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UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

PETROLEUM WAX DEPOSITION AND PRODUCTION GEOCHEMISTRY:

EXPERIMENTAL RESULTS AND FIELD EXAMPLES

A Dissertation

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

Doctor of Philosophy

By

ELI D. TCHOUPAROVA-PETZEVA

Norman, Oklahoma

1999

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PETROLEUM WAX DEPOSITION AND PRODUCTION
GEOCHEMISTRY:
EXPERIMENTAL RESULTS AND FIELD EXAMPLES

A Dissertation APPROVED FOR THE
SCHOOL OF GEOLOGY AND GEOPHYSICS

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ACKNOWLEDGMENTS

The development and completion of the present study have been influenced by many people and different organizations. First, I would like to acknowledge the financial support and encouragement of my major Professor R. Paul Philp through the years. I thank him for introducing me to the field of production geochemistry and the geochemistry of high molecular weight hydrocarbons (HMWHCs), and for the incredible chance to work in one of the world's leading groups on petroleum waxes. I thank Professor J. Forgotsen for agreeing to serve as a Co-Chair of my Advisory Committee, and for the discussions we had on different aspects of characterization and interpretation of reservoir performance. I would like to acknowledge Professors M. Engel and D. Deming for helping me identify and work on certain problem areas in the course of this study, and Professor R. Knapp for taking the time to review drafts of several chapters. I thank Dr. N. Nagarajan (Mobil Technology Company) for taking the time and effort to serve as an outside member of my Advisory Committee.

An important stage in the development of the present study was the joint project between the School of Geology and Geophysics (OU), the Petroleum and Geological Engineering Department (OU) and Mobil Technology Company. I appreciate the financial support of Mobil Technology Company during 1995-1996. My participation in the project as well as the incredible experience as an intern in the Recovery Processes Group of Dr. N. Nagarajan broadened very much my understanding about the multifaceted petroleum wax deposition problem and some of the engineering aspects and experimental methods

for evaluation of fluid behavior of waxy oils. I thank Professor Curtis Whitson (present affiliation Department of Petroleum Engineering and Applied Geophysics, NTNU, Trondheim, Norway) for his patience and for the numerous discussions on the principles of thermodynamic modeling of phase behavior of oils and waxes, and for his help and advice in performing the cold finger experiments.

I would like to acknowledge the participation of A. Bishop in the development of Prairie Gem study, the oil samples he collected in 1993, and the establishment of initial contacts with the field owner company. I thank the production companies (Beard Co., Sensor Ltd., and Phoenix PetroCorp Inc.) of Prairie Gem field for providing the initial geologic and production information for the field and permitting to collect oil samples and publish the results of the study. I would like to express my gratitude and appreciation to Kurt Rottmann, a long-term geologist of Prairie Gem field, for his help, advice and numerous discussions through the years. I thank M. Gaenz, B. Broderson, R. Baker, B. McNew for their time and assistance in collecting the oil samples and the discussions on the production history and performance of Bartlesville reservoir in Prairie Gem field.

I thank J. Allen for his help and many discussions on different aspects of instrument performance and geochemical analytical procedures; M. Shaw for his time and assistance in performing the cold finger experiments; and R. Conlon for performing the X-ray diffraction analysis and the useful discussions on sample preparation and results interpretation. The present study has benefited from the discussions with Professor M. Downey, Drs. G. Hieshima, V. Andrusevich, J. Campbell and R. Andrews on the production geochemistry study of Prairie Gem field; with Dr. T. Bence on checking the

reproducibility of oil sample collection; with Drs. M. McCaffrey and A. Holba on reservoir and production geochemistry.

Lastly, but definitely not least I would like to thank my family: My Dad who was the first person to light my interest in petroleum geology when I was still a child and who helped me make some of the most important choices in my professional development; My Mom who dedicatedly has been helping me in any possible way she can to accomplish my professional goals; and my husband, Vladimir Petsev, for his wise advices, encouragement, financial support and love, without which this work would not be possible to be completed.

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ABSTRACT

The present study targets several main aspects of the problem of petroleum wax deposition. The first aspect to be examined is the change in solubility of n-alkane mixtures and wax deposits as related to variability in their compositional characteristics. The approach applied is based on the solubility parameter concept and comparison of theoretical predictions and experimental results derived from solubility measurements of HMW n-alkane mixtures using various geochemical methods and X-ray diffraction. Second, the study examines changes in n-alkane distributions of wax deposits as a function of temperature of deposition. The compositions of wax deposits formed at different laboratory temperatures (cold finger apparatus) and field conditions are compared using quantitative HTGC analysis. Third, the study examines qualitative and quantitative changes in waxes and asphaltenes precipitated from oils produced during the transition from primary to secondary water flood recovery in Prairie Gem field, collected over a period of three years. The samples used in the study include: a standard HMW dominated n-alkane mixture (Polywax 1000); wax deposits formed in a well tubing and a pipeline; and waxes precipitated from both high-wax (Uinta Basin) and low-wax (Prairie Gem field and Gulf of Mexico) oils.

The main conclusions of the study are as follows:

(1) The solubility of wax deposits dominated by n-alkanes varies with their molecular weight, or carbon number, distributions and the choice of “optimum” solvent for the deposits varies according to the compositional characteristics of the wax.

(2) The composition of wax deposits changes with the temperature of deposition, and increases in molecular weight with the increase in temperature of deposition.

(3) Wax deposits formed along the same well tubing or pipeline vary with regard to both composition and solubility. The study suggests that one possible reason for the current inefficiency of methods for wax problem treatment is related to this variability in the properties of wax deposit mixtures.

(4) An increase in concentration of microcrystalline waxes and asphaltenes in produced oils is proposed as an indicator predicting a strong possibility for wax deposition problems in well equipment.

CHAPTER I. INTRODUCTION

The solid material precipitating from oil and depositing in production and transportation facilities and reservoirs have been presenting problems to the petroleum production practices for over a century and occurs in petroleum producing regions worldwide. Solid material deposition, often referred to as “paraffin” or “wax” deposition, presents a problem to petroleum production by reducing reservoir permeability and/or causing formation damage, by plugging and reducing the well tubing and pipelines diameter, all of them resulting in deferred and/or decreased oil production and additional costs for cleaning and remediation. The main types of wax deposit remediation are based on mechanical, thermal, chemical treatments or a combination of them. Although the wax deposition phenomenon has been known for over a century, it is a recurrent problem even today, and the remediation costs continue to escalate, especially with the expansion of petroleum offshore exploration and production. It has been recognized, and there is a consensus now, that the understanding and the predictive methods for paraffin deposition are still unsatisfactory for successful prevention and treatment of the problem.

The composition of wax deposits is a complex mixture dominated by high molecular weight (HMW) hydrocarbons (mainly n-alkanes, with various amounts of cycloalkanes, isoalkanes, alkylaromatics) and polar fractions (resins and asphaltenes), with additional trapped oil, inorganic material and water in various proportions. Both the hydrocarbons and polar fractions in wax deposits represent a large variety of individual compounds and homologues series with different molecular weights and often unknown

structures and physical properties. Thus the properties of the complex mixtures they form are even more obscure, which presents a major obstacle to the development of more effective and less costly remediation methods for wax deposition problems. The use of terms such as “wax” or “paraffin” deposits to refer to the complex composition of petroleum formed solid deposits could be confusing because these terms imply that the deposits exclusively consist of hydrocarbons or n-alkanes (n-paraffins), respectively. “Wax” deposits and deposition are used in the present study being aware of the broader compositional range that the solid deposits represent, which encompasses non-polar, polar and hydrogen bonding-prone fractions.

The main factors known to control wax deposition are reduction in temperature, changes in overall oil composition and the effect of pressure mainly as it affects the oil composition. In addition, wax deposition can be regarded as a result of the decreasing solubility of heavy petroleum fractions in the oil acting as a solvent under changing temperature and pressure conditions.

The present study addresses the problem of petroleum wax deposition specifically with respect to the composition of high molecular weight (HMW) n-alkanes in wax deposits formed in production, transportation facilities and reservoirs, and as revealed by geochemical methods (Chapter II). The presence and preferential concentration of HMW n-alkanes in wax deposits was identified for the first time less than ten years ago (Carlson et al., 1991; del Rio and Philp, 1992 a and b), and prompted scientists to have a new look on the wax deposition problem. The results in the present study are based on both experimental data and field examples. Two main aspects of the problem of petroleum

wax deposition are targeted. First, the solubility of n-alkane mixtures in the carbon number range C_5 to C_{120} as related to the complex composition of wax deposits (Chapter IV. 2). Second, the changes in n-alkane distributions of wax deposits as related to the temperature of wax deposition (Chapter IV. 3). In addition, discussions are presented on the effect of pressure and temperature as factors influencing the deposition and mobilization of waxes and asphaltenes in reservoirs during a transition from primary to secondary recovery by water flooding in a Prairie Gem field case study (Chapter IV. 4). The samples used in the present study include a standard HMW dominated n-alkane mixture, wax deposits formed in a well tubing and a pipeline, and waxes precipitated from both high-wax (Uinta Basin) and low-wax (Prairie Gem field and Gulf of Mexico) oils (Chapter II). The relationships between hydrocarbons and polar fractions in wax deposits and waxes precipitated from oils are discussed in the study on waxes and asphaltenes in produced oils in Prairie Gem field (Chapter IV. 4) and on solubility of n-alkane mixtures with a model resin component (Chapter IV. 2). Several overviews are presented on the geological setting of Prairie Gem field (Chapter III and Appendix III), the problem of petroleum wax deposition (section IV. 2. 1), the composition, classification and origin of petroleum waxes (section IV. 2. 2), the properties of pure n-alkanes and their mixtures (section IV. 2. 3. B), and the solubility parameter concept (section IV. 2. 3. C).

The results and discussion (Chapter IV) are subdivided into four parts. Chapter IV. 1 discusses the reproducibility and precision of analytical procedures and methods, and validity of data used in the study. The validity of data is assessed by analysis of

replicate and control samples, recovery studies of standard compounds, analysis of standard reference mixtures, and addition of internal standards. Several sources of possible errors, specifically for Prairie Gem oils, are examined by experiments designed to target errors associated with the oil sampling procedure, oil sample preparation, and compound determinations. The imprecision of data used in the study are represented by coefficients of variation less than 1% for instrument performance, less than 5% for replicate analysis, and less than 10-15% for different analytical procedures.

Chapter IV. 2 of the results and discussion of the study focuses on the solubility of HMW n-alkane mixtures as related to the composition and solubility of wax deposits. The approach applied in this part of the study is based on the solubility parameter concept and high temperature gas chromatography (HTGC) analysis as a technique for evaluating the solubility of n-alkane mixtures (section IV. 2. 3. C and D). Three previously published methods are applied for calculation of solubility parameters of pure n-alkanes (C_5 - C_{120}). The predictions of these methods about the solubility of n-alkane mixtures in three solvents are compared with the experimental HTGC results on solubility of a standard HMW dominated n-alkane mixture (Polywax 1000) and pipeline wax deposits (section IV. 2. 3. D1, section IV. 2. 3. D2, section IV. 2. 3. E1). The method that gives predictions closest to the experimental results is validated for further use in the study. Experimental results from filtration of Polywax 1000 in different solvents at room temperature and X-ray diffraction analysis are further discussed with regard to differences in the crystallization behavior of HMW n-alkanes in studied solvents (section IV. 2. 3. D2). In addition, the solubility parameter concept is applied to predict the effect of

different proportions of a model polar fraction (resin) on the order of solvents with best solvency capacities for the HMW dominated n-alkane mixture (section IV. 2. 3. D3). Based on these results, a procedure for solubility parameter calculation of n-alkane mixtures, as determined by HTGC analysis is suggested, and is applied to evaluate the choice and efficiency of solvents used for wax precipitation and dissolution by two laboratory techniques (section IV. 2. 3. E2).

Chapter IV. 3 of the results and discussion of the study explores the changes in molecular weight distributions of n-alkanes in wax deposits formed under different temperature conditions. Presented results are based on both wax deposits formed during laboratory simulated wax deposition at different temperatures using a cold finger apparatus (section IV. 3. 1), and wax deposits formed at different depths of the same well tubing and a pipeline (section IV. 3. 2).

Chapter IV. 4 presents results on the changes in waxes and asphaltenes in produced oils collected over a period of about three years from the Bartlesville reservoir in Prairie Gem field, and covering a period of transition from primary to secondary recovery by water flooding. Processes and factors that could have facilitated wax and asphaltene deposition and mobilization in the reservoir are discussed by attempting to constrain the knowledge accumulated in previous studies with known facts from the production history of the field.

Chapter V presents a summary of the conclusions reached in different sections of Chapter IV, and provides the final conclusions and recommendations of the study. Chapter VI lists all cited references in the previous chapters in an alphabetical order.

All the geochemical analyses and experimental work have been performed at the geochemistry laboratories of Professor R. P. Philp (School of Geology and Geophysics). The X-ray diffraction analyses were performed at the School of Geology and Geophysics X-ray Laboratory by Ron Conlon. The cold finger experimental results were obtained by integrated geochemical and engineering experimental methods and have been performed in a collaborative project between the School of Geology and Geophysics (Professor R. P. Philp), and the Petroleum Engineering Department (Professor C. Whitson, present affiliation Department of Petroleum Engineering and Applied Geophysics, Norwegian Institute of Technology, NTNU, Trondheim, Norway) at the University of Oklahoma, and sponsored by Mobil Technology Company (Project leader Dr. N. Nagarajan) during 1995-1996.

CHAPTER II. EXPERIMENTAL

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II. 1. SAMPLES

Standard compounds and mixtures. Standard individual nC_{17} , nC_{20} , nC_{30} , nC_{40} alkanes, pristane and anthracene have been purchased from Sigma Chemical Company (St. Louis, MO) with a manufacturer-stated purity of approximately 99% and 99.9% (for anthracene). Standard nC_{50} , nC_{60} alkanes (>99% and > 98% purity, respectively) and phenanthrene (>99.5% purity) have been purchased from Fluca Chemie and Aldrich Chemical Company (Milwaukee, WI), respectively. Polywax 1000 is a commercial name of a product purchased from Petrolite Company, and represents a synthetic non-polar polyethylene wax. At room temperature, Polywax 1000 appears as solid white granules.

Prairie Gem oils. Oil samples have been collected from the well-heads of producing wells in Prairie Gem field, and are grouped in fourteen sets according to the time of sampling (**Table II. 1**). The sample collection covers a period from January 1993 to July 1995. The first two sets of oil samples were collected in the last year (1993) of primary production in the field by A. Bishop. The rest of the sample sets were collected during the water flooding initiated in December 1993, and the frequency of sample collection during the water flood was once a month during the period from 9/94 to 3/95

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well name	well #	RPP # (lab #)	Perforation interval (ft); date	Producing formation; Top-bottom depth (ft)	Initial API °, date	Initial GOR; date	Acid Treat. (gal.)	Hydr. Frac.	Choke size	Date of oil sample collection														Notes
										I 1/93	II 11/93	III 9/94	IV 10/94	V 1/95	VI 3/95	VII 4/95	VIII 4/95	IX 5/95	X 5/95	XI 6/95	XII 6/95	XIII 7/95	XIV 7/95	
Acree 1	2221	1572	4550-4590	Bartlesville	36 2/80	796 2/80	yes 2000	yes	16/64"	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
Ben Green 1	2621-w	1565	4642-4670	Bartlesville			yes 1500	yes		+	+	+	+	+	+	+								Frac: 120,000 #sd + 40,000 gals gel wtr
Betty Laub 1	2241-w	1611	4573-4614	Bartlesville	35 12/79	387 12/79	no		20/64"	+	+	+	+	+	+	+	+	+		+	+	+	+	
Carpenter 2	2332-w	1571	4635-4675	Bartlesville	37 1/81	2479 1/81	yes	yes	17/64"	+	+		+	+	+									
Cartine 1	2231		4570-4590	Bartlesville	37.5 3/79	553 3/79	no	no							+	+	+	+	+	+	+	+	+	
Castino A1	2251		4572-4612	Bartlesville	34.5 10/79	462 10/79	not reported	not reported			+	+		+		+	+	+	+	+	+	+	+	
Cleta 1	2271		4590-4620	Bartlesville	37 3/80	1741 3/80	yes 2000	yes	16/64"			+	+		+	+								
Oroen 2	2352-w	1607	4606-4652	Bartlesville	37 4/80	86 4/80	yes 1200	yes	32/64"	+	+													Frac: 90,000#sd. + 109,000 gals wtr.
Green A2	2362	1608	4607-4637	Bartlesville	37 9/80	451 9/80	yes	yes	32/64"	+	+	+	+	+										
Hagar 3			4619-4659	Bartlesville	37 1/81	3000 1/81	yes 500	yes	n.d.									+	+	+	+	+	+	Frac: 7000#sd. + 80,000 gals gel
Ingram 1	1531	1569	4580-4598	Bartlesville	38 10/79	4626 10/79	yes 1000	not reported	24/64"	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
Ingram 3	1533		4524-4550	Bartlesville	37 8/80	1786 8/80	yes	yes	n.d.		+													Frac: 53,000#sd. + 48,500 gal. gel wtr.
Paschall 1	1551	1609	4568-4608	Bartlesville	33(41) 12/79		yes	yes	3/4"	+	+	+	+	+	+	+	+	+	+	+	+	+	+	Frac: 33,240#10/20sd.+40,000 bal. Versa gel (KCl)
Paschall 2	1552	1566	4562-4600	Bartlesville	n.d.		yes 2000	yes	32/64"	+	+	+	+	+		+	+	+	+	+	+	+	+	Frac: 54,000 #sd. + 40,000 gal. KCl
Shebeck 2	1542		4501-4528	Bartlesville	n.d.		yes 2000	yes	1/2"					+	+									Frac: 57,000 gel
Shebeck 3	1513-w	1610	4562-4584	Bartlesville	34.8 4/81	2562	yes	yes	24/64"	+	+													

Table II.1 (continue)

well name	well #	RPP # (lab #)	Perforation interval (ft); date	Producing formation; Top-bottom depth (ft)	Initial API °; date	Initial GOR; date	Acid Treat (gal)	Hydr. Frac.	Choke size	Date of oil sample collection														Notes
										I 1/93	II 11/93	III 9/94	IV 10/94	V 1/95	VI 3/95	VII 4/95	VIII 4/95	IX 5/95	X 5/95	XI 6/95	XII 6/95	XIII 7/95	XIV 7/95	
Colonial Royalties 1	2651	1612	4700-4730	Bartlesville 4705->4765 Pink 4585-4705	38 9/81	3913 9/81	yes 4000	yes	12/64"	+	+													Frac: 102,000#sd. + 84,000 gal gel wtr, DST1 4735-4765 / Blav.
Mathews 3		1567	4486-4530 4408-4430	Bartlesville 4482-4562 Red Fork 4408-4430	32 3/84	1066 3/84	yes 750 yes 500	yes yes	n.d.	+	+													Frac: 26,000#sd., type, am. fluid not reported Frac: 91,000#sd., type, am. fluid not reported
Nina Balca 2		1570	4600-4650 10/80 4351-4356 12/81	Bartlesville 4600->4679 Upper Skinner 4350-4430	37 10/80 35 12/81		yes 2500 yes 500	yes yes		+	+													Frac: 42,000#sd. + 15,000 gal gel wtr
Shebeck 1		1568	4565-4606	Bartlesville 4566-4606 ?			yes 2000	yes		+	+													Frac: 60,000 gal gel wtr.
Shebeck A2	1512	1613	4544-4632 4632->4670 TD	Bartlesville Miss. Lime	40 1/63			yes	1"	+	+	+	+	+	+									Well completed in 1/63. Bartlesville int. 4620-4632 limestone; Bartlesville int. 4600-4620 sand. DST6 4628-4670 / Blav. + Miss. / packer leakage / gas DST7 4550-4670 / Blav. + Miss. / gas+oil After DST6,7, casing 5 1/2" set at 4631 ft. Visible fractures in Miss. w/ good fluorescence. Oil is produced from Miss. Lime
Prudence Silverthorne 1	2382-w	1573	4598-4620 2/81 4452-4458 4/89	Bartlesville 4598-? Lower Skinner 4450-4490?	37 2/81 45 4/89	4100 2/81 39760 4/89	yes 3000 yes 500	yes yes	n.d. 15/64"	+	+													Frac: 13,700 gal wtr.

(sets III to VI), and then every two weeks (sets VII to XIV). The sampling procedure consisted of letting the oil flow from the well head for 5 to 10 min, and then collecting the oil sample in a pre-labeled 50 ml vial with a Teflon covered cap. After transportation to the lab, the samples were kept in a refrigerator at 5 to 10°C. At room temperature the oils represent a dark brown to black liquids.

Oils used in the comparison of wax precipitation techniques. Two oil samples have been used for comparison of the “DCM” (dichloromethane) and “acetone” techniques for wax precipitation. The oils selected from the Uinta Basin and the Prairie Gem field had different physical properties and different geological histories (**Table II. 2**).

Table II. 2. Geologic summary for samples used in the comparative study of wax precipitation techniques

Samples		Geologic summary of samples			
Oils	Physical state @ room temperature	Possible source rocks	Depositional environment of source rocks	Age of source rocks	Migration distance (expected)
Ute Tribal 2-D Uinta Basin	Solid	Bituminous shales Green River- Wasatch	Lacustrine	Eocene (Tertiary)	no or short
Green A2-I Prairie Gem	Liquid	Black shales Woodford	Marine	Late Devonian (Paleozoic)	medium to long

The oil examined from the Uinta Basin and collected from the Wasatch reservoir (well Ute Tribal 2-8D), Duchesne field by Tim Ruble was a yellowish-brown solid at

room temperature. The most probable source rocks for this oil are the Eocene Green River Wasatch bituminous shales (Ruble, 1996), deposited in a lacustrine environment and probably sourced from an input of fresh aquatic fauna/flora and a high contribution of Tertiary terrestrial plants. A short distance secondary migration is expected for this oil.

The other oil examined was produced from the Bartlesville reservoir in Prairie Gem field (well Green A2-I), and was a black liquid at room temperature. The most probable source rocks for this oil are considered to be the Upper Devonian Woodford marine black shales, with possible contributions from the Pennsylvanian and Ordovician black shales. The organic matter in Woodford shales is reported to be dominated by marine microflora and microfauna (spores, acritarchs, plankton algae as Tasmanite sp., Radiolaria), sponges, and some contribution from terrestrial plants (Kirkland *et al.*, 1992). The migration distance from source rocks to present day filled reservoirs is considered to be medium to long distance (Northcut and Johnson, 1996).

Oil used in cold finger experiments. A five gallon stock tank oil sample produced from Gulf of Mexico was provided by Dr. Nagarajan, Mobil Technology Company for the cold finger experiments. Further information regarding well name, location, reservoir and production conditions has not been released by the company. The five gallon oil sample has been transported to the University of Oklahoma in a closed container. At room temperature, the oil represented a black liquid. The initial five gallon oil was subdivided into aliquots of 450 ml for use in the cold finger experiments after a thermal pre-treatment procedure was applied. The procedure consisted of attaching the five gallon oil container to a rocker, and heating it in an oven up to 70°C for 7 hours. Manual

shaking of the oil container was applied every one hour for 10-15 minutes. This procedure was applied in order to achieve as much homogenization and wax dissolution as possible before dividing the oil into aliquots of 450 ml for use in the cold finger experiments. During the thermal pre-treatment, a plastic glove was attached to the opening of the container in order to reduce the pressure build-up resulting from gases released during the heating and confined to a fixed volume. The glove was removed before taking the 450 ml aliquots, and the light components collected there have been lost. The aliquots were taken from the heated oil directly into the bottles used in the cold finger experiments. The 500 ml bottles with oil were stored at 5-10°C prior to use in the cold finger experiments.

Pipeline wax deposit samples (called # 9 and # 10 in the present study) have been collected at two different locations of the same pipeline and provided by Dr. Nagarajan, Mobil Technology Company. Any additional information regarding the sample and pipeline locations, gathering system, composition of oil(s) flowing through the pipeline has not been released. The wax deposit samples arrived in plastic bags and represented medium to dark brown colored solids at room temperature.

Well tubing (rod) wax deposits formed at different depths of a well located in Oklahoma and producing oil by pumping from the Viola Formation were collected and provided by Professor Curtis Whitson. The samples were collected when the rods were taken to the surface for cleaning operations after a wax deposition problem occurred in this well. Only the relative depths of sample location were available, and therefore the samples are called in the present study as “deeper” and “shallower” deposits. The deeper

sample is roughly approximated as collected close to about 8000 ft. of depth (C. Whitson, personal communication).

II. 2. METHODS

Asphaltene / Maltene separation. Whole oils (~100 mg) were dissolved in a small amount of methylene chloride and the asphaltenes precipitated with an excess of n-pentane (50:1 v/v) and allowed to stand at 5°C overnight. The n-pentane insoluble fraction (asphaltenes) was separated from the n-pentane soluble fraction (maltenes) by centrifugation at 1500 rpm for 25 min and subsequent decanting of the pentane. The maltene fraction was concentrated by rotary evaporation of the solvent at 40°C. The asphaltene fraction was recovered in methylene chloride, transferred to 4 ml vial, and the solvent evaporated under nitrogen. The recovered amount of asphaltenes was calculated as follows:

$$\% \text{ Asphaltenes} = ((\text{Asph. wt.})/(\text{Oil wt.})) * 100$$

High-performance liquid chromatography (HPLC). The maltene fractions were separated into saturate, aromatic and NSO fractions based on the method described in McDonald and Kennicutt (1992). The system used for the analysis included a programmable solvent deliver system ELDEX model 9600 with Rheodyne 71 valve injector and Spectroflow 782 absorbence detector with deuterium (190-380 nm) and tungsten (380-700 nm) light sources (KRATOS Analytical). It was equipped with 25 cm x 9.4 mm partisil 5µm PAC (cyano/amino bonded phase 1:2), Magnum 9, preparative

HPLC column commercially available from Whatman Inc. The program used hexane, methylene chloride and ethyl acetate as eluting solvents (flow rate 5 ml/min) for the saturate, aromatic and NSO fractions, respectively. The best separation was achieved using collection times of 0 to 5.3 min, 5.3 to 10.2 min and 10.2 to 16.55 min for the saturate, aromatic and NSO fractions, respectively. The separation between the fractions was periodically checked by GC of the eluted material. Preceding each HPLC analysis, the system was flushed thoroughly with hexane and at least one blank analysis performed in order to assure that the column was clean from any previously adsorbed material, and that the pressure through the system is uniform. The collected saturate, aromatic and NSO fractions were concentrated by rotary evaporation of the hexane, methylene chloride and ethyl acetate at 50°C, 40°C, and 60°C, respectively. The recovered amounts of saturate, aromatic and NSO fractions, as percentages of the maltene fraction, were calculated as follows:

$$\%SAT = ((SAT \text{ wt.}) / (SAT \text{ wt.} + ARO \text{ wt.} + NSO \text{ wt.})) * 100$$

$$\%ARO = ((ARO \text{ wt.}) / (SAT \text{ wt.} + ARO \text{ wt.} + NSO \text{ wt.})) * 100$$

$$\%NSO = ((NSO \text{ wt.}) / (SAT \text{ wt.} + ARO \text{ wt.} + NSO \text{ wt.})) * 100$$

Isolation of branched and cyclic alkane fractions from the total saturate fractions was achieved using Silicalite (a synthetic zeolitic form of silica) for sorption of alkanes (West et al., 1990)

Wax precipitation was compared using two techniques. The first one described in Burger et al. (1981) was based on precipitation of wax material from oils using a petroleum ether:acetone (1:3 by volume) mixture at -20°C, followed by filtration and

recovery of wax fractions using toluene. The second technique was developed by Bishop (1994, unpublished report) targeting precipitation of high molecular weight n-alkanes above nC_{35} - C_{40} . The procedure consisted of precipitation of wax in methylene chloride at -20°C , and followed by filtration and recovery of the wax material using boiling cyclohexane. A comparison of the two procedures is presented in **Table II. 3**. The last column in the table describes some modifications in the technique suggested as result of the reproducibility evaluation.

Filtration experiments were performed at room temperature with Polywax 1000 standard and pipeline wax deposit # 10 solutions in carbon tetrachloride and p-xylene, and carbon tetrachloride, cyclohexane and p-xylene, respectively. Before the filtration, Polywax 1000 granules were ground manually in an agate mortar to powder, and 200 mg of the powdered sample mixed with 50 ml solvent. The same amount of solvent (50 ml) was added to 500 mg of wax deposit # 10. The solutions for both Polywax 1000 and the wax deposit were prepared by heating the sample/solvent mixtures in a heating basket to temperatures close to the boiling point of the corresponding solvent in order to achieve as much sample dissolution as possible. Then, the solutions were left to cool and equilibrate to room temperature for at least 2 hours, and after that used in the filtration experiments. The temperatures of visually observed dissolution of the Polywax 1000 sample during the heating and the first cloudiness of the solutions during the cooling were measured on the external glass surface of the vials with a mercury thermometer. The filtration was performed using a porcelain Büchner funnel with an added pre-measured disposable filter ($0.450\ \mu\text{m}$ pore size) and applying a light vacuum. The solutions were transferred to the

PROCEDURE	ACETONE (Burger <i>et al.</i> , 1981)	DCM (Bishop, 1994)	DCM (modified)
<u>PRECIPITATION</u>			
Initial amount of oil	5000 mg	100 mg	3000 mg
Solvent(s) for precipitation	Petroleum ether : Acetone (1:3 v/v)	DCM	DCM
Concentration of oil in solution	3.4 wt %	0.3 wt%	1 wt. %
Time of precipitation	2 hrs	>12 hrs	>12 hrs
Temperature of precipitation	-20C	-20C	-20C
<u>FILTRATION</u>			
Funnel	Porcelain w/ fixed perforated plate	Glass w/ fritted glass support	Porcelain w/ fixed perforated plate
Filter pore size	1.5 mm	0.045 mm	1.5 mm
<u>RECOVERY OF WAXES</u>			
Solvent	Toluene physical transfer of filter cake and filter	Cyclohexane boiling	Cyclohexane boiling

Table II. 3. Wax precipitation procedures

filter/funnel with a Pasteur pipette. In the case of Polywax 1000 solution in carbon tetrachloride, a white deposit was observed to form on the pipette during this transfer, and may partially account for the observed losses (section IV. 2. 3. D2). The filtrate was collected in a 150 ml Erlenmeyer flask, transferred into a 50 ml pre-measured vial, and the solvent evaporated under nitrogen flow in a water heating bath. The precipitate, collected on the filter, was washed with 10-20 ml of solvent, and together with the filter carefully removed out of the funnel to dry at room temperature. After the complete solvent evaporation from the filtrate and precipitate, which was determined when no further weight loss occurred, the amount of precipitate was determined as the difference between (filter+precipitate) weight and the initial filter weight. The amount of filtrate was determined as the difference between (vial+filtrate) weight and initial vial weight.

Wax deposition with a cold finger apparatus. The cold finger and 500 ml glass bottles used in the presented study have been donated by Shell U.S. Co. to the Petroleum and Geological Engineering Department (PGE) at the University of Oklahoma, where the experiments were performed. The cold finger represents a modification of the cold finger described in Kruka et al. (1995) in that it consists of one cold surface instead of three. The cold finger modification used in the present study allowed the formation of larger amount wax deposits that can be collected and used in the subsequent HTGC analysis.

The settings of the equipment are as described in Kruka et al. (1995), and the procedure has been developed and tested by Shell (unpublished data). In brief, the apparatus consists of an insulated water bath container that is heated and stirred by a hot plate/ magnetic stirrer, a 500 ml (3.0 in. I.D.) bottle containing the oil, placed in the water

bath and independently stirred, and a cold finger placed within the oil bottle during the analysis. The water bath surface was covered with styrofoam “pop-corn” to prevent evaporation and ensure stability in water and oil temperatures. During analysis, the temperature of the oil was maintained at 18-20°F above the set temperature of the cold finger in each experiment. Temperatures of the water bath, oil and cold finger were recorded using thermocouples and data was transferred to a computer every 60 sec during the analysis. The computer program for temperature data recording from all the thermocouples was written and installed by Professor C. Whitson. The achieved precision in detected temperatures was $\pm 0.5^\circ\text{F}$. A mixture of water and ethylene glycol (70:30 v/v) was used as a circulating coolant to control the temperature of the cold finger. Duration of each experiment was 17 hours. The cold finger was removed from the oil after completion of the test, allowed to drip dry and rinsed with methyl-ethyl ketone (MEK) by submerging the finger and deposited material several times in MEK. The MEK is supposed to remove the residual oil deposited with the wax on the cold surface (Kruka et al., 1995). After a rotary evaporation of the solvent, the collected material was referred to as “MEK recovery”. If there was a film visual under a magnifying glass or an accumulation of wax, the finger was placed in another bottle with approximately 400 ml toluene and stirred at temperatures of 130-140°F for about three hours, which was considered a sufficient amount of time for all of the wax material to be dissolved in the toluene. The toluene was removed by rotary evaporation. The wax material was further transferred using toluene in a 20 or 50 ml vial (depending on the amount of deposited wax), and the solvent completely evaporated under nitrogen flow in a water heating bath.

The collected material was called “toluene recovery” and is considered to contain the wax material deposited at the pre-set temperature of the cold finger (Kruka et al., 1995). A new aliquot of the original oil was used in each experiment. The finger surface was polished with an emery cloth (1200 size) before each experiment to ensure the smoothness of the finger.

The cloud point (temperature of initiation of wax deposition) was determined to be in the narrowest temperature interval where presence and absence of wax deposits is observed by a series of experiments at different set temperatures of the cold finger. The temperature difference between consecutive experiments could be narrowed to 5°F.

Gas chromatography (GC) and HTGC analyses of whole oils and waxes were performed on a Hewlett Packard 5890 gas chromatograph with an on-column injector system and a flame ionization detector (FID). Whole oil GC analyses were undertaken using a 30 m x 0.32 mm i.d. DB-1 column with a film thickness of 0.25 µm and temperature program from 20°C to 300°C at a rate of 4°C/min and a final hold time of 48.5 min. The HTGC analysis of waxes was performed using a 30 m x 0.32 mm i.d. DB-1 HT column with 0.1 µm film thickness and a temperature program from 80°C to 350°C at 4°C/min with a final hold time of 51 min. For selected high molecular weight wax samples, HTGC analysis was performed on a gas chromatograph GC 8000 Top series, equipped with a 25 m x 0.32 mm i.d. HT5 column bonded with a non-polar (5% phenyl equiv. polysiloxane-carborane) phase and with film thickness of 0.1 µm. Temperature programs were from 60°C to 420°C at 6°C/min. or from 40°C to 370°C at 4°C/min. with a final hold time of 37 min. Wax samples were dissolved in hot p-xylene (or other solvent

dissolved in hot p-xylene (or other solvent as discussed in the following chapters) before injection. One microliter air gap in the syringe barrel was maintained above and below the sample plug to assure complete emptying of the needle during injection. Detector temperature was set at 10°C higher than the corresponding maximum column program temperature to prevent condensation effects. Quantitation of components was performed by using deuterated C₂₄ and C₃₆ alkanes as internal standards for the whole oils and waxes, respectively.

Quantitative GC analysis of the whole oils was performed using a deuterated alkane as internal standard (n-C₂₄D₅₀; Cambridge Isotope Laboratories, MA). The internal standard method is considered to give the most accurate quantitative results in gas chromatography (e.g., Scott, 1995). A major advantage of the method is that it compensates for variations in injected sample volume and instrument performance since the added standard peak area varies correspondingly with the peak areas of the sample compounds. The n-C₂₄D₅₀ standard compound elutes between the n-C₂₃ and n-C₂₄ alkanes without interference with other compounds. The concentration of the internal standard was commonly adjusted at the beginning of analysis to give about 75% of the height of the tallest peak in the chromatogram. The general procedure followed was to dilute the sample and standard separately, mix the diluted solutions, and inject the mixture into the GC. The standard solution was prepared by dissolving 0.5 mg of n-C₂₄D₅₀ in 10 ml carbon disulfide. The oil solutions were usually prepared at a concentration of 2 mg per ml carbon disulfide. Before the analysis, the oil and standard solutions were mixed in proportion 100 µl : 25 µl, corresponding to adding 1.4 µg

standard to the oil solution. The 1 µl injected volume of the sample and standard solution contained 0.011 µg of the standard compound and 1.6 µg of the oil sample. The calculation procedure of individual components concentration uses the fact that the area of the peak is proportional to the total mass of solute in the peak (e.g., Scott, 1995). Peak integration was performed using Nelson 3000 series chromatography data system software. Best results were obtained with noise threshold, area threshold and minimum peak width settings of 20. The software draws a baseline from which peak areas (or heights) are calculated on a cluster-by-cluster basis, i.e., baseline is drawn from the start of the first peak in each cluster to the end of the last peak. The automatic peak integration was checked for each sample and manual corrections were made if necessary. The amount of individual components was calculated as follows:

$$\frac{(\text{peak area of component})}{(\text{peak area of int. std.})} \times 0.011 \text{ µg int. std.} = \frac{\text{µg of component in 1 µl injected}}{\text{solution}}$$

$$\frac{(\text{µg of injected component})}{(1.6 \text{ µg of sample injected})} \times 1000 = \text{ng of component in µg oil}$$

The quantitative HTGC analysis of waxes and oils followed the same general procedure. The internal standard used was deuterated alkane (n-C₃₆D₇₄; Cambridge Isotope Laboratories, MA). The standard compound elutes between n-C₃₅ and n-C₃₆ without interference from other compounds. The standard solution was prepared by diluting 0.5 mg of n-C₃₆D₇₄ in 10 ml p-xylene. The wax solutions were prepared at concentrations of 1 mg to 4 mg per ml p-xylene based on considerations either not to overload the column or to achieve representative chromatograms. The wax and standard solutions were mixed in proportion 100 µl : 25 µl, and 1 µl of it injected in the gas

chromatograph. The Polywax 1000 solutions in carbon tetrachloride, cyclohexane and p-xylene were prepared from a powdered sample at a concentration of 0.5 mg per ml solvent, and were always heated initially close to the boiling point of the corresponding solvent. Three standard n-C₃₆D₇₄ solutions (0.5 mg/10 ml) were prepared in carbon tetrachloride, cyclohexane and p-xylene, respectively, and added to the Polywax 1000 sample solutions in a proportion such that 1 µl injected (sample+standard) solution to have 0.42 µg Polywax 1000 and 0.008 µg n-C₃₆D₇₄ internal standard. Peak integration was commonly performed on baseline subtracted chromatograms in order to adjust for the baseline increase above 300°C due to column bleed.

X-ray diffraction analysis was performed in the School of Geology and Geophysics X-ray diffraction laboratory by Ron Conlon. The analysis was carried out on a Rigaku automated diffractometer equipped with a graphite monochromator and using $\lambda_{K\alpha}$ copper radiation. The focused monochromatic beam was obtained with a filament intensity of 30 mA at 40 kV. Scans were performed from 3 to 70 degrees 2 θ at 0.05 degree per second. The X-ray diffractometer charts were obtained with Jade software. The accuracy of measurements is $\pm 0.01^\circ 2\theta$ or $\pm 0.02 \text{ \AA} d$ (as determined by Ron Conlon).

X-ray diffraction analysis was performed on a powdered Polywax 1000 sample and on the material crystallized at room temperature from two solutions of Polywax 1000 in carbon tetrachloride and p-xylene. The powdered sample was mounted on a glass slide while the solutions of Polywax 1000 in carbon tetrachloride and p-xylene were prepared by mixing 50 mg of the powdered sample with 1 ml solvent, and heating the mixtures in a

heating basket to achieve dissolution. Then the solutions were poured carefully on a thin section glass plate and air dried at room temperature before analysis.

CHAPTER III. STRATIGRAPHY OF BARTLESVILLE SAND

Summaries on the regional geologic setting and evolution of geological provinces in Oklahoma, regional stratigraphy and local structural elements in the vicinity of Prairie Gem field are included in **Appendix III (Figures III. 1, III. 2 and III. 3)**. The present Chapter gives a brief summary on the stratigraphy and depositional environments of the Cherokee Group and specifically of Bartlesville interval. The major oil producing reservoirs in Prairie Gem field are Bartlesville, Red Fork, Lower Skinner and Upper Skinner sandstones. The most recent publications of the Oklahoma Geological Survey have covered in considerable detail the depositional environments, distribution, well log characteristics and lithology of oil reservoirs associated with Bartlesville, Red Fork and Skinner plays in Oklahoma (Northcut and Johnson, 1996; Andrews *et al.*, 1996; Andrews *et al.*, 1997a; Andrews *et al.*, 1997b, and references therein). The Bartlesville reservoir discussed in the present study belongs to the Cherokee Group of the Middle Pennsylvanian Desmonesian series which is the subsurface analog of Krebs and Cabaniss Groups (**Figure III. 4**). The Bartlesville sand is a subsurface analog of the Bluejacket Sandstone from the upper part of the Boggy Formation (Krebs Group).

The deposition of the Cherokee Group strata was preceded by the Late Morrowan Wichita orogeny, and was followed by the Arbuckle tectonic activity, both of which constitute this region's equivalent of the Hercynian orogeny (North, 1985). The formation of Cherokee Group sequence is influenced by the development of the Arkoma Basin to the south which started to rapidly subside during post-Morrowan, pre-Atokan time and continued through Middle Pennsylvanian. Folding of strata occurred during pre-Cabaniss time, probably after deposition of Boggy, Thurman, and Stuart (pre-Senora) Formations (Joseph, 1987).

System	Series	Group	Formal surface names of formations or members		Formal and informal subsurface names	
Pennsylvanian	Desmonesian	Marmaton	Ft. Scott Limestone	Higginsville Limestone Little Osage Shale Blackjack Creek Ls.	Oswego lime	"Wheeler sand"
				Excello Shale Breezy Hill Ls.		
		Cabaniss	Senora Formation	Lagonda Sandstone	Cherokee Group	Prue sand
				Verdigris Limestone		Verdigris Limest.
				Croweburg coal		Henryetta coal
				Oowala Sandstone		Upper Skinner sand
				Mineral coal		Morris coal
				Chelsea Sandstone		Middle Skinner sand Lower Skinner sand
				Tiawah Limestone		Pink lime
			Thurman	Stuart Shale Arkoma only		Stuart Shale Arkoma only
				Thurman Ss. Arkoma only		Thurman Ss. Arkoma only
		Krebs	Boggy Fm.	Taft Sandstone		Red Fork sand Burbank sd., Earlsboro sd.
				Inola Limestone		Inola Limestone
				Bluejacket Sandstone		Bartlesville sand Glenn sand, Salt sand
			Savanna Fm.	Doneley Limestone Sam Creek Ls. Spaniard Limestone		Brown lime
			McAlester Fm.	Keota Sandstone Tamaha Sandstone Cameron Sandstone Lequire Sandstone Warner Sandstone McCurtain Shale		Upper Booch sand Taneha sand Tucker sand Lower Booch sand
			Hartshorne Sandstone	Hartshorne Sandstone		Hartshorne sand

Figure III. 4. Stratigraphic nomenclature of the Krebs, Cabanis, and lower Marmaton Groups of the Desmonesian Series (modified after Andrews *et al.*, 1997a,b).

The Cherokee Group sequence consists mainly of alternation of shales and sandstones, and sporadic coal horizons. Several marker horizons have been recognized within the sequence of the Cherokee Group for a long time (Oakes, 1953; Cole, 1956; Cole, 1969; and references therein). They are mainly thin limestone bodies formed during periods of transgression, and include Brown lime, Inola Limestone, Pink lime, Verdigris Limestone, and Oswego lime (**Figure III. 4**). Those markers delineate the intervals containing major sandstone bodies within the Cherokee Group, namely Bartlesville sand, Red Fork sand, Skinner sand, and Prue sand. These sandstones have common lithological characteristics, and are classified as orthoquartzites, where well developed sand bodies exist, or as subgraywackes. The sandstones are very fine- to medium grained, poor to well sorted, highly micaceous, argillaceous with numerous carbonaceous partings (Cole, 1969). Two types of shales have been recognized - greenish-gray shales considered to be formed in more oxygenated environments and gray shales considered to be formed in marine environment. The cyclic sequence of the Cherokee Group is considered to have resulted from a series of transgressions and regressions, with an overall transgression dominant, and general WNW-ESE direction, most likely from the Arkoma Basin (Shulman, 1966; Dogan, 1970; Joseph, 1987). Cherokee strata were deposited on an eroded, stream-dissected surface formed on the SE dip of older exposed rocks ranging from Late Cambrian-Early Ordovician (Arbuckle) to Morrowan (Wapanuka) which is evidenced by the lateral variations in thicknesses of the interval from the Mississippian-Pennsylvanian unconformity to the Brown lime (Dogan, 1970; Rottmann, 1997). The thickness of Cherokee Group sequence from Brown lime to Verdigris Limestone increases from NW (150 feet) to SE (1000 feet), and reflects the proximity to the Arkoma Basin. Several unconformities are suggested within the Cherokee Group sequence - top of Atoka and top of Boggy Formation. However, evidence for their subsurface equivalents is difficult to be recognized because none of

those units is truncated, and those that do disappear laterally are result of onlap at the base of the sequence or facies changes into shales (Cole, 1969).

Bartlesville stratigraphy

The Bartlesville interval in Prairie Gem field is part of the Bartlesville play in Oklahoma. The play is distributed mainly on the Cherokee Platform (**Figure III. 5**). To the east and south, the play is limited by its outcrops along the Ozark Uplift and the front of Ouachita mountains uplift (Arkoma basin). To the west, the play is bounded by the limit of sand deposition, or onlap, of Bartlesville around the Nemaha uplift. To the west of the Nemaha uplift and central Oklahoma uplift, in the Anadarko basin, the Bartlesville interval is represented only by marine shales with scattered shallow-marine sands and shoreface-sand deposits. On the Oklahoma City uplift, the Bartlesville interval either was not deposited or was removed by erosion (Andrews et al., 1997a).

The Bartlesville interval is delineated from the top of the Brown lime to the base of the Inola Limestone (**Figure III. 4**). At western locations close to the Nemaha tectonic zone, one or both Brown lime and Inola Limestone are absent mainly due to onlap or erosion by the overlying horizons (e.g., Paradise field, Payne Co.; Ohio-Osage field, Osage Co.; Andrews et al., 1997a). Brown lime in general consists of tan, brown to gray thin limestones, finely crystalline and slightly dolomitic, interbedded with dark shale (Dogan, 1970). The bottom of the Bartlesville interval usually contains several (2 to 8) feet of shale that underlies the Bartlesville sand. Wherever the Brown lime onlaps the Booch interval, the base of Bartlesville is the pre-Desmonesian unconformity. Inola Limestone has a characteristic log signature represented by a sharp kick on the resistivity log (usually the shallow recording), sharp response on the density log, and small response on the GR log. At the surface, the Inola Limestone consists of up to four thin limestone beds, and it is overlain and underlain by beds of black (“hot”) shales. The “hot” shales are easily recognized with their high GR, low resistivity response, and increase in borehole

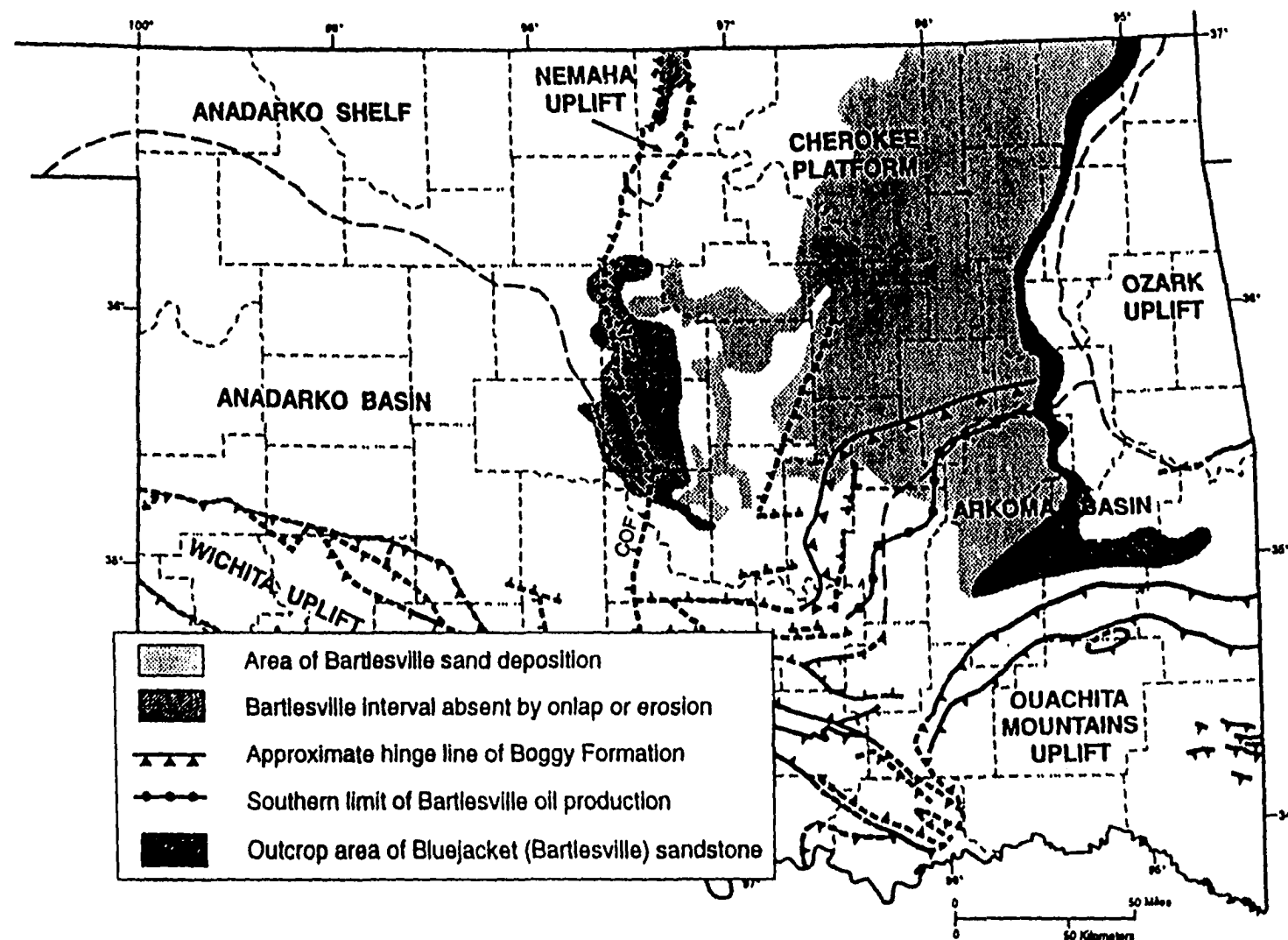


Figure III.5. The Bartlesville oil play in Oklahoma. The play is limited on the east by the outcrop of the Bluejacket Sandstone and on the west and southwest by the limit of Bartlesville sand deposition. NFZ-Nemaha fault zone; COF-central Oklahoma fault zone (after Andrews *et al.*, 1997a).

diameter as registered on the caliper log, thus providing additional criteria for well log identification of the Inola Limestone.

The present day regional dip of Bartlesville sand is to the west of the Ozark uplift and increases from the outcrop on the east to about 2400 ft at the western sand limit. The thickness of the interval, however, generally increases from the west and southwest to the east and northeast. The thickest sandstone bodies (>100 ft) within the interval are located mainly in the eastern and northern areas of the play distribution (**Figure III. 5**). Several authors discuss the presence of pre-Desmonesian drainage system. Based on a sand isopach map of the interval between the Mississippian-Pennsylvanian unconformity and the Hartshorne sand, two major channels with NW-SE trend are delineated in the region to the SE of the Seminole-Cushing Ridge (Cole, 1969). It is suggested that the distribution of the Bartlesville fluvial dominated systems has been controlled to some extent by the ancient topography. The regional interpretation of the depositional environments and facies of Bartlesville interval delineates subaerial upper and middle delta plain deposits in the north-northeastern parts of the Bartlesville play area of distribution (Andrews *et al.*, 1997a, and references therein). In areas of closer proximity to the Prairie Gem field, Bartlesville sand thickness is generally less than 50 feet, and the sequence of the interval becomes more shaly. There is a discussion as to the origin of the sandstones. Some authors consider that none of the regressions that formed the Bartlesville sandstone bodies in proximity to Prairie Gem field progressed to a stage of a well developed alluvial plain (e.g., Verish, 1979; Andrews *et al.*, 1997a) while others consider the origin of the sandstones to be related to recurring meandering alluvial systems (Rottmann, personal communication).

samples to be distributed in a number of series over time. In order to perform comparison of data for samples collected and analyzed at different times, a lot of attention was directed to the evaluation of the results reproducibility. Reproducibility, as defined by the Instrument Society of America (Considine and Considine, 1989), is a measure of the closeness of agreement among repeated measurements under the same operating conditions over a period of time. Quantitatively, all the reproducibility results in this study are expressed using the coefficient of variation of replicate and control samples, and define the range of imprecision of analytical procedures and methods. Good levels of imprecision commonly cited in the geochemical literature are represented by coefficients of variation less than 1% for instrument performance precision, up to 5% for replicate analysis, and up to 10-15% for different analytical procedures (e.g., Hopfgartner et al., 1990; Ludwig, 1995; Dyson, 1995). Only results having these imprecision limits are used in the present study. In addition to the analysis of replicate and control samples, the validity of data is assessed based on recovery studies of standard compounds, analysis of standard reference mixtures, and addition of internal standards. Several sources of possible errors in oil composition determination are examined by experiments designed to target errors associated with the oil sampling procedure, oil sample preparation, and compounds determination.

Asphaltene / maltene isolation. The reproducibility of the procedure was checked by applying it five times on the same oil sample (**Table IV. 1. 1**). The coefficient of variation for the recovered amounts of maltenes and asphaltenes is 6.2% and 16.1%, respectively. The higher variability in the amount of asphaltene precipitates may be

Table IV.1.1 Reproducibility of asphaltene precipitation

Sample	Oil (mg)	Maltene (mg)	Maltene (%)	Asphaltene (mg)	Asphaltene (%)	Loss (mg)	Loss (%)
P2-II-1	108.7	77.7	71.4	1.7	1.5	29.3	27.0
P2-II-2	127.3	80.1	62	2.2	2	45.0	35.3
P2-II-3	107.8	77.4	71.8	2.2	2	28.2	26.1
P2-II-4	104.4	75.3	72.1	1.4	1.4	27.7	26.5
P2-II-5	108.2	77	71.1	1.8	1.7	29.4	27.2
Mean		77.5	69.7	1.9	1.7		
Std.Dev.		1.7	4.3	0.3	0.3		
Coef. variation (%)		2.2	6.2	18.5	16.1		

Table IV.1.3. Reproducibility of HPLC analysis

Sample	Run #	Maltene (mg)	SAT (mg)	SAT (%)*	ARO (mg)	ARO (%)	NSO (mg)	NSO (%)	Loss (mg)	Loss (%)
P2-2	34	20	8.71	43.5	3.1	15.6	1.5	7.4	6.7	33.5
P2-3	47	20	8.34	41.7	3.2	16.0	1.4	6.8	7.1	35.5
P2-3	49	20	8.9	44.5	3.3	16.3	1.4	7.1	6.4	32.2
P2-3	50	20	10.4	51.9	3.8	19.1	1.7	8.6	4.1	20.5
P2-4	66	20	7.8	39.0	3.0	15.2	1.3	6.3	7.9	39.6
P2-4	67	20	8.3	41.5	3.4	16.8	1.4	7.0	6.9	34.8
P2-5	68	20	8.9	44.5	3.0	15.2	1.5	7.3	6.6	33.0
P2-5	69	20	7.8	39.0	2.9	14.7	1.3	6.6	8.0	39.8
P2-5	70	20	8.0	40.2	3.4	17.1	1.5	7.3	7.1	35.6
Mean			8.6	42.9	3.2	16.2	1.4	7.2		
Std.Dev.			0.8	4.0	0.3	1.3	0.1	0.7		
Coef. variation (%)			9.3	9.3	8.3	8.2	9.1	9.1		

* percent of injected amount maltene fraction (20mg)

Table IV.1.4. Reproducibility of B/C fraction isolation

sample	run #	SAT (mg)	ISO (mg)	Iso (%) *	sample	run #	SAT (mg)	ISO (mg)	ISO (%)
st-ii	56	8.2	5.9	71.8	mat-ii	57	7.5	4.9	64.8
st-ii	77	9.1	6.6	71.9	mat-ii	76	6.4	4.4	68.7
Mean				71.8					66.8
Std.Dev.				0.1					2.7
Coef. Variation (%)				0.1					4.1

* percent of saturate fraction

related to co-precipitation of HMW n-alkanes having similar solubility towards the n-pentane. Losses during the procedure account to 25%-30% of the original amount of oil. These losses are large, and most probably could be related to high amounts of volatile compounds in the oil sample that could be easily lost during the rotary evaporation step of the procedure.

HPLC analysis. Several experiments were performed initially to quantitatively evaluate the amount of recovered saturate and aromatic fractions by using individual and mixtures of standard compounds as shown in Table IV. 1. 2.

Table IV. 1. 2. Results of experiments to evaluate the recovery of saturate and aromatic compounds by HPLC analysis.

Standard compound or mixture	Injected amount (mg)	Recovered amount	
		(mg)	%
n-C ₂₀ + n-C ₃₀ alkanes	2	1.99	99.5
Phenanthrene	1	0.90	90
Aromatic fraction* + deuterated C ₂₄ alkane	4.425 (4 + 0.425)	4.2	95

* obtained by a previous HPLC separation of maltene fraction

In addition, validation solution standard consisting of n-C₁₇, pristane, phenanthrene and anthracene was run through the system and checked by GC for the separation of the saturates and aromatics.

The reproducibility of the HPLC analysis was determined by applying the procedure nine times on the maltene fraction obtained from the same oil - Paschall 2-II

(Table IV. 1. 3). Maltene fractions were separated independently four times from the same oil, and repeatedly run by HPLC from one to three times. The coefficient of variation for the amounts of the saturate, aromatic and NSO fractions recovered from the same oil is within 10% (range 8.2 to 9.3%). Material loss is in the range of 30% to 40% of the initial amount of the maltene fraction or 3.8% to 7.6% of the original amount of oil. Since the experiments on saturate and aromatic fractions recovery by HPLC using standard compounds (Table IV. 1. 2) showed 0.5% to 10% losses, it could be expected that the loss of volatile compounds and/or an incomplete recovery of the NSO fraction by the HPLC procedure contribute to the rest of thus determined losses.

Isolation of branched/cyclic fraction. The reproducibility of this analysis was checked by running duplicate analysis for the saturate fractions of two oils as shown in Table IV. 1. 4. The coefficient of variation is within 5%.

GC of whole oils. Since the oil samples were collected at different times during a period of about three years, and stored in lab for different periods of time, a lot of attention was directed towards the GC analysis reproducibility over time. This was an important step that permitted definition of the limitations and ranges of possible errors that may have been introduced to the data set. Several factors that may influence the reproducibility in the oil composition as determined by GC analysis were examined:

- well-head sampling procedure
- oil heterogeneity in the sample vial
- evaporation

The well head sampling procedure was tested by collecting a series of oil samples from the well-head of the same producing borehole, with a time difference intervals between the samples ranging from 1 to 50 min. The samples were analyzed by quantitative GC and the results are presented in **Figure IV. 1. 1** and **Table IV. 1. 5**. The composition of the oils is generally similar with a coefficient of variation in the concentration of individual n-alkanes and isoprenoids commonly within 10%. Oils collected for flow periods of less than 6 min showed a variation in the concentrations of n-C₁₀ to n-C₁₂ alkanes of about 1 mg/ml oil. Most of the samples used in the present study were collected after 5-10 min flow time from the well head. Considering the above results, it may be expected that some of the oils could have variations in the n-C₁₀ to n-C₁₂ alkanes range due to the sampling procedure.

After the Prairie Gem oil samples were allowed to stand at 5-10°C for several weeks, or months, gravitational segregation could be observed visually within the vials. Possible errors that may be introduced to the GC analysis of whole oils (C₁₀₊ range) due to insufficient homogenization of the sample were examined by carrying out several experiments. Oil samples for GC analysis were taken from the bottom and top of a vial prior to mixing, and then after thoroughly mixing the oil using ultrasonic bath and shaking the same vial. The results are presented in **Figure IV. 1. 2**, and demonstrate a significant variation in the concentration of individual components in the order of 20 to 30% (**Table IV. 1. 6**), corresponding to differences in concentration of up to 4 mg/g oil. The variation in oil composition of the samples from the top of the vial and after the oil has been homogenized is smaller, in the order of 5 to 10%, and corresponds to differences

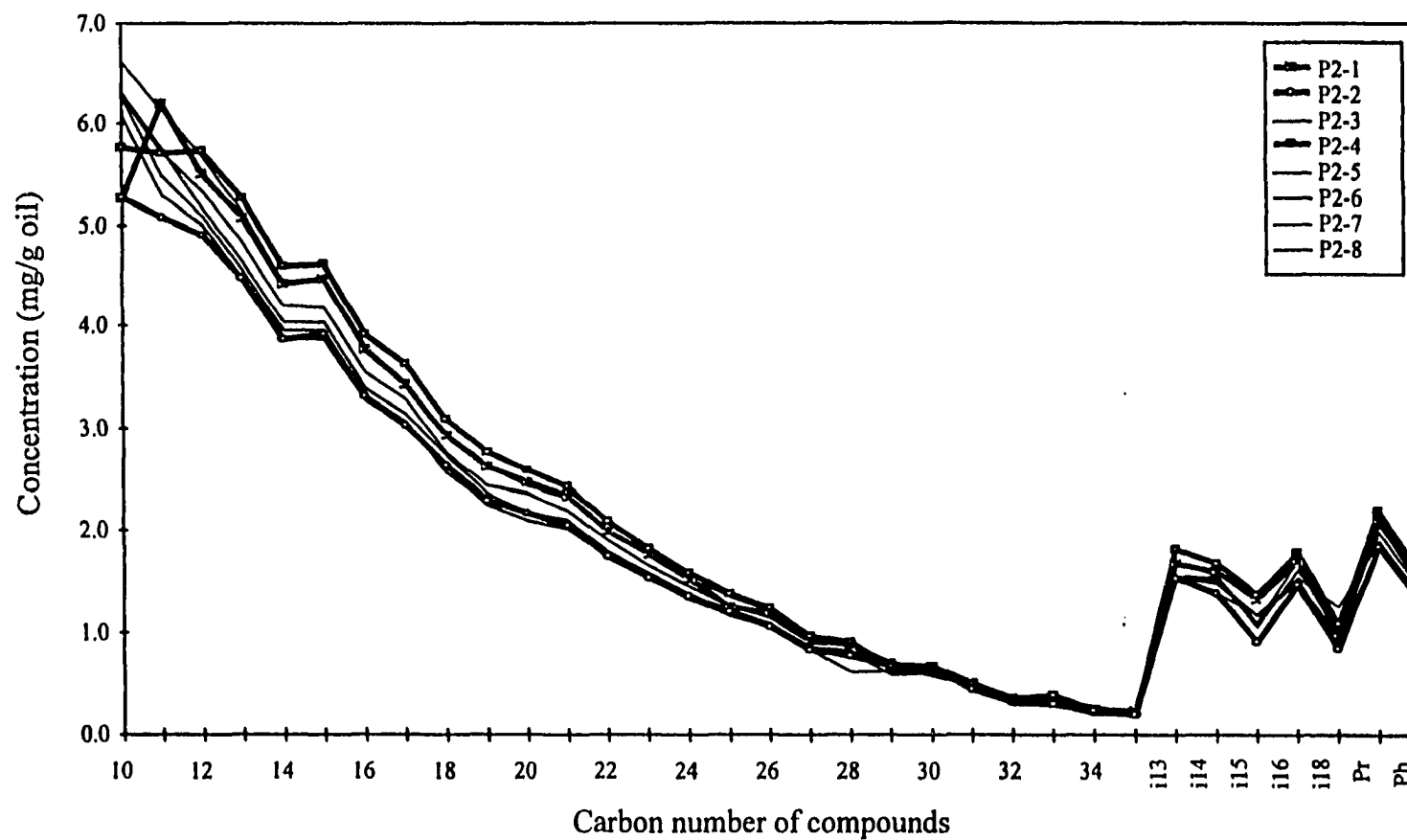


Figure IV. 1. 1 Reproducibility of well head sampling procedure. Samples collected after 1 min (P2-1), 6 min (P2-2, P2-3, P2-4), and 50 min (P2-5, P2-6, P2-7, P2-8) flowing time.

Table IV.1.5. Reproducibility of well head sampling procedure

run #	std 25	std 26	std 29	std 30	std 31	std 32	std 33	std 34	mg/g oil	mg/g oil	mg/g oil	mg/g oil	mg/g oil	mg/g oil	mg/g oil	mg/g oil	Mean	Std. Dev.	CV(%)
comp #	P2-1	P2-2	P2-3	P2-4	P2-4	P2-4	P2-7	P2-8	P2-1	P2-2	P2-3	P2-4	P2-5	P2-6	P2-7	P2-8			
10*	46858	48473	46850	43752	58395	46804	85188	87814	83	53	81	86	83	83	83	86	8.0	0.50	8.4
11	57529	47838	40847	43318	84180	45221	87128	83023	82	81	83	87	88	87	88	81	5.7	0.38	6.7
12	91142	45982	38421	43552	48874	42218	82982	48700	88	49	80	87	82	83	81	87	5.3	0.31	5.9
13	47088	41888	34382	38988	43728	38220	47431	44817	81	45	45	83	48	48	48	81	4.8	0.31	6.5
14	40988	38181	29878	34881	38028	33183	41083	38834	44	38	38	48	40	42	40	44	4.2	0.29	6.8
15	41441	38888	29833	35070	37855	33043	41080	38878	48	39	39	48	40	42	40	48	4.2	0.29	6.9
16	34985	31072	25140	29888	31888	28050	34813	32884	38	33	33	38	34	38	33	37	3.5	0.24	6.8
17	31814	28400	23278	27534	29804	28018	31880	30183	34	38	38	38	31	33	31	38	3.3	0.23	6.9
18	27182	24858	20078	23472	29858	21731	28583	25742	28	28	28	31	27	28	28	28	2.8	0.19	6.6
19	24305	21488	17182	20837	22181	18178	23522	22847	28	23	22	28	24	24	23	28	2.4	0.19	7.9
20	22832	20318	18080	18802	20422	18888	22807	21183	28	22	21	28	22	24	22	24	2.3	0.18	7.6
21	21841	18182	15428	18354	18770	17335	21354	20288	23	20	20	24	21	22	21	23	2.2	0.15	7.1
22	18480	18347	13241	15880	18820	18841	18428	17538	20	17	17	21	18	18	18	20	1.9	0.14	7.4
23	18348	14380	11874	13808	14831	13888	18373	15258	18	18	18	18	18	17	18	17	1.8	0.11	6.9
24	14103	12873	10188	11888	12828	11481	13882	13251	18	14	13	18	14	15	13	18	1.4	0.10	6.7
25	11583	11245	8811	10454	11388	9887	12225	11788	12	12	12	14	12	13	12	13	1.2	0.08	6.3
26	10877	9800	8103	8383	10287	9011	11018	10518	12	11	11	12	11	11	11	12	1.1	0.07	6.3
27	8484	7788	8380	7301	8108	7078	8701	8322	08	08	08	10	08	08	08	10	0.9	0.05	6.0
28	8138	7218	4722	6888	7743	8888	8258	7848	08	08	08	08	08	08	08	08	0.8	0.10	11.8
29	8428	8318	4788	8078	8282	8225	8114	8088	07	07	08	07	07	07	08	07	0.7	0.04	5.4
30	8181	8028	4753	8045	8451	8000	8282	8843	07	08	08	07	08	08	08	07	0.6	0.03	5.1
31	4848	4124	3471	2781	4543	3871	4708	4344	08	04	08	08	08	08	08	08	0.5	0.02	5.1
32	3148	2837	2487	2877	3134	2828	3080	3104	03	03	03	04	03	03	03	04	0.3	0.02	6.0
33	2828	2788	2208	2802	2853	2888	2818	2843	03	03	03	04	03	03	03	03	0.3	0.03	10.8
34	2247	2030	1774	1754	2218	1810	2502	2408	02	02	02	02	02	02	02	03	0.2	0.02	7.1
35	2137	1882	1437	1471	1843	1820	1778	1828	02	03	02	02	02	02	02	02	0.2	0.02	11.4
113	15558	14388	11758	13788	14582	12257	18030	14887	17	15	15	18	15	18	18	17	1.6	0.11	6.6
114	14822	13001	11801	12783	13648	12188	14458	13588	18	14	18	17	18	18	14	18	1.5	0.10	6.6
115	12338	8558	8928	10433	11088	8382	12250	8818	13	08	12	14	12	11	12	11	1.2	0.15	12.6
116	15808	13800	11478	13581	14511	12788	15803	14837	17	15	15	18	18	18	18	17	1.8	0.12	7.3
118	9034	7807	7285	8241	11818	8822	9354	8480	10	08	10	11	13	11	08	10	1.0	0.13	12.9
Pr	18457	17312	14118	18870	17888	18718	18420	18308	21	18	18	22	18	20	19	21	2.0	0.14	8.9
Ph	13882	12417	10288	12018	12858	11335	14122	13350	18	13	13	18	14	14	14	15	1.4	0.10	6.8
STD**	30848	31258	25584	25308	31358	28328	34852	28105											

* Carbon number of n-alkanes and isoprenoids

** Area of internal standard

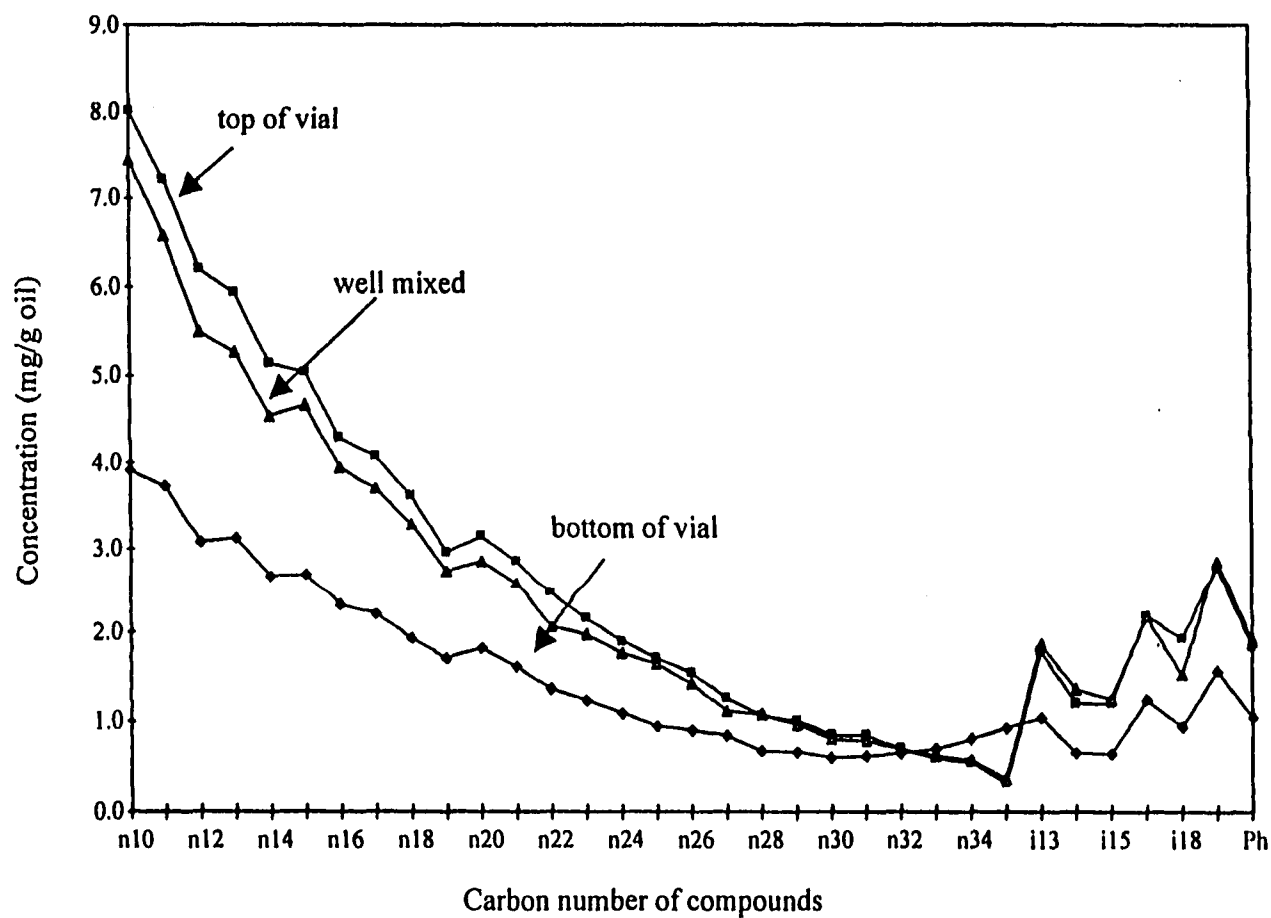


Figure IV.1.2. Test results on oil compositional heterogeneity in a sample vial.

Table IV.1.6. Test of the oil composition heterogeneity in a sample vial

Compound	mg/g oil #402 bottom of vial	mg/g oil #400 top of vial	mg/g oil #411 well mixed	mean (3 samp)	std dev (3 samp)	CV(%) (3 samp)	mean 400,411	std. dev. 400,411	CV. (%) 400,411
n10	3.9	8.0	7.4	6.5	2.2	34.4	7.72	0.41	5.26
n11	3.7	7.2	6.6	5.8	1.8	31.7	6.89	0.45	6.56
n12	3.1	6.2	5.5	4.9	1.6	33.2	5.85	0.30	8.54
n13	3.1	5.9	5.3	4.8	1.5	30.7	5.60	0.47	8.36
n14	2.7	5.1	4.5	4.1	1.3	31.0	4.84	0.42	8.76
n15	2.7	5.0	4.7	4.1	1.3	30.4	4.85	0.27	5.51
n16	2.3	4.3	3.9	3.5	1.1	29.9	4.11	0.24	5.92
n17	2.2	4.1	3.7	3.3	1.0	29.6	3.89	0.26	6.75
n18	1.9	3.6	3.3	2.9	0.9	30.4	3.45	0.23	6.63
n19	1.7	3.0	2.7	2.5	0.7	27.1	2.85	0.16	5.49
n20	1.8	3.1	2.9	2.6	0.7	26.7	3.00	0.21	6.86
n21	1.6	2.9	2.6	2.4	0.7	27.9	2.72	0.18	6.75
n22	1.4	2.5	2.1	2.0	0.6	28.4	2.26	0.28	12.31
n23	1.2	2.2	2.0	1.8	0.5	27.3	2.07	0.13	6.26
n24	1.1	1.9	1.8	1.6	0.4	27.2	1.83	0.09	5.09
n25	0.9	1.7	1.6	1.4	0.4	29.3	1.67	0.04	2.60
n26	0.9	1.5	1.4	1.3	0.3	26.3	1.48	0.08	5.43
n27	0.8	1.3	1.1	1.1	0.2	19.6	1.19	0.10	8.28
n28	0.7	1.1	1.1	0.9	0.2	24.2	1.07	0.02	1.42
n29	0.7	1.0	1.0	0.9	0.2	21.0	0.99	0.03	2.74
n30	0.6	0.8	0.8	0.8	0.1	17.7	0.83	0.03	3.40
n31	0.6	0.8	0.8	0.8	0.1	15.9	0.82	0.04	4.75
n32	0.7	0.7	0.7	0.7	0.0	4.0	0.70	0.00	0.43
n33	0.7	0.6	0.6	0.6	0.1	9.1	0.61	0.03	4.22
n34	0.8	0.5	0.6	0.6	0.1	22.5	0.56	0.02	3.73
n35	0.9	0.3	0.4	0.5	0.3	62.5	0.35	0.04	11.54
i13	1.0	1.8	1.9	1.6	0.5	29.2	1.83	0.06	3.26
i14	0.7	1.2	1.4	1.1	0.4	34.4	1.28	0.11	8.69
i15	0.6	1.2	1.3	1.0	0.3	32.5	1.23	0.03	2.68
i16	1.2	2.2	2.2	1.9	0.5	29.0	2.18	0.01	0.34
i18	0.9	1.9	1.5	1.5	0.5	33.6	1.73	0.29	16.55
Pr	1.6	2.8	2.9	2.4	0.7	30.1	2.82	0.06	2.04
Ph	1.1	1.8	1.9	1.6	0.5	29.6	1.87	0.05	2.63
	#402 bottom of vial	#400 top of vial	#411 well mixed	mean	std dev.	CV. (%)	mean	std. dev.	CV. (%)
sum10-20/sum21-31	2.8	3.2	3.1	3.0	0.2	7.0	3.13	0.03	0.99
sum15-20/sum21-26	1.8	1.8	1.8	1.8	0.0	2.1	1.84	0.01	0.56
sum10-15/sum16-20	1.7	1.8	1.8	1.7	0.1	4.2	1.78	0.01	0.64
sum10-15/sum21-26	1.7	1.8	1.8	1.7	0.1	4.2	1.78	0.01	0.64
n17+18+19+n27+28+29	2.7	3.2	3.1	3.0	0.3	9.3	3.14	0.09	2.97
i18+19+20/n16+17+18	0.6	0.5	0.6	0.6	0.0	2.7	0.56	0.02	3.63
Pr/Ph	1.5	1.5	1.5	1.5	0.0	0.8	1.51	0.01	0.39
Pr/n17	0.7	0.7	0.8	0.7	0.0	6.4	0.73	0.06	8.78
Ph/n18	0.5	0.5	0.6	0.5	0.0	6.6	0.54	0.05	9.27
Pr+Ph/n17+18	0.6	0.6	0.7	0.6	0.0	6.4	0.64	0.06	8.97
n31/n19	0.4	0.3	0.3	0.3	0.0	13.7	0.29	0.00	0.74
n35/19	0.5	0.1	0.1	0.3	0.2	93.8	0.12	0.02	16.98

in the concentration of individual compounds of up to 1 mg/g oil. These observations suggest, as expected, that the gravitational segregation of the oil within the sample vial results in a concentration of the higher density oil material like asphaltenes and higher molecular weight n-alkanes ($> n-C_{30}$) at the bottom of the vial which decreases the absolute amounts of C_{10} - C_{30} n-alkanes and increases the ratios consisting of higher to lower molecular weight n-alkanes (**Table IV. 1. 6** and **Figure IV. 1. 2**). These results demonstrated that significant errors can be introduced to the quantitative GC analysis as well as to the amount of precipitated wax, due to insufficient sample mixing. Based on that observation, special attention was paid to homogenizing the samples prior to analysis, and eliminating some of the data considered to be unreliable for the reasons discussed above.

