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EDWIN EARL TUCKER

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HYDROGEN BONDING EQUILIBRIA IN DILUTE SOLUTION

VAPOR PRESSURE AND VAPOR DENSITY STUDIES

APPROVED BY

DISSERTATION COMMITTEE

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DEDICATED WITH LOVE TO MY PARENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

HYDROGEN BONDING EQUILIBRIA IN DILUTE SOLUTION. VAPOR DENSITY AND VAPOR PRESSURE STUDIES

CHAPTER I

INTRODUCTION

It is surprising, in view of the many publications on hydrogen bonding, that there is general agreement on the types and energies of hydrogen bonds formed only for one specific class of compounds: carboxylic acids. The predominant polymeric species formed by association of carboxylic acids in dilute solution and in the vapor phase is a cyclic dimer. The enthalpy of formation of the dimer in the vapor phase is -14.0 ± 1. kcal/mole and does not seem to depend strongly on characteristics such as the molecular weight of the acid or the type of substituents attached to the carboxyl group.

Agreement about the self-association properties of carboxylic acids is primarily due to the fact that apparently only one polymeric species is formed under the conditions of the experiments and, further, that a considerable fraction of the total acid is present in the associated form both in the vapor phase and in dilute solution. To a large degree, systems involving other types of hydrogen bonding molecules do not exhibit the same characteristics as the carboxylic acid systems. It is common to find systems where two, three or more associated species are present and no one species is predominant.

Pimentel and McClellan, in their 1960 monograph on the hydrogen bond,[1] commented that very few hydrogen bonded systems had been studied systematically, that the solvent effect on complexes was not clear and that often serious questions arise concerning the nature of bonded species. This monograph stressed the need for accurate thermodynamic values for hydrogen bonding systems.

These authors' comments are particularly applicable when hydrogen bonding systems involving water, alcohols and amines are considered. Systems involving these compounds are somewhat unusual in comparison to carboxylic acids. In the vapor phase the extent of association in these compounds is quite small, usually on the order of two to three percent. However, in solution, for water and methanol, as the concentration is increased aggregates of these compounds begin to form and at high concentrations a very large fraction of the total water or alcohol present exists in an associated form.

Due to the paucity of literature data on the relative proton donating abilities of water and methanol as hydrogen bonding acids the present study was undertaken quantitatively to compare the hydrogen bonding reactions between water and methanol with the base diethylamine in several media. A brief review of some pertinent literature concerning both pure component association and association in mixed systems will be given here.

Association in Water and Water Solutions

Many attempts have been made to describe the structure of liquid water. There is little doubt that the anomalous properties of water are due primarily to extensive hydrogen bonding. As yet, no completely

satisfactory structural model for liquid water has been developed. One problem concerning the extent of hydrogen bonding in liquid water is a point of strong contention: the question as to whether water contains definite structural entities or is simply a three dimensional network with maximal hydrogen bonding.[2-4]

Rather than studying the properties of water or solutions where water is the major component, Christian and coworkers have studied solutions in which water is the minor component.[5-8] The rationale here is that one may start out by dissolving water in nonpolar solvents where water behaves ideally and gradually progress to solvents which dissolve more and more water. In this manner the types of associated species which form as the water concentration increases may be studied.

The solute-isopiestic technique developed by Christian et al., which utilizes titration of samples by the Karl Fischer method for water analysis, has been used to study solutions of water in carbon tetrachloride, toluene, benzene, cyclohexane, 1,2 dichloroethane and 1,1,2,2 tetrachloroethane. Johnson[7] found that water is primarily monomeric in the first four of these solvents but partially associates to form either trimers or tetramers in the chlorinated hydrocarbons. However, another worker in this laboratory found that water is approximately 10% associated in benzene by using the same technique.[9]

The association of water in dichloroethane or tetrachloroethane was about equally well described by either a monomer-trimer or by a monomer-tetramer equilibrium. However, Masterton and Gendrano[10] concluded from a similar study of water in dichloroethane that the association could be described by monomer-dimer or monomer-trimer equilibrium but not by monomer-tetramer.

Vapor pressure studies of water association in more reactive solvents of low volatility have been reported by Johnson et al..[8] Association is well described by a monomer-dimer equilibrium in a few solvents but the majority seem to be better described by a monomer-trimer or a monomer-tetramer equilibrium. With the exclusion of such solvents as nitrobenzene, in which a monomer-dimer equilibrium is definitely better, the conclusion has been reached that solvents with a single basic site stabilize the formation of a cyclic water trimer. No concerted effort has been made to obtain values of enthalpies and entropies for the solubility and association of water in the organic solvents although water solubility by the solute isopiestic method has occasionally been determined at two or three temperatures, notably in carbon tetrachloride[11] and benzene.[9] The enthalpy for formation of a water trimer has been reported as roughly -15.0 kcal/mole in 1,2 dichloroethane from measurements at 10 and 25°.[7]

Infrared spectroscopy, which is probably the most frequently used method for studying hydrogen bonding systems, has been used very little for studying dilute solutions of water in organic solvents due to the experimental difficulties involved. One study of the infrared spectra of water in dichloroethane has recently been reported.[12]

Association of Alcohols

Quite a large body of literature exists concerning the self-association of alcohols both in the vapor phase and, most especially, in solution in organic solvents.[1] Alcohol association in the vapor phase is generally thought to follow the monomer-dimer-tetramer equilibrium proposed by Weltner and Pitzer as a result of their heat

capacity studies on methanol vapor.[13] Heat capacity data for other alcohols seem to be satisfactorily explained by this model according to Berman.[14] In this reference Berman asserts that PVT (pressure-volume-temperature) data for alcohol vapors are rather insensitive to any associated species other than a dimer. However, recent precise PVT data on methanol vapor taken in this laboratory by Mr. Sutton B. Farnham indicate that not only is the PVT method sensitive to species other than dimers but that there is little necessity to assume the presence of a measurable quantity of methanol dimer in the vapor phase at room temperature.[15]

The association of alcohols in solution in nonpolar solvents has been studied by several techniques. Probably the most widely used method has been infrared spectroscopy, both in the fundamental hydroxyl stretching region and in the first overtone region.[16-20] The solvent which is most commonly employed is carbon tetrachloride. Other methods which have been used are nuclear magnetic resonance (NMR),[21-24] vapor pressure,[25-27] ultrasonics,[28,29] and dielectric measurements.[30,31]

Although it is generally accepted that, at alcohol concentrations greater than a few tenths molar, alcohols are highly associated in nonpolar solvents there has been much controversy over the types of polymeric species present in the lower concentration region. One particular associated alcohol species which has been proposed, a cyclic dimer, is discussed at some length in almost all reports concerning alcohol association. This species was proposed from the infrared spectra of methanol suspended in solid nitrogen at 20° K (matrix isolation method).[32] Other results interpreted as supporting the presence of this species in

solution in carbon tetrachloride are those of Liddel and Becker[33] who studied the temperature dependence of the absorbance of the peak at ca. 3500 cm^{-1} in the fundamental hydroxyl stretching region. Liddel and Becker obtained a ΔH of $-(9.2 \pm 2.5)$ kcal/mole for methanol assuming that the peak at ca. 3500 cm^{-1} was due to a dimeric species and that no associated species absorb at the monomer peak at ca. 3600 cm^{-1}. The enthalpy values obtained for ethanol and t-butanol dimers were considerably smaller in magnitude.

The cyclic dimer has been accepted as not only an existing species but also as an important one by some authors (for example, 31,34). The existence of this species has been vigorously attacked recently by Fletcher and Heller.[35] These authors contend that many workers assume the presence of a cyclic dimer in alcohol association data when in fact careful analysis of the data may show no detectable dimer, either cyclic or linear. In a later publication these authors conclude that very small quantities of an acyclic dimer can be seen in infrared spectral data.[36]

There is no general agreement as to which polymeric entities are important in alcohol solutions. Association models usually tend to be of the type where one or more smaller polymers (dimer, trimer or tetramer) may be important with a variety of larger unspecified polymers existing in either cyclic or linear form. A model of this type was probably first proposed by Mecke[37] who assumed that a unique equilibrium constant existed for a dimer and that successive additions of monomers to a growing polymer had the same equilibrium constant.

Models which employ only one or two distinct associated species have been proposed. Fletcher and Heller[35] concluded from a study of 1-octanol association in n-decane in the infrared overtone region that a monomer-tetramer model provided the best fit of the data for solutions from 10^{-4} molar to pure 1-octanol. They further concluded that two types of tetramers were present, linear and cyclic, and stated that tetramers were the predominant associated species in alcohol solutions in nonpolar solvents.

Amine Association

All evidence seems to indicate that primary and secondary amines are only slightly associated in the vapor phase or in nonpolar solvents. Lambert and Strong[38] measured the second virial coefficients for a series of seven amines, including ammonia and the primary, secondary and tertiary methyl- and ethyl-amines. A ΔH of -3.3 kcal/mole was obtained for the diethylamine dimer in vapor phase.

Several recent reports have concerned the association of amines in nonpolar solvents as measured by the NMR technique. Murphy and Davis[39] have measured chemical shifts for several amines in cyclohexane as a function of temperature and concentration. They reported equilibrium constants for dimer formation. Springer and Meek[40] have reported a tetramer constant for diethylamine in cyclohexane of 1.75×10^{-3} (M^{-3}). Feeney and Sutcliffe[41] have reported a tetramer constant of 2.5×10^{-4} (M^{-3}) for diethylamine in CCl_4, also from NMR measurements.

The self-association of methyl-, ethyl- and n-propylamines has been studied by vapor pressure measurements in hydrocarbon solvents.[42] Again, the results indicate small degrees of association at low concentrations.

Water-Amine Complexes in Organic Solvents

Probably the only equilibrium constants for hydrogen bonding between water and aliphatic amines in organic solvents have been reported by Gregory.[43] This study reported equilibrium constants for 1:1 complexes of water with cyclohexylamine, N methyl- and N,N dimethylcyclohexylamines in benzene at 25 and 35° using the solute isopiestic technique mentioned previously. Equilibrium constants for the 1:1 complexes of water with triethylamine were also determined in toluene, benzene and cyclohexane at 25°. Dielectric studies were also made of solutions of water and amines in benzene at 25°.

Studies of several types have been done in which water is complexed with weak bases in organic solvents. Mohr, Wilk and Barrow reported the infrared spectra of mixtures of several bases with water.[44] In systems where weak bases were present the spectra indicated the formation of a bridged species involving two molecules of base bonded to one water molecule. One of these systems, water and pyridine dissolved in CCl_4, has been studied by several workers. Siderov[45] reported 1:1 and 2:1 hydrates in the pyridine-water system. Johnson et al.[46] studied mixtures of water and pyridine in several organic solvents, including CCl_4, and found, in addition to a 1:1 complex, the bridged species and also a complex which involved either two or three molecules of water with one pyridine molecule. Equilibrium constants were obtained for these species. An infrared study of the water-pyridine system in CCl_4 at several temperatures has been reported.[47] Equilibrium constants and enthalpies for the 1:1 complex and the bridged species were determined but these values are not available at present.

Alcohol-Amine Complexes

Enthalpies for complex formation in the vapor phase in amine-alcohol mixtures have been reported for three systems. Cracco and Huyskens[48] give a value of -8.9 kcal/mole for the n-butanol-n-butylamine complex from a vapor density study. Clague, Govil and Bernstein,[49] from an NMR study on vapor mixtures, obtained -(5.8 ± 0.7) kcal/mole for the methanol-trimethylamine complex. Hirano and Kozima[50] have studied the interaction of methanol and triethylamine in the vapor phase and in solutions using infrared spectroscopy. They calculated an enthalpy of formation of -8.2 kcal/mole for the vapor phase complex.

Several alcohol-amine systems have been studied in solution by infrared spectroscopy.[51-55] The solvent used in these studies has commonly been CCl_4 despite the fact that many workers have indicated that a precipitate forms when aliphatic amines such as diethyl- and triethylamines are added to this solvent. Some authors have not mentioned the appearance of this precipitate, others have not thought this to be a serious problem and still others have declined to use aliphatic amines in this solvent because of the precipitate formation. Pyridine is one commonly used amine which apparently does not form a precipitate in CCl_4.[51]

The common technique in these infrared studies has been to use very low concentrations of alcohols. There are two primary reasons why low concentrations are used; the necessity for self-association corrections for the alcohol is obviated and, to some extent, the formation of larger complexes which would absorb in the same region as the 1:1 complex is prevented.

Zeegers-Huyskens has reported 1:1 equilibrium constants[52,53] from infrared data in CCl_4 for several alcohol-amine systems at one temperature. Kolbe and Pracejus[54] have determined enthalpies of formation of several alcohol-amine complexes in toluene from infrared spectral data. Gramstad[55] has reported equilibrium constants and enthalpies from IR data for 1:1 complexes of phenol and methanol with several tertiary aliphatic amines. He also found, from refractive index measurements, that pentachlorophenol forms complexes of varying stoichiometry with tertiary amines in CCl_4. The complexes involve one, two and three molecules of the substituted phenol per amine molecule. Measurements on the systems phenol-tertiary amines by the refractive index technique did not show complexes other than the 1:1.

Lamberts and Zeegers-Huyskens[56] reported enthalpies of formation for 1:1 complexes of alcohols and aliphatic amines in CCl_4. A calorimetric method was used to obtain the enthalpies.

The table below summarizes some results of previous studies on 1:1 complex formation between aliphatic amines and aliphatic alcohols.

System	Solvent	Method	$-\Delta H$(kcal/mole)	Ref.
Methanol-triethylamine	CCl_4	IR	6.0	50
Methanol-triethylamine	Toluene	IR	5.2	54
Methanol-triethylamine	CCl_4	IR	3.8	55
Ethanol-diethylamine	CCl_4	Calorimetric	5.0	56
Ethanol-triethylamine	CCl_4	Calorimetric	4.8	56
Ethanol-n-butylamine	Cyclohexane	Calorimetric	7.2	56

The values presented in this table are in accord with Pimentel and McClellan's

comments on the indeterminate nature of solvent effects on hydrogen bonding systems. Toluene, being a more reactive solvent, should retard the formation of the methanol-triethylamine complex but the value of $-\Delta H$ from reference 54 indicates that the complex is stabilized in toluene relative to CCl_4.[55] Reference 50 indicates a higher ΔH in CCl_4 than in toluene but is in poor agreement with reference 55. Also, the $-\Delta H$ values for ethanol-amine complexes in CCl_4 are very little different from the $-\Delta H$ value in toluene and there is a considerable difference between the $-\Delta H$ values for the methanol- and ethanol-amine complexes in CCl_4 obtained by two different methods. The enthalpy of formation of the methanol- and ethanol-pyridine complexes has been reported by Becker[57] to be -3.9 and -3.7 kcal/mole, respectively, in CCl_4 from IR work.

The results of previous investigations have indicated the necessity of detailed studies of the self-association of and interaction between molecules capable of forming hydrogen bonds. Vapor pressure and vapor density methods first used by Christian, Taha and Ling[58-60] have been used in the study presented here for precise determinations of parameters characteristic of the interactions between water and diethylamine and between methanol and diethylamine in several media in the temperature range 25 to 45°. The distribution and self-association of water, methanol and diethylamine in the three slightly volatile solvents n-hexadecane, diphenylmethane and benzyl ether has been studied as a prerequisite for the determination of equilibrium constants and enthalpies describing the heteroassociation of water and methanol with diethylamine. The results of these investigations are compared with relations proposed by Christian et al.[61,62] for correlation of solvent effects on complex formation.

CHAPTER II

OBJECTIVES

The objectives of this research were:

1. To obtain enthalpies and entropies of formation of the 1:1 Complexes water-diethylamine and methanol-diethylamine in the vapor phase.
2. To describe the thermodynamics of self-association of both water and methanol and complexes of water and methanol with the base diethylamine in low vapor pressure organic solvents of varying reactivity.

CHAPTER III

EXPERIMENTAL

Chemicals

Methanol was purchased from Malinkrodt Chemical Company as reagent grade (purity >99%) and was fractionally distilled from magnesium methoxide in a 30 plate Oldershaw Column to remove traces of water. The diethylamine was purchased from J. T. Baker Chemical Company and certified to have purity greater than 99.3%. This amine was fractionally distilled over fresh barium oxide to remove traces of water.

The low vapor pressure solvents used were purchased as practical grade and somewhat more elaborate procedures were followed to purify them. n-Hexadecane was purchased from Matheson, Coleman and Bell Chemical Company and was first treated with concentrated sulfuric acid, washed, passed through a column of activated alumina and finally distilled in a 12 plate Oldershaw Column under 10 mm air pressure. The fraction collected had a boiling point of 150° at this pressure. This product showed no impurity peaks when passed through a gas chromatograph. Diphenylmethane, also a Matheson, Coleman and Bell product, was initially purified by repeated fractional freezing and then distilled under 10 mm air pressure. The

boiling point was 123° at this pressure. This product also showed no impurity peaks when examined on a gas chromatograph. The third solvent, benzyl ether, was considerably more difficult to purify than the first two. This solvent was obtained from two sources, Eastman Chemical Company and Matheson, Coleman and Bell. The ether was distilled under the same conditions as the first two solvents (12 plate column, 10 mm pressure) but the gas chromatographic analysis showed an impurity of ≈ 0.3 mole per cent. Examination of the literature indicated that the ether not only shows the expected behavior in forming peroxides but also readily oxidizes to benzaldehyde and then to benzoic acid on standing. To minimize this process samples were distilled shortly before use, then were frozen and protected from light. Finally, a process of fractional melting was employed immediately prior to sample addition to the apparatus.

Nonetheless, an inordinate amount of work was necessary to obtain the data reported in the appendix for this solvent. The initial vapor pressure studies of water and methanol in this solvent were marred by the appearance of colored deposits on the walls of the apparatus above the solution. This phenomenon generally occurred about 24 to 36 hours after a sequence of runs was started. Several sets of data for both methanol and water at each temperature were taken in which these deposits occurred. The deposits did not seem to have great effect on the vapor pressure data since runs made before the deposits appeared agreed fairly well with those made afterward.

Finally, after purification of a sample of ether from Matheson, Coleman and Bell, data were obtained for water and methanol in the

ether, using the same apparatus, which showed no contamination. The qualitative aspects of these data were identical with those taken where contamination did occur and the values of the distribution and association constants were similar.

All the data reported in the Appendix for single and mixed vapor pressure systems using this ether as the solvent were obtained with the sample which showed no contamination. This final distillation product was kept continuously under vacuum and not exposed to light except for short periods of time when samples were withdrawn for use in vapor pressure studies.

Considering the difficulties experienced with this ether it is believed that, although the final data are of high precision, the calculated association and distribution constants are inherently somewhat less accurate than those derived from data in the other two solvents.

Temperature Control and Pressure Measurement

Measurements were taken on all systems at three temperatures, 25, 35 and 45°. Constant temperature baths for all systems consisted of 20 gallon aquariums utilizing water as the bath medium. Temperatures were controlled through the use of mercury contact thermoregulators controlling Model E2 Electronic Relays from Lux Scientific Company. 300 watt light bulbs, painted black, were used as control heaters.

When necessary, cooling was provided by circulating liquid from an external refrigerated bath through a copper coil in the water bath. Good circulation in the water bath was assured by utilizing two pumps with a total capacity of better than 600 gal/hr. Bath temperatures were measured by one degree thermometers (marked at 0.01 degree intervals) at 25 and 35° and by a 0 to 50 degree thermometer (marked at 0.1

degree intervals) at 45°. The bath temperature was controlled to better than ±0.01 degree at 25 and 35°. Control precision probably approached ±.02 degree at 45° although changes of this magnitude could not be observed on the thermometer.

The basic types of apparatus used in this study have been described previously.[59,60,63] Pressure measurements were made by two different methods. Diethylamine distribution, water distribution and alcohol-amine and water-amine data in diphenylmethane (DPM) were taken using closed-end mercury manometers. A Gaertner M911 Cathetometer (with 50 part vernier) was used to measure the difference in mercury levels. The cathetometer could be read to ±0.01 mm. A Texas Instruments Fused Quartz Precision Pressure Gage was used for pressure measurements for all data other than those mentioned above. This instrument employs photoelectric nulling of a reflected light beam from a mirror attached to a fused quartz Bourdon tube. The minimum resolution of the instrument used in this study was 0.003 mm absolute.

PVT and Vapor Density Systems

The PVT system was composed of two Pyrex flasks (with approximate volumes of 2.0 and 0.6 liters) connected through a Manostat Teflon needle valve (A78-425-01). Connection of the small flask to the TI pressure gage was through a 1 mm i.d. Pyrex capillary. The first step in experimental procedure was the addition of a sample through a mercury-covered sintered glass disc of fine porosity. Once a desired pressure had been obtained in both flasks the valve was closed and the small bulb attached to the TI gage was evacuated through a Delmar stopcock for a short period of time. After closing the

outlet valve and when equilibrium was established in this side of the system the connecting needle valve was opened and the pressure in both flasks allowed to reach equilibrium. The measured quantities P_F, the final equilibrium pressure in the total system, P_L, the initial pressure in the large flask, and P_S, the residual pressure in the small flask, together with the volume ratio (R_V) of the large flask to the total system were used in a least squares treatment of the vapor system. The volume ratio (R_V) was determined with dry nitrogen. The equilibrium pressure in both flasks (P_F) becomes the initial pressure in the large flask (P_L) for the next expansion and in this manner a series of stepwise pressure measurements from high pressure to low are made.

The vapor density system was similar to that described by Christian, et al.[58] It consisted of a three liter Pyrex flask with a Delmar stopcock for evacuation. The mercury covered sintered glass disc was attached to the system by a 24/40 female ground joint seated on a 24/40 male joint in a mercury well. Teflon sleeves were used on ground joints to prevent freezing. Pressure measurements were made with the TI gage rather than with a mercury manometer.

This vapor density system offers a rapid and convenient method of determining the 1:1 formation constant for systems of two interacting vapors which are not highly associated. The procedure may be described using the methanol-diethylamine system as an example. Increments of methanol were delivered to the evacuated system through the mercury-covered disc using an RGI Precision Micrometer Buret of 0.25 ml volume. When a liquid sample had vaporized through the disc the equilibrium pressure was measured and the process repeated from five to ten times.

When this "calibration" run was completed the system was reevacuated to a pressure less than 0.02 torr and a large increment of diethylamine (DEA) was added, from a previously degassed liquid sample attached to the flask by a Fischer-Porter Teflon needle valve (795-005), to give a pressure of 50-100 torr. Then the process of adding increments of methanol was repeated as exactly as possible. The total pressure of methanol in the system was kept low to avoid the necessity for self-association corrections for the alcohol. The maximum pressure of methanol used at 25° was roughly 30 torr. The measured quantities for this system are P_M, the pressure of methanol as a function of the volume of methanol added, Π_A, the formal, or ideal gas pressure, of diethylamine in the system which is calculated from the initial pressure of amine using the association constant from the PVT study of DEA, and P_T the total pressure of amine plus methanol at points corresponding to the exact amount of methanol added in the calibration run. The analysis presented in the next chapter is based on these three pressures.

Vapor Pressure Systems

The basic apparatus used in the vapor pressure studies consisted of two Pyrex flasks with a combined volume of about 800 cc which was determined accurately by weight using liquid water. The smaller flask was connected to the TI gage by a 1 mm i.d. Pyrex capillary wrapped with a silicone rubber heating tape from the TI capsule to a short distance below the water surface in the thermostatted bath. The heating tape was kept at a temperature roughly equivalent to the capsule temperature (45°) to prevent condensation in the connecting tube at bath temperatures above 25°.

The larger flask, which contained the non-volatile solvent, was joined to the smaller through a Fischer-Porter Teflon needle valve (695-005). The large flask had a male 24/40 mercury-cup joint for attaching the mercury-covered sintered glass disc for sample addition of either methanol or water using the 0.25 ml microburet. The small flask had attached to it through a Fischer-Porter Teflon needle valve (795-005) a reservoir of liquid diethylamine.

Prior to commencing a set of experiments a volume ranging from about 100 to 250 cc of the particular solvent was weighed into the apparatus. The system was then evacuated at room temperature to a pressure approaching the vapor pressure of the solvent and the pressure was monitored for several hours to check for leaks.

The vapor pressures of the three solvents used were sufficiently low so that no Raoult's Law corrections were necessary at the temperatures employed. Both n-hexadecane (HX) and benzyl ether (BZE) have vapor pressures below 0.01 torr at 25°. Diphenylmethane (DPM) has a vapor pressure somewhat higher at room temperature ($\simeq$ 0.015 torr).

In order to minimize the number of sample changes employed one sample of a solvent might be used for vapor pressure data on two single volatile component systems such as water and methanol. Another sample of the same solvent would be used for diethylamine (DEA) distribution and the study of the two volatile component systems water-DEA and methanol-DEA.

When one solvent sample is used for several runs it is necessary to insure that no appreciable amount of solvent is pumped away in the evacuation process at the end of a run at one temperature. One

precaution taken was to avoid pumping on the system at temperatures higher than 25°. The system was evacuated at 25° and then the bath temperature was raised to 35° or 45°. When the run at the higher temperature was completed the bath was cooled to 25° before pumping out the system. Due to the extremely low vapor pressures of HX and BZE at 25° there was little fear that significant quantities of these solvents would be pumped into the cold trap attached to the vacuum pump. There was some question as to whether DPM, with its higher vapor pressure at 25°, would be lost from the system. Fortunately, DPM has a very strong characteristic odor which enables the detection of very small quantities of this compound. Inspection of the cold trap after each pumpdown at 25° failed to show the presence of detectable quantities of DPM and in the case of the other two solvents failed to show any liquid material not soluble in water. A further precaution taken was to stagger the sequence of runs, starting at 25° with one run and then concluding the work after taking data at 35° and 45° with a run at 25°. This process failed to show systematic errors which could be ascribed to loss of solvent.

One potentially large source of systematic error in experiments of this type should be discussed. To speed equilibrium in these systems it is advantageous to agitate the solution by some means. In the systems presented here this was done by placing a magnetic stirring bar in the solution and driving it by a submersible magnetic stirrer (TRI-R Instruments) mounted underneath the solution flask in the water bath. Initially, stirring bars coated with Teflon were used for this purpose. These stirring bars were commercially produced and presumably "vacuum tested." However, it was found that

in several circumstances contamination of the solution was evident. In one case, a DPM solution, under vacuum, was left sitting for several days and a large brown deposit formed on the bottom of the solution flask around the stirring bar. Contamination in this case was probably enhanced because the bar had been cleaned with a strong oxidizing agent prior to placing it in the solution. Similar problems caused the rejection of a considerable amount of experimental data.

This problem may be partially avoided by using Pyrex sealed stirring bars. However, these bars are not infrequently broken and this presents a worse contamination problem. A compromise was effected by enclosing a Pyrex covered stirring bar in heat-shrinkable Teflon tubing to soften contact between the bar and the glass flask. Primarily this type of bar was used in the two volatile component vapor pressure experiments.

Single Volatile Component Vapor Pressure Studies

All the single component studies with the exception of DEA and water distributions in DPM were done using the apparatus described previously. DEA and water distributions in DPM were done using an apparatus which was very similar. The only difference was that closed-end mercury manometers were used to measure pressure and this necessitated corrections to the total system volume due to mercury displacement with increasing or decreasing pressure.

Samples of water or methanol were added to the evacuated solvent systems at 25, 35 and 45^{o} through the mercury covered sintered glass disc attached to the large flask. The stopcock between the two flasks was always kept open in the water or methanol work. The microburet

was calibrated by adding samples to an evacuated weighing bottle through a similar disc. By knowing the weight of solute added, measuring the equilibrium vapor pressure above the solution and knowing both vapor and solution volumes it was possible to calculate the solute concentration at any point. Separate burets were used for water and methanol and, when not in use, these burets were kept in chambers thermostatted at 25°. A drying tube was attached to the methanol buret holder.