To check if, and to what extent, the composition of collected oil samples change after different storage periods at 5-10°C, three experiments were performed and the results are presented in **Figure IV. 1. 3**. An oil sample collected in 9/94 was prepared (diluted in carbon disulfide) and analyzed by GC in the same month (sample oil 119). Secondly, this prepared sample was kept at 5-10°C for about an year, and analyzed again by GC in 10/95 (sample oil 394). Finally, the oil collected in 9/94 was prepared and analyzed one year later in 10/95 (sample oil 344). All samples were mixed as well as possible before the analysis. The results show that the oil analyzed soon after collection from the well head differs significantly from the other two samples, particularly in regard to the higher absolute concentration of the nC_{10} - C_{15} alkanes (up to 5 mg/g oil), which can most probably be attributed to evaporation of these relatively higher volatility

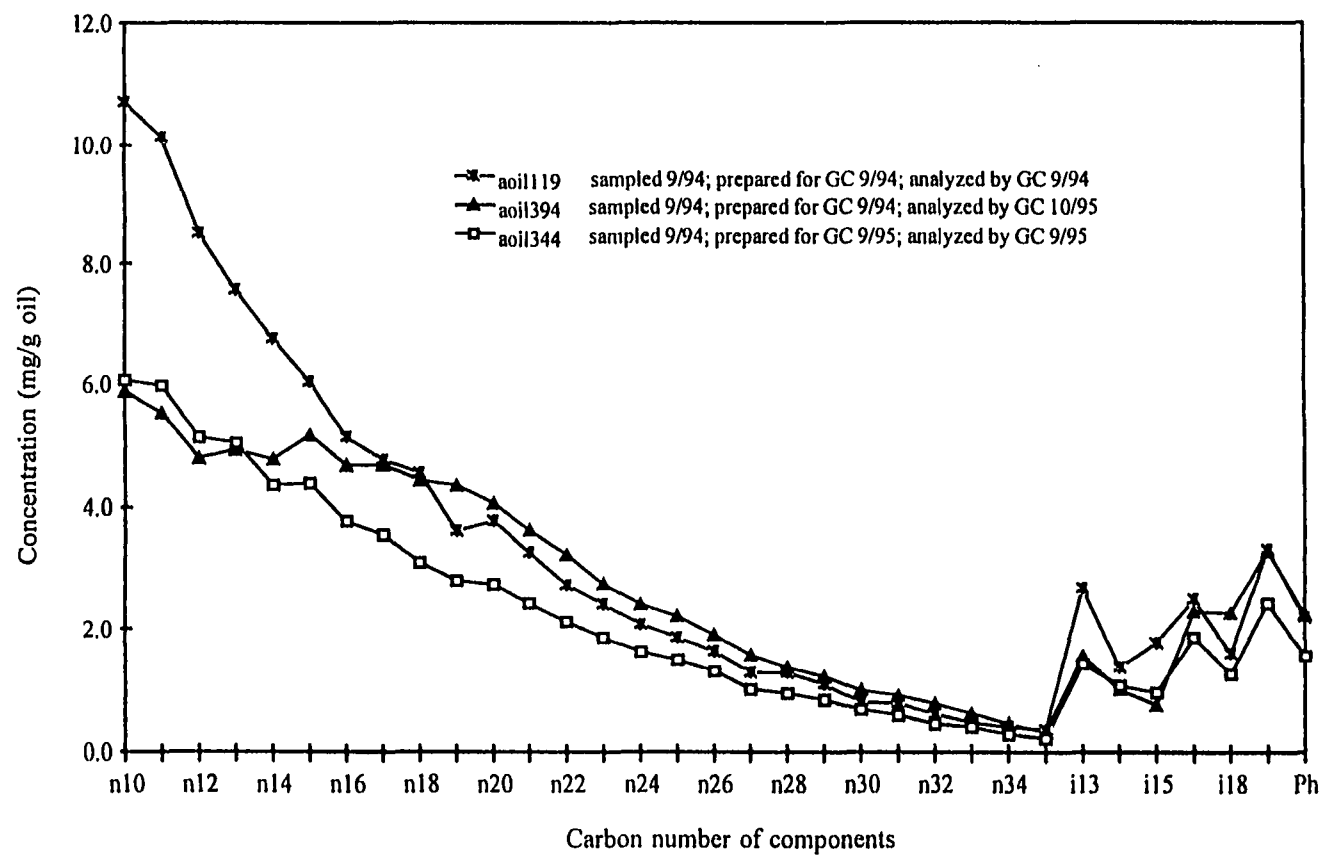


Figure IV. 1. 3. Reproducibility of GC analysis over time and the effect of evaporation (Acree1-IV).

compounds after one year of storage. These experiments demonstrated that the quantitative GC analysis should be applied as soon as possible after the sample collection, which, however, was not always possible.

In addition to the above discussed experiments designed to test the influence of different factors on compositional reproducibility of studied samples, the whole oil quantitative GC analysis was routinely checked by replicate analyses of control oil samples every 10 to 15 runs. The results of these control sample analyses showed variations up to 5% (**Figure IV. 1. 4**). Other studies have reported coefficients of variation of 11.4% and 20% for the nC_{15} relative concentrations and of 13.9% and 10% for pristane/phytane ratio in condensates and oils, respectively (Curiale and Bromley, 1996). The good reproducibility of our results reflects good reproducibility in instrument performance and injection technique.

Wax precipitation. As described in Chapter II, two techniques for wax precipitation have been compared - the “acetone” technique (Burger *et al.*, 1981), and the “DCM” technique (Bishop, 1994) developed for targeting precipitation of HMW n-alkanes. Two different oils were used in these experiments as discussed in Chapter II.

Wax yields and composition of wax fractions. The reproducibility of injection in HTGC was evaluated qualitatively by running the same sample three times (**Figure IV. 1. 5**). The reproducibility results of wax precipitation experiments from the two oils by the acetone and DCM techniques are presented in **Figures IV. 1. 6, IV. 1. 7 and IV. 1. 8**. The results demonstrate a consistency in the n-alkane distribution of the waxes precipitated by the acetone technique for both oils. The coefficients of variation in the wax yields

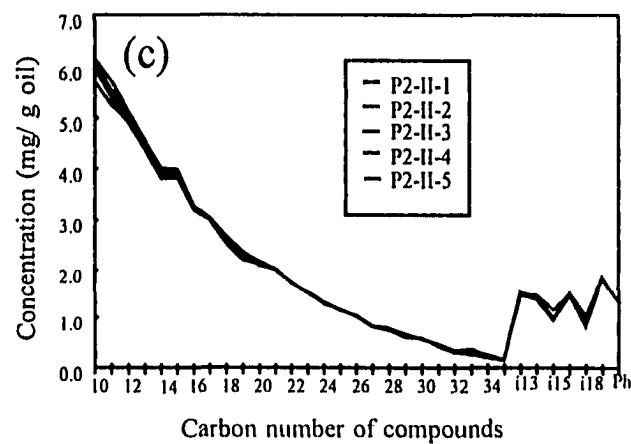
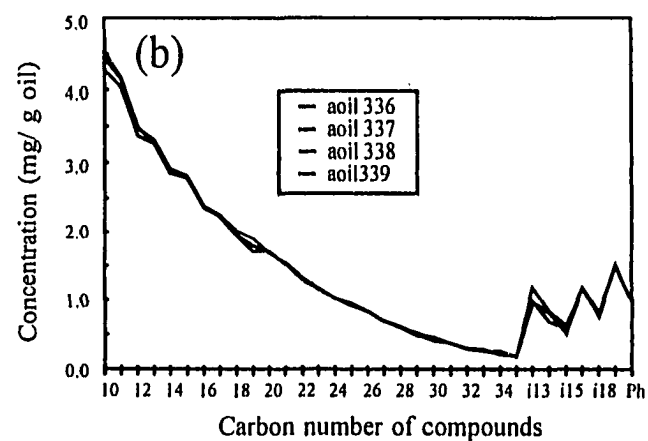
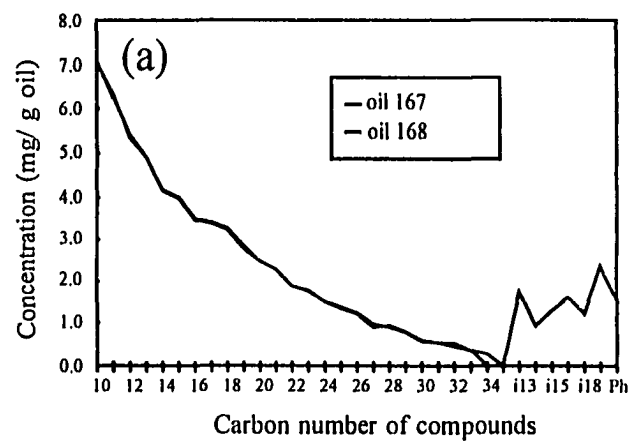


Figure IV. 1. 4 Examples of GC analysis reproducibility as checked in (a) 9/94; (b) 8/95; and (c) 9/98.

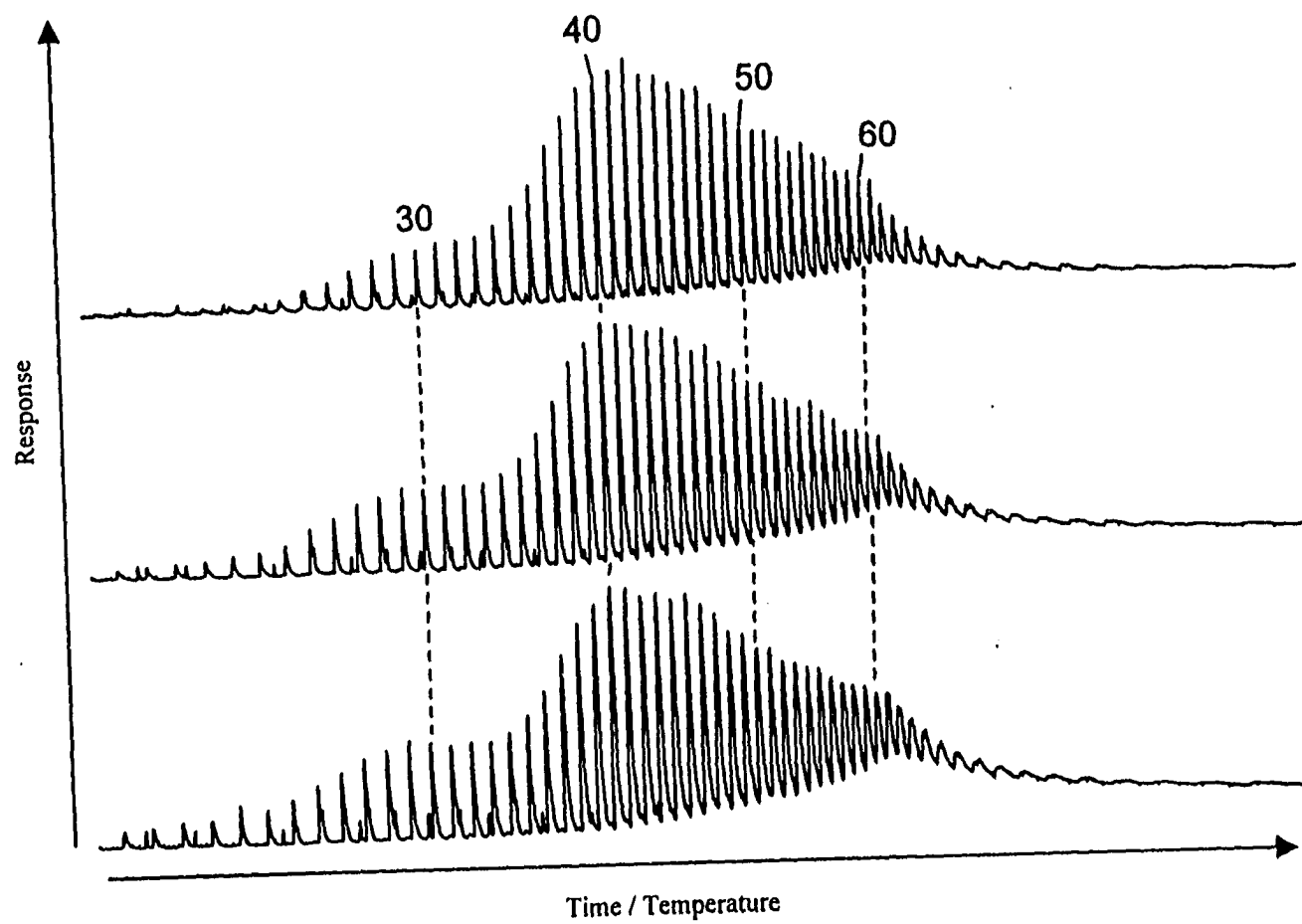


Figure IV.1.5 Reproducibility of HTGC injection technique, Uinta oil.

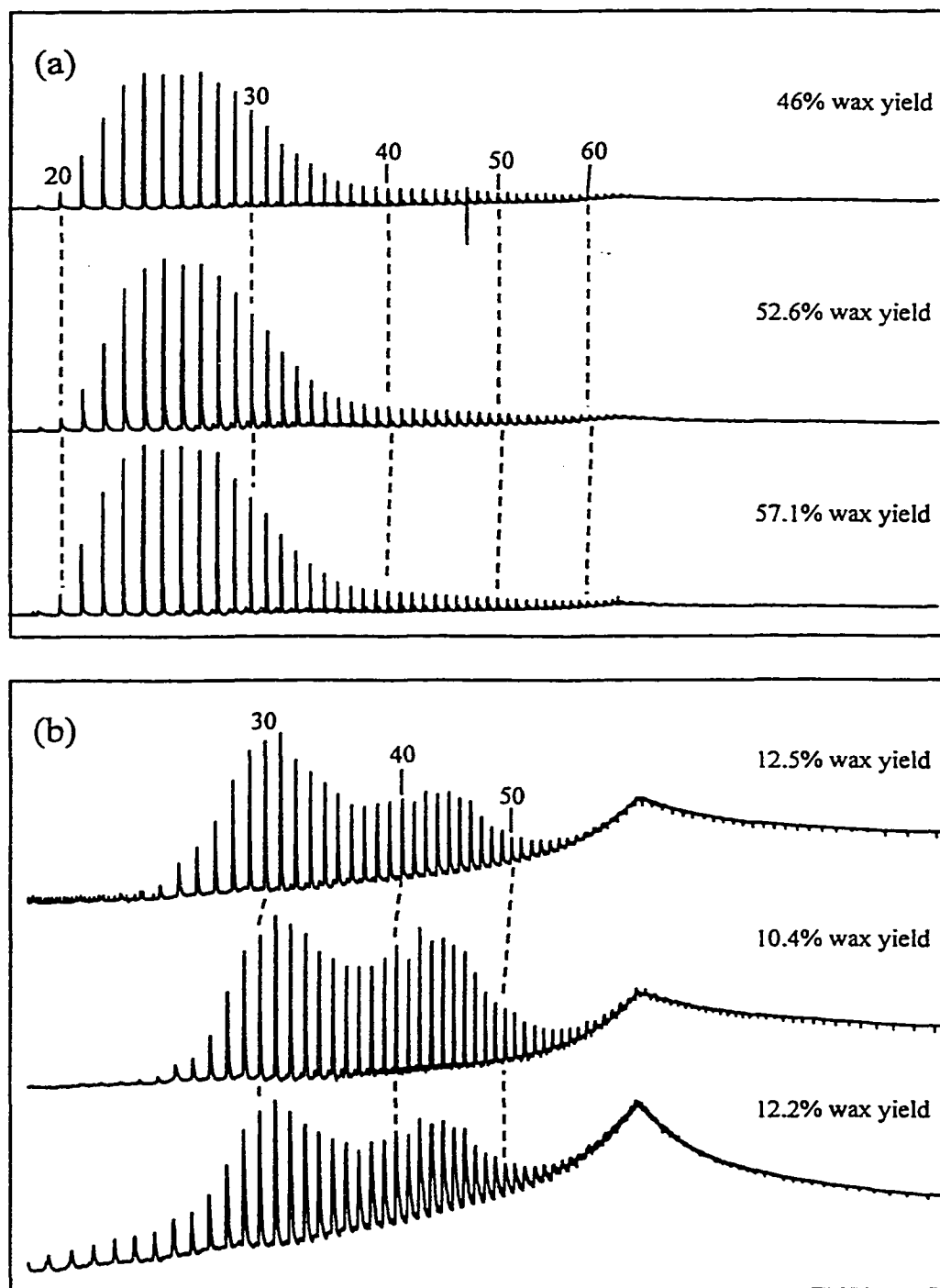


Figure IV. 1. 6 Reproducibility in composition of wax precipitates obtained by the acetone technique from (a) Uinta oil and (b) Prairie Gem oil.

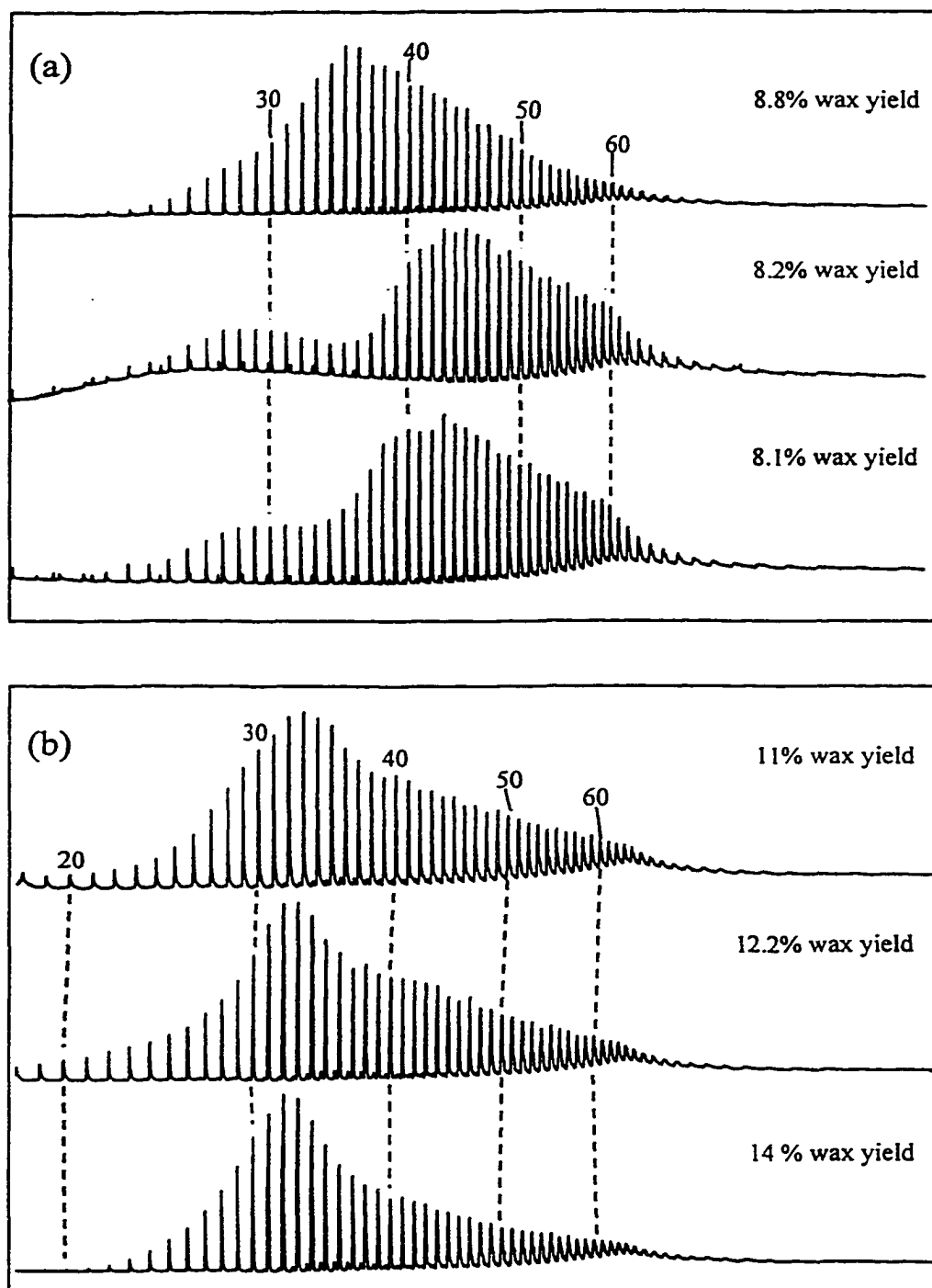


Figure IV. 1. 7. Reproducibility in composition of wax precipitates obtained by the DCM technique from Uinta oil using different initial amounts of oil for precipitation (a) 100 mg oil, 0.3 wt% oil concentration; (b) 3 g oil, 1 wt % oil concentration.

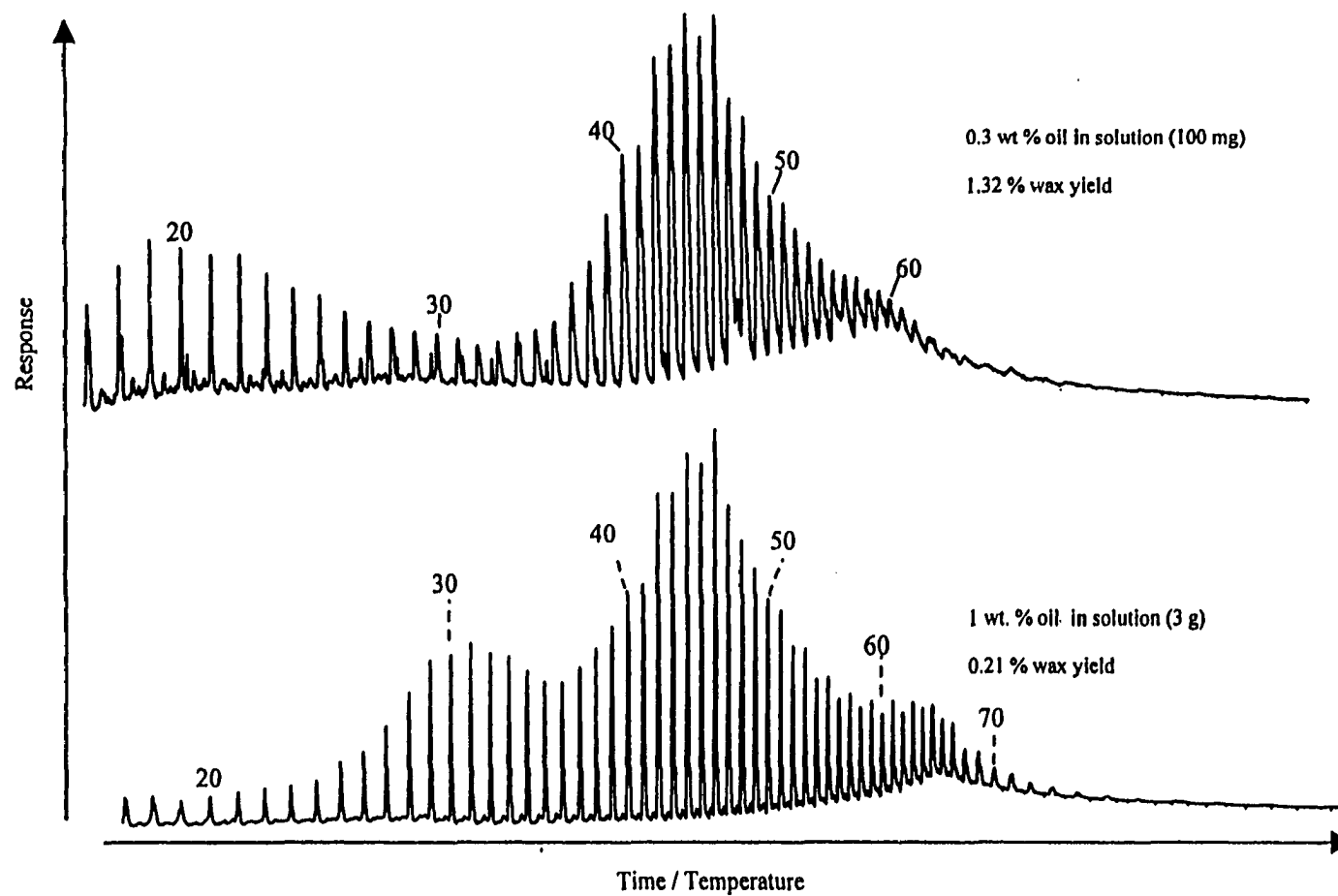


Figure IV.1.8. HTGC of wax fractions obtained by the DCM technique with different initial oil concentrations in the solution for wax precipitation, Prairie Gem oil (Green A2-1).

obtained from the Uinta oil and Prairie Gem oil are 10.8 % and 9.7 %, respectively. The waxes precipitated from the Uinta oil by the DCM technique showed inconsistency in the compositional reproducibility experiments even though the coefficient of variation in the wax yields was lower (5%). An increase in the initial amount of oil from 100 mg to 3 g corresponding to an increased oil concentration in the solvent for precipitation from 0.3 wt.% to 1 wt.% resulted in an improved compositional reproducibility of the waxes precipitated by the DCM technique (**Figure IV. 1. 7**). Related to that, the filtration step of the procedure was modified accordingly to use a porcelain funnel with a fixed perforated plate and 1.5 μm filter (**Table II. 3**). The coefficient of variation in the wax yields under the modified conditions of the technique was 12%. An improvement in the composition of the wax precipitated by the DCM technique with increased oil concentration was observed also for the Prairie Gem oil (**Figure IV. 1. 8**).

Quantitative HTGC analysis results. The reproducibility results of quantitative HTGC analysis of waxes precipitated by both techniques for the Uinta and Prairie Gem oils are presented in **Figure IV. 1. 9** and **Table IV. 1. 7**. The coefficients of variation for the majority of the n-alkanes in the wax fractions are below 5-6% which can be regarded as a good reproducibility (Conder and Young, 1979; Ludwig, 1995). The imprecision of individual n-alkane concentration measurements increases when the compounds are present in low abundance which causes errors in the peak area estimations. Two additional factors contribute to increase the imprecision in the higher molecular region - possible co-elution between n-alkanes and branched/cyclic alkanes (Ludwig, 1995), and a decreasing response on the high temperature gas chromatograms (Thomson and Rynaski,

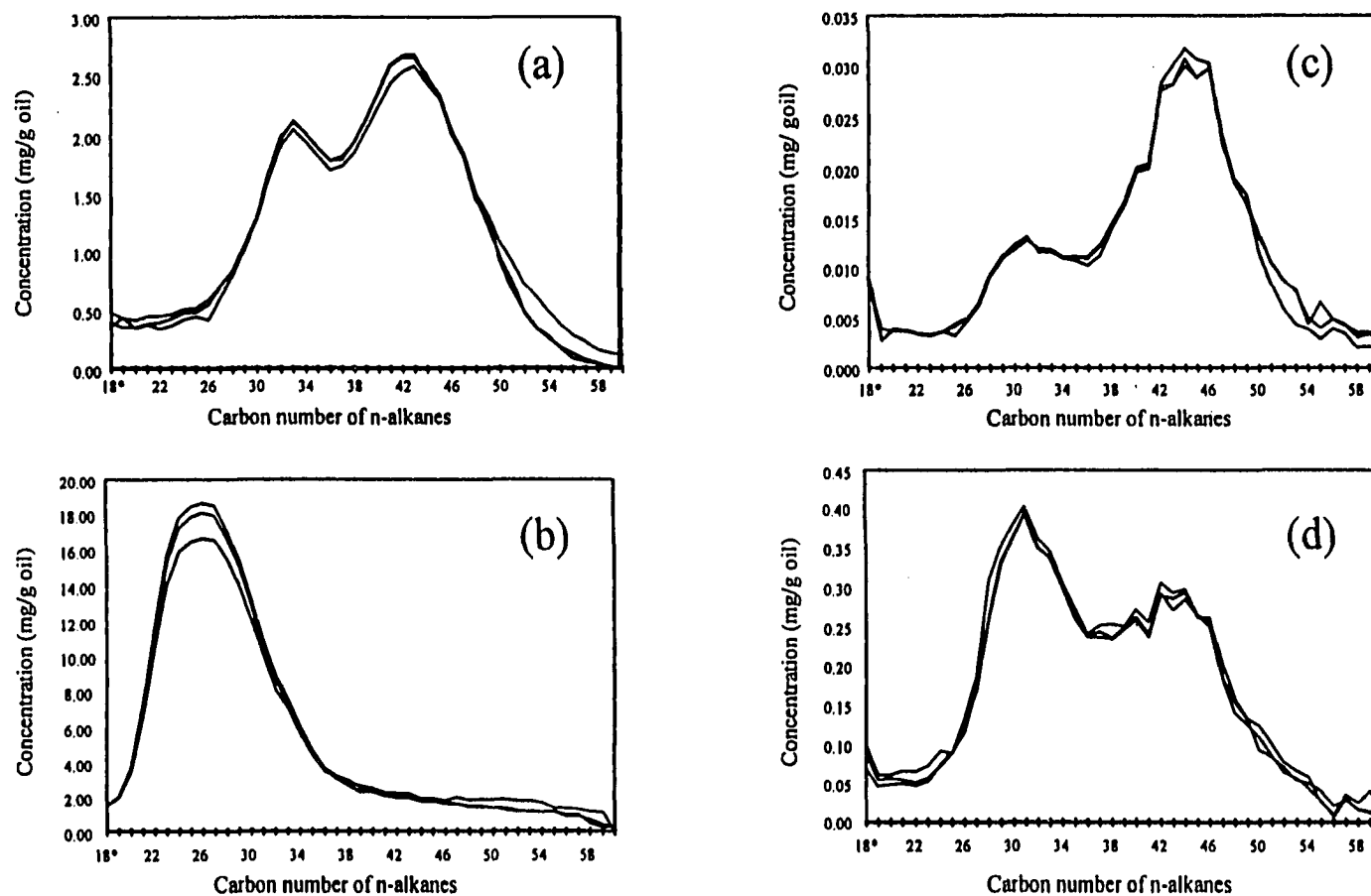


Figure IV. 1. 9. Quantitative HTGC reproducibility results (3 runs for each sample) for wax fractions precipitated from Uinta oil by the DCM (a) and acetone (b) techniques, and from Prairie Gem oil by the DCM (c) and acetone (d) techniques.

Table IV.1.7. Reproducibility of HTGC analysis of wax fractions obtained by the acetone and DCM techniques for Uinta and Prairie Gem oils (3 runs for each sample).

Uilta oil				P.Gem oil				Uilta oil				P.Gem oil				
Concentration area								mg/g wax								
samp.#	45A wax	51 wax	54 wax	56 wax	45A wax	51 wax	54 wax	56 wax	45A wax	51 wax	54 wax	56 wax	45A wax	51 wax	54 wax	56 wax
18 ^a	12259	12338	16537	16524	12153	11552	3736	3339	3318	28383	21368	29741	2.86	2.97	2.96	4.01
19	16277	16035	21727	14919	11123	13758	2355	2095	2217	9620	10357	9223	3.80	3.86	3.89	3.62
20	28696	29192	39930	14259	11159	10752	2330	2173	2321	12847	9690	12810	6.70	7.03	7.14	3.46
21	54250	56256	77421	15365	12026	11821	2515	2102	2374	12891	9794	11989	12.66	13.55	13.85	3.73
22	87013	90546	125827	15488	12322	10668	2482	1968	2237	11704	9074	10878	20.30	21.81	22.51	3.76
23	115123	120901	167654	16090	13458	11691	2770	2205	2522	11400	8770	10436	26.86	29.12	29.99	3.91
24	129897	135809	188534	17548	14892	13266	3475	2779	3560	12306	9486	11838	30.31	32.71	33.73	4.26
25	134143	140694	195353	17922	15046	13953	3365	3395	4335	15172	11024	10589	31.30	33.88	34.95	4.35
26	135882	142510	197780	20344	17098	13194	4991	4680	5474	17020	13147	15008	31.70	34.32	35.38	4.94
27	134874	141186	196345	24016	21451	18913	6922	6341	8275	22398	17172	20487	31.47	34.00	35.12	5.83
28	126195	131438	181433	28349	25679	24450	11565	9844	12307	31985	24105	29895	29.44	31.65	32.46	6.88
29	114336	118647	163942	34991	32262	31270	13119	12401	15678	38190	28854	35873	26.68	28.57	29.33	8.49
30	98544	101722	139583	43737	40181	39993	14081	13629	17052	40735	30922	40135	22.99	24.50	24.97	10.62
31	82085	83945	115278	55407	51163	51932	14925	14713	18421	43566	33698	42703	19.15	20.22	20.62	13.45
32	66176	68021	94086	65320	60746	61591	13518	13151	16491	40369	31283	37382	15.44	16.38	16.83	16.36
33	57828	57880	80083	69595	65307	65285	12865	12677	15802	39414	31010	37419	13.49	13.94	14.33	16.89
34	45990	46010	64126	66314	62098	62446	11391	11293	14036	37103	29208	35478	10.73	11.08	11.47	16.09
35	36407	35680	50400	62171	58547	58882	10210	9812	12508	37792	28788	34710	8.49	8.59	9.02	15.09
36	28727	28820	39250	58139	55083	55403	8987	8926	11164	36828	29308	33301	6.70	6.94	7.02	14.11
37	26339	24349	34657	59362	56218	55718	9400	8932	11437	41064	32548	36205	6.15	5.86	6.20	14.41
38	23264	20764	31589	63026	59764	60309	9458	8840	11105	49980	38063	45930	5.43	5.00	5.65	15.30
39	21705	18089	27083	69755	65751	66503	9344	9301	11701	57536	44042	53266	5.06	4.36	4.84	16.93
40	20419	18428	25330	76409	72622	73424	10173	9787	12357	68638	52285	64136	4.76	4.44	4.53	18.54
41	18619	16469	22875	82722	79174	80122	9570	8952	11346	69977	53159	65139	4.34	3.97	4.09	20.08
42	18235	15580	22149	85769	81435	82394	11403	11023	13606	95495	72862	92034	4.25	3.75	3.96	20.82
43	17991	15549	21433	87565	81426	82662	10932	10269	13446	96101	74591	97926	4.20	3.74	3.83	21.25
44	16065	13928	19074	82383	76873	76300	11089	10751	13763	104602	79230	103260	3.75	3.35	3.41	19.99
45	15982	14301	18746	78364	71489	72471	9913	9987	12340	98435	76460	99941	3.73	3.44	3.35	19.02
46	14734	12700	18146	69674	62078	62820	9615	9422	12293	101260	78795	98593	3.44	3.06	3.25	16.91
47	16325	12775	17403	62805	55984	56800	7501	6868	8655	79402	60152	73152	3.81	3.08	3.11	15.24
48	15096	11431	16058	51276	44667	45560	5901	5323	7239	64400	49255	62118	3.52	2.75	2.87	12.44
49	15570	11453	15740	44802	40388	38089	5022	4771	6249	56070	43945	56975	3.63	2.76	2.82	10.87
50	15431	11422	15029	36573	28501	29378	4662	4165	4474	44373	35826	37693	3.60	2.75	2.69	8.88
51	15483	10016	14610	31083	20614	23231	3778	3286	3982	36229	27699	27317	3.61	2.41	2.61	7.54
52	14789	9039	12719	24876	15169	14713	2937	2480	3381	29954	23053	19212	3.45	2.18	2.28	6.04
53	14926	9258	12232	20860	10881	10560	2507	2175	3566	25790	20442	14063	3.48	2.23	2.19	5.06
54	13763	8937	11702	16690	8728	8014	2217	1678	2378	17231	11662	12549	3.21	2.15	2.09	4.05
55	11483	8917	12410	12783	5386	5914	980	1072	1946	13753	17419	9551	2.68	2.15	2.22	3.10
56	11130	6757	10355	9815	2856	4163	382	283	1036	16638	13052	12729	2.60	1.63	1.85	2.38
57	10536	6914	10437	8119	2045	2687	1324	1189	1379	14730	11691	11290	2.46	1.67	1.87	1.97
58	9433	5292	5488	5773	1550	1628	957	614	809	10670	9393	6944	2.20	1.27	0.98	1.40
59	8948	3245	2374	4802	766	635	1528	453	613	11594	9424	7145	2.09	0.78	0.42	1.17
60		1871	2950	4115	330	589	670	181	279	10182	8403	6417	0.00	0.45	0.53	1.00
STD**	30539	29585	39828	29357	26624	26747	27530	27814	34668	62729	48632	59880				

* Carbon number of n-alkanes; ** Area of internal standard

Table IV.1.7 (continue)

Concentration	Ums oil	Ums oil	Ums oil				Ums oil	Ums oil	Ums oil				P.Osm oil	P.Osm oil	P.Osm oil				P.Osm oil	P.Osm oil	P.Osm oil					
run #	mg/g oil	mg/g oil	mg/g oil	mean	std. dev.	CV(%)	mg/g oil	mg/g oil	mg/g oil	mean	std. dev.	CV(%)	mg/g oil	mg/g oil	mg/g oil	mean	std. dev.	CV(%)	mg/g oil	mg/g oil	mg/g oil	mean	std. dev.	CV(%)		
comp. #	41A wss	41A wss	41A wss				51 wss	51 wss	51 wss				54 wss	54 wss	54 wss				54 wss	54 wss	54 wss					
18	1.51	1.54	1.56	1.54	0.03	2.00	0.49	0.40	0.38	0.42	0.06	14.39	0.10	0.09	0.07	0.09	0.02	17.33	0.008	0.008	0.009	0.009	0.009	3.13E-04	6.5	
19	3.00	3.03	3.05	3.03	0.02	1.30	0.44	0.36	0.43	0.43	0.05	11.36	0.06	0.06	0.05	0.06	0.01	14.41	0.003	0.004	0.003	0.003	0.003	6.30E-04	19.7	
20	3.57	3.70	3.76	3.64	0.13	3.33	0.43	0.34	0.35	0.38	0.04	10.15	0.06	0.06	0.05	0.06	0.01	11.68	0.004	0.004	0.004	0.004	0.004	1.34E-04	3.6	
21	6.66	7.13	7.29	7.03	0.33	4.61	0.45	0.39	0.38	0.41	0.04	9.41	0.07	0.06	0.05	0.06	0.01	14.92	0.004	0.004	0.004	0.004	0.004	5.11E-05	1.4	
22	10.66	11.40	11.83	11.34	0.39	3.24	0.46	0.40	0.35	0.40	0.06	13.90	0.07	0.05	0.05	0.06	0.01	17.79	0.003	0.003	0.003	0.003	0.003	5.23E-05	1.5	
23	14.14	15.32	15.79	15.08	0.51	3.64	0.48	0.44	0.38	0.43	0.05	11.77	0.07	0.06	0.05	0.06	0.01	17.31	0.003	0.003	0.003	0.003	0.003	7.29E-05	2.1	
24	13.95	17.21	17.75	16.97	0.92	3.43	0.32	0.49	0.43	0.48	0.04	9.33	0.09	0.07	0.08	0.08	0.01	13.19	0.004	0.004	0.004	0.004	0.004	2.44E-05	0.7	
25	16.47	17.83	18.39	17.57	0.99	3.63	0.33	0.49	0.43	0.49	0.04	7.83	0.09	0.09	0.09	0.09	0.00	1.36	0.004	0.004	0.003	0.004	0.004	6.26E-04	13.8	
26	16.09	18.06	18.63	17.79	1.00	3.60	0.60	0.56	0.43	0.53	0.09	17.05	0.13	0.12	0.13	0.01	6.93	0.005	0.003	0.003	0.003	0.003	3.15E-04	4.4		
27	16.36	17.90	18.49	17.63	0.99	3.39	0.71	0.70	0.61	0.68	0.05	7.93	0.19	0.17	0.18	0.01	4.91	0.007	0.007	0.006	0.006	0.006	1.42E-04	3.2		
28	15.30	16.66	17.08	16.41	0.82	3.01	0.84	0.84	0.79	0.82	0.05	3.18	0.31	0.26	0.26	0.28	0.03	18.07	0.009	0.009	0.009	0.009	0.009	1.34E-04	1.5	
29	14.04	15.04	15.44	14.84	0.72	4.93	1.04	1.03	1.02	1.03	0.02	1.79	0.35	0.33	0.33	0.34	0.34	0.01	2.33	0.011	0.011	0.011	0.011	0.011	1.44E-04	1.3
30	12.10	12.99	13.14	12.71	0.54	4.78	1.29	1.31	1.30	1.30	0.01	0.67	0.38	0.36	0.37	0.37	0.37	0.01	2.39	0.012	0.012	0.012	0.012	0.012	3.19E-04	2.7
31	10.00	10.64	10.63	10.32	0.40	3.90	1.64	1.67	1.69	1.67	0.02	1.43	0.40	0.39	0.39	0.40	0.01	1.51	0.013	0.013	0.013	0.013	0.013	2.07E-04	1.6	
32	8.13	8.63	8.86	8.54	0.37	4.38	1.93	1.98	2.00	1.97	0.04	1.83	0.36	0.35	0.35	0.36	0.01	2.04	0.012	0.012	0.012	0.012	0.012	2.01E-04	1.7	
33	7.10	7.34	7.54	7.33	0.23	3.00	2.06	2.13	2.13	2.10	0.04	1.83	0.35	0.34	0.34	0.34	0.00	1.43	0.012	0.012	0.012	0.012	0.012	1.21E-04	1.0	
34	5.65	5.83	6.04	5.84	0.20	3.33	1.96	2.03	2.03	2.01	0.04	1.87	0.31	0.30	0.30	0.30	0.00	1.19	0.011	0.011	0.011	0.011	0.011	9.30E-05	0.8	
35	4.47	4.51	4.73	4.58	0.15	3.19	1.84	1.91	1.91	1.89	0.04	2.19	0.28	0.26	0.26	0.27	0.01	2.51	0.011	0.011	0.011	0.011	0.011	2.10E-04	1.9	
36	3.33	3.63	3.70	3.63	0.09	3.41	1.72	1.80	1.80	1.77	0.03	2.54	0.24	0.24	0.24	0.24	0.00	0.90	0.011	0.011	0.011	0.011	0.011	4.34E-04	4.1	
37	3.24	3.09	3.26	3.20	0.10	3.99	1.76	1.83	1.81	1.80	0.04	2.31	0.23	0.24	0.24	0.24	0.25	0.01	3.00	0.012	0.012	0.012	0.012	0.012	6.34E-04	5.5
38	3.06	2.63	2.97	2.82	0.17	4.17	1.87	1.95	1.96	1.93	0.05	2.69	0.23	0.24	0.24	0.24	0.24	0.01	4.34	0.013	0.014	0.014	0.014	0.014	2.74E-04	1.9
39	2.67	3.29	3.35	3.30	0.19	7.63	2.06	2.13	2.16	2.13	0.05	2.43	0.25	0.25	0.25	0.25	0.25	0.00	0.73	0.017	0.017	0.016	0.017	0.017	2.56E-04	1.1
40	2.51	3.34	3.38	3.41	0.09	3.67	2.26	2.37	2.39	2.34	0.07	2.88	0.27	0.26	0.26	0.26	0.27	0.01	2.53	0.020	0.020	0.020	0.020	0.020	2.37E-04	1.1
41	2.29	3.09	3.15	3.18	0.10	4.63	2.43	2.58	2.60	2.55	0.08	3.31	0.26	0.24	0.24	0.23	0.01	4.09	0.021	0.020	0.020	0.020	0.020	2.60E-04	1.3	
42	2.24	1.97	2.09	2.10	0.13	6.32	3.34	2.66	2.68	2.62	0.07	2.85	0.31	0.29	0.29	0.30	0.01	2.89	0.022	0.022	0.022	0.022	0.022	3.60E-04	1.3	
43	2.21	1.97	2.02	2.07	0.15	6.11	2.59	2.66	2.69	2.64	0.05	1.82	0.29	0.27	0.29	0.29	0.01	2.69	0.028	0.028	0.030	0.029	0.029	1.09E-03	3.6	
44	1.97	1.77	1.80	1.84	0.11	6.07	3.44	2.51	2.48	2.48	0.04	1.43	0.30	0.29	0.29	0.29	0.01	2.06	0.031	0.030	0.032	0.031	0.031	8.91E-04	2.9	
45	1.96	1.81	1.77	1.83	0.10	3.38	2.32	2.33	2.33	2.34	0.02	0.75	0.27	0.27	0.26	0.27	0.00	0.60	0.029	0.029	0.029	0.031	0.030	1.03E-03	2.3	
46	1.81	1.61	1.71	1.71	0.10	3.84	2.06	2.03	2.04	2.04	0.03	0.89	0.26	0.25	0.26	0.26	0.01	2.33	0.030	0.030	0.030	0.030	0.030	3.16E-04	1.1	
47	2.00	1.62	1.64	1.72	0.22	12.38	1.86	1.83	1.83	1.84	0.02	0.86	0.30	0.18	0.19	0.19	0.01	5.47	0.023	0.023	0.022	0.023	0.023	4.13E-04	1.0	
48	1.83	1.43	1.31	1.46	0.22	13.57	1.52	1.46	1.46	1.49	0.03	2.04	0.16	0.14	0.15	0.15	0.01	3.85	0.019	0.019	0.019	0.019	0.019	2.37E-04	1.2	
49	1.91	1.43	1.40	1.43	0.26	15.94	1.33	1.33	1.34	1.29	0.03	3.79	0.14	0.13	0.13	0.13	0.00	3.24	0.016	0.017	0.018	0.017	0.017	5.68E-04	3.4	
50	3.09	4.43	4.43	4.39	0.27	16.90	1.00	0.93	0.93	0.99	0.06	0.38	0.13	0.11	0.10	0.11	0.01	13.49	0.013	0.014	0.012	0.013	0.013	1.07E-03	8.0	
51	1.90	1.37	1.38	1.32	0.24	22.33	0.93	0.67	0.73	0.70	0.13	16.09	0.10	0.09	0.09	0.09	0.01	9.79	0.011	0.010	0.008	0.010	0.010	1.33E-03	12.7	
52	1.83	1.15	1.20	1.39	0.37	26.90	0.74	0.50	0.48	0.57	0.14	33.35	0.08	0.07	0.07	0.07	0.01	8.96	0.009	0.009	0.006	0.008	0.008	1.63E-03	21.1	
53	1.83	1.17	1.13	1.39	0.39	27.93	0.63	0.36	0.34	0.44	0.16	33.35	0.07	0.06	0.05	0.06	0.01	10.96	0.008	0.008	0.004	0.007	0.007	1.93E-03	29.4	
54	1.69	1.13	1.10	1.31	0.33	35.30	0.49	0.28	0.26	0.35	0.13	37.07	0.06	0.04	0.03	0.03	0.01	14.53	0.003	0.004	0.004	0.004	0.004	6.00E-04	13.3	
55	1.41	1.13	1.17	1.24	0.15	12.27	0.38	0.18	0.19	0.23	0.13	45.24	0.03	0.03	0.04	0.03	0.01	33.57	0.004	0.007	0.003	0.003	0.003	1.88E-03	41.5	
56	1.37	0.86	0.87	1.07	0.27	21.85	0.29	0.09	0.14	0.17	0.10	64.00	0.01	0.01	0.02	0.01	0.01	58.27	0.003	0.003	0.004	0.003	0.004	3.77E-04	12.6	
57	1.29	0.86	0.90	1.05	0.22	20.64	0.24	0.07	0.09	0.13	0.09	72.15	0.04	0.03	0.03	0.03	0.00	9.68	0.004	0.004	0.003	0.004	0.004	2.44E-04	12.9	
58	1.16	0.67	0.53	0.70	0.33	43.83	0.17	0.03	0.03	0.09	0.07	75.32	0.03	0.02	0.02	0.02	0.01	26.15	0.003	0.004	0.002	0.003	0.003	7.30E-04	24.8	
59	1.10	0.41	0.32	0.58	0.46	79.74	0.14	0.02	0.02	0.06	0.07	110.12	0.04	0.01	0.01	0.02	0.02	74.60	0.003	0.004	0.002	0.003	0.003	7.49E-04	24.5	
60	0.60	0.24	0.28	0.17	0.15	87.41	0.12	0.01	0.02	0.03	0.06	122.37	0.03	0.00	0.01	0.01	0.01	76.21	0.003	0.003	0.002	0.003	0.003	6.49E-04	23.9	

CV - coefficient of variation

1992) causing, for example, the response of a standard n-C₆₀ alkane to be only about one third of the response of n-C₃₀ alkane given equal initial concentrations of the injected compounds (Philp *et al.*, 1995). A number of factors are discussed as potential causes for the decreasing response of the higher carbon number n-alkanes, including the poor solvent solubility of these compounds, and the difficulty in eluting them from the HTGC column due to their high boiling points. The most likely effect of these factors is an underestimation of compound concentrations in that carbon number region (Philp *et al.*, 1995). Some results, especially regarding the solubility of mixtures of HMW n-alkanes in different solvents will be discussed in Chapter IV.2.

Quantitative HTGC analysis on gas chromatograph GC 8000 Top series was performed on selected samples, which allowed to use higher upper end analytical temperatures and detect higher molecular weight compounds. The reproducibility of injection and relative response factors were tested using a standard n-alkane mixture consisting of equal amounts nC₂₀, nC₃₀, nC₄₀, nC₅₀, and nC₆₀ alkanes in cyclohexane (Table IV. 1. 8). The mixture was prepared in two different ways in order to test for the effect of mutual solubility of the n-alkanes. First, each standard n-alkane was individually dissolved in cyclohexane (1 mg/ml), and equal volume aliquots from the heated individual solutions were mixed. Second, equal amounts (1 mg) of each n-alkane were mixed and 5 ml of solvent added, and then heated to obtain dissolution. In both cases, one microliter injected solution was calculated to correspond to 33 nanograms of each n-alkane if assuming that all n-alkanes have been dissolved completely during the solution preparation and before injection. The reproducibility results (four consecutive runs for each solution) demonstrate an imprecision of the analysis less than 3.3%. Better

(a)

run #	n-C ₂₀	n-C ₃₀	n-C ₄₀	n-C ₅₀	n-C ₆₀
wax1	0.93	1.00	1.00	0.94	0.64
wax135	0.95	1.00	1.00	0.97	0.68
wax136	0.94	0.99	1.00	0.96	0.65
wax137	0.94	1.00	1.00	0.95	0.63
mean	0.94	1.00	1.00	0.96	0.65
std. dev.	0.01	0.00	0.00	0.01	0.02
CV (%)	0.87	0.34	0.00	1.35	3.32

(b)

run #	n-C ₂₀	n-C ₃₀	n-C ₄₀	n-C ₅₀	n-C ₆₀
wax145	0.75	1.00	0.78	0.88	0.68
wax146	0.74	1.00	0.78	0.87	0.68
wax147	0.75	1.00	0.78	0.87	0.68
wax148	0.75	1.00	0.78	0.87	0.68
mean	0.75	1.00	0.78	0.87	0.68
std. dev.	0.00	0.00	0.00	0.00	0.00
CV (%)	0.67	0.00	0.00	0.57	0.00

Table IV. 1. 8. Reproducibility results and relative response factors for a standard n-alkane mixture consisting of equal amounts nC₂₀, nC₃₀, nC₄₀, nC₅₀, nC₆₀ alkanes in cyclohexane. Mixtures were prepared by (a) diluting each n-alkane individually and then mixing the solutions, and (b) mixing an equal weight of each of the n-alkanes and then adding the solvent. See additional discussion in text. HTGC temperature program 60-370°C @ 6°C/min, detector temperature at 390°C.

reproducibility, particularly for the HMW nC_{50} and nC_{60} alkanes, was obtained from the solution prepared as initial mixture of all n-alkanes (**Table IV. 1. 8b**). The results in **Table IV. 1. 8**, also, demonstrate the previously observed by Philp et al. (1995) decrease in response factors with increasing carbon number of n-alkanes. However, the mixture prepared by adding all n-alkanes and then dissolving them together in a solvent showed a relatively higher response factor for nC_{60} and a decreased response for nC_{20} , nC_{40} and nC_{50} alkanes compared to the mixture prepared by individually dissolving each n-alkane in a solvent.

IV. 2. COMPOSITION OF WAX DEPOSITS

VS.

SOLUBILITY OF HIGH MOLECULAR WEIGHT (HMW)

n-ALKANE MIXTURES

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IV. 2. 1. OVERVIEW OF THE PETROLEUM WAX DEPOSITION PROBLEM

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IV. 2. 1. A. The problem of wax deposition

Deposition of solid material in reservoirs, production and transportation facilities occurs in petroleum producing regions worldwide and is a problem that has been known for almost a century. Solid deposition during petroleum production is commonly referred to as the “wax “ or “paraffin” problem based on the abundant presence of n-alkanes (n-paraffins) in high-wax oils and associated solid deposits. It is a recurrent and very costly

problem in petroleum production practices. Solid deposits may form within the reservoir during production causing reduction in permeability and/or formation damage, and resulting in a large restriction of production (Civan, 1996a and b). In addition, deposits which form in the production tubing may cause back-pressure into the reservoir which results in a decreased fluid withdrawal rate and will further delay or decrease the production (Carnahan, 1989). In production equipment, solid deposits usually form near areas of restricted flow (e.g., chokes, collars) associated with pressure differentials. In certain situations, uplift of reservoirs containing high-wax oils may result in paraffin deposition prior to production as a result of the accompanying temperature decrease (Trindade et al., 1996).

Another major area of concern relates to deposits formed in pipelines, which can cause reduction in the internal diameter of tubing resulting in pressure decrease and reduced oil pumping rates. In addition, severe start-up problems after shutting down pipelines for cleaning operations can arise from increased viscosity and high yield stress of the gelled oil. “Paraffin” problems occurring in oil pipelines, especially offshore, have been associated with significant production losses and expenses. Leontaritis (1996a) estimated that four days of shutdown/clean up cost for an 8-inch submarine crude oil pipeline could amount to US \$2.5 to 4 million depending on the crude oil price and rate of production.

Waxes also play a role in the emulsification of crude oils, which can present problems during the refining process. The role of waxes relates to the stability of water-in-oil emulsions and it is considered that wax crystals by themselves are interfacially

active or can adsorb resins and asphaltenes which will make them interfacially active (Musser and Kilpatrick, 1998). The wax crystals are capable of being adsorbed on the water-oil surface, and together with the resins and asphaltenes form a rigid film that surrounds the water droplet resulting in increased stability of the emulsion.

Various methods have been applied to remediate “paraffin” problems in production/transportation facilities, including mechanical (e.g., using scrubbers or “pigging”), thermal (e.g., heating, hot oil treatment), chemical (e.g., using solvents like p-xylene or chemicals as dispersants and paraffin inhibitors), or a combination of treatments. Some of the first attempts to mitigate these problems were recorded in the beginning of the twentieth century (Reistle, 1932, and references therein) but even today “paraffin” deposition is a recurring problem, and the remediation costs continue to escalate, particularly with the expansion of the offshore shelf and deep water exploration and production.

There is a consensus at the present time that the understanding of and predictive methods for, “paraffin” deposition are still unsatisfactory for successful prevention and treatment of the problem (Monger-McClure et al., 1999). An expression of the organized effort of the domestic petroleum industry to target the paraffin problems was the formation of DeepStar industrial consortium in the early 90’s, with a number of projects initiated to deal with different aspects of the wax deposition problem.

IV. 2. 1. B. Factors controlling wax deposition

The main factors known to control wax deposition from petroleum are changes in overall oil composition, reduction in temperature, and the effect of pressure mainly as it affects oil composition (e.g., Reistle, 1932; Mozes, 1982; Hansen et al., 1991; Misra et al., 1995; Leontaritis, 1996b, 1997). These factors are closely associated with processes related to petroleum generation history of the source rock, migration history, reservoir history, production history and transportation conditions of the crude oils.

Wax deposition can also be related to the changing solubility behavior of the complex mixture of heavy components in crude oils (Carnahan, 1989). As a result of the reduction in temperature and pressure, and changes in oil composition during the geological history or production/transportation of petroleum, the solubility of higher molecular weight fractions decreases to the extent that they can precipitate from the original oil solution.

B1. Oil composition as a controlling factor for wax deposition.

Composition of wax deposits

The composition of whole oils and petroleum waxes in oils, melting points of individual components and mixtures, and their concentrations determine several very important properties of crude oils. These properties relate to temperature of wax deposition (oil cloud point) and change in flow behavior of the oil that will ultimately lead to wax deposition problems in reservoirs, drilling and transportation facilities. Wax

deposition can be regarded to occur as a result of the changing solvency capacity of the oil towards its heavy fractions, as discussed earlier. However, the relationships between oil type (paraffinic, naphthenic, aromatic), wax type (macrocrystalline, microcrystalline, intermediate) and wax concentration in oils, and how they affect the solubility behavior of heavy components are not completely understood at the present time.

The solid material deposits formed in production facilities are complex mixtures dominated by high molecular weight hydrocarbons (n-alkanes, cycloalkanes, isoalkanes, alkylaromatics) and non-hydrocarbons (resins, asphaltenes), with some additional trapped oil, inorganic material and water in various proportions. The major groups of components that constitute the “paraffin” deposits are very different in their chemical structure and physical properties, ranging from nonpolar n-alkanes to the highly polar and hydrogen bonding prone heteroatom constituents of the asphaltenes. Moreover, each of these groups represents a range of different homologous series and individual compounds with large variations in molecular weights, and often unknown structures and physical properties. For example, the number of possible structural isomers increases exponentially with molecular weight, and only for the homologous series of n-alkanes increases from 3 (nC_5) to 36.6×10^4 (nC_{20}), 62.4×10^{12} (nC_{40}) to 5920×10^{36} (nC_{100}), (based on theoretical calculations; Boduszynski, 1988). The properties of the complex mixtures formed by the hydrocarbons and non-hydrocarbons in “paraffin” deposits are even more obscure, which presents a major obstacle in the development of more effective and less costly “paraffin” deposit remediation methods. The lack of sufficient knowledge about the composition, even of the major groups of components constituting the “paraffin”

deposits, and thus the properties of the complex mixtures they form and their mutual interactions, has been recognized as an area which definitely requires further studies (e.g., Boduszynski, 1988; Al-Zaid *et al.*, 1998).

B2. Temperature as a controlling factor for wax deposition

The formation of wax deposits is strongly influenced by reduction in temperature, which leads to a decrease in solubility of heavy hydrocarbons and formation of wax crystals. With a further decrease in temperature, the concentration of wax crystals increases and at a certain threshold level they will precipitate from solution. The possibility of adsorption of resins and asphaltenes with the HMWHC resulting in their co-precipitation has been discussed in several studies (Becker, 1997; Musser and Kilpatrick, 1998), and could be related to the higher adhesive properties of higher molecular weight hydrocarbons (HMWHC) compared to the lower molecular weight homologues (see below).

The temperature of first wax deposition is defined as the cloud point of the oil, i.e., the highest temperature at which formation of wax crystals can be detected (e.g., Rønningsen *et al.*, 1991; Monger-McClure *et al.*, 1999). The methods used for cloud point determination include the American Society for Testing and Materials ASTM D97 (IP15) procedure, cold finger (CF) apparatus measurements, differential scanning calorimetry (DSC), cross-polarized microscopy (CPM) with a temperature controlled stage with or without video-camera attachment, filter plugging (FP), Fourier transform infrared (FTIR) energy scattering, viscometry (Hunt, 1962; Russel and Chapman, 1971;

Bern and Withers, 1980; McClaflin and Whitfill, 1983; Rønningsen et al., 1991; Hansen et al., 1991; Kruka et al., 1995; Magri et al., 1997; Monger-McClure et al., 1999). The cloud point determination by ASTM D97 (IP15) procedure is applicable only for transparent oils since it relies on the visual observation of a distinct cloudiness in the oil on cooling (Brownawell and Holliday, 1962; Kruka et al., 1995). The cold finger method is applicable for both transparent and black oils, and is one of the methods utilized in the present study (Chapter II). With regard to other methods for cloud point determination listed above, detection of wax crystal formation from a preheated oil sample is achieved by: measuring the heat release associated with wax crystallization (DSC); the increase in differential pressure across a filter (FT); the increase in energy scattering with wax solidification (FTIR); the microscopic observation of wax crystal (CPM) formation, based on their property to rotate polarized light in contrast to the liquid hydrocarbons; and the deviation from linearity in measuring the changes in viscosity of oil sample with decrease in temperature. The cloud point measurements by these methods are commonly performed at very low cooling rates (less than 0.5-1°F/min), to prevent any supercooling effect. A recent study, part of the DeepStar project, systematically evaluated the results of cloud point measurements obtained by several of these methods (DSC, CPM, FT, FTIR) on thirteen oils from various locations, and found that wax-detection sensitivity is method- and oil composition-dependent (Monger-McClure et al., 1999). The CPM method was found to have the highest sensitivity compared to the other methods studied and, correspondingly, it provided highest values of the cloud point. The overall agreement between the methods was found to be about $\pm 3^{\circ}\text{F}$.

The wax concentration of an oil influences both the cloud point and rheological behavior of the oil (Hansen et al., 1991). The cloud point of refined base oils mixed with different amounts of a macrocrystalline wax (m.p.42-43°C) was found to increase rapidly with an increase in wax concentration up to 15%, and then increases linearly with wax concentration from 15% to 50%, as described by Al-Ahmad et al. (1993). The effect of an increasing microcrystalline wax (C_{50+}) content in an oil on the cloud point can be derived from the experimental data presented by Monger-McClure et al. (1999). The cloud point of fourteen oils produced at the same geographic location was found to increase as a logarithmic function of the content of HMW n-alkanes (C_{50+} fraction) in the oils as determined by HTGC analysis. **Figure IV. 2. 1** was constructed using the data presented by Al-Ahmad et al. (1993) and Monger-McClure et al. (1999) in order to compare the results of these two studies. A comparison of the data shows that a very small increase (0.05-0.2 wt.%) in concentration of HMW (C_{50+}) n-alkanes increases the cloud point of the oil with 20-30°C. A much larger increase in concentration of macrocrystalline waxes (20-40 wt.%) is required to achieve the same increase in oil cloud point. It should be noted that the methods for cloud point determination were based on the ASTM procedure in the study of Al-Ahmad et al. (1993), and as an average of results from four methods (DSC, CPM, FP, FTIR), in the study of Monger-McClure et al. (1999).

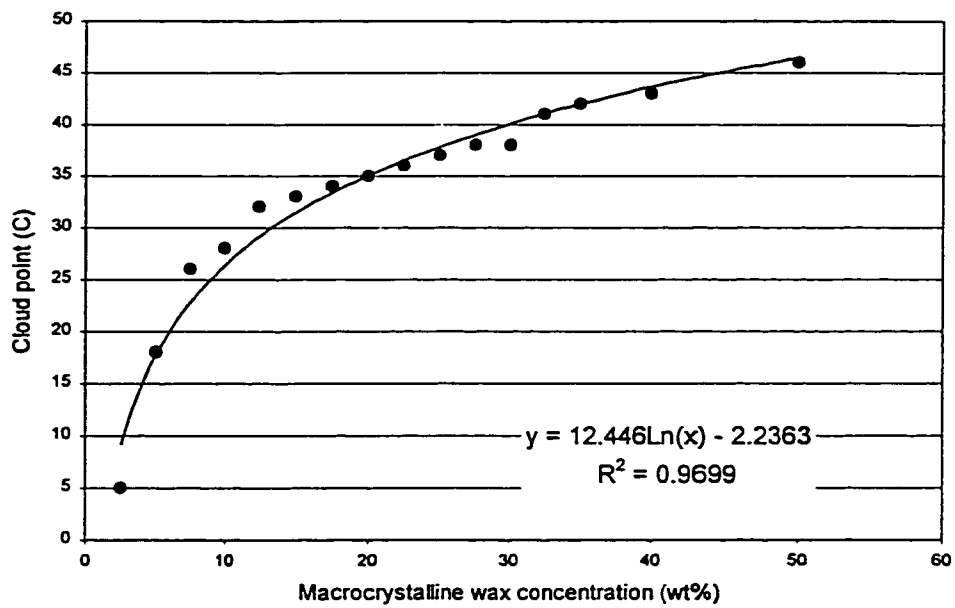
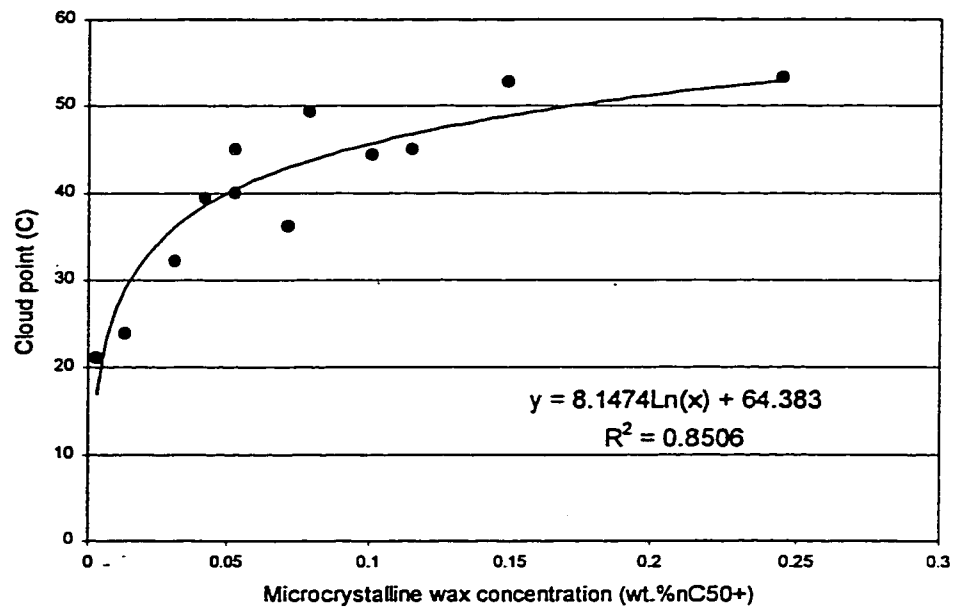


Figure IV. 2. 1. Relationship between cloud point and content of microcrystalline wax (a) and macrocrystalline wax in oils (b). Data from Monger-McClure et al. (1999) and Al-Ahmad et al. (1993).

B3. Pressure as a controlling factor for wax deposition

Pressure can affect cloud point of oils in two contrasting ways. First, with increasing pressure, the melting points of pure n-alkanes increase, which results in an increased cloud points of the oils at higher pressures (Brown *et al.*, 1994; Leontaritis, 1996b; Pan *et al.*, 1996; Monger-McClure *et al.*, 1999). An increase in cloud point of 2°C/100 bar was suggested as a reasonable estimate for the effect of pressure on cloud point of any dead oils (Brown *et al.*, 1994). Second, at higher pressures, the solubility capacity of light hydrocarbon components (methane, ethane, propane) for the wax forming n-alkanes (above C₂₀) increases significantly, and therefore increasing amounts of solution gas in the oil result in a cloud point depression in the order of 10-17°C (Rønningsen *et al.*, 1991; Pan *et al.*, 1996; Leontaritis, 1996; Monger-McClure *et al.*, 1999). Experimental results with live oils have demonstrated that with increasing pressure the cloud point is initially depressed due to dissolution of light ends in the liquid phase, and at pressures exceeding the bubble point of studied oils, the cloud point starts to increase linearly with pressure (Brown *et al.*, 1994).

IV. 2. 1. C. The role of geochemistry in the evaluation of wax deposition

problems

As discussed earlier, wax deposits are very complex mixtures of different compound groups and are far from being understood comprehensively with regard to their composition and properties. The heavy petroleum fractions, which dominate wax

deposits, are particularly difficult to characterize compositionally. Present day geochemical methods for studying heavy molecular weight petroleum fractions represent one of the few available and reliable means to evaluate qualitatively and quantitatively the composition of wax deposits on a component-by-component basis. The technological developments achieved during the last two decades have made it possible to utilize gas chromatographic methods to the characterization of heavy petroleum fractions (Pereira and Aquino Neto, 1999). The advancement in technology of thermostable stationary phases and column coatings, and the introduction of the first commercially available high temperature columns for GC analysis (Lipsky and Duffy, 1986a and b) opened a new frontier for the investigation of high molecular weight compounds above C₄₀ in oils and solid wax deposits (Carlson *et al.*, 1991; del Rio and Philp, 1992a; Philp and Mansuy, 1997). The method has become known as the high-temperature, high-resolution-gas chromatography (HT-HRGC) or simply HTGC, denoting GC analysis with final temperatures above 350°C as opposed to the conventional GC with maximum final temperatures up to 300°C. The use of hydroxy-terminated polymethylsilicone stationary phases with increased thermal stability was introduced by Lipsky and McMurry (1983) and Lipsky and Duffy (1986a and b). The aluminum-clad columns originally used for HTGC were later replaced by “high temperature” polyimide, and nowadays by the “second generation” fused silica-lined steel capillary columns (Pereira and Aquino Neto, 1999). The upper end operating temperatures of the HTGC analysis that can be achieved today is in the range of 400°C to 480°C, depending on the choice of stationary phase and type of column coating material.

These technological developments in chromatographic techniques presented a solution to one of the major limitations of conventional GC analysis of oils and heavy petroleum fractions, which was previously limited to an upper carbon number n-alkane detection of C_{30} - C_{35} under the conventional maximum column temperatures of 300°C . The application of HTGC analysis to high molecular weight standard hydrocarbon mixtures (usually polyethylene) demonstrated the ability to detect n-alkane distributions up to nC_{120} (Thomson and Rynaski, 1992). The comparison of carbon number distributions of high-boiling point, n-alkane dominated wax samples, both synthetic and obtained from oil storage sludge, by high temperature gas chromatography and supercritical fluid chromatographic techniques demonstrated a good agreement between the two techniques. These results, in addition to almost complete recovery of samples, suggested the absence of thermal cracking or decomposition of n-alkane dominated wax mixtures during the HTGC analysis (Thomson and Rynaski, 1992).

The first applications of HTGC analysis to produced oils and wax deposits were presented by Carlson et al. (1991) and del Rio and Philp (1992a and b) and demonstrated that hydrocarbon distributions in various oils extend far above (nC_{75} - nC_{80}) the earlier known carbon number ranges (nC_{35} - C_{40}). Further studies of del Rio et al. (1992), Carlson et al. (1993), Philp (1994a), Philp et al. (1995) found that high molecular weight n-alkanes are preferentially concentrated in the solid wax deposits. HTGC analysis of the solid deposit and produced oil revealed that, despite the very low concentrations of HMW compounds in the oil, they are the predominant hydrocarbons in the associated deposit

(del Rio et al., 1992a and b). Similarities in the biomarker assemblages of saturate fractions of the oil and wax deposit confirmed a common origin.

As a result of geochemical analysis, evidence started to accumulate which demonstrated that not only could “high-wax” oils, commonly considered to be generated from terrestrial type organic matter (Hedberg, 1968), but also “low-wax” oils, formed from marine source rocks, cause severe wax deposition problems (del Rio et al., 1992a and b; Philp, 1994; Philp et al., 1995). In addition, another previously unknown relationship was discovered, namely the co-existence of HMWHC and asphaltenes. Pyrolysis and HTGC analysis of asphaltenes obtained by the commonly used precipitation method with an excess of light hydrocarbon solvent, such as n-pentane, demonstrated the presence of HMW alkanes in the asphaltene and their co-precipitation with the asphaltenes (del Rio and Philp, 1992a; del Rio et al., 1992; Philp et al., 1995; Chouparova and Philp, 1998; Thanh et al., 1999). Several years later, an analytical method for removing those HMWHC from the asphaltene fraction was developed by Thanh et al. (1999) and Hsieh (1999).

In addition to the n-alkanes, which are commonly found as the dominant hydrocarbon series in petroleum waxes, other series of closely co-eluting monocyclic and acyclic branched alkanes, and alkylaromatics, have been identified above C₄₀ in oils with different origins using HTGC-MS analysis (Gallegos et al., 1991; del Rio et al., 1992b; Carlson et al., 1993; Hsieh, 1999; del Rio et al., 1999). The results of these studies expanded the range of homologous series of hydrocarbons identified in earlier studies (e.g., Reid, 1966) that have a potential to be used as HMW biomarkers. The application

of HTGC to non-hydrocarbon fractions of crude oils has not been as intensive as it has been for elucidating the corresponding hydrocarbon composition. In addition to the studies revealing the association of HMWHC with asphaltenes discussed above (del Rio and Philp, 1992a), Gallegos *et al.* (1991) published the first report on direct HTGC/MS analysis of metalloporphyrins, which are generally associated with the resin and asphaltene fractions of crude oils. The isotopic composition of HMWHC is another area that has started to receive scientific attention only in recent years. The carbon isotopic composition of individual n-alkanes (C_{22} to C_{74}) in ozocerite solid bitumen from Uinta Basin was shown to be uniform across the carbon number range studied, suggesting that both the LMW (C_{20} to C_{35}) and HMWHC have similar origins (Carlson *et al.*, 1997).

The presence of HMWHC in immature rock extracts from Green River Formation confirmed the primary source signal of these compounds and suggested their possible use as HMW biomarkers for correlation studies (Mueller and Philp, 1998). The ability to examine the composition of heavy petroleum fractions on a component by component basis by HTGC has the potential to open a huge area of investigation related to the HMW biomarkers and their precursors. During the past 20-30 years, biomarkers have proved to be extremely useful and with many applications especially in petroleum exploration (Eglinton and Calvin, 1967; Lopatin, 1971; Tissot *et al.*, 1977; Didyk *et al.*, 1978; Seifert and Moldowan, 1978, 1981; Waples, 1980; Mackenzie *et al.*, 1982; Leythaeuser *et al.*, 1983; Mackenzie and McKenzie, 1983; McKenzie *et al.*, 1983; Mackenzie, 1984a and b; Abbott *et al.*, 1985; Beaumont *et al.*, 1985; Philp, 1985a and b; Moldowan *et al.*, 1985; Waples, 1985; Bonilla and Engel, 1986; Philp and Gilbert, 1986; Philp and Lewis, 1987;

Volkman, 1986; Philp and Oung, 1988; Waples and Machihara, 1990; Peters and Moldowan, 1992; Hunt, 1995). Most of the recognized biomarkers are concentrated in the heavier end petroleum fractions, in contrast to the compounds resulting from kerogen degradation which are most abundant in the low and medium carbon number ranges ($<C_{25}$) (Tissot and Welte, 1984). The lower molecular weight (LMW) hydrocarbons generated from the kerogen under thermal stress dilute the biomarkers usually preserved as bitumen in the source rocks. In addition, petroleum migration processes tend to lower the biomarker concentrations. An expansion of the trend in geochemistry towards detection and identification of more polar biomarkers and their HMW precursors was discussed and predicted almost fifteen years ago (Philp, 1985b).

As discussed above, the role of geochemistry in elucidating the complex problem of wax deposition is very important and most probably will grow in the future. One of the biggest advantages of the geochemical methods is that they permit direct and compound specific information to be derived about the petroleum. The main limitations of geochemical methods are related to the analytical techniques and the samples obtained for analysis. The importance of developing new analytical techniques is well illustrated by the expanded applications of biomarkers and HMWHC to solving problems related to the petroleum industry as result of developments in GC-MS, MS-MS, GC-MS/MS, and more recently HTGC techniques (e.g., Philp, 1985a and b; Moldowan *et al.*, 1989; Dahdah and Wavrek, 1997). Limitations introduced by the samples used in petroleum geochemistry studies have also been recognized and an increasing number of studies in recent years has addressed these problems by comparison of the data obtained from different types of

samples. In addition to the samples collected from produced reservoir fluids (oil, gas, water) and cores at the surface, well test fluids (drill stem test, DST, and repeat formation test, RFT), bitumen from reservoir cores, and petroleum fluids trapped in the fluid inclusions of reservoir cores, have been studied (e.g., Thompson, 1987; Leythauser and Ruckheim, 1989; Horstad et al., 1990; Hillebrand and Leythauser, 1992; Baskin and Jones, 1993; Wilhelms and Larter, 1994a and b; Hall et al., 1994; Larter and Aplin, 1995; Bement et al., 1996; Wilhelms et al., 1996; Carrigan et al., 1997; Baylis, 1998; Hwang et al., 1998).

IV. 2. 1. D. The integration of petroleum geochemistry and petroleum engineering studies

An increasing awareness of the need for an integrated and interdisciplinary approach towards solving problems in natural systems has been demonstrated in a number of studies. The integration of geological and geochemical, geological and geophysical, geological and engineering methods is a relatively well established and a routine practice nowadays, and has proven to give excellent results in both petroleum exploration and production (e.g., Mitchum et al., 1977; Vail et al., 1977a,b and c; Tissot et al., 1978; Tissot and Welte, 1984; Forgotsen, 1993; Garvey et al., 1993; Forgotsen et al., 1997).

The integration of petroleum geochemistry with petroleum engineering is not so routinely accepted approach even though it has been utilized in an increasing number of

studies (Werner et al., 1996; Leontaritis, 1997; Pan et al., 1997; di Primio et al., 1998; Meulbroek et al., 1998; Khavari-Khorasani et al., 1998a and b). These studies presented results based on: integration of PVT analysis and modeling with geochemical compositional data applied for prediction of petroleum fluids phase behavior and wax deposition; recognition of mixing effects; volumetric evaluation of complex reservoir filling histories; modeling progressive fractionation of oil by gas related to migration fractionation phenomena; prediction of expelled fluids composition and assessment the nature and relative importance of source; maturity and migration related factors to the distribution of heavy and light oils.

Integration of geochemistry with petroleum engineering concepts can be found in earlier studies. For example, Whitson (1980) pointed the attention of the engineering community towards the significant errors that may be introduced into phase behavior modeling of petroleum fluids, based on equation of state, by the common practice of lumping the C_{7+} fraction as one component and giving it average physical and thermodynamic properties. Today the progress in this direction has resulted in incorporation of GC and HTGC results in the modeling and has led to improving the modeling predictions by approximating only the C_{40+} and C_{60+} fractions as one component (Pan et al., 1997). A strong recognition of the value of HTGC analysis was presented in a recent study by Monger-McClure et al. (1999) who compared the predictions from a number of thermodynamic models, regarding the conditions of wax deposition, with field data. It was demonstrated univocally that the models utilizing HTGC data outperformed significantly the models using less specific information (e.g.,

average parameters for lumped components). The incorporation of engineering concepts is evident in a number of geochemical studies discussing the mechanisms of petroleum generation and expulsion, migration, reservoir filling and mixing as reflected in the works of Ungerer et al. (1983), Tissot and Welte (1984), England et al. (1987), England (1990), Larter and Mills (1992), Larter and Aplin (1995).

IV. 2. 2. OVERVIEW AND DISCUSSION ON THE CLASSIFICATION AND ORIGIN OF PETROLEUM WAXES

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IV. 2. 2. A. Definitions

Wax, petroleum wax and wax deposit

The term “wax” has two major connotations: waxes in living systems (animals and plants), and waxes in petroleum. In addition, the term “wax” has been used to refer to the solid material that can precipitate from petroleum in reservoirs, production and transportation facilities.

Animal and plant waxes are part of the lipid fraction of various living organisms and represent mixtures of high-molecular weight compounds including acids, alcohols, wax esters, ketones, hydrocarbons (Hamilton, 1995). The sources of waxes in living organisms are abundant, and waxes have been isolated from the outer layers of bacteria, roots, stems, leaves, fruits and flowers of plants, exudates of insects, skin and hair of some animals, and the bodies of certain marine and land animals. Some of the commercially used waxes of this type include carnauba wax, extracted from an exudate on the leaves of the carnauba palm; candelilla wax obtained from a coating on the stem of a leafless desert shrub, which contains a tacky resin in addition to the large amount of

hydrocarbons; beeswax which is an exudate of honeybee and a good solvent for other waxes; wool wax obtained from sheep wool. For practical reasons during manufacture, waxes are defined mainly based on their physical properties, one of them being the requirement that waxes be solids at 20°C. Waxes obtained from living organisms and plants comprise only 10% of the commercially used waxes by the industry today, with the remaining 90% coming from the petroleum-derived waxes (Hamilton, 1995).

Petroleum wax refers to the solid **hydrocarbons** separated from the intermediate and high-boiling range lubricating petroleum fractions during the refining process. In the literature, it has been noted that “...petroleum wax is a broad and rather poorly defined term” (Hedberg, 1968). Despite this fact, it appears most authors agree that petroleum waxes are dominated by n-alkanes, with smaller amounts of other hydrocarbon compound classes, of sufficiently high molecular weights to be solids at ambient conditions (Wright and Mitchell, 1921; Reistle, 1932; Sachanen, 1950; Mozes, 1982; Carlson et al., 1993). In the present study, “petroleum wax” refers to the hydrocarbons in oils that are solid at room temperature and the fractions obtained by laboratory methods for wax precipitation.

Wax (paraffin) deposits refer to the solid material that can precipitate from oil and accumulate in reservoirs, production and transportation facilities. Referring to these solid deposits as wax or paraffin deposits implies that the deposits consist exclusively of hydrocarbons. As discussed in section IV. 2. 1, these deposits represent mixtures of hydrocarbons and non-hydrocarbons, along with trapped oil, water and inorganic material (Reistle, 1932). In the present study, the term “wax (paraffin) deposits” is used with the

knowledge that under circumstances such deposits may contain non-hydrocarbon material.

Distribution of hydrocarbons in petroleum waxes and wax deposits

The upper carbon number range of the hydrocarbon components in petroleum waxes and wax deposits is not well defined, but a number of recent reports based on HTGC analysis, has demonstrated the presence of n-alkanes up to C_{75} - C_{80} , with corresponding molecular weights of 1050-1120 amu (Trestianu et al., 1985; del Rio et al., 1992; Philp et al., 1995; Pereira and Aquino Neto, 1999). Based on mass spectrometry and gel permeation chromatography, presence of n-alkanes as high as nC_{100} and branched and cyclic alkanes up to C_{110} have been identified in oils and petroleum derived waxes (Musser and Kilpatrick, 1998; del Rio et al., 1999; del Rio and Philp, 1999).

The wax content of oils can vary significantly and in some oils is sufficiently high to cause the whole oil to be solid under ambient conditions. The use of the term “high-wax” oil, however, is quite inconsistent among different studies, which is partially related to the different methods used for estimation of wax content. Hedberg (1968), for example, defined high-wax oil as having wax content greater than 5 wt.% of the oil. The wax content was determined from reported cloud point data of distilled fractions and/or pour-point and viscosity data for the oils. Hedberg (1968) specifically pointed out in his paper that these methods for wax content determinations are quite arbitrary and could be a source of significant errors. For example, oil having a high pour point may be a result of high asphaltene content as well as of high paraffin content. Other authors defined high-

wax oils specifically having a n-C₂₂ to n-C₃₁ content greater than 10 wt.% based on GC analysis (Saikia and Dutta, 1980). In addition, ultra-high-wax oils were distinguished by some authors as having a wax content of more than 30 wt.% as determined by GC analysis of n-alkanes obtained after isolation of the saturate and branched/cyclic fractions (Yongsong *et al.*, 1992). The definitions based on GC analysis generally follow the discussions of Martin *et al.* (1963) who found high-wax oils to be characterized with a typical n-alkane (C₂₀-C₃₅) content of 15-20% that may exceed 30% in some oils.

A widely accepted technique in the petroleum industry for wax separation and estimation of wax content is the method of Burger *et al.* (1981), referred to in the present study as the “acetone” technique (see Chapter II, Experimental). It should be pointed out that the wax content determined by this method not only includes hydrocarbons but also some resin and asphaltene material. A recently published study presented experimental evidence that the amount of material precipitated by acetone is a function not only of the wax, but also of the resin and asphaltene content in the oils (Musser and Kilpatrick, 1998). The elemental analysis results presented in the study showed a relatively low H/C ratio and a high heteroatom content of the acetone wax precipitate, suggesting that polar material co-precipitates with the wax. The results from sequential elution chromatography of the precipitate with solvents and solvent mixtures of increasing polarity demonstrated that the “acetone” precipitate is composed mainly of resins, asphaltenes and wax (Musser and Kilpatrick, 1998).

There are significant discrepancies related to determination of wax content and the definition of high-wax oils. The wax content determined by quantitative GC or HTGC

analysis refers only to the hydrocarbons, because the other fractions are usually not quantifiable by this method. It allows for compositional identification of the hydrocarbon distributions, including the HMWHC range, and thus represents a reliable method for defining hydrocarbon wax content. Therefore, the high-wax oil definitions, based on GC analysis, discussed earlier appear to be the most reasonable (Martin *et al.*, 1963; Saikia and Dutta, 1988; Yongsong *et al.*, 1992). The definition of a high-wax oil followed in the present study is an oil with a total n-alkane content (C_{18} to C_{35} , or a macrocrystalline type wax), as determined by HTGC analysis, higher than 10 wt.% of the oil. In addition, the physical state of the oil at ambient conditions (solid vs. liquid) can be used as a first approximation of high-wax vs. low-wax oils, prior to GC or HTGC analysis.

IV. 2. 2. B. Classification of petroleum waxes

Petroleum waxes are commonly classified in the petroleum industrial literature as macrocrystalline (or paraffin), intermediate, and microcrystalline (or amorphous) types based on the size of wax crystals formed (Jowett, 1984; Speight, 1991). Macrocrystalline waxes are obtained from the intermediate boiling range lubricating oil fractions in the refining process while the microcrystalline waxes are derived from the high-boiling lubricating oil fractions or residuum. The classification of petroleum waxes proposed by Mozes (1982) provides a useful link between the composition of waxes and some of their physical properties and is followed in the present study (**Table IV. 2. 1**).

Macrocrystalline and microcrystalline waxes are dominated by lower molecular

COMPOSITION/ PHYSICAL PROPERTIES	MACROCRYSTALLINE ("PARAFFIN") WAX	MICROCRYSTALLINE ("AMORPHOUS") WAX
N-ALKANES DOMINANT RANGE	C ₁₈ -C ₃₀	>C ₃₀ -C ₅₀
AMOUNT OF OTHER HC (ISO-, CYCLOALKANES, ETC)	LOWER	HIGHER
MELTING POINT RANGE	40-60°C	>60-90°C
ADHESION	LOWER	HIGHER
SOURCE FRACTIONS	LIGHT DISTILLATE	HEAVY DISTILLATE RESIDUAL OIL PIPELINE AND TANK WAX DEPOSITS

Table IV. 2. 1. Classification of petroleum waxes (after Mozes, 1982)

weight (LMW) range (C_{18} - C_{30}), and higher molecular weight (HMW) range (above C_{30} - C_{50}) n-alkanes, respectively. As a result of these compositional differences, microcrystalline waxes have a much higher melting point range (above 60-90°C) compared to the macrocrystalline waxes (40-60°C). Microcrystalline waxes, therefore, will be in a solid state over a much broader temperature range than macrocrystalline waxes, and will also be the first to precipitate from solution on cooling. In addition, microcrystalline type waxes have “substantially higher” adhesive properties than macrocrystalline type waxes as discussed by Mozes (1982). Recent studies have shown that H/C ratios for macrocrystalline waxes (1.92-2.05) are slightly higher than in microcrystalline waxes (1.85-1.90) related to the higher proportions of cyclic hydrocarbons in the latter type waxes (Musser and Kilpatrick, 1998). In addition, microcrystalline waxes often contain higher proportions of branched alkanes (Mozes, 1982; Jowett, 1984; Musser and Kilpatrick, 1998). The intermediate type waxes represent mixtures of macrocrystalline and microcrystalline type waxes in different proportions, and with intermediate properties. The use of the terms “macrocrystalline” and “microcrystalline” waxes in the present study typically refers to the carbon number distribution and concentration of n-alkanes. Estimates for the amount of macro- and microcrystalline type waxes in a sample refer to the sum of all nC_{20} - C_{35} alkanes and the sum of all nC_{35+} alkanes, respectively, as determined by quantitative HTGC analysis.

IV. 2. 2. C. Origin of petroleum waxes in high-wax and low-wax oils

Historically, most of the information about the origin of high-wax oils has been derived based on conventional GC analysis, which mainly detects the presence of LMWHC (macrocrystalline type waxes) in oils, and probably should be revisited in order to determine the possible presence of HMWHC (microcrystalline type waxes) in high-wax oils. High-wax oils are characterized with a high total wax content (more than 10 wt.%, see section IV. 2. 2. A) and compositionally are dominated by LMWHC (macrocrystalline type waxes) and lower concentrations of HMWHC (microcrystalline type wax), for example, the Uinta oil discussed in section IV. 2. 3. E of the present study. Generally, the concentration of HMWHC in oils is low (less than 0.5-1 wt. %; section IV. 2. 1. A; **Figure IV. 2. 1**), and oils that contain mainly HMWHC (microcrystalline type wax) will be characterized as low-wax oils based on definitions of total wax content. The wax composition in low-wax oils, however, is not limited to microcrystalline type waxes. Low-wax oils may contain also the macrocrystalline type waxes but with concentrations that are lower than in the high-wax oils. An example is the Gulf of Mexico oil discussed in Chapter IV. 4. Thus, both macro- and microcrystalline type waxes (LMW and HMWHC) can be present in high-wax and low-wax oils.

The recognition of high concentrations of LMWHC in high-wax oils precedes the recognition of HMWHC in oils by at least 80 years, and therefore there is a proportionately much larger amount of published information about the origin of high-

wax oils compared to HMWHC. Therefore any discussion concerning the origin of LMWHC and HMWHC in high-wax and low-wax oils should always be considered in the light of the historically determined analytical developments in petroleum geochemistry and the accumulation of knowledge about the origin of crude oils as a whole (Eglinton and Murphy, 1969; Tissot and Welte, 1984; Engel and Macko, 1993; Philp, 1994a; Hunt, 1995; Pereira and Aquino Neto, 1999).

In the context of the above considerations, the following summary will discuss some of the main ideas related to the origin of LMW and HMWHCs and the geological conditions that can affect the concentration of these hydrocarbons as well as the macro- and microcrystalline wax types in oils. The origin of LMWHC and HMWHC in high-wax and low-wax oils will be discussed in relation to the biomolecular precursors in living organisms, the lipid compositions in recent sediments, type of organic matter and kerogen, depositional environments, the importance of climate, maturity and generation, expulsion and primary migration, secondary migration, and thermal alteration in reservoired oils.

C1. Origin of macrocrystalline (LMWHCs) and microcrystalline (HMWHCs)

type waxes

The major groups organisms considered to contribute to the composition of organic matter in source rocks, and ultimately crude oils, are bacteria, phytoplankton, zooplankton and higher plants (e.g., Tissot and Welte, 1984; Engel and Macko, 1993). The lipid fraction in these organisms is usually the one best preserved during diagenesis,

and therefore a main contributor to the source rock's organic matter. Generally, the lipid content of marine organisms is higher than that of higher plants. However, certain parts of the higher plants such as barks, leaves, spores, pollen, seeds and fruits may be enriched in lipids and lipid-like substances (e.g., waxes, cutin, suberin).

Marine organisms use the lipids for food storage, insulation, and buoyancy in water, while the higher plants use them as external lipids to prevent water from leaving the plant and to minimize mechanical damage and fungal/insect attack on external surfaces. Fatty acids, alcohols and esters in addition to free hydrocarbons, all constituents of the lipid fraction in different organisms, have been considered as possible precursors for n-alkanes (e.g., Martin et al., 1963; Tissot and Welte, 1984; Bradshaw and Eglinton, 1993). Branched and straight chain alkanes in the carbon number range C_{10} to C_{20} could be derived from the branched fatty acids in bacteria and the straight chain even carbon numbered fatty acids in phytoplankton, respectively. Mid-chain branched monomethyl alkanes, most commonly encountered in mid to late Proterozoic rocks and oils, have been found in large amounts in cyanobacteria and hot spring cyanobacterial mats (Shiea et al., 1990). More recently large amounts of carboxylic acids were found in symbiotic bacteria living exclusively on demosponges that could be related to the origin of these alkanes present in rock extracts and oils (Thiel et al., 1999). Alkanes in the higher carbon number range (nC_{25} to nC_{33}) with strong odd over even carbon number predominance (usually by a factor of 10 or more) are generally considered to be derived from cuticular waxes of continental higher plants (e.g., Tissot and Welte, 1984, and references therein; Rieley et al., 1991; Simoneit, 1993). Odd carbon number (CN) dominated n-alkanes can be either

directly synthesized by the plants or derived through an early diagenetic transformations from even carbon number acids or esters. Generally, an odd-even predominance in alkane distributions is considered a feature of the immature soluble organic matter in source rocks, which becomes disguised by the later generation of hydrocarbons from kerogen (e.g., Tissot and Welte, 1984, and references therein; Huang, 1999).

Suzuki and Taguchi (1984) studied the diagenetic alteration of lipids during diagenesis in a series of naturally matured samples to depths corresponding to the beginning of the oil generation window. They found that the distribution of extractable n-alkanes showed a shift toward LMW (e.g., from nC_{30} to nC_{18}) range with increasing depth of burial while the n-alkane distributions from kerogen bound fractions consistently had higher abundances of higher molecular weight n-alkanes (C_{30} - C_{35} and possibly higher), NSO-compounds and asphaltenes.

Studies on coal wax compositions have shown that the major components in wax extracts from lignitic coals are the esters of aliphatic acids (C_{20} - C_{22}) and alcohols (Rodae et al., 1995; Bougers et al., 1996). In a study on the composition of a coal-bed wax, Dong et al. (1993) reported the major components in the wax to be n-alkanes (55.6%), branched/cyclic alkanes (26%), and several homologous series of alkylbenzenes (5.7%) up to C_{40} . The origin of straight chain alkylaromatics and alkylcyclohexanes is still under discussion because of the apparent lack of logical precursors in living organisms, in contrast to the alkylaromatics with isoprenoid side chain which are derived from carotenoid pigments (Rubinstein and Strausz, 1979; Fowler et al., 1986; Hoffmann et al., 1987; Williams et al., 1988; Sinninghe Damste et al., 1988; Schwark and Puttmann,

1990; Requejo *et al.*, 1992; Dong *et al.*, 1993; Hartgers *et al.*, 1994). These biomarkers are suggested as indicators for prolific bacterial growth in a stratified water column in subtropical to tropical marine environments (Requejo *et al.*, 1992). A recent study on the composition of pyrolysates of HMW sedimentary fractions (kerogen, asphaltenes, and polars) proposed that aryl isoprenoids are more likely to be derived from thermal cracking of bound diaromatic carotenoids rather than by cleavage of free carotenoids as suggested previously (Hartgers *et al.*, 1994). The main mechanisms proposed for the origin of n-alkylaromatics and n-alkylcyclohexanes are related to processes active during diagenesis and catagenesis. One possible mechanism suggests that the straight chain alkylcyclohexanes and alkylbenzenes may have the same fatty acid precursors as the n-alkanes, but are formed as a result of cyclization/aromatization, and decarboxylation of straight chain fatty acids, respectively (Rubinstein and Strausz, 1979; Fowler *et al.*, 1986; Hoffmann *et al.*, 1987; Dong *et al.*, 1993). An alternative mechanism for the formation of these hydrocarbons was proposed by Williams *et al.* (1988). The results of their heating experiments suggested that benzene, toluene, and cyclohexane can be alkylated by long-chain alcohols in the presence of kerogen.

It has been proposed that HMWHC could be formed by oligomerization of lower molecular weight precursors during diagenesis (del Rio and Philp, 1992b), based on the earlier artificial maturation experiments of Rubinstein and Strausz (1979) and de Leeuw *et al.* (1980), who obtained di- and trimerization products when heating phytol and fatty acids, respectively, in the presence of clay catalysts. The heating experiments of del Rio and Philp (1992b), using naturally occurring fatty acids (C₁₆-C₂₆), demonstrated the

formation of complex mixtures of HMWHC ($>C_{40}$) and organic sulfur compounds. The maximum recovered amount of generated hydrocarbons was found to be 30-40% of the weight of the original fatty acids. The formation mechanisms for these HMW compounds were shown to be oligomerization processes giving di- and trimerization products of the original fatty acids. It was suggested that not only fatty acids but other organic compounds with appropriate functional groups, and under appropriate conditions, may oligomerize to form HMW compounds. Another very intriguing result of this study was the effect of elemental sulfur on the formation of HMW compounds in these experiments. It was found that the presence of elemental sulfur inhibits the oligomerization process leading to the formation of decarboxylation products. In support of the possible origins of the HMWHC discussed above are the results of Carlson *et al.* (1997). Based on the similarities in the carbon isotopic composition of LMW (C_{20} - C_{40}) and HMW n-alkanes in wax samples from Alberta Basin, Canada, and Uinta Basin, Utah, it was concluded that both groups of hydrocarbons have a common biological or diagenetic origin.

An alternative origin of HMWHC relates to the in-reservoir thermal alterations of crude oils (del Rio and Philp, 1992a; del Rio *et al.*, 1992; Philp *et al.*, 1995). It was proposed that the HMWHC may be chemically bound to the asphaltenes and under high temperatures and/or pressures in deep reservoirs could be released as free hydrocarbons. The reservoir temperature conditions where degradation of asphaltenes to hydrocarbons may occur was discussed by Schenk *et al.* (1997) in an experimental closed-system pyrolysis study on the secondary oil to gas cracking of reservoired terrigenous wax-rich

and marine-sourced oils. The degradation of asphaltenes into hydrocarbons appears to occur in the zone of early gas generation at around 160°C, with variations depending on the heating rates of the particular basin (Schenk *et al.*, 1997). A study of the formation of ozocerites in the Dead Sea region presents one possible field example of HMWHC with such an origin (Nissenbaum and Aizenshtat, 1975). The high molecular weight n-alkanes ($>C_{30}$) are abundant in this region's ozocerites and have been proposed as possibly being released under higher temperatures from underlying heavy oil accumulations and precipitated in secondary migration conduits.

C2. Geological conditions that could affect the concentration of

macrocrystalline (LMWHC) and microcrystalline (HMWHC) type waxes in oils

A detailed literature review has suggested that several factors can be related to the occurrence of high concentration of waxes in oils. These main factors are kerogen type, depositional environment, climate, petroleum generation, primary and secondary migration, post-accumulation reservoir alterations. Traditionally the origin of high-wax oils has been viewed as being related to an association with terrestrial organic matter and lacustrine, fluvial and deltaic-type depositional environment. A number of studies has presented evidence for the existence of such a relationship but the studies of Hedberg (1968) and Hunt (1954, 1991, 1995) appear to be the main cornerstones in the process of clarifying the significance of high-wax oils with respect to the genesis of petroleum.

Hedberg (1968), in his classic paper based on analysis of physical properties (API gravity, pour point, cloud point), wax content and the geographical and geological

distribution of more than 300 high-wax oils from all continents, suggested the existence of a major relationship between those oils and terrestrially sourced organic matter. The specific characteristics associated with the occurrence of high-wax oils included: (1) predominantly shale-sandstone sequences deposited under non-marine or brackish water conditions; (2) common occurrence of coal beds and/or oil shales in the sequences containing high-wax oils; (3) Devonian to Pliocene age range of sedimentary sequences containing high-wax oils, with the predominance of these oils in Cretaceous-Tertiary and Carboniferous age strata that could be related to the peaks in land plant evolution during these periods; (4) the oils produced in these sequences are high-wax, low sulfur in contrast to the low wax, high sulfur oils formed in marine environments.

In later years, a number of studies of “classic” high-wax Tertiary oils from India and China has confirmed this type of association of high-wax oils with terrestrially sourced organic matter and freshwater environments of source rock deposition (Saikia and Dutta, 1980; Samanta *et al.*, 1994; Yongsong *et al.*, 1991). Other areas of known high-wax oils include Indonesia (Mahakam delta), Australia (Gippsland Basin), Argentina, Venezuela, Brazil and West Africa. In a recent regional study, Waseda and Nishita (1998) compared the geochemical characteristics of terrigenous- and marine-sourced oils from Hokkaido, Japan, and confirmed the major findings of Hedberg (1968). Based on biomarker correlations, they established that high-wax oils (>5 wt.% wax, method of wax determination not reported) with low sulfur content (< 0.1-0.2 wt.%) were generated mainly from the Paleogene coal-bearing formations dominated by terrigenous organic matter and deposited under highly oxic conditions. Low-wax oils (< 1 wt. %

wax) with higher sulfur content (0.1-0.2 wt.%) were correlated with the Miocene marine shales.

The association of high-wax oils with coals and Type III kerogens was specifically discussed by Hunt (1991) in his review of oil and gas generation from coal and other terrestrial organic matter. It was shown that some maceral groups (wax and liptinite) have a high hydrogen content and their oil generative potential is comparable with Type I and II kerogens. Cutinite, alginite, resinite, sporinite, and suberinite, all belonging to the liptinite group are hydrogen-enriched macerals with oil-generation potential. Organic matter sources enriched with alginite, cutinite and sporinite tend to generate waxy oils, while organic matter enriched in resinites often results in generation of naphthenic oils (Hunt, 1991). Extracts of immature coals, enriched with different liptinitic maceral components, suberinite and cutinite, were shown to be characterized by n-alkane distribution maximizing at different carbon numbers - C_{23} and C_{29} , respectively (Khavari-Khorasani and Michelsen, 1991). Similar distributions were observed also in the pyrolyzates of these two types of coals. A marked variability in thermal stability and composition of generated hydrocarbons, even within the same maceral, was indicated by the series of studies on resinite (Lewan and Williams, 1987; Khavari-Khorasani, 1987; Khavari-Khorasani and Murchison, 1988; Snowdon, 1991). Tegelaar *et al.* (1989) reported a group of biological precursors present in the leaf cuticle of an extant vascular plant that could generate high amounts of nC_{20} - C_{35} alkanes. Artificial maturation experiments showed a high generation potential of this biopolymer for n-alkanes in the range C_{15} - C_{35} and the formation of methyl-branched alkanes.

One of the most widely studied examples of high-wax oils being associated with lacustrine and fluvial deltaic source rocks is the Green River Formation in Uinta Basin, Utah. The Green River Formation is a mixture of open lacustrine, marginal lacustrine and alluvial facies contributing different types of kerogen mixtures to the sedimentary sequence (Tissot *et al.*, 1978; Hunt, 1991). The open lacustrine facies, characterized by oil shales dominated by kerogen Type I, are restricted to the deepest lake facies. Kerogens from Green River oil shales are representative of Type I kerogens and are considered to be derived mainly from the lipid fraction of algae, and terrestrial spores and pollen (Tissot *et al.*, 1978; Hunt, 1991). The source rocks in the basin are generally considered to belong to the deep open lacustrine facies (kerogen Type I). The marginal lacustrine facies, characterized by kerogen Types I and II, and the alluvial facies of the Wasatch formation, mainly of kerogen Type III, become predominant from the basin's center to the edge of the lake deposits. The high-wax oils production is mainly from the sequence comprising the marginal lacustrine and alluvial facies. Ruble (1996) suggested that the source of the waxy oils is a distinct sulfur-rich Type I kerogen belonging to the nearshore open lacustrine source rocks of the basal black shales identified to belong to the lower Green River Formation.

The above discussion based on results of published studies demonstrates that the high-wax oils can be related to Types I, II and III kerogens. The compositional variability that can exist in mixtures of kerogens, and even within the same type kerogen, suggests that a relative predominance of one or another component (s) in the kerogen (kerogen mixture), with significantly different kinetic oil generation characteristics, may

significantly affect the amount, maturity, timing and composition of generated oils, and could result in formation of both high-wax and low-wax oils containing both macro- and microcrystalline type waxes.

The importance of warm climates as related to the formations of high-wax oils and bitumens has been addressed by several studies. Martin *et al.* (1963) discussed that the higher production of saturated fatty acids by plants under warm climate conditions is one factor contributing to the occurrence of high-wax oils (high concentration of $nC_{20}-C_{35}$ alkanes). A regional study of wax-bearing Cenozoic lignites in the former USSR by Serova (1987) showed a close relationship between the high-wax content coal bitumens and the flourishing of angiosperm plants in the Paleogene-Neogene. A strong relationship was also found between the amount of wax content and the paleoclimatic zone of coal formation. For example, the highest wax content (75-85%) in coal bitumens was found in lignites formed in subtropical paleoclimatic zones and, with increasing distance from the subtropical Eocene climatic belt, the wax content showed a sharp decrease. Similar trends between wax content and changing climates during Eocene-Miocene in the region were observed along the stratigraphic section from Eocene (75-85% wax content in coals) to Oligocene (55-75% wax content in coals) and Miocene (30-60% wax content in coals) strata, corresponding to the major cooling climatic cycle that started in the Oligocene.

Another factor that can affect the concentration of macrocrystalline and microcrystalline waxes in oils is related to the hydrocarbon expulsion and primary migration restrictions in massive coal beds (Hedberg, 1968; Hunt, 1991). Hunt (1991) noted that coals can have oil generation potential, especially when enriched in the

hydrogen-rich liptinites. However, massive coal beds are characterized with high adsorptive capabilities, and a predominant micropore size range (0.8-2 nm, encompassing 30-76% of pore volume in Alberta coals, for example), which have been recognized as two important factors influencing expulsion and primary migration of high-wax oils. For the case of Alberta coal, macropores (>50 nm) constitute 19-50% of pore volume, with the remaining pore volume distributed between mesopores (2-50 nm) and ultramicropores (<0.8 nm). A comparison with the diameters of complex hydrocarbon ring structures (about 2 nm), and small asphaltenes (about 5 nm) led to the suggestion that newly generated liquid material would not be able to migrate out of a large portion of coal's pore volume (e.g., at least 30-76%) until the coal is fractured. This would result in the free hydrocarbons being physically trapped inside the coal pores (Hunt, 1991).

The importance of kerogen type variations in coals and the coal adsorptive capacity as key controlling factors for the composition of expelled fluids from coals has been discussed in a number of studies (Killops et al., 1998; Inan et al., 1998; Isaksen et al., 1998). In addition, it has been noted that high amounts of generated hydrocarbons would be necessary to overcome coal sorptive capacity and promote expulsion. In such cases, the expulsion of aliphatic liquids from coals would be facilitated once the concentration of generated hydrocarbons reaches sufficiently high levels so that not all of them are partitioned into bound and adsorbed phases (Isaksen et al., 1998). Consequently, the expelled fluids will be enriched in aliphatic components with minor concentrations of aromatics and polars. In contrast, the expulsion of oil from hydrogen-poor kerogens would be limited by the insufficient amount generated compounds necessary to overcome

the coal sorptive capacity, and this type of coal would be more prone to gas generation, rather than liquid and specifically high-wax oil formation (Killops et al., 1998; Inan et al., 1998; Isaksen et al., 1998).

Exploring the association between oil shales and high-wax oils, Hunt (1991, 1995) pointed out that oils that have been generated from oil shales tend to be high-wax oils, reflecting the highly aliphatic nature of the predominant kerogen types, and the need for further cracking for expulsion to occur. However, the restriction to expulsion/primary migration identified in the case of oil shales is that there is often little water and/or gas in fractured oil shale reservoirs, such as Green River Formation, and thus no driving mechanisms to assist the migration of a viscous, waxy oil. Additional factor that could influence the amount of generated n-alkanes has been recognized recently to be the heating rate of generation (Dieckmann et al., 1999). The results of this study demonstrated that at lower heating rates the ratio of n-alkanes (nC_{6+}) to aromatics increases.

The effect of secondary migration on waxy (LMW and HMW) hydrocarbons does not appear to have been studied to any significant extent. One possible reason, specifically related to the HMWHC, is that the presence of HMWHC may have been overlooked in earlier studies on secondary migration related to analytical limitations for detection of HMW compounds. Results of several recent studies will be discussed below, presenting evidence related to the deposition of petroleum waxes along secondary migration pathways, in reservoirs, and the influence of secondary alteration processes on reservoired oils. All of these processes could affect the concentration and composition of

petroleum waxes. Manning and Gize (1993) observed a number of different phases in petroleum inclusions of fluorite and distinguished clear wax precipitate and a black organic precipitate (possible asphaltene) in the inclusions, in addition to the hydrocarbon vapor and liquid phases, aqueous fluid and inorganic phases. More recently, Ruble et al. (1997) demonstrated the presence of high-wax oils trapped in fluid inclusions of reservoir rocks and indicative of the mixing of oils from two different source rocks, which allowed to elucidate multiple charges in reservoir filling. One field example relating the occurrence of high-wax oils with migrational fractionation processes was discussed by Shuichang and Digang (1997). Based on the distribution and composition of low-maturity gas-condensates and waxy oils in the same clastic sequence of the Tarim Basin, it was suggested that they are genetically related and result from processes of migrational fractionation leading to an increased wax content of the residual oils.

A preferential decrease in concentration of HMWHC relative to the LMWHC could occur during secondary migration processes, since HMW n-alkanes have significantly higher melting points compared to the LMW n-alkanes, and they will start to experience liquid-solid phase changes at higher temperatures and earlier stages of migration (section IV. 2. 3). In addition, higher adsorptive properties of HMWHC and the geochromatographic processes associated with oil migration (Bonilla and Engel, 1986, 1987; Kroos et al., 1991; Brothers et al., 1991; Philp and Engel, 1987; Clark et al., 1999) could further promote a decrease in concentration of HMW n-alkanes at much earlier stages compared to the LMW n-alkanes. Additional specifics in the processes of generation (e.g., heating rate), migration (e.g., pressure-temperature related to the

supercritical condition and solubility of the oil towards HMW vs. LMWHC) and in-reservoir thermal alterations (e.g., post-accumulation burial/uplift of reservoir, multistage hydrocarbon accumulation, biodegradation) are other options that may lead to variability in concentration of LMW and HMWHC in oils.

Based on the results of published studies presented above, several comments can be made regarding expulsion and migration processes, specifically related to the high concentration of LMW (C_{20} - C_{35}) n-alkanes in high-wax oils and the commonly observed low concentrations of HMW (C_{35} - C_{80+}) n-alkanes in oils of different origin. The discussion in Hunt (1991) paper regarding the restriction to expulsion/primary migration of complex HMW molecules due to their larger sizes compared to the predominant micropore range in coals, raised the question if similar considerations would be valid specifically for the HMW n-alkanes. In an attempt to address this question, quantitative estimates of the average lengths and volumes of n-alkanes in the carbon number range C_5 - C_{120} are presented in **Table IV. 2. 2** and **Figure IV. 2. 2**, following the calculation procedure described in **Appendix IV. 2. 1**. The calculations are performed assuming a fully extended chains of the n-alkanes, which may be to some extent a reasonable assumption, considering that source rock oil generation occurs under high (supercritical) pressure-temperature conditions. The estimates suggest an average length below and above 2 nm for nC_{20} - C_{100} alkanes and nC_{100} - C_{120} alkanes, respectively. Considering the pore diameters ranges in coals discussed by Hunt (1991), the HMW n-alkanes above nC_{100} have lengths that would represent a restriction to their expulsion from the predominant micropore range (0.8-2 nm) in coals. However, LMW (nC_{20} - C_{35}) alkanes

CN n-alkanes	Length (nm)	Volume (nm ³)
5	0.45	0.03
10	0.64	0.07
20	0.90	0.21
30	1.10	0.38
40	1.27	0.59
50	1.42	0.82
60	1.56	1.08
70	1.68	1.36
80	1.80	1.66
90	1.91	1.98
100	2.01	2.31
110	2.11	2.67
120	2.20	3.04

Table IV. 2. 2. Average length and volume estimates of n-alkane molecules (for procedure of calculation, see Appendix IV. 2. 1).

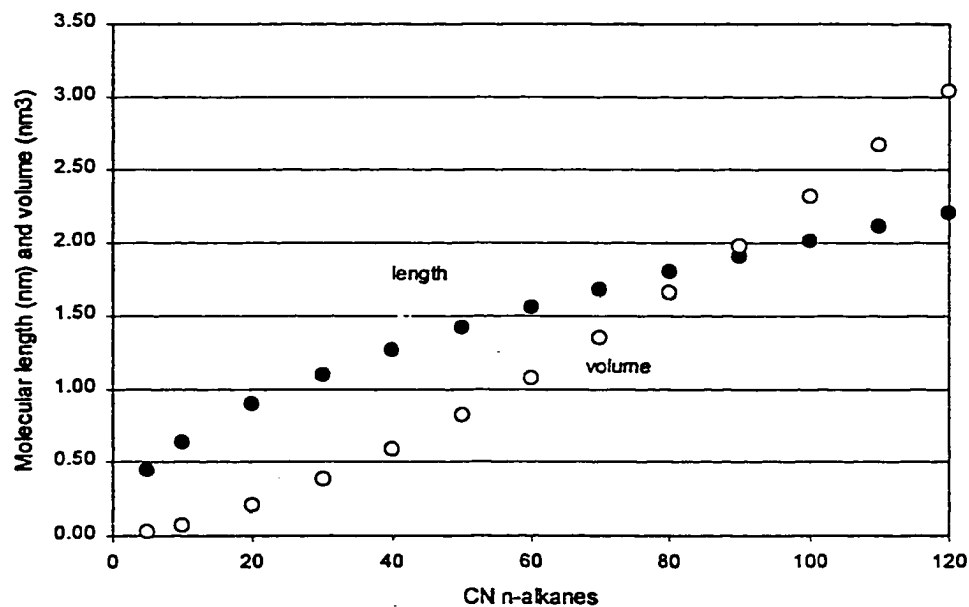


Figure IV. 2. 2. Plot of calculated average molecular length and volume of n-alkanes in the carbon number range C₅ to C₁₂₀.

and a part of the HMW (nC_{35} - C_{100}) alkanes have sizes that do not appear to represent a restriction for their expulsion from the micropores (0.8-2 nm). If the sizes of LMW and nC_{35} - C_{100} HMW alkanes do not represent restriction for their expulsion from the dominant micropore range in coals, then restrictions of other character can be expected to be more important for the observed high and low concentrations of LMW (nC_{20} - C_{35}) and HMW n-alkanes, respectively, in high-wax oils generated from coals. Other considerations include differences between adsorption capabilities and/or type of organic matter capable of generating high amounts of LMW versus HMW n-alkanes. Higher adsorption abilities are characteristic for the HMW n-alkanes compared to the LMW n-alkanes (see **Table IV. 2. 1** and discussion in section IV. 2. 3), and could be an important factor for their preferential retention in the pore volume of coals by adsorption to mineral surfaces and/or polar fractions such as resins and asphaltenes. Regarding type of organic matter, several studies have shown the existence of insoluble biopolymers and hydrogen-rich macerals that are capable of generating high amounts of C_{15} - C_{35} n-alkanes, but to our knowledge no studies are available presenting data for proto-kerogen components capable of generating high concentration of specifically HMW ($>C_{40}$) n-alkanes. The above discussed line of considerations could be valid for source rocks other than coals (e.g., marine shales), since the pore size in most source rocks falls in the range of 1-3 nm (Tissot and Welte, 1984; Werner *et al.*, 1996).

C3. Summary

(1) Petroleum wax refers to the mixture of hydrocarbons in oils that are solid at ambient conditions (e.g., n-alkanes $>C_{18-20}$). The upper carbon number ranges are not well defined, but hydrocarbon distributions extending to nC_{80} have been commonly identified by HTGC in oils and wax deposits. Petroleum waxes are generally dominated by n-alkanes, with smaller amounts of iso-, cycloalkanes and alkylaromatics.

(2) Biomolecular precursors for n-alkanes, iso-alkanes, cycloalkanes, alkylaromatics, with molecular weights range sufficiently broad and high to account for the presence of these compounds in petroleum waxes, are present in both marine and terrestrial organisms.

(3) Evidence has been presented for a common biological and/or diagenetic origins of LMW and HMWHC (Carlson *et al.*, 1997) as well as for a diverse origin (higher plant and microbial for LMW and HMWHC, respectively, Rieley *et al.*, 1991). HMWHC can be formed by oligomerization processes under high thermal stress and/or by thermal alteration of asphaltenes in reservoired oils.

(4) Both macrocrystalline (nC_{20} to C_{30-35} alkanes) and microcrystalline waxes can be present in high-wax and low-wax oils. The concentration of macrocrystalline waxes is commonly high in high-wax oils. Microcrystalline waxes are generally present at much lower concentration levels compared to macrocrystalline waxes in oils.

(5) Possible explanations for the low concentration range of microcrystalline waxes (HMWHC) commonly found in oils of different origins could be related to: (a) their origin from the soluble organic matter in rocks and/or early kerogen degradation at

low maturities; (b) their higher adsorption capabilities and higher melting points as compared to the LMW (C₂₀-C₃₅) n-alkanes, which may preferentially restrict their primary migration, and/or promote their adsorption along secondary migration pathways and in reservoirs based on the principles of geochromatography.

(6) HMWHC have been found to be ubiquitous in both terrestrial and marine source rock bitumens and oils. They have a potential to become a very important biomarker group for source-source, source-oil and oil-oil correlations and may prove to be very useful as indicators of generation, migration (including inter- and intra-reservoir migration) conditions and charge history of petroleum reservoirs.

IV. 2. 3. SOLUBILITY VS. COMPOSITION OF n-ALKANE MIXTURES

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IV. 2. 3. A. Introduction and purpose of the study

Petroleum waxes by definition are dominated by n-alkanes with more than 18-20 carbon atoms (see section IV. 2. 2). The high molecular weight (HMW) nC_{35+} alkanes, specifically, have been observed to concentrate in the petroleum wax deposits (e.g., Carlson *et al.*, 1991, 1993; del Rio and Philp, 1992b; see overviews in sections IV. 2. 1 and IV. 2. 2). One of the main processes leading to wax precipitation and deposition is related to variations in solvency capacity of oil acting as a solvent towards its heavy fractions under changing temperature, pressure and oil composition (e.g., Carnahan, 1989; see overviews in sections IV. 2. 1 and IV. 2. 2). Two main problems arise when attempting to evaluate the solubility of n-alkane mixtures in wax deposits and petroleum waxes. First, field wax deposits and petroleum waxes, precipitated from oils by most of the laboratory methods, represent complex mixtures of hydrocarbons (n-alkanes, iso-

alkanes, cycloalkanes, aromatic hydrocarbons) and non-hydrocarbons (mainly concentrated in the resin and oil asphaltene fractions) in various proportions. The solubility behavior of these various compound classes is very different and has not been completely elucidated and the solubility of mixtures they form is even more uncertain. Second, available experimental data on physical properties and solubility of HMW n-alkanes and n-alkane mixtures, which dominate the hydrocarbon composition of wax deposits, are insufficient at the present time.

The present part of the study explores the relationship between composition (carbon number and concentration distribution) of n-alkane mixtures and their solubility in different solvents with special emphasis on the HMW n-alkane mixtures. The approach used is based on the solubility parameter concept, developed by Hildebrand and Hansen during the period 1916-1967. Three methods for calculation of solubility parameters of n-alkanes (C_5 - C_{120}) are discussed and their predictions are compared with experiments on solubility of a standard n-alkane mixture dominated by HMW alkanes and pipeline wax deposits. In addition, the solubility parameter concept is applied to evaluate the choice and efficiency of solvents used in two laboratory techniques for wax precipitation and dissolution.

The results of the present study address the following questions:

(1) Is it possible to predict the optimum solvent, i.e., the solvent that would dissolve the largest amount of solute, for n-alkane mixtures of increasing molecular weight?

(2) Which of the three methods for calculating solubility parameters of pure n-alkanes is most reliable?

(3) How can the solubility parameters of n-alkane mixtures be calculated from quantitative high temperature gas chromatography (HTGC) analysis?

(4) What is the effect of different proportions of polar fractions (e.g., resins) on the choice of optimum solvent for dissolution of mixtures of n-alkanes and resins?

(5) Can the solubility parameter concept be applied for evaluation of solvents for more efficient precipitation or dissolution of petroleum waxes, depending on their compositional characteristics?

The importance of answering these questions relates to increasing the efficiency of recovery, fractionation and quantitative estimation of n-alkane mixtures in petroleum waxes and wax deposits by laboratory techniques, with possible applications for improving the efficiency of chemical treatment of wax deposition problems in the field.

Since the behavior of n-alkane mixtures is the main topic of this study and the approach is based on the solubility parameter concept, an overview on the properties of pure n-alkanes and n-alkane mixtures and the solubility parameter concept (sections IV. 2. 3. B, C) is given prior to discussing results obtained in the present study (sections IV. 2. 3. D, E, F).

IV. 2. 3. B. Properties of n-alkanes and their mixtures

Available data on the properties of pure n-alkanes becomes very limited in the higher molecular weight range ($> C_{30}$; Table IV. 2. 3) covering only a relatively small

CN C_nH_{2n+2}	Name	B.p.(C)	m.p. (C)	Difference m.p. even-odd CN	MW	Density (g/cm ³)		Refractive index	
						liquid	solid	liquid	solid
3	propane	-42.1	-188.0	-16.0	44				
4	butane	-0.5	-138.0	50.0	58				
5	pentane	36.1	-130.0	8.0	72	0.6260		1.3579	
6	hexane	68.7	-95.0	35.0	86	0.6590		1.3748	
7	heptane	98.4	-91.0	4.0	100	0.6840		1.3876	
8	octane	125.7	-57.0	34.0	114	0.7030		1.3974	
9	nonane	150.8	-54.0	3.0	128	0.7180		1.4054	
10	decane	174.1	-30.0	24.0	142	0.7300		1.4119	
11	undecane	195.9	-26.0	4.0	156	0.7400		1.4176	
12	dodecane	216.3	-10.0	16.0	170	0.7490		1.4216	
13	tridecane	243.0	-5.5	4.5	184	0.7560		1.4233	
14	tetradecane	253.5	6.0	11.5	198	0.7630		1.4290	
15	pentadecane	270.5	10.0	4.0	212	0.7690		1.4315	
16	hexadecane	287.0	18.0	8.0	226	0.7730		1.4345	
17	heptadecane	303.0	22.0	4.0	240		0.7780		1.4369
18	octadecane	306.0	28.0	6.0	254		0.7770		1.4349
19	nonadecane	330.0	32.0	4.0	268		0.7770		1.4409
20	eicosane	343.0	36.8	4.8	282		0.7890		1.4425
21	heneicosane	356.5	40.5	3.7	296		0.7919	1.4240	1.4441
22	docosane	368.6	44.4	3.9	310		0.7944	1.4358	1.4455
23	tricosane	380.0	47.6	3.2	324	0.7785		1.4270	1.4468
24	tertacosane	391.3	54.0	6.4	338	0.7786	0.7991	1.4383	1.4283
25	pentacosane	401.9	54.0	0.0	352	0.7785	0.8012	1.4380	1.4491
26	hexacosane	412.2	56.4	2.4	366	0.7783		1.4357	
27	heptacosane	442.0	59.5	3.1	380	0.7796		1.4345	
28	octacosane	431.6	64.5	5.0	394	0.7792	0.8067	1.4330	
29	nonacosane	440.8	63.7	-0.8	408	0.7797	0.8083		1.4529
30	triacontane	449.7	65.8	2.1	422	0.7795	0.8097	1.4352	
40	tetracontane		81.4	15.6	562				
43					604	0.7812		1.4340	
50	pentacontane	421.0	92.0		702				
60	hexacontane		98.9		842				
70	heptacontane		105.2		982				
100	hectane		115.2		1402				

Table IV. 2. 3. Physical properties of pure n-alkanes (Lide, 1999). Data for liquid and solid state are distinguished according to temperature of measurements of density and refractive index relative to the melting point of the compounds. CN - carbon number of n-alkanes.

domain of the possible carbon number range n-alkanes present in petroleum waxes (C_{20} - C_{30}). An increasing number of studies dealing with different aspects of the properties of n-alkanes and n-alkane mixtures have been recently published (Ksiazczak *et al.*, 1994; Srivastava *et al.*, 1995; Letoffe *et al.*, 1995; Achour *et al.*, 1992, 1995, 1996; Smith and Teja, 1996; Clavel-Grunbaum *et al.*, 1997; Dirand *et al.*, 1998; Chevallier *et al.*, 1999a and b). The following summary discusses the physical properties, molecular structure, crystal behavior and solubility of pure n-alkanes and their binary, ternary and multicomponent mixtures (Appendix IV. 2. 2). The results in discussed published studies have been obtained based on: X-ray diffraction methods (Schaerer *et al.*, 1955; Ohlberg, 1959; Ungar, 1983; Srivastava *et al.*, 1992; Achour *et al.*, 1996; Dirand *et al.*, 1998; Chevallier *et al.*, 1999a and b); differential thermal analysis (DTA; Ungar, 1983; Kim *et al.*, 1989; Chevallier *et al.*, 1999b); differential scanning calorimetry (DSC; Maroncelli *et al.*, 1985; Handoo *et al.*, 1989; Letoffe *et al.*, 1995; Srivastava *et al.*, 1993, 1995; Achour *et al.*, 1996); Raman and infrared spectroscopy (Maroncelli *et al.*, 1985; Kim *et al.*, 1989; Clavel-Grunbaum *et al.*, 1997).

B1. Properties of n-alkane homologous series

n-Alkanes are straight chain saturated hydrocarbons and form a homologous series with a general formula C_nH_{2n+2} , where n can vary from one to possibly thousands. Molecules of n-alkanes consist of single C-C and C-H bonds, and since the electronegativities of carbon and hydrogen are very close, the covalent bonds formed are the least polar single bonds in organic molecules. n-Alkanes are generally stable and

unreactive, and in a solid state form molecular crystals held by the relatively weak intermolecular forces. An increase in carbon number and molecular weight of individual n-alkanes is associated with an increase in their melting and boiling points, density, refractive index and viscosity (Table IV. 2. 3), and a decrease in solubility. The increase in molecular size results in a greater thermal energy necessary to overcome the intermolecular forces of the solid material, and hence higher melting points. Longer molecules also have greater surface areas which facilitates stronger intermolecular interactions, and decrease their solubility.

The crystal properties of n-alkanes and their mixtures have profound effect on their melting point, phase transition behavior and solubility, which are very important for better understanding of the petroleum wax deposition problem (see section IV. 2. 1). Two distinct trends in pure n-alkane properties exist for this homologous series. They relate to differences in the properties of even versus odd carbon number n-alkanes up to about C₂₅, and lower (up to about nC₃₆) versus higher molecular weight homologues. In addition, the crystal and solubility behavior of n-alkane mixtures (binary, ternary and multicomponent) differ from the properties of pure n-alkanes and show some trends depending on the average carbon number of the mixture, and the carbon number range and concentration of individual components.

*B2. Crystal behavior of pure n-alkanes and n-alkane mixtures at “room”
temperature*

Pure n-alkanes. The crystals of pure solid n-alkanes are generally considered to consist of extended chains arranged in a zigzag manner and comprised of numerous molecules aligned in a highly ordered array (**Figure IV. 2. 3**). Experimental studies have demonstrated that crystals of pure odd carbon number n-alkanes in the range C_{11} to C_{29} form orthorhombic systems, while even carbon number n-alkanes form triclinic (C_{18} to C_{24}) or monoclinic (C_{28} to C_{36}) structures (**Figure IV. 2. 4**). Both triclinic and monoclinic crystal systems have been reported for the pure n- C_{26} alkane (Schaerer *et al.*, 1955; Ohlberg, 1959; Ungar, 1983; Achour *et al.*, 1995). In the higher molecular weight ($>C_{40}$) range of the homologues series, the structures of pure n C_{46} and n C_{50} alkanes were reported as orthorhombic with chain packing perpendicular to the lamellar surfaces (Kim *et al.*, 1989), similar to odd carbon number n-alkanes up to about C_{36} . However, it is worth noting that with increasing molecular weight, the length of crystallographic long axis c of the orthorhombic unit cell of pure n-alkanes (C_{13} to C_{61}) increases from about 4 nm to 15 nm (Dirand *et al.*, 1998; Chevallier *et al.*, 1999a).

Pure even- and odd-carbon number n-alkanes in the range up to about C_{25} have been known to form two series differing in physical and crystallographic properties (e.g., Solomons, 1980; Mozes, 1982). Even carbon number n-alkanes have higher melting points compared to the odd carbon number homologues (**Figure IV. 2. 5**), a relationship not observed for their boiling points (**Table IV. 2. 3**). The contrast of this trend between even and odd carbon number n-alkanes is very strong in the range C_4 to about C_{16} , and it

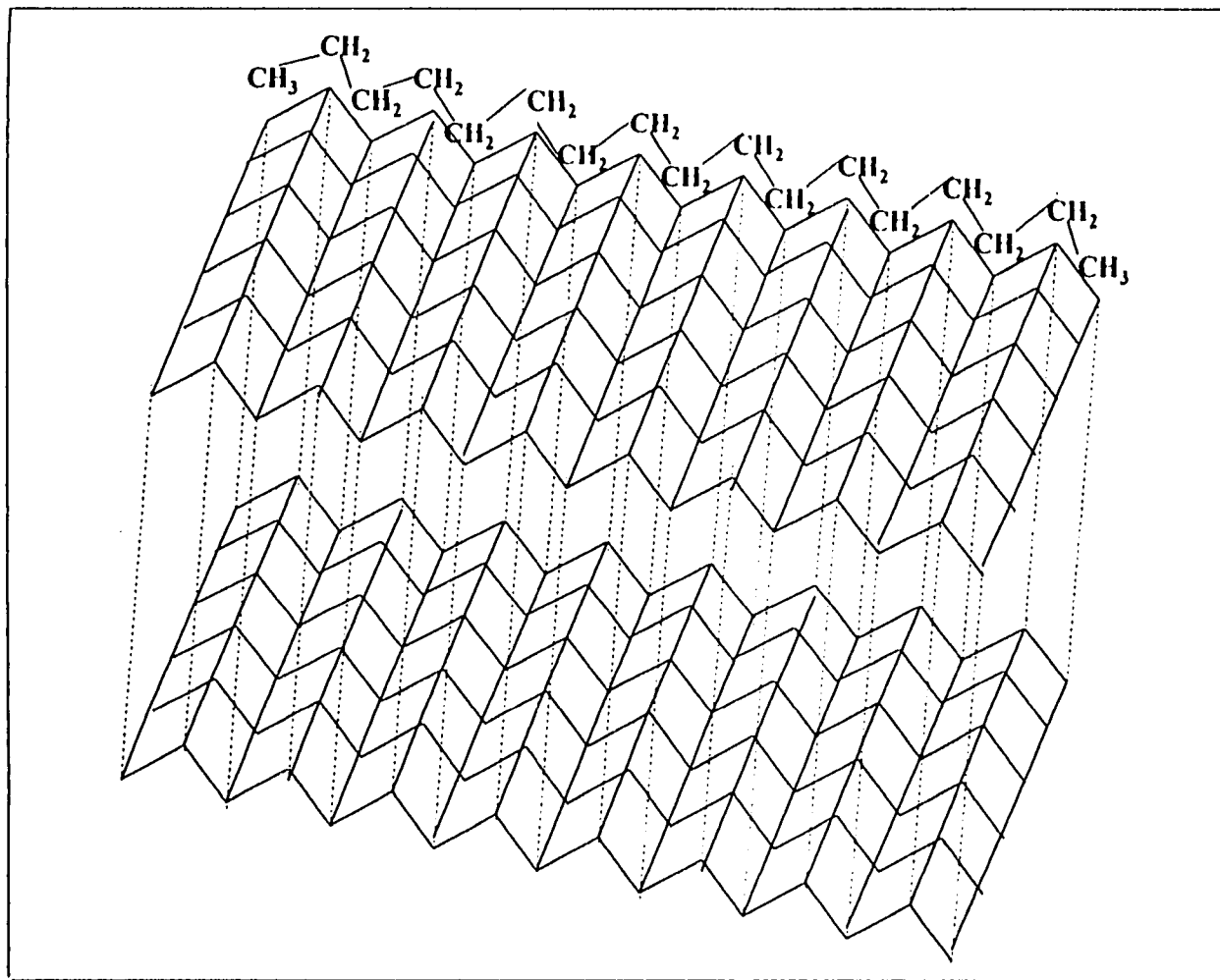


Figure IV. 2. 3. Arrangement of n-alkanes in a wax crystal (Becker, 1997)

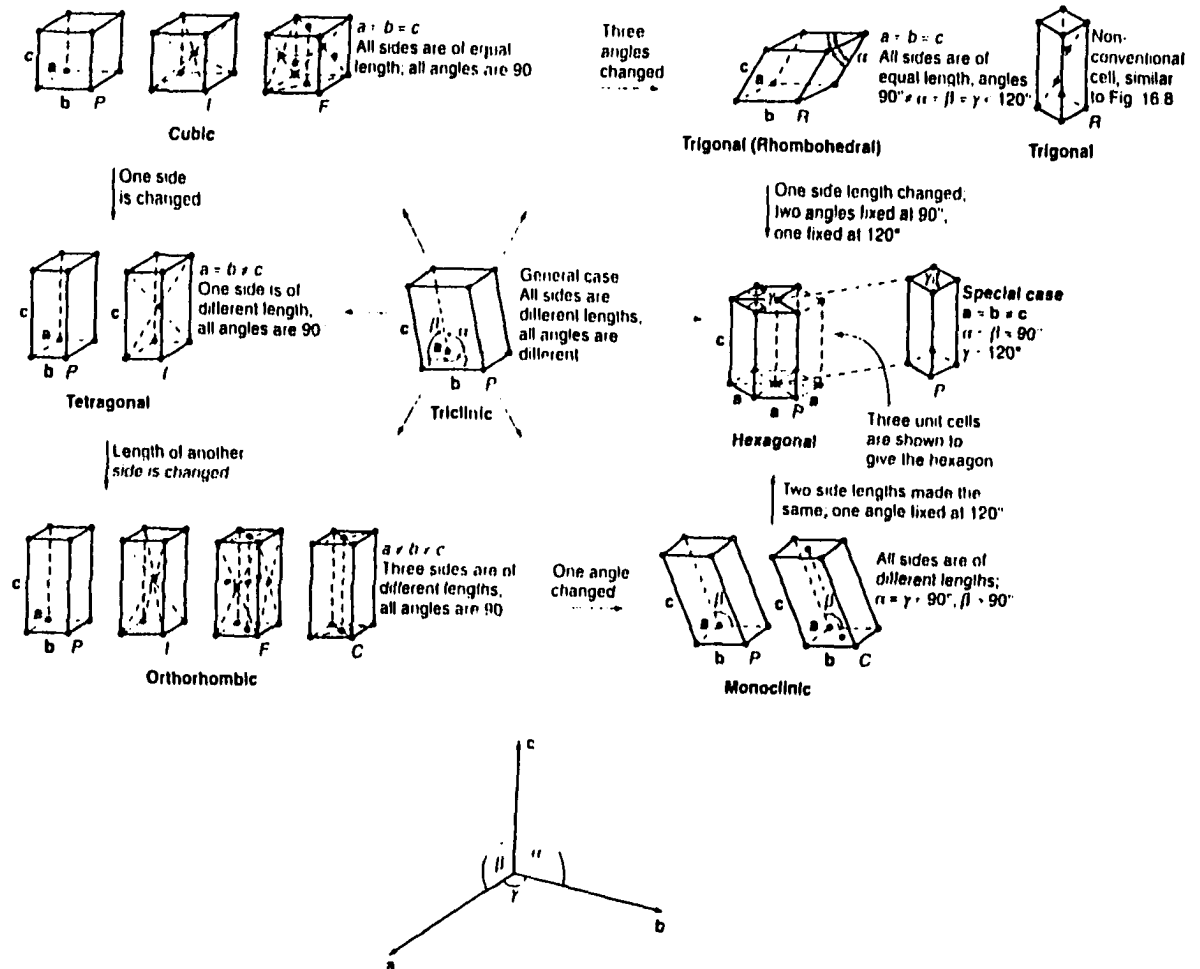


Figure IV. 2. 4. The seven crystal systems and three-dimensional Bravais lattice types (after Laidler and Meisner, 1995).

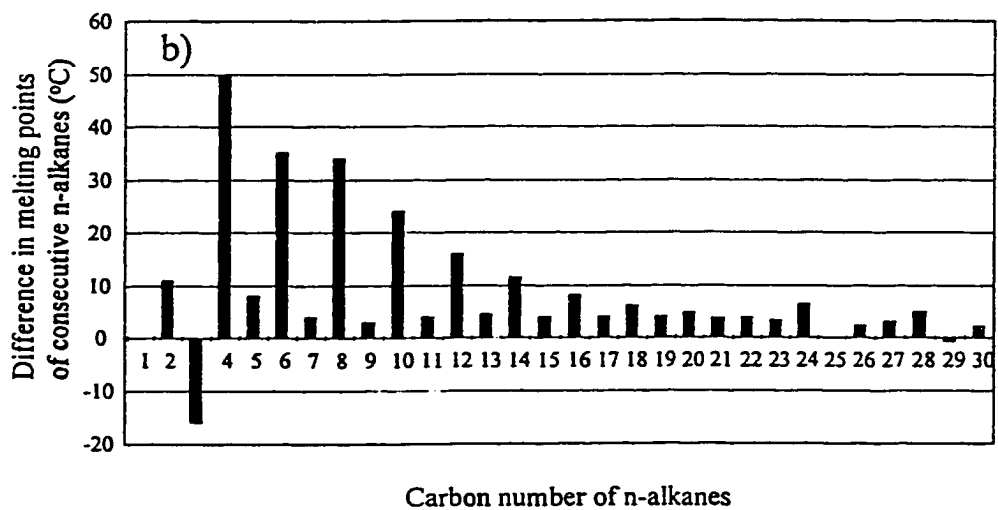
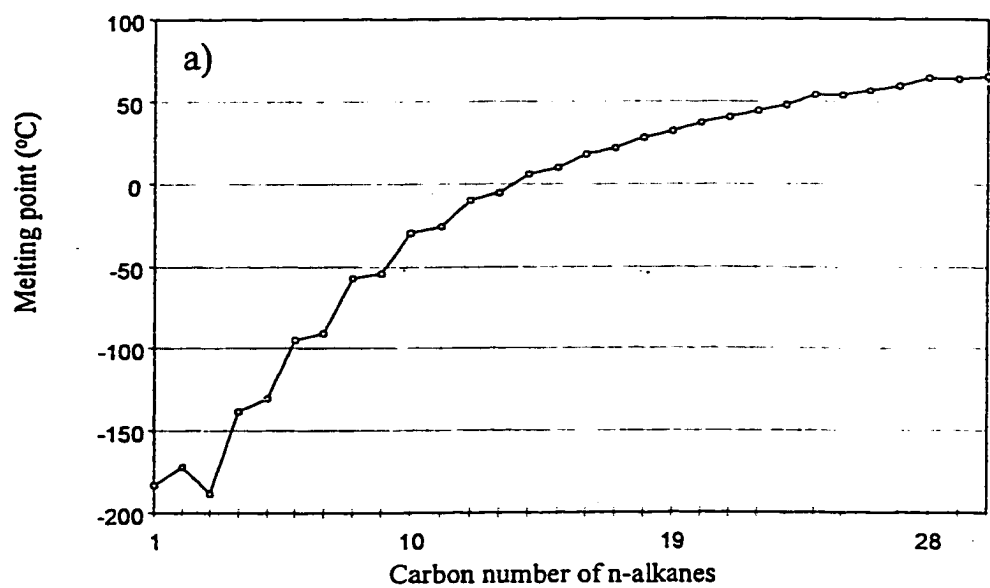


Figure IV. 2. 5. Melting point data of n-alkanes (a); difference in melting points of consecutive carbon number n-alkanes (b). Data for n-alkane melting points from Lide (1998).

could be followed up to C_{25} . For higher carbon number components, the physical property database for n-alkanes decreases sharply and there are significant variations in the values of melting points obtained from different sources related to differences in the techniques of measurement, sample preparation, and influence of solid-solid transition temperatures on melting point measurements. The variations in the melting points of odd and even carbon number n-alkanes up to about C_{25} have been attributed to differences in their molecular and crystal structures allowing even carbon number chains to be packed more closely in the crystalline state (Solomons, 1980). Even carbon number n-alkanes have the end carbon atoms on opposite sides of the chain while odd carbon number chains have the end carbon atoms on the same side of the chain. Since the n-alkane crystal is held together by bonding associated with the end methyl groups and by intermolecular forces between $-CH_2-$ groups of neighboring chains, the chains with even carbon number of atoms pack more closely, allowing the intermolecular forces to be more effective and leading to higher melting points (Ohlberg, 1959; Becker, 1997). For even carbon number n-alkanes, the additivity of intermolecular forces between $-CH_2-$ groups of neighboring chains results in a decrease in the angle that the chain makes with the basal plane. For odd carbon number n-alkanes, the additivity of intermolecular forces between $-CH_2-$ groups of neighboring chains results in a decrease of the cross sectional area of the chain and an increase in chain length (Ohlberg, 1959). More recent studies on solubility of pure n-alkanes (C_{20} to C_{24}) in ethylbenzene at room temperature have presented evidence that the odd-numbered n-alkanes are more soluble than their homologues with even-carbon numbers, confirming the inverse relationship between melting point and

solubility (Ghogomu *et al.*, 1989; **Figure IV. 2. 6b**). The explanation of this observation was related to the alternation of properties in the crystal structures of even and odd n-alkanes at ambient conditions.

Binary n-alkane mixtures. Binary mixtures (prepared as solid solutions of pure components) of odd (C_{19} to C_{27}), even (C_{20} to C_{36}) and odd-even n-alkanes form several solid phases at different concentration ratios of the components (Maroncelli *et al.*, 1985; Achour *et al.*, 1995; Dirand *et al.*, 1998). The phase diagram for the binary system C_{24} - C_{26} is shown in **Figure IV. 2. 7**. At high concentrations (>95%) of the end members in a mixture, two terminal solid solutions (γ_o) form that correspond to the phases formed by the pure end members. At various other concentrations of the components (>5%), several other intermediate solid orthorhombic phases have been identified ($\beta'_1, \beta'_2, \beta''$), demonstrating that binary n-alkane mixtures do not form a continuous homogeneous orthorhombic solid solution at “room” temperatures. The structural characteristics of these intermediate orthorhombic phases were found to be different from the structural characteristics of the orthorhombic phases of pure odd n-alkanes or the terminal phases of their binary mixtures stable at room temperature (Dirand *et al.*, 1998).

Multicomponent n-alkane mixtures. Several orthorhombic solid phases with different long c-axis crystallographic parameters have been reported as stable at room temperature for ternary (C_{22} - C_{23} - C_{24}) and quaternary (C_{22} - C_{26} - C_{30} - C_{34} and C_{24} - C_{28} - C_{32} - C_{36}) solid solutions of n-alkanes (Clavel-Grunbaum *et al.*, 1997; Dirand *et al.*, 1998;

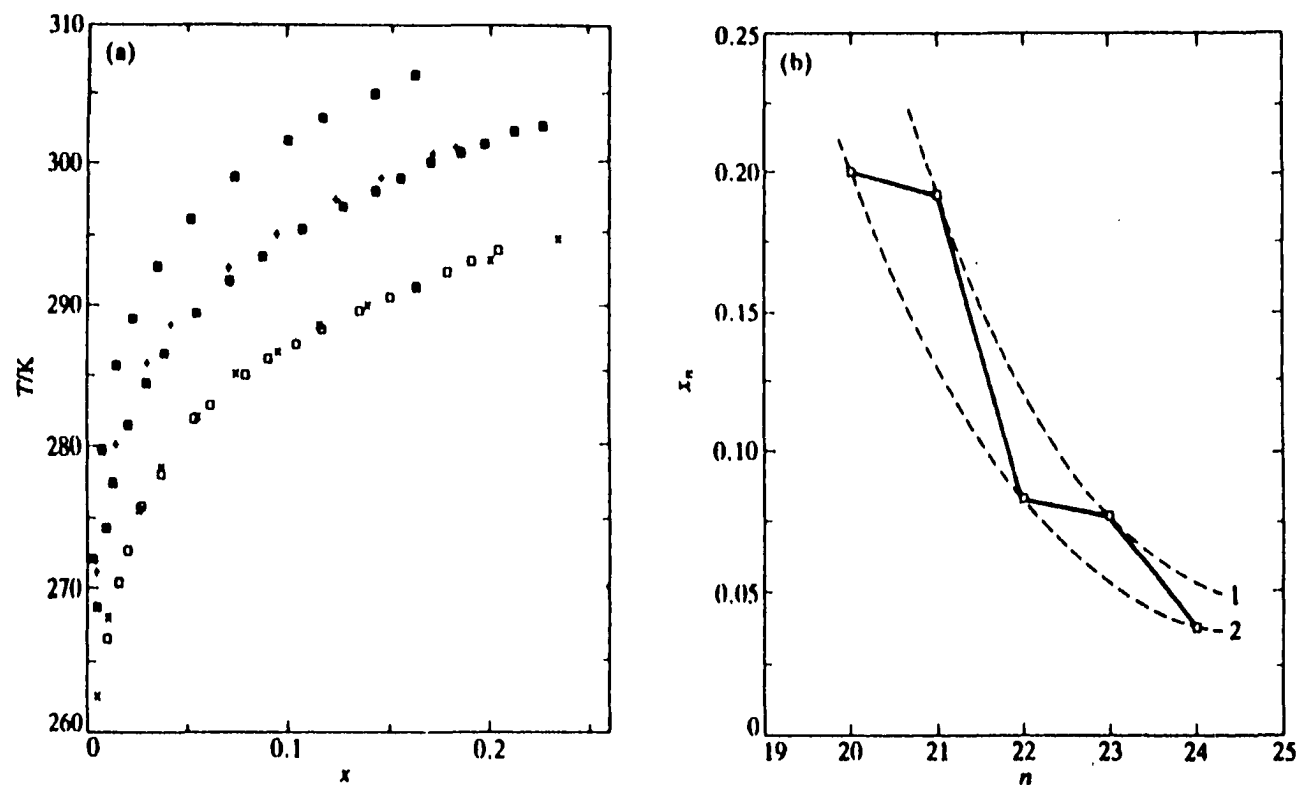
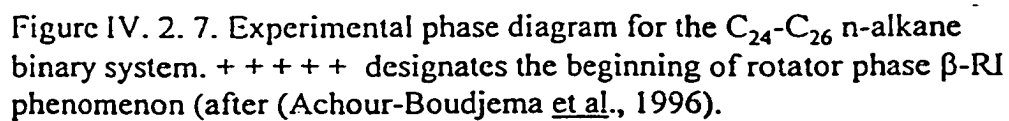


Figure IV. 2. 6. Experimental solubilities for pure n-alkanes in ethylbenzene. (a) Temperature of crystallization as function (x - mole fraction) for nC_{24} , nC_{23} , nC_{22} , nC_{21} , nC_{20} alkanes. (b) Solubilities (x_n - mole fraction) of nC_{20} - nC_{24} alkanes at 293.15 K as function of carbon number n ; 1 - odd carbon number, 2 - even carbon number n-alkanes (after Ghoghomu et al., 1989).



Chevallier et al., 1999a). In addition, experimental results suggested that multicomponent (>4 component) mixtures with a continuous distribution of consecutive carbon number n-alkanes form a single orthorhombic solid phase. Petroleum derived multicomponent n-alkane mixtures with consecutive carbon number components, corresponding to macrocrystalline type waxes (m.p. 33-42°C and 52-62°C, **Table IV. 2. 1**), have been shown to form a single orthorhombic phase (Srivastava et al., 1993; Dirand et al., 1998). In addition, this phase was found to be identical to one of the intermediate solid phases formed by binary or ternary mixtures of consecutive carbon number n-alkanes (Dirand et al., 1998). However, the possibility of domains of two, three or more phases forming at different concentration distributions of the components in multicomponent mixtures has not been excluded (Dirand et al., 1998). Both an orthorhombic and an amorphous solid phases were observed for a multicomponent, non-consecutive carbon number n-alkane mixture (dominated by even carbon number components in the range C₂₀ to C₃₃; Chevallier et al., 1999a) as well as for a multicomponent mixture of consecutive carbon number n-alkanes extending from nC₂₀ to nC₄₂, with a maximum in n-alkane distribution at nC₂₄ (Dirand et al., 1998).

Structural studies of n-alkane mixtures dominated by HMW hydrocarbons (microcrystalline type waxes) are quite scarce. The stable phase at room temperature for this type of wax has been reported to have an orthorhombic structure (Mozes, 1982; Srivastava et al., 1993). Because of the similarities in structure and properties of HMW n-alkanes and commercial polymers, it is interesting to mention some features of the crystal behavior, specifically of high density polyethylenes (HDPE). The HDPE represent

saturated aliphatic hydrocarbons with a low number of branches (2-3 per 1000 carbon atoms) and a range of molecular weights. The HDPE are characterized with densities of at least 0.941 g/cm^3 , and molecular weights from 500-1000 to over ten million (for comparison see **Table IV. 2. 3**). The principal crystalline form of HDPE is orthorhombic with crystallographic parameters $a=0.740 \text{ nm}$, $b=0.493 \text{ nm}$, $c=0.2534 \text{ nm}$ and the polymer chains aligned in crystallographic c-axis direction (Kissin, 1996).

Crystal behavior and solubility of n-alkane mixtures at "room" temperature.

Solid phases formed by both pure n-alkanes (C_{23} to C_{28}) and binary mixtures (C_{26}/C_{28}) in organic solvents are dependent on the concentration of the n-alkanes (Dirand et al., 1998). At low n-alkane concentrations in solutions, the solid formed corresponds to the triclinic, monoclinic or orthorhombic phase of the pure n-alkane or the orthorhombic phase of the binary mixture. At high n-alkane (pure or binary mixture) concentrations, the solid phase has the characteristics of the "rotator" phase (α -RII) of the pure n-alkane or binary mixture, normally observed in solid solutions with increasing temperature. These findings appear to be in agreement with the results of Srivastava et al. (1993) who studied multicomponent, macrocrystalline type waxes and found that the presence of solvent converts some of the orthorhombic lattices of n-alkane mixtures into a hexagonal form. However, it was pointed out that the nature of the solvent would influence this process. In addition, the orthorhombic phase formed at a low concentration of the binary (C_{26}/C_{28}) mixture in heptane was found to be enriched in the heavier (C_{28}) n-alkane. Similarly, the solid solutions formed by multicomponent mixtures most likely will be dominated by the heavier components as discussed by Dirand et al. (1998).

Properties of pure vs. mixtures of n-alkanes at "room" temperature. The differences in properties and behavior of pure n-alkanes and n-alkane mixtures have been attributed mainly to mixing effects and chain length differences of components in a mixture.

Mixing effect. Differences between the properties of pure n-alkanes and n-alkane mixtures have been reported in a number of studies (e.g., Mozes, 1982; Ghoghomu et al., 1989; Dirand et al., 1998). An enhanced solubility of a component in binary and ternary n-alkane mixtures, compared to the solubility of the pure component in organic solvents or solid solutions, has been noted in the studies of Domanska (1987) and Ghogomu et al. (1989). A lower solid-solid phase transition temperature of a mixture compared to the individual components is always observed, given equal melting points of a pure n-alkane and n-alkane mixture (Mozes, 1982).

The conformational disorder in the interlamellar regions of phases formed by n-alkane mixtures has been discussed and related to the formation of different solid phases, and presents an explanation for differences in the behavior of pure components versus mixtures (Maroncelli et al., 1985; Kim et al., 1989; Clavel-Grunbaum et al., 1997). One main difference between n-alkane mixtures (binary, ternary, quaternary with CN range C₂₀ to C₄₀) and pure n-alkanes was found to be the degree of conformational disorder in the interfacial region between lamellas (Clavel-Grunbaum et al., 1997). The conformational disorder in the interlamellar region increases in mixtures compared to pure n-alkanes because of an increase in the concentration of gauche bonds, primarily

around the chain ends as discussed by Maroncelli et al. (1985) and Kim et al. (1989), (Appendix IV. 2. 3). In addition, the concentration of gauche bonds was found to vary with the concentration of components as shown by the experimental results with a binary n-alkane mixture C_{46}/C_{50} where the maximum of conformational disorder is reached in a 1:1 mixture (Kim et al., 1989).

Effect of chain length differences of components in mixtures. Variations in chain lengths of n-alkanes forming a mixture has been found to influence both the miscibility and type of solid phases formed (Kravchenko, 1946; Mozes, 1982). Recent studies, based on Raman and infrared spectroscopy, have confirmed that differences in chain length of components in a mixture influence its crystal behavior (Maroncelli et al., 1986; Kim et al., 1989; Clavel-Grunbaum et al., 1997). A conformational analysis of binary equimolar n-alkane mixtures (C_{30} to C_{40}) with a various chain length mismatch ($\Delta n=1$ to 10) has demonstrated that the disorder in interlamellar regions increases linearly up to a chain length difference of four carbons. This has been related to the effect of gauche bonds, which allow the chains to extend laterally (in direction parallel to the lamellar surface) and permits denser chain packing resulting in formation of stable or nearly stable solid solutions for systems with less than a four carbon number chain mismatch. (Clavell-Grunbaum et al., 1997). A dramatic increase in microphase separation was found to occur at larger chain length differences of the components in binary systems (Clavell-Grunbaum et al., 1997). At a greater chain length mismatch ($\Delta n > 4$), chain end packing becomes increasingly more difficult, and the stability of the mixtures diminishes resulting in microphase separations. The chain extends a minimum of four carbons above the

surface defined by the neighboring chains, which results in bending of the chain. Thus, the results presented above suggest that mixtures of n-alkanes with a narrow carbon number range would be more stable and less soluble than broader carbon number range mixtures. Furthermore, the conformational disorder analysis in binary mixtures with increasing molecular weight (C_{30}/C_n , where n varies from 30 to 40 carbons) has demonstrated that with an increase in chain length difference, the interlamellar disorder increases linearly up to $n=36$, and then decreases. The ordering occurring at HMW mixtures ($n>36$) was attributed to the formation of micro-domains, which are conformationally ordered as they grow.

Based on the findings of Clavel-Grunbaum et al. (1997) on the conformational disorder in mixtures, Dirand et al. (1998) and Chevallier et al. (1999a and b) proposed a probable molecular configurations in packing layers of orthorhombic phases formed by multicomponent, macrocrystalline type waxes (m.p. 52 to 62°C) (**Figure IV. 2. 8**). These multicomponent n-alkane mixtures formed a single lamellar structure of molecule layer stacking. The crystallographic long axis c parameter of this lamellar structure was found to correspond to a chain length of a hypothetical orthorhombic n-alkane with a carbon number equal to the average carbon number of the mixture. In this case, the molecules that are longer than the average carbon number of the mixture, must bend to insert themselves between the molecule layer stacking crystallographic planes and must find a smaller partner (among the components in the mixture) in order to maintain a coherent molecule layer (**Figure IV. 2. 8**). The formation of several orthorhombic phases and an amorphous solid in the non-consecutive carbon number multicomponent mixtures (even

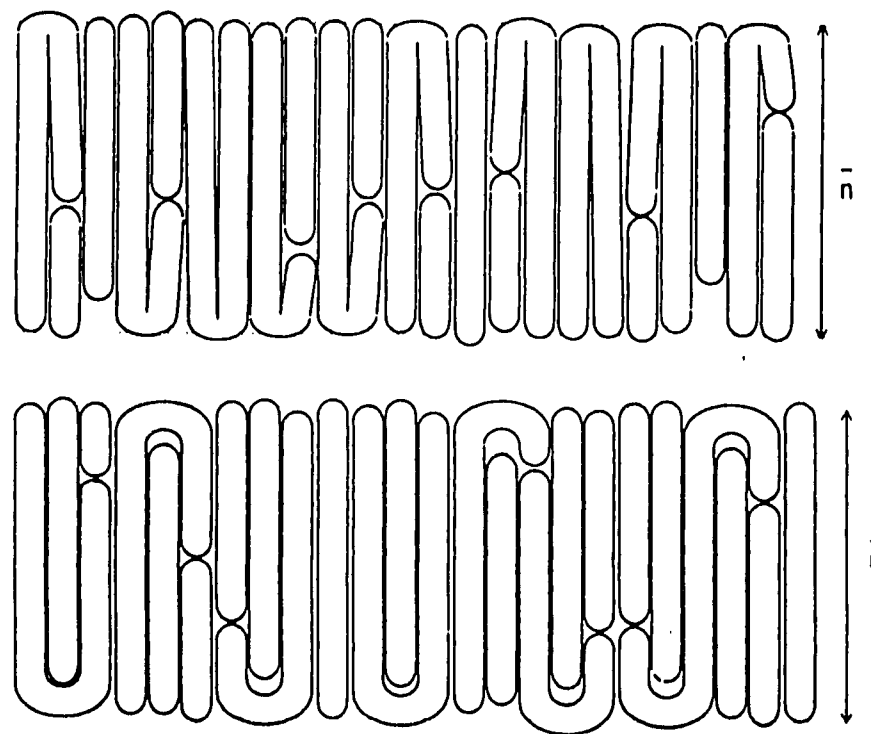


Figure IV. 2. 8. Probable configurations of n-alkane molecules (multicomponent macrocrystalline wax) in a stacking layer of orthorhombic (β) or rotator α -R11 solid solutions. The crystallographic long c parameter of the phase corresponds to a chain length of a hypothetical n-alkane with a carbon number quasi-equal to the average carbon atom n of the multicomponent mixture. Molecules with carbon chain longer than n bend and associate themselves with shorter molecules in order to maintain a coherent molecule layer (after Dirand *et al.*, 1998 and Chevallier *et al.*, 1999a and b)

carbon number dominated nC_{20} - C_{33} alkanes) was related to the larger number of “uncoupled” molecules with multi-length chains that can not form a single lamellar structure.