A different procedure was used for amine distribution since, due to the high volatility of the amine, it was impossible to make accurate additions with a buret. To overcome this problem the amine was added to the system with the use of the liquid sample attachment mentioned previously. The stopcock connecting the large and small flasks was closed after evacuation of the system. At this point the pressure in the entire system was very low (about 0.02 → 0.06 torr generally). The TI gage was reset to indicate a pressure of zero. Then the stopcock connecting the small flask to the previously degassed liquid sample of DEA was opened. After a suitable pressure of amine had built up in the small flask the stopcock was closed and the equilibrium pressure measured. At this point, the valve connecting the small flask and the larger, solvent containing, flask was opened. When equilibrium was attained between solution and vapor the pressure was read, the connecting stopcock closed and the process repeated. The number of moles of DEA introduced into the system was calculated from the initial and final pressures in the small flask using the known association constant for the vapor and the volume of the small flask.

From the measurements for single component distribution the total number of moles added to the system and the vapor pressure above the solution are known. By knowing the vapor volume above the solution the number of moles in the vapor may be calculated and subtraction of this quantity from the total number of moles of amine, water or methanol added gives the number of moles in solution.

The molar concentration of the solute may, in some cases, simply be calculated by dividing the number of moles in solution by the solvent volume. If solution concentrations become large enough corrections must be made for the molar volumes of the solutes. In some instances these corrections are negligible (water in HX and in DPM) but in other systems they are occasionally large enough to change the solution volume by two per cent or so. At the concentrations employed it was sufficient to assume that the molar volume of the solute was equal to its molecular weight divided by its density. Examination of published molar volume data indicated that this was a very satisfactory correction at the concentration ranges employed in this study.

Two Volatile Component Systems

Although the data obtained were not so easily interpreted the experimental procedures followed in the systems with two volatile components involved a simple combination of those previously discussed. Briefly, DEA was added from the liquid addition flask as described previously for DEA distribution until a desired amine concentration was reached in the initially evacuated solvent system. After attainment of equilibrium increments of either water or methanol were added through the disc. When equilibrium was established for an increment

the total pressure was measured and then the next increment was added. At each temperature generally two different amine concentrations were used. The experimental data consisted of sets of total pressure, added moles of amine and added moles of water or methanol.

Equilibrium in Vapor-Solution Systems

There are several factors governing the speed at which equilibrium is attained in these solution systems. The physical arrangement of the system, in two respects, is quite important. Both the surface area of the solvent and the rate of agitation of the solvent or solution are quite important. The ratio of surface diameter to depth of solution was generally larger than a factor of two and stirring was rapid enough to produce a vortex extending about 3/4 of the distance to the flask bottom effectively increasing the available surface area.

It was generally found that in single component distribution studies equilibrium was reached in approximately 20 minutes at 25^{o}. At high solute pressures equilibrium is somewhat slower due to the fact that the solute vapor pressure is readily attained by vaporization of a small fraction of the liquid added through the disc.

In the two volatile component distribution studies it might have been expected that equilibrium would be significantly slower. However, this was not generally the case. One reason for this is that the amine pressure was quite low in all systems. Another reason is that the vapor concentrations of either water or methanol were not as high in the mixed systems as in the single component distribution systems. It was noticed that, in the case of the water-amine systems, equilibrium became appreciably slower when the total vapor pressure

of the system exceeded the vapor pressure of water at that temperature. This effect was not noticed with methanol since very substantial concentrations of methanol could be reached without approaching a total pressure equivalent to the methanol vapor pressure at the system temperature.

CHAPTER IV

DATA TREATMENT AND RESULTS

Vapor Phase Data

Diethylamine Association

If the assumption is made that all deviations from the ideal gas law in vapors of compounds capable of forming hydrogen bonds can be explained on the basis of the formation of specific molecular complexes the total pressure of the vapors may be represented as a sum of the partial pressures of the assumed species

$$P_T = p_A + P_{A_2} + P_{A_3} + \ldots \quad (1)$$

where p_A, P_{A_2}, P_{A_3}, etc. are pressures of monomer, dimer, trimer, etc.. The formal pressure or that pressure the vapors would exert if they behaved ideally may be represented as

$$\Pi_A = p_A + 2K_2 p_A^2 + 3K_3 p_A^3 + \ldots \quad (2)$$

where Π_A is formal pressure which is equivalent to the total moles of A in the system times (RT/V) and the successive K's are equilibrium

constants defined by

$$K_n = \frac{P_{An}}{(p_A)^n} \tag{3}$$

Using these equations and assuming as a first approximation that the only associated species is a dimer the PVT data for diethylamine were analyzed. The three measured pressures are expressed as

$$P_S = p_A + K_2 p_A^2 \tag{4}$$

$$P_L = p_A + K_2 p_A^2$$

$$P_F = p_A + K_2 p_A^2$$

where the p_A values are not identical. The set of formal pressure expressions are

$$\Pi_S = p_A + 2K_2 p_A^2 \tag{5}$$

$$\Pi_L = p_A + 2K_2 p_A^2$$

$$\Pi_F = p_A + 2K_2 p_A^2$$

Also, if the set of equations (5) with the correct value of K_2 is a good representation of the data, then the following relationship holds

$$\Pi_L = \frac{\Pi_F}{R_V} - \Pi_S\left(\frac{1 - R_V}{R_V}\right) \tag{6}$$

where R_V is the volume ratio (VL/VT) of the large bulb volume to the total system volume.

To determine whether the sets of equations 4 and 5 are a good representation of the PVT data an optimizing procedure was used. An initial value of K_2 was assumed; this value was used with P_F and P_S to calculate values of p_A. These p_A values with the assumed K_2 value were used to calculate values of Π_F and Π_S. The calculated Π values were used with the volume ratio in equation 6 to calculate a value of Π_L. The calculated value of Π_L and the assumed value of K_2 were used to calculate a p_A value which was finally utilized with the K_2 value to calculate a value of P_L. This P_L value was then compared with the observed P_L value. K_2 was systematically changed until the minimum in root mean square deviation (RMSD) was reached. RMSD is defined as

$$\text{RMSD} = \left(\sum_{i=1}^{n} (P_i - P_i\text{Cal})^2/n - p \right)^{\frac{1}{2}} \qquad (7)$$

where n is the number of experimental points and p is the number of parameters (one in the present case).

The assumption of a dimerization equilibrium appeared to represent the PVT data for DEA within experimental error which made unnecessary the use of additional parameters. Equilibrium constants and RMSD's for dimer formation at 25, 35 and 45° are presented in Table 1.

Water and Methanol Association with Diethylamine

The assumption that all deviation from the ideal gas law is due to complex formation was also applied in dealing with mixtures of methanol and water with diethylamine. The two mixtures were treated

TABLE 1

Vapor Phase Association Constants for Diethylamine and 1:1 Complexes of Water and Methanol with Diethylamine*

T(°C)	K_2(torr^{-1})	K_{11}(torr^{-1})	K_{11}(torr^{-1})
	$(DEA)_2$	H_2O-DEA	MeOH-DEA
25	$(0.80\pm0.01) \times 10^{-4}$	$(4.24\pm0.09) \times 10^{-4}$	$(7.30\pm0.05) \times 10^{-4}$
35	$(0.64\pm0.01) \times 10^{-4}$	$(2.93\pm0.05) \times 10^{-4}$	$(4.92\pm0.03) \times 10^{-4}$
45	$(0.53\pm0.01) \times 10^{-4}$	$(2.09\pm0.04) \times 10^{-4}$	$(3.35\pm0.02) \times 10^{-4}$

*See last section in this chapter for a note on error calculations, etc.

identically so only the expressions for the water-DEA mixture will be presented. The formal pressure of water in the system is expressed as

$$\Pi_W = p_W + K_{WA} p_W p_A \tag{8}$$

where no self-association of water is considered. The formal pressure of amine in the system is

$$\Pi_A = p_A + 2K_2 p_A^2 + K_{WA} p_W p_A \tag{9}$$

and the total pressure in the system is

$$P_T = p_A + K_2 p_A^2 + p_W + K_{WA} p_W p_A \tag{10}$$

These equations are solved by expressing p_W as a function of Π_W, p_A and K_{WA} from equation (8). Substitution is made for p_W in equation (9) to obtain a cubic in monomer amine pressure (p_A). Using an assumed value of K_{WA} the polynomial is solved numerically for a p_A value; this value is substituted into (8) to calculate a p_W value. These values of p_A and p_W with the assumed K_{WA} are used to calculate a P_T value according to (10). The process is continued until a K_{WA} value is obtained which produces a minimum RMSD.

The assumption that only the one to one complexes of water-DEA and methanol-DEA form under the conditions of the experiments was sufficient to fit the vapor density data within experimental error. The equilibrium constants, their standard errors and the RMSD's for the fits at 25, 35 and 45° are presented in Table 1.

The enthalpy and entropy changes for these association reactions may be determined from the expression

$$\Delta G^{o} = -RT\ln K_{a} = \Delta H^{o} - T\Delta S^{o} \qquad (11)$$

where K_a is the equilibrium constant for the reaction (it is assumed that the error involved in replacing activities with concentrations in the equilibrium constant expression is negligible) and ΔH^{o} and ΔS^{o} are assumed to be invariant over the temperature range involved. The least squares values of ΔH^{o} and ΔS^{o} for the DEA dimer and the 1 to 1 complexes of water-DEA and methanol-DEA are given in Table 2. Van't Hoff plots for the equilibrium constants are given in Figure 1.

Vapor Pressure Data

Single Component Distribution Data

The distribution of a volatile solute between the vapor phase and a non-volatile solvent may be mathematically described as follows. If no association occurs in either phase Nernst's distribution law is expressed as

$$K_D = \frac{C_B^{\,S}}{C_B^{\,V}} \qquad (12)$$

where $C_B^{\,S}$ is the molar concentration of solute B in solution and $C_B^{\,V}$ is the molar concentration of the solute in the vapor phase which is simply the pressure of B divided by the product of the gas constant and the temperature in ^{o}K (P_B/RT). If aggregates of the solute form in solution

TABLE 2

Thermodynamic Parameters for the Vapor Phase Association of Diethylamine and the Association of Water and Methanol with Diethylamine

(Diethylamine)$_2$

ΔH_2^o = -(3.82±0.06) kcal/mole

ΔS_2^o = -(18.4±0.2) eu

Water-Diethylamine

ΔH_{11}^o = -(6.63±0.05) kcal/mole

ΔS_{11}^o = -(24.5±0.2) eu

Methanol-Diethylamine

ΔH_{11}^o = -(7.31±0.02) kcal/mole

ΔS_{11}^o = -(25.7±0.1) eu

A standard state of one atmosphere is used here.

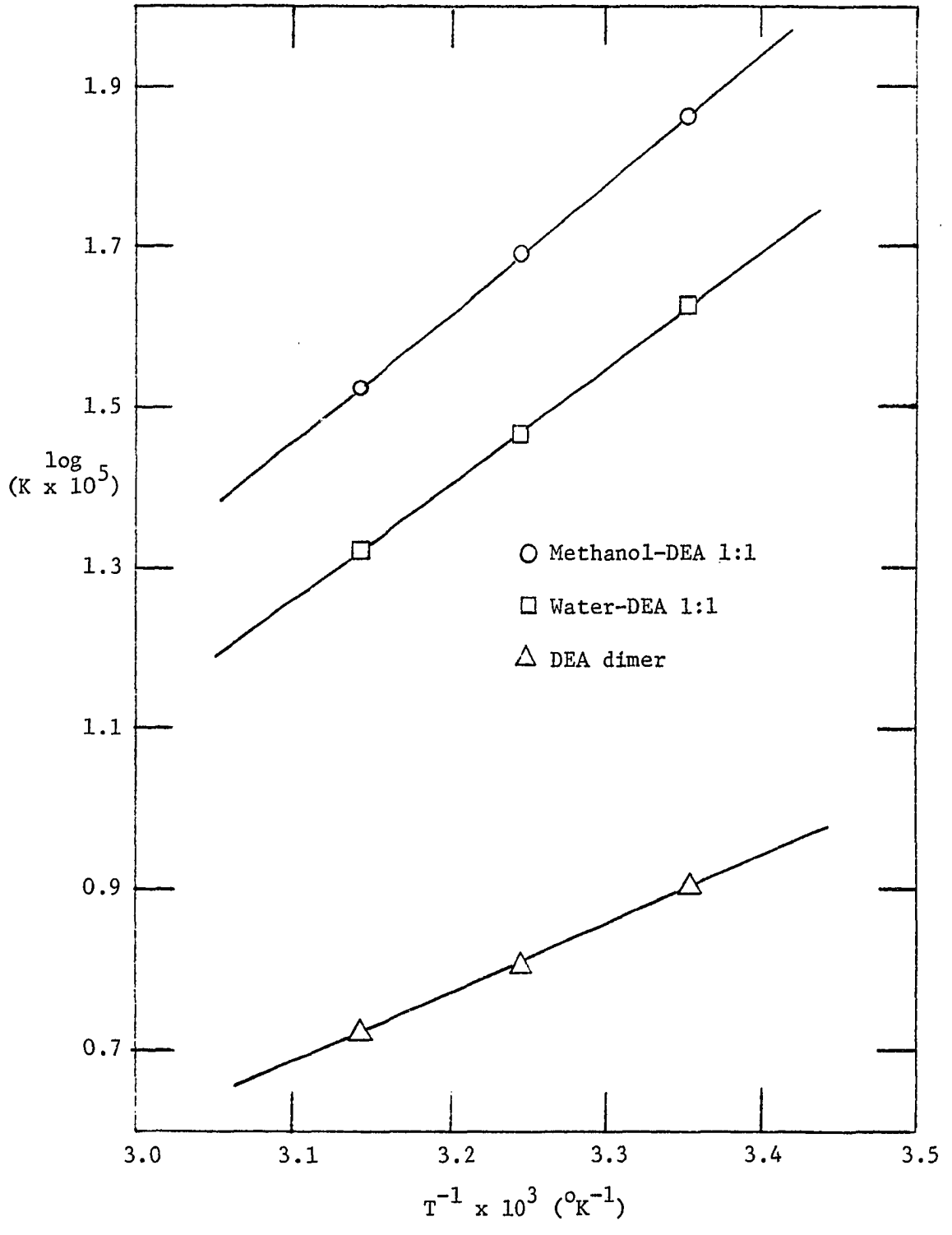

Figure 1. Van't Hoff plots for the vapor phase self-association of diethylamine and the 1:1 complexes of water and methanol with diethylamine.

the formal or analytical concentration may be expressed, assuming that the activity coefficient of each species is unity, as

$$f_B = C_B + 2C_{B_2} + 3C_{B_3} + \ldots \tag{13}$$

where C_B, C_{B_2}, C_{B_3}, etc., are concentrations of monomer, dimer, trimer, etc.. By introducing formation constants defined as

$$K_n = \frac{C_{Bn}}{(C_B)^n} \tag{14}$$

equation 13 may be transformed to

$$f_B = C_B + 2K_2C_B^{\ 2} + 3K_3C_B^{\ 3} + \ldots \tag{15}$$

There is rarely any convenient method of directly determining the monomer concentration C_B in solution. However, if parameters are known to describe the vapor phase association or equally, if this is negligible, then equation (12) may be used to good effect by expressing C_B in solution as $K_DC_B^{\ V}$. With this substitution equation 15 becomes

$$f_B = K_DC_B^{\ V} + 2K_2(K_DC_B^{\ V})^2 + 3K_3(K_DC_B^{\ V})^3 + \ldots \tag{16}$$

With measured values of f_B and $C_B^{\ V}$ one may assume any functional dependence of f_B on $C_B^{\ V}$ according to (16) and by using a computer program for polynomial regression determine the goodness of fit of the assumed form in terms of the RMSD, the least squares values of K_D and the equilibrium constants and their standard errors.

A computer program was written to fit vapor pressure data to equation (16) to four terms. This program was capable of fitting equations in the form of (16), using any desired exponent for a particular term. The inverse matrix solution[64] was used to solve the normal equations since evaluation of the diagonal terms of the inverse matrix enables the calculation of the errors in the coefficients. Instability problems were avoided by using Double Precision storage.

In fitting data to equation (16) one looks for a functional form which gives the smallest standard deviation between observed and calculated f_B values. However, there are other restrictions on this process due to the fact that the coefficients of the polynomial are related to equilibrium constants. If a particular functional form has a term with a negative coefficient then this term is discarded because a negative equilibrium constant has no physical significance. In addition, if sets of data are taken at several temperatures a plot of the logarithm of the equilibrium constants versus reciprocal temperature (van't Hoff plot) should be linear. Thus, there are several criteria by which the "best fit" of a particular set of data is judged.

Diethylamine Distribution

Distribution and association constants for DEA in the three solvents n-hexadecane (HX), diphenylmethane (DPM) and benzyl ether (BZE, are presented in Table 3. As expected from previous reports very little association was detectable in these solvents at the concentration levels employed in this study. A monomer-only fit was reasonably good for these systems but significant improvement in the fit was noticed when a second-order term was added for DEA in HX and BZE. The data

TABLE 3

Distribution and Association Constants for Diethylamine in Three Non-Volatile Solvents at 25, 35 and 45°

T(°C)	K_D	$K_2(M^{-1})$	RMSD(M)
	n-Hexadecane		
25	206.1±0.8	0.251±0.014	0.0004
35	157.0±0.1	0.124±0.003	0.0001
45	113.6±0.1	0.123±0.003	0.0001
	Diphenylmethane		
25	288.5±0.5	-	0.0011
35	204.1±0.4	-	0.0010
45	148.1±0.3	-	0.0007
	Benzyl Ether		
25	276.6±0.5	0.121±0.003	0.0003
35	199.1±0.3	0.066±0.003	0.0004
45	139.8±0.1	0.083±0.001	0.0002

scatter was somewhat worse for DEA in DPM and no improvement resulted from a monomer-dimer fit for these data. The dimer equilibrium constants are quite small and do not show good temperature dependence. No improvement in the fit was gained by adding other terms or replacing the dimer term with a trimer or tetramer. Figure 2 shows the van't Hoff plots of K_D for DEA distribution between the vapor phase and each solvent. Table 4 gives the least squares values of ΔE_D^o and ΔS_D^o for the three systems.

Water Distribution and Association

Table 5 gives RMSD values for several fits for water distribution between the vapor phase and each solvent. In HX water appeared to be monomeric at all three temperatures and no improvement in the fit was obtained by including terms higher than the monomer in equation (16). For water in both DPM and BZE substantial improvements in RMSD were obtained by including associated species in the fit. The assumptions of a monomer-dimer (1-2) equilibrium in DPM and a monomer-dimer-trimer (1-2-3) equilibrium in BZE appear to provide the best fits. Table 6 gives the least squares values of the distribution and association constants for water in the three solvents. Figure 3 shows the temperature dependence of K_D in these solvents. Table 7 gives the least squares values of the thermodynamic parameters for water in the three solvents.

Methanol Distribution and Association

Among the three single component distribution systems the methanol-solvent systems were quite unusual in that in concentration

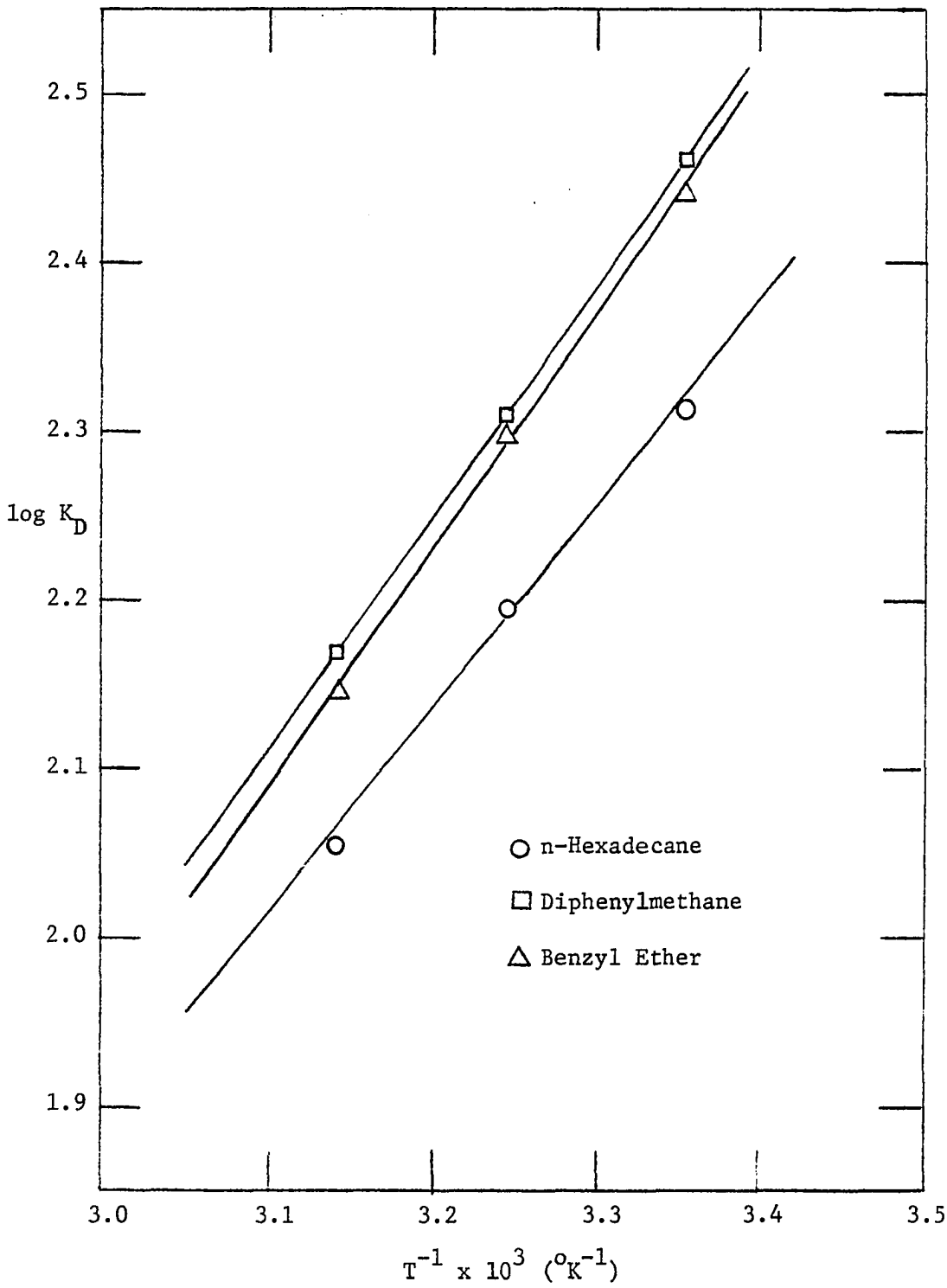

Figure 2. Van't Hoff plots for distribution of diethylamine between the vapor phase and three non-volatile solvents.

TABLE 4

Thermodynamic Parameters for Distribution of Diethylamine in Three Non-Volatile Solvents

n-Hexadecane

ΔE_D^o = -(5.60±0.04) kcal/mole

ΔS_D^o = -(10.2±0.1) eu

Diphenylmethane

ΔE_D^o = -(6.2?±0.01) kcal/mole

ΔS_D^o = -(11.81±0.02) eu

Benzyl Ether

ΔE_D^o = -(6.43±0.03) kcal/mole

ΔS_D^o = -(12.35±0.10) eu

Based on standard state of one mole per liter.

TABLE 5

RMSD's for Several Least Squares Fits of Water in Three Non-Volatile Solvents at 25, 35 and 45°

		Hexadecane	
Fit	25°	35°	45°
		RMSD(M) x 10^4	
1	0.20	0.22	0.20
		Diphenylmethane	
	25°	35°	45°
		RMSD(M) x 10^4	
1	2.16	4.67	5.69
1-2	0.93	0.93	1.01
1-3	1.00	1.00	1.61
1-4	1.13	1.30	2.13
1-2-3	0.94*	0.90	0.93*
1-2-4	0.94*	0.88	0.95*
1-3-4	0.95*	0.96*	1.16*
		Benzyl Ether	
	25°	35°	45°
		RMSD(M) x 10^4	
1-2	1.67	2.96	2.09
1-3	1.86	2.43	2.81
1-4	4.26	5.85	6.32
1-2-3	0.63	0.93	0.25
1-2-4	0.75	0.90	0.38
1-3-4	0.55*	1.28*	0.80*

*These fits gave a negative parameter (usually the highest-order term).

TABLE 6

Distribution and Association Constants for Water in Three Non-Volatile Solvents at 25, 35 and 45°

T(°C)	K_D	$K_2(M^{-1})$	$K_3(M^{-2})$
		n-Hexadecane	
25	2.147±0.007	-	-
35	1.865±0.003	-	-
45	1.708±0.002	-	-
		Diphenylmethane	
25	20.66±0.10	1.84±0.15	-
35	16.40±0.05	1.53±0.06	-
45	13.25±0.03	1.17±0.04	-
		Benzyl Ether	
25	72.44±0.17	0.55±0.04	2.79±0.23
35	51.22±0.13	0.46±0.04	2.51±0.16
45	37.02±0.03	0.50±0.01	1.56±0.04

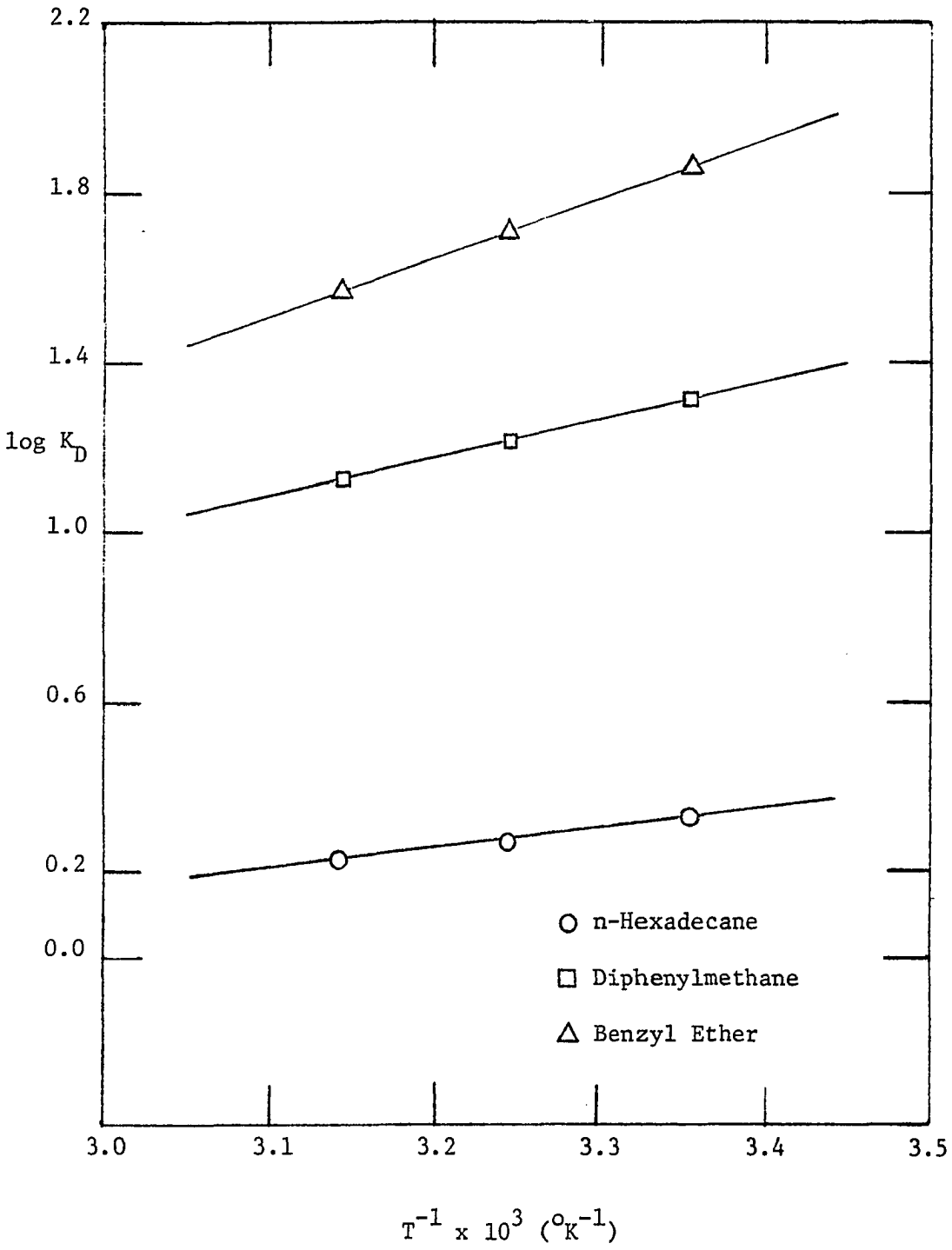

Figure 3. Van't Hoff plots for distribution of water between the vapor phase and three non-volatile solvents.