B3. Crystal behavior of pure n-alkanes and n-alkane mixtures with increasing temperature

Several solid-solid transitions have been reported to occur in both pure n-alkanes and their mixtures with increasing temperature. These solid-solid transitions are accompanied by the formation of orientationally disordered (plastic) crystalline phases, called “rotator” phases. The transition from the stable phase at room temperature to solid phases stable at higher temperatures is accompanied by changes in thermal energy and is commonly studied by differential thermal analysis (DTA) and differential scanning calorimetry (DSC; Ungar, 1983; Maroncelli et al., 1985; Kim et al., 1989; Handoo et al., 1989; Letoffe et al., 1995; Srivastava et al., 1993, 1995; Achour et al., 1996; Chevallier et al., 1999b). The existence of “rotator” phases, has been observed several degrees below the melting point for odd (C_9 to about C_{43}) and even (C_4 , C_{18} -suspected, C_{20} to about C_{44}) carbon number n-alkanes (e.g., Mozes, 1982; Ungar, 1983; Domanska, 1987; Dirand et al., 1998). Both α and β “rotator” phases have been reported with hexagonal (rhombohedral) and orthorhombic structures, respectively (e.g., Ungar, 1983; Handoo et al., 1989).

Pure n-alkanes. Odd carbon number pure n-alkanes with low molecular weight (C_{11} - C_{21}), which have orthorhombic structures at “room” temperature, undergo transition into an orthorhombic “rotator” phase (β -RI), and melt before being able to form hexagonal crystals. In addition to this transition, higher molecular weight odd carbon number n-alkanes (e.g., C_{23} , C_{25}) undergo a further transition into a hexagonal “rotator” (α -RII) modification below the melting point (Ungar, 1983). In contrast, even carbon number n-alkanes (C_{20} to C_{40}), with triclinic or monoclinic structures stable at “room” temperature, undergo transition directly to the hexagonal (α -RII) phase before melting, (Table IV. 2. 4; Mozes, 1982; Kim *et al.*, 1989; Ksiazczak *et al.*, 1994; Achour *et al.*, 1996). With increasing carbon number of the n-alkane homologues, the temperature range where the hexagonal lattice is stable decreases and finally disappears in the carbon number region above ca. C_{40} (Mozes, 1982; Jowet, 1984). Recent experimental data have confirmed the lack of a higher temperature hexagonal (α) form in pure nC_{46} and nC_{50} alkanes (Kim *et al.*, 1989).

Binary, ternary and quaternary n-alkane mixtures. The intermediate orthorhombic solid phases ($\beta'1$, $\beta'2$, β'' ; Figure IV. 2. 7) that are formed by binary, ternary and quaternary n-alkane mixtures and are stable at room temperature, show transitions to an orthorhombic “rotator” state (β -RI) with increasing temperature. With a further increase in temperature, a transition to a hexagonal “rotator” phase (α -RII) just below the melting point has been observed (Dirand *et al.*, 1998). This behavior of the intermediate orthorhombic solid phases in n-alkane mixtures with increasing temperature

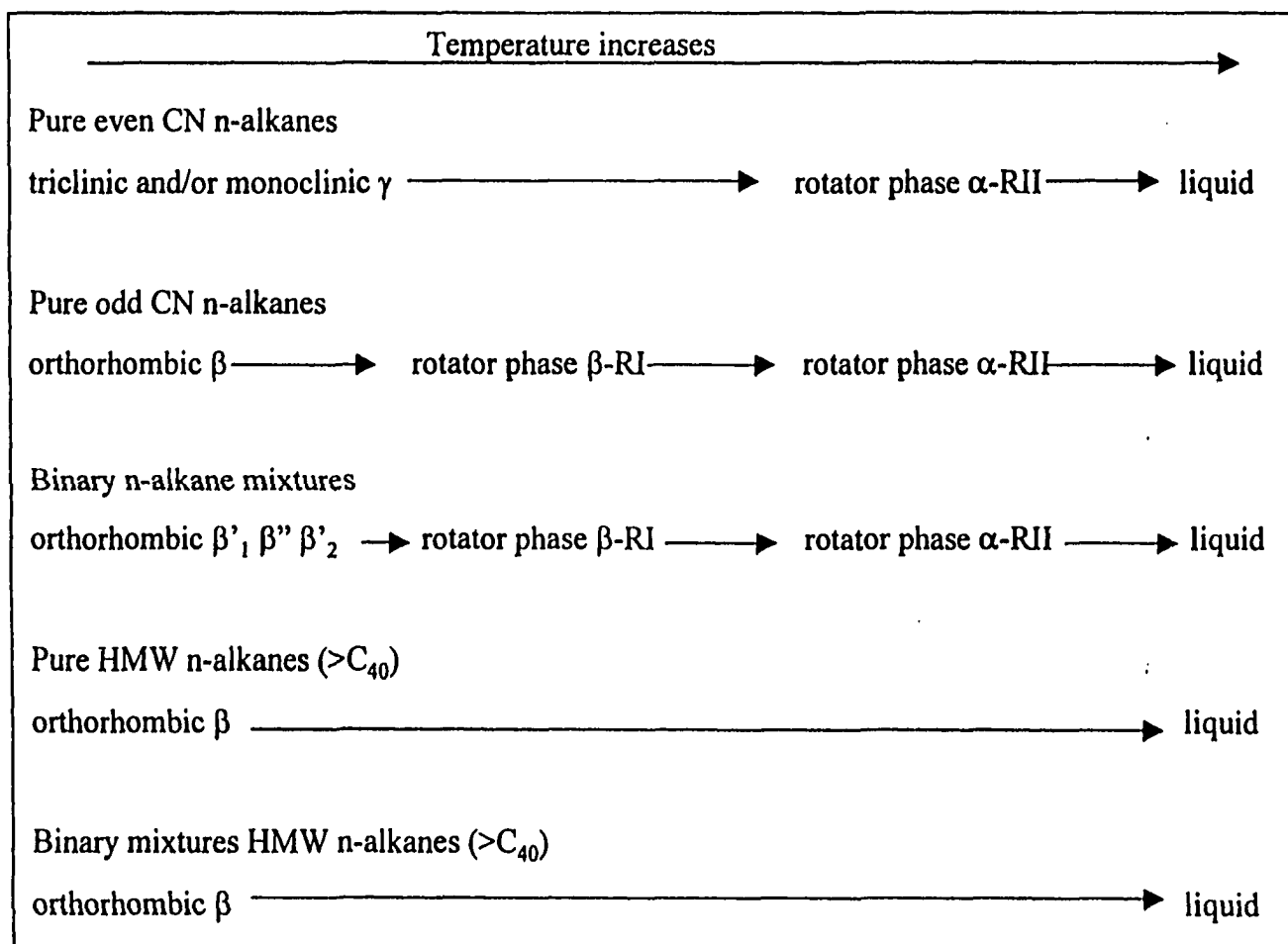


Table IV. 2. 4. Phase transitions with increasing temperature for pure n-alkanes and n-alkane mixtures (see Appendix IV. 2. 2. for references)

was found to be identical to the behavior of the pure odd-numbered n-alkanes (Achour et al., 1996; Chevallier et al., 1999a). For binary even carbon number C_{24} - C_{26} systems, the transformation of terminal triclinic (γ) to orthorhombic (β -RI) phase on heating has been related to straightening up of the n-alkane chains, which become perpendicular to the stacking planes of the molecules, **Figure IV. 2. 7** (Achour et al., 1995). The higher molecular weight binary C_{46}/C_{50} n-alkane mixture, similarly to the pure components, does not form a high-temperature α -RII phase as discussed by Kim et al. (1989). These results are in agreement with the findings of earlier studies that with an increase in the average chain length (molecular weight) of mixtures, the temperature range where the hexagonal lattice is stable decreases and disappears after ca. C_{40} , similarly to the pure HMW components (Mozes, 1982; Jowet, 1984).

Multicomponent n-alkane mixtures. Multiple solid-solid transitions have been reported for multicomponent hydrocarbon mixtures based on differential scanning calorimetry (DSC) thermograms of a series of petroleum derived wax fractions with increasing melting point and carbon number range of n-alkane distributions (Srivastava et al., 1993). The results showed several orthorhombic-orthorhombic transitions and an orthorhombic-hexagonal transition in the lower melting point wax mixtures (macrocrystalline type). In addition, the solid-solid transitions in waxes were found to be dependent on the distribution of n-alkanes (average chain length) and their relative concentration (chain-length disorder; Srivastava et al., 1993). The solid-solid transition temperatures of macrocrystalline waxes with a broad n-alkane carbon number range and

complex composition are lower compared to both individual n-alkanes and narrower carbon number range mixtures (Mozes, 1982). An increase in melting points (molecular weight) of n-alkane mixtures has been found to correspond to a reduced number of orthorhombic-orthorhombic transitions (Srivastava *et al.*, 1993). The highest melting point wax mixture (carbon number distribution maximizing at C₄₀, corresponding to a microcrystalline type wax, **Table IV. 2. 1**) showed neither orthorhombic-orthorhombic nor orthorhombic-hexagonal transitions, but only one orthorhombic-liquid transition, confirming the results of earlier studies of Jowet (1984) and Handoo *et al.* (1989). The solid-liquid transition takes place over a wide temperature range, indicating the co-existence of several phases in the wax mixture. Thus, both the higher molecular weight individual n-alkanes (above ca. C₄₀) and the mixtures they form, corresponding to a microcrystalline type waxes (**Table IV. 2. 1**), do not exhibit transition points, i.e., the phase stable below the melting point is the orthorhombic phase (Mozes, 1982).

The effect of other hydrocarbon fractions added to n-alkanes, on the solid-solid transition behavior of the resulting mixtures, was experimentally studied and discussed by Srivastava *et al.* (1995). Differential scanning calorimetry (DSC) analysis of n-alkane mixtures (macrocrystalline type) obtained by urea adduction and of total saturate fractions demonstrated that the solid-solid transition peaks, observed for the n-alkane mixtures were not detected in the DSC curves of the total saturate fractions. This observation was attributed to the effect of iso- and cycloalkanes present in the total saturate fractions and acting as solvents for the n-alkanes. In contrast, adding an aromatic fraction, previously separated from the same distillate, to the n-alkane mixture resulted in

three to four times increase in the energies associated with the solid-solid transitions. Co-crystallization of the long n-alkyl chains of the alkylaromatics with the n-alkanes was discussed as a possible contributing factor for the observed transitional energy increase (Srivastava et al., 1995).

The phase transition phenomena were found to influence one important, from a practical view point, physical characteristic of waxes and wax deposits, namely the degree of their hardness (extent of needle penetration). Hard wax deposits have been known as very difficult for remediation (e.g., Mozes, 1982). It has been found that as soon as the temperature gets close to the first solid-solid phase transition temperature the wax becomes very soft (Srivastava et al., 1993). In contrast, waxes that lack solid-solid phase transitions (like the microcrystalline type waxes having only orthorhombic-liquid transition) are hard even when the temperature is close to their melting point.

At molecular and crystal levels, solid-solid phase transitions are associated with a relaxation of the molecular packing in a crystal and a rapid decrease in ordering which facilitates easier reorganization and formation of a new form of the solid (Ksiazczak et al., 1994). In hexagonal structures (α -RII), the long molecules are capable of free rotation around their longitudinal axis, and the solid wax materials formed are relatively soft (Mozes, 1982). More recent studies have demonstrated that higher conformational disorder is an important characteristic of the high-temperature hexagonal phase (α -RII) and distinguishes it from the low-temperature orthorhombic phase in both pure odd n-alkanes and their binary mixtures (C_{19}/C_{21}) at different concentrations (Maroncelli et al., 1985). The presence of both orientational disorder about chain axis and a longitudinal

disorder due to translation along the chain direction is characteristic for the hexagonal phase.

Macrocrystalline type waxes that undergo this transitional phase upon heating form a single phase of α -RII type. The crystallographic long-axis c parameter of this phase corresponds to a chain length of a hypothetical n-alkane with carbon number quasi-equal to the average carbon number of the mixture (n), **Figure IV. 2. 8** (Chevallier *et al.*, 1999b). Molecules longer than the average CN of the mixture must therefore fold over to fit within the crystallographic planes. However, in this case, the orientational oscillations around the long axis are restricted and only the small molecules which are rigid may freely rotate around their long c -axis in the α -RII rotator phase. In orthorhombic crystals, the free rotation is not possible and such wax materials are more rigid (Mozes, 1982).

Several important points that need to be considered when studying petroleum wax deposition by laboratory methods, based on the above discussion, should be noted. The choice of standard compounds and/or standard mixtures for HTGC, cloud point determination methods or evaluation of additives for chemical remediation, should take into account the following differences in n-alkane properties:

- (1) behavior of pure n-alkanes versus n-alkane mixtures;
- (2) behavior of standard n-alkane mixtures with consecutive versus non-consecutive carbon number distributions;
- (3) chain length difference (Δn) of components in a standard mixture leading to stable solutions when $\Delta n < 4$, and microphase separations if $\Delta n > 4$, or in other words a

higher stability of narrower carbon number range mixtures compared to broader carbon number range distributions;

(4) range of carbon number distribution and the concentrations of individual components, especially in the HMW ($>C_{40}$) region.

IV. 2. 3. C. Solubility parameter concept

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Dissolution of a solid in a liquid initially requires the orderly crystal structure of the solid to be destroyed in order to form the more disorderly arrangement of the molecules in solution, and second, the molecules to be separated from each other. The energy required for this process of overcoming lattice energies and intermolecular attractions comes from the formation of new attractive forces between the solute and solvent (Solomons, 1980). Therefore, the development and selection of methods for solubility prediction require understanding of the nature and relative importance of the intermolecular forces and interactions between solute-solute, solvent-solvent, and solute-solvent systems. The solubility parameter concept accounts in a quantitative manner for the main molecular interactions between solvent and solute, and characterizes the type and magnitude of energies holding a unit volume of material together.

C1. Definition and meaning of the solubility parameter

The concept of solubility parameters, as it relates to the internal energy of solutions, was developed by J. H. Hildebrand and Scatchard in the period 1916-1949, and further extended by Hildebrand and Scott (1950), Hildebrand et al. (1970), and Hansen (1967, 1969, 1970). The concept was first applied for the purposes of polymer sciences and paint industry, and later has found applications in many other areas, such as

pharmaceutical, liquid and gas chromatography (e.g., Karger et al., 1976; Lipson and Guillet, 1982), and cosmetics (Barton, 1991).

Internal pressure is the energy required to vaporize one cubic centimeter of a substance. Hildebrand and Scatchard proposed that molecules with similar internal pressures would attract and interact with each other. The cohesive energy density (CED) describes this internal energy and it can be calculated from physical properties (**Appendix IV. 2. 4**). The solubility theory predicts that dissolution of a solute will occur in a solvent or solvent blend of similar CED values.

Hildebrand and Scott (1950) proposed that

$$\Delta H_M = V_M [(\Delta E_1/V_1)^{1/2} - (\Delta E_2/V_2)^{1/2}]^2 \phi_1 \phi_2 \quad (1)$$

where ΔH_M is the overall heat of mixing, V_M is total volume of the mixture, ΔE is the energy of vaporization of component 1 or 2, V is the molar volume of component 1 or 2, ϕ is the volume fraction of component 1 or 2 in the mixture.

The expression $(\Delta E/V)$ is the energy of vaporization per cubic centimeter and is often referred to as the “internal pressure” or “cohesive energy density” (CED). Rearrangement of (1) gives

$$\Delta H_M / (V_M \phi_1 \phi_2) = [(\Delta E_1/V_1)^{1/2} - (\Delta E_2/V_2)^{1/2}]^2 \quad (2)$$

The equation expresses that the heat of mixing per cubic centimeter at a given concentration is equal to the square of the difference between the square roots of the cohesive energy densities of the components (solute-solvent). Based on this equation, the solubility parameter is defined as $\delta = (\Delta E/V)^{1/2}$ or $\delta^2 = \text{CED}$, and equation (2) can be expressed as

$$\Delta H_M / (V_M \phi_1 \phi_2) = (\delta_1 - \delta_2)^2 \quad (3)$$

The $CED^{1/2} = \delta$ is one measure of the intensity of all types intermolecular interactions in a pure liquid or solid, and the strengths of solvent-solvent and solute-solute bonds are related to it. The theoretical prediction is that the smaller the difference between solubility parameters of solute (δ_1) and solvent (δ_2), the higher is the solubility. The maximum solubility is reached when $\delta_1 = \delta_2$, and the mixture behaves ideally.

C2. Partial solubility parameters

The solubility parameter concept proposed by Hildebrand, later known as regular solution theory, provides good predictions for the solubility of nonpolar solutes in nonpolar solvents when the primary intermolecular forces are the London dispersion forces (Barton, 1991). In the early sixties, Blanks and Prauznitz (1964) demonstrated that division of cohesion energy for polar solvents into nonpolar and polar parts leads to a system with two parameters having good predictive capabilities. Burrell (1968) and Hansen (1967, 1969) made further developments by subdividing the polar part into a dipole-dipole contribution and a hydrogen bonding contribution, and introduced the concept of three dimensional solubility parameter system. The concept is based on the assumption that the energy of vaporization, i.e., the total cohesive energy which holds a liquid (solid) together, can be divided into contributions from dispersion (London) forces, E_d , permanent dipole-permanent dipole forces, E_p , and hydrogen-bonding forces, E_h .

$$E = E_d + E_p + E_h \quad (4)$$

Dividing by the molar volume ($V = MW/d$, where MW is molecular weight, d is density) of a solvent (solute) gives

$$\frac{\underline{E}}{V} = \frac{\underline{E}_d}{V} + \frac{\underline{E}_p}{V} + \frac{\underline{E}_h}{V} \quad (5)$$

$$\text{or} \quad \delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (6)$$

where $\delta = (E/V)^{1/2} = (\text{cohesive energy density})^{1/2}$ is the total solubility parameter equation of Hildebrand and Scott (1950), which accounts for all types of intermolecular interactions. The three partial solubility parameters ($\delta_d, \delta_p, \delta_h$) account for the different types of intermolecular interaction between solute and solvent molecules.

The three components of the total solubility parameter (δ) are the solubility parameter due to dispersion forces $\delta_d = (E_d/V)^{1/2}$, the solubility parameter due to dipole-dipole forces $\delta_p = (E_p/V)^{1/2}$, and the solubility parameter due to hydrogen bonding forces $\delta_h = (E_h/V)^{1/2}$ (**Appendix IV. 2. 5**). It should be noted that the hydrogen-bonding component also includes any specific type of interaction between the molecules, including permanent dipole-induced dipole forces, as specifically discussed by Hansen (1969).

It should be pointed out that the three components of the solubility parameter characterize the magnitude and the nature of the energies holding a unit volume of a solvent (material) together, and not only the strength of a particular type of bond (Hansen, 1969). The total solubility parameter (δ) of a material has been represented as a point in three-dimensional space defined with axes $x - \text{two times } \delta_d$, $y - \delta_p$, and $z - \delta_h$, where the three partial solubility parameter vectors meet. Thus, total and partial solubility

parameters define an idealized solubility sphere with a radius R . For two substances (solute – i , and solvent – j), the radius of interaction between them can be represented by the distance (${}^{ij}R$) between the centers of the solubility spheres as suggested by Hansen (1967)

$${}^{ij}R = [4(\delta_d^i - \delta_d^j)^2 + (\delta_p^i - \delta_p^j)^2 + (\delta_h^i - \delta_h^j)^2]^{1/2} \quad (7)$$

where ${}^{ij}R$ is radius of interaction between solute (i) and solvent (j).

If the calculated radius of interaction between solute and solvent ${}^{ij}R$ is less than the radius of the solute solubility sphere (R), i.e., the solvent's solubility sphere falls within the solute's solubility sphere, then the solvent will probably dissolve the solute. Thus the solubility condition can be expressed as ${}^{ij}R < R$, where R is the radius of the solubility sphere of the solute (Hansen, 1967, 1982; Barton, 1991).

If the solvent's solubility sphere falls out of the solute's solubility sphere, the solvent is predicted as a poor solvent for the solute (${}^{ij}R > R$). Thus, the radius of interaction ${}^{ij}R$ between solute and solvent can be used as a quantitative measurement of the degree of solubility parameter match between the two substances. The “best” solvents or solvent mixtures for a particular solute would be those with equal or very similar values of all the solubility parameter components, as shown by equation 7, and the ${}^{ij}R$ value will be approximating zero.

In addition, the solubility parameters of a blend of solvents can be calculated using the volume fraction (ϕ_i) and solubility parameter (δ_i) of a solvent mixture with i components,

$$\delta_{\text{blend}} = \sum \phi_i \delta_i \quad (8)$$

The partial solubility parameter values for a solvent blend can be calculated in three separate equations using the three solubility parameter values for each solvent in the blend (Archer, 1996).

The partial (or Hansen) solubility parameter concept provides a better understanding for the different types intermolecular interactions between solute and solvent, compared to the regular solution theory, and have proven to give excellent results for practical applications in many different industries. Because of these advantages, this concept was chosen for use in the present study and applied to obtain some theoretical predictions about the order of solubility of HMW n-alkane mixtures in different solvents.

IV. 2. 3. D. Solubility of mixtures of n-alkanes in the carbon number range

C₅-C₁₂₀

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This section discusses three main groups of results from the present study. First, methods for calculation of solubility parameters of pure and mixtures of n-alkanes, and predictions of “best” choice solvents for mixtures of increasing molecular weight. Second, experimental results on the solubility and crystallization behavior of a standard high molecular weight (HMW) dominated n-alkane mixture in different solvents. Third, the effect of different proportions of non-hydrocarbons (e.g., resins) on the choice of “best” solvent for n-alkane/resin model mixture.

D1. Solubility parameter calculations for nC₅-C₁₂₀ alkanes and n-alkane mixtures

Most of the methods available for solubility parameter measurements and calculations from physical properties are not applicable for non-volatile substances such as HMW n-alkanes (Appendix IV. 2. 4). Another option is to use methods for calculation of solubility parameters based on molecular formula. These methods apply an approach commonly known as the group contribution, and are based on the assumption of additivity of measured property values for individual groups in a molecule. The

molecular formula of n-alkane homologues can be represented as $\text{CH}_3-(\text{CH}_2)_n-\text{CH}_3$, and known values for $-\text{CH}_3$ and $-\text{CH}_2-$ groups would allow the application of group contribution methods.

Three methods for calculation of solubility parameters of n-alkanes up to $n\text{C}_{120}$ are compared in the present study. Method 1 and Method 2 (**Appendix IV. 2. 6**) are based on the molar constants (G_i) for $-\text{CH}_3$ and $-\text{CH}_2-$ groups provided by Small (1953) and Hoy (1970), and correlations between density and molecular weight of n-alkanes provided in the recent studies of Riazi and Al-Sahhaf (1995) and Jianzhong *et al.* (1998). The solubility parameters of individual n-alkanes are calculated using $\delta = d \sum G_i / \text{MW}$ (Small, 1953), where δ is the total solubility parameter, d is density, $\sum G_i$ is the sum of molar constants of all $-\text{CH}_3$ and $-\text{CH}_2-$ groups in an n-alkane molecule, and MW is the n-alkane molecular weight (**Appendix IV. 2. 6**). Density estimates based on correlation with molecular weight were necessary to be applied because of the lack of measured data specifically in the HMW range n-alkanes above $n\text{C}_{30}$. A review of the engineering literature shows that a significant number of studies have been published in recent years, related to the development of thermodynamic models for solid-liquid equilibrium of heavy petroleum fractions, and in response to the increased need for achieving better predictive methods for petroleum wax deposition (Leontaritis, 1996b; Lira-Galeana *et al.*, 1996; Civan, 1996b; Calange *et al.*, 1997; Lee and Yoo, 1998; Monger-McClure *et al.*, 1999; Andersen and Speight, 1999; Wang *et al.*, 1999). Generally, there are two main ways in which these models have been developed. The first is based on cubic equations of state, which are generally extensions of the van der Waals equation (e.g., Won, 1986;

Riazi and Al-Sahhaf, 1995; Leontaritis, 1997; Calange *et al.*, 1997) and the second is based on the so-called perturbed chain theory (e.g., Carnahan and Starling, 1972; Beret and Prausnitz, 1975; Kim *et al.*, 1986; Whiting and Prausnitz, 1982; Peters *et al.*, 1988; Brown *et al.*, 1994; Jianzhong *et al.*, 1998). The second group of models is developed for mixtures, including high-boiling point hydrocarbons, and is theoretically valid for a wide range of molecular weights, temperatures and densities of the components. The predictive capabilities of these two groups of models have been evaluated to give comparable results, except near the critical region where the models based on perturbed chain theory demonstrate superior results (Pauly *et al.*, 1998; Vimalchand and Donohue, 1989).

The correlations between density and molecular weight presented in a model, based on equation of state (Riazi and Al-Sahhaf, 1995) and in a model based on the perturbed chain theory (Jianzhong *et al.*, 1998), have been used in the present study to determine the n-alkanes density, a missing parameter in Equation 9 for calculation of the total solubility parameter of HMW pure n-alkanes (**Appendix IV. 2. 6**). Since the molar attraction constants necessary to estimate ΣG in Equation 9, are valid at room temperature, the density correlations for n-alkanes were applied for the same conditions. A comparison of density correlations for n-alkanes in the carbon number range C_5 - C_{120} by both models are presented in **Figure IV. 2. 9**. It is apparent that both correlations give very similar values for the density of n-alkanes in this carbon number range at ambient conditions. A comparison between the estimated densities with the experimental data available up to nC_{30} is also presented, and demonstrates a good correlation. The densities of n-alkanes in the carbon number range C_5 - C_{120} , calculated as an average of the two

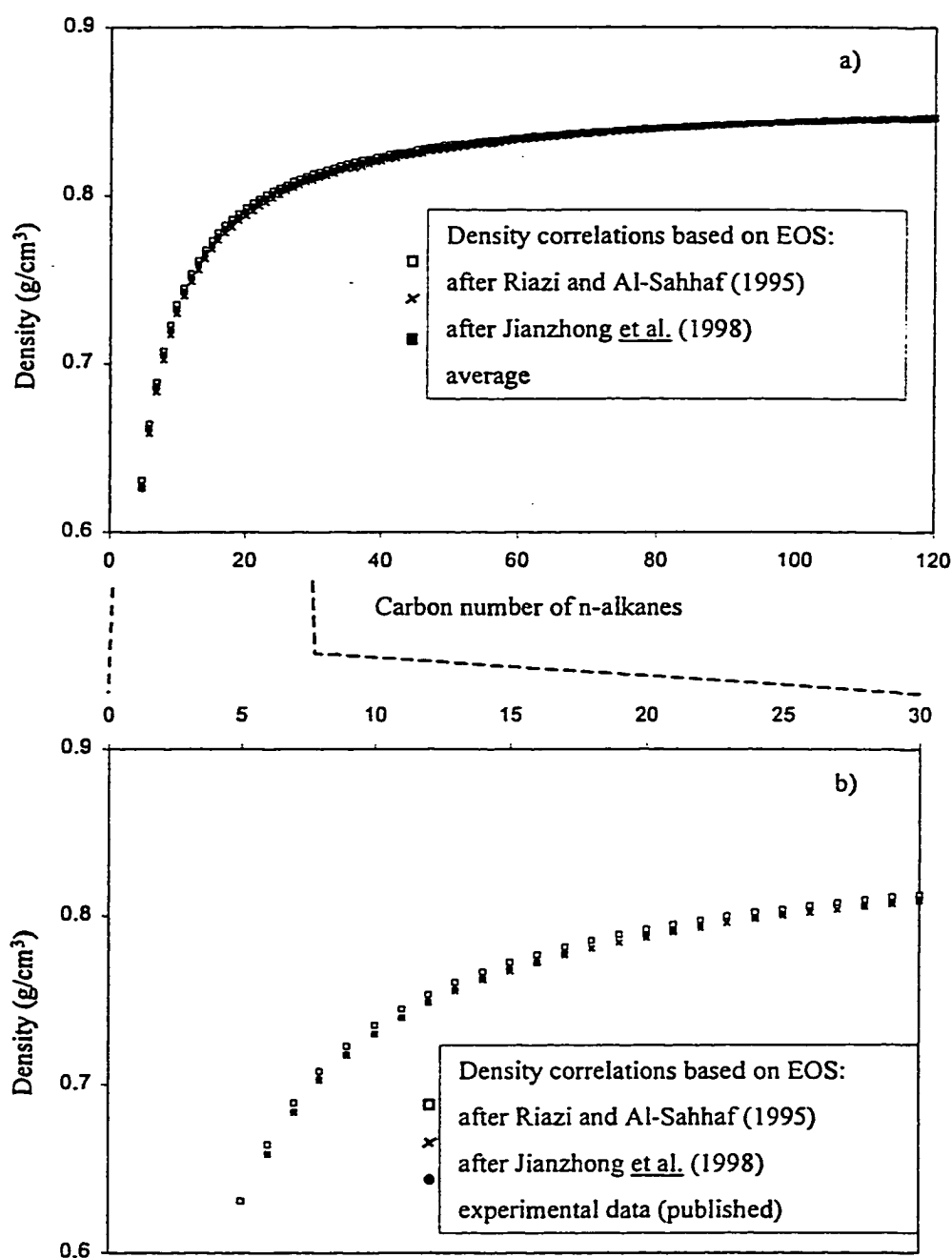


Figure IV. 2. 9. Density correlations for n-alkanes based on EOS (a), and their comparison with published experimental data (Lide, 1999), (b) .

density correlations (Riazi and Al-Sahhaf, 1995; Jianzhong *et al.*, 1998), are used in the calculations of the solubility parameters of pure n-alkanes by Methods 1 and 2.

A method for calculation of total solubility parameter, based on knowledge of the molecular structure only, was presented by Fedors (1974). The method is based on additive contribution of groups in a molecule to the energy of vaporization and molar volume of the whole molecule (**Appendix IV. 2. 6**). The method has been developed specifically to be applicable for non-volatile substances as polymers. This method is directly followed in the present study for calculation of solubility parameters of pure n-alkanes (C₅-C₁₂₀) and is designated as “Method 3”. This method, similarly to the other two methods, has been developed for ambient pressure-temperature conditions.

The above described three methods were applied to calculate the solubility parameters for individual n-alkanes in the carbon number range from C₅ to C₁₂₀ at ambient conditions and the results are presented in **Figure IV. 2. 10**. The solubility parameters calculated by all three methods increase with increasing carbon number and molecular weight of individual n-alkanes and cover a range from 12.3 to 17.4 (J/cm³)^{1/2} (**Table IV. 2. 5a**; **Figure IV. 2. 10**). It should be noted that such a trend has been reported in previous studies for aliphatic hydrocarbon solvents, polyethylenes and their chloro-derivatives, while the polar solvents and polyethylene hydroxy-derivatives have showed a decrease in total solubility parameters with increasing molecular weight (Seymour, 1982; Barton, 1991, and references therein).

The calculated solubility parameter values obtained by the three methods demonstrate differences exceeding 1 (J/cm³)^{1/2} for the same carbon number n-alkanes

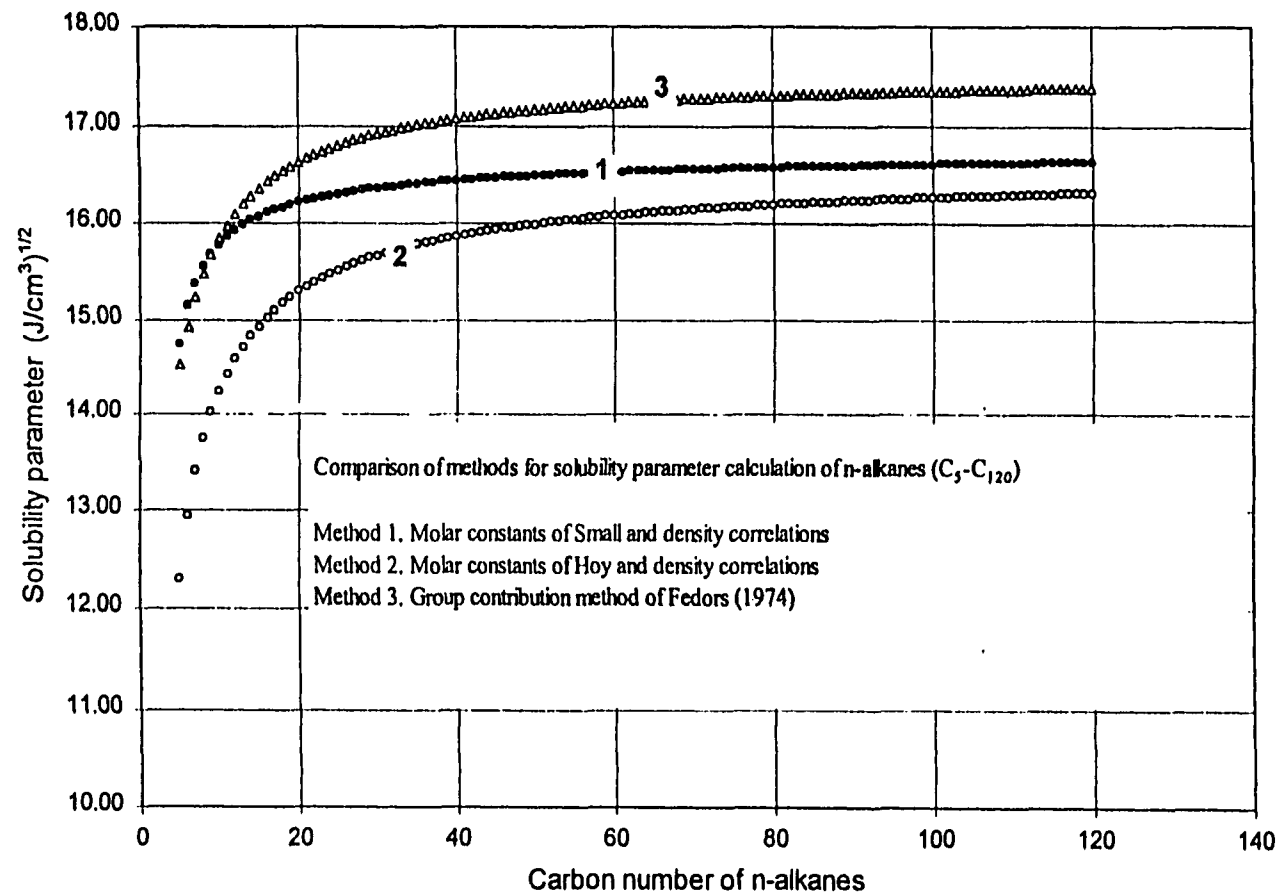


Figure IV. 2. 10. Solubility parameters of n-alkanes (C_5 - C_{120}) as calculated by Methods 1, 2, 3.

a)

Total solubility parameter ($\delta = \delta_d$) of n-alkanes														
	nC ₃	nC ₁₀	nC ₂₀	nC ₃₀	nC ₄₀	nC ₅₀	nC ₆₀	nC ₇₀	nC ₈₀	nC ₉₀	nC ₁₀₀	nC ₁₁₀	nC ₁₂₀	Standard Mix
Method 1*	14.74	15.78	16.21	16.36	16.44	16.49	16.52	16.55	16.57	16.59	16.61	16.62	16.63	16.40
Method 2	12.29	14.24	15.29	15.67	15.87	15.99	16.08	16.14	16.19	16.23	16.26	16.29	16.31	15.78
Method 3	14.53	15.84	16.63	16.92	17.07	17.17	17.23	17.27	17.31	17.33	17.36	17.37	17.39	17.00
*Method 1 - molar constants of Small (1953) and density correlations of Riazi and Al-Sahhaf (1995) and Jianzhong <i>et al.</i> (1998); Method 2 - molar constants of Hoy (1970) and density correlations of Riazi and Al-Sahhaf (1995) and Jianzhong <i>et al.</i> (1998); Method 3 - group contribution method of Fedors (1974).														

b)

$\delta_1 = \delta_d = 15.5, \delta_p = 0, \delta_h = 0$		$\delta_1 = \delta_d = 16.0, \delta_p = 0, \delta_h = 0$		$\delta_1 = \delta_d = 16.5, \delta_p = 0, \delta_h = 0$		$\delta_1 = \delta_d = 17.0, \delta_p = 0, \delta_h = 0$		$\delta_1 = \delta_d = 17.5, \delta_p = 0, \delta_h = 0$		$\delta_1 = \delta_d = 18.0, \delta_p = 0, \delta_h = 0$	
solvent	r	solvent	r	solvent	r	solvent	r	solvent	r	solvent	r
n-decane	0.6	n-decane	0.4	n-hexadecane	0.2	cyclohexane	0.4	carbon tetrachloride	0.8	decalin	0.1
n-hexadecane	1.8	n-hexadecane	0.8	n-eicosane	0.2	n-eicosane	0.8	decalin	1.1	carbon tetrachloride	0.7
n-eicosane	2.2	n-eicosane	1.2	cyclohexane	0.6	n-hexadecane	1.2	cyclohexane	1.4	cyclohexane	2.4
cyclohexane	2.6	cyclohexane	1.6	n-decane	1.4	carbon tetrachloride	1.7	n-eicosane	1.8	toluene	2.4
carbon tetrachloride	4.6	carbon tetrachloride	3.6	carbon tetrachloride	2.7	decalin	2.1	n-hexadecane	2.2	n-eicosane	2.6
decalin	5.1	decalin	4.1	decalin	3.1	n-decane	2.4	toluene	2.6	n-hexadecane	3.2
p-xylene	5.3	p-xylene	4.6	toluene	3.9	toluene	3.2	p-xylene	3.3	p-xylene	3.4
toluene	5.6	toluene	4.7	p-xylene	3.9	p-xylene	3.5	n-decane	3.4	n-decane	4.4

Table IV. 2. 5. Comparison of methods for calculation of the total solubility parameter ($\delta_d = \delta$) of n-alkanes in the carbon number range C₃-C₁₂₀ and a standard n-alkane mixture consisting of equal concentrations of nC₂₀, nC₃₀, nC₄₀, nC₅₀, nC₆₀ (a). Radius of interaction (r) for n-alkane mixtures or individual compounds with total solubility parameter in the range 15.5 to 18.0 with a set of selected solvents (b). For n-alkanes, the polar and hydrogen bonding contribution to the solubility parameter are assumed to be zero, and the total solubility parameter is represented only by its dispersion contribution. Refer also to Figure IV. 2. 12 and Appendix IV. 2. 5.

(Figure IV. 2. 10). Method 2 gives consistently lower values for the solubility parameters of n-alkanes along the studied carbon number range compared to the other two methods. Methods 1 and 3 provide similar δ values only for the gasoline range n-alkanes (C_5 to about C_{12}), where the deviation from Method 2 calculated values is in the order of 1 to $2.5 \text{ (J/cm}^3\text{)}^{1/2}$. After about nC_{12} , the solubility parameter values obtained from Method 3 are consistently higher than those obtained by the other two methods (in the order of 0.5- $1.3 \text{ (J/cm}^3\text{)}^{1/2}$; Figure IV. 2. 10).

The solubility parameters calculated by Methods 1, 2, and 3 refer to the total (or Hildebrand) solubility parameter. In view of the three-dimensional solubility parameter concept of Hansen, the total solubility parameter (δ) is related to the partial solubility parameters due to dispersion (δ_d), dipole-dipole (δ_p) and hydrogen bonding (δ_h) interactions by the equation $\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$. For non-polar hydrocarbons, such as n-alkanes, the main intermolecular interactions are governed by the dispersion forces, and the total solubility parameters can be assumed as mainly determined by the partial solubility parameter due to dispersion ($\delta = \delta_d$). Such an assumption does not account for the dipole-induced dipole interactions that could occur in a case of n-alkanes in polar solvents. The energy of these interactions is considered by Hansen (1969) to contribute to the value of δ_h . By accepting the above discussed assumption in the present study, the total solubility parameters of n-alkanes calculated by Methods 1, 2, and 3 can be regarded as equal solely to the solubility parameter due to dispersion interaction ($\delta \approx \delta_d$, $\delta_p = 0$, $\delta_h \approx 0$).

The solubility parameters of mixtures of n-alkanes are calculated in the present study using a mixing rule of the form $\delta = \sum \phi_i \delta_i$, where ϕ_i and δ_i are the fraction and the solubility parameter, respectively, of i individual n-alkanes in the mixture. The solubility parameter calculation of individual n-alkanes (δ_i) is performed by the Method 3, which is the one justified later on in this Chapter to give predictions closest to the experimental results on solubility of HMW dominated standard n-alkane mixture (see section IV. 2. 3. C2). The fraction of individual n-alkanes in a mixture is determined by quantitative HTGC analysis as a ratio of the concentration of i-th n-alkane to the sum of concentrations of all n-alkanes detected by HTGC. An example of solubility parameters calculated for a standard n-alkane mixture, consisting of equal amounts of pure nC₂₀, nC₃₀, nC₄₀, nC₅₀ and nC₆₀ alkanes, is presented in **Table IV. 2. 5b**. In this example, $\delta = \delta_d$ values calculated by Methods 1, 2 and 3 are presented and demonstrate a variation from $15.8 \text{ (J/cm}^3\text{)}^{1/2}$ to $17 \text{ (J/cm}^3\text{)}^{1/2}$ according to the method of calculation.

Calculated solubility parameters for pure n-alkanes by Methods 1, 2, and 3 show differences exceeding $1 \text{ (J/cm}^3\text{)}^{1/2}$ (**Figure IV. 2. 10**). The significance of these differences among the methods is evaluated according to their effect on the choice of “best” solvent for dissolution of pure and/or mixtures of n-alkanes by applying the proposed by Hansen equation (Equation 7, section IV. 2. 3. B2). Data for total and partial solubility parameters of a significant number of solvents are readily available in the literature (e.g., Barton, 1991; Archer, 1996). Data for selected solvents are presented in **Table IV. 2. 6**. Using Equation 7 and a database of about 300 solvents (Archer, 1996), the match between the solubility parameters of n-alkanes and different solvents is

Solubility parameters of selected solvents				
Solvent	delta D	delta P	delta H	delta total
Acetone	15.5	10.4	7.0	19.9
Benzene	18.4	0.0	2.0	18.5
Carbon disulfide	20.4	0.0	0.0	20.4
Carbon tetrachloride	17.8	0.0	0.6	17.8
Chloroform	17.8	3.1	5.7	18.9
Cyclohexane	16.8	0.0	0.2	16.8
Decalin	18.0	0.0	0.0	18.0
Ethyl acetate	15.8	5.3	7.2	18.2
Ethyl benzene	17.8	0.6	1.4	17.9
Furan	17.8	1.8	5.3	18.7
Methanol	15.1	12.3	22.3	29.6
MEK	16.0	9.0	5.1	19.1
MethylCHx	16.0	0.0	1.0	16.0
Methylene chloride (DCM)	18.2	6.4	6.2	20.3
o-Xylene	17.8	1.0	3.1	18.1
p-Xylene	17.6	1.0	3.1	17.9
Pyridine	19.0	8.8	5.9	21.8
Quinoline	19.4	7.0	7.6	22.0
THF (tetrahydrofuran)	16.8	5.7	8.0	19.5
Tetralin	19.7	2.1	2.9	20.0
Toluene	18.0	1.4	2.0	18.2
Water	16.5	23.5	14.8	32.3
2,2,4-Trimethylpentane	14.1	0.0	0.0	14.1

Table IV. 2. 6. Solubility parameter values for selected solvents in $(\text{J}/\text{cm}^3)^{1/2}$. Data from Archer (1996).

expressed as the radius of interaction ${}^{ij}R$ (**Table IV. 2. 5b**). The radii of interaction (${}^{ij}R$) between n-alkanes of increasing molecular weight and approximately 300 solvents were calculated for several solubility parameters ($\delta = \delta_d$) chosen in the range from 15.5 to 18 (J/cm³)^{1/2}, defined by Methods 1, 2, and 3. The results of these calculations are presented in **Table IV. 2. 5b** for a selected set of solvents, sorted in the order of decreasing ${}^{ij}R$ values.

The interpretation of these results relates to the criteria for evaluation of the best match between solute and solvent, which determines the extent of solubility of a solute in a solvent, as described by Hansen's extension of the regular solution theory (see section IV. 2. 3. B2). The solvents with partial solubility parameters closest to the ones of the solute would give the lowest values for ${}^{ij}R$ according to Equation 7, and they would be the ones that are predicted by the solubility parameter concept to dissolve the solute in larger amounts. The ideal solvent for a particular solute would be the one with the same partial solubility parameters as the solute, and will result in ${}^{ij}R$ values equal to zero. This criterion allows to define an order of solvents with increasing solubility (decreasing ${}^{ij}R$ values) for a particular solute. Another criterion is related to the solubility condition ${}^{ij}R < R$ defined by the partial solubility parameters (Equation 7), where R is the solubility radius of the solute (see section IV. 2. 3. B2). The problem that arises in using this criterion for n-alkanes relates to the lack of published data or estimates for the solubility radius (R) of n-alkanes in the studied carbon number range. Therefore, the first discussed criterion is used in the present study to evaluate the solubility of pure and/or mixtures of n-alkanes in different solvents.

The first row in **Table IV. 2. 5b** shows the solvent predicted to be closest to the “ideal” solvent for n-alkanes or mixtures of n-alkanes with $\delta_d = \delta$ ranging from 15.5 (J/cm³)^½ to 18 (J/cm³)^½. It is apparent that with increasing $\delta_d = \delta$, corresponding to an increase in carbon number and molecular weight of n-alkanes, the order of solvents with the lowest $\bar{r}$ values, i.e., those that would “best” dissolve a solute with such δ value, changes. Thus, n-decane (nC₁₀) is the solvent of “best” choice (lowest $\bar{r}$) for n-alkanes (or mixtures) with $\delta = \delta_d$ of 15.5 (J/cm³)^½ and 16 (J/cm³)^½, while cyclohexane, carbon tetrachloride and decalin, become the “best” match solvents for solutes with $\delta = \delta_d$ of 17 (J/cm³)^½, 17.5 (J/cm³)^½ and 18 (J/cm³)^½, respectively. An illustration, using data in **Table IV. 2. 5b**, of how the radius of interaction ($\bar{r}$) of different solvents changes with the increase of molecular weight (carbon number) and solubility parameters of n-alkanes is presented in **Figure IV. 2. 11**. This type of plot has not been encountered by the author in the literature, even though a number of other different types of plots and solubility maps are often used depending on the type of studied substances (Barton, 1991, and references therein). The most commonly applied plots to evaluate the solubility of polymers, resins and plasticizers, for example, include plots of δ_p vs δ_h , δ_{total} vs δ_h , and ternary diagrams of fractional Hansen parameters.

Considering the concept of three-dimensional parameters (see discussion in section IV. 2. 3. B), the plot in **Figure IV. 2. 11** represents how the solubility regions of n-alkanes with increasing solubility parameter ($\delta_d = \delta$) change with respect to the solubility region of a particular solvent, defined by the distance between the centers of the solubility regions $\bar{r}$ of solute and solvent. The results in **Figure IV. 2. 11** demonstrate

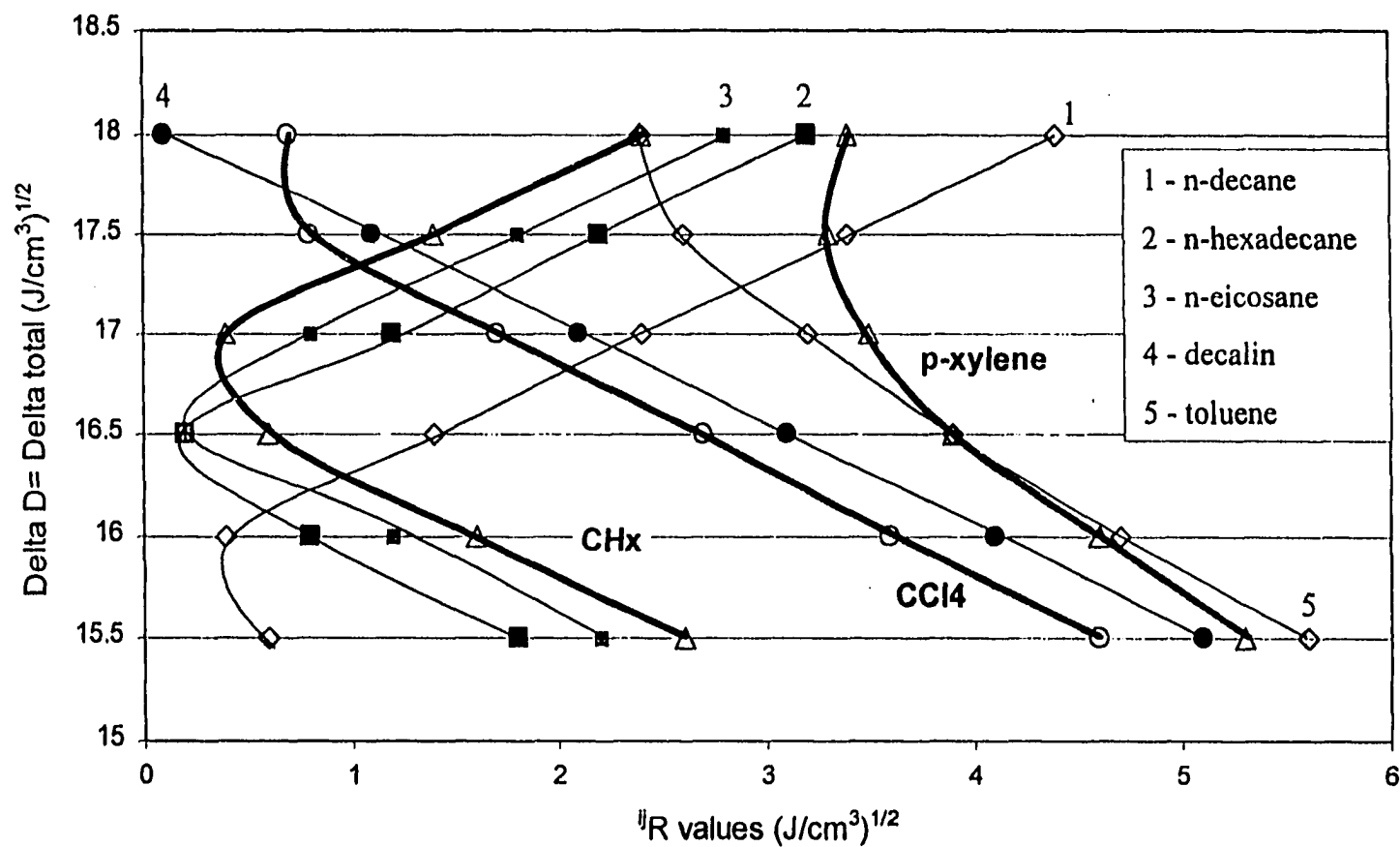


Figure IV. 2. 11. Changes in radius of interaction (i_jR) of solvents with increasing molecular weight and solubility parameter of n-alkanes.

that the solubility of pure and/or mixtures of n-alkanes of increasing molecular weight (solubility parameter) in a particular solvent represents a curve, which reaches a maximum for a certain molecular weight (solubility parameter) n-alkanes. Therefore, applying the same solvent for pure and/or mixtures of n-alkanes with largely different molecular weights would lead to a significant variability in the amount of different n-alkanes which dissolve.

The results in **Table IV. 2. 5** and **Figure IV. 2. 11** also present the evaluation of the significance in the differences of the n-alkane solubility parameters calculated by Methods 1, 2, and 3. For example, the solubility parameter of nC₈₀ alkane calculated by Method 1 is 16.6 (J/cm³)^{1/2}, by Method 2 – 16.2 (J/cm³)^{1/2}, and by Method 3 – 17.3 (J/cm³)^{1/2}. A referral to **Figure IV. 2. 11** suggests that these differences are significant with regard to the “best” choice of a solvent(s) (corresponding to lowest ^{ij}R values). Thus, for the nC₈₀ alkane with a solubility parameter of 16.6 (J/cm³)^{1/2}, the “best” solvents would be n-hexadecane and eicosane; if the solubility parameter of nC₈₀ is 16.2 (J/cm³)^{1/2}, then the “best” choice solvents would be n-decane and n-hexadecane, and if the solubility parameter of nC₈₀ is 17.3 (J/cm³)^{1/2}, then the best choice solvents would be cyclohexane and carbon tetrachloride.

Additional results related to the solubility of n-alkane mixtures and petroleum wax deposits will be presented later on in this Chapter, but even at this point, the presented results suggest to have a practical meaning to both the laboratory study and field treatment of wax deposits and waxes in oils. For example, it can be predicted that solvents such as carbon tetrachloride and decalin will dissolve the largest amount of a

high molecular weight n-alkane mixture, characterized by $\delta = \delta_d$ of 17.5-18 (J/cm³)^{1/2}, while a solvent such as n-decane will most efficiently dissolve a mixture of lower molecular weight hydrocarbons with $\delta = \delta_d$ of 16 (J/cm³)^{1/2}. Both oils and wax deposits are complex mixtures of different classes compounds. Oils contain a wide range of molecular weight n-alkanes, while wax deposits often have concentrated abundances of HMW n-alkanes. The results discussed above mean that laboratory methods and field treatments of wax deposition problems using the same solvent will vary in their efficiency, and suggest one possible reason for the general inefficiency of methods for wax treatment.

Based on the results presented in **Table IV. 2. 5b** and **Figure IV. 2. 11**, three solvents, namely p-xylene, cyclohexane and carbon tetrachloride were chosen to evaluate experimentally the solubility of a standard HMW dominated n-alkane multicomponent mixture (Polywax 1000). The choice of p-xylene was based on the fact that it is a common solvent used to study waxes in the laboratory. It is also one of the commonly utilized solvents for treatment of paraffin problems during production and forms the structural basis of many commercial solvents for chemical treatment of wax problems (Ferworn *et al.*, 1997). However, based on the results presented in **Table IV. 2. 5b** and **Figure IV. 2. 11**, p-xylene is not the best choice of a solvent for pure and mixtures of n-alkanes and is predicted to be outperformed by a number of other solvents, including cyclohexane, carbon tetrachloride and decalin. The choice of carbon tetrachloride and cyclohexane for further experimental work was based on the marked variability in the ^{ij}R values between these solvents and solutes with increasing $\delta = \delta_d$ values (**Table IV. 2. 5b**).

The experimental results with Polywax 1000 standard n-alkane mixture are described in the following section, and will be compared with the following predictions derived from **Figure IV. 2. 11** and **Table IV. 2. 5**:

- (1) p-xylene should be the poorest solvent for the Polywax 1000 n-alkane mixture;
- (2) cyclohexane should be a superior solvent compared to carbon tetrachloride if $\delta_d = \delta$ of Polywax 1000 is anywhere in the range from 16 to about $17.3 \text{ (J/cm}^3\text{)}^{1/2}$;
- (3) carbon tetrachloride will be a superior solvent compared to cyclohexane if $\delta_d = \delta$ of Polywax 1000 mixture is higher than about $17.3 \text{ (J/cm}^3\text{)}^{1/2}$.

D2. Solubility of Polywax 1000— experimental results

Polywax 1000. A commercially available Polywax 1000 was chosen for the experimental work on the solubility of n-alkane mixtures (sample description in Chapter II). Three different types of analyses were performed in order to evaluate the solubility behavior of Polywax 1000 in different solvents: (1) quantitative HTGC analysis of heated solutions (0.5 mg/ml) of Polywax 1000 in carbon tetrachloride, cyclohexane and p-xylene; (2) filtration experiments at room temperature of solutions (4 mg/ml) of Polywax 1000 in carbon tetrachloride and p-xylene with a following HTGC analysis of the obtained filtrates; (3) X-ray analysis (room temperature) of powdered Polywax 1000 and crystallized from solutions in carbon tetrachloride and p-xylene (for sample and method description refer to Chapter II).

In order to optimize the detection of HMW n-alkanes present in the Polywax 1000, the solution was heated before HTGC analysis. Under these conditions, Polywax

1000 is characterized with a strong predominance of even carbon number n-alkanes with a maximum in the region C_{58} - C_{60} , and a carbon number distribution extending from about nC_{14} to nC_{80} (**Figure IV. 2. 12**).

Quantitative HTGC analysis was performed on solutions of Polywax 1000 in three solvents, p-xylene, cyclohexane and carbon tetrachloride (**Appendix IV. 2. 7**). The results of these analyses are presented in **Figure IV. 2. 13**, and interestingly enough demonstrate 2.5 to 4 times higher total n-alkane recovery in C_{65} to C_{75} range from the carbon tetrachloride solution compared to the cyclohexane and p-xylene solutions, respectively. The concentration of individual n-alkanes in the carbon tetrachloride solution was 10-15 ng/ μ l and over 15 ng/ μ l higher as compared to the cyclohexane and p-xylene solutions, respectively. Changes in the distribution of n-alkanes from the different solutions are not observed.

A factor, other than solubility, that could possibly influence the quantitative HTGC results would be volume differences of the solvents at close to the boiling point temperatures that could affect the actual amount of sample introduced on the HTGC column. However, a comparison of the cubic thermal coefficients of expansion for the solvents (1.14×10^{-3} , 1.15×10^{-3} and $1.00 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$, for CCl_4 , CH_x and p-xylene, respectively) suggests the volume change for p-xylene is the lowest, and could not be therefore a reason for introducing a smaller amount of sample onto the HTGC column. Thus, the HTGC results show that an increasing amount of Polywax 1000 is dissolved in the order of solvents from p-xylene to cyclohexane and to carbon tetrachloride. A comparison with the predictions stated at the end of the previous section and **Figure IV.**

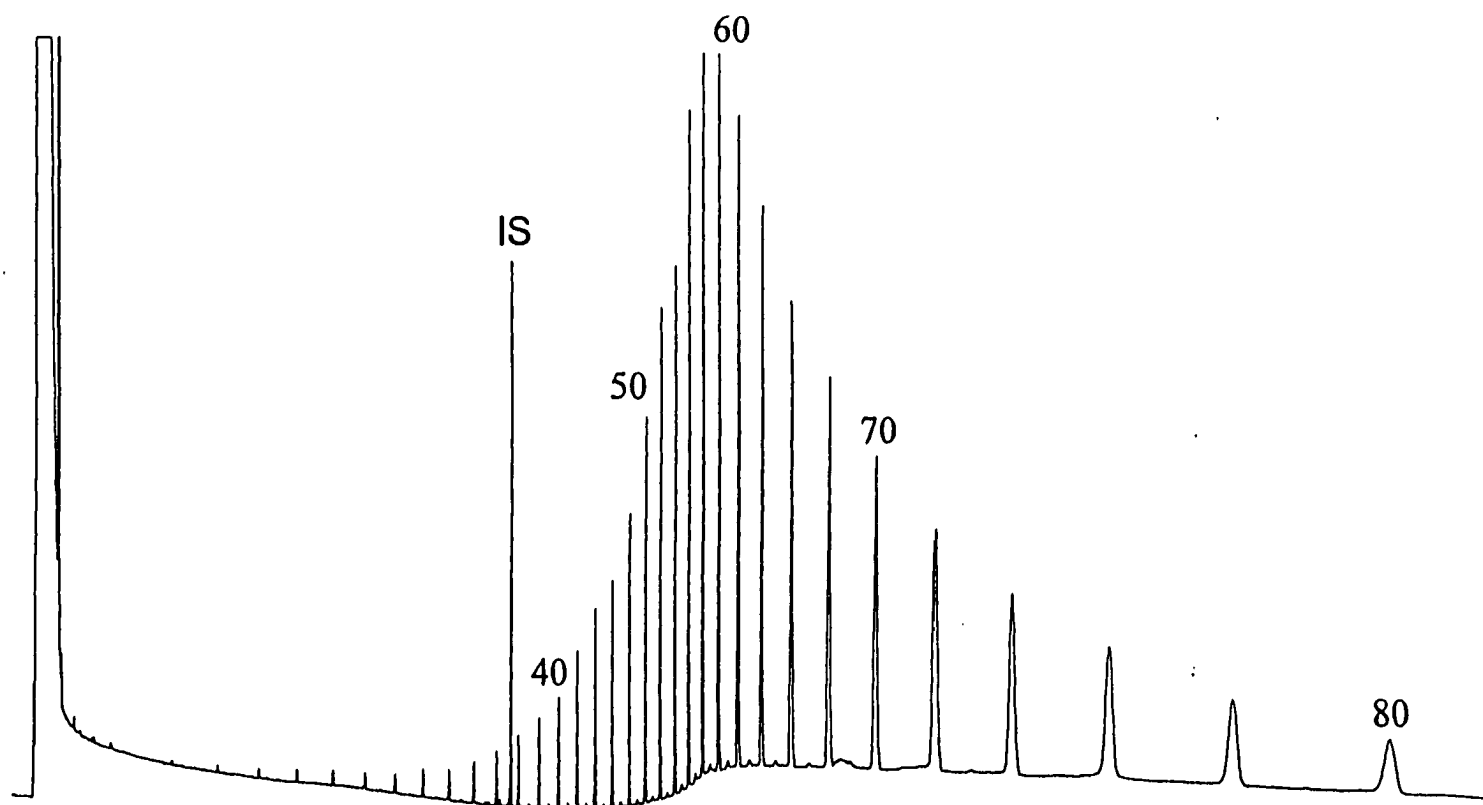


Figure IV. 2. 12. HTGC chromatogram of Polywax 1000 dissolved in carbon tetrachloride. HTGC oven temperature program 60-400°C @10°C/min, detector temperature 410°C, sample solution heated before injection.

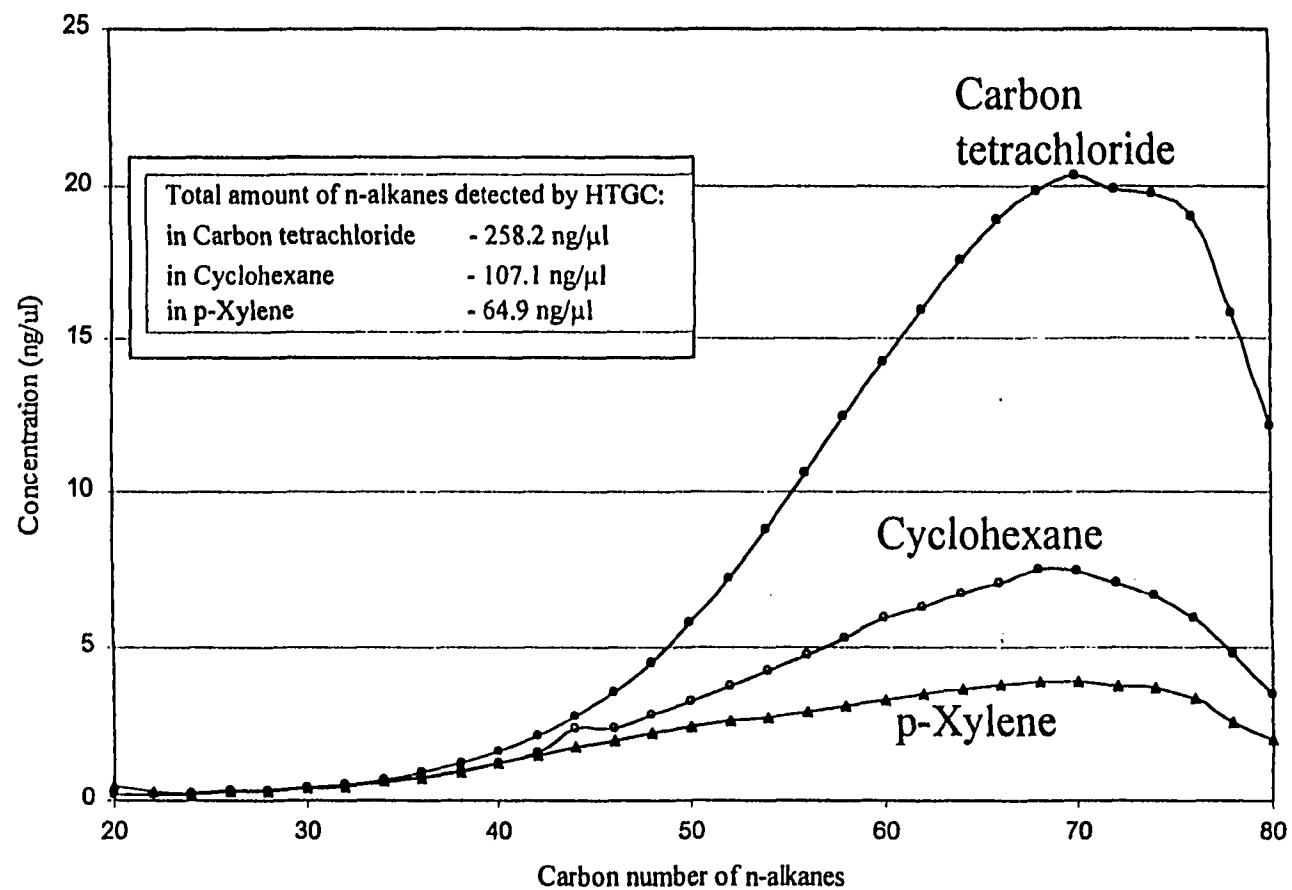


Figure IV. 2. 13. Quantitative HTGC analysis results for Polywax 1000 solutions in carbon tetrachloride, cyclohexane and p-xylene. HTGC program 60-400°C @ 10°C/min, detector temperature @ 410°C, solutions heated before injection.

2. 11 suggests that experimentally observed order of solubility of Polywax 1000 in the solvents by HTGC should be valid for n-alkane mixtures with solubility parameter ($\delta_d = \delta$) values higher than about $17.3 \text{ (J/cm}^3\text{)}^{1/2}$. This prediction is further used to evaluate which of the Methods 1, 2 and 3, discussed in section IV. 2. 3. C1, will give values for the solubility parameter of Polywax 1000 closest to $17.3 \text{ (J/cm}^3\text{)}^{1/2}$. The solubility parameters of Polywax 1000, calculated based on HTGC analysis by using Methods 1, 2 and 3, are $16.5 \text{ (J/cm}^3\text{)}^{1/2}$, $16.1 \text{ (J/cm}^3\text{)}^{1/2}$, and $17.2 \text{ (J/cm}^3\text{)}^{1/2}$, respectively. Because of the possible extension of the carbon number distribution of Polywax 1000 above the HTGC detection limit, these calculated values should be considered slightly lower with respect to the complete carbon number distribution of the sample. Thus from the calculated solubility parameters of Polywax 1000 and reference to **Table IV. 2. 5a** it is proposed that only Method 3 could give delta values above $17 \text{ (J/cm}^3\text{)}^{1/2}$ for the HMW n-alkane mixtures up to C_{120} that would be consistent with the experimental results on order of solubility of Polywax 1000 in p-xylene, cyclohexane and carbon tetrachloride. Based on that, Method 3 is used in further calculations of solubility parameters of n-alkane mixtures in petroleum waxes and wax deposits.

Filtration experiments at room temperature. Filtration experiments, as described in Chapter II, were performed in order to evaluate the solubility of Polywax 1000 in p-xylene and carbon tetrachloride at room temperature. The Polywax 1000 solutions were heated initially (close to the boiling point of the solvent) to dissolve as much as possible of the solute. The visually observed dissolution of Polywax 1000 in both solvents

occurred at approximately the same temperature of 70°C. Then, the solutions were left to equilibrate at room temperature for at least couple of hours prior to use in the filtration experiments. During the cooling period, the formation of solid from the solutions could be visually observed, suggesting that the cloud point of the solutions (concentration 4 mg/ml) is higher than the room temperature. The first observed cloudiness occurred at a higher temperature ($\approx 34^{\circ}\text{C}$) for the p-xylene solution compared to the carbon tetrachloride solution ($\approx 31^{\circ}\text{C}$), suggesting a relatively higher cloud point for the p-xylene solution of Polywax 1000. In addition, differences in morphology of the solid forming from the two solutions could be observed. The solid crystallizing from the carbon tetrachloride solution appeared to form better defined, more compact, and relatively larger size particles, whilst the solid crystallizing from the p-xylene solution was forming large amounts of very fine, snowflake-like material distributed as “puffy clouds”. Similar reductions in the average size of wax crystals as result of adding o-xylene to oil was observed by Ferworn et al. (1997) based on cross polar microscopy. After the Polywax 1000 solutions equilibrated to room temperature, the majority of crystallized material separated at the bottom of the p-xylene vial, and at the top of the carbon tetrachloride vial, reflecting density differences between solute and solvents. The density segregation appeared to occur faster with the carbon tetrachloride than with the p-xylene solution.

The above observations suggest that the solutions used in the filtration experiments do not represent true solutions at room temperature, in which the solute particles consist of individual molecules, but rather suspensions or colloidal dispersions. In suspensions, the solute particles contain more than one molecule and are large enough

to be visually observed, while in colloidal dispersions, the particles may contain more than one molecule but are not large enough to be visually observed even under a microscope. The pore size of the filter used was 450 nm (0.45 μm), which should allow all of the colloidal particles (5 nm to 200 nm; Laidler and Meiser, 1995) to pass through it as well as some portion of the larger size particles. The amount of sample collected as filtrate residue (after complete solvent evaporation), was used as a measure of the dissolved sample, and the amount of sample trapped on the filter (precipitate) was used as a measure of the undissolved part of the sample at room temperature.

The results from the filtration experiments are presented in **Table IV. 2. 7** and demonstrate that the carbon tetrachloride filtrate residue is almost three times larger (33.7% of original sample amount) compared to the p-xylene filtrate (12.1% of original sample amount). The amount of material trapped on the filter by carbon tetrachloride and p-xylene is 56.5% and 88.5% of the starting sample amount, respectively. These results indicate a higher solubility of Polywax 1000 in carbon tetrachloride than in p-xylene at room temperature, and they are in agreement with the HTGC results of heated Polywax 1000 summarized in **Table IV. 2. 5** and **Figure IV. 2. 11** (section IV. 2. 3. C1).

The obtained filtrates were analyzed by quantitative HTGC analysis to determine whether there were any differences in the carbon number distributions of the material from the filtrates of the carbon tetrachloride and p-xylene solutions. (**Appendix IV. 2. 8**, **Figures IV. 2. 14** and **IV. 2. 15**). Both filtrates were characterized by carbon number distributions extending to nC_{70} , suggesting that the highest carbon number n-alkanes have been trapped on filter (compare **Figures IV. 2. 14**, **IV. 2. 15** and **IV. 2. 12**, **IV. 2.**

Sample weight mg	Solvent volume ml	Solvent density g/cm ³	Solution concentration wt. %	Filtrate*		Precipitate*		Loss	
				mg	%**	mg	%**	mg	%**
202.7	p-xylene (50)	0.8611	0.46	24.5	12.1	163.4	80.6	14.8	7.3
204.3	carbon (50) tetrachloride	1.5940	0.25	68.8	33.7	100.4	49.1	35.1	17.2

Table IV. 2. 7. Results of filtration experiments at room temperature with Polywax 1000 solutions in p-xylene and carbon tetrachloride.

* after complete solvent evaporation

** relative to initial sample amount

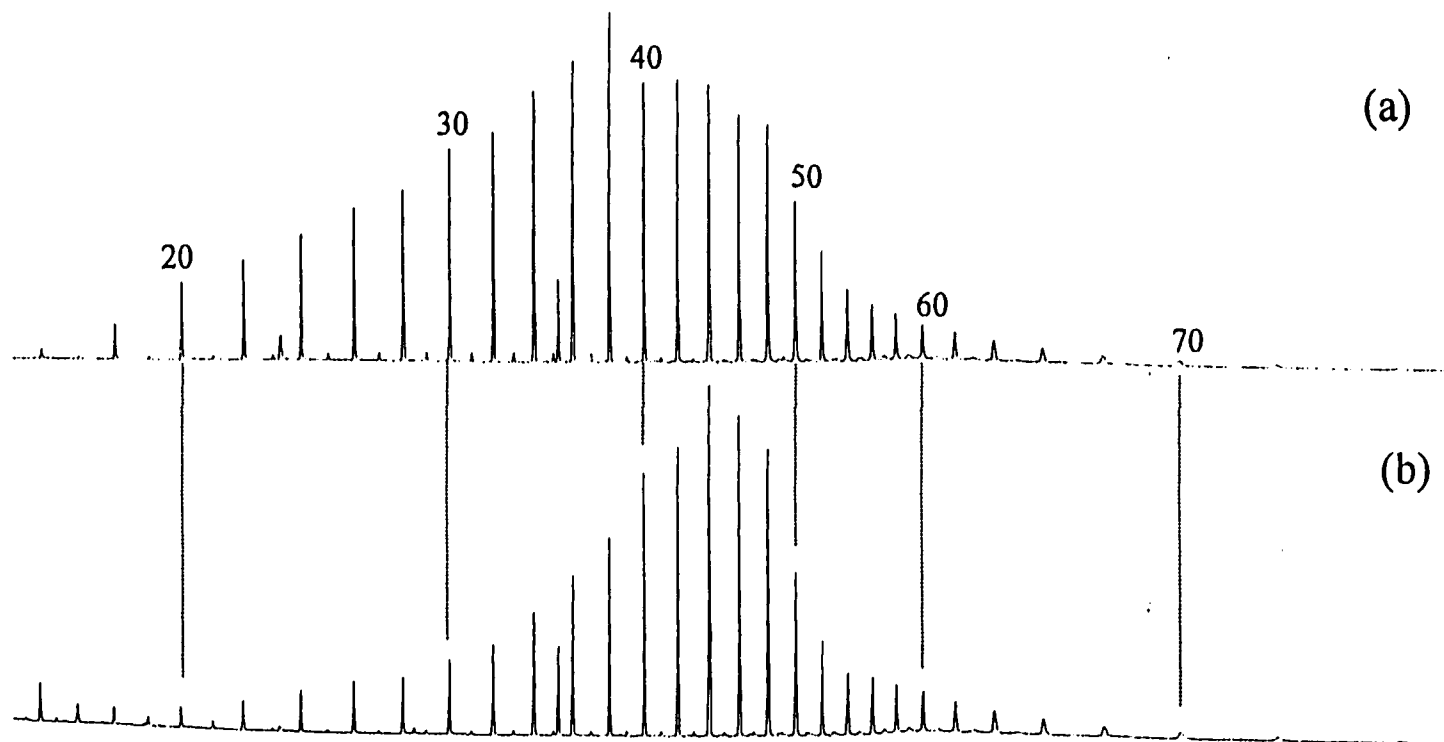


Figure IV. 2. 14. HTGC chromatograms of filtrates of Polywax 1000 solutions in (a) carbon tetrachloride; (b) p-xylene. Note the difference in carbon number distribution between the filtrates and the whole samples (Figure IV. 2. 12).

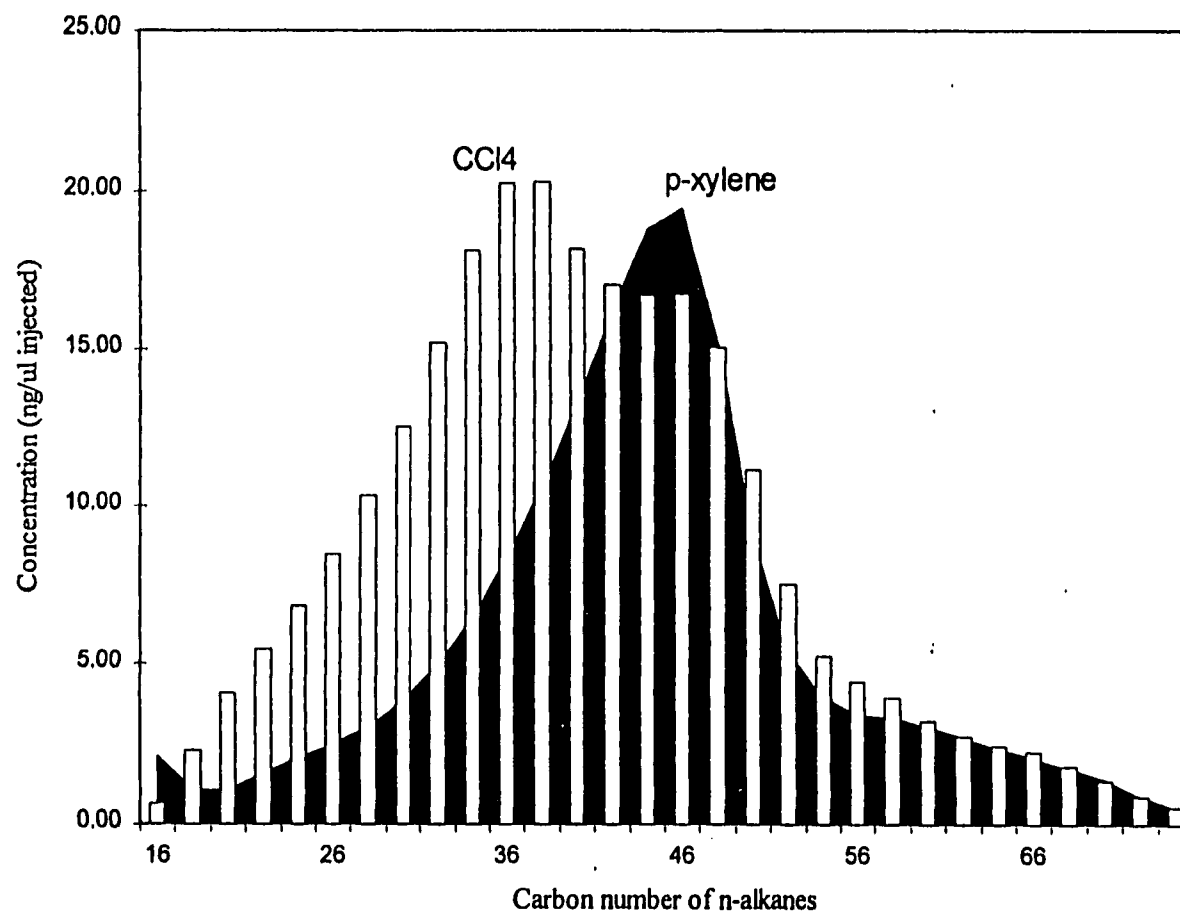
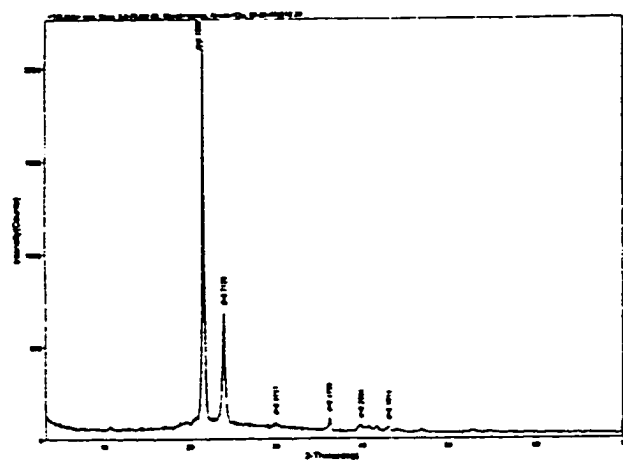


Figure IV. 2. 15. Quantitative HTGC analysis results of filtrates from Polywax 1000 solutions in carbon tetrachloride and p-xylene.

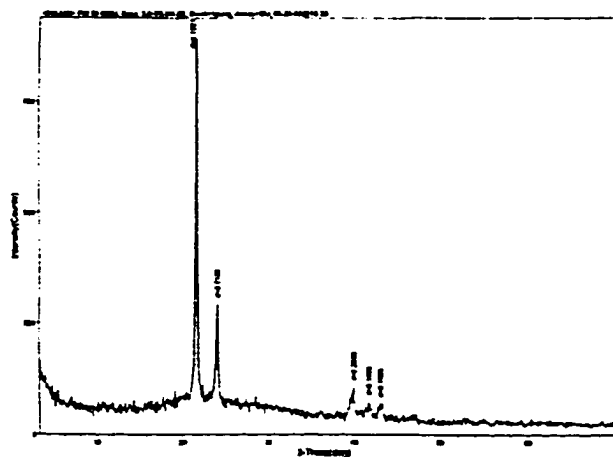
13). The n-alkane distribution in the carbon tetrachloride filtrate maximizes at nC_{38} and it is shifted to nC_{44} in the p-xylene filtrate (**Figure IV. 2. 14**). Another interesting result relates to the larger amounts (up to 13 ng/ μ l) of individual nC_{18} to nC_{40} alkanes present in the carbon tetrachloride filtrate compared to the p-xylene filtrate (**Figure IV. 2. 15**). These higher concentrations of n-alkanes in the carbon tetrachloride filtrate apparently contribute to the higher total amount of the material collected as filtrate. To a smaller extent, the nC_{50} to nC_{60} alkanes also showed a higher recovery (in the order of 1 ng/ μ l) in the carbon tetrachloride. Higher concentrations of n-alkanes in the p-xylene filtrate were present in a much narrower carbon number range (C_{44} - C_{48}) and in smaller amounts in the order of 2-3 ng/ μ l, compared to the carbon tetrachloride filtrate. Based on the quantitative HTGC results, the composition of both filtrates can be characterized as mixtures of macrocrystalline and microcrystalline waxes (**Table IV. 2. 1**). The p-xylene filtrate consists of 17% macrocrystalline wax (nC_{16} - nC_{34}) and 83% microcrystalline (nC_{36+}) wax, while the carbon tetrachloride filtrate contains twice as much macrocrystalline wax (33%; **Appendix IV. 2. 8**). This major difference in the composition of carbon tetrachloride and p-xylene filtrates suggests that the effect of these solvents on the solubility of Polywax 1000 at room temperature could be related to differences in the crystallization behavior of the n-alkane mixture from different solvents. In order to further test this possibility, X-ray diffraction analysis was performed on material crystallized from solutions of Polywax 1000 in carbon tetrachloride and p-xylene, and the results are discussed below. It should be noted here that this analysis was performed at a very late stage of the study and replicate analyses were not performed.

X-ray diffraction analysis was carried out on the following samples: (1) a powdered sample of Polywax 1000; (2) material crystallized from solution of Polywax 1000 in carbon tetrachloride; and (3) material crystallized from p-xylene (sample preparation and experimental conditions of X-ray analysis as described in Chapter II). The X-ray diffractograms of these samples are presented in **Figures IV. 2. 16a-c**, respectively. Powdered Polywax 1000 sample has a diffraction pattern similar to those published in previous studies (Dirand et al., 1998; Chevallier et al., 1999a), and suggests an orthorhombic structure (**Figure IV. 2. 17**). A computer library search, performed at the School of Geology and Geophysics X-ray laboratory by Ron Conlon, provided an excellent match with the data presented in **Table IV. 2. 8**. Based on the results of this match, the orthorhombic unit cell parameters are defined as 0.7455 x 0.4966 x 0.2589 nm, and are similar with the cell parameters of high density polyethylene discussed in section IV.2. 3. A. The n-alkane mixture that crystallized from the carbon tetrachloride solution shows a similar orthorhombic structure. Interestingly, the X-ray diffractogram of the material that crystallized from the p-xylene solution suggests that a part of it is with an orthorhombic structure, but the rest of it exists as an amorphous solid forming the large hump on the diffractogram (**Figure IV. 2. 16c**).

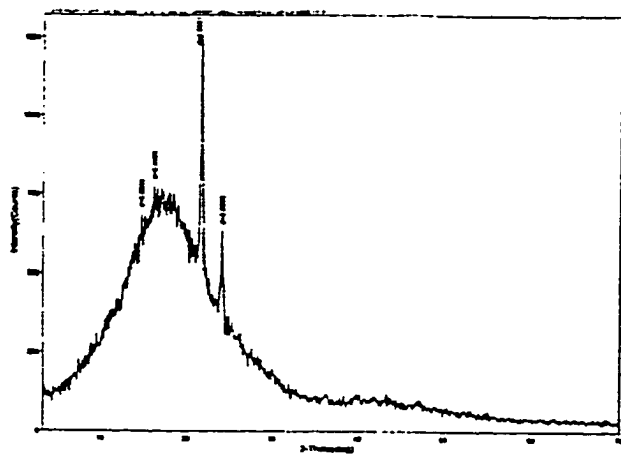
The model proposed by Dirand et al. (1998) and Chevallier et al. (1999a,b) of a single lamellar structure of molecule layer packing (**Figure IV. 2. 8**) is defined by a single family of diffraction lines (0 0 *l*) at low θ (1-10°), (**Figure IV. 2. 17**). Small intensity diffraction lines in this region appear to be present in **Figure IV. 2. 16b** and **c**.



(a)



(b)



(c)

Figure IV. 2. 16. X-ray diffractograms of Polywax 1000: (a) powder sample; solid crystallized from (b) carbon tetrachloride solution and (c) p-xylene solution.

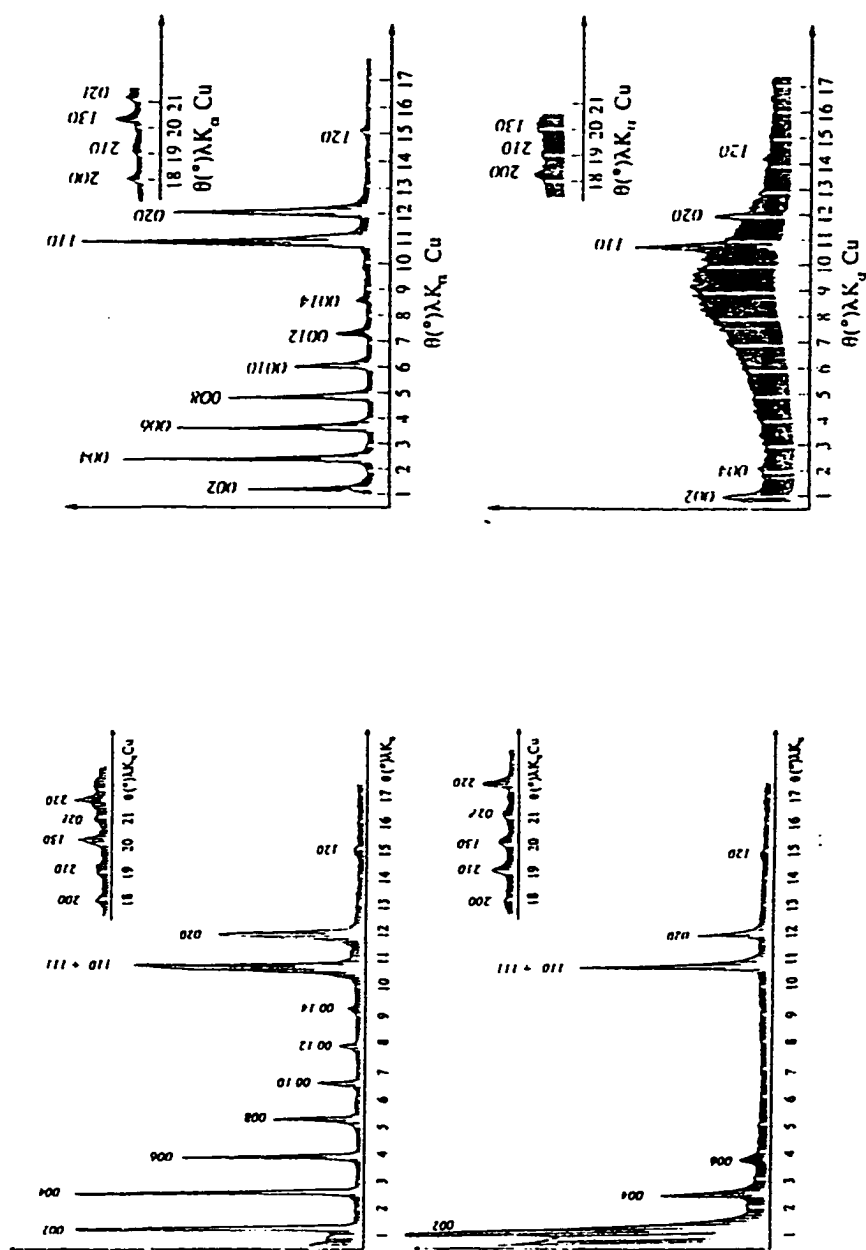


Figure IV. 2. 17. X-ray diffractograms showing (a) the structural identity between the orthorhombic β_2' intermediate solid solution of binary n-alkane mixture (C_{23} :85 mol% C_{25}) and (b) the orthorhombic solid solution of commercial wax (m. p. 52-54°C); (c) the orthorhombic intermediate solid solution β_1'' of binary n-alkane mixture (C_{26} :50 mol % C_{28}); (d) heavy crude oil; after Dirand *et al.* (1998) and Chevallier *et al.* (1999a).

Reflections				
2 Theta (deg)	d(Å)	h	k	l
21.482	4.1330	1	1	0
23.849	3.7280	2	0	0
29.950	2.9810	2	1	0
36.145	2.4830	0	2	0
39.204	2.2960	0	1	1
40.566	2.2220	3	1	0
41.107	2.1940	1	1	1
42.485	2.1260	2	0	1
43.759	2.0670	2	2	0

Table IV. 2. 8. X-ray diffraction data for Polywax 1000 match substance.

The above authors discussed that in order to increase the intensity of diffraction lines (0 0 λ), and obtain a preferential crystallographic orientation, the samples should be better prepared by melting and slow cooling on a water surface. This type of sample preparation was not attempted in the present study.

Discussion on the specifics of Polywax 1000 crystallization from carbon tetrachloride and p-xylene solutions.

The process of crystallization from solution occurs as a result of the supersaturation taking place during the cooling and is generally considered to involve the two phenomena of nucleation and crystal growth (Mozes, 1982; Manahan, 1986). Nucleation consists of the uniting of several (at least 4 or 5) molecules to form extremely small solid particles or nuclei. Larger amounts of solid material could be formed by further nucleation. Alternatively, solid particles can condense on existing nuclei through the process of particle growth. A predominant process of nucleation leads to a huge number of very small particles while a predominant process of particle growth favors fewer but larger particles. The relative predominance of both nucleation or particle growth depends upon the degree of supersaturation. However, the nucleation increases exponentially with supersaturation while particle growth increases in approximately linear fashion with the degree of supersaturation. Related to that, a low degree of supersaturation favors particle growth as a predominant mechanism of solid formation (Manahan, 1986). The physical appearance of the solid particles formed at a low degree of supersaturation is usually compact in shape (Walton, 1966). At a higher degree of

supersaturation, favoring nucleation, the rate of growth becomes so rapid that the heat, which is liberated by the formation of the new solid phase, can not easily be dissipated. As a consequence, a dendritic growth (snowflake type) occurs, so that the surface area of the growing particle to be maximized and to enable the crystal to evolve the heat to its surroundings.

Differences in both solid morphology and concentration of Polywax 1000 on a wt/wt basis in the carbon tetrachloride and p-xylene solutions appear to be related to different mechanisms of solid formation. The formation of compact and larger size particles, and the lower solute concentration (wt/wt) in the carbon tetrachloride solution (Table IV. 2. 7) are in support for a predominant particle growth mechanism of solid formation. This type of predominant solid formation mechanism will be in agreement with the higher amount of filtrate recovered from the Polywax 1000-CCl₄ solution, since the particle growth mechanism favors the formation of fewer even though relatively larger size solid particles. On the other hand, the formation of large amounts of very fine, snowflake-like solid material and the higher solute concentration (wt/wt) of the p-xylene solution supports a predominant mechanism of solid formation by nucleation. The p-xylene is also characterized with a relatively higher thermal conductivity (0.130, 0.124, and 0.118 W/m K at 25, 50 and 75°C) compared to carbon tetrachloride (0.099, 0.093, and 0.088 W/m K at 25, 50 and 75°C), a condition that could favor dissipation of the heat released during solidification of n-alkane mixture and a dendritic type growth. The effect of p-xylene to reduce the size of solid formed is apparently not a sufficient condition to

be an effective solvent for Polywax 1000, because the amount of total formed solid is not influenced. Similar results have been published for the effect of o-xylene on the reduction of the size but not the amount of wax crystals for a North Sea oil, based on temperature controlled microscopy observations (Ferworn et al., 1997). Moreover, addition of xylenes to oil or pure nC_{28} , nC_{32} , nC_{36} alkanes have resulted in cloud point increase of the system, as demonstrated by the data of Erickson et al. (1993) and Ferworn et al. (1997), and is confirmed by the observations in the present study with the HMW dominated Polywax 1000.

As discussed in section IV. 2. 3. B, n-alkane mixtures at room temperature form solids with orthorhombic structures. The X-ray diffraction results for the powdered Polywax 1000 (**Figure IV. 2. 16**) confirm these observations. The even number predominance of n-alkanes in the Polywax 1000 does not lead to formation of an amorphous solid as the one observed for an even carbon number dominated macrocrystalline type wax (nC_{20} - C_{33} alkanes) by Chevallier et al. (1999a). This difference in the results could be attributed to the predominantly high molecular weight (HMW) n-alkane distribution in Polywax 1000. Similarities in structure of powdered Polywax 1000 and the solid crystallized from the carbon tetrachloride solution further suggest that carbon tetrachloride does not significantly change the orthorhombic structure of Polywax 1000. This result can be related to the results of Dirand et al. (1998), who observed that the structure of solid formed from solutions with low solute concentration has the characteristics of the solute mixture (see discussions in section IV. 2. 3. B). On the other

hand, presence of both crystalline (orthorhombic) and amorphous solids in the material crystallized from the p-xylene solution suggests that p-xylene to some extent changes the orthorhombic structure of Polywax 1000. Srivastava et al. (1992) observed the formation of amorphous solid, consisting of thin, flat, plate-type crystallites for a macrocrystalline-type wax in aromatic and iso-/cycloalkane solvent mixture. For the case of the wax-solvent system studied by these authors, it was shown that the amorphous solid develops due to the formation of a hexagonal structure and is associated with a large amount of solvent trapped in the layered structure formed by the thin plates of the crystallites. Dirand et al. (1998) discussed that at high n-alkane (binary n-alkane mixture C₂₆/C₂₈) concentrations in solvent solutions, the solid formed has the characteristics of the rotator (α -RII) phase of the binary mixture, which is normally observed only with increasing temperature (see discussions in section IV. 2. 3. B). Based on these results of Srivastava et al. (1992) and Dirand et al. (1998), the presence of the amorphous solid formed from the p-xylene solution (higher Polywax 1000 concentration, wt/wt), can be related to the formation of solid with a hexagonal structure. However, HMW n-alkanes and mixtures show neither solid-solid transitions nor formation of hexagonal (rotator) phases with increasing temperature (see discussions in section IV. 2. 3. B). Lower molecular weight n-alkanes (below ca. nC₃₆-C₄₀) do experience an orthorhombic-hexagonal solid-solid transition below the melting point. Considering that Polywax 1000 is dominated by HMW n-alkanes, but also contains a range of lower molecular weight n-alkanes, it can be expected that the amorphous solid formed from the p-xylene solution results mainly from the interaction of the solvent with the LMW n-alkanes in the mixture. The rest of

the solid with an orthorhombic structure, formed from the same solution most probably consists of the HMW n-alkanes present in Polywax 1000 and is not changed by the solvent. Such interpretation of the X-ray diffraction results is consistent with the determined depletion of LMW (C_{18} - C_{40}) n-alkanes in the p-xylene filtrate (Figures IV. 2. 14 and IV. 2. 15), and suggests that the p-xylene precipitate is likely to consist of mixed amorphous/orthorhombic solid. Such solid, as discussed in section IV. 2 3. B, will be softer compared to a crystalline solid formed by HMW n-alkanes only (as expected to be the one formed from the carbon tetrachloride solution). One possible reason why p-xylene interacts more strongly with the LMW n-alkanes compared to carbon tetrachloride could be related to the rod-like shape of the molecule that could fit better and closer to the rod-like shape of LMW n-alkane molecules (Conder and Young, 1979).

D3. Solubility of hydrocarbon / non-hydrocarbon mixtures

Petroleum wax deposits consist not only of hydrocarbons, but various proportions resins and asphaltenes, water, trapped oil and inorganic material (section IV. 2. 1). In order to get closer to the actual composition of solid petroleum wax deposits, the results in this section discuss the predicted changes in the solubility of mixtures of n-alkanes with resins, one of the major non-hydrocarbon groups. The specific question addressed in this section is if and how the choice of a “best” solvent for a particular n-alkane/resin mixture might be changed according to the different proportions of n-alkanes and resins. The discussion is based on calculated solubility parameters of a model n-alkane mixture with different proportions of resin, and their radii of interaction with different solvents.

The solubility parameter of a mixture consisting of n-alkanes and resin was calculated assuming one of the components to be an n-alkane mixture with $\delta = \delta_d$ of $17.3 \text{ (J/cm}^3\text{)}^{1/2}$, $\delta_p = 0$, $\delta_h = 0$, and the other component to be a “hydrocarbon resin” with partial solubility parameters as provided by Archer (1996), **Table IV. 2. 9**. The formula $\delta = \sum \phi_i \delta_i$, where ϕ_i and δ_i are the fraction and solubility parameters of the two components was used for calculation. The solubility of three mixtures with relative proportions of the n-alkanes and resin being 0.5-0.5, 0.3-0.7, and 0.7-0.3 are investigated. The calculated solubility parameters for these mixtures and the match with a database of solvents, sorted in order of decreasing $^i j R$ values for selected solvents, are presented in **Table IV. 2. 9a** and **b**. The results discussed earlier in section IV. 2. 3. D2. demonstrated that an n-alkane mixture with $\delta = 17.2 \text{ (J/cm}^3\text{)}^{1/2}$ is “best” dissolved in carbon tetrachloride. The addition of different proportions of resin to a similar solubility parameter n-alkane mixture show that the “best” choice solvents change significantly (**Table IV. 2. 9**). With an increasing proportion of the resin in the n-alkane/resin mixture from 30 % to 50 % to 70 %, the solvents with lowest $^i j R$ values (first row in **Table IV. 2. 9b**), or solvents with a highest solvency capacity for the particular mixture, change from triethylamine to ethyl benzene to p-xylene, respectively. These results present a good illustration regarding the specificity of “best” choice solvent according to the composition of the petroleum wax mixture. It should be pointed out that the n-alkane/resin mixture discussed here is a simple example with fixed solubility parameters for the components. In actual petroleum wax deposits formed even in the same well or pipeline, the

a)

	delta D	delta P	delta H
n-alkane mixture	17.3	0.0	0.0
HC resin	17.6	1.2	3.6
n-alkane/HC resin mixture			
0.7-0.3	17.4	0.4	1.1
0.5-0.5	17.4	0.6	1.8
0.3-0.7	17.5	0.8	2.5

b)

n-alkane/HC Resin mixture					
0.7 - 0.3 mix		0.5 - 0.5 mix		0.3 - 0.7 mix	
solvent	ljR	solvent	ljR	solvent	ljR
triethylamine	0.8	ethyl benzene	0.9	p-xylene	0.7
carbon tetrachloride	1.0	triethylamine	1.1	o-xylene	0.9
ethyl benzene	1.0	p-xylene	1.4	toluene	1.3
mesitylene	1.4	toluene	1.5	ethyl benzene	1.3
cyclohexane	1.6	carbon tetrachloride	1.6	triethylamine	1.7
decalin	1.7	o-xylene	1.6	carbon tetrachloride	2.1
toluene	1.8	mesitylene	1.8	mesitylene	2.3
n-eicosane	2.0	cyclohexane	2.1	cyclohexane	2.8
p-xylene	2.1	decalin	2.3	decalin	2.8
o-xylene	2.2	n-eicosane	2.5	n-eicosane	3.2
n-hexadecane	2.3	n-hexadecane	2.8	n-hexadecane	3.4

Table IV. 2. 9. Solubility parameters for mixtures of n-alkanes with different proportions of resin (a), and their radii of interaction with a selected set of solvents (b).

composition of both hydrocarbons and non-hydrocarbons could vary, as demonstrated later in this Chapter.

Another major group of non-hydrocarbons present in the petroleum wax deposits are asphaltenes. Asphaltenes are defined as a petroleum fraction, which precipitates in an excess of light hydrocarbons. The content and composition of asphaltenes vary not only with the origin of the oils, but also with the method of precipitation (e.g., Yen and Chillingarian, 1994). Despite the large number of studies on asphaltenes and resins, the type of association between them and the micelles they form is still under discussion and investigation (e.g., Pfeifer and Gaal, 1940; Speight, 1999; Artok *et al.*, 1999). Even more obscure and less studied is the nature of the association between resins and asphaltenes on the one hand, and the HMW hydrocarbons on the other. The type and properties of particles formed by the association between HMW n-alkanes, resins and asphaltenes are not completely clear. It is not clear, for example, if the HMW n-alkanes are occluded in the resin-asphaltene matrix or resin-asphaltenes are trapped as occlusions during the crystallization of n-alkanes, or if both types of particles may be formed under different conditions. Knowledge of the nature of these particles is very important because it will determine if they are hydrophobic or hydrophilic in nature, and their related behavior and interaction with the rest of the oil.

It should be noted here that the regular solution theory and total solubility parameter have been applied for the evaluation and modeling of asphaltene solubility and precipitation in a number of studies (Yen and Chillingarian, 1994; Wilhelms and Larter, 1994a and b; Speight and Long, 1996; Speight, 1999; Andersen and Speight, 1999;

Browarzik *et al.*, 1999; Wang *et al.*, 1999). Generally, models incorporating the total solubility parameter to predict phase behavior and precipitation of asphaltenes regard the oil as a two component system, consisting of asphaltenes and de-asphalted oil only. Thus, the changes in phase equilibrium of the system are caused by changes in the solubility parameter of either of the two pseudocomponents (Andersen and Speight, 1999).

Higher proportions of asphaltenes in solid wax deposits will most likely significantly change the solubility and the choice of a “best” solvent for such mixtures. In the present study, asphaltenes are not included for two main reasons: (1) the compositional variability in asphaltenes, due to both oil origin and method of precipitation, which relates to variability in dispersion, polar and hydrogen bond strengths of interactions in different asphaltenes, and (2) the lack of Hansen solubility parameters for asphaltenes published in the literature.

D4. Conclusions

With respect to the problem of wax deposition, the results and information presented in section IV. 2. 3. D can be summarized as follows:

- n-alkane mixtures of different molecular weights present in wax deposits are dissolved most efficiently by different solvents, depending on carbon number distribution.

- the choice of solvent for sample dilution used for quantitative HTGC analysis can significantly affect (2 to 4 times) the estimated amount of n-alkanes in wax deposits.

- a procedure for the calculation of solubility parameters of n-alkane mixtures in petroleum waxes and wax deposits is proposed, based on quantitative HTGC analysis and Method 3 (Fedors, 1974). The method of choice for the solubility parameter calculation is validated by experimental results on solubility of a standard HMW dominated n-alkane mixture.

- carbon tetrachloride dissolves a higher amount of the HMW dominated n-alkane mixture (Polywax 1000) compared to cyclohexane and p-xylene (HTGC results). At the same (room) temperature below the cloud point, Polywax 1000 solution in carbon tetrachloride forms a smaller amount (1.5 times) of precipitate compared to p-xylene solution. However, the carbon tetrachloride precipitate is expected to be harder than the one formed from a p-xylene solution, and could be more difficult for remediation.

- presence of higher proportions non-hydrocarbons in wax deposits significantly changes the choice of a solvent for best dissolution.

IV. 2. 3. E. Solubility of wax deposits and petroleum waxes

In the present section, the procedure for solubility parameter calculation and evaluation of “best” choice solvent (developed in section IV. 2. 3. D) has been applied to evaluate the solubility of actual wax deposits and petroleum waxes. Two main groups of results are presented in this section. First, the solvents used in the previous section are applied to evaluate their effect on two samples of solid deposits collected at different locations of the same pipeline. Second, comparisons of n-alkane recovery efficiency between two laboratory techniques for wax precipitation using a high-wax and a low-wax oils are performed and the results discussed in terms of the choice of solvents used for precipitation and recovery of waxes.

E1. Pipeline wax deposits

As an extension of the results presented in previous section IV. 2. 3. D, the results in this section explore the effect of the same solvents on actual pipeline solid wax deposit samples (# 9 and # 10). Quantitative HTGC analyses were performed on heated solutions of the pipeline waxes in carbon tetrachloride, cyclohexane and p-xylene. Filtration experiments at room temperature were performed with sample # 10 solutions in carbon tetrachloride, cyclohexane and p-xylene, similar to the ones performed with the standard n-alkane mixture (section IV. 2. 3. D and Chapter II).

HTGC chromatograms and quantitative results for both pipeline samples in carbon tetrachloride, cyclohexane and p-xylene are presented in **Figure IV. 2. 18a-d**. The

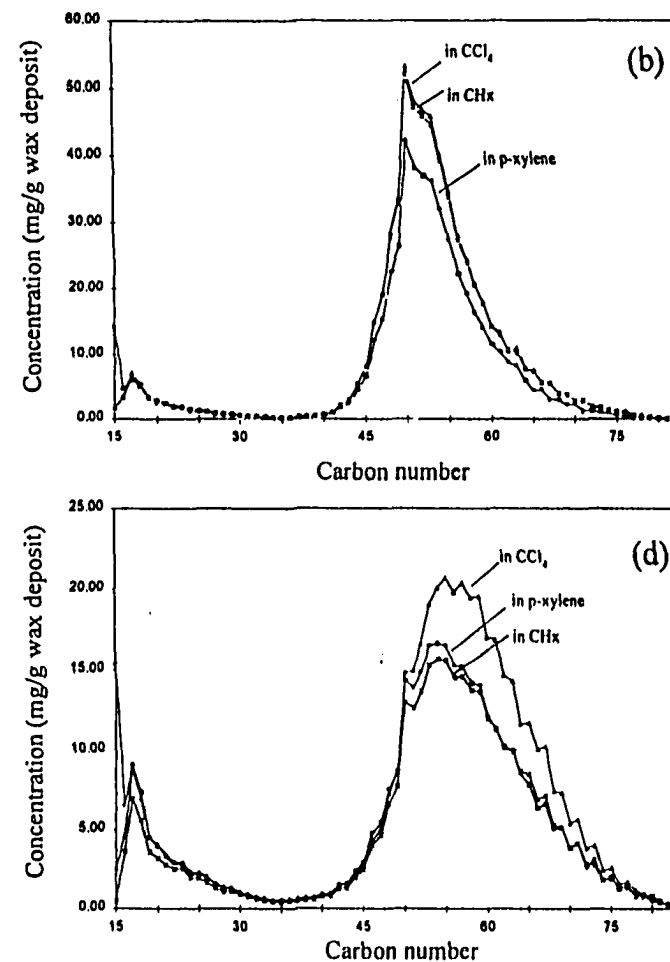
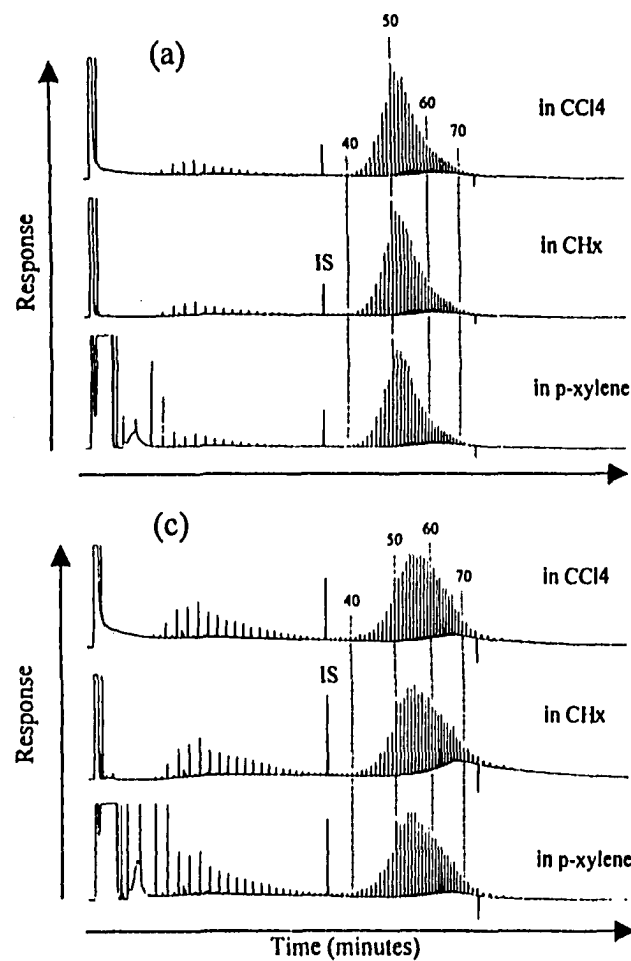


Figure IV. 2. 18. HTGC chromatograms and quantitative HTGC analysis results for pipeline sample # 9 (a, b) and # 10 (c, d) using carbon tetrachloride, cyclohexane and p-xylene as solvents. HTGC program 60-400°C @ 10°C/min, detector temperature @ 410°C, solutions heated before injection.

n-alkane distribution in both pipeline wax deposits maximizes in the HMW range from nC_{40} to nC_{80} (**Figure IV. 2. 18a and b**). Presence of n-alkanes in the carbon number range below nC_{35} , evident on the chromatograms, can be attributed to a certain amount of trapped oil with the pipeline deposits. The n-alkane distribution in pipeline sample # 9 maximizes at nC_{50} and is shifted slightly towards the nC_{55} - nC_{60} alkanes in sample # 10. The quantitative HTGC results demonstrate differences in the amount of n-alkanes present in the samples. In addition, the samples show different solubility behavior in the three solvents. The results in **Table IV. 2. 10** and **Figure IV. 2. 18c and d** demonstrate approximately one and a half times higher total n-alkane amounts and almost three times higher maximum concentration of individual n-alkanes in wax deposit # 9 than in wax deposit # 10. For wax # 9, similarly high total amount of n-alkanes (60% of the wax deposit) is recovered by carbon tetrachloride and cyclohexane, followed by p-xylene (50% of the wax deposits; **Table IV. 2. 10**). On an individual component basis, n-alkane concentrations up to 10 mg/g higher are recovered from the carbon tetrachloride and cyclohexane solutions (specifically in the carbon number range nC_{50} - nC_{55}) than by p-xylene solution (**Appendix IV. 2. 9**). For the pipeline wax deposit # 10, the highest total amount of n-alkanes, representing 43% of the wax deposit, is recovered from the carbon tetrachloride, followed by the p-xylene (37%) and cyclohexane (33%) solutions (**Table IV. 2. 10**). On an individual component basis, carbon tetrachloride recovers up to 5 mg/g of wax deposit more of the n-alkanes than both the cyclohexane and p-xylene. These results suggest an order of increasing solubility of wax # 9 from p-xylene to cyclohexane

Solvent	Initial solute concentration	Pipeline wax # 9 HTGC recovery (total n-alkanes)		Pipeline wax # 10 HTGC recovery (total n-alkanes)	
	ng/ul	ng/ul	%*	ng/ul	%*
Carbon tetrachloride	800	495.5	61.9	345.4	43.2
Cyclohexane	800	481.5	60.2	263.1	32.9
p-Xylene	800	417.6	52.2	294.1	36.8

Table IV. 2. 10. Summary of quantitative HTGC analysis results for pipeline wax deposit samples # 9 and # 10 using carbon tetrachloride, cyclohexane and p-xylene as solvents; solutions heated before injection; * refers to the initial solute concentration.

SOLVENTS					WAX #10-23	
Name	B.p.	Density @20°C	Volume	Weight	Weight	Wt.% in solution
	(°C)	(g/ml)	(ml)	(g)	(g)	
Carbon tetrachloride	77	1.5940	50	79.7	0.4942	0.6
Cyclohexane	81	0.7785	50	38.9	0.5172	1.3
p-Xylene	138	0.8611	50	43.1	0.5156	1.2

Solvent	Precipitate		Filtrate		Loss
	mg	wt.% *	mg	wt.%	wt.%
Carbon tetrachloride	0.1081	22	0.3610	73	5.0
Cyclohexane	0.2480	48	0.2361	46	6.4
p-Xylene	0.2607	51	0.2194	43	6.9

Table IV. 2. 12. Results of filtration experiments at room temperature with a pipeline wax deposit sample # 10 using carbon tetrachloride, cyclohexane and p-xylene as solvents; * refers to the original amount of sample.

and carbon tetrachloride, and for wax # 10 from cyclohexane to p-xylene to carbon tetrachloride.

The solubility parameters of the HTGC determined n-alkane mixtures in both pipeline wax samples were calculated using the procedure discussed in sections IV. 2. 3. D (Appendix IV. 2. 6, Table IV. 2. 5, Figure IV. 2. 11), and resulted in values of $17.10 \text{ (J/cm}^3\text{)}^{1/2}$ and $17.14 \text{ (J/cm}^3\text{)}^{1/2}$ for pipeline wax samples # 9 and # 10, respectively. In contrast to the determined order of solubility by HTGC, these values are very similar and suggestive of similar solubility behavior for the n-alkane mixtures present in both wax deposits, provided the samples consist only of n-alkanes in the carbon number range detectable by HTGC. The results shown in Figure IV. 2. 11 suggest that an n-alkane mixture with a solubility parameter of $17.1 \text{ (J/cm}^3\text{)}^{1/2}$ dissolves most readily in cyclohexane (lowest $\bar{u}_R$), followed by carbon tetrachloride and p-xylene (increasing $\bar{u}_R$), which does not correspond to the observed solubility order from the HTGC results (Figure IV. 2. 18). The inconsistency between observed and predicted results may be related to an incomplete detection of the n-alkane distribution and/or co-elution effects in the HMW region that could lead to an undefined range of errors in the solubility parameter calculation. On the other hand, larger proportions of compounds other than n-alkane may affect the solubility behavior of the samples.

An n-alkane mixture with a solubility parameter in the order of $17.3 \text{ (J/cm}^3\text{)}^{1/2}$ will have similar $\bar{u}_R$ values in both carbon tetrachloride and cyclohexane which will be higher than in p-xylene (Figure IV. 2. 11). This pattern corresponds to the solubility order for sample # 9 based on HTGC results. It can also be determined from Figure IV. 2. 11 that

the solubility order for sample # 10 based on HTGC results is not in agreement for any pure n-alkane mixture with solubility parameters in the range from 15 (J/cm³)^{1/2} to 18 (J/cm³)^{1/2}. An alternative explanation for this observation is that compounds other than n-alkanes in the pipeline wax samples change their solubility pattern .

The HTGC results of the wax deposits demonstrate that there are differences in their n-alkane contents and hence the content of other compounds in the deposits. Wax sample # 10 would appear to have a higher content of non-n-alkane compounds than sample # 9 (**Figure IV. 2. 18d**, **Table IV. 2. 10**). To test how the presence of polar fractions may influence the predicted solubility pattern of the wax deposits, solubility parameters for several different proportions n-alkane/hydrocarbon resin mixtures and their radii of interaction (^{ij}R) with the three solvents were calculated. Two cases were considered, when the solubility parameter ($\delta_d = \delta_{total}$) of the n-alkane mixture is 17.1 (J/cm³)^{1/2} and 17.3 (J/cm³)^{1/2}, respectively (**Table IV. 2. 11**). The solubility parameter provided for a hydrocarbon resin (Archer, 1996) was used in the calculations. The results of these calculations are presented in **Table IV. 2. 11a** and **b** and suggest that a pattern consistent with the solubility order for sample # 9, as determined by HTGC, occurs for an n-alkane/resin mixture (65/35) when the solubility parameter of the n-alkane mixture is 17.1 (J/cm³)^{1/2}. A similar pattern is observed for n-alkane/resin mixture (90/10) when the solubility parameter of the n-alkane mixture is 17.3 (J/cm³)^{1/2}. A solubility pattern for sample # 10 consistent with the HTGC results occurs for a case of 65/35 n-alkane/resin mixture with a solubility parameter of the n-alkane mixture being 17.3 (J/cm³)^{1/2} (**Figure IV. 2. 18** and **Table IV. 2. 11**). The n-alkane/resin mixtures that contain more than 50%

(a)

n-alkane mixture ($\delta_{\text{total}} = \delta_d = 17.1 \text{ (J/cm}^3)^{1/2}$) with different proportions of hydrocarbon resin									
90:10		75:25		65:35		45:55		25:75	
solvent	$\bar{U}_R$	solvent	$\bar{U}_R$	solvent	$\bar{U}_R$	solvent	$\bar{U}_R$	solvent	$\bar{U}_R$
cyclohexane	0.8	cyclohexane	1.1	carbon tetrachloride	1.3	p-xylene	1.2	p-xylene	0.5
carbon tetrachloride	1.2	carbon tetrachloride	1.3	cyclohexane	1.5	carbon tetrachloride	1.8	carbon tetrachloride	2.4
p-xylene	3.0	p-xylene	2.4	p-xylene	2.0	cyclohexane	2.3	cyclohexane	3.0

(b)

n-alkane mixture ($\delta_{\text{total}} = \delta_d = 17.3 \text{ (J/cm}^3)^{1/2}$) with different proportions of hydrocarbon resin									
90:10		75:25		65:35		45:55		25:75	
solvent	$\bar{U}_R$	solvent	$\bar{U}_R$	solvent	$\bar{U}_R$	solvent	$\bar{U}_R$	solvent	$\bar{U}_R$
carbon tetrachloride	1.0	carbon tetrachloride	0.9	carbon tetrachloride	1.1	p-xylene	1.2	p-xylene	0.1
cyclohexane	1.0	cyclohexane	1.4	cyclohexane	1.7	carbon tetrachloride	1.7	carbon tetrachloride	2.9
p-xylene	2.9	p-xylene	2.3	p-xylene	1.9	cyclohexane	2.4	cyclohexane	3.6

Table IV. 2. 11. Calculated radii of interaction ($\bar{U}_R$) of modeled n-alkane/resin mixtures with studied solvents. Two cases are presented for an n-alkane mixture with solubility parameter of $17.1 \text{ (J/cm}^3)^{1/2}$ (a) and solubility parameter of $17.3 \text{ (J/cm}^3)^{1/2}$ (b) with an increasing proportion of hydrocarbon resin from 10% to 75%. The solubility parameters in $\text{(J/cm}^3)^{1/2}$ for the hydrocarbon resin are $\delta_d = 17.6$, $\delta_p = 1.2$, $\delta_h = 3.6$.

resin have highest solubilities in p-xylene, compared to cyclohexane and carbon tetrachloride. Such a pattern of solubility was not observed in any of the pipeline wax samples studied by HTGC, which implies that the amount of resin in these wax deposit samples is less than 50%. It should be pointed out again that the examples presented above on mixtures of n-alkanes with polar fractions represent rather simplified models of the wax deposits. The polar part of these mixtures is assumed to consist only of one component (a hydrocarbon resin), thus eliminating the effect of other possible resin components with different solubility characteristics and the effect of asphaltenes. Despite this simplification, it has been demonstrated that the HTGC results reflect the influence of possible non-hydrocarbons on the solubility of the samples. Additional experimental data based on amounts, composition, and structural relationships between hydrocarbon and non-hydrocarbon classes of compounds could be incorporated in the future to refine the predictions for solubility of these wax deposits.

Filtration experiments were performed at room temperature (see section IV. 2. 3. C for comparison with similar experiments with Polywax 1000) with wax sample # 10 to evaluate the filtrate and precipitate yields in solutions of carbon tetrachloride, cyclohexane and p-xylene. Solutions were prepared using wax deposit amount of 500 mg in 50 ml of solvent. This sample amount is higher than that used in the Polywax 1000 (200 mg) experiments because the pipeline deposits were expected to represent a mixture of n-alkanes and other components in contrast to Polywax 1000. The filtration results presented in **Table IV. 2. 12** demonstrate that the amount of filtrate recovered from carbon tetrachloride (73% of wax deposit) at room temperature is 27-30% higher than

that recovered from the cyclohexane (46% of wax deposit) and p-xylene (43% of wax deposit) solutions. These results are consistent with the HTGC results of the heated pipeline wax # 10 solutions which demonstrated a 6-10% higher total n-alkane recovery in carbon tetrachloride (43%) than the other two solvents (**Figure IV. 2. 18, Table IV. 2. 10**). The higher yields from the filtration experiments vs. the HTGC experiments can be explained by losses or higher imprecision of quantitative HTGC analysis in the HMW region (section IV. 2. 1) and/or presence of non-hydrocarbon fractions in the filtrate that also can not be accounted for by HTGC.

The results presented above can be summarized as follows:

- (1) HTGC results show an increasing solubility for the pipeline wax deposits from p-xylene and cyclohexane to carbon tetrachloride, consistent with the standard Polywax 1000 results, and suggest that the amount of n-alkanes in both pipeline waxes is relatively high.
- (2) Differences in total n-alkane recovery content between pipeline waxes # 9 and # 10 imply a higher contribution of non-n-alkane components in sample # 10 and/or incomplete detection of the n-alkanes by HTGC.
- (3) The observed solubility order of pipeline waxes # 9 and # 10 based on HTGC analysis was found to match several model n-alkane/resin compositions:

wax # 9

- 100% n-alkane mixture or 90:10% n-alkane/resin mixture, if the n-alkane mixture solubility parameter is $17.3 \text{ (J/cm}^3\text{)}^{1/2}$

- 65:35% n-alkane/resin mixture if the n-alkane mixture solubility parameter is $17.1 (\text{J}/\text{cm}^3)^{1/2}$

wax # 10

- 65:35% n-alkane/resin mixture if the solubility parameter of the n-alkane mixture is $17.3 (\text{J}/\text{cm}^3)^{1/2}$

E2. Comparison of two laboratory techniques for wax precipitation

The two techniques compared in this section are the “acetone” technique (Burger *et al.*, 1981) and the “DCM” (dichloromethane) technique (Bishop, 1994). These techniques have been applied to oils chosen to be representative of a high-wax oil (Uinta Basin with a total nC_{20+} alkane content of ca. 37%), being a solid at ambient conditions, and a low-wax oil (Prairie Gem field, Oklahoma, with a total nC_{20+} alkane content of 5%), being a liquid at ambient conditions (**Figure IV. 2. 19** and **Appendix IV. 2. 10**; **Figure IV. 2. 20** and **Appendix IV. 2. 10**). Additional sample, method information and reproducibility results of the techniques are discussed in Chapter II.

The purpose of the experiments discussed in this section is to evaluate the efficiency of n-alkanes recovery in wax precipitates obtained by both techniques for the Uinta Basin and Prairie Gem oils. Based on these results, acetone technique was chosen for further use in the study on waxes in produced oils from Prairie Gem field (Chapter IV. 4).

Quantitative HTGC analysis has been utilized previously to estimate the concentration of different groups hydrocarbons (n-alkanes, branched and cyclic alkanes,

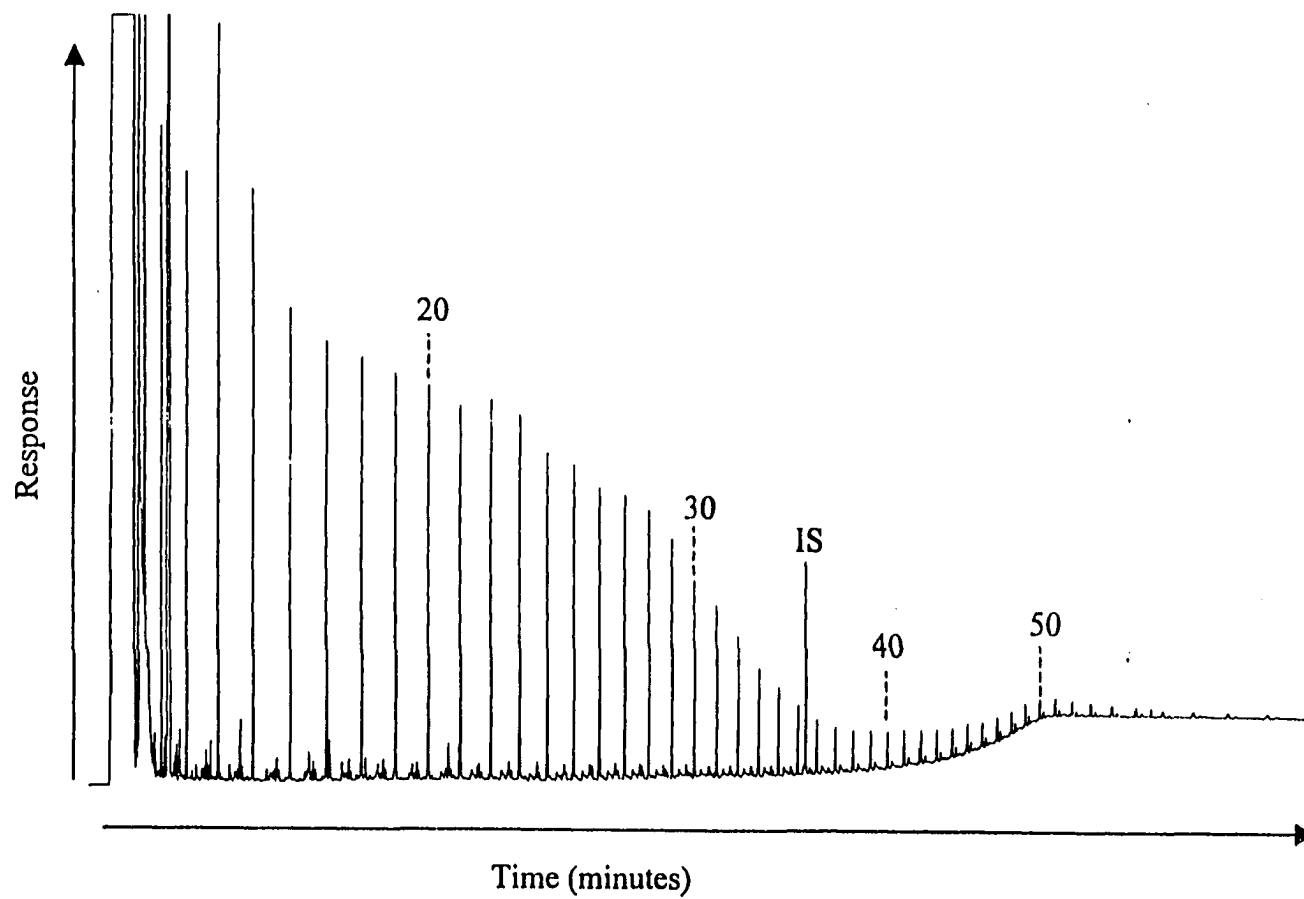


Figure IV. 2. 19. HTGC chromatogram of Uinta Basin high-wax whole oil. Numbers refer to carbon number of n-alkanes. IS-internal standard deuterated C_{36} alkane. HTGC 80-350°C @ 4°C/min.

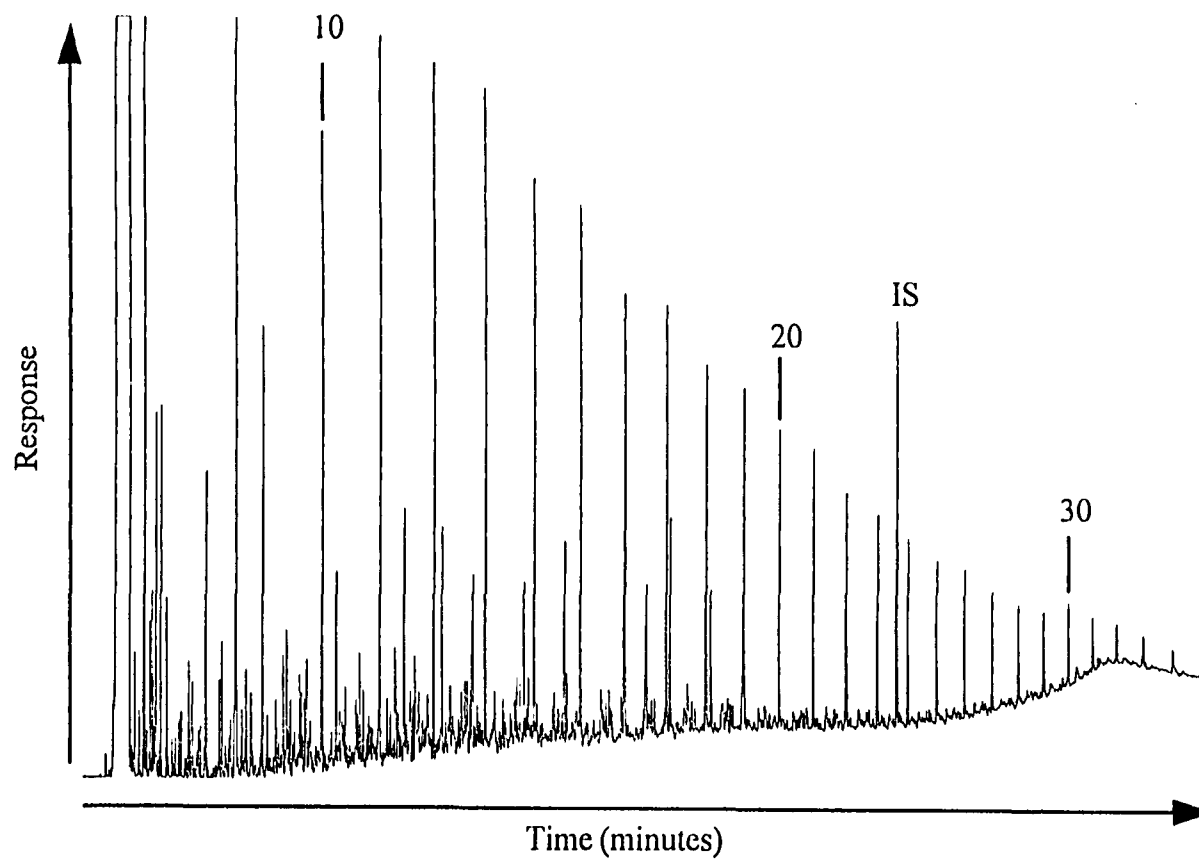


Figure IV. 2. 20. Gas chromatogram of Prairie Gem low-wax whole oil. Numbers refer to carbon number of n-alkanes. IS-internal standard, deuterated C_{24} alkane. GC 20-300°C @ 4°C/min.

aromatics) in synthetic and refined waxes (e.g., Barker, 1995). In the present study, HTGC is used to determine the concentration distributions of n-alkanes only, which are generally the major hydrocarbon components in petroleum waxes. A comparison of the n-alkane concentrations between the wax and non-wax fractions, and the initial oil sample, is used to perform mass balance calculations and evaluate the recovery efficiency of the techniques. The procedure for calculating solubility parameters of n-alkane mixtures with or without presence of polars (section IV. 2. 3. D) is applied to discuss the recovery efficiency results with regard to the solvents used for precipitation and dissolution of wax fractions by the two techniques.

Carbon number distributions of n-alkanes in wax and non-wax fractions

Uinta oil. The total wax yield obtained from the Uinta oil by the DCM technique (12.2% of the oil) is approximately five times lower than the yield obtained by the acetone technique (52.6% of the oil; **Table IV. 2. 13**). The composition of the precipitate from the DCM technique is characterized by a bimodal n-alkane distribution maximizing at about C_{32} - C_{34} and C_{43} , respectively (**Figure IV. 2. 21a**). The wax fraction obtained by the acetone technique is characterized by a unimodal distribution of the n-alkanes with a maximum in the carbon number range C_{20} - C_{35} (**Figure IV. 2. 21a**).

The carbon number range of n-alkanes in the non-wax fraction obtained by DCM technique is dominated by compounds up to C_{35} while the non-wax fraction obtained by acetone technique is characterized mainly by n-alkanes with carbon numbers up to C_{25} (**Figure IV. 2. 21b**). A comparison of n-alkane distributions in wax and non-wax fraction

Results	Uinta oil	Prairie Gem oil
(a) Precipitation		
acetone wax yield (% oil)	52.6	10.4
acetone non-wax yield (% oil)	39.0	69.2
total mass loss (% oil)	8.4	22.4
DCM wax yield (% oil)	12.2	0.2
DCM non-wax yield (% oil)	63.0	82.8
total mass loss (% oil)	24.8	17.0
(b) HTGC analysis		
Total amount of nC ₁₈₊ alkanes (% oil):		
in whole oil	36.8	4.9
acetone wax	23.0	0.8
DCM wax	6.7	0.1
acetone non-wax	9.5	3.2
DCM non-wax	19.6	4.4

Table IV. 2. 13. Summary of results on laboratory wax precipitation of high-wax Uinta oil and low-wax Prairie Gem oil by the acetone and DCM techniques. (a) precipitation results; (b) HTGC results.

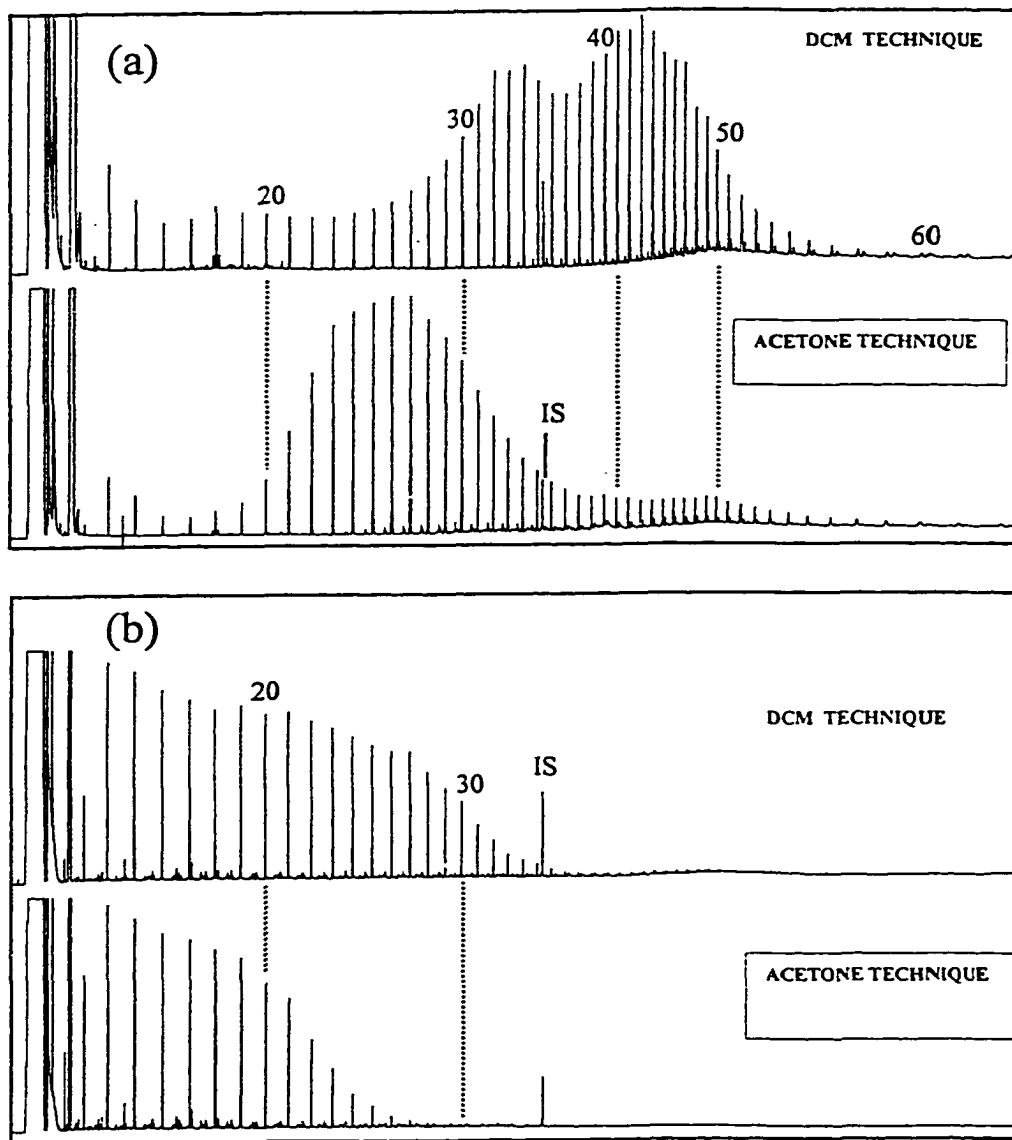


Figure IV. 2. 21. HTGC chromatograms of wax (a) and non-wax (b) fractions precipitated from Uinta oil by DCM and acetone techniques. Amount of internal standard in wax and non-wax fractions is 10.6 ng/ μ l and 11.4 ng/ μ l injected solution, respectively. HTGC 80-350°C @ 4°C/min.

demonstrates that DCM technique preferentially recovers the n-alkanes with more than 30-35 carbon atoms in the wax fraction while the acetone technique recovers a much broader carbon number range n-alkanes starting at approximately nC₂₂.

Prairie Gem oil. The wax fractions recovered from the Prairie Gem oil by both DCM and acetone techniques were characterized by bimodal distributions of n-alkanes, maximizing in the carbon number ranges C₃₀-C₃₁ and C₄₄-C₄₇ (**Figure IV. 2. 22**). The DCM wax precipitate showed a relative enhancement in the distribution of C₄₀-C₅₀ n-alkanes compared to the acetone wax precipitate (**Figure IV. 2. 22**).

Recovery efficiency of the techniques

Comparison of the results from quantitative HTGC analysis of the whole oil, acetone and DCM wax and non-wax fractions for the Uinta and Prairie Gem oils are presented in **Figure IV. 2. 23**, **Table IV. 2. 13** and **Appendix IV. 2. 10**. The results demonstrate significant variations in the concentrations of individual n-alkanes recovered from the same oil. The results suggest that the acetone technique has a much higher efficiency in separating n-alkanes in the wax fraction compared to the DCM technique for both Uinta and Prairie Gem oils. The maximum concentration of individual n-alkanes recovered in the DCM wax fraction from Uinta oil, which is in the C₃₅-C₅₃ carbon number region, does not exceed 30% of the initial concentration of compounds in the oil (calculated based on data in **Appendix IV. 2. 10**). More than 50-70% of the individual n-alkanes above nC₂₂- nC₂₄ present in the Uinta whole oil are recovered in the acetone wax fraction. With regard to the Prairie Gem oil, the maximum amount individual n-alkanes

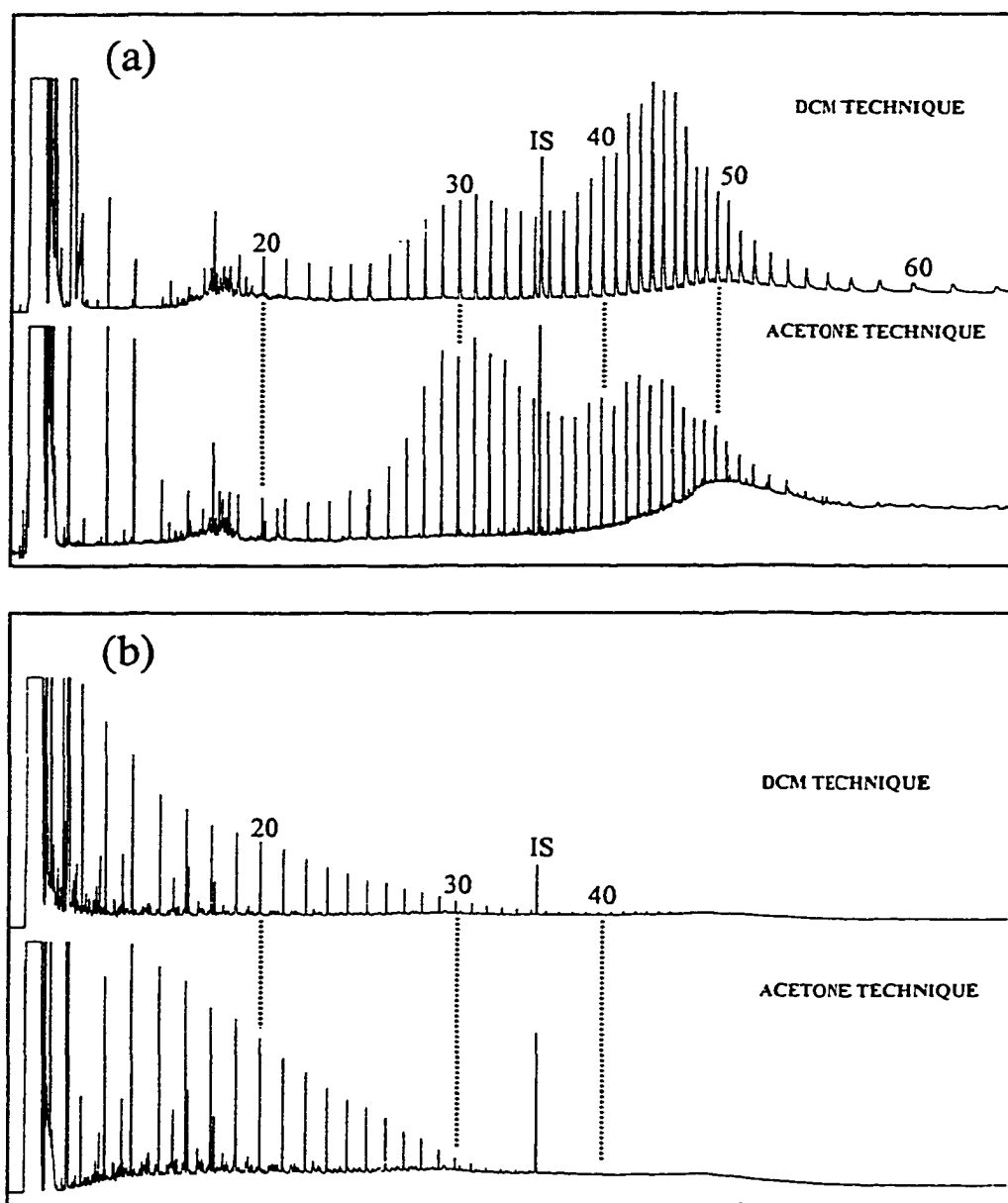


Figure IV. 2. 22. HTGC chromatograms of wax (a) and non-wax (b) fractions precipitated from Prairie Gem oil by DCM and acetone techniques. Amount of internal standard in both wax fractions is 10.6 ng/ μ l injected solution, 11.4 ng/ μ l in DCM non-wax and 19 ng/ μ l in acetone non-wax fractions. HTGC 80-350°C @ 4°C/min.

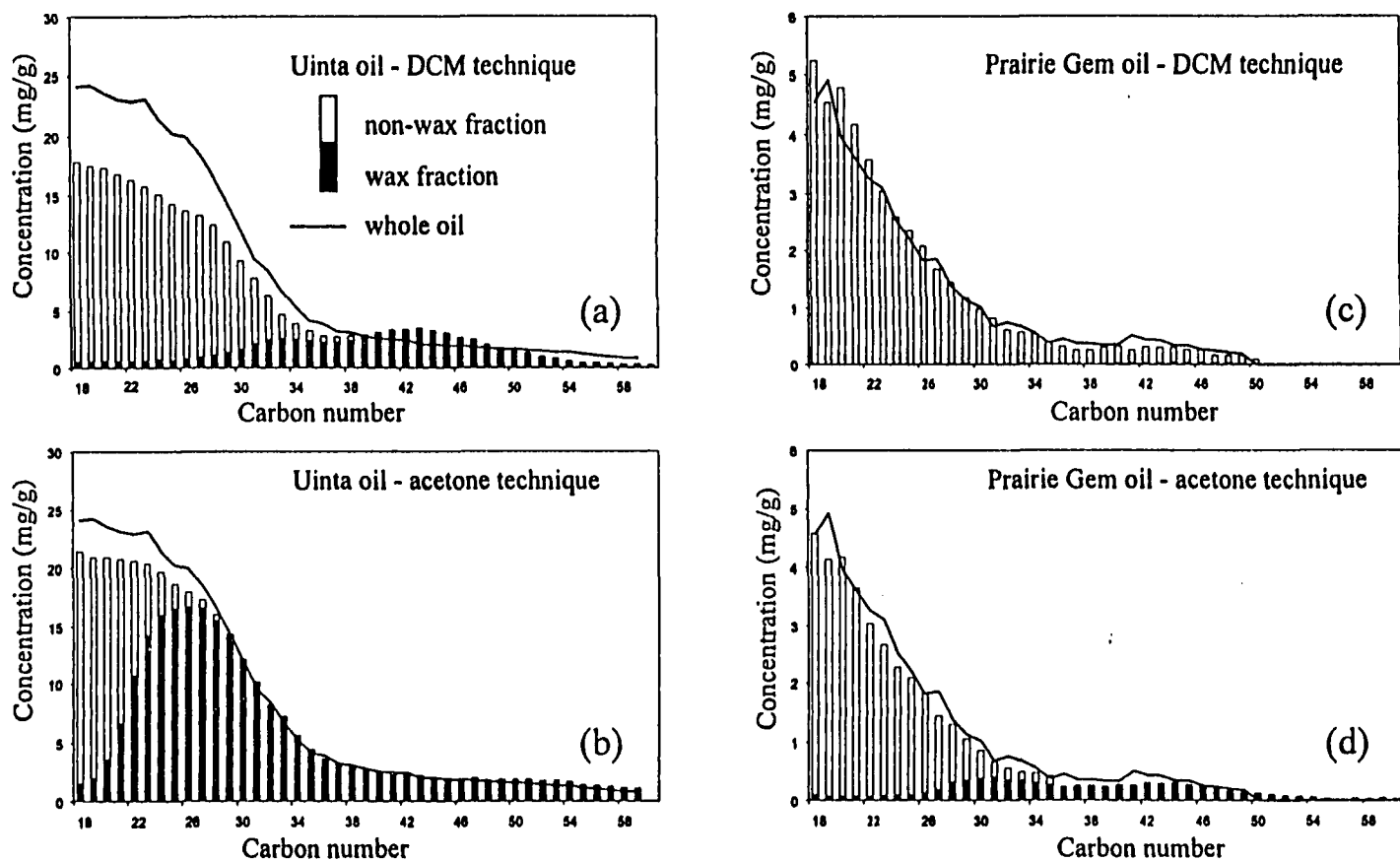


Figure IV. 2. 23. Carbon number distribution analysis of n-alkanes in whole oil, wax and non-wax fractions obtained by the acetone and DCM techniques for Uinta (a, b) and Prairie Gem (c, d) oils. Component concentrations in wax fractions (a, b) higher than in the whole oil could be attributed to the larger imprecision of quantitative HTGC analysis in the HMW region for the whole oil as discussed in Chapter IV. 1.

above nC_{32} recovered by the DCM technique is 9%, while the acetone technique recovers more than 50% of each of the individual n-alkanes in the same carbon number range in the wax fraction. The maximum losses of individual n-alkanes using the DCM technique varies in the ranges 30-95% and 30-50% for the Uinta and Prairie Gem oils, respectively, while the maximum losses associated with the acetone technique is in the range of 5-15% and 20-40%, for Uinta and Prairie Gem oils, respectively. Total mass losses of the DCM technique are 24.8% and 17% for the Uinta and Prairie Gem oils, respectively, while the total losses associated with the acetone technique are 8.4% and 22.4% for the Uinta and Prairie Gem oils, respectively (**Table IV. 2. 13**).

With regard to the acetone technique, a lower recovery efficiency is observed for the LMW n-alkanes for both the Uinta (C_{18} to C_{22}) and Prairie Gem (C_{18} to C_{27}) oils (**Figure IV. 2. 23, Appendix IV. 2. 10**). For Uinta oil, 50% to 80% of the $n-C_{18}$ to $n-C_{22}$ individual n-alkanes remain in the non-wax fraction, 6% to 46% are recovered in the wax fraction, and losses in this carbon number region are 10% to 13%. For Prairie Gem oil, 70% to 90% of the individual n-alkanes in the C_{18} - C_{27} region remain in the non-wax fraction, 2% to 50% are recovered in the wax fraction, and the losses are 8% to 30%, on a component by component basis (calculated based on data in **Appendix IV. 2. 10**).

In summary:

(1) The DCM technique preferentially recovers HMW n-alkanes above nC_{25} - C_{30} in the wax fraction although the recovery efficiency of n-alkanes in wax fractions by this technique is very poor for both oils.

(2) The acetone technique recovers much broader carbon number range of n-alkanes in the wax fraction (above nC_{18}), specifically for the high-wax oil, compared to the DCM technique. The recovery efficiency of the acetone technique in separating n-alkanes in the wax fraction is good. A decreased recovery efficiency is observed for the LMW n-alkanes, using this technique.

(3) The n-alkane recovery efficiency for the low-wax oil (Prairie Gem) by both techniques is much lower compared to the high-wax oil (Uinta Basin).

Discussion

One possible reason for the decreased recovery efficiency of the LMWHCs using the acetone technique may be related to the temperature conditions of the filtration step, which are not continuously controlled. Even though all the glassware, solvents and filters are cooled to -20°C before the filtration, and the filter kept cool by pouring chilled solvent during the filtration step, the actual temperature of filtration was probably higher than the desired filtration temperature (-20°C). Since the solubility of n-alkanes increases with decreasing carbon number and increasing temperature, it could be anticipated that at relatively elevated temperatures during the filtration step some of the LMW n-alkanes (particularly the lower melting point nC_{18} - nC_{22} alkanes) will be re-solubilized in the solvent and not trapped as solids at the filter.

The quantitative HTGC results demonstrate that the acetone technique has a decreased n-alkane recovery efficiency for a broader carbon number range in the case of the low wax Prairie Gem oil (nC_{18} - C_{27}) compared to the high wax Uinta oil (nC_{18} - C_{22}).

One possible reason for this is the insufficient degree of supersaturation of n-alkanes during the precipitation stage. Another possible reason could be the presence of relatively high amounts of compounds other than n-alkanes above C_{18} that could interfere with the n-alkane crystallization/precipitation and solubility.

The quantitative HTGC results demonstrate that total n-alkane content of the low-wax Prairie Gem oil (5% of the oil) is more than seven times lower compared to the high wax Uinta oil (37% of the oil). The maximum individual n-alkane concentration in Prairie Gem oil is five times lower compared to the Uinta oil (**Figure IV. 2. 23, Table IV. 2. 13**). Precipitation of wax components involves the formation of a supersaturated solution on cooling, hence the concentration of individual components in the original oil/solvent solution is an important factor for their complete precipitation and recovery. The acetone technique uses a blend of acetone with petroleum ether (3:1 v/v), where acetone is considered the main wax precipitating solvent and the petroleum ether is used to dissolve the “oil” (non-waxy components) and reduce the oil content in the wax precipitate (Nathan, 1955; Burger *et al.*, 1981). Solubility of a macrocrystalline type wax (nC_{18} - C_{30} alkanes) at 0°C has been reported as 0.018 g wax/100 ml acetone (Mozes, 1982). Based on quantitative HTGC results, it can be estimated that Prairie Gem oil contains 39.6 mg/g of nC_{18} - nC_{30} n-alkanes and the Uinta oil contains 276.3 mg/g of nC_{18} - nC_{30} alkanes. Thus, 5 g oil diluted in 110 ml acetone (acetone technique procedure **Table IV. 1. 10**) will correspond to a nC_{18} - C_{30} alkane concentration of 0.18 g per 100 ml acetone and 1.26 g per 100 ml acetone for the Prairie Gem and Uinta oils, respectively, or exceed ten and seventy times the concentration needed for a saturated solution. At the

lower temperature for precipitation (-20°C), even higher levels of supersaturation can be expected, and therefore the lack of supersaturation as a factor contributing to the low recovery efficiency of the acetone technique in the LMW n-alkane range could be ruled out.

Another possible reason for the decreased recovery of the n-alkanes by both the acetone and DCM techniques for the Prairie Gem oil could be related to the large percentage (95%) of other compounds as determined from the HTGC and HPLC analyses. These compounds could be hydrocarbons such as lower than nC_{18} alkanes, aromatics, branched-, iso- and cycloalkanes as well as non-hydrocarbons such as resins and asphaltenes, and they could be regarded as representing a complex composition solvent blend for the n-alkanes. Pedersen *et al.* (1991) reported for oils with a pronounced aromatic/naphthenic character that the acetone technique had a reduced efficiency but they could not provide an explanation for these observations.

HPLC and molecular sieving analyses of Prairie Gem oils demonstrates that the amounts of both branched/cyclic (25-30%) and aromatic fractions (16-20%) are higher than the amounts of n-alkanes (9-13%). The amounts of NSO and asphaltene fractions vary between 4-9% and 1-5% of the oil, respectively (**Table IV. 2. 14**). This overall composition corresponds to a mixed aromatic-naphthenic type oil. However, considering the large losses and the reproducibility results (section IV.1, **Tables IV. 1. 1** and **IV. 1. 3**), the average composition of the Prairie Gem oil at the beginning of the asphaltene isolation-HPLC procedures could be reconstructed to be approximately 14% n-alkanes, 44% branched/cyclic hydrocarbons, 18% aromatic hydrocarbons, 21% NSO (resin) and

Well/Fraction	SAT	B/C	ALK	ARO	NSO	ASPH	Loss
	% oil	% oil	% oil	% oil	%oil	% oil	% oil
Acree1-II	42.8	31.8	11.0	19.1	8.6	1.2	28.3
Green A2-II	37.5	24.1	13.4	18.3	4.7	2.5	37.0
Green A2-III	38.4	29.5	8.9	18.0	3.9	1.8	37.9
Ben Green-II	35.9	24.8	11.1	16.2	3.8	1.2	42.9
Ben Green-III	40.7	29.1	11.6	17.2	4.1	4.0	34.0
Mathews 3-II	38.6	26.5	12.1	19.1	5.1	5.0	32.2
N.Bales 2-II	35.9	25.8	10.1	19.3	5.1	4.3	35.4
Mean	38.5	27.4	11.2	18.2	5.0	2.9	35.4

Table IV. 2. 14. Results of HPLC, asphaltene precipitation (n-pentane) and molecular sieving analyses for oils produced at different wells in Prairie Gem field.

3% asphaltenes. Such a reconstructed composition of the Prairie Gem oil would classify it as a naphthenic type oil (e.g., Tissot and Welte, 1984; Speight, 1991). Different proportions of branched-, cyclic- and n-alkanes in the losses may change the evaluated oil type to be paraffinic-naphthenic (both paraffins and naphthenes less than 40% of the oil) or paraffinic (amount of paraffins higher than naphthenes and higher than 40% of the oil). It should be noted here that one possible reason for the difference in estimated total amount of n-alkanes by HPLC/molecular sieving analyses (at least 11% of the oil) and HTGC (5% of the oil) for Prairie Gem oil could be related to the solvent used for sample dilution in HTGC analysis. The comparison of the wax techniques was performed at the early stages of the work and the HTGC analysis was carried out using p-xylene as a solvent for sample dilution. The results developed later on the solubility of Polywax 1000 demonstrated that up to four times higher amount of n-alkanes could be recovered when using carbon tetrachloride or cyclohexane instead of p-xylene for sample dissolution in HTGC analysis of waxes (**Figure IV. 2. 13**, section IV. 2. 3. D). This type of reasoning may account to some extent also for the large losses associated with the recovery efficiency of DCM technique in case of the high-wax Uinta oil (**Figure IV. 2. 23a**).