TABLE 7

Thermodynamic Parameters for Distribution and Association of Water in Three Non-Volatile Solvents

n-Hexadecane

$\Delta E_D^o = -(2.13 \pm 0.03)$ kcal/mole

$\Delta S_D^o = -(7.64 \pm 0.10)$ eu

Diphenylmethane

$\Delta E_D^o = -(4.17 \pm 0.02)$ kcal/mole $\quad \Delta H_2^o = -(4.25 \pm 0.18)$ kcal/mole

$\Delta S_D^o = -(9.95 \pm 0.04)$ eu $\quad \Delta S_2^o = -(13.0 \pm 0.6)$ eu

Benzyl Ether

$\Delta E_D^o = -(6.33 \pm 0.01)$ kcal/mole $\quad \Delta H_2^o \simeq -2.0$ kcal/mole

$\Delta S_D^o = -(14.70 \pm 0.02)$ eu

$\Delta H_3^o = -(5.5 \pm 0.3)$ kcal/mole

$\Delta S_3^o = -(16.3 \pm 0.8)$ eu

Standard state is one mole per liter.

ranges readily obtainable a very high degree of association was observed. A plot of solute vapor pressure versus formal concentration for either the DEA or the water systems shows little or no curvature because (1) amines are only very slightly associated up to much higher concentration levels than those used here and (2) the solubility of water in solvents of the types used here is so small as to preclude substantial concentrations of associated species. Figure 4 shows the vapor pressure of methanol above solutions of methanol in n-hexadecane as a function of methanol concentration at three temperatures. (A few points were selected randomly from the large number of data points for the methanol-n-hexadecane system in the Appendix.) The extreme curvature of the lines indicates a high degree of methanol association in this solvent.

Table 8 presents RMSD's for numerous fits of the methanol vapor pressure data in the three solvents. What is readily obvious from the RMSD's for the methanol-HX system is that one three parameter fit is outstanding, the 1-3-8 fit. Only two fits have no negative parameters and lower RMSD's. These are the 1-2-4-9 and 1-3-4-9. However, the dimer and trimer constants in these two fits do not have good temperature dependence.

The RMSD's for fits in the two more reactive solvents, DPM and BZE, present a slightly different picture. For three parameter fits a sharp minimum is shown for 1-3-8 and 1-3-9 fits. When four parameter fits are considered the two fits 1-2-3-8 and 1-2-4-9 appear to provide significant improvements over the three parameter fits.

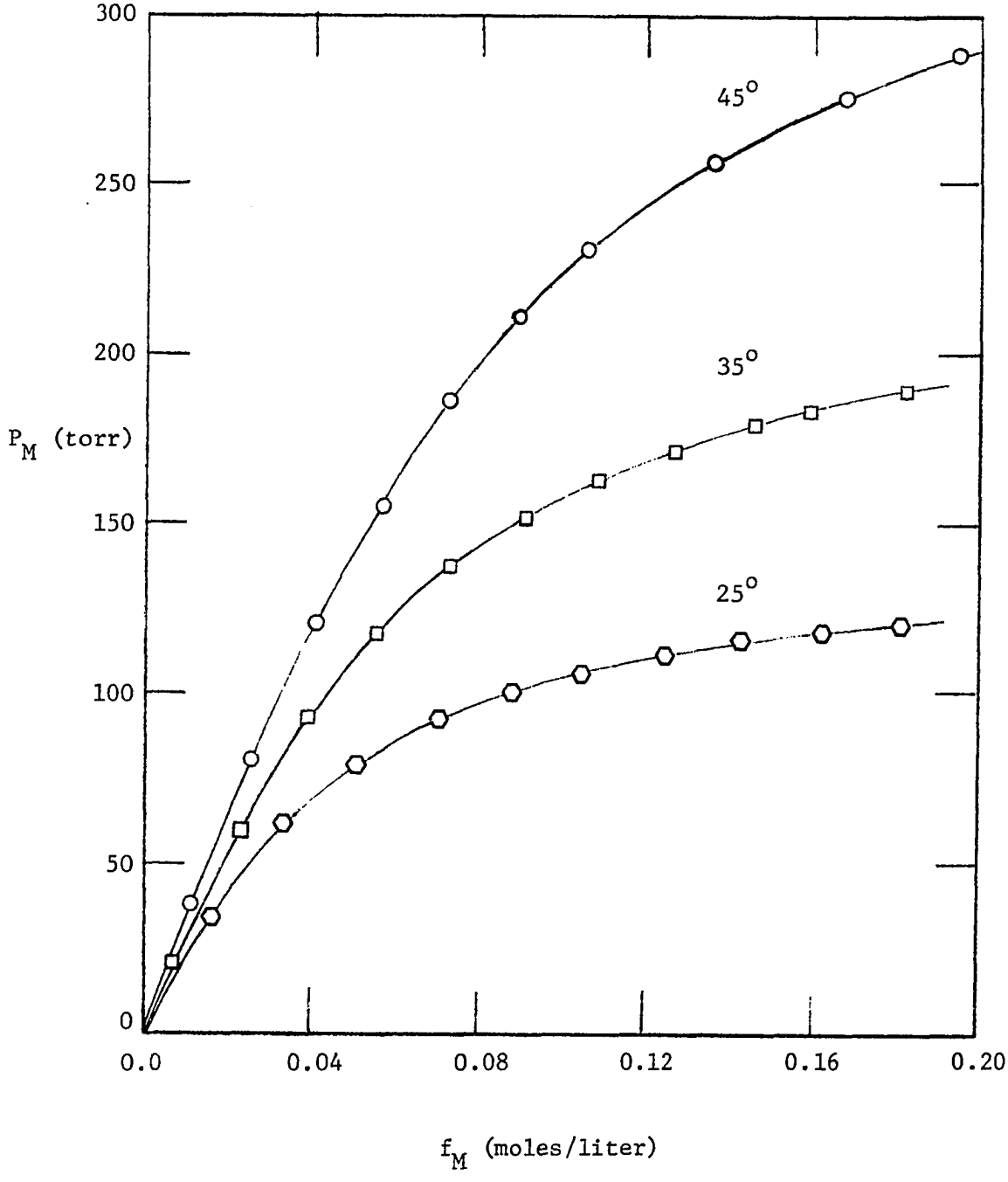

Figure 4. Vapor pressure of methanol versus formal concentration of methanol in n-hexadecane at 25, 35 and 45°. Points are experimental; lines are calculated on the basis of the 1-3-8 model.

TABLE 8

Comparison of RMSD's for Several Fits of Vapor Pressure Data for Methanol in Three Non-Volatile Solvents at 25, 35 and 45°

	n-Hexadecane		
Fit	25°	35°	45°
	RMSD's(M) x 10^4		
1-2	100.0*	126.0*	84.6
1-3	70.0	87.3	55.2
1-4	45.2	56.8	32.0
1-2-4	27.1*	34.5*	20.0*
1-3-4	21.8*	27.4*	16.3
1-3-6	10.2*	12.9*	7.2
1-2-8	4.7	5.1	6.2
1-3-8	2.3	2.7	1.8
1-4-8	4.0	5.3	4.0
1-2-9	9.4	10.6	10.3
1-3-9	3.9	3.5	3.6
1-2-3-8	2.4(-2)	2.7	1.8(-2)
1-2-4-8	2.6(K_2=3.4)	3.0(K_2=3.0)	2.0(K_2=1.4)
1-3-4-8	2.4(-4)	2.5(-4)	1.8
1-2-3-9	1.9(-2)	1.5(-2)	1.9(-2)
1-2-4-9	1.7(K_2=0.86)	1.5(K_2=1.14)	1.5(K_2=0.75)
1-3-4-9	1.7(K_3=22.4)	1.4(K_3=21.5)	1.5(K_3=10.7)
	Diphenylmethane		
	25°	35°	45°
	RMSD's(M) x 10^4		
1-2-4	48.8(-2)	40.5(-2)	35.1(-2)
1-3-6	21.3	18.7	17.3
1-2-8	17.5	20.3	22.9
1-3-8	6.2	5.1	5.7
1-4-8	20.5	23.6	26.0

*indicates one or more negative parameters; (-n) indicates that K_n was negative in that fit.

TABLE 8 - continued

	Diphenylmethane		
	25°	35°	45°
	RMSD's(M) x 10^4		
1-2-9	27.4	30.0	32.6
1-3-9	4.5	2.9	4.7
1-4-9	17.7	-	-
1-2-3-8	4.6	1.8	2.2
1-2-4-8	5.7	3.5	2.1
1-3-4-8	4.4(-4)	1.9(-4)	3.4(-4)
1-2-3-9	4.4(-2)	3.0(-2)	4.7
1-2-4-9	4.2	1.8	1.4
1-3-4-9	-	2.9	4.7

	Benzyl Ether		
	25°	35°	45°
	RMSD's(M) x 10^4		
1-3	108.4	75.0	70.3
1-4	44.2	55.7	59.3
1-2-3	65.0(-2)	48.8(-2)	48.4(-2)
1-3-6	22.0	19.3	19.9
1-4-6	44.4(-6)	44.0(-6)	45.6(-6)
1-2-8	39.8	40.5	42.6
1-3-8	9.8	11.6	12.4
1-4-8	45.1(-8)	48.0(-8)	49.9(-8)
1-2-9	52.4	51.4	53.0
1-3-9	7.4	10.1	10.4
1-4-9	45.2(-9)	49.4(-9)	51.4(-9)
1-2-3-8	3.1	5.0	5.0
1-2-4-8	2.4	1.8	4.2
1-3-4-8	5.4(-4)	7.8(-4)	7.5(-4)
1-2-3-9	6.2	7.7	6.7
1-2-4-9	1.2	2.2	3.5
1-3-4-9	7.1(-4)	9.3(-4)	8.6(-4)

From considering all these fits and neglecting those fits with a negative constant it appears that there is a choice between two fits: the 1-2-4-9 which consistently has a somewhat lower RMSD but has poor temperature dependence for the dimer constant in HX and the 1-2-3-8 fit which loses a dimer constant in HX but the resulting 1-3-8 fit in HX and the 1-2-3-8 fits in DPM and BZE have excellent temperature dependence for all constants.

On the basis of RMSD alone the 1-2-4-9 fit is the best overall fit but there are certain indications that a trimer is an important species in the low concentration region.

An additional fitting technique which was used on all the methanol data was to consider the first ten terms in equation (16). A Gaussian elimination procedure[65] was used to obtain the least squares solution to this tenth order equation. A series of ten coefficients were obtained and in each instance the trimer and octamer constants were positive and the tetramer and the ninth-order equilibrium constants were negative. The program was run using Double Precision arithmetic to minimize the problem of roundoff error in the elimination procedure.

Also, the four parameter program mentioned previously was extended to five parameters by the addition of a generalized matrix inversion subroutine. To check the accuracy of the procedure the input data matrix whose elements ranged in value from 10^2 to 10^6 was multiplied by the inverse obtained by the subroutine to see if a close approximation of the identity matrix was obtained. Double Precision arithmetic was also used here. The off-diagonal elements, which should be zero ideally, ranged in value from 10^{-9} to 10^{-16} with the great majority in the 10^{-12}

region indicating that roundoff error was not a severe problem.

Two five parameter fits were tried on all methanol distribution data. The first four terms were common (1-2-3-4) and the last term was either 8 or 9. Table 9 lists the values of all positive constants and their errors for the two five parameter fits of the methanol distribution data. The fits of the data for the HX system gave the most unequivocal results. At each temperature, for the 1-2-3-4-8 fit, both dimer and tetramer coefficients were negative. For the 1-2-3-4-9 fit of the HX data the dimer coefficients at 25 and 35° were negative and the dimer coefficient at 45° had a standard error of ±92 per cent. In terms of the number of observations the HX data contain more than half the total number of data points taken on all three methanol distribution systems. Also, at the same activity of methanol over the solution, a much larger fraction of the total methanol is associated in this solvent. For these two reasons this set of data should probably be given greatest weight in the process of determining a particular association model.

The five parameter fits for the other two alcohol-solvent systems are less clear-cut. Of the six five parameter fits with the 8 term present all but one have values of trimer constants which would make the trimer a considerably more important species than the tetramer. Five of the six five parameter fits for methanol in diphenylmethane indicate that the trimer term is more important than the tetramer term since at a given monomer concentration (C_M) of 0.1 molar the K_4 value has to be larger than the K_3 value by almost a factor of eight in order for the trimer and tetramer terms to be equivalent.

Unfortunately, no unequivocal decision can be made from the evidence of these fits as to which fit (1-3-8 and 1-2-3-8 or 1-2-4-9)

TABLE 9

Comparison of Two Five Parameter Fits of Methanol Vapor Pressure Data for Three Methanol-Non-volatile Solvent Systems

T(°C)	n	$K_2(M^{-1})$	$K_3(M^{-2})$	$K_4(M^{-3})$	$K_n(M^{-n})$
			n-Hexadecane		
25°	8	neg.*	204.±41.	neg.	$(9.2\pm1.7)10^7_9$
	9	neg.	40.±27.	1065.±295.	$(1.7\pm0.3)10^9$
35°	8	neg.	121.±25.	neg.	$(1.1\pm0.2)10^7_8$
	9	neg.	37.±14.	252.±96.	$(1.5\pm0.2)10^8$
45°	8	neg.	35.±11.	neg.	$(1.8\pm.3)10^6_7$
	9	0.61±0.56	2.±8.	226.±60.	$(1.6\pm.3)10^7$
			Diphenylmethane		
25°	8	neg.	4.9 ±1.4	neg.	859.±149.
	9	neg.	1.8 ±1.0	4.9±2.0	2605.±442.
35°	8	0.16±0.08	2.9 ±0.4	neg.	280.±21.
	9	0.48±0.07	0.96±0.30	4.0±0.6	718.±48.
45°	8	0.45±0.06	0.9 ±0.2	1.5±0.4	90.±6.
	9	0.65±0.05	neg.	4.0±0.3	195.±11.
			Benzyl Ether		
25°	8	0.43±0.03	0.49±0.08	0.70±0.09	5.4±0.3
	9	0.55±0.03	0.06±0.06	1.39±0.08	8.0±0.4
35°	8	0.49±0.03	0.09±0.09	0.88±0.10	2.3±.2
	9	0.56±0.04	neg.	1.23±0.12	3.1±.3
45°	8	0.35±0.06	0.26±0.14	0.44±0.14	1.1±0.2
	9	0.39±0.05	0.10±0.11	0.65±0.12	1.3±0.2

*indicates a negative equilibrium constant.

is best. The general impression is that there is some preference for a trimer term as opposed to either a dimer or tetramer term. The 1-3-8 and 1-2-3-8 fits are therefore proposed as the most satisfactory for the methanol distribution data. Evidence will be given later to support the premise that the fit including a trimer term is likely to be more widely applicable for alcohol association data.

Table 10 presents the values of distribution and association constants for methanol in the three solvents. Figure 5 shows van't Hoff plots for K_D for methanol in the three solvents. The least squares values of the thermodynamic parameters derived from the temperature dependence of the constants in Table 10 are given in Table 11.

Although methanol is not highly associated in the vapor phase it is necessary, in the vapor pressure work presented here, to calculate monomer pressure from the observed methanol pressures in order to obtain precise values for distribution and association constants. It may be noted that assumption of any reasonable association model in the vapor phase for methanol does not displace the order of the hierarchy of fits for the vapor pressure data. The PVT work[15] mentioned previously was initially fit by the customary 1-2-4 model for methanol vapor association with the surprising result of a negative dimer constant at 15°. When it became apparent that the 1-3-8 fit for methanol in n-hexadecane was highly satisfactory the methanol PVT data were fit by this model and the result was that the 1-3-8 model provided a better fit of the PVT data for methanol vapor than any previously proposed model for the association of methanol in the vapor phase. Accordingly, the values of enthalpy and entropy obtained for trimer and octamer formation

TABLE 10

Distribution and Association Constants for Methanol in Three Non-volatile Solvents at 25, 35 and 45°

T(°C)	K_D	$K_2(M^{-1})$	$K_3(M^{-2})$	$K_8(M^{-7})$
			n-Hexadecane	
25	8.249±0.025	-	83.8±1.6	$(1.80\pm0.05)10^8$
35	7.070±0.029	-	42.6±1.1	$(1.84\pm0.07)10^7$
45	6.063±0.013	-	25.4±0.4	$(2.27\pm0.05)10^6$
			Diphenylmethane	
25	51.92±0.47	0.32±0.07	3.05±0.24	1007.±84.
35	38.52±0.14	0.27±0.02	2.41±0.07	291.6±10.0
45	29.73±0.10	0.22±0.02	1.73±0.05	83.5± 2.9
			Benzyl Ether	
25	112.58±0.43	0.199±0.016	1.05±0.03	4.95±0.20
35	78.50±0.47	0.183±0.024	0.830±0.041	2.34±0.17
45	56.39±0.30	0.164±0.019	0.663±0.030	1.11±0.08

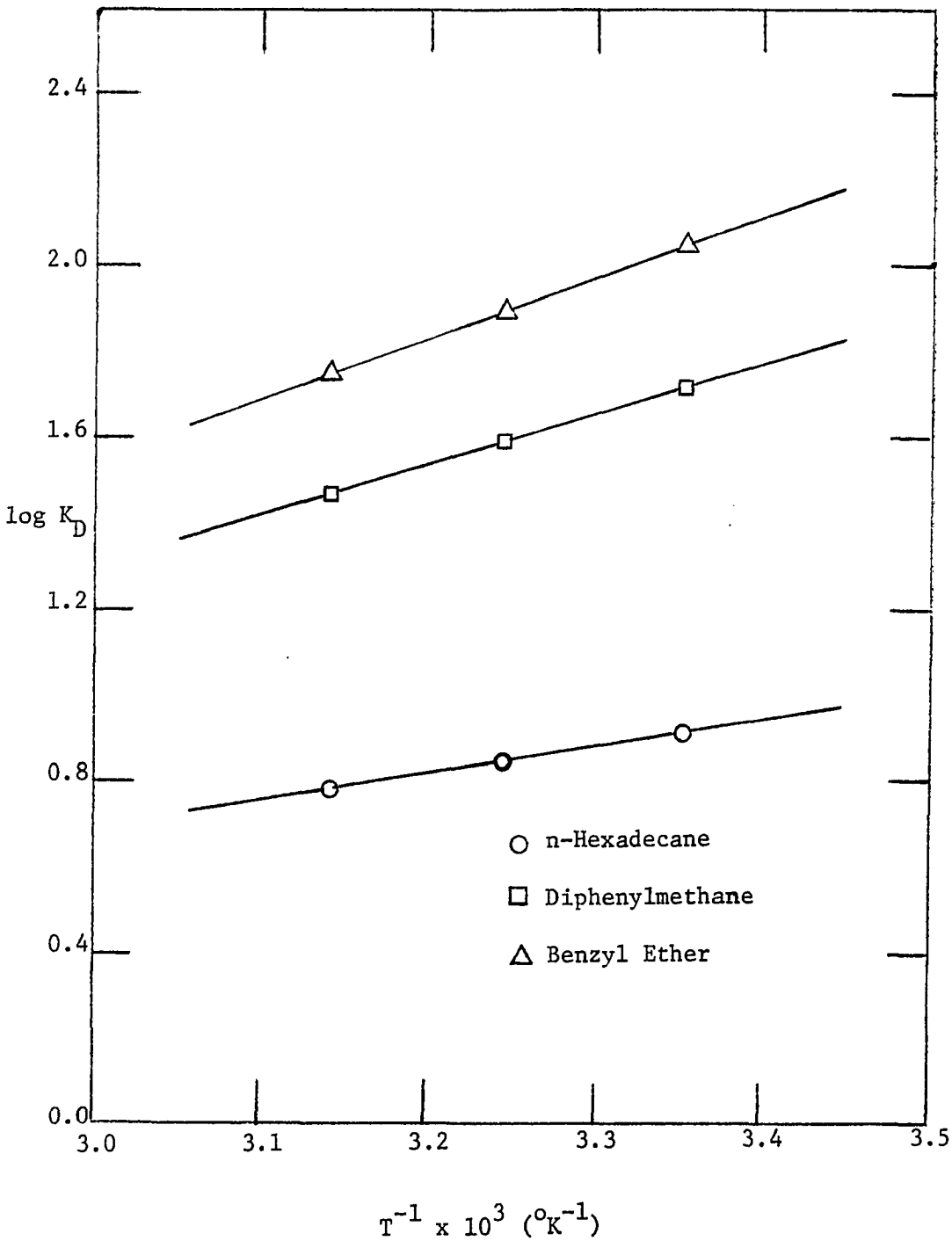

Figure 5. Van't Hoff plots for the distribution of methanol between the vapor phase and three non-volatile solvents.

TABLE 11

Thermodynamic Parameters for Distribution and Association of Methanol in Three Non-volatile Solvents

Hexadecane

ΔE_D^o = -(2.90±0.01) kcal/mole ΔH_3^o = -(11.27±0.09) kcal/mole

ΔS_D^o = -(7.53±0.03) e.u. ΔS_3^o = -(29.0±0.3) eu

ΔH_8^o = -(41.23±0.08) kcal/mole

ΔS_8^o = -(100.5±0.3) e.u.

Diphenylmethane

ΔE_D^o = -(5.26±0.02) kcal/mole ΔH_2^o = -(3.40+0.33) kcal/mole

ΔS_D^o = -(11.78 ±0.07) eu ΔS_2^o = -(13.7±1.0) eu

ΔH_3^o = -(5.33±0.10) kcal/mole ΔH_8^o = -(23.45±0.14) kcal/mole

ΔS_3^o = -(15.6±0.3) eu ΔS_8^o = -(64.5±0.5) eu

Benzyl Ether

ΔE_D^o = -(6.52±0.01) kcal/mole ΔH_2^o = -(1.86±0.25) kcal/mole

ΔS_D^o = -(14.47±0.04) eu ΔS_2^o = -(9.5±0.8) eu

ΔH_3^o = -(4.35±0.10) kcal/mole ΔH_8^o = -(14.11±0.14) kcal/mole

ΔS_3^o = -(14.5±0.3) eu ΔS_8^o = -(44.1±0.5) eu

Standard state is one mole/liter.

of methanol in the vapor phase from the PVT study of methanol vapor were used to calculate equilibrium constants for vapor association for the purpose of obtaining monomer methanol pressure from the observed methanol pressures over solutions of methanol in n-hexadecane, diphenylmethane and benzyl ether. The values of the thermodynamic parameters obtained from the 1-3-8 fit of the PVT data[15] for methanol vapor and used in the present work to calculate monomer methanol pressure for use as defined in equations (12) and (16) are presented in Table 12.

TABLE 12

Enthalpy and Entropy Values for Methanol Trimer and Octamer Formation in the Vapor Phase[15]

ΔH_3^o = -(12.53±0.12)kcal/mole	ΔS_3^o = -(44.2±0.4)eu
ΔH_8^o = -(67.84±0.28)kcal/mole	ΔS_8^o = -(216.9±0.9)eu

Standard state is one atmosphere.

Vapor Pressure Data for Two Volatile Components

The method of data analysis for these systems was somewhat more involved than that for the single component distribution systems since no quantity very directly related to a monomer concentration in solution could be measured. The three measured quantities for these systems are P_T, total pressure, N_A, moles of DEA added, and N_W or N_M, the moles of water or methanol added. The method of analysis will be presented using the water-DEA system as an example.

The observables, P_T, N_A and N_W may be converted to a molar concentration scale. This is readily done for P_T by dividing by the product

of the gas constant and the absolute temperature (RT) when P_T is expressed in torr and the units of R are liter-torr/degree-mole. P_T may, from the results of the vapor density study, be expressed as

$$P_T = p_A + p_W + P_{WA} \tag{17}$$

where p_A and p_W are monomer pressures of DEA and water and P_{WA} is the pressure of the complex. Division by RT gives

$$C_T^V = C_A^V + C_W^V + C_{WA}^V \tag{18}$$

with the superscript to indicate vapor phase concentration. DEA vapor association is neglected here because at the concentrations employed the amine dimer pressure is negligible. The introduction of the vapor phase association constant (K_{WA}^V) in molar units gives

$$C_T^V = C_A^V + C_W^V + K_{WA}C_W^V C_A^V \tag{19}$$

for the vapor phase concentration.

At any point it is not possible to employ a conventional concentration scale for the two solutes because each single component is distributed between the vapor and solution phases and the quantity of one component in solution at a certain point is not susceptible to measurement. What can be done is to define a hypothetical concentration which assumes that all of a component is present in solution and then add the necessary terms to account for the vapor phase quantities.

This hypothetical concentration will be symbolized by f*. As an example a single volatile component system may be used to illustrate the meaning of this definition where no association is considered in either phase.

Let N_B^T, N_B^V and N_B^S be the total moles of component B present in the system, the number of moles of B in the vapor phase and the number of moles in solution, respectively. The customary molar concentration scale is

$$f_B = \frac{N_B{}^S}{V_S} \tag{20}$$

where V_S is the solution volume.

f* is expressed as

$$f^* = \frac{N_B{}^T}{V_S} \tag{21}$$

From this equation and using the fact that $N_B{}^T = N_B{}^S + N_B{}^V$

$$f^* = \frac{N_B{}^S + N_B{}^V}{V_S} = C_B{}^S + \frac{N_B{}^V}{V_S} \tag{22}$$

where $C_B{}^S$ is the molar concentration of B in solution. $N_B{}^V$ is equal to $C_B{}^V V_V$, the vapor concentration times the vapor volume. Utilizing the distribution expression ($K_D = C_B{}^S / C_B{}^V$) equation 23 may be obtained.

$$f^* = C_B{}^S + \frac{C_B{}^S V_V}{K_D V_S}$$

or

$$f^* = C_B{}^S + C_B{}^S \frac{R_{VS}}{K_D} \tag{23}$$

R_{VS} is the ratio of the vapor volume to the solution volume.

In this manner a formal concentration expression may be written for each component in the mixed system. The formal amine concentration is expressed as

$$f^*_A = C_A + 2K_2C_A^2 + \frac{R_{VS}C_A}{K_A} + \frac{R_{VS}K^V_{WA}C_WC_A}{K_WK_A} + K^S_{WA}C_WC_A \quad (24)$$

and for water

$$f^*_W = C_W + \frac{R_{VS}C_W}{K_W} + \frac{R_{VS}K^V_{WA}C_WC_A}{K_WK_A} + K^S_{WA}C_WC_A \quad (25)$$

where only a 1:1 complex is assumed in solution, K_A and K_W are distribution constants for monomers of amine and water, K^V_{WA} is the vapor phase association constant (in molar units) for the 1:1 complex and K^S_{WA} is the unknown equilibrium constant in solution. C_A and C_W are monomer concentrations in solution.

Equation (24) contains the only necessary self-association term for the amine. In solvents where water associates with itself, and for all solvents for methanol, terms must be added to account for the self-association. For the water-amine system in BZE the term $(2K_2C_W^2 + 3K_3C_W^3)$ must be added to equation (25); the water-amine system in DPM requires only addition of $2K_2C_W^2$. For the mixed system, methanol-DEA in DPM, equation (25) would take the form

$$f^*_M = C_M + \frac{R_{VS}C_M}{K_M} + \frac{R_{VS}K^V_{MA}C_MC_A}{K_MK_A} + K^S_{MA}C_MC_A + 2K_2C_M^2 + 3K_3C_M^3 + 8K_8C_M^8 \quad (26)$$

where only a one to one complex of methanol-DEA is assumed. If complexes are formed which incorporate more than one molecule of either amine or water or methanol other terms must be added to equations (24) and (25). For example if a complex involving two molecules of water to one of amine is formed the term $K_{21}^{S} C_W^2 C_A$ must be added to equation (24) and twice this term ($2K_{21}^{S} C_W^2 C_A$) must be added to equation (25). In this way sets of equations are constructed to account for complex formation and self-association in solution.