In addition to the HPLC results, aromatics eluting in the region before nC_{20} on the HTGC chromatograms appear to be present in both the acetone and DCM wax precipitates of Prairie Gem oil (**Figure IV. 2. 20**). The presence of series of iso-, cycloalkanes and alkylaromatics is also evident on HTGC chromatograms of the wax precipitates from both Prairie Gem and Uinta samples, based on a comparison of the elution sequence with published studies (Carlson *et al.*, 1993). These hydrocarbons

appear as series of small peaks between the n-alkanes in carbon number region above nC_{30} , and their identification has been discussed in the recent studies of Hsieh (1999) and del Rio and Philp (1999). In the present study, further identification and/or quantitation of these compounds have not been performed. The occurrence of branched/cyclic alkanes and aromatic hydrocarbons in the wax precipitates suggests that they have co-precipitated with the n-alkanes, trapped on the filter, recovered by the solvents (toluene in the acetone technique and boiling cyclohexane in the DCM technique) and detected by HTGC as part of the wax fractions. This observation is in contrast with the results of Pan *et al.* (1996) for the composition of wax precipitates from a model synthetic oil consisting of n-alkanes, aromatics and iso-/cycloalkanes in the carbon number range C_5 - C_{45} , which concluded that the precipitated wax does not contain aromatics. If this model is correct, then the presence of aromatic hydrocarbons in wax precipitates from oils in the present study could be attributed to interactions between these compounds and the resins and asphaltenes, which were not included in the model oil of Pan *et al.* (1996). The influence of aromatic hydrocarbons and branched/cyclic alkanes on solubility/precipitation behavior of n-alkane mixtures can be related to the results of Handoo *et al.* (1989) and Srivastava *et al.* (1992). These studies demonstrated that increased amounts of both branched/cyclic alkanes and aromatic hydrocarbons interfere with the crystallization process of nC_{20} - nC_{28} alkane mixtures. The results discussed in section IV. 2. 3. D of the present work demonstrated that there are also differences in the solubility and crystallization behavior of the HMW n-alkanes in p-xylene and cyclohexane. Large amounts of branched/cyclic hydrocarbons acting as a solvent for the n-alkanes can lead

to lowering of the melting point or liquid-solid transition temperature of the precipitate (Srivastava *et al.*, 1995). In this case, relatively elevated temperature conditions for filtration combined with a lower melting point precipitate could result in larger amounts of the wax precipitate recovered as non-wax fraction and reduced efficiency of the techniques for the Prairie Gem oil. Another possibility is that large amounts of branched/cyclic and aromatic hydrocarbons can promote an incorporation of resinous and asphaltene material within the precipitate, resulting in the formation of a solid material with mixed nonpolar/polar properties. The presence of resins and asphaltenes in wax precipitates formed by the acetone technique has been experimentally identified in the recent study of Musser and Kilpatrick (1998).

The interactions between a mixed non-polar/polar wax precipitate and the solvents used for wax precipitation and recovery by DCM and acetone techniques are explored in a quantitative manner by applying the procedure for solubility parameter calculation of n-alkane/resin mixtures discussed in section IV. 2. 3. D. First, the solubility parameters of the n-alkane mixtures in whole oils, acetone and DCM wax precipitates were estimated for both Uinta and Prairie Gem samples. For the Uinta sample, the solubility parameters for the n-alkane mixtures present in the whole oil and acetone wax precipitate determined by HTGC are the same $16.9 \text{ (J/cm}^3)^{1/2}$, and a little higher, $17.0 \text{ (J/cm}^3)^{1/2}$, for the DCM wax precipitate, reflecting the higher molecular weight distribution of n-alkanes recovered in this wax fraction. For the Prairie Gem sample, the solubility parameters of the n-alkane mixtures in the oil, acetone and DCM wax precipitates were $16.8 \text{ (J/cm}^3)^{1/2}$, $17.0 \text{ (J/cm}^3)^{1/2}$, and $17.1 \text{ (J/cm}^3)^{1/2}$, respectively. Thus, the solubility parameter range of n-alkane mixtures present in oils and fractions for both Uinta and Prairie Gem samples is

rather narrow ($16.8\text{--}17.1 \text{ (J/cm}^3)^{1/2}$). Reference to **Figure IV. 2. 11** and **Table IV. 2. 15** suggests that cyclohexane is predicted to be a much better solvent than toluene. The results from the n-alkane recovery efficiency experiments using the DCM technique, which uses cyclohexane as a solvent for wax precipitate recovery, however, demonstrate a significantly lower n-alkane recovery compared to the acetone technique, which uses toluene as a recovery solvent for the precipitate. The contradiction between these results suggests again that the composition of wax precipitates includes compounds other than n-alkane. In order to explore what would be the influence of polar fractions present in the wax precipitates on the choice of the best solvents, the solubility parameters of an n-alkane mixture with different proportions of hydrocarbon resin were calculated. The n-alkane mixture was considered to have a solubility parameter of $16.9 \text{ (J/cm}^3)^{1/2}$. The results (**Table IV. 2. 16a**) suggest that the presence of more than 50% resin in the wax precipitate results in toluene being a better solvent for the n-alkane/resin mixtures than cyclohexane, consistent with the experimental results on the higher recovery efficiency for the acetone technique. The possibility of adsorption or even absorption between n-alkanes and resins/ asphaltenes during the crystallization process has been discussed in several studies (Becker, 1987; Musser and Kilpatrick, 1998), and suggests that the better solvents for solubilizing resins/asphaltenes could promote the recovery of the associated n-alkane crystals (**Table IV. 2. 16a**). Thus, it can be concluded that the most probable reason that the acetone technique gives a higher n-alkane recovery is that the precipitates represent a nonpolar/polar mixture and not only hydrocarbons. Therefore, toluene

Uinta acet wax, delta=16.9	$\bar{U}R$	Prairie Gem acet wax, delta=17.0	$\bar{U}R$
cyclohexane	0.3	cyclohexane	0.4
n-eicosane (mp 36-38 C)	0.6	n-eicosane (mp 36-38 C)	0.8
diisopropyl naphthalenes 1,4-and 2,6-isomers	0.7	diisopropyl naphthalenes 1,4-and 2,6-isomers	0.9
p-cymene (4-isopropyltoluene)	0.9	p-cymene (4-isopropyltoluene)	1.0
n-hexadecane (mp 18 C)	1.0	n-hexadecane (mp 18 C)	1.2
carbon tetrachloride	1.9	carbon tetrachloride	1.7
methylcyclohexane	2.1	triethylamine	1.9
triethylamine	2.1	decalin (mixture of cis and trans isomers)	2.1
n-decane	2.2	trans-decalin	2.1
n-nonane	2.2	mesitylene	2.1
Texasolve s-66 (mineral spirits)	2.2	methylcyclohexane	2.2
Texsolve s (mineral spirits)	2.2	ethyl benzene	2.3
decalin (mixture of cis and trans isomers)	2.3	n-decane	2.4
trans-decalin	2.3	n-nonane	2.4
mesitylene	2.3	Texasolve s-66 (mineral spirits)	2.4
ethyl benzene	2.4	Texsolve s (mineral spirits)	2.4
n-octane	2.6	n-octane	2.8
Texasolve s-lo (low aromatics/odor mineral spirits)	2.6	Texasolve s-lo (low aromatics/odor mineral spirits)	2.8
Texsolve c (commercial heptane)	3.1	toluene	3.2
heptane	3.2	Texsolve c (commercial heptane)	3.3
toluene	3.3	heptane	3.4
Texasolve h (hexane-heptane mixture)	3.5	benzene	3.4

Table IV. 2. 15. Radii of interaction ($\bar{U}R$) for n-alkane mixtures as determined by HTGC of acetone wax precipitates from the high-wax Uinta oil and the low-wax Prairie Gem oil with different solvents. Lower $\bar{U}R$ values suggest higher solubility. Based on this condition, cyclohexane is evaluated as the "best" solvent for the n-alkane mixtures in acetone wax precipitates from both Uinta and Prairie Gem oils.

(a)

n-alkane mixture ($\delta_{\text{total}} = \delta_d = 16.9 \text{ (J/cm}^3)^{1/2}$) with different proportions of hydrocarbon resin									
90:10		75:25		50:50		25:75		10:90	
solvent	ψ_R	solvent	ψ_R	solvent	ψ_R	solvent	ψ_R	solvent	ψ_R
solvents for wax recovery									
cyclohexane	0.5	cyclohexane	1.0	toluene	1.7	toluene	1.5	toluene	1.6
toluene	2.9	toluene	2.4	cyclohexane	1.9	cyclohexane	2.9	cyclohexane	3.5
solvents for wax precipitation									
DCM	8.9	DCM	8.3	DCM	7.5	DCM	6.7	DCM	6.2
acetone	12.6	acetone	12.2	acetone	11.6	acetone	11.1	acetone	10.8

(b)

HC resin 100%	ψ_R
p-xylene	0.5
o-xylene	0.7
toluene	1.8
furan	1.8
ethyl benzene	2.3
benzene	2.6
triethylamine	2.7
chloroform	2.9
carbon tetrachloride	3.3
mesitylene	3.3
decalin	3.9
cyclohexane	3.9
methylene chloride	5.9
tetrahydrofuran	6.5
quinoline	7.9
pyridine	8.4
methyl ethyl ketone	8.6
nitrobenzene	8.8
acetone	10.7

Table IV. 2. 16. Calculated radii of interaction (ψ_R) of (a) modeled n-alkane/resin mixtures with solvents used for precipitation and recovery of wax fractions by the acetone and DCM techniques; (b) pure hydrocarbon resin with selected list of solvents. The solubility condition is defined by $\psi_R < R$, where R is the radius of a solubility sphere of solute. For pure "HC resin", $R=10$.

(acetone technique, **Table II. 3**) which dissolves polars better than cyclohexane (DCM technique) results in a higher amount of n-alkanes recovered from the precipitate.

The solvents used for precipitation of waxes by the acetone (acetone) and DCM (methylene chloride) techniques can be evaluated on similar arguments. The radii of interaction (${}^i jR$) of a resin (100%) with a list of selected solvents are presented in **Table IV. 2. 16b**. If the radius of the solubility region of the solute (R) is known, then the solubility condition is determined by ${}^i jR < R$, or the precipitation condition would be determined by ${}^i jR > R$. A commonly recommended value for R of resins is 10 (Barton, 1991; Archer, 1996). Hence, methylene chloride, which has an ${}^i jR$ value (5.9) lower than R (10), will solubilize the resin while the acetone with ${}^i jR$ value (10.7) slightly higher than the boundary condition for R (10) is likely to precipitate it. Based on such discussion, one possible reason for the poor recovery efficiency observed for the DCM technique for both oils studied can be attributed to the lack of precipitation in methylene chloride for the n-alkanes associated with the resinous material.

Conclusions on the recovery efficiency of wax precipitation techniques

(1) The developed procedure for solubility evaluation of n-alkane mixtures with or without non-hydrocarbons (section IV. 2. 3. D), applied to the solvents used for wax precipitation and dissolution allowed several reasons for the observed differences in recovery efficiency of the techniques to be identified.

(i) Lack of precipitation of mixed n-alkane/resin (or in general nonpolar/polar) particles in DCM compared to acetone.

(ii) Lack of dissolution of mixed n-alkane/resin particles by cyclohexane (DCM technique) in contrast to toluene (acetone technique).

(2) The decreased recovery efficiency of both the acetone and DCM techniques for the low-wax Prairie Gem oil can be related to the naphthenic nature of the oil, and relatively large amounts of aromatic hydrocarbons and resins ($\approx 20\%$ each). Large proportions of branched/cyclic and aromatic hydrocarbons in the oil can act as solvents for the n-alkanes. A large amount of aromatic hydrocarbons is likely to promote solvent trapping and the co-precipitation of resins (and possibly asphaltenes). A large amount of branched/cyclic alkanes trapped with the wax precipitate will reduce the melting point of the precipitated mixture, and at elevated filtration temperatures will promote some portions of the precipitate to be redissolved by the solvents used for washing (methylene chloride and acetone/petroleum ether blend) and thus recovered in the non-wax fraction.

E3. A recommendation for using partial solubility parameters as first criteria in solvent order selection for laboratory studies on HMW petroleum fractions

Several examples were discussed in the present chapter that showed that the order of solvents with increasing solvency capacity for a particular solute could be predicted reasonably well using the partial solubility parameters proposed by Hansen (1967, 1969). Many experimental studies use sequential solvent extraction (or elution) schemes for petroleum fractionation. However the criteria for solvent selection are rarely discussed, and are usually based on previous experimental studies on the recovery of different fractions by a large number of tested solvents. The partial solubility parameters are

readily available for a significant number of solvents (e.g., Barton, 1991), and can be calculated for different solvent blends. These solvent (or solvent blend) characteristics can be used as initial criteria to select and develop different schemes for sequential solvent extraction and contribute to a more efficient experimental evaluation of different classes compounds, specifically for the heavy petroleum fractions.

Several examples of published experimental schemes in engineering and geochemistry studies for obtaining different petroleum fractions are presented in **Table IV. 2. 17**. The partial and total solubility parameters of these solvents or solvent blends have been calculated for the purposes of illustrating and discussing the information provided by these parameters and their usefulness as solvent selection criteria. The studies of McLean and Kilpatrick (1997) and Boduszynski (1988) present two examples of experimental schemes where, as shown by the calculated solubility parameters, the chosen solvents for sequential fractionation are arranged in order of systematically increasing total solubility parameter (**Table IV. 2. 17**). A good example of how partial solubility parameters can be used to obtain narrower solubility compound classes is provided by a comparison of the solvents used in the studies of Boduszynski (1988) and McLean and Kilpatrick (1997). A fraction that is soluble in DCM:MeOH (80:20) and is insoluble in toluene (**Table IV. 2. 17**, solvents used in Boduszynski, 1988) can be considered as defined to be within the total solubility parameter range of 18.2 to 21.4 $(\text{J}/\text{cm}^3)^{1/2}$ of the two solvents. The partial solubility parameters of these solvents, however, show that they define a rather broad range of polar, δ_p from 1.4 to 7.6 $(\text{J}/\text{cm}^3)^{1/2}$, and hydrogen bonding, δ_h from 2 to 9.4 $(\text{J}/\text{cm}^3)^{1/2}$, solubility parameters. For comparison,

Table IV. 2. 17. Examples of published experimental schemes for solubility petroleum fractionation and extraction. The solubility parameters of solvents and solvent blends are calculated for the purposes of the present study. δ_{total} , δ_d , δ_p , δ_h refer to the total and partial solubility parameters. * thermal treatment.

Solvent (solvent blend)	Recovered fraction (wt.%)			Calculated solubility parameters (this study)			
				δ_{total}	δ_d	δ_p	δ_h
McLean and Kilpatrick (1997)	Oil fractionation						
Heptane:Toluene (68:32)	saturates, aromatics (71-95)			16.2	16.2	0.5	0.6
Acetone:DCM:Toluene (40:30:30)	resins (3-19)			19.0	17.1	6.5	5.3
THF:Acetone (80:20)	asphaltenes (0.4-2)			19.4	16.5	6.6	7.8
Chlorobenzene @70 °C	polar asphaltenes 1 (0.4-3)			19.6	19.0	4.3	2.0
Pyridine	polar asphaltenes 2 (<0.05-0.6)			21.8	19.0	8.8	5.9
Boduszynski (1988)	Petroleum non-distillable residue						
n-pentane	n-pentane soluble			14.6	14.6	0.0	0.0
cyclohexane	C11x soluble/n-C5 insoluble			16.8	16.8	0.0	0.2
toluene	Tol soluble/C11x insoluble			18.2	18.0	1.4	2.0
DCM:MeOH (80:20)	DCM:MeOH soluble/ Tol insoluble			21.4	17.6	17.0	9.4
Wilhelms et al. (1996)	Crashed reservoir rocks						
	SAT	ARO	RES				
DCM *	55-70	12-26	10-32	20.3	18.2	6.4	6.2
Chloroform *	10-40	<7	52-87	18.9	17.8	3.1	5.7
THF:DCM:MeOH (50:47:3) *	<4	<7	91-99	20.0	17.4	6.2	7.6
Schwark et al. (1997)	Reservoir core cleaning						
DCM:MeOH (93:7)	"free" oil			20.6	18.0	6.8	7.3
THF:Acetone:MeOH (50:25:25)	"adsorbed" oil			21.4	16.1	8.5	11.3
Toluene	18% of adsorbed asphaltenes			18.2	18.0	1.4	2.0
Chloroform	40% of adsorbed asphaltenes			18.9	17.8	3.1	5.7
Tol:MeOH (70:30)	30% of adsorbed asphaltenes			19.5	17.1	4.7	8.1
Chloroform:Acetone (70:30)	73% of adsorbed asphaltenes			18.9	17.1	5.3	6.1
Chloroform:MeOH (70:30)	97% of adsorbed asphaltenes			20.9	17.0	5.9	10.7
Muller and Philp (1998)	Source rock extraction for HMWHIC						
	SAT	ARO	RES	ASPH			
DCM:MeOH (50:50)	30	12	25	33	23.9	16.7	9.4
p-xylene	29	18	21	32	17.9	17.6	1.0
p-xylene (sonication)	41	21	25	13	17.9	17.6	1.0

the study of McLean and Kilpatrick (1997) uses several solvents with polar and hydrogen bonding parameters within the 1.4 to 7.6 (J/cm³)^{1/2}, and 2 to 9.4 (J/cm³)^{1/2} ranges, respectively, and recovers several resin and asphaltene fractions. Several studies discussed by Schwark *et al.* (1997) are included in the table with the percentage of recovered asphaltenes from reservoir cores by using different solvents. The solubility parameters calculated for these solvents demonstrate that they are characterized with relatively constant and strong dispersion solubility parameter (δ_d), and with an increasing strength of both polar and hydrogen bonding solubility parameters (δ_p and δ_h), leading to a consequently higher recovery of adsorbed on the rock matrix asphaltenes from 18% to 97% (**Table IV. 2. 17**). On the other hand, when the sequence of solvents does not follow a systematic increase in total or partial solubility parameter, either the separated fractions are rather broad and/or a significant amount of similar compound classes appear in several solubility fractions (**Table IV. 2. 17**).

In summary, the usefulness of partial solubility parameters to provide quantitative evaluation about the solvent or solvent blend properties appears to be insufficiently exploited in the laboratory geochemistry studies, and therefore their application as initial criteria for solvent selection is recommended.

IV. 2. 4. CONCLUSIONS ON SOLUBILITY OF WAX DEPOSITS

- (1) Mixtures of n-alkanes with largely different molecular weight distributions have optimum solubility in different solvents. Laboratory and/or field treatment of such

mixtures with the same solvent (or solvent blend) would result in a significant variability of the amount of different n-alkanes dissolved and ultimately a decreased efficiency of the treatment method.

- (2) A procedure for the solubility parameter calculation of HMW dominated n-alkane mixtures, based on quantitative HTGC analysis and Method 3 for solubility parameter calculation for pure n-alkanes (Fedors, 1974), was found to give predictions closest to the experimental solubility results.
- (3) The application of this procedure to evaluate the solubility of wax deposits and petroleum waxes was demonstrated by several examples, and presents a way to model the solubility of wax deposits in cases of limited experimental compositional data for the non-hydrocarbon fractions that may be present in the waxes.

IV. 3. COMPOSITION OF WAX DEPOSITS

VS.

TEMPERATURE OF WAX DEPOSITION

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The main factors controlling petroleum wax deposition are temperature, pressure and oil composition (see section IV. 2. 1). The results discussed in this part of the study are mainly concerned with the effects of temperature on the composition of n-alkanes in wax deposits, whilst pressure and oil composition are kept constant. Samples obtained from wax deposition simulation experiments at different temperatures and field wax deposits formed at different depths from the same well (rod waxes) and a pipeline have been studied. Simulation experiments were performed using a cold finger apparatus (see Chapter II), which allows control over the temperature conditions of the cold surface where the wax deposition occurs. Similar experiments are commonly used to determine the cloud point of black oils (Kruka et al., 1995). In addition to determining the cloud point of the oil, the cold finger experiments were used to collect the deposited material, which was then analyzed by HTGC. The HTGC analysis was used to evaluate what type of changes, if any, occur in the n-alkane distributions of the wax deposits formed at different temperatures from the same oil. Since the cold finger laboratory experiments were performed at ambient pressure conditions using the same oil, the results could be

used to evaluate solely the effect of temperature on the distribution of n-alkanes in wax deposits.

The rod waxes used in this study were collected from a well producing oil from the Viola Formation in Oklahoma (Chapter II). Based on the information provided by Professor Curtis Whitson, who collected the samples, the well is only producing oil from the Viola Formation and the possibility of commingled oil production with other reservoirs is very low. A different set of wax deposit samples formed in the same pipeline were provided by Mobil and information about the gathering system, composition of oil(s) flowing through the pipeline, and exact locations of samples has not been released. Changes in the composition of wax deposits formed at different depths of the same well and pipeline would apparently relate to difference in temperature conditions. However, specifics in pumping rates, fluid dynamics and pressure induced changes in oil composition in well tubing and pipeline could be some of the other factors that may influence the composition of field wax deposits.

IV. 3. 1. LABORATORY SIMULATION OF WAX DEPOSITION

Laboratory simulation of wax deposition using a cold finger submerged in hot oil has been described in a number of studies (Hunt, 1962; Kolesnik et al., 1971; Bern et al., 1980; Woo et al., 1984; Weingarten and Euchner, 1986). Modification of the cold finger used in the present study is described in Kruka et al. (1995) and the analytical procedure discussed in Chapter II.

A five-gallon aliquot of the whole oil used in the cold finger experiments was subjected to a thermal pretreatment described in Chapter II, which involved shaking and heating at 80°C for 12 hours. The pretreatment procedure was carried out in order to homogenize the oil and dissolve as much wax as possible prior to dividing the initial five-gallon oil sample into 450 ml aliquots, which were used in the cold finger experiments. Prior to initiation of the cold finger experiments, wax and asphaltene precipitates were obtained from the whole oil by the acetone and n-pentane precipitation, respectively (Table IV. 3. 1). The HTGC chromatograms of the whole oil, wax and asphaltene fractions are shown in Figure IV. 3. 1. The n-alkane distribution observable in the whole oil extends to about nC₅₀, but the higher molecular weight components are hardly distinguishable on the chromatogram (Figure IV. 3. 1a). The quantitative HTGC results suggest a maximum individual n-alkane concentration of about 13 mg/g oil (Figure IV. 3. 2). However, the concentrations of LMW n-alkanes (e.g., up to nC₁₅-nC₂₀) are likely to be reduced as a result of the thermal pretreatment of the oil. The concentration of all the n-alkanes detected above nC₁₈ represents 7.7% of the oil, and according to the definitions used in the present study (section IV. 2. 2. C), this oil can be classified as low-wax oil (Appendix IV. 3. 1). The wax precipitate represents 12.2 wt.% of the oil (Table IV. 3. 1) and is characterized by an n-alkane distribution maximizing at nC₂₄-nC₂₆ (Figure IV. 3. 1b). The higher amount of wax precipitate (12.2 wt.% of the oil) compared to the total nC₁₈₊ alkanes (7.7 wt.% of the oil) is related to the fact that the wax precipitate does not represent a pure n-alkane mixture (see sections IV. 2. 3. D and IV. 2. 3. E). The total amount of nC₁₈₊ alkanes in the wax precipitate represents 26 wt.% of the wax precipitate

Asphaltene	Malltene	Loss
% oil	% oil	% oil
0.46	76.30	23.24
Acetone wax precipitate		
Wax	Non-wax	Loss
% oil	% oil	% oil
12.2	77.3	10.5

Table IV. 3. 1. Results of wax (acetone technique) and asphaltene (n-pentane) precipitation from the oil used in the cold finger experiments.

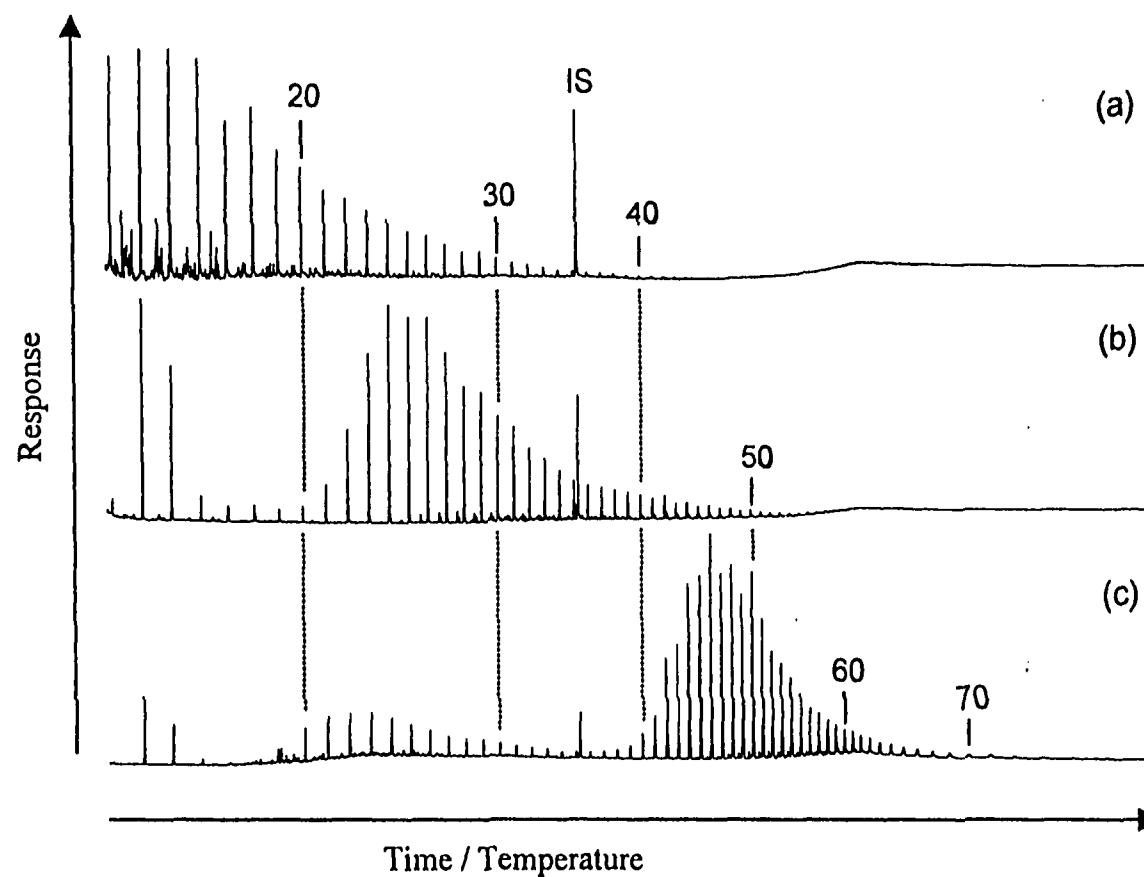


Figure IV. 3. 1. HTGC chromatograms of whole oil (a), acetone wax precipitate (b) and asphaltene n-pentane precipitate (c) of Gulf of Mexico oil used in cold finger experiments. Temperature program 40-400°C at 6°C/min. All samples dissolved in p-xylene and heated before injection.

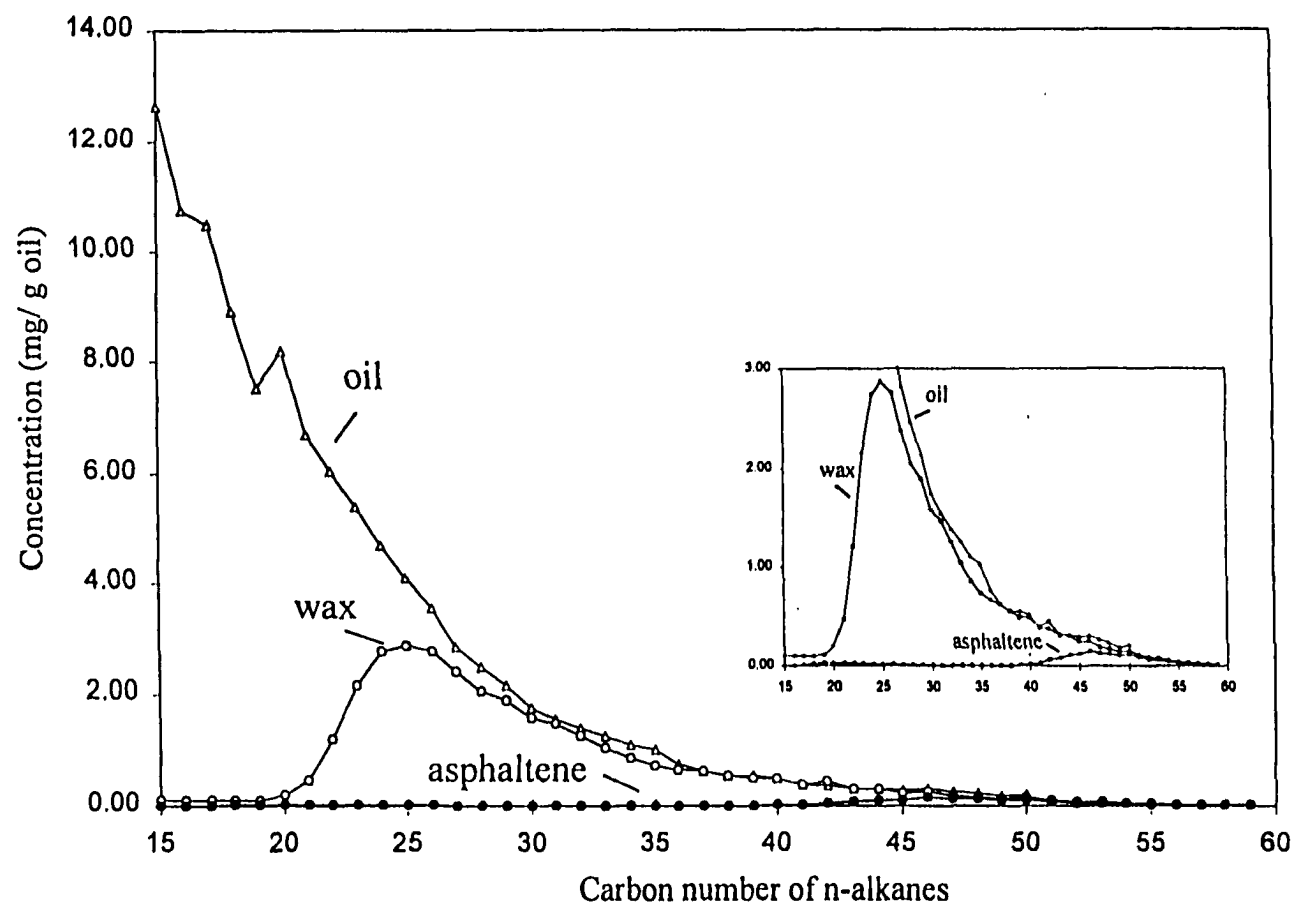


Figure IV. 3. 2. Quantitative HTGC results for n-alkane distributions recovered in acetone wax and asphaltene precipitates in comparison to the concentration of n-alkanes in the whole oil. The inset presents a portion of the diagram with an expanded vertical scale up to 3 mg/g oil.

and 3.1 wt.% of the oil (**Appendix IV. 3. 1**). The difference between nC_{18+} alkanes determined in the whole oil and wax precipitate could be attributed to the decreased recovery efficiency of the acetone technique as established in section IV. 2. 3. E2. Quantitative HTGC results suggest that the majority of HMW n-alkanes ($>C_{30}$) present in the oil are recovered in the wax precipitate, and represent 10 wt.% of total acetone wax precipitate or 1.2 wt.% of the oil (**Figure IV. 3. 2**). Thus, the wax fraction can be characterized as an intermediate type wax (section IV. 2. 2), consisting of macrocrystalline (nC_{20} - nC_{30}) and microcrystalline ($>nC_{35}$) type waxes in ratio 2.6:1. The HTGC chromatogram of the asphaltene demonstrates a significant abundance of HMW ($>C_{40}$) n-alkanes with a distribution maximizing in the range nC_{44} - nC_{50} (**Figure IV. 3. 1c**). Total asphaltene fraction represents 0.5 wt.% of the oil (**Table IV. 3. 1**). Total amount of n-alkanes above C_{18} in the asphaltene fraction represents 39 wt.%, and the total amount of n-alkanes above C_{35+} represents 32 wt.% of the asphaltenes (**Appendix IV. 3. 1**).

One purpose of the cold finger experiments was to determine the oil cloud point, which consists of locating two close temperatures where no wax deposit forms, and then where the first wax deposit forms. The cloud point is defined to be within this temperature interval. Cold finger experimental results with the oil used in this study are presented in **Table IV. 3. 2**. No wax was deposited at 54.4°C and the first visible wax deposit was observed to form at 51.7°C, and the cloud point of the oil was determined to be $53.1 \pm 1.4^\circ\text{C}$. The first significant wax deposit formation occurs at 40.5°C, which is more than ten degrees below the cloud point. The wax deposits formed between 51.7°C

Experiment #	Temperature		Toluene (wax)	MEK
	°F	°C	recovery mg	recovery mg
18	9	-13.0	23477.29	2186.94
14	40	4.4	3356.92	1685.78
13	60	15.6	3608.91	1170.26
12	80	26.7	2721.37	484.04
5	90	32.2	247.90	964.78
6	95	35.0	1301.00	589.30
15	100	37.8	340.68	487.00
7	105	40.5	203.60	475.40
11	110	43.3	73.22	336.14
8	115	46.1	279.00	363.30
16	120	48.9	53.88	119.76
9	125	51.7	68.20	446.40
17	130	54.4	no wax	136.03
10	135	57.2	no wax	-

Table IV. 3. 2. Results of cold finger experiments on wax deposition at different temperatures. The cloud point is determined to be at $53.1^{\circ}\text{C} \pm 1.4^{\circ}\text{C}$. The amount of wax deposits dissolved in methyl ethyl ketone (MEK) is considered to represent the majority of the oil trapped with the deposit.

and 43.3°C appeared as very tiny films of wax covering the cold finger, mixed with oil. The HTGC analysis of the wax deposits (toluene recovery as defined in Chapter II) complemented these observations and suggested that the waxes consist mainly of HMW ($>C_{40}$) n-alkanes with the trapped oil consisting of LMWHC (**Figure IV. 3. 3**). The cloud point was determined on thermally pre-treated oil, which may have reduced the concentration of lower molecular weight n-alkanes and may change the cloud point of the oil (Brownawell and Hollyday, 1962).

A plot of the amount of trapped oil (MEK recovery as defined in Chapter II) in wax deposits formed at different temperatures (**Figure IV. 3. 4, Table IV. 3. 2**) demonstrates a linear trend increasing with decreasing temperature. It should be noted that MEK does not remove all of the trapped oil, as evidenced by the distribution of LMW n-alkanes on HTGC chromatograms of the deposits, and may contribute to some variation in the amounts of trapped oil (**Figure IV. 3. 3**). A plot of the amount of wax (toluene recovery) deposited on the cold finger at different temperatures below the cloud point is presented in **Figure IV. 3. 5**. Based on these results, several stages of wax deposition can be distinguished to occur at different temperature intervals (**Figure IV. 3. 3, Table IV. 3. 2**). The deposits in the range 51.7°C to 37.8°C are characterized by small amounts of wax (53 mg to 73 mg), with large portions of trapped oil. A rapid increase (20 to 50 times) in amounts of wax deposits (1000 mg to 3600 mg) occurs in the temperature range 35°C to 4.4°C. And a further increase of more than ten times ($>24,000$ mg) wax deposit compared to the preceding temperature interval is observed at -13°C. The trend for the amounts of deposit at different temperatures shows similarities with the

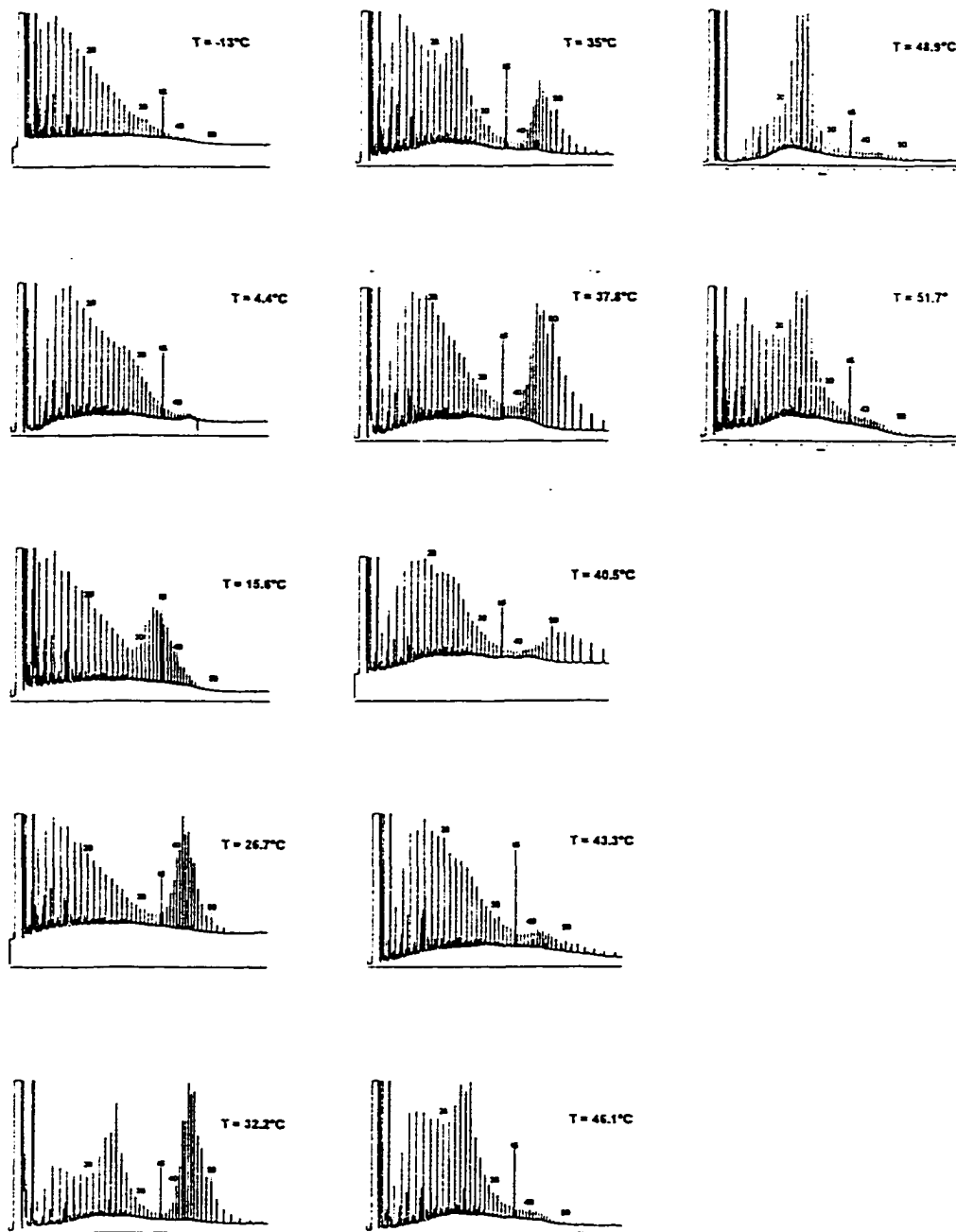


Figure IV. 3. 3. HTGC chromatograms of wax deposits (toluene recovery) formed at different temperatures of deposition by cold finger experiments.

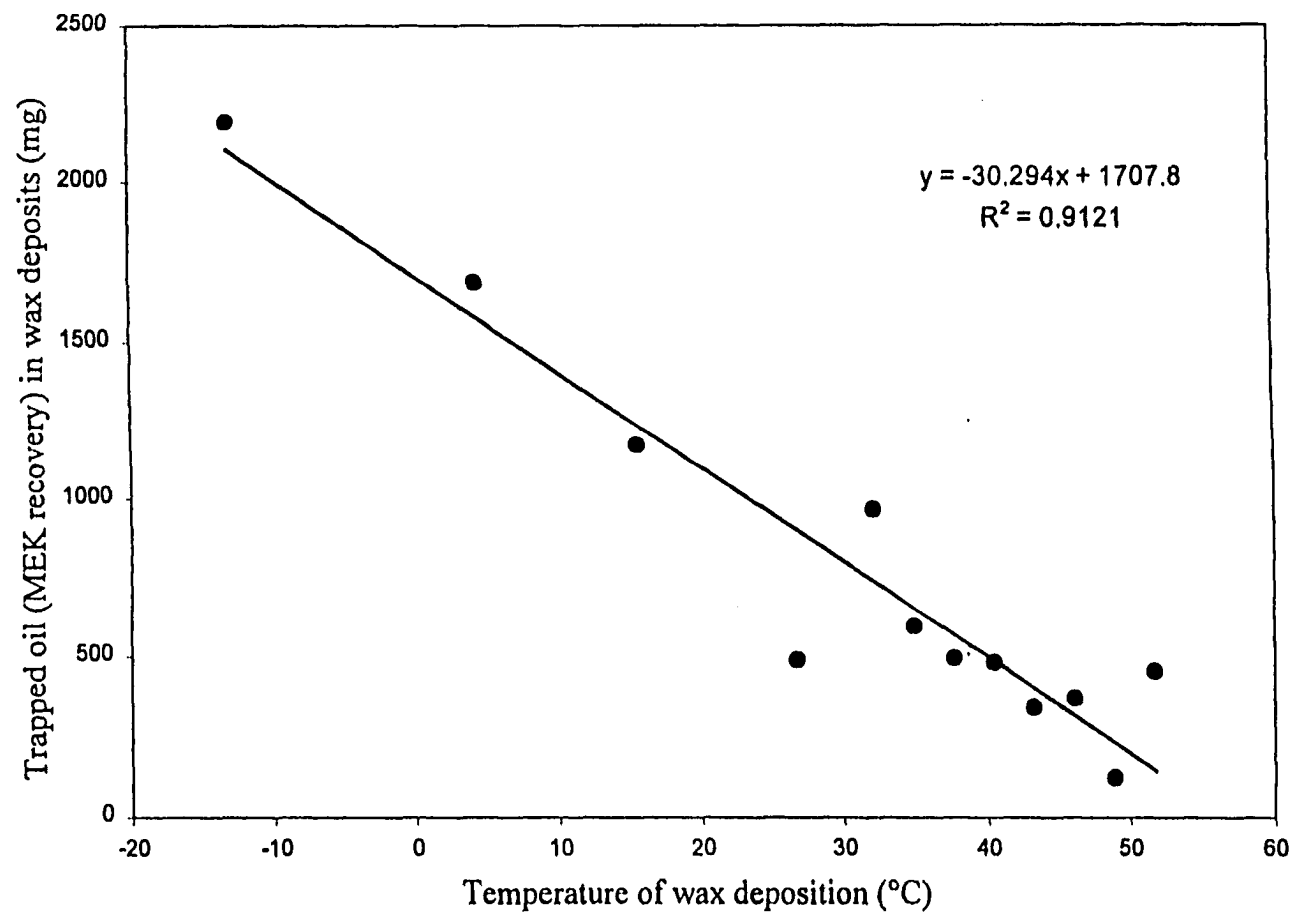


Figure IV. 3. 4. Amount of trapped oil recovered by methyl ethyl ketone (MEK) in wax deposits formed during the cold finger experiments at different temperatures of deposition.

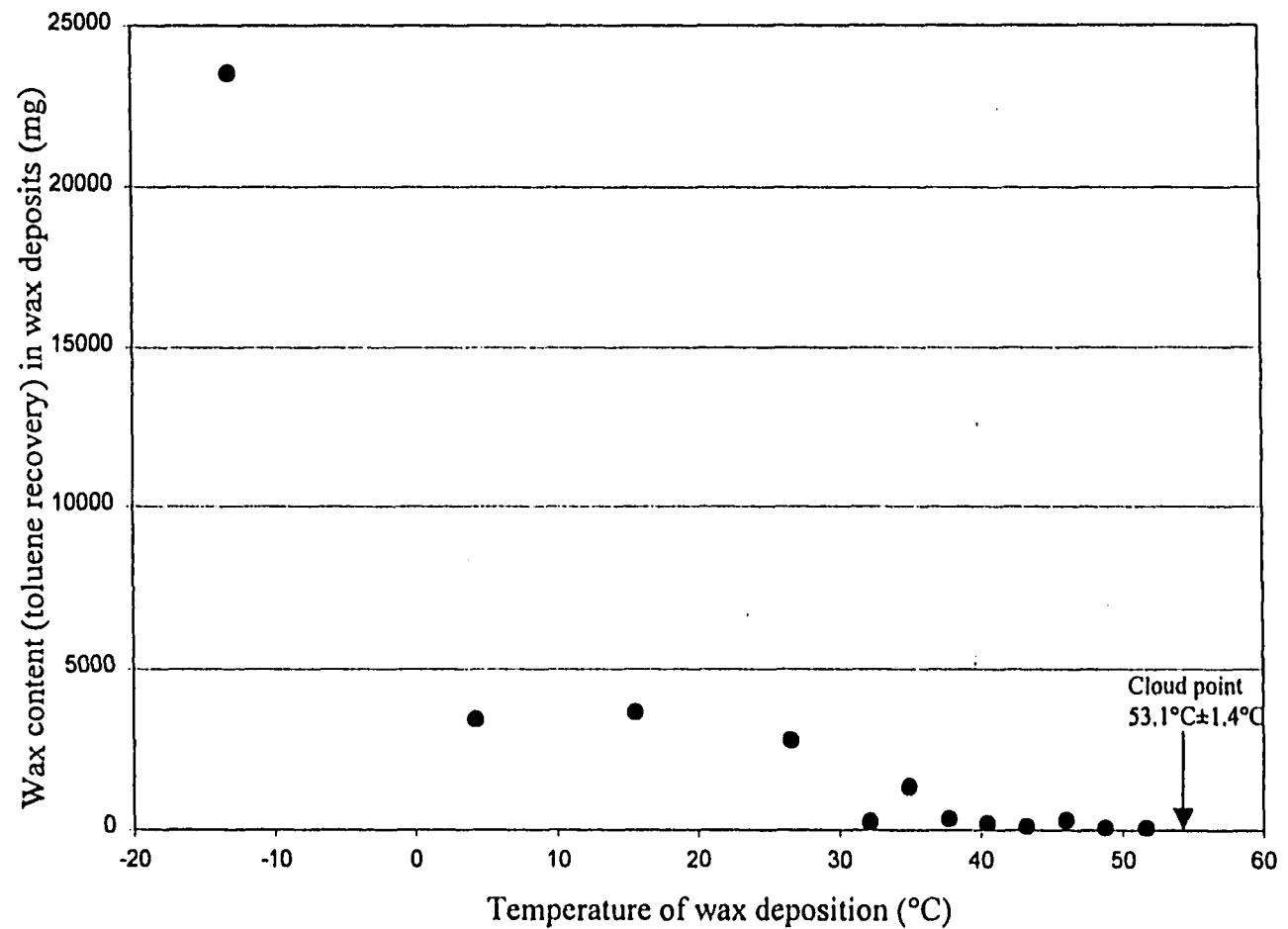


Figure IV. 3. 5. Amount of wax recovered by toluene in wax deposits formed during cold finger experiments at different temperatures of deposition.

nuclear magnetic resonance (NMR) results presented by Pedersen et al. (1991b) and cold finger measurements by Kolesnik et al. (1971). In both studies, an intermediate temperature interval exists, where the amount of deposited wax increased rapidly. The temperature range was 20°C to -15°C in the oils studied by Pedersen et al. (1991b) and 20°C to 5°C and 10°C to -5°C for the oils studied by Kolesnik et al. (1971). For the oil in the present study this range is at relatively high temperatures, extending from 35°C to 4.4°C. This interval can be regarded to correspond to a region of decreased solubility of the most abundant wax components in the oil (and therefore is oil specific). A comparison of the n-alkane distributions in the asphaltene and waxes deposited between 40.5-26.7°C show a similarity in the distribution of HMW n-alkanes, maximizing at nC₄₄-nC₅₀ (**Figures IV. 3. 1c** and **Figure IV. 3. 3**). The nC₃₅ n-alkanes can be regarded mainly as trapped oil and at lower temperatures (15.6°C and 4.4°C) there is a progressive contribution of LMW macrocrystalline type wax (**Figures IV. 3. 3** and **Figure IV. 3. 1b**).

The second increase in the amount of deposited wax was observed at the lowest temperature (-13°C; **Figure IV. 3. 5**) and can be related to solidification of the whole oil while approaching the glass transition temperature. The glass transition temperature is where the part of the oil matrix, which can not crystallize, transforms into a frozen solid (a glass), which drastically reduces molecular mobility and increases the oil viscosity (Hansen et al., 1991). At the end of the cold finger experiment (-13°C), the wax deposit was more than 2.0 inches thick and most of the oil had a high viscosity, suggesting glass transition temperature very close to -13°C for this oil.

Another purpose of the cold finger experiments was to study the composition of wax deposits formed at different temperatures using HTGC analysis (**Figure IV. 3. 3**). The chromatograms demonstrate a considerable increase in the HMW ($>nC_{30}$) n-alkane distributions in the temperature deposition range from 40.5°C to 15.6°C, corresponding to the beginning of the first temperature interval for a rapid wax deposit formation. Additionally, the maximum of the HMW n-alkane distributions in this temperature interval demonstrates a subsequent shift towards lower molecular weight n-alkanes at lower temperatures (**Figure IV. 3. 6**). For example, the maximum of n-alkane distribution at 37.8°C is at nC_{50} , and it shifts to nC_{42} at 26.7°C and nC_{33} at 15.6°C. Shifts in maximum of n-alkane distributions towards LMW components have been observed for petroleum distillate fractions of decreasing boiling range (Krishna *et al.*, 1989), for waxes precipitated from the same oil at decreasing temperatures of precipitation (Rønningsen *et al.*, 1991) as well as in a model n-alkane mixture consisting of nC_{18} - nC_{30} components in decane (Pauly *et al.*, 1998).

The results of quantitative HTGC analysis of wax deposits formed at different temperatures are presented in **Figure IV. 3. 7**. In order to correct for the presence of trapped oil in the deposits, a manipulation of the quantitative HTGC data was performed by presenting the wax components as a percentage of the total wax distribution. Thus, for the deposits formed at temperatures in the interval from 40.5 to 32.2°C, the wax components distribution was determined to begin at nC_{35} (**Figure IV. 3. 3** and **Figure IV. 3. 7**), and individual n-alkanes were presented as a percentage of the total sum of nC_{35+} components (**Figure IV. 3. 8**). For the wax deposits formed at 26.7°C, 15.6°C and

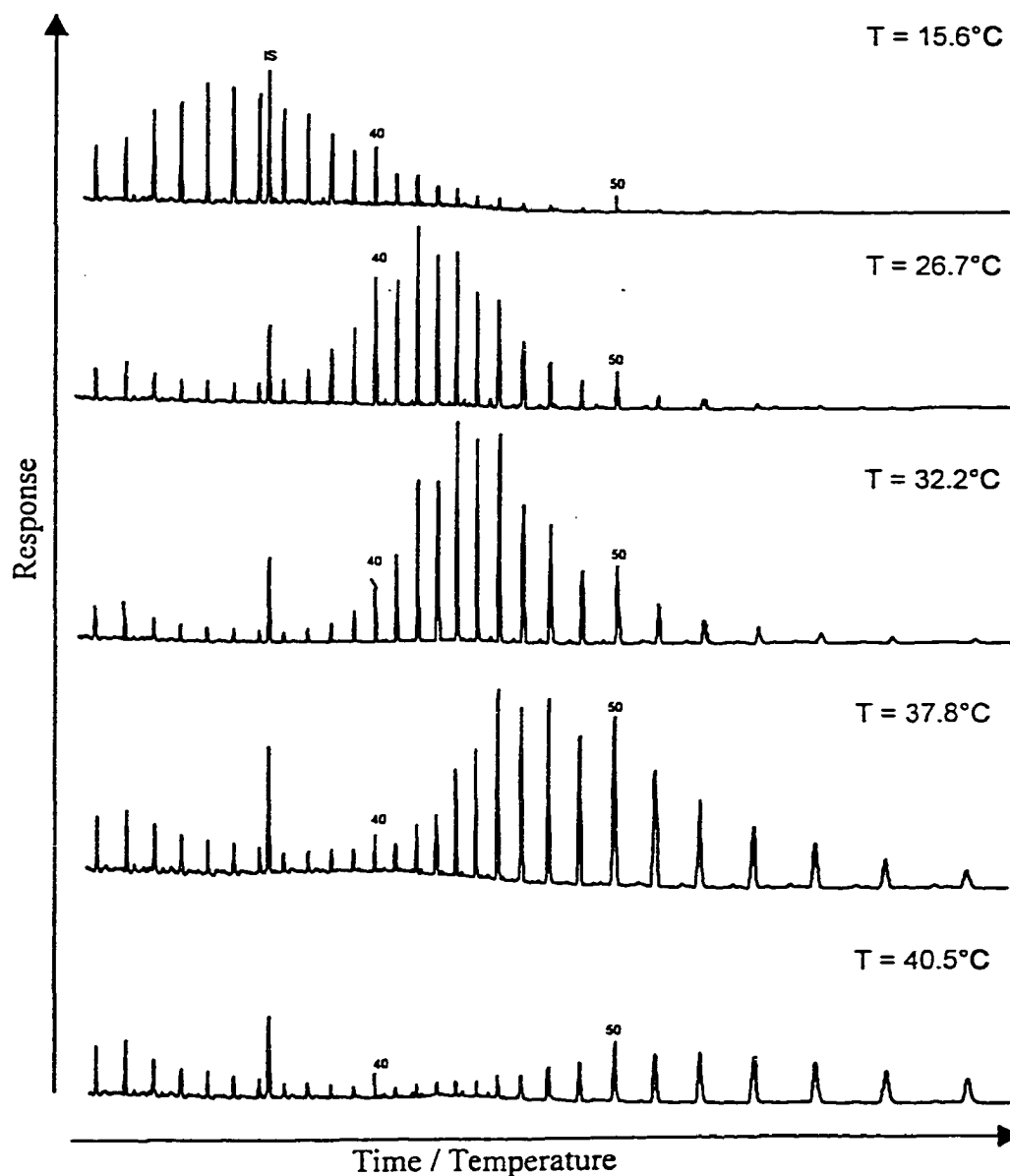


Figure IV. 3. 6. Partial HTGC chromatograms of wax deposits formed during cold finger experiments at different temperatures. Note the shift in maximum of n-alkane distribution towards lower carbon number components with decreasing temperature of deposition.

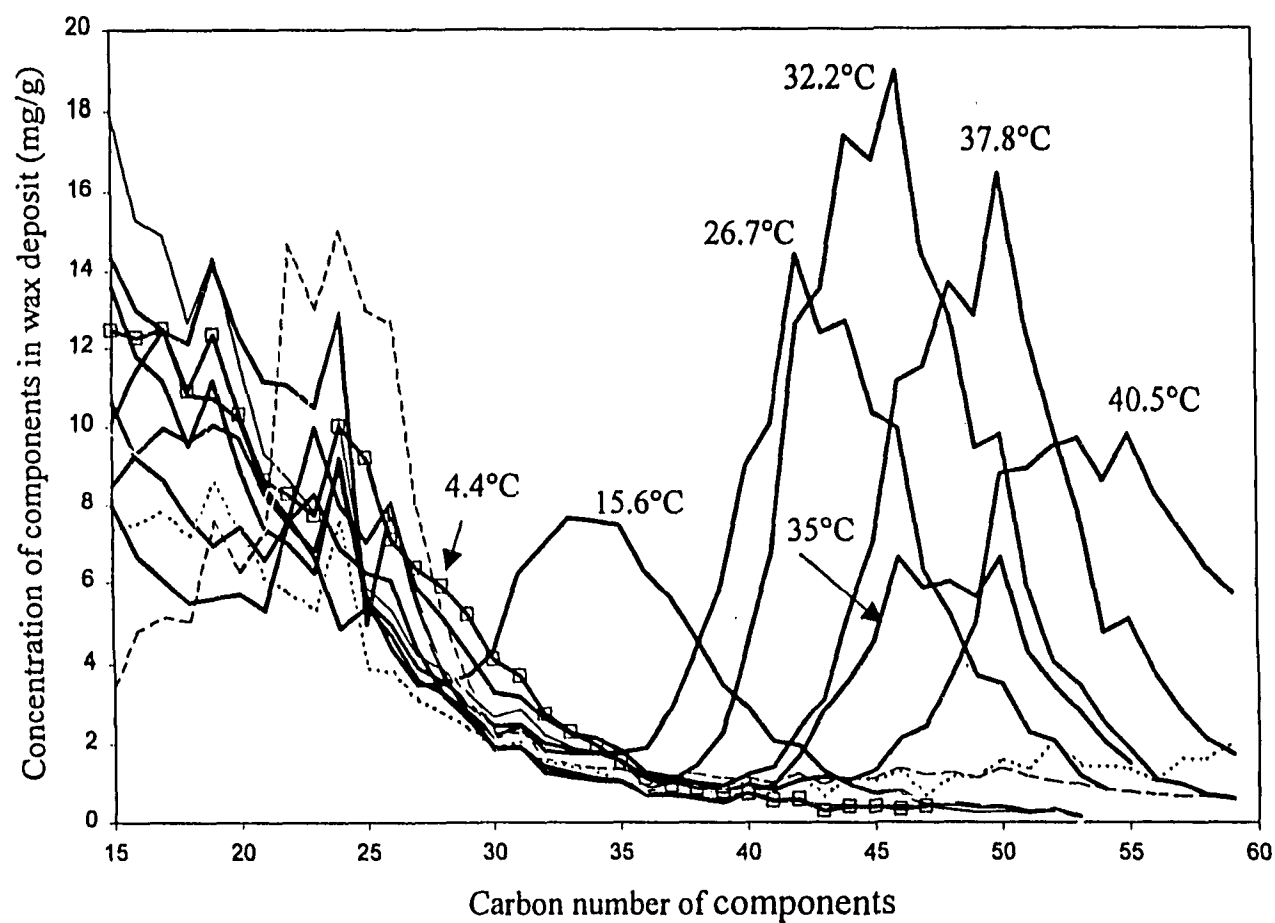


Figure IV. 3. 7. Quantitative HTGC results for n-alkane distributions in wax deposits formed during the cold finger experiments at different temperatures of deposition.

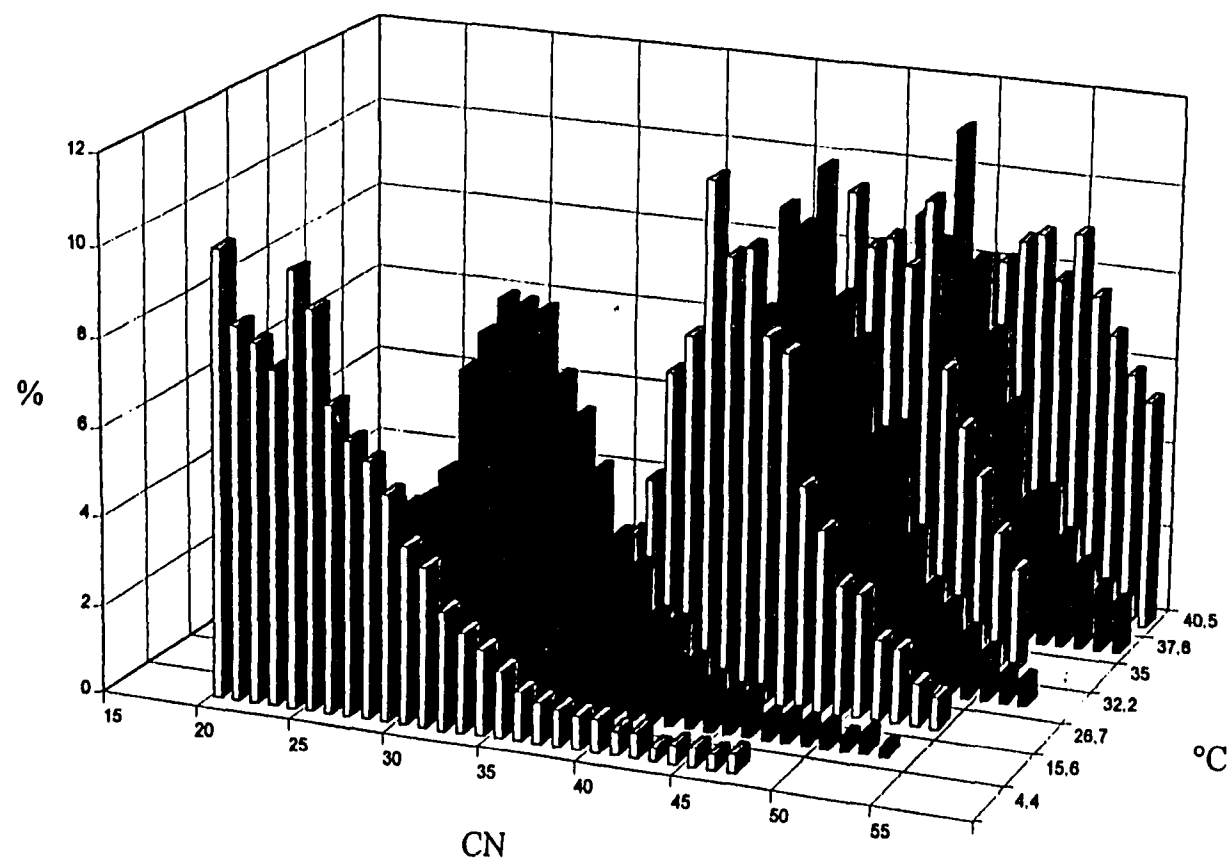


Figure IV. 3. 8. Carbon number (CN) distribution of n-alkanes in wax deposits formed at different temperatures during cold finger experiments. Concentration of n-alkanes is expressed as a percentage (wt/wt) of total nC_{20+} , nC_{27+} , nC_{33+} and nC_{35+} components in the deposits formed at 4.4°C, 15.6°C, 26.7°C and 32.2, 35, 37.8, 40.5°C, respectively, based on quantitative HTGC analysis results.

4.4°C, the wax component distribution was calculated as a percentage of the sum of all n-alkanes above nC_{33+} , nC_{27+} and nC_{20+} alkanes, respectively (**Figure IV. 3. 8**). These results illustrate the significant shift in the maxima of n-alkane distributions from nC_{35} to nC_{25} in wax deposits formed throughout the temperature interval 40.5 to 4.4°C, respectively. In addition, at the higher temperatures (40.5°C to 26.7°C) the deposits are characterized by a narrow carbon number range distribution (ca. 20 carbon numbers from nC_{60} to nC_{42}) compared to those at lower temperatures (15.6°C and 4.4°C), which cover at least 30-40 carbon numbers (**Figure IV. 3. 7** and **Figure IV. 3. 8**).

The results described above suggest that wax deposits formed under the higher temperatures of a reservoir, well equipment and/or pipeline, will be dominated by HMWHCs, and at lower temperatures the compositions will change towards distributions dominated by more of the lower molecular weight components. These distributions can be related to variations in melting points and solubilities of the HMW hydrocarbons. In offshore pipelines, for example, the composition of wax deposits should change from a broad carbon number n-alkane distribution (both LMW and HMW ranges) in the cooler offshore part of the pipeline to a narrow, predominantly HMW n-alkane distribution in the onshore part of the pipeline, located at relatively higher temperatures. The narrow, HMW dominated n-alkane solid mixtures are much more stable and less soluble compared to the broad carbon number range n-alkane mixtures (section IV. 2. 3. C). Chemical remediation of such a profile of wax deposits using one solvent or solvent blend is not likely to efficiently dissolve the waxes deposited at different temperatures. In the case of wax deposits formed in producing oil well tubings at moderate climates where

the lower temperatures will be determined by surface temperature conditions (e.g., 15–20°C), the results suggest that wax deposits will be dominated mainly by HMW n-alkane distributions. The profile of wax deposits from the reservoir to the surface should still show a variability in composition and shifts towards relatively LMW components at lower temperatures, but the whole range of n-alkanes in the wax deposits is likely to be in the HMW range (above nC_{35}). Wax deposits such as these would require treatment with solvents like cyclohexane and carbon tetrachloride (see results in section IV. 2. 3. C). The type of oil (paraffinic, naphthenic, aromatic) and relative proportions of non-hydrocarbons (resins and asphaltenes) in the deposits could require further modifications to the solvent choice for most efficient treatment.

Recognition that wax deposits vary in their composition with respect to n-alkanes as a function of temperature is particularly important for the development of thermodynamic models with better predictive capabilities. Many currently available models (Won *et al.*, 1986; Hansen *et al.*, 1988; Pedersen *et al.*, 1991b; Ungerer *et al.*, 1995), directed to predict the phase behavior of reservoir fluids, are based on the assumption that all wax components (heavier and lighter) precipitate at the cloud point temperature (Pauly *et al.*, 1998). Considering the experimental results in the present study, such an assumption would, for example, model a wax deposit with the composition formed at 4.4°C to be considered as formed at 51.7°C (**Figure IV. 3. 3**). In addition, it is not well understood from a geochemical point of view how the other classes hydrocarbon and non-hydrocarbon compounds that comprise the wax deposits behave as a function of temperature. Apparently, a detailed compositional characterization of different classes

compounds in wax deposits and oils and their close integration with modeling is necessary in order to improve the predictions for wax deposition occurring in production equipment and reservoirs.

IV. 3. 2. FIELD WAX DEPOSITS – ROD WAXES AND PIPELINE WAXES

Wax deposits from the rods of producing oil well, and collected at two different depths were analyzed by HTGC (**Figure IV. 3. 9a**), and demonstrate that the deposit formed at the shallower depth is characterized by an n-alkane distribution maximizing at nC₃₅. The deposit formed at the deeper part of the well tubing shows an n-alkane distribution maximizing at nC₅₁. The n-alkane distributions in both samples are relatively narrow, encompassing approximately 23 and 26 carbon number ranges of n-alkanes for the shallower and deeper samples, respectively (**Figure IV. 3. 9b**, **Appendix IV. 3. 2**). The significant shift (16 carbon number n-alkanes) in n-alkane distributions in the rod waxes is consistent with the changes in the composition of the wax deposits using the cold finger apparatus. The consistency of these results suggests temperature to be a main factor controlling wax deposition in the well tubing. In addition, the consistency of these results suggests that the compositional information revealed by a geochemical study of wax deposits could be used to predict the relative temperature of wax deposition

Another example of wax deposition (**Figure IV. 3. 10**) is based on wax deposits formed at two different locations of the same pipeline (section IV. 2. 3. D) provided by Mobil without prior knowledge of the relative sample location with respect to

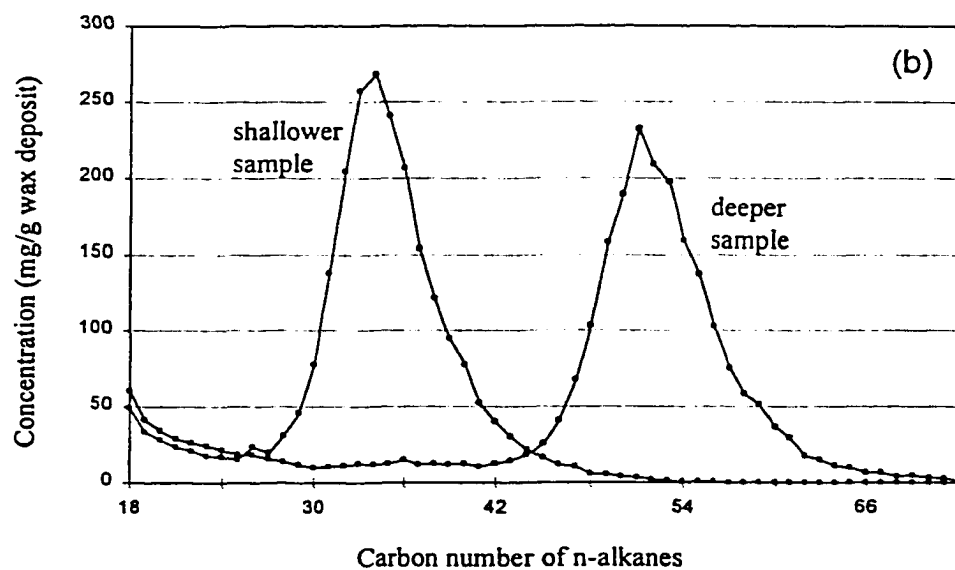
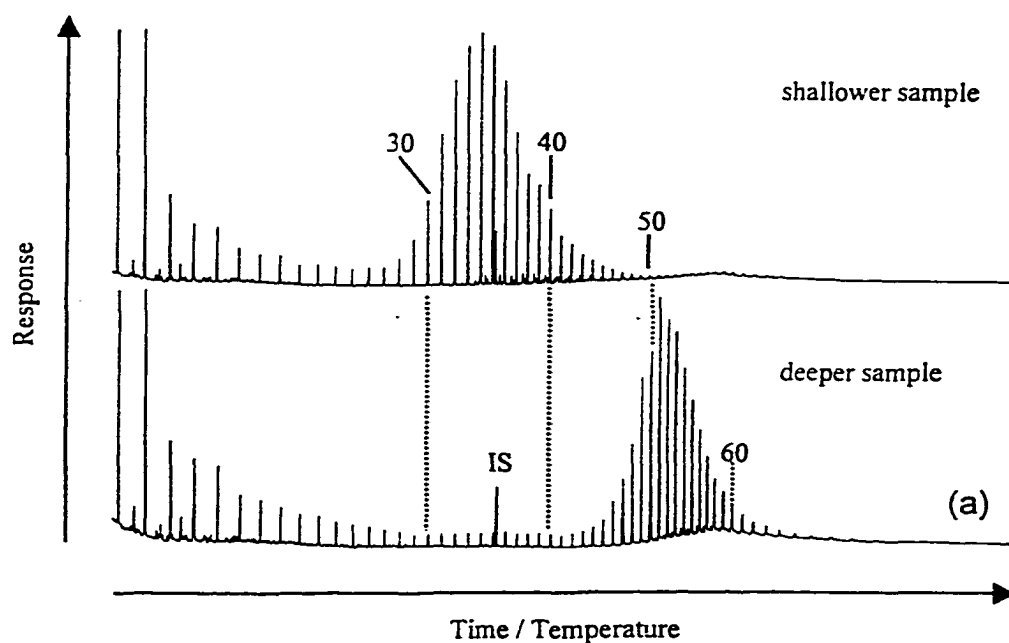


Figure IV. 3. 9. HTGC chromatograms (a) and quantitative HTGC results (b) for two rod wax deposit samples collected at different depths from Viola Formation oil producing well in Oklahoma. Note the significant shift in carbon number distribution towards higher molecular weight n-alkanes in the deeper sample. Samples dissolved in p-xylene and heated before injection.

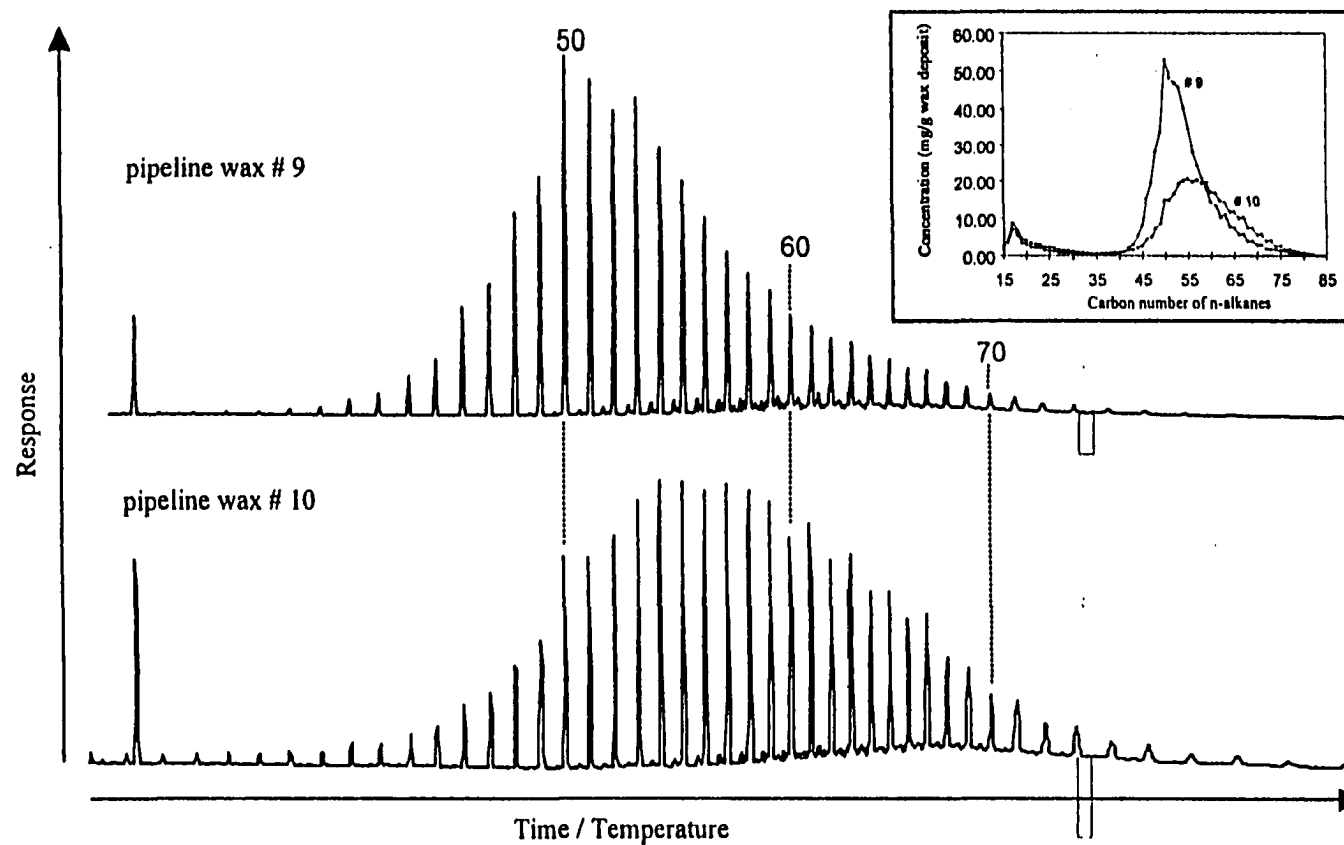


Figure IV. 3. 10. HTGC chromatograms of wax deposits formed in the same pipeline at two different locations. The inset presents the results of quantitative HTGC analysis of the samples. Temperature program 60-400 at 6°C/min. Samples dissolved in carbon tetrachloride and heated before injection.

temperature of deposition. An attempt was made to predict the relative temperature of deposition of each sample relative to the other, based solely on the geochemical interpretation of HTGC analysis of these samples. The chromatograms of the samples did not show a drastic shift in n-alkane distributions as was previously observed for the rod wax deposits. A slight shift, however, in the maximum of n-alkane distribution towards HMW components was observed to occur from wax deposit # 9 (nC_{50}) to wax deposit # 10 (nC_{54} - nC_{57}). Quantitative HTGC results further demonstrated that the HMW n-alkane concentration in wax # 9 is more than twice that for wax # 10, and as discussed in section IV.2.3.D, it may contain higher proportions of non-hydrocarbons that are not detected by HTGC. These characteristics suggested that sample # 10 was likely to have been deposited at a higher temperature than sample # 9, later confirmed by Mobil as correct.

IV. 3. 3. CONCLUSIONS

(1) Cold finger experiments demonstrated two temperature regions of rapid increase in the amount of wax deposit that could be regarded as being determined by processes of a different nature. The first interval of a rapid deposit growth (35°C to 4.4°C) could be related to subsequent crystallization of the most abundant HMW and LMW n-alkanes, respectively, in the oil, and therefore this temperature interval will be oil specific. The second interval (-13°C and possibly lower) relates to solidification of the oil matrix in approaching the glass transition temperature, it is not influenced by the wax content of

the oil and correlates with the concentration of lighter components in the oil matrix (Hansen et al., 1991).

(2) The n-alkane composition of wax deposits changes with the temperature (depth) of deposition as demonstrated by both laboratory and field formed wax deposits. At higher temperatures of deposition, the n-alkane distribution in wax deposits is dominated by components with a higher molecular weight compared to wax deposits formed at lower temperatures. Thus, the n-alkane composition of wax deposits formed within the same production tubing/pipeline is not constant but increases in molecular weight with the increase in temperature, and the proportions of hydrocarbon/non-hydrocarbons in formed deposits may change.

(3) The results presented in this study demonstrated that compositional characterization of wax deposits by geochemical methods can predict correctly the relative temperature conditions of wax deposition. Further integration of detailed geochemical characterization of different classes compounds in oils and wax deposits formed at different temperatures with thermodynamic modeling is very important for development of better predictive models of wax deposition, its prevention and remediation.

IV. 4. PRODUCTION GEOCHEMISTRY STUDY

IN PRAIRIE GEM FIELD, OKLAHOMA

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IV. 4. 1. INTRODUCTION

Reservoirs, production equipment and transportation facilities, including pipelines are the main areas where wax deposition can cause problems to petroleum production. The results discussed in Chapter IV. 3 presented several examples of wax deposition occurring in oil pipelines and well tubing. The results discussed in this part of the study relate to the deposition of waxes and asphaltenes in reservoirs, their mobilization under varying reservoir pressure and temperature conditions during production, and deposition in well tubing. The study was performed on oils produced from Bartlesville reservoir in the Prairie Gem field, Lincoln Co., Oklahoma, during a period corresponding to the transition from primary to secondary recovery by water flooding. The main purpose of the study was to monitor the wax and asphaltene content and composition in oils produced from the same well (Paschall 2) for a period of about three years, and to compare variations in the oil composition with the sequence of production events (**Figure**

IV. 4. 1 and Figure IV. 4. 2). The main production events during the period of oil sample collection from Paschall 2 well included an increase in oil production as a response of the well to water flooding and a wax deposition problem in well tubing that was subsequently treated with injection of hot oil and additives. Wax and asphaltene fractions were isolated using the acetone precipitation technique and n-pentane method, respectively, as described in Chapter II.