The solution of equations (19), (24) and (25) is accomplished in the following manner. Equation (19) is rearranged to

$$C_W^V = \frac{C_T^V - C_A^V}{1 + K_{WA}^V C_A^V} \tag{27}$$

and, by introducing the distribution constant for each monomer,

$$\frac{C_W^S}{K_W} = \frac{C_T^V - C_A^S/K_A}{1 + K_{WA}^V C_A^S/K_A}$$

or

$$C_W = \frac{C_T^V - C_A/K_A}{1/K_W + K_{WA}^V C_A/K_W K_A} \tag{28}$$

an expression for C_W, the monomer concentration in solution, is obtained in terms of the total vapor phase concentration, the monomer amine concentration in solution and known constants. This expression for C_W is substituted into equation (24) and when fractions are cleared the result is a polynomial in terms of C_A, the monomer amine concentration, known constants, and the unknown solution equilibrium constant(s).

An optimizing procedure was used to obtain the best value of K^S_{WA}. An initial guess of K^S_{WA} is made and this value is used to obtain a value of C_A, via an iterative process, from the polynomial in C_A. This C_A value and the assumed K^S_{WA} are substituted into equation (28) to calculate a C_W value. The values of C_A, C_W, and K^S_{WA} are then used to calculate an f^*_W value which is compared with the measured f^*_W. The process is continued until the value of K^S_{WA} which minimizes the RMSD between all values of f^*_W and f^*_W(calcd.) is obtained. Essentially the same process is carried out when larger complexes than the one to one are present. In these cases one seeks to find the values of two or more equilibrium constants which produce a minimum in the RMSD.

The least squares values of equilibrium constants for complex formation between water and DEA in each solvent are presented in Table 13. The assumption of only a 1:1 complex in HX and DPM was sufficient to explain the data. However, in BZE the data clearly indicated the formation of a complex incorporating more than one water molecule. A two parameter fit of the data resulted in a considerable decrease in RMSD over the one parameter fit. The RMSD's for the 1:1 complex fit were all almost an order of magnitude larger than the RMSD's for the two parameter fit which assumed the additional presence of the species $(water)_2$-$(amine)_1$. It may be noticed from the table that the constants for the water-amine complexes in BZE at 35° are somewhat out of line with the constants at 25 and 45°. To be specific the K_{11} value appears to be too low and the K_{21} value too high. Part of this difficulty is due to the substantial errors in the small dimer and trimer constants for water association in this solvent since small changes in these

TABLE 13

Association Constants for the 1:1 Complexes Water-Diethylamine in Three Non-volatile Solvents at 25, 35 and 45°

T(°C)	$K_{11}(M^{-1})$	$K_{21}(M^{-2})$	RMSD(M)
		n-Hexadecane	
25	10.97±0.12		0.00005
35	8.05±0.09		0.00005
45	5.72±0.04		0.00003
		Diphenylmethane	
25	8.52±0.06		0.0003
35	6.93±0.04		0.0003
45	5.28±0.05		0.0003
		Benzyl Ether	
25	2.81±0.07	9.7±0.6	0.0004
35	1.94±0.02	8.1±0.1	0.0002
45	1.93±0.03	4.4±0.2	0.0002

constants directly affect the values of the complex constants K_{11} and K_{21}. Van't Hoff plots for K_{11} in each solvent are given in Figure 6.

Table 14 lists the corresponding equilibrium constants for the methanol-amine systems in the three solvents. In each case the 1:1 fits were quite poor but the addition of a second complex species involving two methanol molecules to one amine provided a satisfactory fit of all the data. Figure 7 presents van't Hoff plots of K_{11} for the methanol-amine system in each solvent. Table 15 compares the enthalpy and entropy of formation of the methanol and water 1:1 complexes with DEA in each solvent. Figure 8 gives van't Hoff plots for K_{21} for the methanol-amine complexes in each solvent and the water-amine complex in BZE. Table 16 gives the least squares values of the thermodynamic parameters for the formation of these 2:1 complexes.

Comments on Notation and Errors in Parameters

The equilibrium constants for 1:1 complex formation are, for clarity, defined by letter subscripts indicating the compounds involved in the reaction only in the equations defining the mathematical relationships. In Tables and in the Discussion the constants are denoted by K_{11} where it will be clearly indicated which 1:1 complex is being discussed. K_{21} is used consistently for the higher order complexes of methanol and water with diethylamine. The symbol M is used in tables to denote molarity. When used as a subscript, C_M or f_M, etc., M is taken to mean methanol.

The errors listed with the least squares values of parameters are all one sigma values. Parameter errors were determined for single component distribution data from the diagonal terms of the inverse

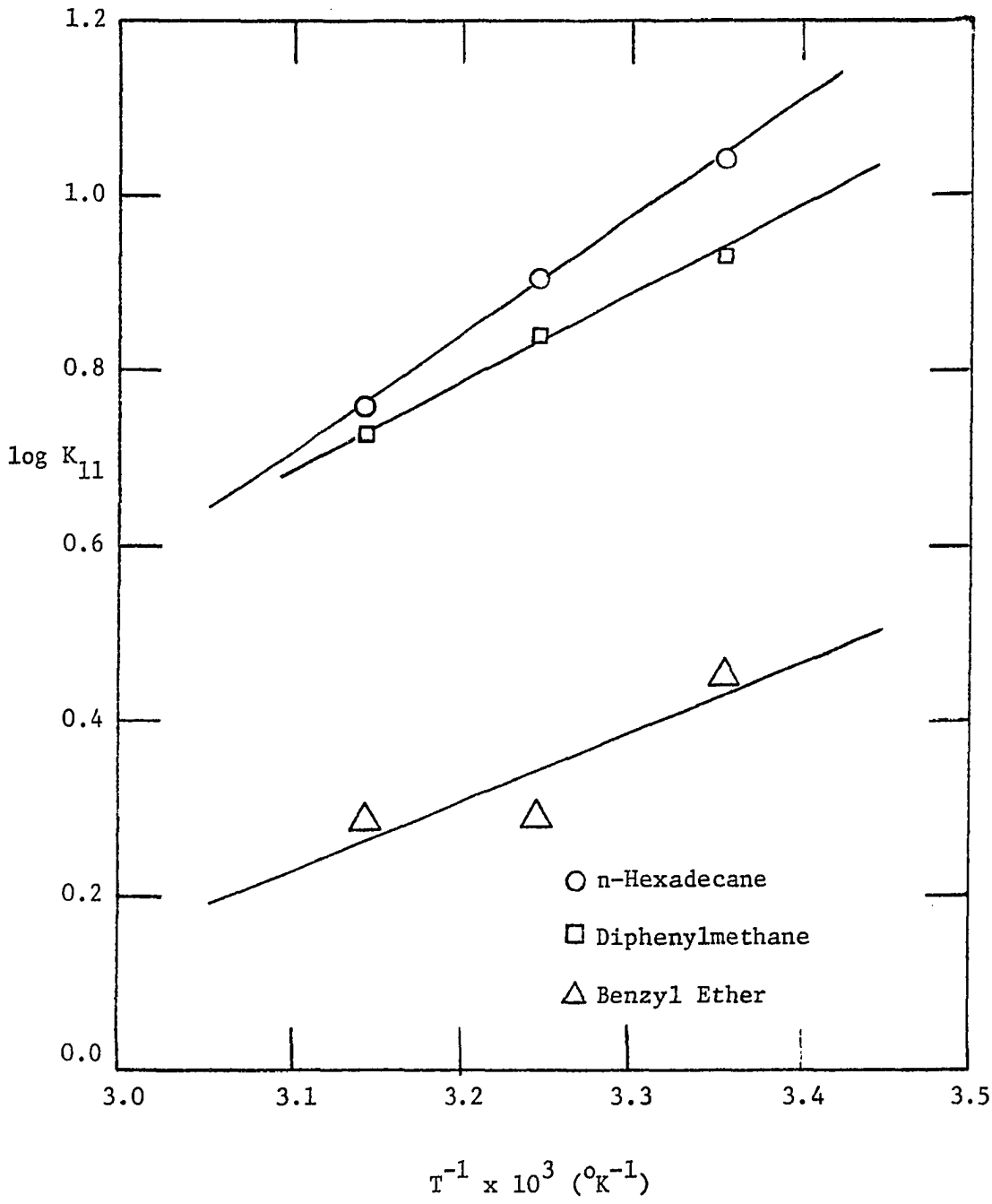

Figure 6. Van't Hoff plots for 1:1 complex formation between water and diethylamine in three non-volatile solvents.

TABLE 14

Association Constants for Methanol-Diethylamine 1:1 and 2:1 Complexes in Three Non-volatile Solvents at 25, 35 and 45°

T(°C)	$K_{11}(M^{-1})$	$K_{21}(M^{-2})$	RMSD(M)
		n-Hexadecane	
25	8.76±0.44	299.1±11.5	0.0004
35	6.67±0.21	139.6± 5.2	0.0004
45	5.45±0.12	69.2± 2.5	0.0003
		Diphenylmethane	
25	4.78±0.28	22.7± 2.4	0.0010
35	4.06±0.05	14.95±0.36	0.0002
45	3.26±0.04	7.60±0.34	0.0002
		Benzyl Ether	
25	2.75±0.12	7.1±0.4	0.0018
35	2.34±0.05	4.6±0.2	0.0009
45	2.03±0.06	2.8±0.2	0.0012

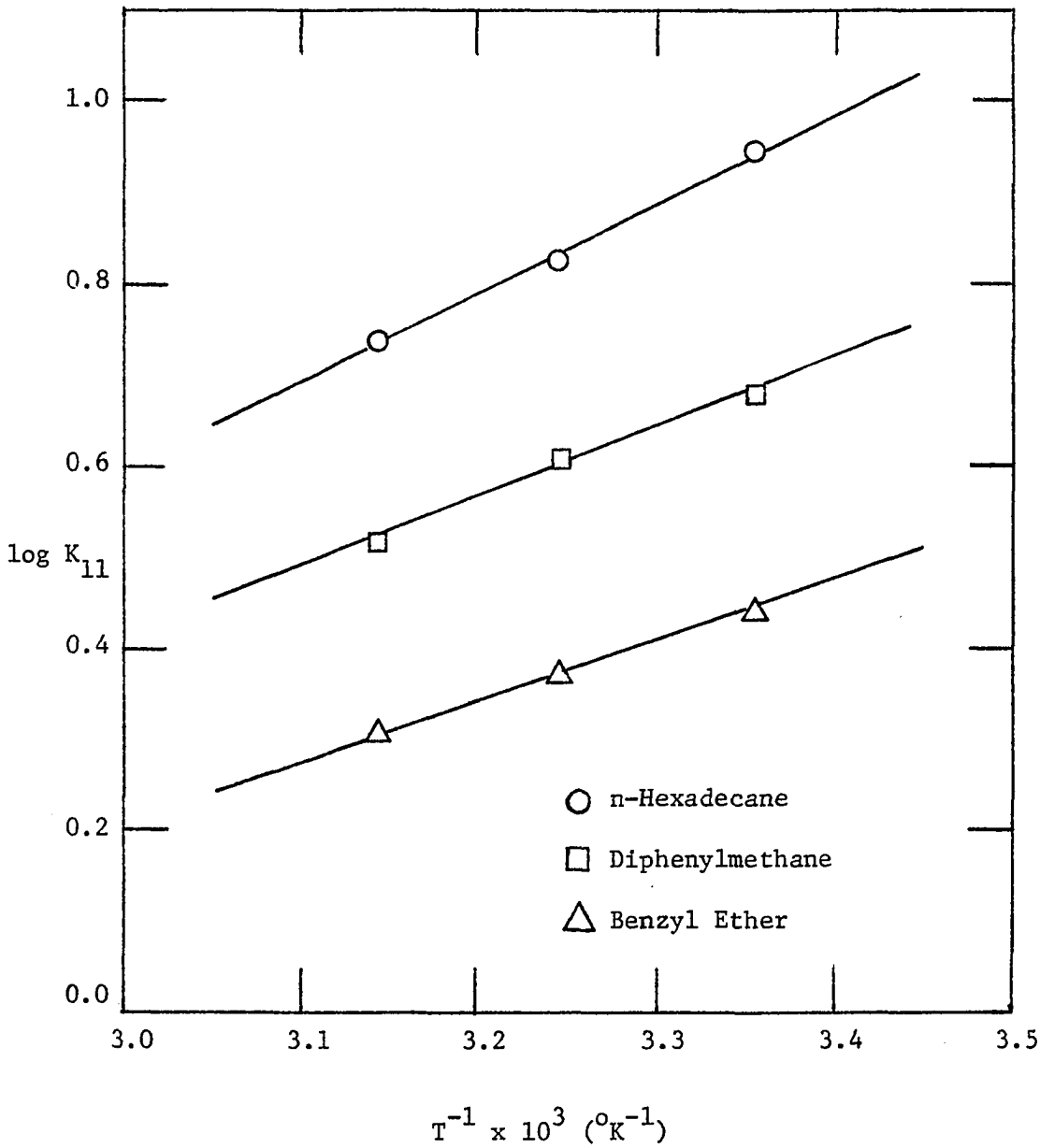

Figure 7. Van't Hoff plots for 1:1 complex formation between methanol and diethylamine in three non-volatile solvents.

TABLE 15

Thermodynamic Parameters for the One to One Complexes of Water and Methanol with Diethylamine in Three Non-volatile Solvents

	Water-DEA	Methanol-DEA
n-Hexadecane		
	ΔH^{o}_{11} = -(6.13±0.04) kcal/mole	ΔH^{o}_{11} = -(4.48±0.09) kcal/mole
	ΔS^{o}_{11} = -(15.8±0.1) eu	ΔS^{o}_{11} = 0(10.7±0.3) eu
Diphenylmethane		
	ΔH^{o}_{11} = -(4.50±0.05) kcal/mole	ΔH^{o}_{11} = -(3.58±0.09) kcal/mole
	ΔS^{o}_{11} = -(10.8±0.2) eu	ΔS^{o}_{11} = -(8.9±0.3) eu
Benzyl Ether		
	ΔH^{o}_{11} = -(3.56±0.26) kcal/moie)	ΔH^{o}_{11} = -(2.86±0.08) kcal/mole
	ΔS^{o}_{11} = -(10.0±0.8) eu	ΔS^{o}_{11} = -(7.6±0.3) eu

Standard state is one mole per liter.

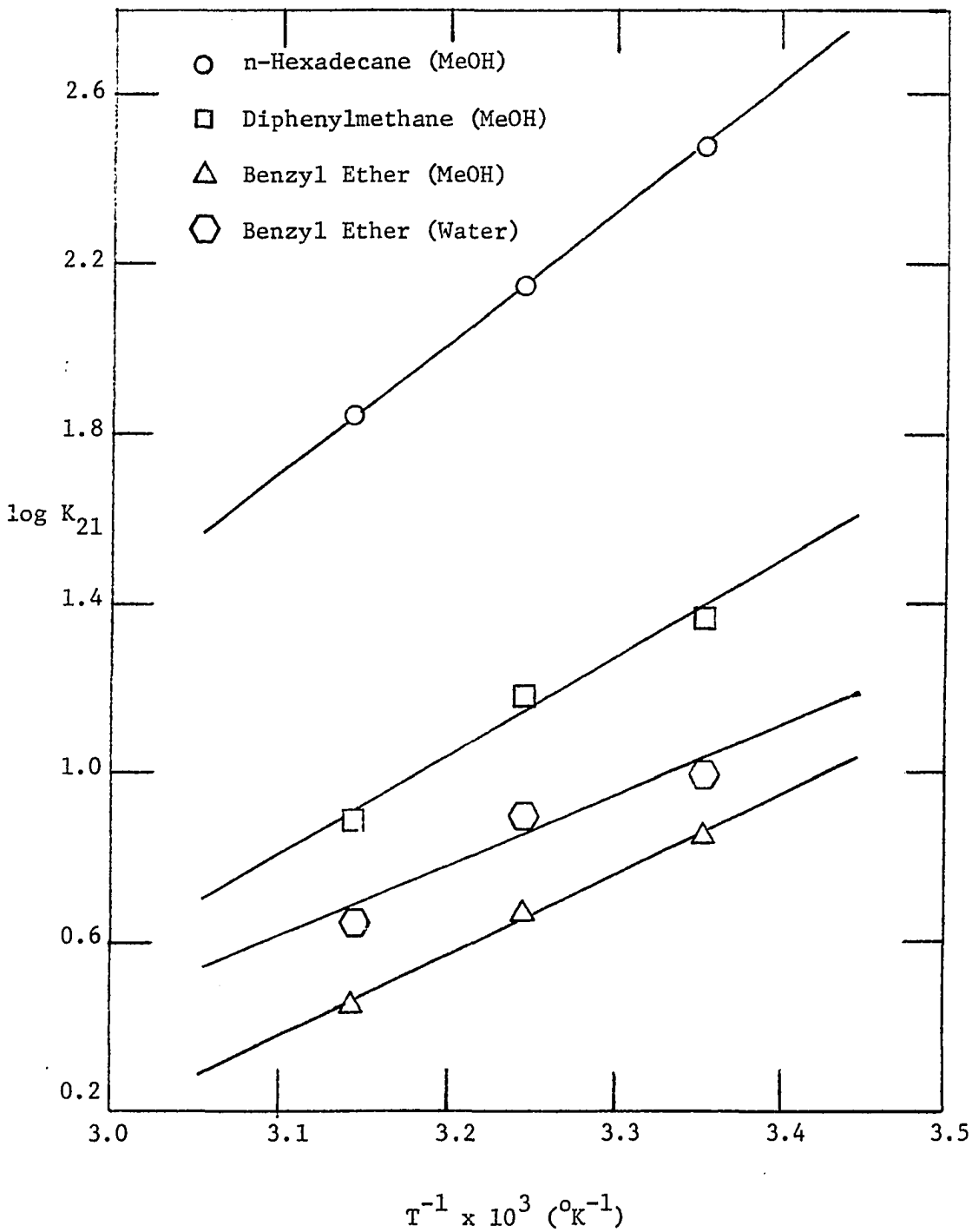

Figure 8. Van't Hoff plots for two to one complexes of methanol and water with diethylamine in three non-volatile solvents.

TABLE 16

Thermodynamic Parameters for Two to One Complexes of Water and Methanol with Diethylamine in Three Solvents

	$(Methanol)_2$-DEA	$(Water)_2$-DEA
n-Hexadecane		
ΔH^o_{21}	-(13.80±0.09) kcal/mole	
ΔS^o_{21}	-(35.0±0.3) eu	
Diphenylmethane		
ΔH^o_{21}	-(10.23±0.25) kcal/mole	
ΔS^o_{21}	-(28.0±0.8) eu	
Benzyl Ether		
ΔH^o_{21}	- (8.71±0.13) kcal/mole	-(7.5±0.4) kcal/mole
ΔS^o_{21}	-(25.3±0.4) eu	-(20.6±1.4) eu

Standard state is one mole per liter.

matrix mentioned earlier. In mixed systems errors in one and two parameter fits were determined from the behavior of contour lines around the minimum in RMSD.[67,68]

CHAPTER V

DISCUSSION AND CONCLUSIONS

The discussion of the results of this study is divided into five major sections. In the first section the results of the PVT and vapor density studies will be discussed. A comparison of the results of the distribution and association studies for diethylamine, water and methanol in the solvents n-hexadecane, diphenylmethane and benzyl ether will be given in the second section. The third section will compare the results of measurements on complex formation in the solvent systems involving two volatile components. A comparison of the parameters descriptive of 1:1 complex formation with the relations proposed by Christian et al. to correlate solvent effects on complex formation will be presented in the fourth section. A short summary and some proposals for future work will conclude this chapter.

Vapor Phase Association

The results of the PVT study on diethylamine vapor indicate that very little association occurs in the vapors of this compound at room temperature. At 25^{o} and a DEA pressure of 100 torr the pressure of the assumed associated species, a dimer, is less than 0.8 torr. The small enthalpy of association reported in this work (-3.82 kcal/mole) is comparable to the value of -3.3 kcal/mole determined

by Lambert and Strong[38] from second virial coefficient measurements. Only qualitative comparison of these enthalpies should be made since Lambert and Strong consider part of the non-ideality in DEA vapor to be due to nonspecific interactions and their reported ΔH value is based on a "corrected" association constant. A more discordant enthalpy value of -5.8 kcal/mole for dimer formation in n-butylamine vapor was determined by Cracco and Huyskens[48] from vapor density measurements.

Table 17 presents equilibrium constants for the 1:1 vapor phase complexes of water-DEA and methanol-DEA at 25° converted from the original units of $torr^{-1}$ to molar units and values of ΔE^{o}_{11} for the complex formation reactions at 25°. These conversions will facilitate comparison in the rest of this chapter.

TABLE 17

Equilibrium Constants in Molar Units and ΔE^{o} Values for Vapor Phase Complex Formation at 25°

System	$K_{11}(M^{-1})$	ΔE^{o}_{11} kcal/mole	
Water-DEA	7.90	-6.04	(ΔH^{o}_{11} = -6.63)
Methanol-DEA	13.6	-6.72	(ΔH^{o}_{11} = -7.31)

The ΔH^{o}_{11} value reported in this study is apparently the first enthalpy for a hydrogen bonded complex of water in the vapor phase. Bacarella et al.[68] have determined a second virial coefficient of

-7500 ml/mole for the interaction of water with dioxane at 25°. This coefficient is equivalent to an equilibrium constant of about 7.5 M^{-1} which compares favorably with the constant of 7.9 M^{-1} for the water-DEA vapor complex determined in the present study.

ΔH^{o} values have been reported for three alcohol-amine 1:1 complexes in the vapor phase. Cracco and Huyskens give -8.9 kcal/mole for the ΔH^{o} of formation of the n-butanol-n-butylamine complex from vapor density studies.[48] Clague, Govil and Bernstein[49] obtained a ΔH^{o} value of (-5.8±0.7) kcal/mole for the methanol-trimethylamine vapor complex from NMR measurements. Hirano and Kozima[50] report a ΔH^{o} of -8.2 kcal/mole for the methanol-triethylamine complex from IR studies on vapor mixtures. Comparison of the above ΔH^{o} values with the ΔH^{o}_{11} value obtained in the present study (-7.31 kcal/mole) for the methanol-DEA vapor complex indicates that no general agreement can be reached on the enthalpy of formation of an alcohol-amine hydrogen bond in the vapor phase.

Distribution and Association Results for Diethylamine, Water and Methanol

Diethylamine Distribution and Association

The results of the distribution of DEA between the vapor phase and the three solvents indicate that, at the concentrations employed in this study, no significant association is present in solution. Association of DEA appears to be limited to one or two per cent in HX and BZE. It is somewhat surprising that association was not detected in DPM whereas in BZE--a more reactive solvent which would be expected

to retard polymer formation--some association is detected. This discrepancy is probably due to the fact that a considerably higher amine concentration level was attained in BZE than in DPM. Also, the data for the DEA-DPM system are less precise than the data for the other DEA-solvent systems. Gregory[43] did not detect association in several amine systems studied by partitioning the amines between water and organic solve[illegible]ine concentrations up to 0.5 molar in the organic [illegible]

determined from the present study do no[illegible]erature dependence to enable the calcu[illegible]s for DEA. Amine concentrations used i[illegible]enthalpies have been determined are a[illegible]arger than those used in the present study.[illegible]e association which have been reported v[illegible]/mole per bond.[39,40,41]

The [illegible]energy of solution of one mole of a solute from the ideal gas phase to the infinitely dilute solution) for DEA distribution between the three solvents and the vapor phase reflect the fact that the amine hydrogen is a very weak acid in the hydrogen bonding sense. ΔE_D^o for DEA in DPM is not much larger in absolute value than ΔE_D^o for DEA in HX. The latter solvent, n-hexadecane, is one of the most nearly inert solvents available. In this sense an inert solvent is one which has no functional group substituents (O, F, Cl, Br, NO_2, etc.) or aromatic rings to interact strongly with a solute. It has been recognized for some time[1] that solvents possessing an aromatic ring, such as benzene or DPM, are not inert solvents in the hydrogen bonding sense.

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The equilibrium constants determined from the present study do not show sufficiently good temperature dependence to enable the calculation of association enthalpies for DEA. Amine concentrations used in work from which association enthalpies have been determined are at least an order of magnitude larger than those used in the present study. The enthalpy values for amine association which have been reported vary from -0.6 to -2.0 kcal/mole per bond.[39,40,41]

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Proton donating molecules such as alcohols interact strongly with solvents possessing an aromatic ring. The small difference in ΔE_D^o's on going from HX to DPM shows the presence of only very weak interactions between the amine hydrogen and the aromatic ring. When the amine is dissolved in the even more basic solvent BZE there is virtually no change in ΔE_D^o compared to the value for DEA in DPM. This reinforces the belief that the amine hydrogen is a very weak donor.

Water Distribution and Association

The water distribution data presented in this work reflect the very high precision which is obtainable using the mercury-covered sintered glass disc inlet valve in conjunction with an accurate microburet to add samples of a vaporizable liquid to a vacuum system. Initially, some of the RMSD values in Table 5 for the least squares fits for distribution of water in the three low vapor pressure solvents were viewed with skepticism. The RMSD's for water in HX are all on the order of 2×10^{-5} M. Calibration of the microburet was done with the aid of a single pan balance which had a precision of ±0.1 mg. It was evident from replicate sample additions to the evacuated weighing bottle that the precision of sample addition was better than the precision of the balance. In fact, the standard deviation in weight for a series of samples was estimated as about 0.05 mg of water. If the error in water concentration at any point in the water-HX systems is taken as equal to the RMSD then the calculated uncertainty in milligrams of water is about 0.07 for a 200 cc volume of solution. These calculations indicate that the water distribution data using HX as the solvent are near the limit of precision of the method.

The distribution data for the system water-DPM are of good precision but the RMSD values are considerably higher than those for the data on the water-HX system. There is little difference in the relative precision of the data for the two systems but comparison on an absolute scale is disappointing. No readily obvious explanation for this difference is available but it may be noted that the pressure measurements on the water-DPM system, made by measuring the height difference of two mercury columns with a cathetometer, are very possibly subject to larger random errors than the TI gage measurements on the water-HX system.

The RMSD values in Table 5 for the water-BZE system are generally lower than those for the water-DPM system. At 45° the RMSD value for the 1-2-3 fit for water in BZE is comparable to the RMSD values for the water-HX system even though the water concentration in BZE is roughly 40 times as large as the water concentration in HX.

The ΔE_D^o values for water in the solvents HX, DPM and BZE, unlike the ΔE_D^o values for DEA, increase very markedly from the first solvent HX to the third, BZE, indicating the increasing interaction of water with the solvent as the electron donor properties of the solvent become more pronounced.

The evidence that an appreciable amount of the total water present in DPM exists in complexed form was somewhat surprising. A previous report from this laboratory[69] indicated that self-association of water in DPM at 25° was negligible. Another worker in this laboratory, also using the vapor pressure technique, has confirmed that water apparently associates in DPM at 25° and that roughly 10 per cent of the water present

in DPM at unit water activity consists of polymeric species.[70] The measured monomer distribution constant for water in DPM agrees very well with the value reported in the present study (K_D = 20.68 compared to this work, Table 6, K_D = 20.66).

Association of water in BZE is much better described by assuming the presence of two associated species than by any one of the fits 1-2, 1-3 or 1-4. The 1-2 is the best single associated species fit; the 1-3 is somewhat worse and the 1-4 fit is considerably poorer than either. The temperature dependence of the dimer and trimer constants for water in BZE is not very good. It is ironic that the water distribution data mentioned previously, which were taken in the presence of colored deposits on the walls of the sample flask, showed quite good temperature dependence (ΔH_2^o = -1.8 and ΔH_3^o = -5.5 kcal/mole).

Methanol Distribution and Association

The ΔE_D^o values for methanol in HX, DPM and BZE show the same trend that the ΔE_D^o values for water in these solvents show--a considerable increase in the magnitude of ΔE_D^o as the solvent becomes more reactive.

The model proposed by this author to explain some deviations from ideality which exist in methanol-solvent systems is somewhat unusual. No previously proposed association models for alcohols have correlated association data so well over such a wide activity range in the low concentration region. Except for recently proposed 1-4 model of Fletcher and Heller,[35] attempts to describe the thermodynamics of hydrogen bonding in alcohol-solvent systems usually involve description of association in the low concentration region by a monomer-n-mer equilibrium or a determination of activity coefficients for solutions

throughout a concentration range from 0 to 1 mole fraction of the alcohol.

Fletcher and Heller proposed a monomer-tetramer (1-4) equilibrium to explain infrared spectra in the overtone region for mixtures of 1-octanol in n-decane over the entire composition range to pure alcohol. Measurements were made at temperatures between 5 and 100° and enthalpies of formation of linear and cyclic tetramers of -16.5 and -20.3 kcal/mole, respectively, were calculated. Fletcher and Heller concluded that the predominant alcohol polymer in non-polar solvents was a tetramer even though their attempt to prove tetramer predominance by fits of other workers' alcohol data met with limited success.[35]

Liddel and Becker[33] give enthalpy values for dimer formation for methanol, ethanol and t-butanol in CCl_4 from IR studies of the fundamental hydroxyl stretching region for dilute solutions of these alcohols. The ΔH_2 values obtained were -(9.2±2.5), -(7.2±1.6) and -(4.8±1.1) kcal/mole, respectively, for methanol, ethanol and t-butanol. The assumption was made that these dimers were cyclic with two hydrogen bonds.

Wolff and Hoppel[26] recently reported vapor pressure measurements for the system methanol-n-hexane throughout the composition range at temperatures between 35 and 75°. The vapor pressure measured in these systems is not that due to methanol only, as is essentially the case in the present study, since n-hexane has a vapor pressure roughly comparable to methanol in the temperature range 35° to 75°. These authors fit their vapor pressure data with an equation used by

Redlich and Kister[71] in which the logarithm of the activity coefficient of a component is expressed by a series expansion in terms involving the mole fraction of that component. In order to obtain reasonable agreement it was necessary for Wolf and Hoppel to use 11 terms in the expansion for the 35° data. A solvation energy of -2.6 kcal/mole was reported for methanol in n-hexane; this value is comparable to the ΔE_D^o value of -(2.90±.01) kcal/mole obtained in the present study for methanol in HX. Wolff and Hoppel[26] calculated an average hydrogen bond energy of methanol polymers in n-hexane of -5.8 kcal/mole. An average value of energy per bond from the present study would be about -5.3 kcal/mole for methanol in HX.

The three references discussed above are perhaps typical of approaches used in studies of alcohol-solvent systems. It was thought by this author that perhaps a more meaningful comparison of association in different alcohol systems could be obtained if the associative properties of different alcohols could be compared on the basis of one association model. Such an association model would not only have to be adequate for correlating data of the same type for several alcohols but would also have to be in accord with different types of data such as vapor pressure, infrared spectral (IR) and nuclear magnetic resonance (NMR) data for the same alcohol. Since the 1-3-8 model was capable of fitting the vapor pressure data for methanol in n-hexadecane to a high degree of precision the decision was made to try to extend this model to treatment of IR and NMR data for alcohol solutions.

Application of the 1-3-8 Model to IR Data

Copies of IR data for methanol, ethanol and t-butanol solutions

in CCl_4 were graciously provided by Dr. E. D. Becker. These data formed the basis for the article by Liddel and Becker.[33] The spectra were recorded in the fundamental hydroxyl stretching region through the temperature range -10 to 45°. Formal concentrations of the alcohols were varied from 0 to 0.2 molar for methanol and ethanol and from 0 to 1.0 molar for t-butanol.

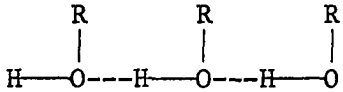
In order to fit IR data for alcohol solutions it is necessary to make some reasonable assumptions about the structures of the assumed associated species present. For the 1-3-8 model the first assumption is that the trimer is linear with two hydrogen bonds. This may be justified by the fact that, for a given hydrogen bond A-H...B, there is general agreement that the bond is strongest when the AHB angle is 180 degrees.[1] The electrostatic model of the hydrogen bond predicts a large decrease in the hydrogen bond energy as the AHB angle deviates from 180 degrees. If a cyclic trimer is considered, the AHB angle deviates almost 50 degrees from linearity.[17]

The structure of the assumed species, the octamer, could either be a chain or linear structure or a cyclic one. A cyclic species would have eight hydrogen bonds which would be linear. If the octamer is assumed to be linear one might expect the presence of substantial concentrations of chain polymers with less than eight alcohol units. The presence of a large cyclic species of unique stability would arbitrate for decreased importance of chain polymers with nearly the same number of monomer units.

A short discussion of qualitative characteristics of IR spectra in the fundamental OH stretching region is necessary before presenting the procedure used to analyze Liddel and Becker's data.

The infrared spectra of many alcohol solutions in CCl_4 in the region 3700-3300 cm^{-1} are quite similar. Three absorption bands, varying in shape and intensity as alcohol concentration increases, commonly appear. The absorption peak near 3600 cm^{-1} is assigned to monomeric molecules, the peak near 3500 cm^{-1} has ordinarily been assumed to exhibit approximate dimer dependence and the peak near 3300 cm^{-1} is considered to be due to interior hydroxyl groups in large polymers (future reference will assume for convenience that the peaks occur at 3600, 3500, and 3300 cm^{-1}). The extent of interference of the "dangling" or nonbonded OH of linear polymers at the monomer peak has often been discussed but few authors have considered this to be a serious problem. The work of Smith and Creitz[16] indicated that discernible interference at the monomer peak occurs. Coburn and Grunwald[17] made a correction for this effect in their work with ethanol in CCl_4. A recent article by Bellamy and Pace[72] strongly supports the view that the end OH in linear polymers is virtually indistinguishable from the monomer OH. The results of difference spectra obtained by Bellamy and Pace indicate that absorption by the end OH in linear methanol polymers occurs only 5 cm^{-1} from the monomer absorption in CCl_4.

By assuming that the end OH in linear polymers absorbs at the monomer frequency an analysis of IR data in the fundamental region is readily performed. The linear trimer below has three OH absorptions which are assumed to be different. OH(I) has already been assigned as



(I) (II) (III)

absorbing at the monomer frequency. OH(II) should be comparable to an OH group in the interior of a cyclic polymer and should absorb at 3300 cm^{-1}. If it is assumed that all polymers higher than trimer are cyclic and absorb only at 3300 cm^{-1} then one OH is left, OH(III), and one major peak is unassigned. With the assignment of OH(III) as the bond responsible for the 3500 cm^{-1} peak it was possible to determine the applicability of the 1-3-8 model to IR data for alcohol solutions in the 3700 - 3300 cm^{-1} region. It may be noted here that the assumptions made above lead to assignments similar to those made by Smith and Creitz.[16]

The absorbance per unit length at the monomeric frequency, A_{3600}, may now be expressed as

$$A_{3600} = E_M^o \ (C_M + K_3 C_M^3) \tag{29}$$

where it is assumed that the ratio of absorptivities (E^I/E_M^o) for OH(I) and monomeric OH is unity and C_M is monomer methanol (alcohol) concentration. Since the absorptivity of OH(I) should be enlarged in comparison to an OH not acting as a donor it might be expected that the ratio of absorptivities above would be somewhat larger than unity but the assumption is probably improved by the fact that OH(I) absorbs at slightly lower frequency than the monomer. The formal alcohol concentration is expressed as:

$$f_M = C_M + 3K_3 C_M^3 + 8K_8 C_M^8 \tag{30}$$

The solution of equations (29) and (30) is accomplished by use of the two parameter optimum seeking program mentioned earlier. Using measured values of A_{3600} and E_M^o and initial estimates of K_3 and K_8, equation (29) is solved by an iteration method to give a monomer concentration which is used with K_3 and K_8 to calculate an f_M value according to equation (30). This process is repeated for each of the data points and K_3 and K_8 are changed systematically until the minimum in RMSD is reached.

For data at each of seven temperatures between -10 and 45°, 1-3-8 and 1-2-8 fits were tried on Liddel and Becker's data. It was found that the 1-3-8 fit was generally better for all three alcohols--indicating that the IR data are more nearly in accord with the presence of a linear trimer rather than a linear dimer when the assumption is made that a cyclic octamer is the only other associated species present. The temperature dependence of both trimer and octamer constants was quite good with the exception of the trimer constant for methanol in CCl_4 at 25°. RMSD's and equilibrium constants for the 1-3-8 fits of Liddel and Becker's IR data for methanol, ethanol and t-butanol in CCl_4 are presented in Table 18.

It should be noted that, although good temperature dependence was obtained for K_3 and K_8 from 1-3-8 fits of these IR data for alcohol solutions in CCl_4, a factor is present which might markedly affect the calculated ΔH's. The molar absorptivity (E_M^o) of alcohols in CCl_4 has been shown to change with temperature.[33] In assuming (equation (29)) that E^I/E_M^o is constant it is assumed that this ratio does not change with temperature. The ratio probably does change slightly with

TABLE 18

RMSD's and Equilibrium Constants for 1-3-8 Fits of Liddel and Becker's IR Data[33]

TEMPERATURE	-10	0	5	10	15	25	35	45
Methanol								
RMSD(M)	0.0048	0.0047		0.0042	0.0052	0.0010	0.0017	0.0005
$K_3(M^{-2})$	$(3.2\pm0.4)10^2$	$(1.7\pm0.2)10^2$		71.±10.	51.±13.	6.2±0.5	5.4±0.5	1.2±0.1
$K_8(M^{-7})$	$(1.6\pm0.3)10^9$	$(9.4\pm1.6)10^7$		$(4.7\pm0.5)10^6$	$(9.7\pm2.3)10^5$	$(1.24\pm0.02)10^5$	$(7.6\pm1.6)10^3$	$(2.5+0.1)10^3$
Ethanol								
RMSD(M)	0.0080	0.0066	0.0056		0.0046	0.0041	0.0037	0.0033
$K_3(M^{-2})$	$(3.1\pm0.6)10^2$	$(1.3\pm0.3)10^2$	85.±15.		33.±6.	16.±3.	6.7±1.5	2.8±1.0
$K_8(M^{-7})$	$(2.2\pm0.6)10^9$	$(1.0\pm0.2)10^8$	$(2.6\pm0.5)10^7$		$(1.6\pm0.2)10^6$	$(1.4\pm0.2)10^5$	$(1.5\pm0.5)10^4$	$(3.5\pm1.9)10^3$
t-Butanol								
RMSD(M)	0.0048	0.0035	0.0022		0.0016	0.0024	0.0027	0.0033
$K_3(M^{-2})$	$(5.9\pm0.1)10^2$	$(2.22\pm0.05)10^2$	$(1.34\pm0.02)10^2$		57.2±0.8	25.7±0.7	14.0±0.6	8.9±0.7
$K_8(M^{-7})$	$(1.59\pm.08)10^9$	$(5.1\pm0.2)10^7$	$(9.7\pm0.3)10^6$		$(6.0\pm0.1)10^5$	$(4.2\pm0.2)10^4$	$(4.5\pm0.3)10^3$	$(6.1\pm0.5)10^2$

Errors are ± one sigma value.

temperature and more refined analyses of IR data for alcohols in CCl_4 should attempt to account for this factor.

Fletcher and Heller's spectral data[35] for 1-octanol in n-decane were also used to test the 1-3-8 model. These authors assumed that no overlap of nonbonded OH's occurred at the monomer peak in the first overtone region. It is not certain that the no overlap assumption used by Fletcher and Heller is valid. However, since intensities of absorption bands are very markedly reduced in the overtone region compared to the fundamental region, it is possible that interference by the end OH in chain polymers is less noticeable in the overtone region. Further studies on this point would be quite valuable.

If the condition of no overlap at the monomer peak in the overtone is accepted then Fletcher and Heller's data may be fit in the following form

$$f_o = \sum_{n=1} C_n a_1^n \qquad (31)$$

where the coefficients C_1, C_2, . . . C_n are functions of equilibrium constants and monomer absorptivity, a_1 is the absorbance at the monomer peak and f_o is formal 1-octanol concentration. A relative weighting procedure was used by Fletcher and Heller in fitting their data to a sixth-order equation defined by equation (31). They found that the best fits were 1-2-4 and 1-3-4 and concluded that a 1-4 fit was satisfactory since the dimer constant in the 1-2-4 fit did not have good temperature dependence.

The 1-3-8 fit of Fletcher and Heller's 1-octanol data had positive constants which showed good temperature dependence. The relative

standard deviations of the 1-3-8, 1-2-4, 1-3-4 and 1-4 fits were comparable. The best fit for the 1-octanol IR data cannot be determined; the data at 5 and 15° included numerous points with deviations as large as ±15% for these fits. It may be concluded that--with the near equivalence of all these fits and with the presence of numerous data points of substantial error--one cannot definitely state that any particular association model is best for these data.

Application of the 1-3-8 Model to NMR Data for Alcohol Solutions. Assumptions similar to those made in fitting Liddel and Becker's IR data are made in testing the 1-3-8 model on NMR data for alcohol solutions in CCl_4. It is assumed that the chemical shift for the nonbonded proton of OH(I) in the linear trimer is the same as that for the monomer proton (δ_1). The chemical shift for the OH(II) proton is assumed to be the same as that for protons in the interior of the cyclic polymer (δ_8) and the proton of OH(III) is assumed to have a unique shift of δ_3. These assumptions lead to the expression

$$\delta_{obs} = \left[\delta_1 C_M + (\delta_1 + \delta_3 + \delta_8)K_3 C_M^3 + 8\delta_8 K_8 C_M^8\right] / f_M \qquad (32)$$

where δ_{obs} is the observed chemical shift. By using the equilibrium constants from the 1-3-8 fits of Liddel and Becker's data it was possible to calculate values of C_M and then fit equation (32) as a three parameter problem using the matrix inversion least squares program mentioned earlier.

Several sets of published NMR data for methanol, ethanol and t-butanol solutions in CCl_4 were analyzed by fitting the data to equation (32). Some degree of ambiguity was present in the results of the fits.

Two sets of data[21,23] fit by equation (32) gave a δ_3 value somewhat outside the expected range in contrast to the good values of δ_1 and δ_8 obtained. Part of the difficulty is perhaps due to the minor importance of δ_3 in the fit. However, two sets of data on t-butanol in CCl_4 at 21° show quite different dependence of chemical shift on concentration.[21,23] The NMR data of Davis, Pitzer and Rao[23] do not have the same qualitative dependence of chemical shift on alcohol concentration that either Saunders and Hyne's data[21] or Becker, Liddel or Shoolery's data[22] do. A very good fit of the latter authors' data[22] for ethanol in CCl_4 at 27° was obtained. The least squares values of δ_1, δ_3 and δ_8 for these 27° data are presented in the table below.

TABLE 19

Calculated Chemical Shifts* for Ethanol in CCl_4 at 27°

$\delta_1 = -0.41 \pm 0.07$ ppm

$\delta_3 = 1.60 \pm 0.80$ ppm

$\delta_8 = 4.20 \pm 0.05$ ppm

*Shifts are referenced to methyl group resonance of ethanol.

The unexpected result of the 1-3-8 fit of the NMR data for ethanol was that, by using K_3 and K_8 from IR data for ethanol solutions of 0.2 M or less in CCl_4, it was possible to fit chemical shift data for solutions from infinite dilution all the way to pure ethanol at 27° (17M). Figure 9 presents a comparison of experimental chemical

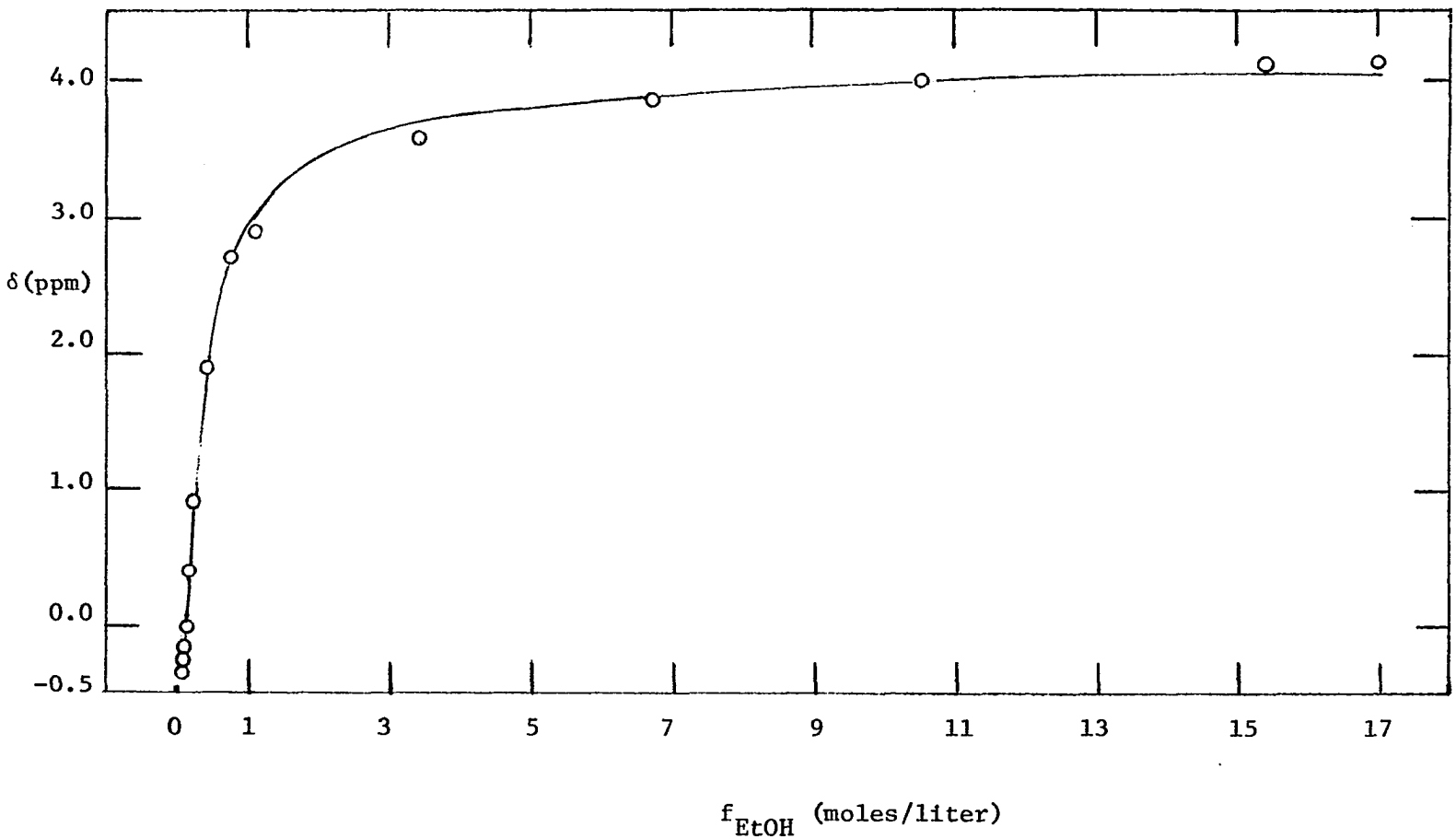


Figure 9. Chemical shift versus formal ethanol concentration in CCl_4 at 27°. Points are experimental.[22] Line is calculated with $K_3 = 11.6\ (M^{-2})$, [4] $K_8 = 10^5 (M^{-7})$ and the chemical shifts in Table 18.

shifts and shifts calculated on the basis of the 1-3-8 model. It should be pointed out that, in effect, five parameters are used in fitting the chemical shift data. However, the result is quite satisfactory in view of the apparent compatibility of the individual sets of IR and NMR data. Also, any fit of NMR data for hydrogen bonding systems must involve two parameters for each species other than the monomer.

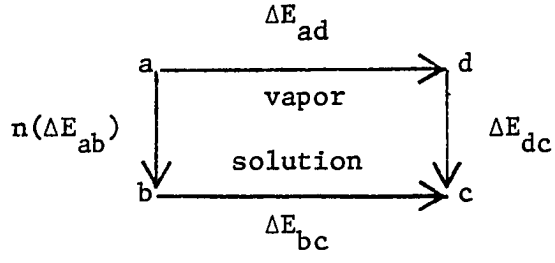
Solvent effect on methanol association. The 1-3-8 model proposed for alcohol solutions in inert solvents must be modified for methanol solutions in the more reactive solvents DPM and BZE. In particular, a small but distinguishable amount of methanol dimer appears to be present. Previous mention was made of the well-documented fact that specific interactions occur between hydroxyl groups and aromatic rings. It was noticed also that water apparently forms dimeric species in DPM and BZE. At this point the hypothesis will be forwarded that the appearance of a dimeric alcohol species in DPM (contrasted to the apparent negligible quantity of methanol dimer in HX) is due to stabilization of the dimer by specific interaction with the solvent, i.e., a trimeric species composed of a dimer-solvent complex. It is proposed that both alcohol and water dimers in the solvents DPM and BZE are stabilized in this manner. Evidence as to the feasibility of this arrangement will be discussed in consideration of the methanol-DEA and water-DEA complexes.

The enthalpies for methanol trimer and octamer formation in the three solvents HX, DPM and BZE very directly reflect the effect of increasing solvent reactivity on heats of formation of polymeric species. The values of $-\Delta H_3^o$ for trimer formation are 11.3, 5.5 and 4.4 kcal/mole in HX, DPM and BZE, respectively. Values of $-\Delta H_8^o$ for octamer formation,

42.1, 23.4 and 14.1 kcal/mole in HX, DPM and BZE, respectively, show an even more pronounced solvent effect.

Plausibility of proposed structures for trimer and octamer of methanol. It is interesting to speculate upon the trends that should be shown by values of energies of vaporization from solution for polymeric species of different structure as the solvent becomes a more effective electron donor. A cyclic polymeric alcohol species has all acidic hydrogens involved in bonding and, in addition, the projecting alkyl groups of the alcohol have a shielding effect which makes the solvent approach more difficult. In effect, it may be said that the cyclic species creates a roughly spherical cavity in the solvent. The linear polymer has one acidic hydrogen not tied up and the chain configuration is more open to interaction with the solvent. Based on these considerations it would be expected that the energy of vaporization from solution for a linear polymer would be more affected by an increase in solvent basicity.

The thermodynamic cycle below represents the processes involved in formation of a polymeric species, containing n monomer units, in both vapor and solution phases. ΔE_{ad}



is the energy change for formation of the polymer from n monomer units in the vapor phase; ΔE_{bc} is the energy change for the corresponding

process in solution; ΔE_{ab} is the energy change for solution of one monomer from the vapor phase and ΔE_{dc} is the energy of solution of the polymer (equivalent in magnitude but opposite in sign to the heat of vaporization). ΔE_{bc} is very closely equivalent to ΔH_n^o for polymer formation in solution since the PV term in solution is negligible.

The laws of thermodynamics require that the energy changes involved in the path abc equal those involved in the path adc and this gives

$$n(\Delta E_{ab}) + \Delta E_{bc} = \Delta E_{ad} + \Delta E_{dc} \qquad (33)$$

so that the energy of solution (or vaporization) of the polymer equals n times the energy of distribution of the monomer plus the energy of formation of the polymer in solution minus the energy of formation of the polymer in the vapor phase. Note that it is not necessary to have a value for the vapor phase polymer formation energy in order to calculate the change in energy of solution or vaporization of the polymer from solution as the solvent is changed since the vapor phase energy of formation is always a constant. By evaluating the left hand side of equation (33) a quantity is obtained which by its change in value as the solvent is changed reflects exactly the change in the energy of solution or vaporization from solution of the methanol polymer. Table 20 summarizes this value for both methanol trimer and octamer for each of the solvents HX, DPM and BZE. The table indicates that the differences in the sums change in the way that would be expected if the methanol trimer is linear and the octamer is cyclic. The first difference for

TABLE 20

Sums of Monomer Distribution and Polymer Formation Energies for Methanol in Three Solvents

Solvent	Trimer(kcal/mole) $-(3x\Delta E_D^o + \Delta E_3^o)$	Difference	Octamer(kcal/mole) $-(8x\Delta E_D^o + \Delta E_8^o)$	Difference
HX	20.0		64.5	
		1.1		1.0
DPM	21.1		65.5	
		2.8		0.8
BZE	23.9		66.3	

the trimer (1.1 kcal) indicates increasing interaction of the end OH with the more basic solvent; the second difference, from DPM to BZE shows a larger interaction with the ether linkage in BZE. In contrast, both differences for the octamer are very nearly constant as the solvent becomes more basic.

If the relative amounts of total methanol present as trimer and octamer on the basis of the 1-3-8 fit for methanol in HX are compared it is seen that the octamer is a considerably more important species, accounting for more than 60% of the total methanol present in HX at 0.2 M at 25°. The situation may be qualitatively described by saying that small concentrations of reactive species, monomers and trimers, are present with a large quantity of end product--the octamer. Pauling[73] has proposed an interesting conjecture on the state of

aggregation in liquid alcohols. It is generally accepted that simple alcohols associate in the solid state to form long chains.[1] However, it is apparent that few hydrogen bonds are broken on melting since alcohols have small heats of fusion. If alcohols existed in the liquid state as long chains a pronounced heat effect should be evident upon melting. To account for the fact that the heats of fusion of two isomeric compounds, ethanol and dimethyl ether are little different, Pauling suggests that liquid alcohols may consist largely of ring polymers since transition from chains in the solid to cyclic aggregates in the liquid would not involve the rupture of hydrogen bonds. The vapor pressure data for methanol from the present study are qualitatively in accord with Pauling's hypothesis since as the methanol concentration is increased an ever larger fraction of the alcohol appears to exist in large aggregates.

Qualifications of alcohol association models. There are several attributes which a successful alcohol association model should possess. Only two distinct types of models exist; one in which allowance is made for all possible polymeric species in a statistical fashion and one for which the assumption is made that only a few associated species occur to any extent in alcohol systems. In proposing the latter type of model an attempt is made to define a mathematical relationship which represents experimental data to a high degree of precision and, in addition, contains a minimum number of adjustable parameters. On a purely pragmatic basis the model need not have any relation to the actual physical situation as long as it predicts and correlates experimental observations within acceptable error limits. However, a general

tendency is to ascribe some degree of correspondence between the assumed structures of the model and the existing structures.

Once having assumed an association model, it is desirable to test the model on systems other than that from which the model was developed. If a model developed on the basis of one type of data on a particular alcohol system can be shown applicable for correlations of different types of data for alcohols of varying molecular structure then a more coherent picture of alcohol association may be developed to aid understanding of the effects of various factors influencing hydrogen bond formation in alcohol systems.