Only in recent years has attention been given towards testing the possible effects of production on oil composition by comparing samples collected over a significant period of time (Whelan et al., 1994; Holba et al., 1996; Hwang and Ortiz, 1997; Korneva et al., 1997). For example, significant changes in wax, resin and asphaltene contents of oils collected over a twenty year period of primary production were reported by Korneva et al. (1997). In terms of secondary recovery operations, Hwang and Ortiz (1997) recently reported results on changes in oil composition during enhanced oil recovery by CO₂ flooding based on oil samples collected at three different times before and after the start of CO₂ injection. Asphaltene and wax contents in produced oils after the initiation of CO₂ injection were found to decrease and the laboratory experiments confirmed the decrease to be induced by the CO₂ flood.

IV. 4. 2. PRAIRIE GEM FIELD PRODUCTION SUMMARY

The geologic setting of Prairie Gem field was discussed in Chapter III. The field is located on the Northeastern Oklahoma (Cherokee) Platform with the main oil

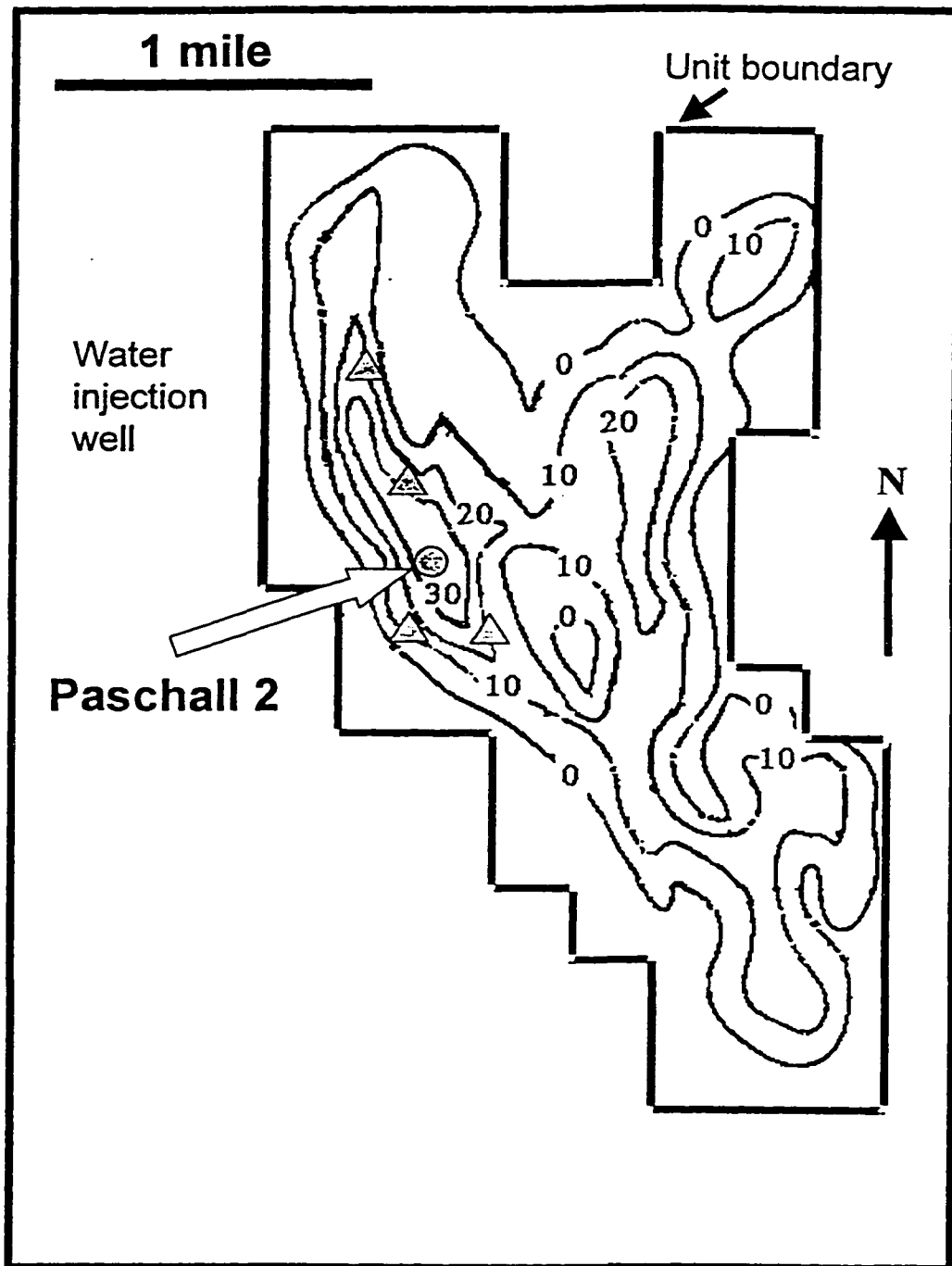


Figure IV. 4. 1. Net isopach map of Bartlesville sand in Prairie Gem field. Locations of monitored well Paschall 2 and water injection wells are shown with a circle and triangles.

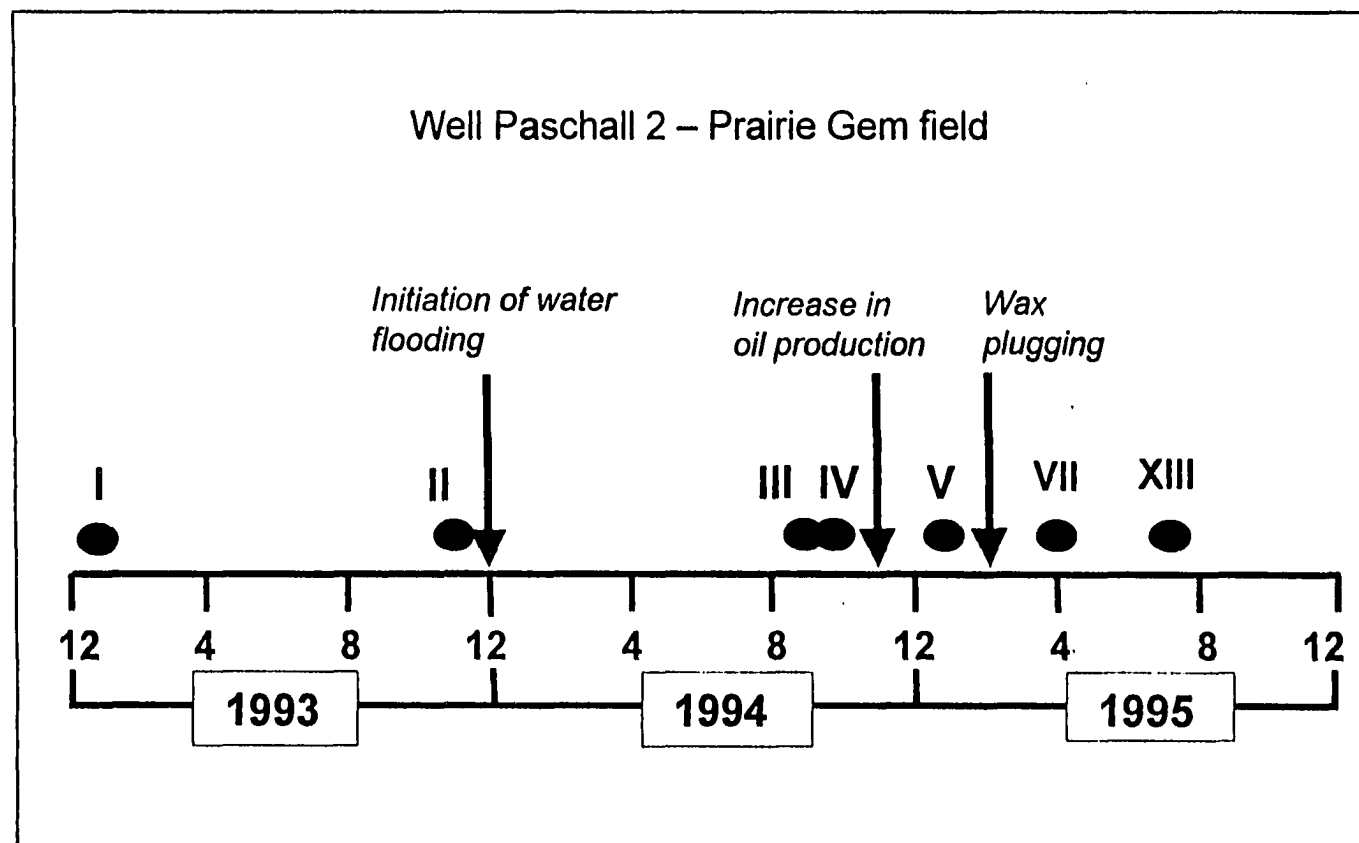


Figure IV. 4. 2. Timing of oil sample collection from Paschall 2 well in relation to the main production events - initiation of water flooding, increase in oil production, well wax plugging.

production coming from the fluvial-deltaic sandstones of the Bartlesville sand (Bluejacket sandstone) deposited during Pennsylvanian time (**Figures III. 1 and Figure III. 4, Appendix III** ; Northcutt and Johnson, 1996). The present average subsea depth to top of the formation is 1402 m, and the average thickness of reservoir is 9 m. The Late Devonian Woodford Formation (marine black shales) is widely distributed in the region and has been correlated geochemically with oils produced from other fields in central and southern Oklahoma (Comer and Hinch, 1987), and is considered the most likely source for the Bartlesville oil in the Prairie Gem field.

The Prairie Gem field was discovered in 1979 and has been in production since 1980. The accumulation has a gas cap in the northeastern part of the field, comprising 10% of the initial volume of total hydrocarbons in place, with an average thickness of 2.6 m. The primary drive mechanisms of the reservoir are solution gas and gas cap, and the average porosity and permeability in the reservoir are estimated to be 12.5% and 20 md, respectively (Rottmann, unpublished report). The initial gravity of the oil measured from one well was 33.5°API @ 60/60°F, and the bubble point pressure measured at reservoir temperature of 45°C (114°F) has been estimated to be 12.9 MPa (1876 psi) based on reservoir fluid PVT analysis (unpublished company report). The bottom hole pressure test at the time of discovery measured an initial reservoir pressure of 12.9 MPa (1879 psi). Reservoir pressure dropped to about 4.1 MPa (600 psi) after the first year of production and to 1.7 MPa (250 psi) after thirteen more years of primary production. The oil column characteristics under initial reservoir conditions and one year before the start of water flooding were estimated to be as follows: a decrease in oil saturation from the initial 75%

to 54.8%, and associated increase in gas saturation from 0% to 20.2%; decrease in solution gas-oil ratio from the initial 478 scf/STB to 44 scf/STB; increase in oil viscosity from the initial 1.0799×10^{-3} Pa s to 3.5701×10^{-3} Pa s. Water saturation was estimated to be 25% (Rottmann, unpublished report). At initial stages of production, all wells in the field were stimulated by hydraulic fracturing.

In December of 1993, after thirteen years of primary production, a water flood program (four injection wells) was initiated in the NW part of the field (**Figure IV. 4. 1**) with an injection rate of about 200 bbl water per day per well (K. Rottmann and M. Gaenz, oral communications). Water for injection operations was supplied from the shallower Layton sand (Rottmann, 1998). Almost one year after the initiation of water flooding, the Paschall 2 well responded with an approximate five fold increase in oil production (**Figure IV. 4. 3**). Several months later oil production was doubled again, but wax plugging of well equipment also occurred. The wax plugging episode in Paschall 2 was treated with injection of hot oil and additives.

IV. 4. 3. RESULTS

The results of this study demonstrate significant variations in the asphaltene and wax content of oil produced from Paschall 2 over a period of about three years, covering the transition from primary to secondary recovery by water flooding. The asphaltene and wax content of the oils varied from 0.7 to 5 wt.%, and from 11 to 33 wt.%, respectively (**Figure IV. 4. 4**). The most drastic increase in asphaltene content and change in the

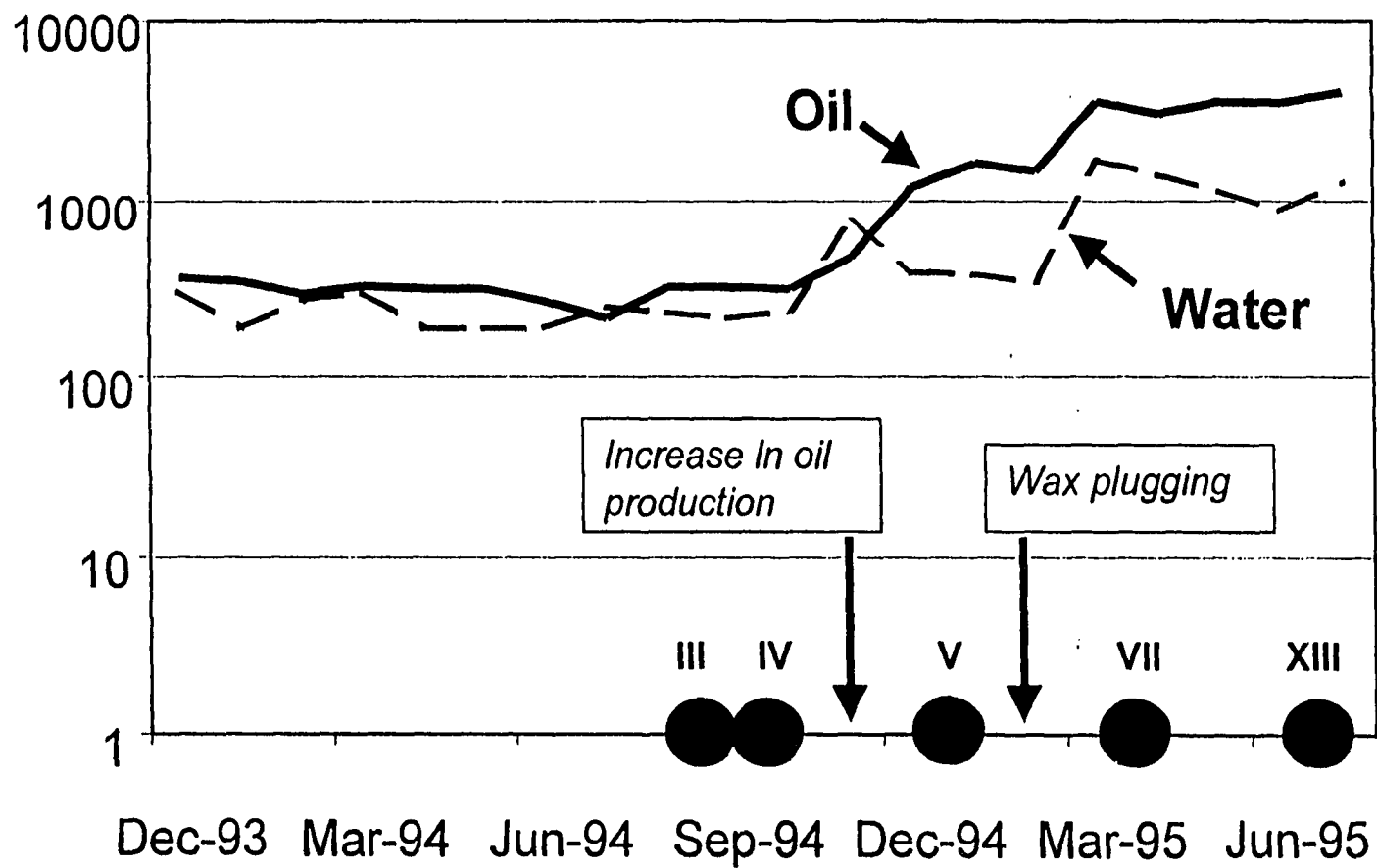


Figure IV. 4. 3. Monthly oil and water production (BOPM, BWPM) for Paschall 2 well after initiation of water flooding in December 1993. Black circles indicate timing of oil sample collection.

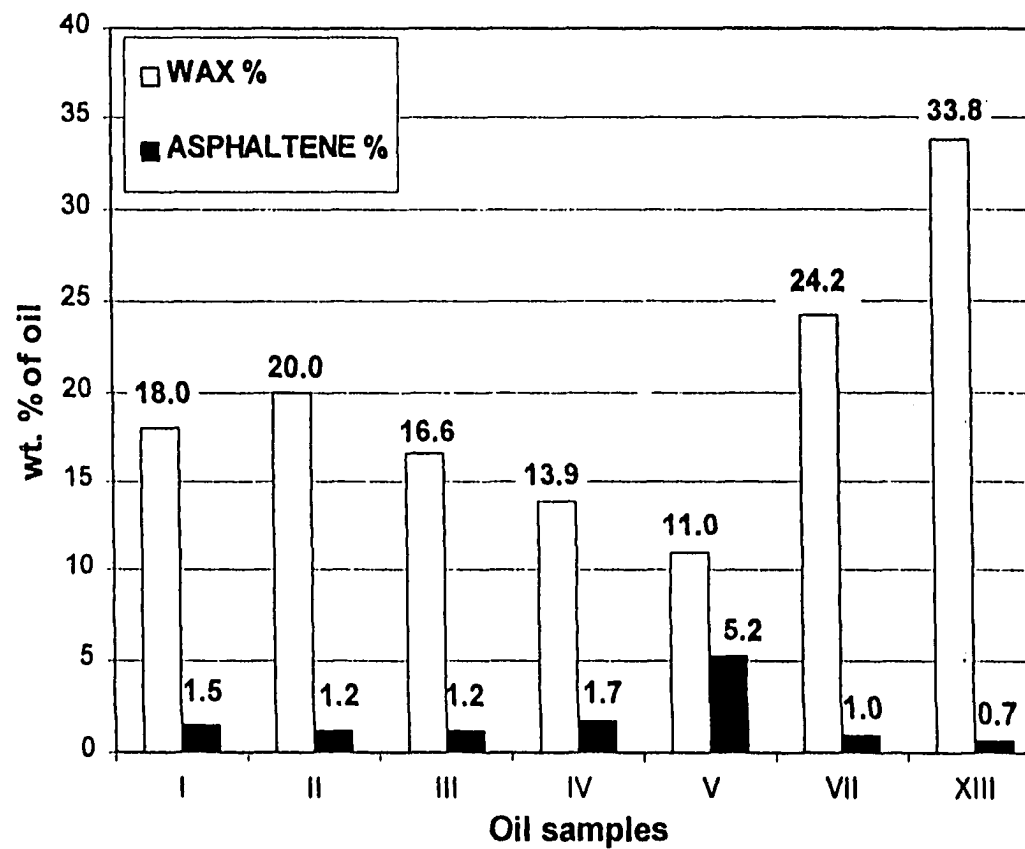


Figure IV. 4. 4. Total wax (acetone precipitate) and asphaltene (n-pentane precipitate) contents in produced oils at Paschall 2 well, Prairie Gem field (for timing of oil sample collection refer to Figure IV. 4. 2).

predominant wax type occurred in oil V, collected within two months after the oil production increase and a month before the occurrence of well wax plugging (**Figures IV. 4. 2 and IV. 4. 4**). The asphaltene content in oil V increased more than three times compared to the earlier produced oils (from 1.7 to 5.2 wt.%). Quantitative HTGC analysis of the asphaltenes precipitated from oil V showed that this fraction contained about 23% of all C_{18} - C_{55} components and more than 80% of nC_{42+} alkanes recovered in the wax fraction (**Figures IV. 4. 5 and IV. 4. 6, Appendix IV. 4. 1**). The amount of all nC_{35} - C_{55} alkanes precipitated with the asphaltenes represents 2.4% of the asphaltene fraction or 0.12 wt.% of the oil (**Appendix IV. 4. 1**). The amount of asphaltenes without the co-precipitated waxy components thus represents 5.08 wt.% of the oil. After the wax problem in the well was treated with hot oil and additives, the asphaltene content in oils VII and XIII dropped to little below the asphaltene content level before the wax plugging episode in the well (**Figure IV. 4. 4**).

Total wax content in oils produced at Paschall 2 well before the wax plugging demonstrates a decreasing trend from 18-20 wt.% (samples I, II) to 11 wt.% (sample V), **Figure IV. 4. 4**. A similar decreasing trend in total wax content from 5.2 to 1.6% has been reported by Woo et al. (1984) and was detected four months prior to the wax deposition problem that occurred in the well monitored over an year period. Based on that observation, the authors proposed that total wax content in produced oils may be an indicator for a potential wax problem in the well.

The quantitative HTGC results for the waxes in oils (I, II, III, IV and V), produced before the well wax plugging, revealed further changes in the predominant wax

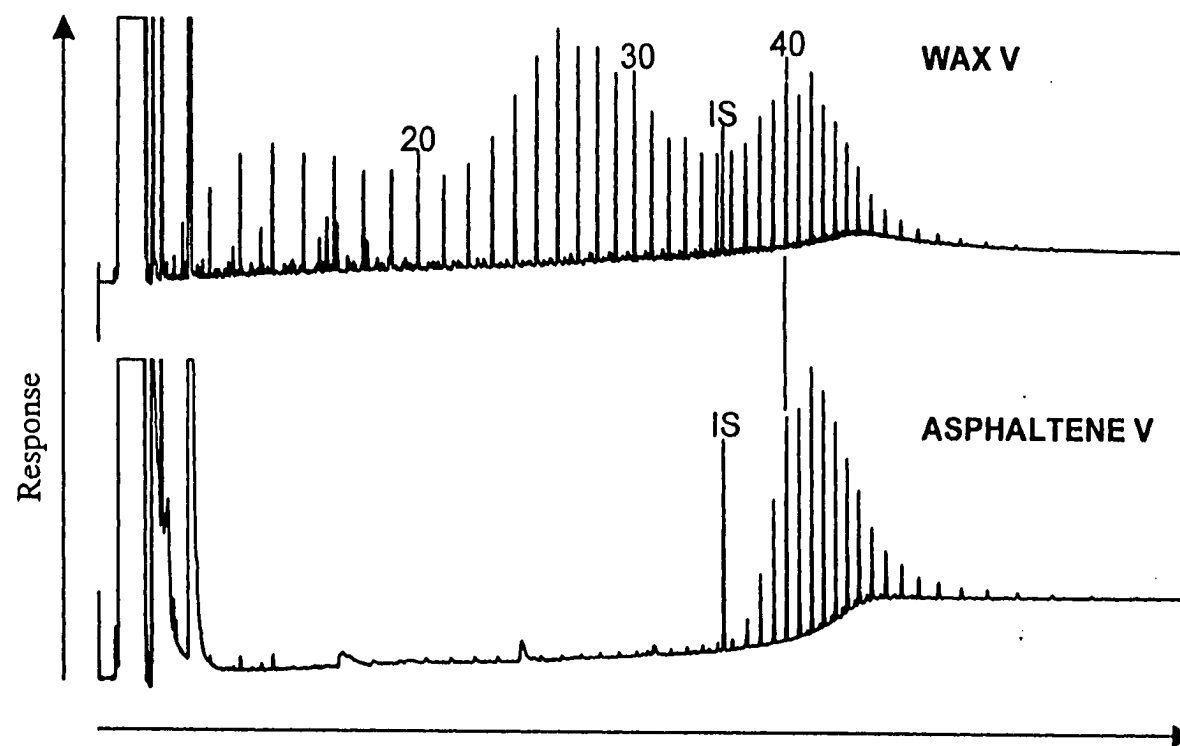


Figure IV. 4. 5. HTGC chromatograms of wax and asphaltene precipitates from oil V, Paschall 2 well.

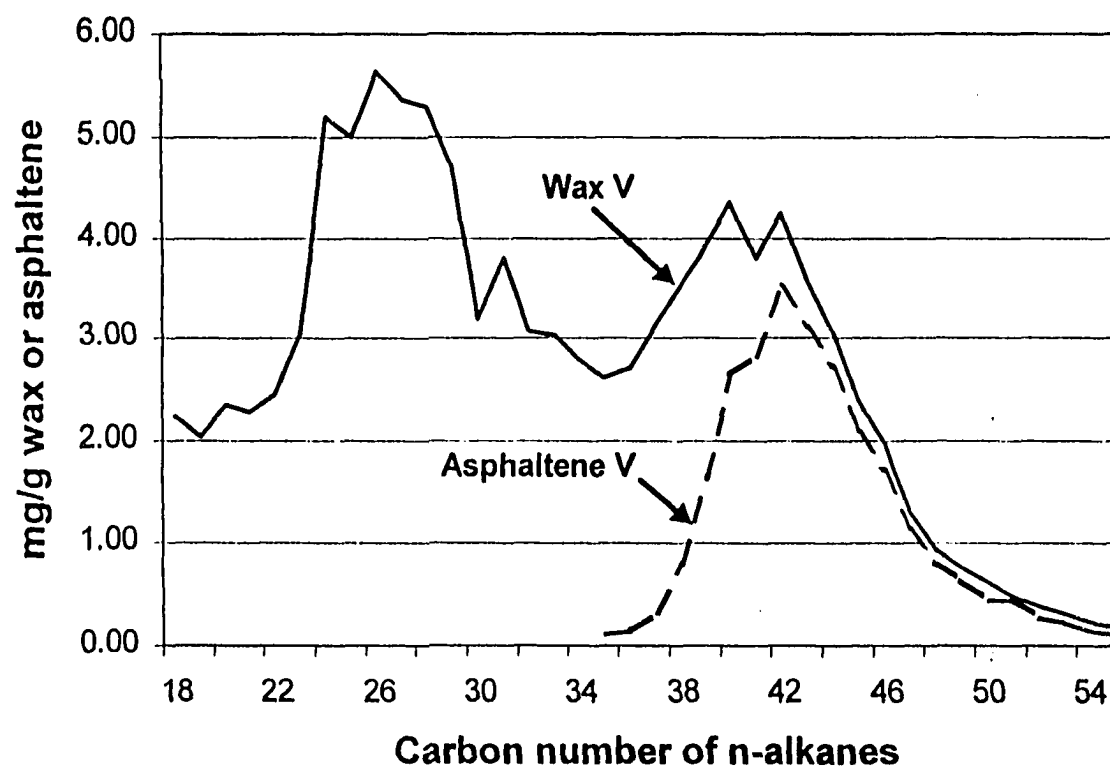


Figure IV. 4. 6. Quantitative HTGC results for n-alkane distributions in wax and asphaltene precipitates from oil V.

type that could be correlated with the decreasing trend in the total wax content of the oils (**Figure IV. 4. 7** and **Figure IV. 4. 8**). In accordance with the petroleum wax classification scheme discussed in section IV. 2. 2. B, macrocrystalline and microcrystalline waxes refer to the distribution of nC_{20} - nC_{35} and nC_{35+} alkanes, respectively, and these wax types can be identified from quantitative HTGC analysis. The amounts of macro- and microcrystalline waxes as percentages of the total nC_{18+} alkanes in the total wax as determined by HTGC, for Paschall 2 oils are summarized in **Figure IV. 4. 9**. The acetone technique was shown to recover 70-80% of nC_{38+} alkanes present in the Prairie Gem oil in the wax fraction (section IV. 2. 3. D) with some variations in the recovery of the macrocrystalline waxes, which defines the possible errors in estimating the relative proportions of macro-and microcrystalline waxes in Prairie Gem oils.

The predominant wax type in all the oils produced at Paschall 2 well, except oil V, is macrocrystalline (**Figure IV. 4. 9**) with amounts ranging from 83% to 93% and exceeding by five to fourteen times the amount of associated microcrystalline wax (**Figure IV. 4. 9**). After initiation of the water flooding, the amount of microcrystalline wax increased slightly in samples III and IV (15 and 17%) to reach a maximum of 42% in sample V, which was collected within two months after the increase in oil production and a month before the well wax-plugging episode (**Figures IV. 4. 9**). As discussed earlier, the amount of asphaltenes, even after correction for the presence of HMW n -alkanes, in oil V also increases significantly (approximately three times). Thus, a month before the wax plugging, the oil produced from well Paschall 2 demonstrates an

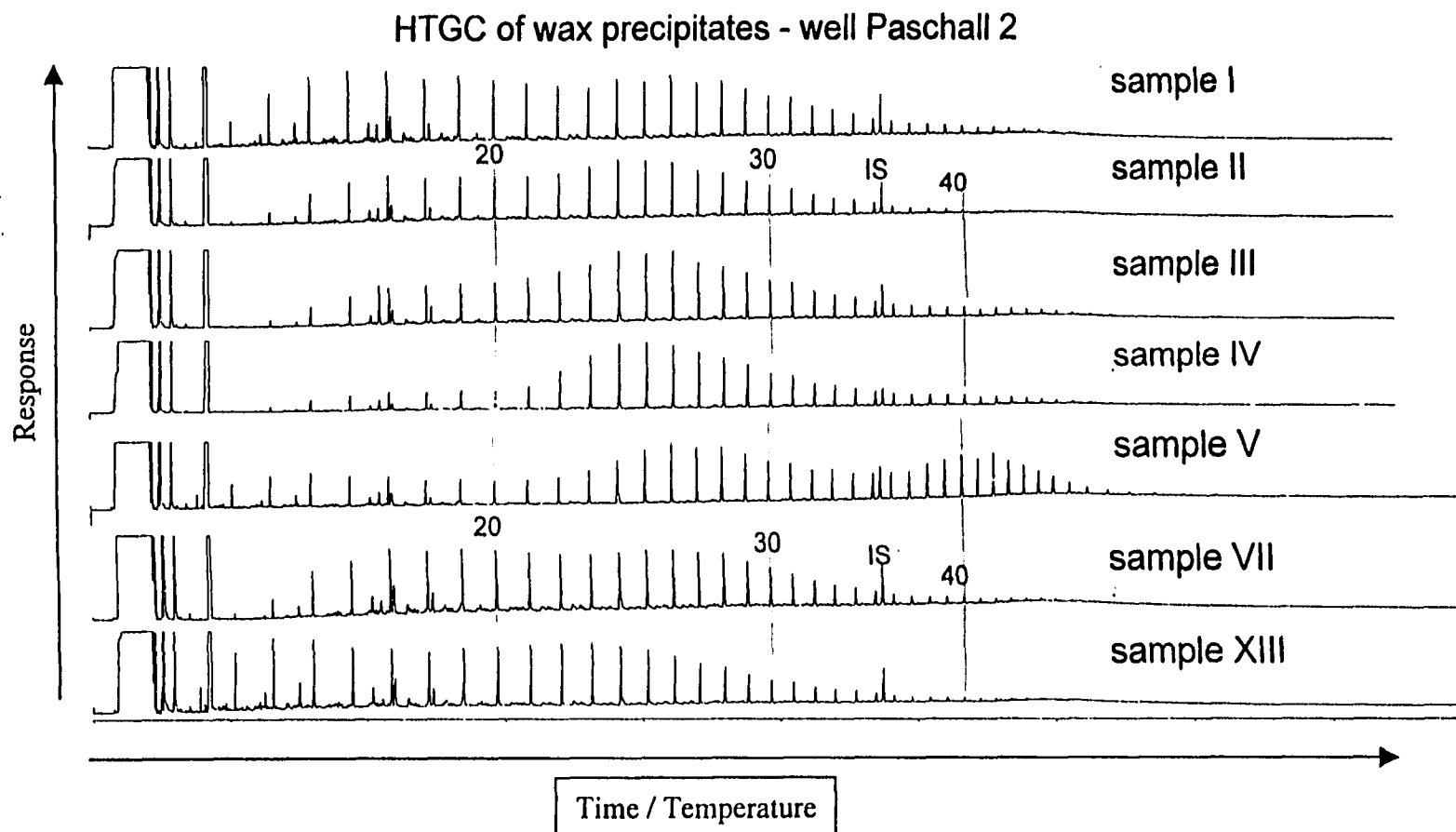


Figure IV. 4. 7. HTGC of wax precipitates from oil samples I through XIII, Paschall 2 well, Prairie Gem field (for timing of sample collection refer to Figure IV. 4. 2).

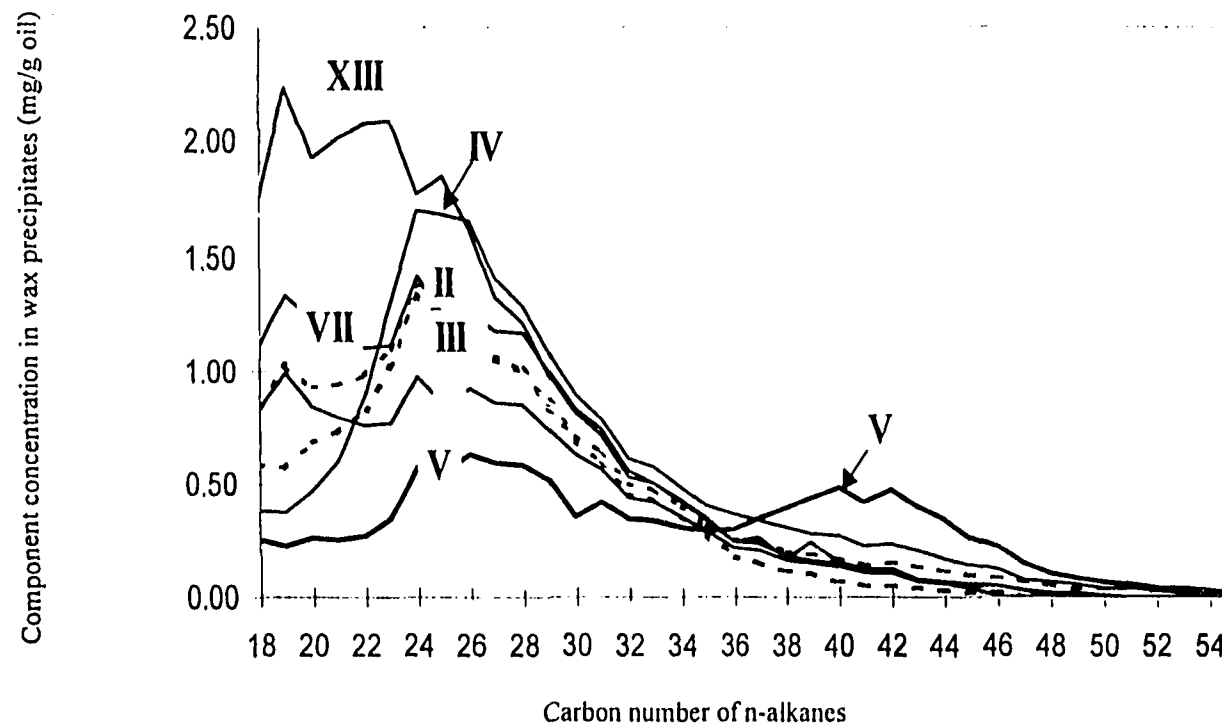


Figure IV. 4. 8. Quantitative HTGC results for the n-alkane distributions in the wax precipitates from oils I through XIII. Note the increase in HMW nC_{35+} alkanes in oil V collected a month before wax plugging in well tubing was observed.

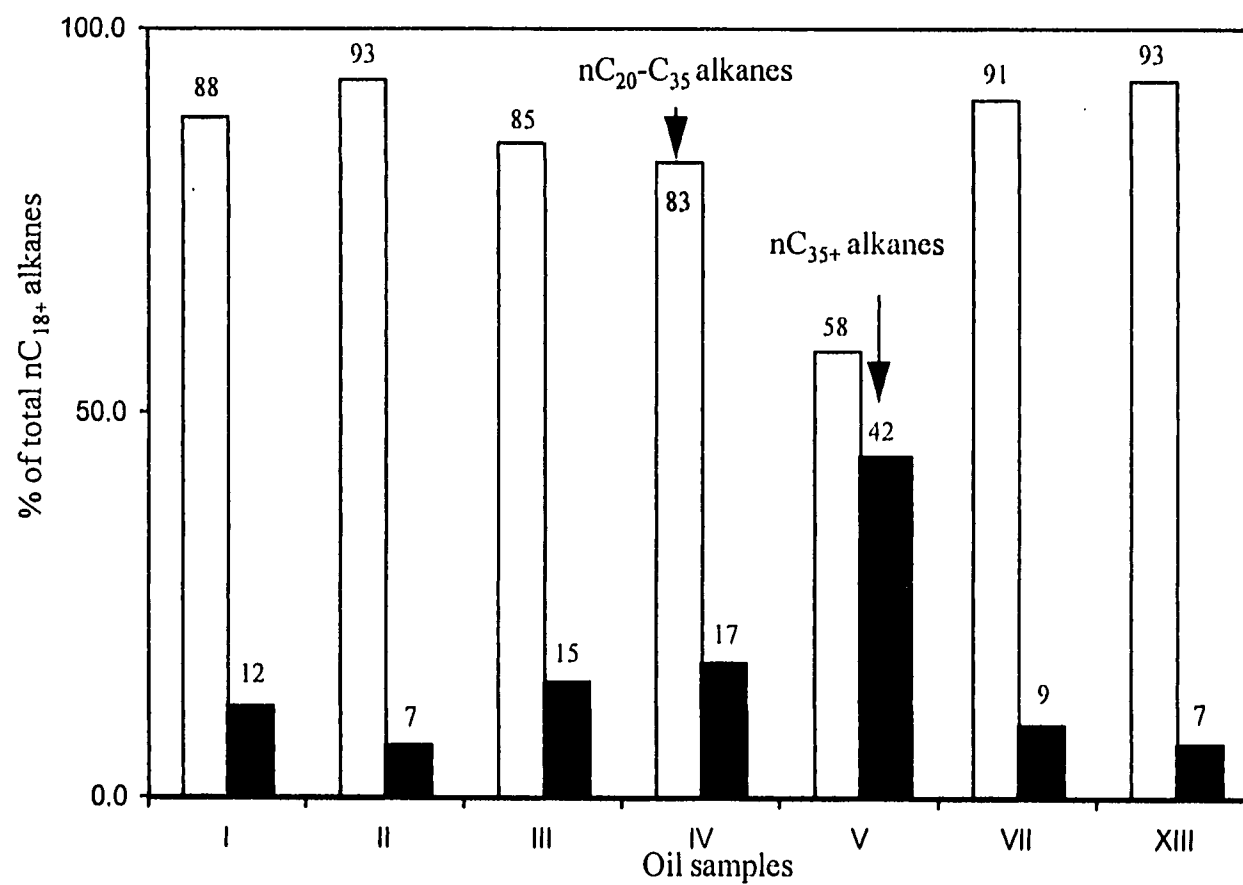


Figure IV. 4. 9. Variations in macrocrystalline ($nC_{20}-C_{35}$ alkanes) and microcrystalline (nC_{35+} alkanes) waxes for oils produced at Paschall 2 well, Prairie gem field. Note the increase in microcrystalline wax for oil V, which corresponds to an increase in asphaltene content (Figure IV. 4. 6) and decrease in macrocrystalline wax and total wax content (Figure IV. 4. 6).

unusually high concentration of microcrystalline wax and asphaltenes. This observation, in addition to the commonly observed preferential concentration of HMW n-alkanes in wax deposits (Carlson et al., 1991, 1993; del Rio and Philp, 1992b; Philp et al., 1995), suggests that well wax deposition problems may be detected ahead of time by monitoring changes in microcrystalline wax and asphaltene contents in produced oils.

The increase in microcrystalline wax in oil V is associated with a decrease in the macrocrystalline wax and total wax content. Total wax content refers to both macro- and microcrystalline waxes, and since macrocrystalline waxes (when present) have much higher concentrations (e.g., 5-15 times, **Appendix IV. 2. 10**) than microcrystalline waxes. Hence the variations in total wax content will be determined mainly by variations in macrocrystalline wax content. A decrease in total wax and/or macrocrystalline wax content in the produced oil has been suggested as an indicator for wax problems (Woo et al., 1984). However, as shown by the Paschall 2 results, the decrease in total wax content will be mainly determined by a decrease in macrocrystalline waxes, and is actually associated with an increase in concentration of HMW n-alkanes (microcrystalline type wax) that are the first components to precipitate with decreasing temperature during production. Therefore, a decrease in total wax content is not a sufficiently specific indicator for predicting wax deposition problems. The relative increase in microcrystalline waxes and asphaltenes in the produced oils are suggested to be more specific indicators for possible well wax deposition problems. This criterion should be used with caution in very cold climates or deep offshore production at low temperatures (section IV. 2. 4).

Oils produced after the clean-up of the plugged well tubing (samples VII and XIII) were characterized with the highest total wax content with regard to both acetone precipitated wax (24 and 34% oil) and macrocrystalline type wax (91 and 93% of total nC_{18+} alkanes; **Figures IV. 4. 4 and IV. 4. 9, Appendix IV. 4. 1**). The increase in total wax and macrocrystalline type wax content after the clean-up operations could be related to the effect of hot oil treatment, which initially dissolves the lower-end (macrocrystalline type) waxes as discussed by King and Cotney (1996).

IV. 4. 4. DISCUSSION

The results presented above demonstrate that the composition of Paschall 2 oils, specifically the wax and asphaltene fractions, varied significantly during the transition from primary to secondary water flood recovery. An increase in asphaltene and microcrystalline wax content in the oil, and decrease in total and macrocrystalline wax content were detected in the produced oils a month before wax deposition in the well tubing occurred. These results suggest that geochemical monitoring of waxes, specifically microcrystalline waxes and asphaltenes, may detect compositional changes at very low concentrations, that have the potential to be used as a method to detect wax deposition problem ahead of their occurrence. An early detection of wax deposition problems would permit the use of some preventive wax treatment (e.g., injection of solvent, dispersants) that could minimize the effect of the increasing asphaltene and microcrystalline wax contents in the oils before a supersaturation level causing their precipitation in well

tubing and interruption of the oil production.

Changes determined in the waxes and asphaltenes of the Paschall 2 oils lead to a number of questions regarding the processes occurring in the reservoir during the production and water flooding that give rise to the observed compositional variations. The interactions and processes that occur in the pore space of reservoirs are very complex, including variability in fluids composition, fluid-fluid and fluid-rock interactions, wettability changes and their development in the framework of the pressure and temperature history of the reservoir. Since the present study does not present evidence to constrain all of these factors, the following discussion attempts to address some of these questions by constraining the knowledge accumulated in previous studies about the phenomena of wax and asphaltene deposition and mobilization in porous media of reservoirs with known facts from the production history in Prairie Gem field.

The increase in both microcrystalline wax and asphaltenes on one hand, and decrease in total alkanes and macrocrystalline waxes on the other, suggest that macrocrystalline and microcrystalline waxes behave in a different way in the pore space of the reservoir (additional discussions on solubility, crystal behavior and adhesive properties in sections IV. 2. 3. A, C and IV. 2. 2. B). HMW n-alkanes show more similarities with the asphaltenes and part of the resins than with the macrocrystalline waxes (Reistle, 1932; Dubey and Waxman, 1991; del Rio and Philp, 1992a and b; del Rio *et al.*, 1992; Platonov *et al.*, 1994; Musser and Kilpatrick, 1998; Thanh *et al.*, 1999). In addition, HMW n-alkanes, asphaltenes and resins are all considered as oil components that may cause wettability alterations of rock surfaces in the pore space of reservoirs from

water-wet to neutral or oil-wet (Jennings, 1957; Andersen, 1986; Buckley *et al.*, 1997).

Asphaltene and wax deposition in reservoirs are affected by the same major factors, namely, temperature, pressure and changes in oil composition. A decrease in temperature decreases the solubility of both asphaltenes (Hirschberg *et al.*, 1982) and n-alkanes. However, the composition of oil, acting as a solvent for the asphaltenes and waxes, may affect the solubility of these fractions in different ways. In addition, reservoir pressure conditions above the bubble point of the oil result in higher amounts of solution gas in the oil. Under such conditions, the oil could be a better solvent for waxes (Reistle, 1932) but a poorer solvent for asphaltenes (Buckley *et al.*, 1997).

In the Prairie Gem field, the bottom hole pressure test, PVT data, and the existence of a small gas cap, suggest that initially the accumulation in Bartlesville reservoir was near or slightly below the bubble point pressure. During primary production the reservoir pressure decreased steeply during the first year (Nov.79-Dec.80) from 12.9 MPa to 4.1 MPa, and then decreased at a lower rate to 1.7 MPa for the next thirteen years until the initiation of water flooding. A production-induced decrease in reservoir pressure below the bubble point is associated with liberation of free gas from the oil and formation of two hydrocarbon phases within the reservoir which compete for space to flow, thus reducing the relative permeability of the reservoir to oil (e.g., Craft, 1991). During primary production in the Prairie Gem field, gas saturation increased from 0 to 20%. The liberation of dissolved gas from the oil decreases the oil mobility due to an increase in viscosity, which has increased more than three times for the period of primary production in Prairie Gem. The increase in oil density (decrease in API gravity)

and viscosity over a longer production history increases the solubility of asphaltenes in the oil and precipitation is generally not favored. Thus, the most likely condition for initial asphaltene precipitation is at the bubble point when the solubility of asphaltenes in the oil is poor (Koots and Speight, 1974; Chang and Fogler, 1993; Wilhelms and Larter, 1994a and b; Tang and Morrow, 1996). Asphaltene precipitation early in the production history of the Prairie Gem field may have caused a change in the wettability of the reservoir at certain zones from predominantly water-wet to neutral and/or oil-wet. With an increase in flow time, the quantity of asphaltenes retained in the porous media would increase, and even non-flocculated asphaltenes could be retained as noted by Turta et al. (1997). Dynamic surface deposition, occurring under the condition of flowing fluids in reservoirs, of both asphaltenes, and microcrystalline waxes and asphaltenes, has been shown to occur under different reservoir porosity, permeability and asphaltene, microcrystalline wax content in the oils (Wang et al., 1999). After initiation of water flooding, asphaltene deposition resulting in pore throat plugging could occur under the conditions of increased rate of fluid flow (Wang et al., 1999). In addition, a continuous increase in pressure above the bubble point could increase the cloud point of the oil (Brown et al., 1994; see discussions in section IV. 2. 2) and facilitate microcrystalline wax precipitation.

Initial wax deposition would be favored by a longer primary production time and indirectly by a declining pressure via the loss of light components from the oil and decrease in temperature. In contrast to asphaltenes, the lower API gravity hydrocarbon solvents are generally poor solvents for waxes (Reistle, 1932). Therefore, the increase in

density and viscosity of oil over longer production time, as observed in Prairie Gem, could be expected to decrease the solubility of waxes and favor their precipitation. Decline in pressure during a long period of primary production is also associated with a certain drop in oil temperature due to gas expansion and may contribute to the process of wax deposition. Near producing wells, the pressure decrease is very rapid and the associated amount of cooling could be relatively large, thus favoring wax precipitation in those regions. Another production event that could have caused cooling in the reservoir is related to the increase in gas-oil ratios observed in many wells in the Prairie Gem field after the first year of production that has been attributed to gas cap penetration. Reistle (1932) has discussed that such a situation may cause cooling of 5 to 10°C. Another possible opportunity for wax deposition in the Bartlesville reservoir of the Prairie Gem is during the well fracture stimulation, applied early in the production history of the field. This common operation increases hydrocarbon production in formations with low permeability. It involves a high injection rate of fluids, that are often cooler than the formation, and results in the development of mainly vertical fractures. The fracture length could be up to 300 m and 0.5 cm wide at the wellbore (Sutton and Roberts, 1974). The greatest cooling effect would be experienced by the part of the fracture closest to the well bore (e.g., 5 to 8°C; Sutton and Roberts, 1974). Waxes can precipitate from the oil during the injection period of hydraulic well stimulation and/or when production resumes and the oil passes through the cooler formation near the fracture. The maximum cooling associated with the discussed possible cooling events in Bartlesville reservoir is 10°C, which could decrease the reservoir temperature (45°C) maximum to 35 °C. Depending on

the cloud point of Bartlesville oils, and considering the results in Chapter IV. 3, it could be speculated that temperature variations during production in Prairie Gem field had been sufficient mainly for microcrystalline wax deposition.

The pore space of the reservoir contains oil fractions with different strengths of interaction with the solid surface. Baldwin and Gray (1973) distinguished three groups of material according to the strength of interaction with the rock surface, based on a three step sequential extraction of whole reservoir cores with solvents of increasing polarity. They found that a fraction of the organic material is held very strongly by the reservoir surface, and consists of large aromatic and heteroatom compounds (possibly asphaltenes). A second fraction of high molecular weight aromatics, and smaller molecules (possibly resins), is held in the reservoir, which interacts mainly with the strongest adsorbed layer. The majority of the oil in the reservoir interacts weakly, if at all, with the rock surface and is similar to the produced oil. Comparable results have been reported in the recent studies of Wilhelms et al. (1996) and Keuser et al. (1997). Using a novel solvent flow-through extraction method Schwark et al. (1997) have shown that the composition of “adsorbed oil” fractions is significantly enriched in resins, asphaltenes, and HMW nC_{35+} alkanes compared to the “free” oil in the reservoir core pore space. A recent study of Guèhènneux et al. (1999) demonstrated that the reservoir core extracts from a field experiencing wax problems is considerably enriched in heavy hydrocarbons compared to the oil. Based on an experimental study using a glass micromodel for the porous medium, Chang and Fogler (1993) proposed that the asphaltene (n-pentane insolubles) deposition occurs in two stages. During the first stage, the less soluble part of the “asphaltenes” form

cluster-like deposits, which reduce the permeability, significantly; the more soluble part of the “asphaltenes” remain in solution, or are attached loosely to these deposits and could be carried away by the fluids. During the second stage, in addition to these cluster-like deposits, the more soluble “asphaltenes” form island-like deposits that may cause a total blockage. The experimental results of Chang and Fogler (1993) also indicated that “asphaltene” deposits can be solubilized and eluted from the porous media using oil soluble amphiphile/alkane solutions.

During water flooding, the reservoir pressure increases and at a certain threshold value of the pressure field, larger amounts of the “non-adsorbed” oil trapped in the pore space of reservoir would become movable. The movable oil could be produced, resulting in an increase of oil production, as observed in Paschall 2 well. Since macrocrystalline waxes have lower adhesive properties compared to the microcrystalline waxes (Table IV. 2. 1), it could be speculated that macrocrystalline waxes are attached more loosely to the other components in the pore space. In such a situation, the macrocrystalline waxes could be produced easily with the rest of the oil, corresponding to the observations in Paschall 2.

With regard to the observed increase in microcrystalline waxes and asphaltenes in oil V, it is possible that under the conditions of continuously increasing pressure and flowing fluid volumes after the water flooding some of the more strongly “adsorbed oil” fractions, enriched in asphaltenes, HMW n-alkanes and resins, in the pore volume of the reservoir will be mobilized as suggested by the models of Chang and Fogler (1993), and Schwark et al. (1997). Resins may play an important role in this process of mobilization

since they can be adsorbed to both asphaltenes and HMW waxes, and can be re-dissolved by lighter oil fractions. Another mechanism of mobilization of these oil fractions from the pore space (and/or fractures) could be related to migration of oil wet clay particles with already adsorbed asphaltenes and possibly HMW n-alkanes. Such particle migration could be triggered by increased flow rates and pressure disturbances associated with the water flooding (e.g., Gabriel and Inamdar, 1983; Boon et al., 1983; Sharma and Yortsos, 1987). Wettability of particles has been found to be of importance for their mobility – particles migrate only if the phase that wets them is mobile (Gabriel and Inamdar, 1983). In addition, particle bridges formed at pore throats are found to be readily disrupted by pressure disturbances and/or flow reversal, and mechanical particle mobilization is found to occur only above some critical flow velocity (Wu and Sharma, 1989). Alternatively, oil-wet clay particles may provide nuclei for adhesion and growth for wax components suspended in the oil.

The wax plugging of the well tubing in Paschall 2 apparently resulted from an increased concentration of HMW waxes and asphaltenes in the oil to a level sufficiently high enough for their precipitation under the prevailing temperature conditions. A change in temperature from 50°C (close to present day Bartlesville reservoir temperature) to 20°C (close to surface temperature) is found to decrease the interfacial tension of a hydrocarbon solution containing wax, resins and asphaltenes relative to the brine solution (Mullagalyamov et al., 1965), and would favor the adhesion of hydrocarbon components to the solid surface of well tubings. The higher adhesive properties and lower solubility of HMW waxes relative to the LMW waxes (**Table IV. 2. 1**; section IV. 2. 3), could further

facilitate their preferential deposition.

IV. 4. 5. CONCLUSIONS

The results presented herein demonstrate significant changes in total wax (nC_{18+} alkanes), macro-, microcrystalline type waxes and asphaltene content in oils produced during the transition from primary to secondary recovery by water flood as monitored in one well over a period of about three years. The time sequence of changes observed in oil composition, compared with the production events, suggests they are likely to be related to the changes in reservoir pressure and temperature during production and water flooding.

The present study demonstrates the potential of geochemistry for prediction of wax deposition problems in well equipment by distinguishing the pattern of oil compositional changes related to specific production operations. The application of quantitative high temperature gas chromatography (HTGC) method permits changes in high molecular weight (HMW) compounds, constituting a wax type with very different properties, to be identified, and the changes in concentration of individual wax components of the oils to be estimated. The method allows also for a semi-quantitative discrimination of the co-precipitated HMW waxy components from the asphaltene content obtained as n-pentane insoluble fraction.

The conclusions of this study can be summarized as follows:

- (1) Geochemical monitoring of waxes and asphaltenes in produced oils can detect

compositional changes at very low concentrations and has the potential to predict wax deposition problems in well production equipment;

(2) The wax deposition problem in Paschall 2 well was preceded by a decrease in the total wax concentration, total nC_{18+} alkanes and macrocrystalline waxes and a concentration increase in microcrystalline waxes and asphaltenes in the produced oils. The increase in concentration of microcrystalline waxes and asphaltenes is suggested as a more specific indicator for up-coming wax deposition problems compared to changes in total wax and/or macrocrystalline wax content. Microcrystalline waxes appear to have much more similarities with the asphaltenes, with regard to solubility/precipitation behavior and adhesive properties, than with the macrocrystalline waxes, which facilitates the common occurrence of microcrystalline waxes and asphaltenes in wax deposits.

(3) An increase of asphaltenes and microcrystalline waxes in produced oil can most likely be related to processes of mobilization of these fractions under increased reservoir pressure and flowing fluid volumes related to water flooding;

(4) Production geochemical monitoring is a relatively novel approach and could be integrated in the future with other time dependent reservoir information. The best compositional characterization of oils during production is provided by geochemical methods. Integration of temporal data on both oil geochemistry and reservoir engineering in the 3-D geological spatial framework of the reservoir is necessary for diagnosing and solving the 4-D production problems often encountered in the petroleum practice.

CHAPTER V. CONCLUSIONS

V. 1. SUMMARY ON THE ORIGIN OF PETROLEUM WAXES

Petroleum wax refers to the mixture of hydrocarbons in oils that are solid at ambient conditions (e.g., n-alkanes $>C_{18-20}$). The upper carbon number ranges are not well defined, but hydrocarbon distributions extending to nC_{80} have been commonly identified by HTGC in oils and wax deposits. Petroleum waxes are generally dominated by n-alkanes, with smaller amounts of iso-, cycloalkanes and alkylaromatics.

Biomolecular precursors for n-alkanes, iso-alkanes, cycloalkanes, alkylaromatics, with molecular weights range sufficiently broad and high to account for the presence of these compounds in petroleum waxes, are present in both marine and terrestrial organisms. LMW and HMWHC may be directly derived from biomolecular precursors or formed by defunctionalization of the precursors during the diagenesis. Evidence has been presented for a common biological and/or diagenetic origins of LMW and HMWHC (Carlson *et al.*, 1997) as well as for a diverse origin (higher plant and microbial for LMW and HMWHC, respectively, Rieley *et al.*, 1991). In addition, oligomerization processes under high thermal stress could form HMWHC. An alternative, post-generation mechanism for HMWHC formation is the thermal alteration of asphaltenes in reservoired oils. It is very likely that HMWHC can have multiple origins (Philp, 1994b).

High-wax oils are usually characterized with a high concentration of macrocrystalline waxes (nC_{20} to C_{30-35} alkanes) but also could have microcrystalline

waxes in lower concentration. High-wax oils are often associated with terrestrially derived organic matter and clastic sedimentary sequences comprising oil shales and coals, and deposited in lacustrine and/or fluvial and deltaic environments of deposition. High-wax oils can be generated from both the highly aliphatic Type I (and II) kerogen and the high-hydrogen content components in Type III kerogen. The occurrence of high-wax oils has been closely related to the primary migration restrictions associated with the high adsorptive capabilities of massive coal beds and the lack of driving mechanisms for migration (absence of gas and water) in immature oil shales. Therefore in these cases, high-wax oils can be expected to have experienced either no or short distance migration. Significant discrepancies exist in the way high-wax oils are defined, particularly as a result of the different methods used to determine wax content of crude oils. Furthermore, the material precipitated from an oil and referred to as wax fraction often contains various proportions of resins and asphaltenes that are taken together with the hydrocarbons as an estimate of the wax content. In the present study, GC and HTGC analysis are considered as one of the more reliable methods for hydrocarbon content estimation and high-wax oils are defined as having at least 10 wt.% total amount of n-alkanes in the carbon number range C_{20} to C_{35} . Low-wax oils could contain macrocrystalline waxes in lower concentration than the high-wax oils and/or microcrystalline waxes, which are generally observed to be present at much lower concentration levels compared to macrocrystalline waxes in oils. Possible explanations for the low concentration range of microcrystalline waxes (HMWHC) in oils could be related to: (a) their origin from the soluble organic matter in rocks and/or early kerogen degradation at low maturities; (b) their higher

adsorption capabilities and higher melting points as compared to the LMW (C_{20} - C_{35}) n-alkanes, which may preferentially restrict their primary migration, and/or promote their adsorption along secondary migration pathways and in reservoirs based on the principles of geochromatography. An additional factor contributing to observed low concentrations of HMWHC could be related to the use of an inappropriate solvent for sample dilution in HTGC analysis for determination of n-alkane content in petroleum waxes (see below).

V. 2. CONCLUSIONS ON SOLUBILITY OF n-ALKANE MIXTURES

- (1) The optimum solvents for n-alkane mixtures with largely different molecular weight distributions that could be present in wax deposits are different. Laboratory and/or field treatment of such mixtures with the same solvent would result in a significant variability of the dissolved amount of different n-alkanes, and ultimately a decreased efficiency of the treatment.
- (2) A considerable increase (2 to 4 times) in quantitative recovery of n-alkane mixtures by HTGC can be achieved by using an optimum solvent for a particular molecular weight distribution mixture, which affects the estimated amount of n-alkanes, and macro- and microcrystalline type waxes in wax deposits and petroleum waxes.
- (3) A procedure for solubility parameter calculation of HMW dominated n-alkane mixtures, based on quantitative HTGC analysis and Method 3 (Fedors, 1974) for solubility parameter calculation for pure n-alkanes, was found to give predictions closest to the experimental solubility results. The proposed procedure allows to

identify the order of solubility of wax deposits in different solvents according to the variation in their compositional characteristics. HMW dominated n-alkane deposits are found to be dissolved in larger amounts by carbon tetrachloride than by cyclohexane and p-xylene. A main limitation of the procedure is related to the limitations of the HTGC analysis. Presence of different proportions non-hydrocarbons (model resin component) with the n-alkanes in wax deposits is predicted to change significantly the choice of a solvent for best dissolution of HMW n-alkane mixture from carbon tetrachloride to triethylamine (30% resin) to ethyl benzene (50% resin) to p-xylene (70% resin). Additional experimental work is necessary in order to evaluate the effect of resins and asphaltenes on the solubility behavior of wax deposits.

- (4) The application of above proposed procedure for evaluating the solubility of wax deposits and petroleum waxes, representing mixtures of both hydrocarbons and non-hydrocarbons, was demonstrated by several examples, and presents a way to model the solubility of wax deposits in cases of limited experimental compositional data for the non-hydrocarbon (polar) fractions. Analysis of solvents for wax precipitation and dissolution using this procedure allowed to identify two possible reasons for the observed low n-alkane recovery efficiency of DCM technique compared to the acetone technique: (a) lack of precipitation of mixed n-alkane/resin (or in general nonpolar/polar) particles in DCM compared to acetone; and (b) lack of dissolution of mixed n-alkane/resin particles by cyclohexane in contrast to toluene.
- (5) Low efficiency of n-alkane recovery in precipitated wax fractions by both studied techniques for the low-wax Prairie Gem oil was related to the naphthenic-aromatic

nature of the oil. Larger proportions of iso-/cycloalkanes and aromatic hydrocarbons in the oils act as solvents for the n-alkanes. Based on the results presented in section IV. 2. 3. D, the aromatic hydrocarbons are likely to promote entrapment of the components acting as solvents (iso-/cycloalkanes, aromatics) with the precipitated mixture. In addition, aromatic hydrocarbons are likely to facilitate a co-precipitation of resins (and possibly asphaltenes). The iso-/cycloalkanes, co-precipitated with the n-alkanes, would have the effect of reducing the melting point of the precipitate, and contribute to a lower recovery at relatively elevated temperature conditions of filtration.

- (6) The Polywax 1000 standard HMW dominated n-alkane mixture was found to form a smaller amount (1.5 times) of precipitate from carbon tetrachloride than p-xylene solutions. However, the carbon tetrachloride precipitate is anticipated to be harder and more difficult for dissolution because of consisting mainly of HMW components forming a crystalline solid. The p-xylene precipitate forming a larger amount is expected to be softer and easier for dissolution because of the identified in this study mixed amorphous/crystalline (LMW/HMW components) nature of the solid.

V. 3. CONCLUSIONS ON COMPOSITION OF WAX DEPOSITS FORMED AT DIFFERENT TEMPERATURES

- (1) The laboratory simulated wax deposit formation using a cold finger apparatus demonstrated two temperature regions of rapid increase in wax deposit amount that

could be regarded as determined by processes of different nature. The first interval of a rapid deposit growth (35°C to 4.4°C) could be related to subsequent crystallization of the most abundant HMW and LMW n-alkanes, respectively, in the oil, and therefore this temperature interval will be mainly wax composition and concentration specific. The second interval (-13°C and possibly lower) relates to solidification of the oil matrix in approaching the glass transition temperature of the oil, it is not influenced by the wax content of the oil and correlates with the concentration of lighter components in the oil matrix (Hansen et al., 1991).

- (2) The composition of wax deposits changes with the temperature of deposition, as demonstrated by both laboratory and field formed wax deposits. The n-alkane composition of wax deposits formed within the same production tubing/pipeline is not constant but increases in molecular weight with the increase in temperature. In addition, the relative proportions of non-hydrocarbons may change in wax deposits formed at different temperatures.

V. 4. CONCLUSIONS ON WAX / ASPHALTENE STUDY IN PRAIRIE GEM FIELD

- (1) Geochemical monitoring of waxes and asphaltenes in produced oils can detect compositional changes at very low concentration levels, and thus has a potential to predict wax deposition problems in well production equipment. Paschall 2 well wax deposition problem is related to the detected ahead of time decrease in concentration

of total wax, total nC_{18+} alkanes and macrocrystalline waxes and an increase in concentration of microcrystalline waxes and asphaltenes in the produced oils. The increase in concentration of microcrystalline waxes and asphaltenes is identified as a more specific indicator for up-coming wax deposition problems compared to changes in total wax and/or macrocrystalline wax content.

- (2) An increase of asphaltenes and microcrystalline waxes in produced oil can most likely be related to processes of mobilization of these fractions under increased reservoir pressure and flowing fluid volumes related to water flooding. The common occurrence of microcrystalline waxes and asphaltenes could be related to the similarities in their solubility/precipitation behavior and adhesive properties.

V. 5. FINAL CONCLUSIONS AND RECOMMENDATIONS OF THE STUDY

- (1) A procedure for solubility parameter determination of HMW n-alkane mixtures is developed and experimentally tested, which combines quantitative HTGC analysis and Method 3 (Fedors, 1974) for solubility parameter calculation of pure HMW n-alkanes. The procedure allows to identify the optimum solvent (from a database of about 300 solvents) for wax deposits with different compositional characteristics. The examples of applying this procedure presented in the study demonstrate a potential to improve the quality and efficiency of different analytical techniques for characterization of petroleum waxes.

- (2) Wax deposits formed along the same well tubing or pipeline have been identified to vary with regard to both composition and solubility. One reason for the current inefficiency of methods for wax problem treatment could be related to this variability in the composition and solubility properties of wax deposit mixtures.
- (3) The results of the study demonstrate the potential of geochemistry to predict correctly wax deposition problems in well equipment and the relative temperature of formation of wax deposits based on the compositional characteristics of waxes. Further integration of geochemical studies with thermodynamic modeling is a necessity for more successful prediction and prevention of wax deposition problems.
- (4) The results of the present study demonstrate that there is a lot of unexploited potential for obtaining useful results for practical laboratory geochemistry studies by applying the solubility parameter concept and therefore its use is recommended in sequential elution and fractionation studies of heavy petroleum fractions.

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APPENDICES

The numbering system of the appendices corresponds
to the chapter number where they are discussed

Appendix III. Geologic setting of Prairie Gem field

Regional tectonic setting and evolution of geological provinces in Oklahoma

Present day major geologic provinces in Oklahoma include several sedimentary basins, uplifts and fault zones, result of a long and complex geological history (**Figure III. 1**). The sedimentary basins comprise: Anadarko, Arkoma, Cherokee Platform, Ardmore, and Marietta Basins. On a regional scale, the major geologic provinces in Oklahoma are result mainly of the active tectonic history involving the southern margin of the North American craton during Precambrian and Paleozoic time when a major ocean margin cycle (“Wilson cycle”) was completed (Arbenz, 1989). The cycle started with the breakup of the mythical “Precambrian Pangea” continent, consisting of North America, Baltica and Siberia, during the Late Precambrian-Early Paleozoic rifting that led to the opening of the Iapetus (proto-Atlantic) Ocean and the formation of the Appalachian-Ouachita continental margin (Bally et al., 1989; Bally, 1989; Thomas, 1991). The rifting propagated in space from the Appalachian to the Ouachita margin. The shift in the spreading center towards the Ouachita margin is considered to have occurred during the latest Precambrian to the Early Cambrian time based on the type and timing of the igneous events along the Southern Oklahoma fault system (Gilbert, 1983; Thomas, 1991). The Southern Oklahoma fault zone represented one of the intracratonic fault systems that extended from the Appalachian-Ouachita orogen into the craton, and formed the Southern Oklahoma aulacogen (**Figure III. 2**). The formation of these intracratonic fault systems has been interpreted as a result of the intersection of the rift with a

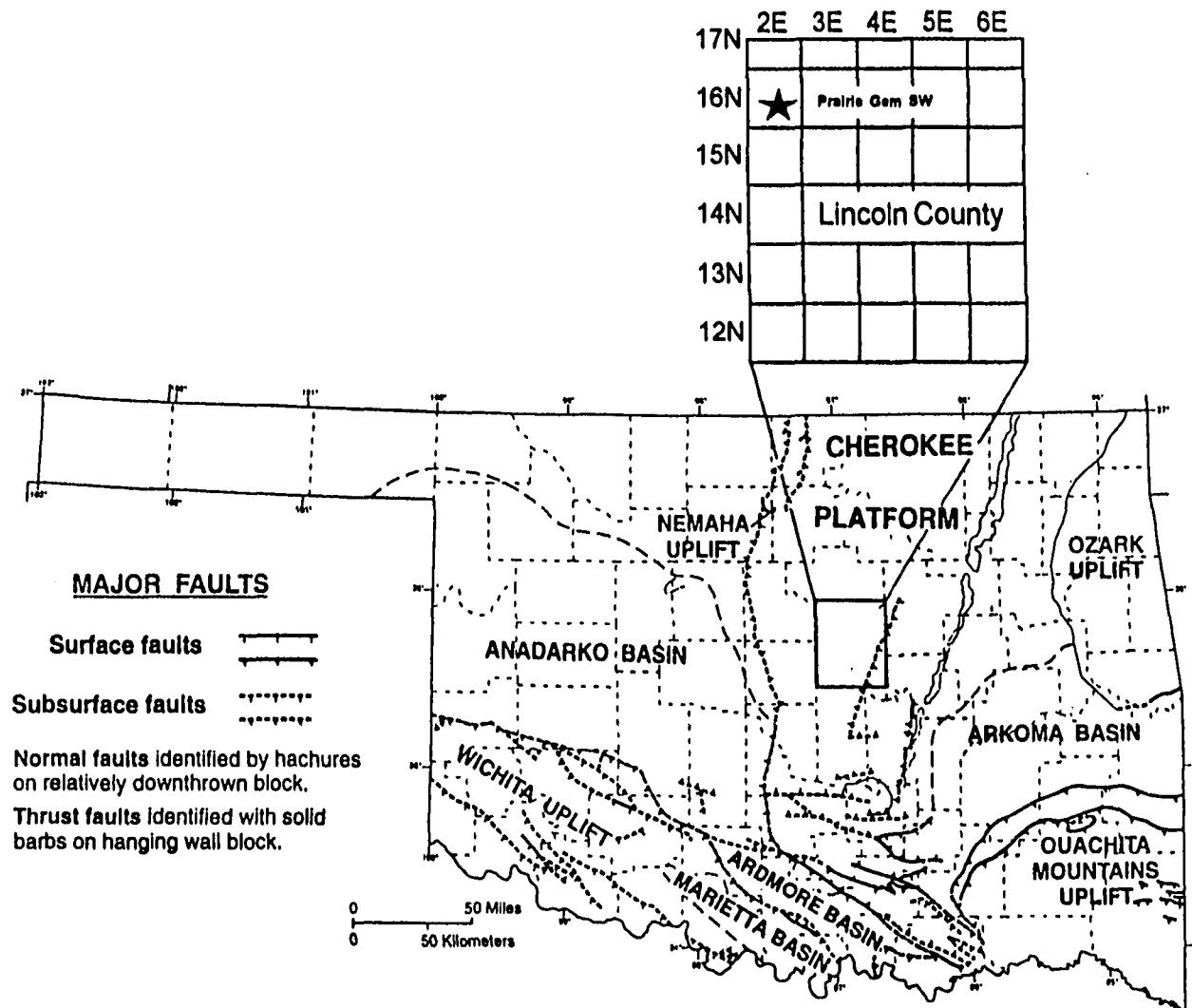


Figure III.1. Major geologic provinces of Oklahoma and location of Prairie Gem field (modified after Northcutt and Campbell, 1996).

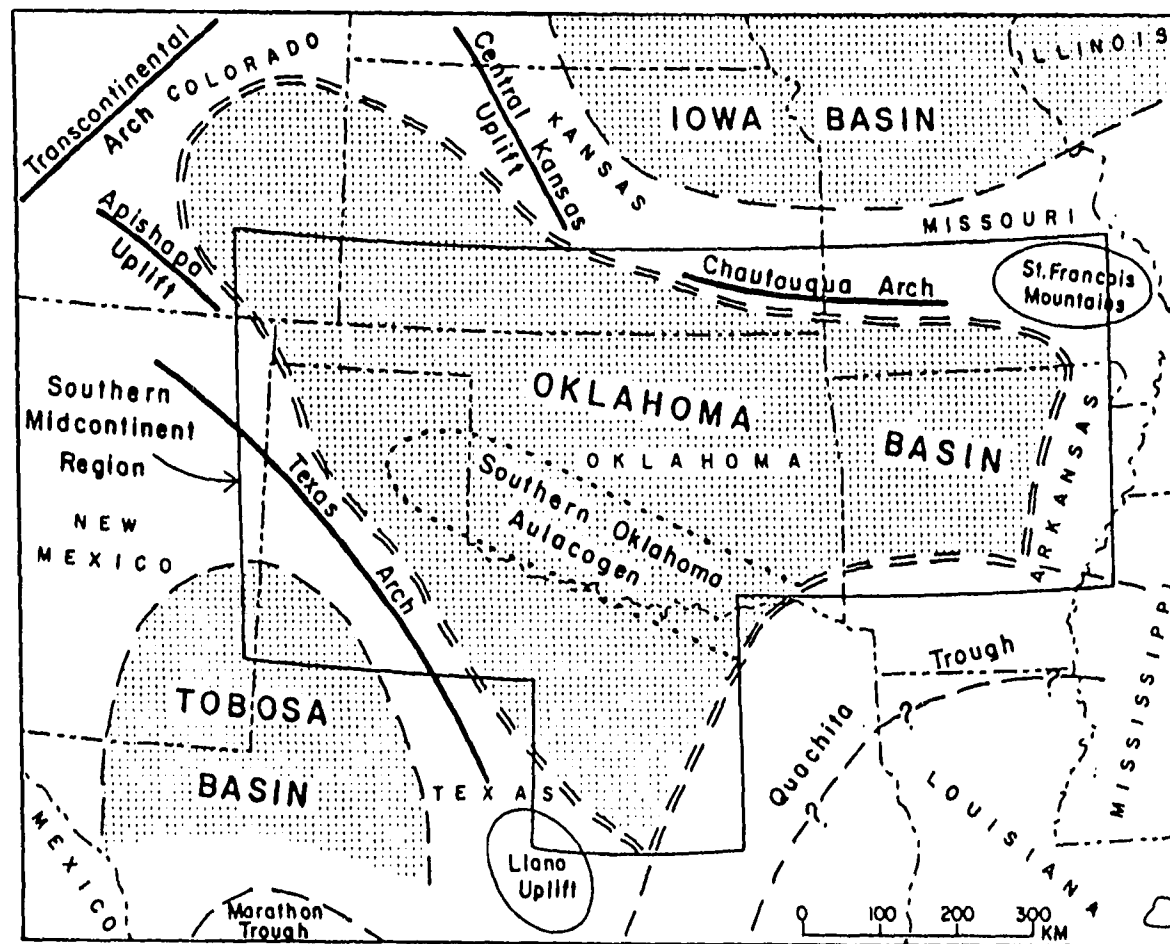


Figure III.2. Map of southwestern United States, showing approximate boundary of the Oklahoma Basin and other major features that existed in early and middle Paleozoic time (after Johnson *et al.*, 1988).

transform fault or as an intersection of two “successful” arms of a three-armed radial rift (rift-rift-rift triple junction; Thomas, 1991). By early Late Cambrian time, a passive margin had been formed along the entire rift system and during the Late Cambrian to Early Mississippian time, the continental margin was trailing and passive. The Wilson cycle involving the southern margin of the North American craton ended in the Mississippian time with the closing of the Paleozoic proto-Atlantic Ocean, and the collision of Gondwana with North America leading to the assembly of Pangea (Arbenz, 1989).

Three major tectonic phases characterized the Phanerozoic evolution of the Southern Mid-continent (Johnson *et al.*, 1989). An early phase of broad subsidence and epeirogenic movements during Late Cambrian through Mississippian, an orogenic phase characterized by uplift and deep subsidence during Pennsylvanian, and a late phase of infilling the basins and epeirogenic movements starting in Permian. During most of the Middle Paleozoic until Pennsylvanian time, three major tectonic provinces existed in Oklahoma: Oklahoma Basin, southern Oklahoma aulacogen, and Ouachita trough (**Figure III. 2**). The Oklahoma Basin was a broad, shelf-like region with predominantly carbonate sedimentation encompassing the Cherokee Platform and the Arkoma protobasin. The southern Oklahoma aulacogen was a depocenter of the Oklahoma basin, and included the Anadarko, Ardmore, and Marietta protobasins, the Arbuckle anticline, and the Wichita Mountain uplift. The Ouachita trough, located along the Ouachita rift margin, was a site of deep-water sedimentation. Most authors agree that by the end of the Early Mississippian, the Ouachita basin became a narrowing trough receiving vast amount of clastics and some southern sourced volcanics. During the Middle Mississippian through Middle Pennsylvanian (late Atokan) time, flysch deposition with very high sedimentation rates was the dominant process for the Ouachita trough (Arbenz,

1989). A series of orogenic pulses in the aulacogen and the Ouachita orogen caused or contributed to the development of the widespread pre-Pennsylvanian unconformity (Late Mississippian-Early Pennsylvanian time), the raising of the Wichita (Wichita orogeny of late Morrowan-early Atokan time), folding and thrusting of the Ouachita foldbelt (Wichita orogeny of Desmonesian-post-Krebs), Arbuckle (Arbuckle orogeny of Late Pennsylvanian time), Nemaha, and Ozark uplifts, and the pronounced down-wrapping of the Anadarko, Ardmore, Marietta, and Arkoma basins during Early, Middle and Late Pennsylvanian time (Johnson et al., 1989).

The Mesozoic, Tertiary and Quaternary evolution in Oklahoma is characterized mainly by erosion. Remnants of Triassic, Jurassic, Cretaceous, Tertiary and Quaternary strata are present mainly in the western parts of Oklahoma. The deposition of these sediments was not influenced by the tectonic provinces that were so pronounced in Pennsylvanian and Permian. The last great marine incursion in the region occurred during Cretaceous when a seaway from west to east covered a part of Oklahoma. The Laramide orogeny during Late Cretaceous-Early Tertiary time which caused the formation of the Rocky Mountains resulted in the withdrawal of the Cretaceous sea and establishment of a eastward and southeastward tilt of the entire region (Johnson et al., 1989).