The development of an association model for alcohols involving only one or two distinct associated species is not simple. On the basis of specific types of data, very different proposals have been made concerning the important associated species in similar or identical alcohol-solvent systems. Perhaps the most recent example is the 1-4 model proposed by Fletcher and Heller.[35] These authors concluded from a study of the infrared spectra of 1-octanol solutions in n-decane that tetramers are the predominant associated species in alcohol solutions in non-polar solvents. An attempt was made to extend this association model to other alcohol solutions. However, other authors have found that if association is to be described by assumption of a monomer-n-mer equilibrium then a monomer-trimer equilibrium provides a better fit of spectral data. For example, Saunders and Hyne obtained good fits of NMR data for both phenol and t-butanol in CCl_4 with a 1-3 model. Storek and Kriegsmann[74] have recently confirmed the superiority of the 1-3 model in fitting NMR data for t-butanol in CCl_4. Also, Fletcher and Heller's fit of other

workers' IR data for phenol in CCl_4 to a 1-3-4 model resulted in showing that the trimer is a considerably more important species than the tetramer in that fit.[35]

The 1-3-8 model proposed in the present study has been successfully applied to data of several types for alcohol systems. It has been capable of correlating PVT data for methanol vapor.[15] The 1-3-8 model has been used to fit infrared spectral data for 1-octanol in n-decane in the overtone region and infrared spectral data from the fundamental hydroxyl stretching region for solutions of methanol, ethanol and t-butanol in CCl_4. Good temperature dependence was obtained for trimer and octamer equilibrium constants from infrared data. The effect of steric hindrance to association for t-butanol is reflected in the magnitudes of the trimer and octamer constants for this alcohol compared to trimer and octamer constants for methanol and ethanol in Table 18. These equilibrium constants indicate that the trimer is considerably more important in t-butanol solutions and that the octamer is less important. Although previously reported NMR measurements for alcohol solutions are not highly consistent the 1-3-8 model offers some promise of a quantitative explanation of the observed chemical shift data for alcohol solutions in non-polar solvents.

In concluding this section a note of caution must be sounded. Although the 1-3-8 model proposed in the present work to correlate association data for alcohols in non-polar solvents appears to be more generally applicable to several types of data for a number of alcohols than any proposed previously the correctness of the model cannot be taken as having been established. Reasonable assumptions about the

structures of the trimer and octamer have been shown to be in relatively good agreement with experimental results but this agreement can only add some measure of plausibility to the model and its structures.

Water and Methanol Complexes with Diethylamine in Solution

Water-Diethylamine 1:1 Complexes

The only previously reported enthalpies and equilibrium constants for water-aliphatic amine complexes in hydrocarbon solvents are those given by Gregory.[43] He determined equilibrium constants at 25 and 35° for the 1:1 complexes of water with cyclohexylamine, N-methylcyclohexylamine and N,N-dimethylcyclohexylamine in benzene. The enthalpy of formation of the water-DEA complex in DPM obtained in the present study (-4.5 kcal/mole) is in agreement with the average of Gregory's values for the water-cyclohexylamine complexes (-4.8 kcal/mole) in the similar solvent benzene. The equilibrium constants for the water-DEA complex at 25° in HX and DPM are significantly larger than the values obtained by Gregory for the water-triethylamine complex in cyclohexane and toluene at 25°. No apparent reason is known for this discrepancy. It is noted that the value of water solubility in cyclohexane used by Gregory was 0.0030 M. Johnson et al.[7] obtained a value of 0.0024 M for water solubility in cyclohexane. Use of the latter value for water solubility would increase Gregory's value for the water-triethylamine constant (7.0 M^{-1}) in cyclohexane by 20 per cent which would give closer agreement with the value obtained in this study for the water-DEA constant (11.0 M^{-1}) in HX. However, there is, as yet, not sufficient information available on the variance of equilibrium

constants with substitution at the amine nitrogen to say whether the equilibrium constants for the diethyl- and triethylamine-water complexes should have nearly equal values in similar solvents.

Methanol-Diethylamine 1:1 Complexes

The enthalpy values for the methanol-DEA 1:1 complex in HX, DPM and BZE are not in very good agreement with the enthalpy values listed in the Introduction for alcohol-aliphatic amine complexes. Only one ΔH^{o} value,[55] for the system methanol-triethylamine in CCl_4, of -3.8 kcal/mole is in reasonable agreement with the ΔH^{o}_{11} values for methanol-DEA listed in the present study. Except for the two alcohol-amine systems in toluene and cyclohexane all the values listed in the table in the Introduction were calculated from data obtained from alcohol-amine solutions in CCl_4. The well-documented fact that precipitates form in amine-CCl_4 solutions introduces the possibility of large systematic errors in enthalpy measurements since this precipitation reaction might well be drastically affected by temperature changes. It has also been noted that the study of intermolecular OH...N bonds to amines by infrared spectroscopy is plagued by the problem of very broad association bands which are not easily defined.[75]

Methanol and Water 2:1 Complexes with Diethylamine

Before considering the implications of the values of thermodynamic parameters for the 2:1 complexes found in this study a short discussion of some pertinent literature will be given.

A topic which has been of increasing interest in recent years has been that of solvent effects on infrared stretching frequencies.[75]

Many of the systems investigated have involved both solutes and solvents capable of entering into hydrogen bonding reactions. Attempts have been made to correlate the frequency shifts on the basis of non-specific interactions by relating frequency shifts to the bulk dielectric properties of the solutions. This approach has not been outstandingly successful.[76] Whetsel and Kagarise[77] studied the carbonyl stretching bands of acetone and cyclohexanone in mixtures of p-cresol and cyclohexane. These authors found that the observed frequency shifts could be explained by assuming the formation of 1:1 and 2:1 p-cresol-ketone complexes at moderate concentrations of p-cresol. Higher order complexes were possibly formed at increased p-cresol concentrations. Whetsel and Kagarise were able to determine equilibrium constants for the 1:1 and 2:1 complexes; the values for the p-cresol-acetone system at 30^{o} were 12.8 M^{-1} for K_{11} and $480M^{-2}$ for K_{21}. There are two possible configurations for the 2:1 complex; one where both p-cresol molecules are bonded to the carbonyl and one where the second p-cresol is bonded to the first p-cresol which is bonded to the carbonyl. Whetsel and Kagarise concluded that due to the small frequency shift observed for the carbonyl absorption, the second structure was more plausible.

Bellamy and Pace[72] have proposed that dimers of alcohols and phenols have chain rather than cyclic structures. This proposition is thought to account for two perplexing problems which arise in consideration of spectra of alcohol solutions. The first of these problems concerns the separation of the OH frequencies near 3500 cm^{-1} and 3300 cm^{-1} of alcohol solutions in CCl_4. As mentioned previously the first of these frequencies is customarily assigned to absorption by

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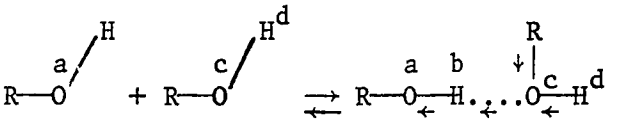
an alcohol dimer and the second to absorption by polymeric alcohol species. The fact that the dimer band is separated from the monomer band (at ≈ 3600 cm^{-1}) by 100 cm^{-1} and that the polymer band is separated from the monomer band by 300 cm^{-1} indicates that the hydrogen bonds are much stronger in the polymer than the bonds linking the dimer according to what is known as the Badger-Bauer rule. This rule proposes that a linear relationship exists between frequency shift and enthalpy of bond formation so that if a larger frequency shift is noticed for one species than another then the bonds in the first are stronger. The Badger-Bauer rule has been shown applicable in some cases but there are several instances in which it clearly gives the wrong prediction.[75]

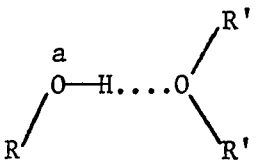
Bellamy and Pace propose that dimers are not cyclic with two weak bonds but are open-chain structures and are linked by a hydrogen bond of ordinary strength while alcohol polymers are cyclic and have unusually strong bonds. The rationale for this suggestion is similar to the "cooperative effect" proposed by Frank and Wen[78] concerning hydrogen bonding in water. This effect may be illustrated by considering the reaction of two alcohol molecules to form a dimer. In the process of forming the hydrogen bond in the dimer pictured below a shift of



electron density takes place in the direction indicated by the arrows.

The net effect of this shift is to render hydrogen atom (d) more acidic and oxygen atom (a) more basic in the sense of the electron density now present at these positions compared to the free molecules. The dimer is now more susceptible to attack at either position. A third alcohol molecule can attach itself at either (a) or (d). In this fashion a polymer is formed and Bellamy and Pace expect that cyclic polymers are formed since in the cyclic configuration all OH groups are participating in the cooperative process.

Bellamy, Morgan and Pace[79] consider the second problem concerning unusual aspects of the spectra of alcohol solutions. A marked decrease in the OH frequency occurring in solutions of phenol in ether upon addition of chloroform to the solution had been reported.[80] Bellamy et al. found that this effect could be rationalized very readily on the basis of the previous suggestion that alcohol dimers were of enhanced reactivity. The OH frequency of the complex formed between an alcohol molecule and an ether should be sensitive to the addition of



a proton donor like chloroform since the oxygen atom (a) becomes more basic upon formation of the alcohol-ether complex. The decrease in the OH stretching frequency upon addition of chloroform may then be explained by the formation of the chloroform-alcohol-ether ternary complex. In situations where an alcohol dimer is present Bellamy et al. expect that the OH stretching frequency would be sensitive to addition of either a proton donor or a proton acceptor since the dimer has increased reactivity at both an acidic and a basic site.

Table 21 compares the values of $-\Delta H^{o}$ obtained in the present study for formation of 1:1 and 2:1 complexes of methanol and water with diethylamine in the non-volatile solvents.

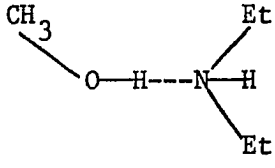
TABLE 21

Comparison of $-\Delta H^{o}_{11}$ and $-\Delta H^{o}_{21}$ for Methanol and Water Complexes with Diethylamine in Three Non-volatile Solvents

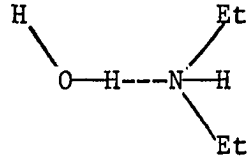
Solvent	System	$-H^{o}_{11}$ (kcal/mole)	$-H^{o}_{21}$ (kcal/mole)
HX	Methanol-DEA	4.48	13.80
DPM	Methanol-DEA	3.58	10.23
BZE	Methanol-DEA	2.86	8.71
BZE	Water-DEA	3.56	7.5

The most plausible structures for the 1:1 complexes with DEA are pictured below.

Methanol-DEA

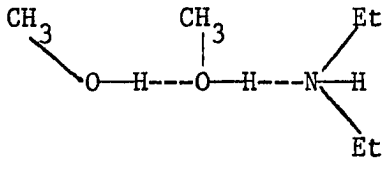


Water-DEA

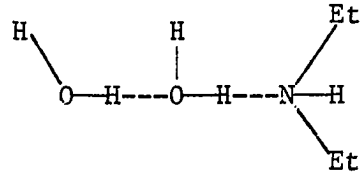


In analogy with these structures the proposed structures for the 2:1 complexes of methanol and water with the amine are:

$(Methanol)_2$-DEA

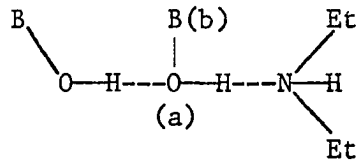


$(Water)_2$-DEA



Assuming that the preceding 2:1 structures are correct the enthalpy values in Table 21 may be taken as the most direct proof presently available of the importance of the cooperative effect in promoting polymer formation in hydrogen bonding systems. Comparison of the enthalpy values for the methanol:DEA 1:1 and 2:1 complexes indicates a substantial increase in stabilization of the hetero-trimer over the 1:1 complex. The ratios of $\Delta H^{o}_{21}/\Delta H^{o}_{11}$ are always significantly larger than 2 even if a substantial margin of error is allowed for. Even in the more reactive solvents DPM and BZE, in which the 1:1 complex has to compete with the solvent for the second methanol monomer, there is still the marked thermodynamic preference for the 2:1 methanol-DEA complex.

The contrast between the large enhancement of the methanol-DEA 2:1 complex in BZE and the much smaller increase in $-\Delta H^{o}_{21}$ for the water-DEA 2:1 complex in BZE, compared to the respective $-\Delta H^{o}_{11}$ values, is surprising. There is a slight problem with the temperature dependence of K_{11} and K_{21} for the water-DEA system in BZE but it is believed that the ratio $-\Delta H^{o}_{21}/-\Delta H^{o}_{11}$ from these data is qualitatively correct. A probable reason for the small enhancement of the ratio $-\Delta H^{o}_{21}/-\Delta H^{o}_{11}$ for the water-DEA system in BZE relative to the methanol-DEA enthalpy ratio may be suggested. The proposed structure for the 2:1 methanol-DEA and water-DEA complexes is



where B is either a methyl group or a hydrogen atom. It is generally established that the electron withdrawing tendency of a hydrogen atom is slightly larger than that of a methyl group. This author proposes that the electron density shift occasioned by the cooperative effect as the 1:1 complex is formed is less effective in promoting the basic nature of oxygen atom (a) in the 1:1 water-DEA complex relative to the methanol-DEA 1:1 complex. Even though $-\Delta H_{11}$ is larger for the water-DEA 1:1 complex than for the methanol-DEA 1:1 complex in BZE and the other two solvents as well, the bleeding away of electron density at oxygen atom (a) by hydrogen atom (b) tends to limit the stability obtained by addition of a second water molecule to the 1:1 water:DEA complex whereas in the methanol-DEA 1:1 complex the electron density at oxygen atom (a) is dissipated by substituent group (b) to a much smaller degree.

It may be noted that the proposed structures for the 2:1 complexes are not the only possible ones. A cyclic trimer structure for the methanol-DEA 2:1 complex could be formed by a hydrogen bond between the amine hydrogen and the oxygen of the second methanol molecule. This possibility cannot be ruled out but it is implausible for two reasons. First, it has been indicated that amine hydrogens are quite poor hydrogen bond acceptors and, even allowing for an increased acidity for the amine hydrogen due to the cooperative effect, it is unlikely that the energy of an amine hydrogen-alcohol oxygen bond would be even as large as the ΔH^{o}_{11} for 1:1 complex formation.

The second reason for the implausibility of the cyclic structure has already been discussed. Again, a large deviation from linearity in

the hydrogen bonds would occur and it is unlikely that the formation of a weak third bond would compensate for energy loss due to distortion of two strong bonds. A similar argument is applicable for the 2:1 water:DEA complex.

The enthalpies for 2:1 complex formation reported in this study appear to be the first values for the heat of formation of hetero-hydrogen bonded complexes involving more than one donor or acceptor molecule. The apparently large increase in complex stability due to the cooperative effect substantiates the qualitative results of Bellamy et al. on solvent effects in alcohol systems. This author is in disagreement with two opinions by Bellamy et al.[72] that 1) appreciable quantities of alcohol dimers exist in non-polar solvents and that 2) alcohol species higher than the dimer have cyclic structures. The strong effect shown in the $-\Delta H^{o}_{21}$ values for the methanol-DEA complexes from the present work would indicate that the formation of trimeric alcohol species is greatly favored over the formation of dimeric species.

The vapor pressure data for methanol in HX indicate that, within the precision of the measurements, a methanol dimer does not appear in measurable quantities in this system. In the solvents DPM and BZE, where interaction with a basic site is possible, small but detectable quantities of methanol dimers are apparently present.

The results obtained by Bellamy et al. in mixed solvent systems support their hypothesis that ternary complexes (proton donor-alcohol-basic solvent) form. Complexes of this type must have chain configurations and the marked frequency shifts promoted by addition of the weak proton donor chloroform to alcohol-basic solvent mixtures support the

apparently strong effect due to the shift of electron density along the bonded chain.

Other results from the present study presumably due to the cooperative effect may be mentioned. The $-\Delta H_2^o$ values for formation of water and methanol dimers in DPM (4.25 and 3.40 kcal/mole, respectively) are surprisingly large compared to the $-\Delta H_{11}^o$ values for 1:1 complexes of water and methanol with DEA in the same solvent (4.5 and 3.6 kcal/mole, respectively) since as a general rule hetero-hydrogen bonded complexes are expected to have appreciably larger values for $-\Delta H^o$ per bond than for similar self-associated complexes. The near equality of the $-\Delta H_{11}^o$ and $-\Delta H_2^o$ values can be rationalized on the basis of dimer-solvent complexes of water and methanol dimers with the aromatic ring. Also, recent unpublished work in this laboratory[15] indicates that in mixtures of fluorinated alcohols and methanol in n-hexadecane the predominant associated species is a hetero-trimer; 1:1 complexes of the alcohols are present in almost indetectable amounts. This is further indication of the instability of alcohol dimers in the absence of solvents with basic sites.

Relations for Predicting Solvent Effects on Association

Christian et al.[46,61,62] have developed relationships to predict the effect of changes in solvent reactivity on molecular complex formation. For a donor-acceptor reaction (A + D → AD) occurring in both the vapor phase and in a solvent a dimensionless parameter, α, is defined as the ratio of the energy of solution of the complex AD to the sum of the energies of solution of the monomers A and D

$$\alpha = \frac{\Delta E_{AD}^{o\ v\to s}}{\Delta E_{A}^{o\ v\to s} + \Delta E_{D}^{o\ v\to s}} \tag{34}$$

where $\Delta E^{o\ v\to s}$ is the energy change for transfer of one mole from the vapor phase to the infinitely dilute solution. It is expected in general that α will have a value less than unity since the reactive sites in the monomers are unable directly to contact the solvent after the complex is formed. In a sense, it may be stated that α represents the fraction of solvation energy retained by the monomers on forming the complex.

If α is strictly independent of temperature a similar relation may be obtained in terms of the free energies of solution

$$\alpha' = \frac{\Delta G_{AD}^{o\ v\to s}}{\Delta G_{A}^{o\ v\to s} + \Delta G_{D}^{o\ v\to s}} \tag{35}$$

where α' should equal α if the temperature independent restriction is met. It is expected that in the absence of strong specific solvent-solute interactions α and α' will not be strongly dependent on either temperature or choice of solvent.

Table 22 gives values of $-\Delta E^{o}$ and $-\Delta G^{o}$ (at 25^{o}) obtained from the present study of water-DEA and methanol-DEA complexes in the vapor phase and in solution in non-volatile solvents. With reference to the previously mentioned thermodynamic cycle (for methanol association) it is noted that ΔE^{o} and ΔG^{o} for transfer of one mole of a 1:1 complex (water-DEA or methanol-DEA) are obtained from use of the experimentally measured ΔE^{o} and ΔG^{o} for complex formation in the vapor phase, monomer

TABLE 22

Free Energies and Energies of Distribution of Monomers and 1:1 Complexes between the Vapor Phase and Three Non-volatile Solvents at 25°

Solute	$-\Delta G^{\circ}_{298}$ kcal/mole	$-\Delta E^{\circ}_{298}$ kcal/mole
	n-Hexadecane	
Water	0.45	2.13
Methanol	1.25	2.90
Diethylamine	3.16	5.60
H_2O-DEA	3.80	7.80
MeOH-DEA	4.15	6.28
	Diphenylmethane	
Water	1.79	4.17
Methanol	2.34	5.26
Diethylamine	3.36	6.29
H_2O-DEA	5.20	8.92
MeOH-DEA	5.08	8.41
	Benzyl Ether	
Water	2.54	6.33
Methanol	2.80	6.52
Diethylamine	3.33	6.43
H_2O-DEA	5.26	10.18
MeOH-DEA	5.19	9.09

All quantities in table referred to standard state of one mole/liter.

distribution between vapor and solution and energy of formation of the 1:1 complexes in solution. A standard state of one mole per liter ideal dilute solution is used; ΔH^{o}_{11} values in the vapor phase are converted to ΔE^{o}_{11} values by subtracting RT and ΔH^{o}_{11} values in solution are virtually identical to ΔE^{o}_{11} values since the PV term in solution is negligible.

The calculated values of α and α' for the 1:1 complexes of water and methanol with DEA are presented in Table 23. It is apparent that both α and α' values decrease in magnitude as the solvent becomes more reactive. The α values for the methanol-DEA 1:1 complex are more nearly constant than the other α and α' values. A decrease in values of the parameter α (and α') as the solvent becomes more reactive has been noted previously by Stevens[81] and Van Duyne[82] in studies on carboxylic acid dimerization in organic solvents. The cycles of thermodynamic values reported here are the first to have been obtained for water-amine and alcohol-amine complexes. Relations may be obtained from equation (35) which enable the calculation of an α' value from the slope of a log-log plot of association constants versus the product of distribution constants for the monomers obtained by determining distribution constants and association constants at one temperature for a series of solvents. Johnson et al.[46] determined 1:1 association constants at 25° for the water-pyridine complex in several organic solvents and obtained an α' value of 0.71.

Christian and Grundnes[62] have proposed a relationship to correlate the energy and free energy of solution of molecules involved in complex formation. From consideration of the energy and free energy relationships for solution of several non-polar gases in organic solvents the relation

TABLE 23

α and α' values for the Water-Diethylamine and Methanol-Diethylamine 1:1 Complexes in Three Non-volatile Solvents

Water-Diethylamine 1:1 Complex

Solvent	α	α'
HX	1.01	1.05
DPM	0.85	1.01
BZE	0.80	0.90

Methanol-Diethylamine 1:1 Complex

Solvent	α	α'
HX	0.74	0.93
DPM	0.73	0.89
BZE	0.70	0.85

$$\Delta G^{o}_{i\ v\rightarrow s} = \beta \Delta E^{o}_{i\ v\rightarrow s} + 0.75\ RT \qquad (36)$$

was proposed. The parameter β has a value of approximately 0.6 for solution of gases in several organic solvents. It is expected that this expression may be useful for relating thermodynamic data for donor, acceptor and complex molecules in a variety of solvents provided that strong specific solute-solvent interactions do not occur. Figure 10 presents a plot of $-\Delta G^{o}$ versus $-\Delta E^{o}$ for the monomeric molecules and 1:1 complexes studied in the present work. Values of $-\Delta G^{o}$ and $-\Delta E^{o}$ are used from Table 22.

The dashed line in Figure 10 is the expected line with a slope of about 0.6 for solution of gases which do not interact strongly with the solvent. As might have been expected from the trend expressed in Table 23 by the α and α′ values there is the appearance of what are apparently strong specific solute-solvent interactions. The points for water and methanol monomer distribution in the three solvents increasingly diverge from the line as the solvent reactivity is increased. The $-\Delta E^{o}_{D}$ values for water and methanol increase more rapidly than the $-\Delta G^{o}_{D}$ values as the solvent becomes more basic. The points for DEA lie very near the line and agree with the previous suggestion that little specific solute-solvent interaction is present in solutions of DEA in HX, DPM and BZE. A fair amount of scatter is evident in the points for the 1:1 complexes. This is partially to be expected since the values of ΔE^{o}_{D} and ΔG^{o}_{D} are calculated from four separate values of energy and free energy, respectively.

1 H_2O-HX
2 H_2O-DPM
3 H_2O-BZE
4 MeOH-HX
5 MeOH-DPM
6 MeOH-BZE
7 DEA-HX
8 DEA-DPM
9 DEA-BZE
10 H_2O-DEA-HX
11 H_2O-DEA-DPM
12 H_2O-DEA-BZE
13 MeOH-DEA-HX
14 MeOH-DEA-DPM
15 MeOH-DEA-BZE

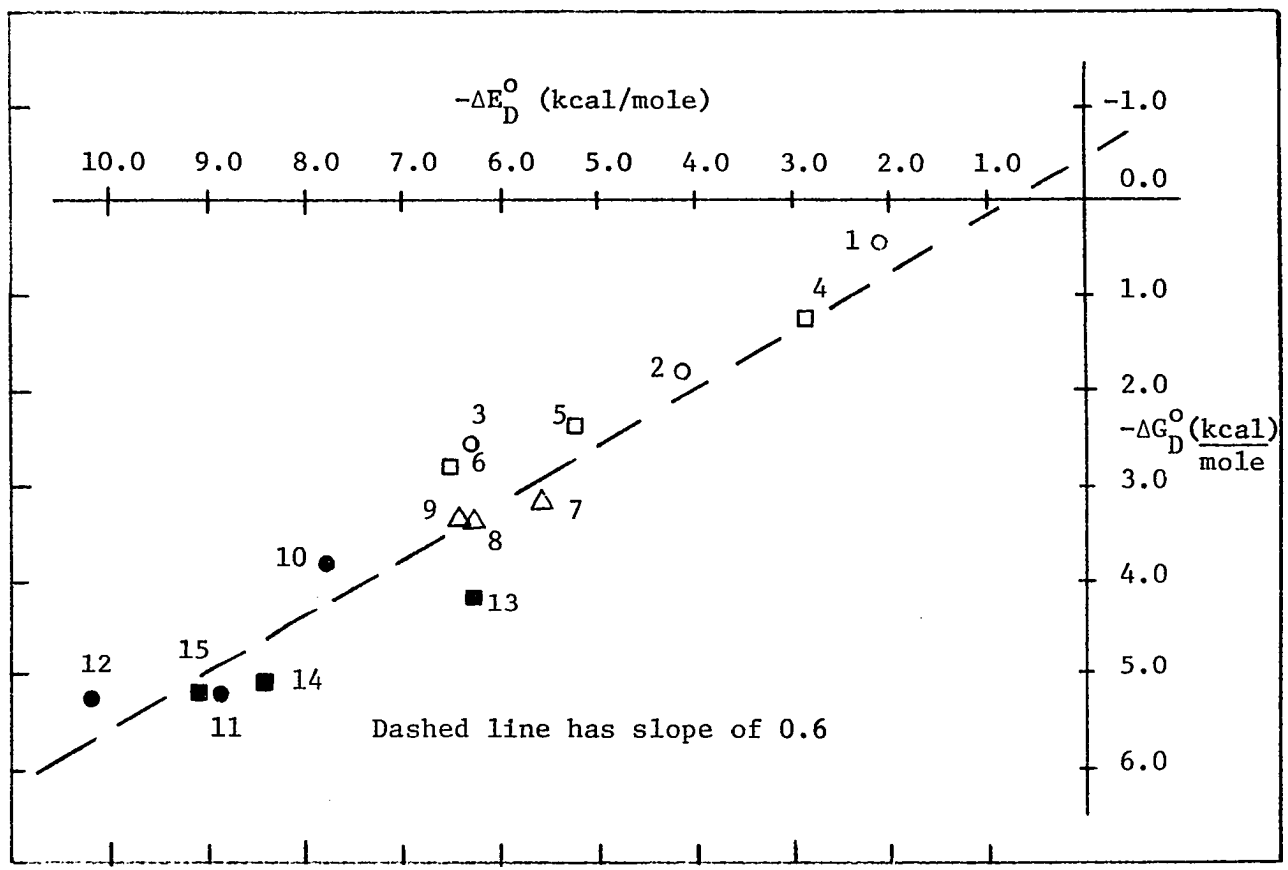


Figure 10. Plot of $-\Delta G_D^o$ versus $-\Delta E_D^o$ for distribution of monomers and 1:1 complexes between the vapor phase and three non-volatile solvents.

A comparison of vapor phase association constants and $-\Delta E^{o}_{11}$ for the 1:1 complexes of water and methanol with DEA (Table 17) with the corresponding quantities in solution (Table 15) is interesting. Since water is generally considered a better acid than methanol it might have been expected that both K_{11} and $-\Delta E_{11}$ for the water-DEA vapor complex would be larger than the K_{11} and $-\Delta E^{o}_{11}$ for the methanol-DEA vapor complex. However, the experimental result is that in the vapor phase methanol apparently forms a stronger bond with DEA than does water. When the K_{11} and $-\Delta E^{o}_{11}$ values are compared in solution the situation is reversed--water uniformly appears to form a stronger bond with DEA than methanol does (1:1 complexes only). Not only are the K_{11} and $-\Delta E^{o}_{11}$ values for the water-DEA complex in solution larger than the K_{11} and $-\Delta E^{o}_{11}$ for methanol-DEA but they are also in the two least reactive solvents unexpectedly large compared to the K_{11} and $-\Delta E^{o}_{11}$ values for the water-DEA complex in the vapor phase. K_{11} (water-DEA at 25°) in HX (11.0 M^{-1}) and also in DPM (8.5 M^{-1}) is larger than the vapor phase K_{11} of 7.9 M^{-1}. $-\Delta E^{o}_{11}$ (water-DEA) is slightly larger in HX (6.13 kcal/mole) than in vapor (6.07 kcal/mole) and becomes smaller (4.5 kcal/mole) in DPM. The result of these comparisons would indicate the existence of some factor leading to the stabilization of the water-DEA 1:1 complex in solution, relative to the vapor phase. Dielectric studies on water-aliphatic amine complexes[43] in organic solvents have indicated that the complexes have much larger dipole moments than would be expected assuming vector additivity of the dipole moments of water and the amine. The possibility exists, therefore that excess dipole-induced dipole interaction in polarizable

solvents is responsible for the anomalous stabilization of the water-DEA complex. Similar dipole enhancement has been reported for alcohol-amine complexes in organic solvents[83] but there is apparently no marked effect in the case of the methanol-DEA complexes. Grundnes and Christian[84] have found that the highly polar charge transfer complex $(CH_3)_3N.SO_2$ is stabilized in heptane and chlorinated hydrocarbons relative to the vapor phase.

The relations proposed by Christian et al. appear to be valuable as first approximations in correlating the thermodynamic properties of hydrogen bonding systems. Comparison of experimentally determined energy and free energy values on the basis of the α and β relations enable the prediction of the effects of increasing solvent reactivity on complex formation. These relations should be further tested on systems for which accurate solvation energies and free energies may be obtained for the species involved in complex formation reactions. Specific effects of donor-acceptor interactions between polar solvents and polar solutes deserve further study.

Summary and Proposals for Future Work

Equilibrium constants, enthalpies and entropies have been determined for diethylamine self-association, the 1:1 complex of water with diethylamine and the 1:1 complex of methanol with diethylamine in the vapor phase. The enthalpy for the water-diethylamine complex appears to be the first reported enthalpy for a hydrogen bonded complex of water in the vapor phase.

Distribution and association equilibrium constants for methanol, water and diethylamine partitioned between the vapor phase and three

non-volatile solvents have been determined at 25, 35 and 45°. Enthalpies and entropies of associated species are reported. A new association model for alcohols is proposed and tested on readily available data for alcohol-solvent systems with excellent results.

The study of three component systems where two volatile components are partitioned between the vapor phase and a non-volatile solvent has enabled the calculation of enthalpies and entropies of association for the 1:1 complexes methanol-diethylamine and water-diethylamine in n-hexadecane, diphenylmethane and benzyl ether. Also, enthalpies and entropies of formation of 2:1 complexes of methanol with diethylamine in each of the solvents n-hexadecane, diphenylmethane and benzyl ether have been determined. Enthalpy and entropy of formation for the 2:1 complex water-diethylamine in benzyl ether are reported. These thermodynamic data for the 2:1 hydrogen bonded complexes of water and methanol give the first quantitative evidence bearing on the supposition that hydrogen bonds are stronger in larger polymers.

The extensive thermodynamic data in this work are used to test relations proposed by Christian et al. and deviate from the proposed relations in such a manner as to indicate strong specific solute-solvent interactions.

Some very desirable directions for future studies in the general area of hydrogen bonding and specifically concerning the results of this study are:

1. Measurement of equilibrium constants and enthalpies for the 1:1 association of water with several electron donors both in the vapor phase and in solutions.

2. Further application of the alcohol association model proposed here to data of several types for alcohol-solvent systems for alcohols of varying molecular weight and structure.
3. Use of solvents which dissolve appreciable quantities of water in an attempt to determine thermodynamic parameters for 2:1 water-base complexes to further assess the importance of the cooperative effect in formation of water polymers.

APPENDIX

PRESENTATION OF EXPERIMENTAL DATA

The primary data collected in this work are tabulated here. A few words of explanation are necessary in order to facilitate any future use of these data.

Whenever the symbols Π or P are used they indicate either a formal or a measured pressure, respectively. These pressures are expressed in torr. The volume ratio for the PVT apparatus with which the PVT data for diethylamine were obtained was 0.71837 at 25° and 0.77572 at 35 and 45°.

All symbols used are defined in the text. Subscripts on symbols (Π_A, P_M, f_W) indicate compounds; A for diethylamine, M for methanol and W for water. In the systems where two volatile components are present it may be emphasized that f* refers to the total moles of a component present divided by the solution volume whereas f is the formal concentration in solution only for single volatile component vapor-solution systems.

Reference 59 discusses in some detail the types of measurements employed in this study.

TABLE 24

PVT Data for Diethylamine Vapor at 25°

P_F	P_S	P_L	P_L(calcd.)
86.54	0.15	120.12	120.10
62.42	0.44	86.54	86.56
44.99	0.39	62.42	62.40
32.43	0.30	44.99	44.98
23.51	0.71	32.43	32.42
17.08	0.64	23.51	23.51
12.35	0.29	17.08	17.07
8.87	0.00	12.35	12.34
111.53	0.22	154.64	154.67
80.33	0.06	111.53	111.53
57.84	0.10	80.33	80.33
41.66	0.25	57.84	57.82
29.98	0.15	41.64	41.64
21.76	0.78	29.97	29.97
15.77	0.49	21.76	21.76
11.63	1.03	15.78	15.78
81.25	0.26	112.73	112.73
58.62	0.49	81.26	81.26
42.32	0.61	58.60	58.60
30.59	0.58	42.32	42.32
22.16	0.66	30.59	30.57
16.06	0.49	22.16	22.15
11.70	0.55	16.06	16.07
8.54	0.46	11.70	11.70
113.30	0.55	156.96	156.98
81.70	0.42	113.30	113.29
58.93	0.48	81.70	81.70
42.51	0.46	58.93	58.91
30.71	0.55	42.51	42.49
22.20	0.47	30.71	30.70
16.16	0.75	22.20	22.20
11.77	0.52	16.16	16.17
8.59	0.48	11.77	11.76
6.27	0.37	8.59	8.58
4.61	0.37	6.27	6.27
79.67	0.29	110.55	110.53
57.53	0.66	79.67	79.68
41.47	0.38	57.53	57.50
29.93	0.42	41.47	41.46
21.64	0.48	29.93	29.91
15.68	0.48	21.64	21.63
11.40	0.43	15.68	15.69
8.32	0.49	11.40	11.39
6.08	0.36	8.32	8.31

TABLE 25

PVT Data for Diethylamine Vapor at 35°

P_F	P_S	P_L	P_L(calcd.)
123.03	0.30	158.17	158.18
95.66	0.34	123.03	123.02
74.33	0.20	95.66	95.64
57.77	0.27	74.33	74.32
44.93	0.41	57.77	57.76
34.92	0.27	44.93	44.91
27.16	0.33	34.92	34.91
21.17	0.40	27.16	27.16
16.53	0.50	21.17	21.16
12.90	0.35	16.53	16.53
125.39	0.42	161.16	161.18
97.49	0.33	125.39	125.36
75.78	0.29	97.49	97.47
58.91	0.31	75.78	75.77
45.79	0.34	58.91	58.89
35.58	0.21	45.79	45.78
27.64	0.19	35.58	35.57
21.50	0.26	27.64	27.63
16.75	0.32	21.50	21.49
13.09	0.39	16.75	16.75
126.74	0.33	162.89	162.93
98.51	0.24	126.74	126.70
76.59	0.33	98.51	98.50
59.54	0.33	76.59	76.58
46.32	0.47	59.54	59.52
36.01	0.29	46.32	46.31
28.05	0.51	36.01	36.00
21.84	0.35	28.05	28.04
17.03	0.40	21.84	21.83
13.28	0.28	17.03	17.03
119.32	0.36	153.36	153.40
92.77	0.34	119.32	119.30
72.13	0.39	92.77	92.76
56.07	0.31	72.13	72.12
43.60	0.40	56.07	56.05
33.91	0.37	43.60	43.59
26.42	0.48	33.91	33.90
20.58	0.38	26.42	26.41
16.06	0.45	20.58	20.57
12.54	0.33	16.06	16.07
125.83	0.36	161.72	161.76
97.83	0.37	125.83	125.80
76.05	0.30	97.83	97.82
59.14	0.36	76.05	76.05
45.97	0.33	59.14	59.12
35.75	0.35	45.97	45.95
27.79	0.27	35.75	35.73
21.64	0.34	27.79	27.78
16.85	0.33	21.64	21.62
13.16	0.37	16.85	16.86

TABLE 26

PVT Data for Diethylamine Vapor at 45°

P_F	P_S	P_L	P_L(calcd.)
120.30	0.35	154.66	154.71
93.57	0.58	120.30	120.29
72.69	0.21	93.57	93.55
56.51	0.34	72.69	72.69
43.98	0.55	56.51	56.49
34.22	0.43	43.98	43.97
26.62	0.34	34.22	34.20
20.74	0.37	26.62	26.62
16.19	0.49	20.74	20.73
12.64	0.34	16.19	16.20
122.18	0.33	157.11	157.13
94.98	0.35	122.18	122.16
73.79	0.20	94.98	94.96
57.35	0.30	73.79	73.78
44.66	0.69	57.35	57.34
34.74	0.44	44.66	44.64
27.02	0.28	34.74	34.73
21.02	0.26	27.02	27.01
16.46	0.69	21.02	21.02
12.84	0.30	16.46	16.47
107.72	0.38	138.54	138.53
83.77	0.52	107.72	107.71
65.19	0.60	83.77	83.78
50.70	0.51	65.19	65.16
39.50	0.70	50.70	50.70
30.82	0.74	39.50	39.49
24.05	0.67	30.82	30.80
18.75	0.41	24.05	24.05
14.66	0.49	18.75	18.76
11.44	0.27	14.66	14.67
108.87	0.68	139.94	139.93
84.76	0.93	108.87	108.86
65.96	0.59	84.76	84.78
51.42	1.05	65.96	65.94

TABLE 27

Vapor Density Data for the System Water-Diethylamine at 25°

Π_A	P_W	P_T	P_T(calcd.)
59.83	3.15	62.63	62.62
59.83	4.76	64.18	64.18
59.83	6.35	65.73	65.74
59.83	7.95	67.29	67.30
59.83	9.54	68.84	68.86
57.58	1.55	58.85	58.83
57.58	3.15	60.40	60.39
57.58	4.75	61.96	61.96
57.58	6.35	63.51	63.52
57.58	7.95	65.07	65.08
85.85	3.15	88.31	88.32
85.85	4.76	89.84	89.86
63.61	1.54	64.81	64.79
63.61	3.13	66.36	66.34
63.61	4.73	67.91	67.90
63.61	6.33	69.47	69.46
63.61	7.92	71.02	71.01
63.61	9.52	72.57	72.56
63.61	11.10	74.11	74.11

TABLE 28

Vapor Density Data for the System Water-Diethylamine at 35°

Π_A	P_W	P_T	P_T(calcd.)
86.72	6.53	92.66	92.63
86.72	9.84	95.87	95.85
86.72	13.13	99.08	99.06
86.72	16.42	102.29	102.27
97.01	3.22	99.58	99.55
97.01	6.52	102.77	102.77
97.01	9.81	105.98	105.98
97.01	13.11	109.17	109.18
97.01	16.39	112.37	112.38
68.79	6.53	74.92	74.90
68.79	9.82	78.16	78.13
68.79	13.12	81.39	81.36
68.79	16.41	84.61	84.58
89.47	3.26	92.16	92.15
89.47	6.57	95.36	95.38
89.47	9.86	98.57	98.59
89.47	13.15	101.78	101.80
89.47	16.45	104.99	105.01
74.72	3.26	77,56	77.56
74.72	6.57	80.78	80.81
74.73	9.86	84.00	84.03
74.73	13.15	87.23	87.25
74.73	16.43	90.44	90.47

TABLE 29

Vapor Density Data for the System Water-Diethylamine at 45°

Π_A	P_W	P_T	P_T(calcd.)
98.39	6.73	104.49	104.48
98.39	10.14	107.83	107.82
98.39	13.54	111.17	111.16
98.39	16.94	114.50	114.49
111.60	3.34	114.23	114.22
111.60	6.75	117.55	117.56
111.60	10.16	120.88	120.89
111.60	13.56	124.20	124.22
111.60	16.96	127.54	127.54
87.06	6.74	93.32	93.29
87.06	10.15	96.66	96.64
87.06	13.55	100.00	99.98
87.06	16.95	103.34	103.32
105.28	3.33	108.00	107.97
105.28	6.75	111.34	111.32
105.28	10.16	114.67	114.65
105.28	13.57	118.00	117.99
105.28	16.97	121.34	121.32
122.86	3.34	125.35	125.34
122.86	6.76	128.66	128.67
122.86	10.17	131.97	132.00
122.86	13.58	135.29	135.32
122.86	16.98	138.60	138.64

TABLE 30

Vapor Density Data for the System Methanol-Diethylamine at 25°

Π_A	P_M	P_T	P_T(calcd.)
52.25	3.42	55.33	55.33
52.25	6.83	58.64	58.62
52.25	10.25	61.93	61.92
52.25	13.65	65.23	65.20
52.25	17.06	68.51	68.49
52.25	20.45	71.77	71.75
52.25	23.84	75.04	75.03
52.25	27.24	78.31	78.31
52.25	30.63	81.57	81.58
52.25	34.03	84.82	84.86
52.54	3.42	55.64	55.62
52.54	6.84	58.96	58.91
52.54	10.25	62.24	62.21
52.54	13.65	65.53	65.49
52.54	17.06	68.80	68.77
52.54	20.45	72.06	72.04
52.54	23.84	75.33	75.31
52.54	27.24	78.58	78.59
52.54	30.64	81.86	81.87
52.54	34.02	85.12	85.14
53.09	3.42	56.17	56.16
53.09	6.83	59.48	59.45
53.09	10.25	62.77	62.74
53.09	13.65	66.06	66.02
53.09	17.06	69.33	69.31
53.09	20.45	72.59	72.57
53.09	23.84	75.85	75.84
53.09	27.24	79.10	79.12
53.09	30.64	82.36	82.40
53.09	34.02	85.62	85.67

TABLE 31

Vapor Density Data for the System Methanol-Diethylamine at 35°

Π_A	P_M	P_T	P_T(calcd.)
68.98	3.54	72.12	72.12
68.98	7.08	75.56	75.54
68.98	10.61	79.01	78.96
68.98	14.16	82.40	82.39
68.98	17.70	85.82	85.82
68.98	21.24	89.26	89.25
68.98	24.79	92.67	92.68
68.98	28.32	96.09	96.10
68.98	31.85	99.51	99.52
68.98	35.36	102.92	102.92
71.39	3.55	74.52	74.50
71.39	7.10	77.95	77.94
71.39	10.64	81.40	81.36
71.39	14.20	84.83	84.80
71.39	17.70	88.26	88.19
78.20	3.54	81.21	81.24
78.20	7.08	84.64	84.65
78.20	10.61	88.05	88.05
78.20	14.16	91.46	91.47
78.20	17.70	94.88	94.89
78.20	21.24	98.31	98.30
78.20	24.79	101.71	101.72
78.20	28.32	105.12	105.12
78.20	31.85	108.51	108.53
78.20	35.36	111.92	111.92
55.93	3.55	59.19	59.19
55.93	7.10	62.63	62.65
55.93	10.64	66.09	66.10
55.93	14.20	69.54	69.56
73.44	3.53	76.54	76.51
73.44	7.09	79.98	79.95
73.44	10.64	83.40	83.38
73.44	14.19	86.83	86.81
73.44	17.73	90.25	90.23
73.44	21.27	93.65	93.65
73.44	24.83	97.06	97.09
73.44	28.37	100.47	100.51
73.44	31.90	103.88	103.92
73.44	35.43	107.29	107.33
64.37	3.53	67.55	67.53
64.37	7.09	71.00	70.98
64.37	10.64	74.44	74.42
64.37	14.19	77.88	77.87
64.37	17.73	81.35	81.31
64.37	21.27	84.78	84.74
64.37	24.83	88.22	88.19
64.37	28.37	91.63	91.63
64.37	31.90	95.05	95.05
64.37	35.43	98.49	98.48

TABLE 32

Vapor Density Data for the System Methanol-Diethylamine at 45°

Π_A	P_M	P_T	P_T(calcd.)
70.17	3.67	73.51	73.50
70.17	7.33	77.08	77.08
70.17	10.98	80.68	80.64
70.17	14.62	84.24	84.21
70.17	18.27	87.78	87.77
70.17	21.90	91.35	91.32
70.17	25.54	94.88	94.88
70.17	29.17	98.42	98.43
70.17	32.80	101.97	101.98
70.17	36.44	105.52	105.53
73.75	3.67	77.05	77.05
73.75	7.33	80.63	80.62
73.75	10.97	84.21	84.18
73.75	14.62	87.79	87.74
73.75	18.27	91.31	91.30
73.75	21.90	94.86	94.85
73.75	25.54	98.40	98.41
73.75	29.17	101.94	101.95
73.75	32.81	105.49	105.50
73.75	36.43	109.04	109.04
62.59	3.67	65.99	65.98
62.59	7.33	69.57	69.56
62.59	10.97	73.15	73.13
62.59	14.62	76.71	76.70
62.59	18.27	80.27	80.28
62.59	21.90	83.85	83.84
62.59	25.54	87.40	87.41
62.59	29.17	90.96	90.97
62.59	32.81	94.51	94.53
62.59	36.43	98.08	98.09

TABLE 33

Vapor Pressure Data for Diethylamine in n-Hexadecane at 25°

P_A	f_A	f_A(calcd.)
1.17	0.0124	0.0131
2.28	0.0251	0.0256
3.38	0.0379	0.0381
4.46	0.0509	0.0507
5.57	0.0635	0.0636
6.62	0.0758	0.0760
7.67	0.0885	0.0886
8.70	0.1010	0.1011
9.72	0.1136	0.1135
10.65	0.1260	0.1250
11.76	0.1388	0.1388
12.81	0.1521	0.1520
13.76	0.1641	0.1641
14.74	0.1765	0.1767
15.68	0.1887	0.1889

TABLE 34

Vapor Pressure Data for Diethylamine in n-Hexadecane at 35°

P_A	f_A	f_A(calcd.)
2.25	0.0187	0.0185
3.74	0.0310	0.0308
5.28	0.0437	0.0436
6.75	0.0560	0.0559
8.25	0.0686	0.0686
9.76	0.0813	0.0813
11.22	0.0938	0.0938
12.56	0.1052	0.1053
13.96	0.1172	0.1174
15.32	0.1290	0.1291
16.71	0.1411	0.1412
18.06	0.1530	0.1530
19.58	0.1664	0.1664
20.92	0.1783	0.1783
22.27	0.1902	0.1902

TABLE 35

Vapor Pressure Data for Diethylamine in n-Hexadecane at 45°

P_A	f_A	f_A(calcd.)
2.27	0.0132	0.0130
4.55	0.0264	0.0262
6.76	0.0391	0.0391
8.97	0.0521	0.0520
11.86	0.0691	0.0690
13.99	0.0816	0.0817
16.58	0.0970	0.0971
18.64	0.1094	0.1095
20.72	0.1222	0.1221
22.77	0.1346	0.1345
25.07	0.1486	0.1486
27.12	0.1612	0.1612
29.22	0.1741	0.1741
32.02	0.1916	0.1916
34.25	0.2056	0.2055

TABLE 36

Vapor Pressure Data for Water in n-Hexadecane at 25°

P_W	f_W	f_W(calcd.)
2.43	0.00029	0.00028
4.92	0.00057	0.00057
7.33	0.00085	0.00085
9.80	0.00114	0.00113
12.23	0.00142	0.00142
14.62	0.00171	0.00169
17.08	0.00200	0.00198
19.41	0.00230	0.00225
2.49	0.00028	0.00029
4.98	0.00056	0.00058
7.42	0.00084	0.00086
9.84	0.00113	0.00114
12.25	0.00142	0.00142
14.72	0.00170	0.00170
17.22	0.00198	0.00199
19.60	0.00227	0.00227
2.40	0.00029	0.00028
4.90	0.00057	0.00057
7.37	0.00085	0.00085
9.97	0.00112	0.00115
12.36	0.00141	0.00143
14.80	0.00170	0.00171
17.36	0.00197	0.00201

TABLE 37

Vapor Pressure Data for Water in n-Hexadecane at 35°

P_W	f_W	f_W(calcd.)
5.35	0.00052	0.00052
9.66	0.00094	0.00094
13.94	0.00135	0.00136
18.24	0.00177	0.00178
22.52	0.00219	0.00219
26.76	0.00261	0.00261
31.05	0.00303	0.00302
35.27	0.00345	0.00343
38.36	0.00378	0.00373
3.16	0.00032	0.00031
7.46	0.00073	0.00073
11.78	0.00115	0.00115
16.09	0.00156	0.00157
20.39	0.00198	0.00198
24.64	0.00240	0.00240
28.91	0.00282	0.00281
33.18	0.00324	0.00323
38.36	0.00379	0.00373
4.28	0.00042	0.00042
8.63	0.00083	0.00084
12.98	0.00124	0.00126
17.29	0.00166	0.00168
21.62	0.00207	0.00210
25.91	0.00249	0.00252
30.20	0.00290	0.00294
34.47	0.00332	0.00336
38.59	0.00375	0.00376

TABLE 38

Vapor Pressure Data for Water in n-Hexadecane at 45°

P_W	f_W	f_W(calcd.)
5.75	0.00050	0.00050
13.81	0.00119	0.00119
20.75	0.00179	0.00179
27.64	0.00238	0.00239
34.56	0.00298	0.00299
41.46	0.00357	0.00358
48.28	0.00418	0.00417
55.08	0.00478	0.00476
5.77	0.00050	0.00050
11.60	0.00099	0.00100
17.37	0.00148	0.00150
23.14	0.00198	0.00200
28.97	0.00247	0.00250
34.70	0.00297	0.00300
40.39	0.00347	0.00349
46.11	0.00397	0.00398
51.76	0.00447	0.00447
57.39	0.00498	0.00497
8.60	0.00075	0.00074
14.41	0.00124	0.00124
20.15	0.00174	0.00174
25.91	0.00223	0.00224
31.65	0.00273	0.00273
37.64	0.00320	0.00325
43.08	0.00373	0.00372
48.75	0.00424	0.00421
54.40	0.00475	0.00470

TABLE 39

Vapor Pressure Data for Methanol in n-Hexadecane at 25°

P_M	f_M	f_M(calcd.)
3.53	0.0016	0.0016
8.76	0.0039	0.0039
13.90	0.0063	0.0062
18.98	0.0087	0.0086
23.99	0.0111	0.0110
28.88	0.0135	0.0133
33.68	0.0159	0.0158
38.36	0.0183	0.0183
42.89	0.0207	0.0208
47.21	0.0232	0.0233
51.35	0.0257	0.0258
5.29	0.0023	0.0023
10.51	0.0047	0.0047
15.59	0.0071	0.0070
20.65	0.0095	0.0094
25.59	0.0119	0.0117
30.48	0.0143	0.0141
35.21	0.0167	0.0166
39.82	0.0191	0.0190
44.26	0.0216	0.0215
48.53	0.0240	0.0241
52.59	0.0265	0.0266
56.43	0.0290	0.0291
60.08	0.0316	0.0317
63.50	0.0341	0.0342
66.68	0.0367	0.0368
69.68	0.0393	0.0394
74.22	0.0437	0.0437
78.28	0.0481	0.0480
81.93	0.0526	0.0524
85.14	0.0571	0.0568
88.10	0.0617	0.0613
90.79	0.0663	0.0659
7.08	0.0031	0.0031
12.25	0.0055	0.0055
20.74	0.0095	0.0094
28.98	0.0135	0.0134
36.93	0.0175	0.0175
44.42	0.0215	0.0216
51.40	0.0257	0.0258
57.84	0.0298	0.0301
63.64	0.0341	0.0344

P_M	f_M	f_M(calcd.)
68.84	0.0384	0.0386
73.48	0.0428	0.0429
77.63	0.0473	0.0473
81.32	0.0517	0.0516
84.64	0.0562	0.0560
87.66	0.0608	0.0606
90.37	0.0653	0.0651
92.82	0.0699	0.0697
95.08	0.0746	0.0744
97.12	0.0792	0.0790
99.02	0.0839	0.0837
100.79	0.0886	0.0884
102.44	0.0933	0.0933
103.95	0.0980	0.0980
105.38	0.1027	0.1028
106.72	0.1074	0.1076
107.98	0.1121	0.1124
109.17	0.1169	0.1172
110.28	0.1216	0.1220
111.35	0.1263	0.1268
112.36	0.1311	0.1316
113.32	0.1358	0.1364
17.34	0.0079	0.0078
33.82	0.0159	0.0159
50.10	0.0248	0.0250
62.58	0.0332	0.0335
71.75	0.0410	0.0413
79.95	0.0499	0.0499
87.76	0.0607	0.0607
92.92	0.0699	0.0699
96.84	0.0783	0.0783
100.57	0.0876	0.0880
103.17	0.0961	0.0955
106.06	0.1055	0.1052
108.60	0.1150	0.1149
110.86	0.1245	0.1246
112.89	0.1340	0.1342
114.54	0.1425	0.1427
116.38	0.1530	0.1531
117.94	0.1625	0.1626
119.32	0.1721	0.1717
120.61	0.1816	0.1807

TABLE 40

Vapor Pressure Data for Methanol in n-Hexadecane at 35°

P_M	f_M	f_M(calcd.)
20.38	0.0076	0.0076
40.09	0.0152	0.0152
58.88	0.0229	0.0229
76.33	0.0308	0.0309
92.17	0.0388	0.0390
106.09	0.0470	0.0472
118.19	0.0554	0.0555
128.53	0.0639	0.0639
137.35	0.0727	0.0725
144.99	0.0815	0.0813
151.58	0.0905	0.0902
157.32	0.0995	0.0993
162.42	0.1086	0.1085
166.94	0.1178	0.1178
170.98	0.1270	0.1271
174.64	0.1362	0.1366
177.96	0.1455	0.1460
180.95	0.1547	0.1553
188.65	0.1827	0.1831
190.83	0.1921	0.1922
192.90	0.2014	0.2014
194.79	0.2108	0.2102
196.67	0.2202	0.2195
6.18	0.0023	0.0023
12.31	0.0045	0.0045
18.35	0.0068	0.0068
24.37	0.0091	0.0091
30.33	0.0114	0.0113
49.62	0.0190	0.0190
67.75	0.0268	0.0269
84.43	0.0347	0.0349
99.29	0.0429	0.0431
112.29	0.0512	0.0513
123.43	0.0596	0.0596
132.98	0.0683	0.0681
141.22	0.0771	0.0768
148.32	0.0860	0.0856
154.46	0.0950	0.0946
159.88	0.1040	0.1037
164.65	0.1132	0.1129
168.93	0.1224	0.1223
172.76	0.1316	0.1316
176.24	0.1408	0.1410
179.39	0.1501	0.1503
182.29	0.1594	0.1597
184.97	0.1687	0.1691

TABLE 41

Vapor Pressure Data for Methanol in n-Hexadecane at 45°

P_M	f_M	f_M(calcd.)
23.57	0.0072	0.0072
46.56	0.0145	0.0144
68.89	0.0219	0.0217
90.36	0.0293	0.0292
110.87	0.0369	0.0368
130.17	0.0445	0.0445
148.13	0.0523	0.0524
164.56	0.0602	0.0603
179.55	0.0682	0.0684
193.02	0.0764	0.0765
205.18	0.0847	0.0848
216.00	0.0932	0.0931
225.76	0.1017	0.1016
234.53	0.1103	0.1102
242.51	0.1191	0.1189
249.73	0.1278	0.1278
256.31	0.1367	0.1367
262.31	0.1456	0.1457
267.86	0.1545	0.1549
272.95	0.1635	0.1640
11.82	0.0036	0.0036
37.47	0.0116	0.0116
57.80	0.0182	0.0181
79.74	0.0256	0.0254
100.73	0.0331	0.0330
120.67	0.0407	0.0406
139.25	0.0484	0.0484
156.49	0.0562	0.0563
172.18	0.0642	0.0643
186.39	0.0723	0.0724
199.16	0.0805	0.0806
210.60	0.0889	0.0888
220.89	0.0974	0.0972
230.15	0.1060	0.1058
238.52	0.1147	0.1144
246.19	0.1234	0.1233
253.08	0.1323	0.1322
259.30	0.1412	0.1411
265.18	0.1501	0.1504
270.11	0.1591	0.1588
275.05	0.1681	0.1680
279.57	0.1771	0.1770
283.74	0.1862	0.1860
287.88	0.1952	0.1956
291.27	0.2044	0.2040