Regional stratigraphy

The geology of Oklahoma is complex but is remarkably well understood based on the numerous investigations in the region (e.g., Oakes, 1953; Huffman, 1959; Dogan, 1970; Pulling, 1979a and b; Campbell et al., 1988; Johnson et al., 1989; Johnson and Cardott, 1992; Northcut and Johnson, 1996; Andrews et al., 1996; Andrews et al., 1997a; Andrews et al., 1997b). Generalized correlation stratigraphic chart of rock units between different sedimentary basins in Oklahoma is presented in **Figure III. 3**. The brief summary that follows is based on previously published works, and will cover mainly the lithological characteristics and depositional environments of the Paleozoic sequence in

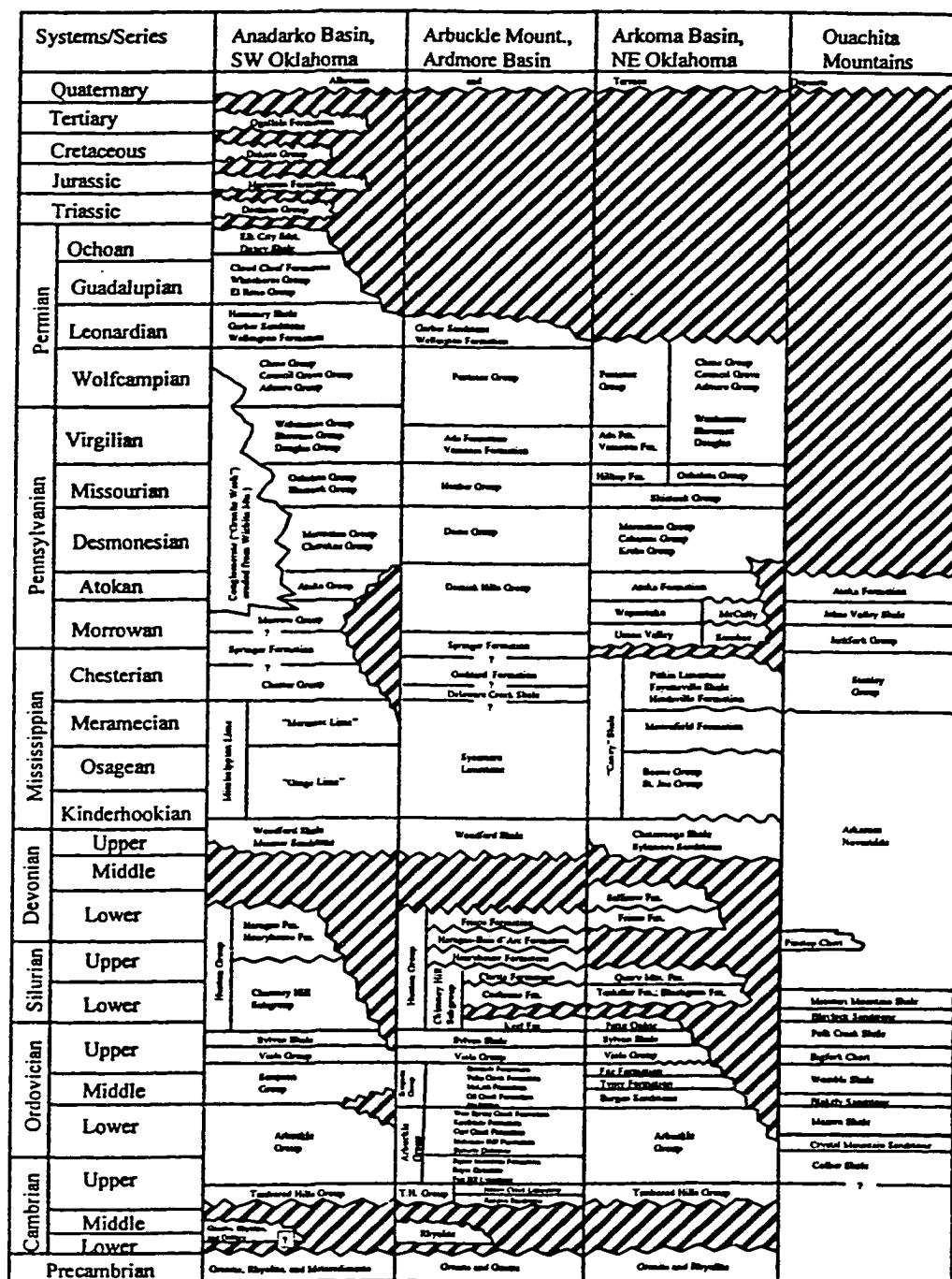


Figure III.3. Generalized correlation of rock units in Oklahoma (from Johnson and Cardott, 1992, based on COSUNA charts by Hills and Kottlowski, 1983; Mankin, 1987).

Cherokee Platform, and adjacent Anadarko and Arkoma Basins. The sequence in these regions includes all of the recognized source rocks and reservoirs in the region.

The pre-Pennsylvanian strata in Oklahoma are mainly shallow-marine carbonates (limestones and dolomites) interbedded with sandstones and shales. As result of the tectonic stability of the craton during this geological period, these strata are widespread and laterally persistent within the Oklahoma Basin. The region was a part of a vast shallow-water platform extending from New York to New Mexico. The Cambrian sequence starts with a basal sandstone reflecting a sea transgression from south and east over a relief of mostly granitic igneous rocks, and grades upward into a succession of shallow-water carbonates. The widespread pre-middle Early Devonian and pre-Late Devonian-Early Mississippian unconformities in the region are result of two major epeirogenic uplifts (**Figure III. 3**). Strata as old as Late and Early Ordovician were eroded during the pre-middle Early Devonian and pre-Late Devonian uplifts, respectively. In late Middle Devonian to early Late Devonian time, a sea transgression from the east resulted in the deposition of the Woodford-Chatanooga black shales. The withdrawal of the Woodford sea was followed by a transgression of shallow, well oxygenated, warm marine waters in Early Mississippian time favorable for deposition of oolitic and crinoidal limestones (Mississippi limestone). In Arkoma Basin, the deposition during this period consisted mainly of calcareous shales ("Caney" Shale). The deposition of sediments in the Late Mississippian (Chesterian) sea was in normal marine waters and resulted in a sequence mainly of shales with some limestones. During this time, an increasingly important factor affecting the sedimentation in the basin became the evolution of the Ouachita Trough (including the future Arkoma and Ardmore Basins), which had been subsiding intensively, with deposition resulting in more than 1500 m thick turbidite shale sequence (Stanley Group). The total thickness of the Mississippian strata is largest in the western part of Anadarko (about 1000 m) and southern part of Arkoma Basins (more than 750 m), reflecting an increasing rate of subsidence in the

centers of the ancestral basins to become predominant in the Pennsylvanian time. The Mississippian-Pennsylvanian boundary is well marked by the pre-Pennsylvanian unconformity, result of an epeirogenic uplift, attributed by some authors to the broad upwrapping of the transcontinental arch (Rascoe and Adler, 1983). In areas with uninterrupted sedimentation (central Anadarko, Ardmore, Arkoma Basins), the Mississippian-Pennsylvanian boundary occurs within the Springer and equivalent Formations (**Figure III. 3**).

The Pennsylvanian sequence in Oklahoma is significantly different in the type of accumulated sediments and reflects the active tectonic history of the region during this time. It consists of marine and non-marine shales, sandstones, conglomerates, and limestones with considerable thicknesses (about 5000 m) formed in the rapidly subsiding basins (Anadarko, Ardmore, Marietta, Arkoma). In the shelf or platform areas, the thicknesses of the Pennsylvanian sequence are in the range of 500 to 1200 m.

During Early Pennsylvanian time (Morrowan and Atokan), most of the Cherokee Platform was land and source of clastic material mainly for the Anadarko Basin where shallow marine sediments (shales, sandstones, limestones) constitute the lower part of the Morrowan sequence, overlain by deposits formed in the progradation phase of deltaic systems, and changing upward to the cyclic sequence of thin marine limestones and shales formed in Atokan time. The contact of Morrowan with Atokan series in the Anadarko Basin ranges from progradational to disconformable. Locally on the northern shelf of the Anadarko Basin, the Atokan series oversteps the limit of the Morrowan series and unconformably onlap Mississippian rocks. In the Arkoma Basin, during Early Morrowan time, the sea transgressed north from the Ouachita Trough onto the Arkoma shelf and deposits characteristic for a shallow-marine bank facies were formed while turbidite deposition continued in the Ouachita Trough to the south. The Atokan sequence in Arkoma Basin is markedly different from the synchronous deposits in the Anadarko Basin mainly due to the much more rapid subsidence in Arkoma Basin, and the existence

of uplifts along the Nemaha tectonic zone which separated the basins. The sequence is represented by thick series of clastic rocks. The development of syndepositional east-trending normal faults was characteristic for the deposition of the middle of Atoka Formation interval (as described in Johnson et al., 1989), and was associated with the beginning of the flexural bending of the southern part of the Arkoma Shelf (which included southern Ozark Uplift and Arkoma Basin) resulting from the continued basin closure. The earliest development of these faults is suggested to have occurred first in the southernmost parts, and that the active faulting migrated northward with time. Thus, the lower Atoka predates such faulting, and the upper Atoka postdates it. The Upper Atoka sediments were deposited in the fully developed Arkoma Foreland Basin.

During Middle Pennsylvanian (Desmonesian) time, the geological development of the Cherokee Platform was largely determined by the development of the Arkoma Basin, and folding of the Ouachitas. The Desmonesian series consists of three groups - Krebs, Cabaniss and Marmaton, with the subsurface equivalent of the first two being the Cherokee Group (**Figure III. 4**). McAlester to Boggy Formations depositional patterns included several major northwestward transgressions followed by regressive southward progradations of fluvial/deltaic systems across the shelf and into the Arkoma Basin. The thicknesses of these Formations show marked increases southward into the subsiding foreland Arkoma Basin. The largest deltaic complex of that time formed the Bartlesville-Bluejacket Sandstone Member of the Boggy Formation. This fluvial system extended through the eastern Kansas and eastern Oklahoma, and entered the Arkoma Basin as an extensive fluvial-dominated deltaic complex. The source of sediments is considered to have been to the north. The thickness of Boggy Formation in the Arkoma Basin reaches 610 m while on the shelf its thickness is less than 150 m. Johnson et al. (1989) suggest that the initial uplift of the Ozark Mountains occurred during late Early Desmonesian time, based on the southwestward deflection in the distribution of the Bartlesville-Bluejacket deltaic complex. Following the Krebs Group deposition, uplift, erosion, and

folding of the Arkoma foreland basin took place. This event is marked by the deposition of the Thurman Sandstone (present only in Arkoma Basin) consisting of fluvial chert-pebble conglomerates transported from the southeast in a narrow successor of Arkoma basin, and they are the first indication for significant uplift of the Ouachita Foldbelt (**Figure III. 4**). Boggy and pre-Boggy rocks are more complexly folded and faulted than the post-Boggy strata and there is a marked difference in strike between them. In addition, some southwest-trending faults, probably associated with the Ozark Uplift, cut the Boggy but do not cut post-Boggy strata (Oakes, 1967). During the deposition of the remainder of the Desmonesian Cabaniss and Marmaton Groups, the successor basin continued to receive terrigenous sediments from the erosion of the Ouachita Foldbelt. The Ouachita Mountains continued to be a primary source of terrigenous sediments to Arkoma through the remainder of Pennsylvanian and into Permian. At the same time, to the northwest in the Cherokee Platform, another fluvial-deltaic (Skinner and Prue) systems developed with northward source of the sedimentary material.

In the Anadarko Basin, the Desmonesian Series consists mainly of cyclic marine limestones and shales, with some lenticular point bar and channel-fill sandstones in the northern shelf areas. The sequence of the Late Pennsylvanian Missourian Series in Anadarko Basin is represented by carbonates at the shelf, which changes to the south to shales and fine-grained sandstones. The Arbuckle Uplift and the Wichita-Amarillo Uplift were active major positive tectonic elements during Missourian time. During Late Pennsylvanian (Virgilian) time, continental to shallow marine shales, siltstones, and mudstones were deposited in central Oklahoma, and prodelta shales and delta-plain sandstones formed in the Anadarko Basin. Wedges of clastic material derived from the Ouachita Mountains accumulated along the eastern margin of the Anadarko Basin during regressive phases of cyclic sedimentation, while carbonate deposition dominated during the transgressive periods. In this manner, a constructional shelf was established along the eastern margin of the Anadarko Basin in Virgilian time.

Local structural elements

In the regional tectonic framework described earlier, the Prairie Gem field (T. 16 N., R. 2 E.; Lincoln Co.) is located on the Cherokee Platform, about 20 miles east of the Nemaha tectonic zone, 20 miles N-NW of the Seminole Cushing ridge and Wilzetta fault zone, and about 90 miles west of the Ozark uplift (**Figure HI. 1**).

The Nemaha tectonic zone divides the Oklahoma Platform into eastern (Cherokee) and western (Anadarko shelf area) parts. The tectonic zone is 400 miles long and extends from Nebraska through eastern Kansas, and into Oklahoma to terminate in the Oklahoma City uplift. The structure is believed to have been an integral part of the 1.1 Ba old Mid-continent rift system, and the results of seismic surveys suggest that the rift system extends to depths above 30 km (Berendsen and Blair, 1995). The Nemaha tectonic zone in Oklahoma consists of crustal blocks typically 5-8 km wide and 8-32 km long, bounded by faults mainly on the east and/or west side (Luza, 1995). Mississippian and older beds are tilted and eroded on the flanks of the uplift, and overlapped by Middle Pennsylvanian strata, which locally lie even on Precambrian rocks (Huffman, 1959). The Nemaha uplift is believed to have been a positive structural feature during most of the Paleozoic time. The major timing of its formation, however, is considered to be in the post-Mississippian (late-post-Morrowan time) related to the Wichita orogeny and the subsidence of the Anadarko Basin (Pulling, 1979a; Joseph, 1987; Berendsen and Blair, 1995). A number of small crustal blocks have been raised sharply along its axis zone (Luza, 1995). An extension of the Nemaha tectonic zone to the south is the Oklahoma City uplift formed in post-Mississippian and pre-Middle Pennsylvanian (probably post-Morrowan) time (Huffman, 1959). The eastern flank of the uplift is characterized with a large fault. According to Luza (1995), the displacement for most of the Oklahoma City faults took place between the end of Devonian (Hunton) time and the end of Middle Pennsylvanian (Oswego) time. Further southern extension of the Nemaha tectonic zone is the McClain County fault zone ending at the Pauls Valley uplift, with a maximum

displacement of 2300 feet. This fault zone represents a major zone of shearing between the Central Oklahoma Platform and the Anadarko basin (Pulling, 1979a). The fault zone is considered active after the deposition of the Springer formation and during the deposition of the Cherokee Group sediments. The initial uplift in Pauls Valley area is considered to have occurred in post-Morrowan time with possible later movements during Late Pennsylvanian (Missourian) related to the folding of Arbuckle Mountains.

The regional stratigraphic profiles and maps presented in previous studies suggest that Nemaha tectonic zone was a structurally and topographically positive feature during the deposition of the Cherokee Group (Dogan, 1970; Andrews et al., 1997a,b). The analysis of thicknesses could be influenced by a number of factors, including facies variations in sandstone deposition especially in fluvial dominated deltaic complexes, differential compaction between sand and shale dominated sequences, contemporaneous fault movement. The interpretation of Andrews et al. (1997a,b) suggests that different parts of the Nemaha tectonic zone have been tectonically active at different periods of time. Thus, the Nemaha tectonic zone in the northwestern part of Logan County has been completely buried by the end of Red Fork, while in the southern part of the same county the zone had not been active during the deposition of Cherokee Group, and just represented a structurally positive feature. A number of local faults in the adjacent areas (Oklahoma, Logan, Payne, Lincoln Counties) to the north, west and south of Prairie Gem are apparent on the Mississippian isopach map of Rottmann (1997). However, it is not clear if any of them were active at later times. A possible presence of a normal NW-SE fault located less than one mile W-NW of Prairie Gem field (NW part) is suggested based on the structure map on top of Pink lime by Shulman (1966). The Central Oklahoma fault zone is interpreted as completely buried by the end of Red Fork and Lower-Middle Skinner in the southern and northern parts of Oklahoma County, respectively (Andrews et al., 1996, 1997a and b).

Another structural element in close geographical proximity to the Prairie Gem field is the Seminole-Cushing ridge with the associated Wilzetta and Keokuk faults to the west and east, respectively. The Wilzetta fault is evident on structure maps on top of Viola, pre-Pennsylvanian unconformity and top of Verdigris in Pottawatomie County (Pulling, 1979a; Joseph, 1987). It appears to be completely buried by the end of the Prue sand deposition (Andrews *et al.*, 1997b). The initial uplift of Seminole-Cushing ridge is believed to have occurred in Middle Devonian time (after the deposition of Hunton Group) associated with major normal faulting along the western flank of the ridge - Wilzetta fault. During post-Mississippian to pre-Desmonesian time (Late Morrowan), major folding of Seminole-Cushing ridge, and rejuvenation of Wilzetta and other NE-SW trending faults took place related to the Pauls Valley uplift to the south. During this period of folding and faulting, the area was tilted toward the east. During Desmonesian time (Cherokee deposition) possible growth faulting with recurrent movement is suggested along Seminole Cushing ridge resulting in formation of thicker sequences on the downthrown side (Lozano, 1969; Pulling, 1979a; Joseph, 1987). In Late Desmonesian time, renewed movement of the Wilzetta fault is reflected on the Verdigris (top of Skinner) structure map of Pulling (1979a) and Joseph (1987). The regional stratigraphic profiles of Andrews *et al.* (1996, 1997a and b) along the western and eastern parts of the Wilzetta fault demonstrate significant thickness reduction mainly for Bartlesville and Lower-Middle Skinner intervals. It appears that the Seminole-Cushing ridge was a relatively high topographic feature on the paleorelief of Bartlesville deposition, and resulted in a reduced thickness of the interval over the ridge. The isopach maps of the interval between the Mississippian-Pennsylvanian unconformity to the base of Bartlesville have shown that a pre-Desmonesian fluvial-deltaic system existed along the ridge, and its distribution is very probable to have influenced the distribution of the overlying Bartlesville interval. The smaller reduction of the Red Fork, compared to the Bartlesville, interval thickness along the western-eastern flanks of the Wilzetta fault

suggests that by the end of Red Fork deposition the topographical lows resulting from the earlier activity of the ridge are almost leveled off. The significant reduction in the thickness of the Lower-Middle Skinner interval is suggestive for some activation of the fault during this time leading to deposition of greater thicknesses along the downthrown western flank of the fault in correspondence with the previous suggestions of Joseph (1987) for the southern portions of Lincoln County. Activation of the fault during the deposition of lower part of Skinner interval appears to be in accordance with the regional folding in Arkoma Basin considered to occur at the beginning of Cabaniss time (**Figure III. 4**). Differential compactions of shale versus sandstone dominated sequences as well as non-deposition or erosion may influence the resulting present day thicknesses, and these factors can not be completely ruled out.

The eastern part of the Seminole-Cushing ridge is bound by the Keokuk fault. The fault is considered completely buried by the end of deposition of the Red Fork interval, apparently much earlier than the western part of the ridge (Wilzetta fault). The difference in the latest timing of activation between the western and eastern flanks of the ridge may be related to the tectonic activity associated with McLain fault and Pauls Valley uplift. Several other faults are suggested on top of Pink lime further NE in Creek County (Hanke, 1967), appearing to be related to the Wilzetta faults to the southwest. West-ward tilting of the area is considered to occur in post-Permian, pre-Cretaceous time (Pulling, 1979a) or at the close of Permian time (Joseph, 1987). Finally, the uplift of the Rocky Mountains in Late Cretaceous and Early Tertiary time established the regional eastward tilting of the Southern Midcontinent, including Cherokee Platform, and the dominant east-flowing river systems (Johnson et al., 1989).

The Ozark Uplift marks the eastern boundary of the Cherokee Platform in Oklahoma. Its present elongation is considered formed during Middle Pennsylvanian time when it underwent a gentle arching and normal faulting along its flanks. Rocks from Precambrian to Middle Pennsylvanian are exposed on the surface in this region.

The analysis of thicknesses of the intervals Brown lime-Verdigris Limestone (Bartlesville to top of Skinner) versus Verdigris Limestone-Checkerboard (upper part of Desmonesian to Missourian), from north to south along the Cherokee Platform, suggests the subsidence to the south increased compared to the northern areas during Late Desmonesian and Missourian time (Dogan, 1970).

The interpretation of paleotransport directions of sand material, especially in fluvial dominated sequences can give indication regarding the paleoslopes in the region. The dominant transport direction during the deposition of the lower part of Desmonesian sequence (Mississippian-Pennsylvanian unconformity to end of Red Fork) is north-south-southeast (Andrews et al., 1997 a and b) while during the deposition of Skinner interval north-south as well as additional well developed west-east trends could be traced (Verish, 1979).

Appendix IV. 2. 1. Calculation of the average length and volume of n-alkanes (C₅-C₁₂₀)

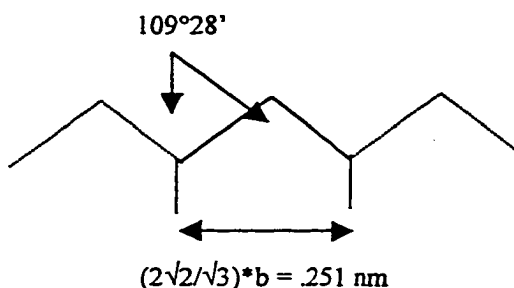
The followed calculation procedure is described by Laidler and Meiser (1995) for linear polymers.

A. Average length (l) calculation of n-alkane molecule.

$$(1) \quad l = b \cdot (8N/3\pi)^{1/2},$$

where b is C-C bond length (0.154 nm), N is number of C-C bonds.

The maximum extension of a hydrocarbon chain occurs when alternate carbon atoms are in a straight line as shown below



Since the angle between carbon-carbon single bonds is the tetrahedral angle, 109°28', in a fully extended hydrocarbon chain, the effective bond length could be approximated as $b \cdot \sqrt{2}$ and the distance between alternate carbon atoms can be estimated as $2\sqrt{2}/\sqrt{3} = 1.633 \cdot b = 0.251 \text{ nm}$. The length (nm) of a fully extended hydrocarbon chain with N carbon-carbon bonds thus can be calculated as $(N/2) \cdot 0.251$.

The effective bond length, considering the tetrahedral angle between C-C bonds, approximated as $b \cdot \sqrt{2}$ gives 0.218 nm. Using Equation (1), the average length in nanometers of a n-alkane chain is calculated as $l = 0.218 \cdot (8N/3\pi)^{1/2}$.

B. Volume calculation of n-alkane molecule.

A somewhat realistic estimate of the volume of a molecule is proposed to be obtained if considering a volume of a sphere with a radius equal to $\sqrt{(l^2/6)}$, where l is the average length of a molecule. Then, the volume is calculated as $V = (4/3)\pi(\sqrt{(l^2/6)})^3$.

Appendix IV. 2. 2.

References to experimental studies on crystal behavior of pure n-alkanes and n-alkane mixtures discussed in the text

<u>Pure n-alkanes</u>	Carbon number range	References*
odd	C ₁₉ -C ₂₉	1, 2, 3, 4, 5
even	C ₁₈ -C ₃₆	3, 6
	>C ₃₆	4
<u>Binary mixtures</u>		
odd-odd	C ₁₉ -C ₂₅	7, 2, 3
even-even	C ₂₀ -C ₃₆	5, 8, 9, 7, 10
	>C ₃₆	9, 4
even-odd	C ₂₂ -C ₃₃	9, 7
<u>Ternary mixtures</u>		
even	C ₂₀ -C ₃₆	9
	>C ₃₆	9
<u>Quaternary mixtures</u>		
even	C ₂₂ -C ₃₆	9, 11
<u>Multicomponent (>4 components) mixtures and petroleum derived waxes</u>		
even CN dominated	C ₂₀ -C ₃₃	11
continuous even-odd	C ₂₀ -≈C ₅₈	11, 7, 12, 13, 14, 15

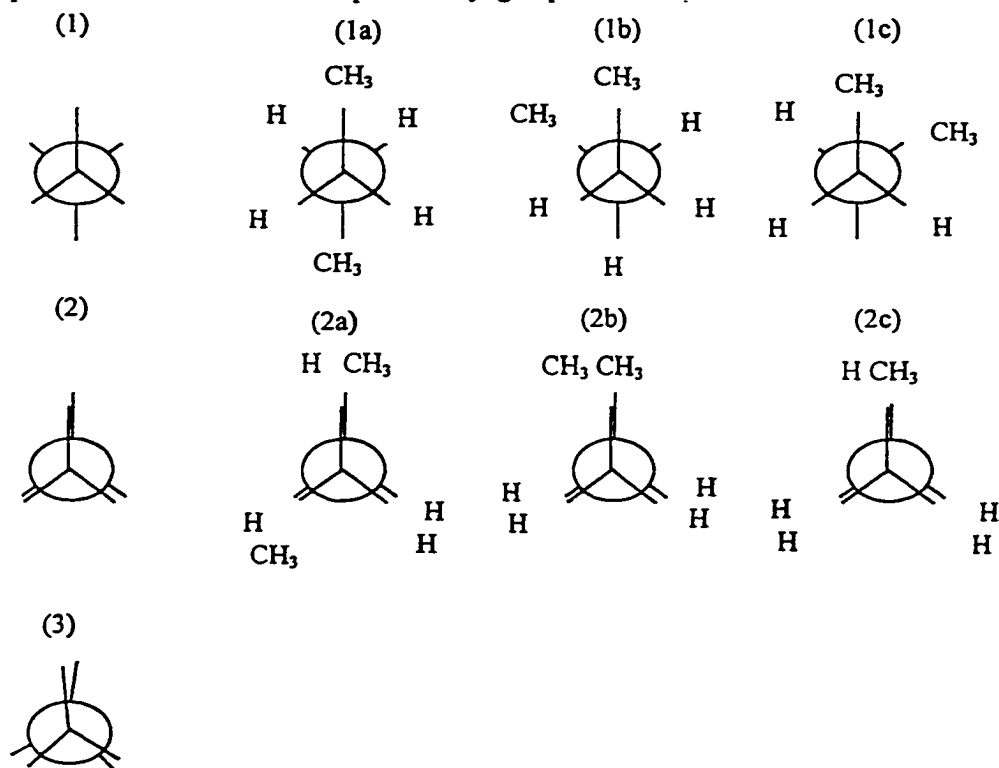
* Note: 1 Maroncelli *et al.* (1985); 2 Ungar (1983); 3 Schaerer *et al.* (1955); 4 Kim *et al.* (1989); 5 Achour *et al.* (1995); 6 Ohlberg (1959); 7 Dirand *et al.* (1998); 8 Chevallier *et al.* (1999b); 9 Clavell *et al.* (1997); 10 Achour *et al.* (1996); 11 Chevallier *et al.* (1999a); 12 Handoo *et al.* (1989); 13 Srivastava *et al.* (1992); 14 Srivastava *et al.* (1993); 15 Srivastava *et al.* (1995).

Appendix IV. 2. 3. Molecular conformations in n-alkanes (after Solomons, 1980)

Groups in a molecule bonded by a single bond can undergo rotation about the bond with respect to each other. Different arrangements of the atoms in space resulting from rotations of groups about single bonds are called conformations. Conformational analysis is the analysis of energy changes that a molecule undergoes as groups rotate about single bonds.

Newman projections (viewing the molecule from one end along the carbon-carbon bond axis) where bonds of the front carbon are presented as , and those of the back carbon as  for staggered conformation (1), eclipsed conformation (2), skewed conformation (3).

Rotation about C2-C3 bond of butane (C_4H_{10}) – 1a, 1b, 1c, 2a, 2b, 2c. Among the staggered conformations, the anti conformation (1a) is the most stable, with the gauche conformations (1b and 1c) having ≈ 0.8 kcal/mol more energy than the anti conformation. The methyl groups in gauche conformations are so close to each other that the electron clouds of the two groups repel each other and the van der Waals forces between them are repulsive. The eclipsed conformations (2a,b,c) have higher potential energy and are less stable due to torsional strain of the molecule. In the case of 2a,c conformations, the potential energy of molecule is increased by the van der Waals repulsions arising from eclipsed hydrogen and methyl groups while the eclipsed conformation 2b has the greatest energy of all because of the large van der Waals repulsive force between the eclipsed methyl groups.



Appendix IV. 2. 4

Methods for calculation of solubility parameter (δ) from physical constants

1. From Heat of Vaporization.

$$\Delta E_{25^\circ\text{C}} = \Delta H_{25^\circ\text{C}} - RT,$$

where ΔH is the latent heat of vaporization at temperature T (K), R is gas constant.

Hilderbrand's equation for nonpolar liquids:

$$\Delta H_{25^\circ\text{C}} = 23.7 T_b + 0.020 T_b^2 - 2950$$

where T_b is the boiling point.

2. From thermal coefficients:

$$\delta \approx (\alpha T / \beta)^{1/2}$$

3. From relationship of pressure to temperature.

δ may be calculated from $(TdP/dT)^{1/2}$, where dP/dT must be determined at constant volume.

4. From van der Waals' Gas Constant.

$$\delta \approx 1.2 a^{1/2} / V$$

5. From Critical Pressure.

$$\delta \approx 1.25 P_c^{1/2}$$

6. From Surface Tension.

Hilderbrand and Scott (1949) equation

$$\delta = 4.1 (\gamma / V^{1/3})^{0.43}$$

where γ is the surface tension.

7. From Kauri-Butanol Values.

$$\delta = 6.3 + 0.03 (KB)$$

8. From Structural Formula.

$$\delta = d \sum G / MW$$

where d is density, $\sum G$ is the sum of molar attraction constants for all the atoms and groupings in a molecule, MW is molecular weight.

Appendix IV. 2. 5.

Intermolecular interactions accounted for by the solubility parameter concept

Induced dipole-induced dipole attractive forces (dispersion or London forces) are present in all molecules, polar and nonpolar, as indicated by quantum mechanical considerations (Grant and Higuchi, 1990). They arise from the instantaneous dipole moments formed when partially polarized bonds (one example is C-H bond) are brought to within an interaction distance. In a given instant, the electrons and charge may be slightly accumulated on one side of the molecule and thus cause a small temporary dipole to occur. This dipole in one molecule can induce instantaneous opposite dipoles in surrounding molecules by distorting their electron clouds. As a result, the electron densities and charge in the molecules shift in opposite directions (e.g., towards carbon in one molecule and towards hydrogen in the other). The dipole of each of the carbon-hydrogen bonds is thus changed in a small way, and causes the instantaneous existence of a dipole moment referred to as induced dipole moment. The result is an increased attraction between the electrons of one carbon-hydrogen bond and the positive charge of the nucleus of the other. This type of forces causes nondirectional attractions to exist between the molecules. Even though the temporary dipoles change constantly, the net result of the dispersion forces in nonpolar substances is represented by weak attractive forces between the molecules and thus makes possible the existence of their liquid and solid physical states.

The London equation of the energy contributed by the dispersion interaction between two similar molecules is given by:

$$E_d \cong \frac{3\alpha^2 I}{4r^6} \quad (\text{IV. 2. 1})$$

where α - molecular polarizability, I - ionization potential, and r - distance of separation of molecules.

Dispersion forces are the main way of interaction between nonpolar molecules. However, even between polar molecules, dispersion forces may predominate over the other attractive forces. Because of the ubiquity and similarity in strength of these forces in different molecules, their usage as to provide selectivity in solubility phenomena is generally considered to be restricted (Peiffer *et al.*, 1980; Grant and Higuchi, 1990).

Permanent dipole-permanent dipole forces exist between polar molecules with a permanent electric dipole moment μ , which are all polarizable to an extent represented by the polarizability α . Dipole moment is a vector, and the overall dipole moment of a molecule is a vectorial sum of the dipole moments of all its bonds and groups. Because of that, the direction of dipole-dipole forces affects the strength of this interaction, and in this way they differ from the dispersion molecular forces. In addition, polar forces are usually stronger than the dispersion forces. The contribution to the energy of interaction due to the polar dipole-dipole attractions is given by the following equation

$$E_p = \frac{2\mu^4}{3kTr^6} \quad (\text{IV.2.2})$$

where μ - permanent dipole moment, k - Boltzman constant, T - absolute temperature, r - distance of separation of molecules.

Dipole-induced dipole forces (Debye forces or induction effect) exist between polar and nonpolar molecules. As a result of its polarizability, a given molecule may participate in an attractive interaction with a neighboring polar or nonpolar molecule. The interaction between a dipole and a nonpolar molecules sets an induced charge in the latter resulting in attractive interaction between them. The induction effect increases the attraction between already polar

molecules, and causes an attraction between a polar and a polarizable nonpolar molecule. For two similar molecules, the contribution of dipole-induced dipole forces to the energy of interaction is given by

$$E_i = \frac{2\alpha\mu^2}{r^6} \quad (\text{IV. 2. 3})$$

where α - polarizability, μ - dipole moment, r - distance of separation of molecules. The energy is attractive, independent of temperature, and can exist provided that at least one of the molecules is polar (Grant and Higuchi, 1990).

The contribution of the dipole-induced dipole (Debye) forces to the total intermolecular energy of interaction is generally considered to be of less importance compared to the other two electrostatic (dipole-dipole and dispersion) forces. However, Debye interactions are often stronger than dispersion forces for highly polar molecules in solvents of low polarity, and comparable to dipole-dipole forces for polar molecules in weakly polar aromatic solvents as discussed by Grant and Higuchi (1990). Peiffer *et al.* (1980), also, pointed out that dipole-induced dipole forces may have a significant effect on the solubility if the dipolar interaction between the molecules is zero or close to zero. The dipole-induced dipole interactions, for example, explain the formation of complex crystal lattices of both very polar and polarizable molecules as well as why a polar compound such as benzil is fourteen times more soluble in the nonpolar but polarizable solvent carbon tetrachloride than in the nonpolar but poorly polarizable solvent n-hexane (Grant and Higuchi, 1990). The same authors suggested that the selectivity of this type of forces could be very useful in explaining and promoting selectivity in solubility phenomena and separation sciences.

Hydrogen bond. Hydrogen is unique among the elements in that all of its electron density is used in bonding when combined with other elements. By sharing electron density with a neighboring atom, the hydrogen nucleus is relatively exposed on the side opposite the bond. Thus, hydrogen atoms interact with the electron density surrounding other atoms in the same or other molecules by weak, but significant, electrostatic interactions. When this attraction is to the electrons of another σ bond, it is called a van der Waals attractive interaction. Hydrogen bond is the term used when the attraction is between a hydrogen atom participating in a polar covalent σ bond and an atom with one or more accessible pairs of electrons (Fox and Whitesell, 1994).

The hydrogen bond is an intermolecular or intramolecular interaction which has a strength similar to that of van der Waals forces but is directional. Hydrogen bond is an electrostatic, spatially oriented, weak interaction between a hydrogen atom participating in a moderately polar covalent σ bond and another electronegative atom bearing at least one lone pair of electrons, as in one of the heteroatoms N, O, P, or S, or a halogen (F, Cl, Br, or I). The magnitude of this attractive interaction increases with the electronegativity of the heteroatom. Strongest hydrogen bonds are formed with N, O, and F. The chlorine and sulfur can sometimes form weaker hydrogen bonds. The hydrogen bond includes total of three atoms: the hydrogen atom and two heteroatoms (typically), both of which are attracted to this single proton. In any hydrogen bond, Debye and London forces will supplement the forces of electrostatic attraction and electron delocalization (or orbital overlap) (Grant and Higuchi, 1990).

Appendix IV. 2. 6.

Methods for solubility parameter calculations of HMW n-alkanes

Method 1: $\delta = d\Sigma G/MW$ where δ - total solubility parameter, d - density, ΣG - sum of group molar attraction constants, MW - molecular weight.

Molar constants (Small, 1953) and density correlations (Riazi and Al-Sahhaf, 1995; Jianzhong *et al.*, 1998)

Method 2: $\delta = d\Sigma G/MW^{***}$ (9)

Molar constants (Hoy, 1970) and density correlations (Riazi and Al-Sahhaf, 1995; Jianzhong *et al.*, 1998)

Group molar attraction constants ($\text{cal}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$):		
	G	G
	Small (1953)*	Hoy (1970)**
-CH ₃	214	147.3
-CH ₂ -	133	131.5

* derived from measurements of heat of evaporation

** derived from measurements of vapor pressure

*** solubility parameter unit conversion: $1 \text{ cal}^{1/2} \text{cm}^{3/2} = 2.05 \text{ J}^{1/2} \text{cm}^{3/2} = 2.05 \text{ MPa}^{1/2} = 6.4 \text{ atm}^{1/2}$

Density correlations for HMW n-alkanes

1. Riazi and Al-Sahhaf (1995)

$$\ln(0.859 - d_{20}) = 88.01379 - 85.7446 \times MW^{(0.01)}$$

where d_{20} - density at 20°C, MW - molecular weight. Limiting value of 0.859 as MW of n-alkanes approaches ∞ .

2. Jianzhong *et al.* (1998)

$$SG^{\circ} = 0.6262 \times (1 + 0.66878721 \times 10^{-1} \times \epsilon_{sg} + 0.59212241 \times 10^{-2} \times \epsilon_{sg}^2) / (1 + 0.62791972 \times 10^{-1} \times \epsilon_{sg} + 0.42682682 \times 10^{-2} \times \epsilon_{sg}^2)$$

where SG° - specific gravity as ratio of density of n-alkane at 20°C to density of water at 4°C;

$$\epsilon_{sg} = (MW - 72.1486)^{2/3};$$

MW - molecular weight of n-alkane.

Method 3: $\delta = (\Delta E/V)^{1/2}$

where $\Delta E = \Sigma \Delta e_i$ and $V = \Sigma \Delta v_i$ and δ - total solubility parameter, ΔE - energy of vaporization, V - molar volume, Δe_i - additive atomic and group contribution to the energy of vaporization, Δv_i - additive atomic and group contribution to the molar volume (Fedors, 1974).

	Δe_i cal/mole	Δv_i cm ³ /mole
-CH ₃	1125	33.5
-CH ₂ -	1180	16.1

Appendix IV. 2. 7.

Quantitative HTGC results for n-alkane carbon number (CN) distributions in solutions of Polywax 1000 in carbon tetrachloride, cyclohexane and p-xylene

CN	Polywax 1000 solutions in								
	Carbon tetrachloride			Cyclohexane			p-Xylene		
	area	ng/μl	mg/g	area	ng/μl	mg/g	area	ng/μl	mg/g
16	241	0.1	0.2						
18	346	0.1	0.3						
20	505	0.2	0.4				1298	0.5	1.2
22	535	0.2	0.5	443	0.2	0.5	693	0.3	0.7
24	675	0.2	0.6	452	0.2	0.5	490	0.2	0.5
26	794	0.3	0.7	689	0.3	0.8	720	0.3	0.7
28	923	0.3	0.8	687	0.3	0.8	768	0.3	0.7
30	1218	0.4	1.0	879	0.4	1.0	964	0.4	0.9
32	1538	0.5	1.3	1014	0.5	1.2	1157	0.5	1.1
34	1996	0.7	1.7	1239	0.6	1.4	1575	0.6	1.5
36	2623	0.9	2.3	1664	0.8	1.9	1903	0.8	1.8
38	3469	1.2	3.0	2081	1.0	2.4	2406	1.0	2.3
40	4566	1.6	3.9	2664	1.3	3.0	3058	1.2	2.9
42	5934	2.1	5.1	3308	1.6	3.8	3700	1.5	3.5
44	7729	2.8	6.6	5028	2.4	5.7	4449	1.8	4.2
46	9937	3.5	8.5	5018	2.4	5.7	5043	2.0	4.7
48	12676	4.5	10.9	5925	2.8	6.7	5619	2.2	5.3
50	16201	5.8	13.9	6951	3.3	7.9	6101	2.4	5.7
52	20234	7.2	17.4	7973	3.8	9.1	6578	2.6	6.2
54	24757	8.8	21.3	9030	4.3	10.3	6891	2.7	6.5
56	29723	10.6	25.5	10096	4.8	11.5	7365	2.9	6.9
58	34812	12.4	29.9	11265	5.3	12.8	7881	3.1	7.4
60	39884	14.2	34.2	12530	5.9	14.3	8389	3.3	7.9
62	44789	16.0	38.5	13362	6.3	15.2	8860	3.5	8.3
64	49323	17.6	42.3	14303	6.8	16.3	9281	3.7	8.7
66	53138	18.9	45.6	15023	7.1	17.1	9596	3.8	9.0
68	55747	19.9	47.9	15970	7.5	18.2	9872	3.9	9.3
70	57135	20.4	49.1	15784	7.5	18.0	9885	3.9	9.3
72	55845	19.9	47.9	15026	7.1	17.1	9538	3.8	9.0
74	55495	19.8	47.6	14119	6.7	16.1	9335	3.7	8.8
76	53344	19.0	45.8	12561	5.9	14.3	8421	3.3	7.9
78	44455	15.8	38.2	10188	4.8	11.6	6515	2.6	6.1
80	33974	12.1	29.2	7479	3.5	8.5	5051	2.0	4.7
82				4023	1.9	4.6			

Appendix IV. 2. 8.

Quantitative HTGC results for n-alkane carbon number (CN) distribution in filtrates obtained at room temperature from carbon tetrachloride and p-xylene solutions of Polywax 1000.

	p-Xylene filtrate		Carbon tetrachloride filtrate	
CN	area	ng/μl	area	ng/μl
16	7166	2.0	2599	0.6
18	3780	1.1	9747	2.3
20	3644	1.0	17566	4.1
22	5461	1.6	23560	5.5
24	7073	2.0	29182	6.8
26	8533	2.4	36320	8.5
28	10448	3.0	44262	10.3
30	13268	3.8	53816	12.6
32	17280	4.9	65082	15.2
34	22646	6.5	77590	18.1
36	29200	8.3	86624	20.2
38	37315	10.7	86839	20.3
40	46546	13.3	77851	18.2
42	56587	16.2	72950	17.0
44	65915	18.8	71534	16.7
46	68123	19.5	71692	16.7
48	53061	15.1	64440	15.0
50	31425	9.0	47684	11.1
52	18847	5.4	32088	7.5
54	13687	3.9	22452	5.2
56	11871	3.4	18874	4.4
58	11439	3.3	16657	3.9
60	10381	3.0	13594	3.2
62	9328	2.7	11444	2.7
64	8074	2.3	10308	2.4
66	7136	2.0	9463	2.2
68	5852	1.7	7588	1.8
70	4865	1.4	5787	1.4
72	2965	0.8	3760	0.9
74	1693	0.5	2319	0.5
total nC ₁₆ -C ₃₄		28.4		84.0
total nC ₃₅ +		141.1		171.4

Appendix IV. 2. 9.

Results of quantitative HTGC analysis of pipeline wax deposit samples # 9 and # 10 in carbon tetrachloride, cyclohexane and p-xylene

Model pipelines									
ON	# 10 in CH ₂	# 10 in p-xylene	# 10 in CCM	# 10 in CH ₂	# 10 in p-xylene	# 10 in CCM	# 10 in CH ₂	# 10 in p-xylene	# 10 in CCM
n-alkanes	area	area	area	ng/L in	ng/L in	ng/L in	mg/g wax deposit	mg/g wax deposit	mg/g wax deposit
14	854	50827		0.4	18.0		0.5	21.7	0.0
15	1028	33028	4648	0.4	12.3	2.1	0.5	15.4	2.6
16	7457	13862	8158	2.9	5.2	3.7	3.5	6.5	4.7
17	14304	18560	15588	5.6	7.3	7.0	6.5	8.1	6.7
18	11463	15846	12378	4.4	5.9	5.5	6.5	7.4	6.9
19	7454	9680	8138	2.9	3.6	3.8	3.5	4.8	4.9
20	8662	8543	7270	2.6	3.2	3.3	3.2	4.0	4.1
21	5778	7051	6185	2.2	2.6	2.8	2.5	3.3	3.5
22	5263	6129	5388	2.0	2.3	2.4	2.5	2.9	3.0
23	5214	5627	5324	2.0	2.2	2.4	2.5	2.8	3.0
24	4103	4671	4188	1.6	1.7	1.9	2.0	2.3	2.3
25	3958	4679	4077	1.5	1.7	1.8	1.9	2.2	2.3
26	3388	4224	3697	1.3	1.6	1.7	1.6	2.0	2.1
27	2701	3333	2835	1.0	1.2	1.3	1.3	1.6	1.8
28	2247	2751	2458	0.9	1.0	1.1	1.1	1.3	1.4
29	2251	2737	2384	0.9	1.0	1.1	1.1	1.3	1.3
30	1856	2176	1912	0.7	0.8	0.9	0.9	1.0	1.1
31	1513	1784	1682	0.6	0.7	0.8	0.7	0.8	0.9
32	1242	1532	1351	0.5	0.6	0.6	0.6	0.7	0.8
33	1064	1332	1221	0.4	0.5	0.5	0.5	0.6	0.7
34	800	1053	975	0.3	0.4	0.4	0.4	0.5	0.5
35	880	1111	1012	0.3	0.4	0.5	0.4	0.5	0.6
36	841	1100	1061	0.4	0.4	0.5	0.5	0.6	0.6
37	836	1210	1145	0.4	0.5	0.5	0.5	0.6	0.6
38	1072	1321	1264	0.4	0.5	0.6	0.5	0.6	0.7
39	1201	1456	1342	0.5	0.5	0.6	0.6	0.7	0.8
40	1510	1824	1660	0.6	0.7	0.7	0.7	0.9	0.9
41	1654	2030	1781	0.6	0.8	0.8	0.8	0.9	1.0
42	2620	3306	2777	1.0	1.2	1.2	1.3	1.5	1.6
43	2734	3385	2701	1.1	1.3	1.2	1.3	1.6	1.6
44	4019	5080	3880	1.6	1.9	1.7	1.9	2.4	2.3
45	5133	6426	4875	2.0	2.4	2.2	2.5	3.0	2.7
46	8262	10223	7711	3.2	3.8	3.4	4.0	4.8	4.3
47	9676	11768	9123	3.8	4.4	4.1	4.7	5.5	5.1
48	13618	16174	13008	5.3	6.0	5.8	6.5	7.5	7.3
49	15953	18619	15451	6.2	6.9	6.9	7.7	8.7	8.6
50	26781	30754	26510	10.4	11.5	11.9	13.0	14.3	14.3
51	26136	29837	26748	10.1	11.1	12.0	12.7	13.9	13.8
52	28218	31886	28688	11.0	11.9	13.3	13.7	14.9	16.8
53	31527	35296	34028	12.2	13.2	15.2	15.3	16.8	19.0
54	32254	35881	35808	12.5	13.3	16.1	16.6	16.8	20.1
55	32148	35286	37010	12.5	13.2	16.6	16.6	16.8	20.7
56	30005	32731	35423	11.8	12.3	15.8	14.8	16.3	18.3
57	30076	32955	36405	11.7	12.1	16.3	14.6	16.2	20.4
58	28301	30447	34791	11.0	11.4	15.8	13.7	14.2	18.4
59	28116	30029	34911	10.9	11.2	15.6	13.6	14.0	18.3
60	24751	26045	30417	9.6	9.7	13.6	12.8	12.1	17.9
61	23373	24233	30084	9.1	9.0	13.5	11.3	11.3	16.8
62	20915	21887	26223	8.1	8.2	11.7	10.1	10.2	14.7
63	20420	21377	25617	7.9	8.0	11.5	9.9	10.8	14.3
64	17824	18280	20861	7.0	6.8	9.3	8.7	8.6	11.7
65	17489	18938	20991	6.8	6.3	9.4	8.5	7.3	11.7
66	14222	13727	18018	5.5	5.1	8.1	6.9	6.4	10.7
67	14742	14201	18282	5.7	5.3	8.2	7.2	6.6	10.3
68	10888	10809	13375	4.2	4.0	6.0	6.3	6.0	7.3
69	10637	11064	13080	4.1	4.1	5.8	6.2	6.2	7.3
70	8063	8384	9772	3.1	3.1	4.4	3.9	3.9	5.6
71	8637	8806	10113	3.4	3.5	4.5	4.2	4.1	6.7
72	6019	5636	6950	2.3	2.2	3.1	2.9	2.8	3.9
73	5725	6720	7241	2.2	2.5	3.2	2.8	3.1	4.0
74	3730	3888	4380	1.4	1.5	2.0	1.8	1.8	2.8
75	3823	4363	4713	1.5	1.6	2.1	1.9	2.0	2.8
76	2932	2720	2752	1.1	1.0	1.2	1.4	1.3	1.8
77	2757	3080	3002	1.1	1.2	1.3	1.3	1.4	1.7
78	1676	1976	2073	0.7	0.7	0.9	0.8	0.9	1.2
79	1858	1707	1696	0.7	0.6	0.8	0.9	0.8	0.9
80	1712	1133	1091	0.7	0.4	0.5	0.8	0.6	0.6
81	1079	634	745	0.4	0.3	0.3	0.8	0.4	0.4
82	524	717	468	0.2	0.3	0.2	0.3	0.3	0.3
83	462		68	0.2		0.0	0.2	0.0	0.0
84	132			0.1			0.1	0.0	0.0
85									

Appendix IV. 2. 9 (continue)

CV	#9 in CH ₄	#9 in p-xylene	#9 in CO ₂	#9 in CH ₄	#9 in p-xylene	#9 in CO ₂	#9 in CH ₄	#9 in p-xylene	#9 in CO ₂
n-alkanes	area	area	area	ng/L in	ng/L in	ng/L in	mg/g wax deposit	mg/g wax deposit	mg/g wax deposit
14	643.0	51187.0	808.0	0.2	18.6	0.3	0.3	21.3	0.3
15	3867.0	31451.0	3302.0	1.2	11.3	1.4	1.4	14.3	1.7
16	8248.0	10434.0	8974.0	2.6	3.8	2.9	3.3	4.8	3.6
17	16126.0	13028.0	13801.0	5.1	4.7	5.7	6.4	6.9	7.1
18	12545.0	11771.0	10800.0	4.0	4.3	4.4	5.8	6.4	6.3
19	8103.0	7051.0	8708.0	2.6	2.6	2.6	3.2	3.2	3.6
20	8991.0	5718.0	5816.0	2.2	2.1	2.4	2.8	2.6	3.0
21	5826.0	4433.0	4783.0	1.9	1.8	2.0	2.3	2.2	2.6
22	4868.0	3910.0	3864.0	1.6	1.4	1.7	1.9	1.8	2.1
23	4635.0	3662.0	3897.0	1.3	1.3	1.6	1.8	1.7	2.0
24	3752.0	2625.0	2737.0	1.2	1.0	1.1	1.5	1.2	1.4
25	3204.0	2502.0	2542.0	1.0	0.9	1.1	1.3	1.1	1.3
26	2879.0	2306.0	2274.0	0.9	0.8	0.9	1.1	1.0	1.2
27	2183.0	1868.0	1730.0	0.7	0.6	0.7	0.9	0.8	0.9
28	1942.0	1483.0	1523.0	0.6	0.5	0.6	0.8	0.7	0.8
29	1874.0	1428.0	1380.0	0.6	0.5	0.6	0.7	0.7	0.7
30	1448.0	1138.0	1155.0	0.5	0.4	0.5	0.6	0.6	0.6
31	1182.0	910.0	817.0	0.4	0.3	0.3	0.5	0.4	0.4
32	981.0	727.0	785.0	0.3	0.3	0.3	0.4	0.3	0.4
33	833.0	624.0	687.0	0.3	0.2	0.3	0.3	0.3	0.3
34	588.0	432.0	448.0	0.2	0.2	0.2	0.3	0.2	0.2
35	622.0	484.0	454.0	0.2	0.2	0.2	0.3	0.2	0.2
36	800.0	483.0	481.0	0.2	0.2	0.2	0.3	0.2	0.3
37	760.0	531.0	533.0	0.2	0.2	0.2	0.3	0.2	0.3
38	889.0	670.0	683.0	0.3	0.2	0.3	0.4	0.3	0.4
39	1177.0	854.0	820.0	0.4	0.3	0.4	0.5	0.4	0.5
40	1740.0	1295.0	1377.0	0.6	0.5	0.6	0.7	0.6	0.7
41	2567.0	1907.0	2015.0	0.8	0.7	0.8	1.0	0.9	1.0
42	5331.0	3850.0	4111.0	1.7	1.4	1.7	2.1	1.8	2.1
43	7261.0	5274.0	5703.0	2.3	1.9	2.4	2.9	2.6	3.0
44	13480.0	8642.0	10412.0	4.3	3.5	4.3	6.4	4.4	6.4
45	20382.0	14505.0	15433.0	6.5	5.3	6.6	8.1	6.6	8.2
46	37329.0	26533.0	28032.0	11.9	9.7	12.1	14.9	12.1	16.1
47	47786.0	33809.0	37227.0	15.2	12.4	15.3	19.0	16.4	19.4
48	69794.0	48536.0	54425.0	22.2	18.0	22.7	27.8	22.6	28.3
49	82531.0	58438.0	64531.0	26.3	21.3	26.9	32.9	26.6	33.6
50	130591.0	82628.0	102263.0	41.8	33.7	42.6	52.8	42.2	52.2
51	118450.0	84028.0	82773.0	37.7	30.6	34.6	47.2	38.3	48.3
52	115238.0	81408.0	80044.0	36.7	28.7	37.5	45.9	37.1	46.9
53	111875.0	78450.0	87843.0	35.6	28.9	36.6	44.3	36.2	45.8
54	98786.0	70102.0	77432.0	31.3	25.5	32.2	39.3	31.9	40.3
55	84747.0	60082.0	66585.0	27.0	21.9	27.7	33.7	27.4	34.8
56	68845.0	48876.0	54086.0	21.9	17.8	22.5	27.4	22.3	28.1
57	60043.0	42317.0	46884.0	18.1	15.4	19.6	23.9	19.3	24.4
58	51530.0	36110.0	38986.0	16.4	13.2	16.7	20.9	16.4	20.8
59	44284.0	31336.0	34638.0	14.1	11.4	14.4	17.8	14.3	18.0
60	35548.0	25283.0	27753.0	11.3	9.2	11.6	14.2	11.6	14.4
61	32525.0	22754.0	25782.0	10.4	8.3	10.7	12.9	10.4	13.2
62	27196.0	19053.0	20240.0	8.7	6.9	8.4	10.8	8.7	10.8
63	25816.0	18112.0	21084.0	8.2	6.6	8.8	10.3	8.3	11.0
64	18282.0	13186.0	15042.0	6.1	4.8	6.3	7.7	6.0	7.8
65	18238.0	9673.0	14381.0	5.8	3.5	6.0	7.3	4.4	7.8
66	14107.0	9801.0	10881.0	4.5	3.6	4.6	6.6	4.8	6.7
67	13815.0	8674.0	10764.0	4.4	2.4	4.5	6.6	3.9	6.6
68	10201.0	6406.0	7530.0	3.2	2.3	3.1	4.1	2.9	3.9
69	8707.0	4679.0	7352.0	3.1	1.7	3.1	3.9	2.1	3.8
70	7088.0	4856.0	5438.0	2.3	1.8	2.3	2.8	2.3	2.8
71	7234.0	2882.0	5328.0	2.3	1.0	2.2	2.9	1.3	2.8
72	4670.0	2689.0	3408.0	1.3	1.0	1.4	1.9	1.2	1.8
73	4561.0	1868.0	3205.0	1.3	0.7	1.3	1.8	0.9	1.7
74	3266.0	2037.0	2862.0	1.0	0.7	1.2	1.5	0.9	1.6
75	2942.0	1156.0	2486.0	0.9	0.4	1.0	1.2	0.6	1.3
76	1817.0	777.0	2425.0	0.6	0.3	1.0	0.7	0.4	1.3
77	1487.0	376.0	1250.0	0.5	0.1	0.5	0.6	0.2	0.7
78	970.0	541.0	1001.0	0.3	0.2	0.4	0.4	0.2	0.6
79	863.0	278.0	851.0	0.3	0.1	0.3	0.3	0.1	0.5
80	480.0	195.0	162.0	0.2	0.1	0.1	0.2	0.1	0.1
81	336.0		247.0	0.1	0.0	0.1	0.1	0.0	0.1
82									
83									
84									
85									

Appendix IV. 2. 10. Results of quantitative HTGC analysis for n-alkanes in Uinta and Prairie Gem whole oils, and wax and non-wax fractions obtained by the acetone and DCM techniques for wax precipitation. Concentration of individual carbon number (CN) n-alkanes is in mg/g oil.

Uinta Basin sample						Prairie Gem field sample					
CN	acetone wax	acetone nonwax	DCMwax	DCMnonwax	whole oil	DCMwax	DCMnonwax	acetone wax	acetone nonwax	whole oil	
18	1.5	19.9	0.50	17.3	24.6	0.008	5.2	0.1	4.5	5.3	
19	2.0	18.9	0.53	17.0	24.1	0.003	4.5	0.1	4.1	4.6	
20	3.5	17.4	0.55	16.8	24.2	0.004	4.8	0.1	4.1	4.9	
21	6.7	14.1	0.55	16.3	23.5	0.004	4.2	0.1	3.6	4.0	
22	10.7	9.9	0.56	15.7	23.1	0.003	3.6	0.1	3.0	3.6	
23	14.1	6.3	0.58	15.2	22.8	0.003	3.0	0.1	2.6	3.3	
24	16.0	3.7	0.71	14.3	23.1	0.004	2.6	0.1	2.2	3.1	
25	16.5	2.2	0.64	13.6	21.4	0.004	2.3	0.1	2.0	2.5	
26	16.7	1.2	0.75	12.9	20.2	0.005	2.1	0.1	1.7	2.2	
27	16.6	0.7	0.89	12.3	19.9	0.007	1.6	0.2	1.3	1.8	
28	15.5	0.5	1.06	11.3	18.5	0.009	1.4	0.3	1.0	1.9	
29	14.0	0.2	1.30	9.6	16.7	0.011	1.2	0.4	0.7	1.4	
30	12.1	0.1	1.63	7.7	14.2	0.012	1.0	0.4	0.5	1.1	
31	10.1	0.1	2.08	5.7	12.0	0.013	0.8	0.4	0.3	1.0	
32	8.1	0.1	2.46	3.8	9.5	0.012	0.6	0.4	0.2	0.7	
33	7.1	0.1	2.61	2.1	8.4	0.012	0.6	0.3	0.2	0.8	
34	5.6	0.0	2.49	1.4	6.7	0.011	0.5	0.3	0.2	0.7	
35	4.5	0.0	2.34	0.9	5.3	0.011	0.4	0.3	0.2	0.6	
36	3.5	0.0	2.22	0.6	4.1	0.011	0.3	0.2	0.0	0.4	
37	3.2	0.0	2.25	0.4	3.9	0.012	0.2	0.3	0.0	0.5	
38	2.9	0.0	2.36	0.4	3.2	0.015	0.2	0.3	0.0	0.4	
39	2.7	0.0	2.62	0.3	3.1	0.017	0.3	0.3	0.0	0.4	
40	2.5	0.0	2.91	0.2	2.7	0.020	0.3	0.3	0.0	0.3	
41	2.3	0.0	3.19	0.1	2.6	0.021	0.2	0.3	0.0	0.3	
42	2.2	0.0	3.30	0.1	2.5	0.028	0.3	0.3	0.0	0.5	
43	2.2	0.0	3.35	0.1	2.5	0.028	0.3	0.3	0.0	0.4	
44	2.0	0.0	3.16	0.1	2.1	0.031	0.3	0.3	0.0	0.4	
45	2.0	0.0	2.99	0.0	2.0	0.029	0.2	0.3	0.0	0.3	
46	1.8	0.0	2.66	0.0	1.9	0.030	0.2	0.3	0.0	0.3	
47	2.0	0.0	2.47	0.0	1.9	0.023	0.1	0.2	0.0	0.3	
48	1.9	0.0	2.04	0.0	1.8	0.019	0.1	0.2	0.0	0.2	
49	1.9	0.0	1.77	0.0	1.7	0.016	0.1	0.1	0.0	0.2	
50	1.9	0.0	1.44	0.0	1.6	0.013	0.1	0.1	0.0	0.2	
51	1.9	0.0	1.23	0.0	1.6	0.011	nd.	0.1	nd.	nd.	
52	1.8	0.0	0.96	0.0	1.5	0.009	nd.	0.1	nd.	nd.	
53	1.8	0.0	0.80	0.0	1.5	0.008	nd.	0.1	nd.	nd.	
54	1.7	0.0	0.56	0.0	1.3	0.005	nd.	0.1	nd.	nd.	
55	1.4	0.0	0.43	0.0	1.3	0.004	nd.	0.0	nd.	nd.	
56	1.4	0.0	0.45	0.0	1.2	0.005	nd.	0.0	nd.	nd.	
57	1.3	0.0	0.38	0.0	1.1	0.004	nd.	0.0	nd.	nd.	
58	1.2	0.0	0.30	0.0	1.0	0.003	nd.	0.0	nd.	nd.	
59	1.1	0.0	0.26	0.0	0.9	0.003	nd.	0.0	nd.	nd.	

Appendix IV. 3. 1. Quantitative HTGC analysis results of n-alkane distributions in the whole oil used in cold finger experiments, and wax and asphaltene fractions obtained by acetone and n-pentane precipitation.

CN	whole oil			acetone wax				asphaltene			
	area	ng/ μ l	mg/g	area	ng/ μ l	mg/g wax	mg/g oil	area	ng/ μ l	mg/g asph.	mg/g oil
15	80034	20.25	12.66	5927	1.29	0.81	0.10				
16	67988	17.20	10.75	5810	1.27	0.79	0.09				
17	66192	16.75	10.47	6103	1.33	0.83	0.10	19748	4.75	2.97	0.01
18	56440	14.28	8.93	5875	1.28	0.80	0.10	34156	8.22	5.14	0.02
19	47746	12.08	7.55	6630	1.45	0.90	0.11	46481	11.18	6.99	0.03
20	51742	13.09	8.18	11964	2.61	1.63	0.20	48638	11.70	7.31	0.03
21	42335	10.71	6.70	28216	6.15	3.84	0.46	42140	10.14	6.34	0.03
22	38223	9.67	6.04	72429	15.79	9.87	1.18	39756	9.56	5.98	0.03
23	34017	8.61	5.38	130312	28.41	17.75	2.13	33895	8.63	5.40	0.02
24	29484	7.46	4.66	165281	36.03	22.52	2.70	30648	7.37	4.61	0.02
25	25928	6.56	4.10	173013	37.71	23.57	2.83	26266	6.32	3.95	0.02
26	22422	5.67	3.55	166352	36.26	22.66	2.72	23911	5.75	3.60	0.02
27	17880	4.52	2.83	143248	31.22	19.52	2.34	19097	4.59	2.87	0.01
28	15640	3.96	2.47	123175	26.85	16.78	2.01	17715	4.26	2.66	0.01
29	13562	3.43	2.14	113937	24.84	15.52	1.86	15026	3.61	2.26	0.01
30	11089	2.81	1.75	95085	20.73	12.95	1.55	11852	2.85	1.78	0.01
31	12485	3.16	1.97	88285	19.24	12.03	1.44	13010	3.13	1.96	0.01
32	8765	2.22	1.39	75224	16.40	10.25	1.23	10077	2.42	1.52	0.01
33	7940	2.01	1.26	62668	13.66	8.54	1.02	9302	2.24	1.40	0.01
34	6979	1.77	1.10	51773	11.29	7.05	0.85	8891	2.14	1.34	0.01
35	6495	1.64	1.03	44469	9.69	6.06	0.73	8284	1.99	1.25	0.01
36	3631	0.92	0.57	40215	8.77	5.48	0.66	6582	1.58	0.99	0.00
37	3955	1.00	0.63	37667	8.21	5.13	0.62	7539	1.81	1.13	0.01
38	3463	0.88	0.55	33480	7.30	4.56	0.55	9348	2.25	1.41	0.01
39	3507	0.89	0.55	29980	6.53	4.08	0.49	13814	3.32	2.08	0.01
40	3238	0.82	0.51	29256	6.38	3.99	0.48	26074	6.27	3.92	0.02
41	2427	0.61	0.38	24053	5.24	3.28	0.39	44366	10.67	6.67	0.03
42	2389	0.60	0.38	27125	5.91	3.70	0.44	96074	23.11	14.44	0.07
43	1958	0.50	0.31	19078	4.16	2.60	0.31	116436	28.01	17.51	0.08
44	1965	0.50	0.31	18460	4.02	2.51	0.30	168934	40.64	25.40	0.12
45	1856	0.47	0.29	14417	3.14	1.96	0.24	181427	43.64	27.28	0.13
46	1914	0.48	0.30	15142	3.30	2.06	0.25	223216	53.70	33.56	0.15
47	1628	0.41	0.26	11246	2.45	1.53	0.18	188354	45.31	28.32	0.13
48	1484	0.38	0.23	10181	2.22	1.39	0.17	184367	44.35	27.72	0.13
49	1150	0.29	0.18	7961	1.74	1.08	0.13	150725	36.26	22.66	0.10
50	1347	0.34	0.21	8935	1.95	1.22	0.15	175051	42.11	26.32	0.12
51				6291	1.37	0.86	0.10	123304	29.66	18.54	0.09
52				5100	1.11	0.69	0.08	97936	23.56	14.72	0.07
53				4698	1.02	0.64	0.08	81575	19.62	12.26	0.06
54				3308	0.72	0.45	0.05	63032	15.16	9.48	0.04
55				2626	0.57	0.36	0.04	45923	11.05	6.90	0.03
56				1978	0.43	0.27	0.03	41655	10.02	6.26	0.03
57				1598	0.35	0.22	0.03	34540	8.31	5.19	0.02
58				1576	0.34	0.21	0.03	28505	6.86	4.29	0.02
59				1148	0.25	0.16	0.02	25692	6.18	3.86	0.02
nC ₁₈₊	485084	123	76.7	1913455	417.1	261	31.3	2575614	620	387	1.8
nC ₃₀₊	89665	23	14.2	773023	169.0	105	12.6	2195885	528	330	1.5
nC ₃₃₊	42407	11	6.7	399988	87.2	54	6.5	2142753	515	322	1.5

Appendix IV. 3. 2. Quantitative HTGC analysis results of n-alkane distributions in wax deposits formed at different depths of well tubing (rod).

CN	shallower sample			deeper sample		
	area	ng/ μ l	mg/g	area	ng/ μ l	mg/g
18	10504	4.53	49.74	10415	5.53	60.74
19	7109	3.06	33.66	7091	3.76	41.33
20	6056	2.61	28.68	5921	3.14	34.53
21	4979	2.15	23.58	4940	2.62	28.81
22	4191	1.89	20.79	4474	2.37	26.09
23	3829	1.65	18.13	4130	2.19	24.08
24	3989	1.55	16.99	3691	1.96	21.52
25	3227	1.39	15.28	3137	1.66	18.29
26	5029	2.17	23.81	3137	1.66	18.29
27	4239	1.83	20.07	2708	1.44	15.79
28	6602	2.84	31.26	2350	1.25	13.70
29	9710	4.18	45.98	2080	1.10	12.13
30	14425	7.08	77.77	1679	0.89	9.79
31	29045	12.51	137.52	1841	0.98	10.74
32	43229	18.43	204.89	1902	1.01	11.09
33	54136	23.40	257.19	2185	1.16	12.74
34	56692	24.43	268.44	2051	1.09	11.96
35	50825	21.90	240.86	2116	1.12	12.34
36	43643	18.81	206.65	2644	1.40	15.42
37	33402	13.96	153.42	1994	1.06	11.63
38	25367	11.02	123.06	2092	1.11	12.20
39	20031	8.63	94.85	2075	1.10	12.10
40	16396	7.06	77.64	2196	1.17	12.81
41	13082	4.78	52.47	1820	0.97	10.61
42	10541	3.68	40.44	2120	1.13	12.36
43	6428	2.77	30.44	2464	1.31	14.37
44	4983	1.97	21.70	1127	1.66	18.24
45	3491	1.50	16.53	4370	2.32	25.48
46	2556	1.10	12.10	7007	3.72	40.86
47	2159	0.93	10.22	11595	6.15	67.62
48	1281	0.55	6.07	17719	9.40	103.23
49	1135	0.49	5.37	27073	14.37	157.88
50	807	0.35	3.82	32502	17.25	189.54
51	653	0.28	3.09	39822	21.13	232.22
52	454	0.20	2.15	35804	19.00	208.79
53	300	0.13	1.42	33789	17.93	197.04
54	194	0.08	0.92	27300	14.49	159.27
55	144	0.06	0.68	23553	12.50	137.37
56	93	0.04	0.45	17656	9.37	102.96
57				12976	6.89	75.67
58				10056	5.34	58.64
59				8825	4.68	51.46
60				6364	3.38	37.11
61				5118	2.72	29.85
62				3094	1.64	18.04
63				2554	1.36	14.89
64				1936	1.03	11.29
65				1689	0.90	9.85
66				1185	0.63	6.91
67				1103	0.59	6.43
68				643	0.34	3.75
69				773	0.41	4.51
70				534	0.28	3.11
71				466	0.25	2.72
72				192	0.10	1.12

Appendix IV. 4. 1. Quantitative HTGC results for n-alkane distributions in acetone wax precipitates from oils (I-XIII) and asphaltene precipitate from oil V produced at Paschall 2 well, Prairie Gem field.

CN	oil I				oil II				oil III				oil IV			
	area	ng/ μ l	mg/g wax	mg/g oil	area	ng/ μ l	mg/g wax	mg/g oil	area	ng/ μ l	mg/g wax	mg/g oil	area	ng/ μ l	mg/g wax	mg/g oil
18	57187	14.8	4.6	0.8	55074	13.5	4.2	0.8	40635	11.1	3.5	0.6	34723	8.6	2.7	0.4
19	68953	17.8	5.6	1.0	66732	16.3	5.1	1.0	39946	11.0	3.4	0.6	34189	8.4	2.6	0.4
20	57703	14.9	4.7	0.8	60959	14.2	4.7	0.9	47646	13.1	4.1	0.7	43573	10.8	3.4	0.5
21	54725	14.1	4.4	0.8	61491	15.0	4.7	0.9	50527	13.9	4.3	0.7	55937	13.8	4.3	0.6
22	52089	13.5	4.2	0.8	64335	15.7	4.9	1.0	57894	15.9	5.0	0.8	82672	20.4	6.4	0.9
23	53090	13.7	4.3	0.8	72387	17.7	5.5	1.1	70617	19.4	6.1	1.0	120999	29.9	9.3	1.3
24	67455	17.4	5.4	1.0	89390	21.9	6.8	1.4	93947	25.8	8.1	1.3	158793	39.2	12.3	1.7
25	59509	15.4	4.8	0.9	91370	22.3	7.0	1.4	86513	23.7	7.4	1.2	156566	38.7	12.1	1.7
26	63653	16.5	5.1	0.9	78387	19.2	6.0	1.2	86445	23.7	7.4	1.2	154639	38.2	11.9	1.7
27	59078	15.3	4.8	0.9	68476	16.7	5.2	1.0	74675	20.5	6.4	1.1	131125	32.4	10.1	1.4
28	58756	15.2	4.7	0.8	65020	15.9	5.0	1.0	70150	19.2	6.0	1.0	120072	29.7	9.3	1.3
29	51101	13.2	4.1	0.7	54139	13.2	4.1	0.8	59625	16.4	5.1	0.9	101201	25.0	7.8	1.1
30	43294	11.2	3.5	0.6	44812	11.0	3.4	0.7	49735	13.6	4.3	0.7	82811	20.5	6.4	0.9
31	39050	10.1	3.2	0.6	38567	9.4	2.9	0.6	44210	12.1	3.8	0.6	72480	17.9	5.6	0.8
32	29666	7.7	2.4	0.4	29212	7.1	2.2	0.4	34892	9.6	3.0	0.5	56445	13.9	4.4	0.6
33	28918	7.5	2.3	0.4	27490	6.7	2.1	0.4	33033	9.1	2.8	0.5	52904	13.1	4.1	0.6
34	24037	6.2	1.9	0.3	22806	5.6	1.7	0.3	27395	7.5	2.3	0.4	44301	10.9	3.4	0.5
35	19741	5.1	1.6	0.3	17799	4.4	1.4	0.3	22140	6.1	1.9	0.3	36567	9.0	2.8	0.4
36	14414	3.7	1.2	0.2	11189	2.7	0.9	0.2	17264	4.7	1.5	0.2	33289	8.2	2.6	0.4
37	14097	3.6	1.1	0.2	9350	2.3	0.7	0.1	17267	4.7	1.5	0.2	31116	7.7	2.4	0.3
38	10523	2.7	0.9	0.2	7070	1.7	0.5	0.1	13422	3.7	1.2	0.2	28310	7.0	2.2	0.3
39	10100	2.6	0.8	0.1	6785	1.7	0.5	0.1	12935	3.5	1.1	0.2	25831	6.4	2.0	0.3
40	8825	2.3	0.7	0.1	4221	1.0	0.3	0.1	11860	3.3	1.0	0.2	24720	6.1	1.9	0.3
41	6800	1.8	0.5	0.1	3200	0.8	0.2	0.0	9791	2.7	0.8	0.1	20563	5.1	1.6	0.2
42	7312	1.9	0.6	0.1	2894	0.7	0.2	0.0	10269	2.8	0.9	0.1	21568	5.3	1.7	0.2
43	5105	1.3	0.4	0.1	2144	0.5	0.2	0.0	8755	2.4	0.8	0.1	19113	4.7	1.5	0.2
44	4351	1.1	0.4	0.1	1622	0.4	0.1	0.0	7901	2.2	0.7	0.1	15463	3.8	1.2	0.2
45	3321	0.9	0.3	0.0	1483	0.4	0.1	0.0	6374	1.7	0.5	0.1	12787	3.2	1.0	0.1
46	3033	0.8	0.2	0.0	1385	0.3	0.1	0.0	5826	1.6	0.5	0.1	11272	2.8	0.9	0.1
47	1952	0.5	0.2	0.0		0.0	0.0	0.0	4466	1.2	0.4	0.1	7156	1.8	0.6	0.1
48	1001	0.3	0.1	0.0		0.0	0.0	0.0	3151	0.9	0.3	0.0	6209	1.5	0.5	0.1
49	1224	0.3	0.1	0.0		0.0	0.0	0.0	2811	0.8	0.2	0.0	4743	1.2	0.4	0.1
50	622	0.2	0.1	0.0		0.0	0.0	0.0	2690	0.7	0.2	0.0	3281	0.8	0.3	0.0
51		0.0	0.0	0.0		0.0	0.0	0.0	2366	0.6	0.2	0.0	3284	0.8	0.3	0.0
52		0.0	0.0	0.0		0.0	0.0	0.0	1825	0.5	0.2	0.0	2296	0.6	0.2	0.0
53		0.0	0.0	0.0		0.0	0.0	0.0	1957	0.5	0.2	0.0	1865	0.5	0.1	0.0
54		0.0	0.0	0.0		0.0	0.0	0.0	1508	0.4	0.1	0.0		0.0	0.0	0.0
55		0.0	0.0	0.0		0.0	0.0	0.0	1125	0.3	0.1	0.0		0.0	0.0	0.0
sum nC18-C3	868264	224.4	70.1	12.5	990647	242.2	75.7	15.1	967885	265.6	83.0	13.8	*****	371.4	116.1	16.1
sum nC35+	112421	29.1	9.1	1.6	69142	16.9	5.3	1.1	165703	45.5	14.2	2.4	309433	76.4	23.9	3.3
sum nC18+	980685	253.5	79.2	14.1	1059789	259.1	81.0	16.2	1133588	311.0	97.2	16.2	*****	447.9	140.0	19.4

Appendix IV. 4. 1. (continue)

CN	wax V			wax VII			wax XIII			asphaltene V		
	area	ng/ μ l	mg/g	area	ng/ μ l	mg/g	area	ng/ μ l	mg/g	area	ng/ μ l	mg/g
			wax oil			wax oil			wax oil			asph.
18	24114	7.2	2.2	59440	14.8	4.6	43742	14.9	5.3			
19	21939	6.5	2.0	70402	17.5	5.5	78430	21.5	6.7			
20	23271	7.3	2.3	64896	16.1	5.0	68466	18.3	5.8			
21	24622	7.3	2.3	61131	15.2	4.7	71421	19.3	6.0			
22	26435	7.8	2.4	58477	14.5	4.3	73799	19.9	6.2			
23	31139	9.8	3.1	58837	14.6	4.6	74092	20.0	6.3			
24	34055	14.6	5.2	74761	18.6	5.8	83033	17.0	5.3			
25	33930	14.0	5.0	63790	16.3	5.1	65770	17.8	5.6			
26	40937	18.1	5.6	66364	16.5	5.2	57590	15.4	4.9			
27	33865	17.2	5.4	61005	15.4	4.8	47000	12.7	4.0			
28	37188	17.0	5.3	61561	15.3	4.8	42974	11.6	3.6			
29	30235	15.0	4.7	52096	13.1	4.1	35115	9.5	3.0			
30	34376	10.2	3.2	43800	10.9	3.4	28667	7.7	2.4			
31	40973	12.2	3.8	38806	9.6	3.0	25137	6.8	2.1			
32	33071	9.8	3.1	29263	7.3	2.3	18038	5.0	1.6			
33	32633	9.1	3.0	26318	6.5	2.0	17611	4.8	1.5			
34	30098	8.9	2.8	22004	5.5	1.7	14977	4.0	1.3			
35	28073	8.3	2.6	17247	4.3	1.3	12214	3.3	1.0			
36	29041	8.4	2.7	12496	3.1	1.0	8464	2.3	0.7			
37	33609	10.0	3.1	12128	3.0	0.9	9073	2.5	0.8			
38	37987	11.3	3.5	9227	2.3	0.7	5865	1.6	0.5			
39	42445	12.6	3.9	8402	2.1	0.7	8464	2.3	0.7			
40	47005	13.9	4.4	7587	1.9	0.6	3374	1.5	0.5			
41	41042	12.2	3.8	6096	1.5	0.5	3792	1.0	0.3			
42	45847	13.6	4.2	6340	1.6	0.5	3470	0.9	0.3			
43	38423	11.4	3.6	3937	1.0	0.3	2374	0.6	0.2			
44	33977	9.8	3.1	3593	0.9	0.3	1939	0.5	0.2			
45	25650	7.6	2.4	2682	0.7	0.2	1208	0.3	0.1			
46	21260	6.3	2.0	2621	0.7	0.2		0.0	0.0			
47	14017	4.2	1.3	1251	0.3	0.1		0.0	0.0			
48	10022	3.0	0.9		0.0	0.0		0.0	0.0			
49	8219	2.4	0.8		0.0	0.0		0.0	0.0			
50	6714	2.0	0.6		0.0	0.0		0.0	0.0			
51	5041	1.5	0.5		0.0	0.0		0.0	0.0			
52	4061	1.2	0.4		0.0	0.0		0.0	0.0			
53	3439	1.0	0.3		0.0	0.0		0.0	0.0			
54	2487	0.7	0.2		0.0	0.0		0.0	0.0			
55	1981	0.6	0.2		0.0	0.0		0.0	0.0			
sum nC18-C35	1967	61.5	6.8	2277	71.2	17.4		2286	71.5	23.8		0.0
sum nC33+	1422	44.4	4.9	233	7.3	1.8		168	5.3	1.8		82.7
sum nC18+	3389	105.9	11.6	2510	78.4	19.1		2455	76.7	25.6		82.7