TABLE 42

Vapor Pressure Data for Diethylamine in Diphenylmethane at 25°

P_A	f_A	f_A(calcd.)
0.90	0.0149	0.0140
1.78	0.0297	0.0276
2.96	0.0475	0.0459
4.00	0.0641	0.0621
6.43	0.0995	0.0998
7.45	0.1158	0.1156
8.55	0.1315	0.1327
9.45	0.1463	0.1466
10.55	0.1631	0.1637
11.78	0.1821	0.1828
12.69	0.1960	0.1969
13.70	0.2123	0.2126
14.68	0.2287	0.2278
15.92	0.2477	0.2470
16.87	0.2618	0.2618

TABLE 43

Vapor Pressure Data for Diethylamine in Diphenylmethane at 35°

P_A	f_A	f_A(calcd.)
1.23	0.0128	0.0131
2.64	0.0281	0.0280
3.94	0.0415	0.0418
5.44	0.0577	0.0578
6.83	0.0720	0.0725
8.30	0.0882	0.0881
9.82	0.1030	0.1043
11.09	0.1166	0.1178
12.83	0.1348	0.1362
13.72	0.1449	0.1457
15.26	0.1622	0.1620
16.27	0.1741	0.1728
17.63	0.1877	0.1872
18.75	0.2006	0.1991

TABLE 44

Vapor Pressure Data for Diethylamine in Diphenylmethane at 45°

P_A	f_A	f_A(calcd.)
1.50	0.0116	0.0112
3.82	0.0282	0.0285
5.72	0.0418	0.0427
7.77	0.0571	0.0580
9.61	0.0709	0.0717
11.41	0.0843	0.0851
13.58	0.1005	0.1013
14.81	0.1106	0.1105
17.18	0.1285	0.1282
18.37	0.1375	0.1371
21.24	0.1588	0.1585
24.56	0.1841	0.1833

TABLE 45

Vapor Pressure Data for Water in Diphenylmethane at 25°

P_W	f_W	f_W(calcd.)
1.81	0.0021	0.0020
3.65	0.0042	0.0041
5.55	0.0063	0.0063
7.40	0.0084	0.0085
9.20	0.0105	0.0106
10.94	0.0127	0.0127
12.70	0.0148	0.0148
14.49	0.0169	0.0171
16.11	0.0191	0.0191
17.80	0.0213	0.0212
1.95	0.0021	0.0022
3.82	0.0042	0.0043
5.69	0.0063	0.0065
7.49	0.0085	0.0086
9.24	0.0106	0.0107
11.00	0.0128	0.0128
12.74	0.0149	0.0149
3.74	0.0042	0.0042
7.31	0.0085	0.0084
9.14	0.0106	0.0105
10.97	0.0127	0.0127
12.73	0.0149	0.0149
14.47	0.0170	0.0170
16.39	0.0192	0.0194
1.86	0.0021	0.0021
5.51	0.0064	0.0063
7.43	0.0085	0.0085
9.18	0.0106	0.0106
10.92	0.0128	0.0127
12.71	0.0149	0.0149
14.38	0.0171	0.0169
16.17	0.0192	0.0191
17.88	0.0214	0.0213
19.64	0.0235	0.0236

TABLE 46

Vapor Pressure Data for Water in Diphenylmethane at 35°

P_W	f_W	f_W(calcd.)
4.63	0.0039	0.0040
9.01	0.0079	0.0079
13.47	0.0119	0.0119
17.85	0.0159	0.0165
22.12	0.0199	0.0199
26.33	0.0240	0.0240
30.52	0.0280	0.0281
34.66	0.0322	0.0333
36.73	0.0342	0.0344
40.59	0.0384	0.0383
2.30	0.0020	0.0020
6.90	0.0059	0.0060
11.26	0.0099	0.0099
15.65	0.0139	0.0139
19.95	0.0179	0.0179
24.20	0.0220	0.0220
28.42	0.0260	0.0260
32.64	0.0301	0.0302
36.70	0.0342	0.0343
40.57	0.0384	0.0383
3.36	0.0030	0.0029
7.99	0.0069	0.0070
12.27	0.0109	0.0108
16.58	0.0150	0.0148
20.97	0.0189	0.0188
25.23	0.0230	0.0230
29.39	0.0270	0.0270
33.48	0.0311	0.0310
36.56	0.0342	0.0342
40.44	0.0384	0.0382

TABLE 47

Vapor Pressure Data for Water in Diphenylmethane at 45°

P_W	f_W	f_W(calcd.)
5.57	0.0036	0.0037
16.33	0.0110	0.0112
21.38	0.0148	0.0148
26.60	0.0185	0.0185
31.68	0.0223	0.0222
36.85	0.0260	0.0260
46.88	0.0336	0.0336
56.75	0.0412	0.0413
61.62	0.0450	0.0451
66.38	0.0489	0.0490
10.86	0.0073	0.0074
18.81	0.0129	0.0129
23.99	0.0166	0.0166
29.15	0.0204	0.0204
34.26	0.0241	0.0241
39.30	0.0279	0.0279
44.39	0.0317	0.0317
49.36	0.0355	0.0355
54.25	0.0393	0.0393
59.16	0.0431	0.0432
63.94	0.0470	0.0470
5.70	0.0036	0.0038
8.40	0.0054	0.0057
13.47	0.0092	0.0092
20.03	0.0139	0.0138
25.20	0.0176	0.0175
30.38	0.0213	0.0212
35.52	0.0251	0.0250
40.55	0.0289	0.0288
45.55	0.0327	0.0326
51.72	0.0374	0.0373
60.26	0.0441	0.0440

TABLE 48

Vapor Pressure Data for Methanol in Diphenylmethane at 25°

P_M	f_M	f_M(calcd.)
7.57	0.0216	0.0215
14.83	0.0433	0.0431
21.69	0.0650	0.0649
28.13	0.0869	0.0869
34.14	0.1089	0.1090
39.72	0.1310	0.1312
44.91	0.1532	0.1537
49.66	0.1756	0.1760
54.02	0.1980	0.1983
58.02	0.2205	0.2207
61.68	0.2431	0.2431
65.04	0.2657	0.2657
68.13	0.2884	0.2885
70.94	0.3111	0.3114
73.51	0.3339	0.3342
75.84	0.3568	0.3570
77.99	0.3796	0.3799
79.91	0.4025	0.4022
7.60	0.0216	0.0216
21.67	0.0650	0.0648
34.09	0.1089	0.1088
44.89	0.1532	0.1535
53.88	0.1980	0.1975
61.57	0.2431	0.2424
68.01	0.2884	0.2876
73.40	0.3340	0.3333
77.94	0.3796	0.3794
81.77	0.4254	0.4255
85.02	0.4712	0.4713
87.88	0.5169	0.5177
90.37	0.5626	0.5635
92.48	0.6083	0.6071

TABLE 49

Vapor Pressure Data for Methanol in Diphenylmethane at 35°

P_M	f_M	f_M(calcd.)
10.19	0.0206	0.0207
19.96	0.0413	0.0413
29.31	0.0622	0.0621
38.19	0.0831	0.0830
46.63	0.1042	0.1041
54.59	0.1254	0.1254
62.09	0.1467	0.1468
69.16	0.1681	0.1684
75.61	0.1897	0.1895
81.86	0.2113	0.2114
87.57	0.2331	0.2329
93.04	0.2549	0.2549
98.10	0.2767	0.2768
102.83	0.2987	0.2988
107.18	0.3208	0.3206
111.31	0.3428	0.3428
115.13	0.3650	0.3650
118.68	0.3872	013870
122.02	0.4094	0.4094
125.11	0.4317	0.4316
130.76	0.4763	0.4764
135.73	0.5209	0.5212
140.10	0.5656	0.5656
144.05	0.6103	0.6106
147.53	0.6549	0.6545

TABLE 50

Vapor Pressure Data for Methanol in Diphenylmethane at 45°

P_M	f_M	f_M(calcd.)
13.17	0.0196	0.0199
25.83	0.0393	0.0397
38.03	0.0591	0.0594
49.76	0.0791	0.0791
61.02	0.0992	0.0990
71.87	0.1193	0.1192
82.25	0.1396	0.1395
92.16	0.1600	0.1599
101.52	0.1806	0.1803
110.51	0.2012	0.2010
119.08	0.2219	0.2219
127.23	0.2427	0.2428
134.92	0.2636	0.2637
142.21	0.2847	0.2847
149.22	0.3057	0.3060
155.76	0.3269	0.3271
161.96	0.3482	0.3483
167.84	0.3695	0.3696
173.41	0.3909	0.3910
178.67	0.4123	0.4125
188.21	0.4554	0.4549
196.88	0.4986	0.4982
204.68	0.5419	0.5418
211.66	0.5853	0.5852
218.01	0.6288	0.6289
223.76	0.6722	0.6725
228.96	0.7157	0.7156

TABLE 51

Vapor Pressure Data for Diethylamine in Benzyl Ether at 25°

P_A	f_A	f_A(calcd.)
1.53	0.0239	0.0228
3.11	0.0474	0.0469
4.67	0.0707	0.0706
6.18	0.0939	0.0939
7.69	0.1174	0.1176
9.13	0.1401	0.1403
10.58	0.1633	0.1634
12.03	0.1865	0.1866
13.45	0.2097	0.2098
14.87	0.2330	0.2330
16.27	0.2563	0.2562
17.67	0.2797	0.2797
19.06	0.3031	0.3030
20.42	0.3261	0.3261
21.82	0.3501	0.3501

TABLE 52

Vapor Pressure Data for Diethylamine in Benzyl Ether at 35°

P_A	f_A	f_A(calcd.)
2.39	0.0255	0.0249
4.84	0.0512	0.0505
7.26	0.0765	0.0760
9.70	0.o021	0.1018
12.11	0.1276	0.1275
14.78	0.1560	0.1562
17.20	0.1822	0.1823
19.47	0.2069	0.2071
21.74	0.2317	0.2319
23.97	0.2562	0.2565
26.20	0.2810	0.2812
28.42	0.3057	0.3059
30.57	0.3300	0.3300
32.67	0.3536	0.3535
34.74	0.3773	0.3770

TABLE 53

Vapor Pressure Data for Diethylamine in Benzyl Ether at 45°

P_A	f_A	f_A(calcd.)
3.87	0.0266	0.0261
7.77	0.0556	0.0553
13.43	0.0962	0.0961
16.17	0.1163	0.1161
19.62	0.1414	0.1414
22.79	0.1649	0.1649
26.07	0.1893	0.1894
29.48	0.2149	0.2150
33.16	0.2427	0.2428
36.23	0.2662	0.2663
39.17	0.2887	0.2888
42.15	0.3117	0.3118
45.56	0.3383	0.3383
48.35	0.3603	0.3602
51.30	0.3835	0.3833

TABLE 54

Vapor Pressure Data for Water in Benzyl Ether at 25°

P_W	f_W	f_W(calcd.)
1.25	0.00507	0.00489
2.55	0.01011	0.01004
3.82	0.01517	0.01517
5.07	0.02024	0.02024
6.31	0.02530	0.02536
8.71	0.03546	0.03554
11.03	0.04565	0.04569
13.28	0.05585	0.05585
15.46	0.06608	0.06605
17.56	0.07633	0.07624
1.25	0.00506	0.00491
3.19	0.01264	0.01260
4.44	0.01770	0.01769
5.69	0.02277	0.02279
6.91	0.02784	0.02789
9.28	0.03801	0.03801
11.59	0.04820	0.04820
13.83	0.05841	0.05839
16.00	0.06864	0.06863
17.06	0.07376	0.07378
18.09	0.07889	0.07888
19.11	0.08403	0.08401
20.12	0.08917	0.08918
21.10	0.09431	0.09434
22.07	0.09946	0.09948

TABLE 55

Vapor Pressure Data for Water in Benzyl Ether at 35°

P_W	f_W	f_W(calcd.)
2.69	0.00728	0.00722
4.49	0.01213	0.01210
6.27	0.01699	0.01699
8.03	0.02185	0.02190
11.47	0.03160	0.03163
14.81	0.04138	0.04137
18.07	0.05119	0.05113
21.24	0.06102	0.06092
24.33	0.07087	0.07076
27.34	0.08076	0.08064
30.26	0.09067	0.09053
33.10	0.10060	0.10051
35.85	0.11056	0.11047
38.53	0.12054	0.12049
41.11	0.13055	0.13044
1.78	0.00486	0.00477
3.60	0.00970	0.00969
5.39	0.01455	0.01459
7.17	0.01941	0.01949
10.62	0.02916	0.02922
14.00	0.03893	0.03897
17.28	0.04873	0.04874
20.48	0.05855	0.05852
23.62	0.06839	0.06844
26.49	0.07777	0.07781
29.46	0.08767	0.08780
32.34	0.09749	0.09782
35.10	0.10754	0.10772
37.77	0.11753	0.11761
40.37	0.12753	0.12756

TABLE 56

Vapor Pressure Data for Water in Benzyl Ether at 45°

P_W	f_W	f_W(calcd.)
4.89	0.00924	0.00921
9.72	0.01850	0.01849
14.46	0.02778	0.02780
19.12	0.03708	0.03715
23.63	0.04643	0.04643
28.07	0.05581	0.05578
32.42	0.06521	0.06518
36.68	0.07463	0.07462
40.84	0.08409	0.08408
44.91	0.09357	0.09355
7.31	0.01387	0.01383
12.09	0.02314	0.02312
16.78	0.03243	0.03243
21.38	0.04176	0.04177
25.87	0.05111	0.05113
30.27	0.06050	0.06051
34.56	0.06991	0.06990
38.79	0.07935	0.07937
42.90	0.08882	0.08883
46.92	0.09832	0.09834
50.85	0.10784	0.10786
54.68	0.11739	0.11737
58.44	0.12697	0.12697
62.11	0.13657	0.13657

TABLE 57

Vapor Pressure Data for Methanol in Benzyl Ether at 25°

P_M	f_M	f_M(calcd.)
7.50	0.0458	0.0465
14.38	0.0917	0.0921
20.69	0.1376	0.1376
26.45	0.1835	0.1832
31.73	0.2295	0.2290
36.57	0.2754	0.2750
41.01	0.3212	0.3211
45.08	0.3671	0.3670
48.83	0.4128	0.4130
52.28	0.4585	0.4589
55.46	0.5041	0.5044
58.39	0.5496	0.5499
61.10	0.5951	0.5950
63.65	0.6404	0.6406
65.99	0.6856	0.6857
68.16	0.7307	0.7305
70.20	0.7757	0.7755
72.10	0.8205	0.8205
73.87	0.8652	0.8651
75.53	0.9098	0.9098
77.08	0.9543	0.9539
78.56	0.9986	0.9986
79.95	1.0428	1.0431
81.25	1.0869	1.0871

TABLE 58

Vapor Pressure Data for Methanol in Benzyl Ether at 35°

P_M	f_M	f_M(calcd.)
10.82	0.0444	0.0451
20.88	0.0889	0.0895
30.22	0.1335	0.1337
38.88	0.1781	0.1779
47.68	0.2273	0.2269
55.04	0.2720	0.2715
61.91	0.3168	0.3164
68.28	0.3615	0.3614
74.18	0.4062	0.4063
79.65	0.4509	0.4509
84.78	0.4956	0.4959
89.55	0.5402	0.5406
93.99	0.5847	0.5851
98.16	0.6291	0.6297
101.98	0.6735	0.6734
112.22	0.8061	0.8058
118.02	0.8940	0.8931
123.25	0.9814	0.9813
127.90	1.0684	1.0690

TABLE 59

Vapor Pressure Data for Methanol in Benzyl Ether at 45°

P_M	f_M	f_M(calcd.)
15.03	0.0428	0.0435
29.17	0.0857	0.0863
42.47	0.1287	0.1289
54.97	0.1719	0.1717
66.67	0.2151	0.2147
77.66	0.2584	0.2579
88.01	0.3018	0.3015
97.66	0.3452	0.3451
106.67	0.3887	0.3885
115.23	0.4321	0.4325
130.62	0.5191	0.5194
144.34	0.6059	0.6069
156.32	0.6926	0.6926
167.03	0.7791	0.7784
176.67	0.8652	0.8646
181.17	0.9082	0.9083
185.33	0.9511	0.9509
189.36	0.9938	0.9943
196.68	1.0791	1.0793
200.05	1.1216	1.1215

TABLE 60

Vapor Pressure Data for the System Water-Diethylamine in n-Hexadecane at 25°

P_T	R_{VS}	f_A*	f_W*	f_W*(calcd.)
7.61	2.922	0.06356	0.00083	0.00075
10.08	2.922	0.06356	0.00166	0.00161
12.57	2.922	0.06356	0.00250	0.00248
15.01	2.922	0.06356	0.00333	0.00334
17.43	2.921	0.06355	0.00416	0.00418
19.79	2.921	0.06355	0.00499	0.00501
22.13	2.921	0.06355	0.00583	0.00582
24.41	2.921	0.06355	0.00666	0.00662
6.58	2.927	0.04946	0.00083	0.00076
9.22	2.927	0.04946	0.00167	0.00165
11.83	2.927	0.04946	0.00250	0.00252
14.41	2.927	0.04946	0.00333	0.00338
17.00	2.927	0.04946	0.00417	0.00424
19.58	2.927	0.04946	0.00500	0.00510
22.08	2.927	0.04945	0.00583	0.00593
13.97	2.912	0.08763	0.00249	0.00246
16.22	2.912	0.08762	0.00332	0.00331
18.45	2.912	0.08762	0.00415	0.00415
20.62	2.912	0.08762	0.00498	0.00496
22.82	2.911	0.08762	0.00581	0.00579
24.91	2.911	0.08762	0.00664	0.00658

TABLE 61

Vapor Pressure Data for the System Water-Diethylamine in n-Hexadecane at 35°

P_T	R_{VS}	f_A*	f_W*	f_W*(calcd.)
13.67	2.880	0.07814	0.00137	0.00139
18.14	2.880	0.07814	0.00274	0.00276
22.67	2.880	0.07814	0.00412	0.00414
27.17	2.880	0.07814	0.00549	0.00552
31.63	2.880	0.07814	0.00686	0.00688
36.05	2.880	0.07814	0.00823	0.00823
40.43	2.880	0.07814	0.00961	0.00956
44.71	2.880	0.07814	0.01098	0.01086
9.15	2.891	0.05290	0.00083	0.00084
13.98	2.891	0.05290	0.00220	0.00223
18.86	2.891	0.05290	0.00358	0.00363
23.74	2.891	0.05290	0.00495	0.00504
28.48	2.891	0.05289	0.00633	0.00640
33.21	2.891	0.05289	0.00771	0.00776
37.96	2.891	0.05289	0.00908	0.00912
42.61	2.891	0.05289	0.01046	0.01045

TABLE 62

Vapor Pressure Data for the System Water-Diethylamine in n-Hexadecane at 45°

P_T	R_{VS}	f_A*	f_W*	f_W*(calcd.)
20.18	2.840	0.09153	0.00136	0.00134
25.20	2.840	0.09153	0.00272	0.00271
30.20	2.840	0.09153	0.00407	0.00408
35.26	2.840	0.09152	0.00543	0.00547
40.28	2.840	0.09152	0.00679	0.00684
45.18	2.840	0.09152	0.00815	0.00817
50.09	2.840	0.09152	0.00951	0.00951
55.02	2.840	0.09152	0.01086	0.1085
59.90	2.840	0.09152	0.01222	0.01219
64.78	2.840	0.09152	0.01358	0.01351
14.40	2.855	0.05432	0.00136	0.00135
19.82	2.855	0.05432	0.00273	0.00274
25.26	2.855	0.05432	0.00409	0.00413
30.61	2.855	0.05432	0.00545	0.00551
35.90	2.855	0.05432	0.00682	0.00686
41.19	2.855	0.05432	0.00818	0.00822
46.50	2.855	0.05431	0.00954	0.00957
51.79	2.855	0.05431	0.01091	0.01093
57.02	2.855	0.05431	0.01227	0.01227
62.24	2.855	0.05431	0.01363	0.01360

TABLE 63

Vapor Pressure Data for the System Methanol-Diethylamine in n-Hexadecane at 25°

P_T	R_{VS}	f_A*	f_M*	f_M*(calcd.)
11.56	2.922	0.05985	0.0061	0.0056
18.02	2.922	0.05984	0.0122	0.0118
24.19	2.921	0.05983	0.0183	0.0181
30.05	2.920	0.05982	0.0244	0.0245
35.58	2.919	0.05980	0.0305	0.0308
40.80	2.918	0.05979	0.0366	0.0371
45.66	2.917	0.05978	0.0427	0.0431
50.23	2.917	0.05977	0.0488	0.0490
54.49	2.916	0.05975	0.0549	0.0546
58.46	2.915	0.05974	0.0610	0.0601
18.55	2.909	0.08900	0.0122	0.0115
23.85	2.909	0.08898	0.0183	0.0178
28.88	2.908	0.08896	0.0244	0.0242
33.64	2.907	0.08894	0.0304	0.0305
38.16	2.906	0.08892	0.0365	0.0369
42.42	2.905	0.08890	0.0426	0.0431
46.42	2.904	0.08888	0.0487	0.0491
50.18	2.903	0.08886	0.0547	0.0549
53.71	2.903	0.08884	0.0608	0.0605

TABLE 64

Vapor Pressure Data for the System Methanol-Diethylamine in n-Hexadecane at 35°

P_T	R_{VS}	f_A*	f_M*	f_M*(calcd.)
25.98	2.872	0.09562	0.0121	0.0119
33.05	2.871	0.09560	0.0181	0.0180
39.90	2.870	0.09558	0.0241	0.0243
46.50	2.869	0.09556	0.0301	0.0305
52.86	2.868	0.09554	0.0362	0.0367
58.95	2.868	0.09552	0.0422	0.0428
64.81	2.867	0.09550	0.0482	0.0489
70.37	2.866	0.09548	0.0542	0.0548
75.71	2.865	0.09546	0.0602	0.0606
85.72	2.863	0.09541	0.0722	0.0718
28.63	2.853	0.14069	0.0120	0.0115
34.55	2.852	0.14066	0.0180	0.0175
40.42	2.851	0.14063	0.0240	0.0236
46.02	2.851	0.14060	0.0300	0.0298
51.43	2.850	0.14057	0.0360	0.0360
56.62	2.849	0.14054	0.0420	0.0421
61.60	2.848	0.14051	0.0480	0.0481
66.33	2.847	0.14048	0.0540	0.0540
70.93	2.846	0.14045	0.0599	0.0598
79.54	2.845	0.14039	0.0719	0.0711

TABLE 65

Vapor Pressure Data for the System Methanol-Diethylamine in n-Hexadecane at 45°

P_T	R_{VS}	f_A*	f_M*	f_M*(calcd.)
32.31	2.846	0.07379	0.0120	0.0118
42.11	2.845	0.07378	0.0180	0.0178
51.78	2.844	0.07376	0.0240	0.0239
61.32	2.844	0.07375	0.0299	0.0301
70.49	2.843	0.07373	0.0359	0.0362
79.49	2.842	0.07372	0.0419	0.0423
88.25	2.841	0.07370	0.0479	0.0483
96.69	2.841	0.07369	0.0539	0.0543
104.88	2.840	0.07367	0.0598	0.0602
120.45	2.838	0.07364	0.0718	0.0717
40.66	2.813	0.15234	0.0119	0.0114
48.42	2.813	0.15231	0.0178	0.0174
56.02	2.812	0.15228	0.0238	0.0235
63.49	2.811	0.15225	0.0297	0.0296
70.76	2.811	0.15222	0.0356	0.0357
77.78	2.810	0.15219	0.0416	0.0417
84.65	2.809	0.15216	0.0475	0.0477
97.77	2.807	0.15209	0.0593	0.0596
110.09	2.805	0.15203	0.0712	0.0711
121.71	2.804	0.15197	0.0830	0.0823

TABLE 66

Vapor Pressure Data for the System Water-Diethylamine in Diphenylmethane at 25°

P_T	R_{VS}	f_A^*	f_W^*	f_W^*(calcd.)
12.50	6.751	0.0946	0.0162	0.0160
14.68	6.753	0.0946	0.0216	0.0213
17.04	6.755	0.0946	0.0271	0.0270
19.35	6.757	0.0946	0.0325	0.0325
21.58	6.759	0.0946	0.0379	0.0378
7.94	6.764	0.0694	0.0082	0.0078
9.76	6.766	0.0694	0.0122	0.0118
11.78	6.768	0.0694	0.0163	0.0162
13.70	6.770	0.0694	0.0204	0.0204
15.64	6.772	0.0694	0.0244	0.0246
17.52	6.773	0.0694	0.0285	0.0287
19.43	6.775	0.0694	0.0326	0.0329
7.06	6.968	0.0509	0.0084	0.0078
9.31	6.970	0.0509	0.0125	0.0123
11.45	6.972	0.0509	0.0167	0.0166
13.61	6.975	0.0509	0.0209	0.0210
15.79	6.977	0.0509	0.0251	0.0254
17.84	6.979	0.0509	0.0293	0.0295
19.84	6.981	0.0509	0.0334	0.0336
21.83	6.983	0.0509	0.0376	0.0377
8.35	6.984	0.0798	0.0083	0.0077
10.29	6.950	0.0798	0.0125	0.0122
12.22	6.952	0.0798	0.0167	0.0166
14.14	6.954	0.0798	0.0208	0.0210
16.02	6.956	0.0798	0.0250	0.0253
17.86	6.958	0.0798	0.0292	0.0294
19.70	6.959	0.0798	0.0333	0.0336
22.16	6.962	0.0798	0.0389	0.0372
10.19	6.928	0.1091	0.0097	0.0088
11.91	6.930	0.1091	0.0138	0.0132
13.62	6.932	0.1091	0.0180	0.0176
15.89	6.934	0.1091	0.0235	0.0235
18.18	6.936	0.1091	0.0291	0.0293
19.74	6.938	0.1091	0.0332	0.0332
21.89	6.940	0.1091	0.0388	0.0387

TABLE 67

Vapor Pressure Data for the System Water-Diethylamine in Diphenylmethane at 35°

P_T	R_{VS}	f^*_A	f^*_W	f^*_W(calcd.)
11.88	6.907	0.0584	0.0111	0.0105
15.48	6.910	0.0584	0.0166	0.0162
19.04	6.914	0.0584	0.0221	0.0219
22.50	6.918	0.0584	0.0276	0.0275
26.02	6.921	0.0584	0.0332	0.0331
29.42	6.925	0.0584	0.0387	0.0386
36.13	6.931	0.0584	0.0497	0.0495
39.59	6.935	0.0584	0.0553	0.0552
16.91	6.893	0.0849	0.0165	0.0162
20.13	6.896	0.0849	0.0220	0.0219
26.61	6.902	0.0849	0.0331	0.0332
29.74	6.906	0.0849	0.0386	0.0387
32.91	6.909	0.0849	0.0441	0.0443
36.03	6.912	0.0849	0.0496	0.0498
39.05	6.915	0.0849	0.0551	0.0551
42.05	6.918	0.0849	0.0606	0.0604
15.02	6.876	0.1055	0.0110	0.0103
18.07	6.879	0.1055	0.0165	0.0161
21.18	6.882	0.1055	0.0221	0.0220
24.21	6.884	0.1055	0.0275	0.0276
15.75	6.910	0.0601	0.0166	0.0165
19.18	6.913	0.0601	0.0221	0.0220
22.75	6.917	0.0601	0.0276	0.0278
29.54	6.924	0.0601	0.0387	0.0388
33.09	6.927	0.0601	0.0442	0.0446
36.42	6.931	0.0601	0.0497	0.0501
39.62	6.934	0.0601	0.0552	0.0553

TABLE 68

Vapor Pressure Data for the System Water-Diethylamine in Diphenylmethane at 45°

P_T	R_{VS}	f^*_A	f^*_W	f^*_W(calcd.)
11.57	6.655	0.0588	0.0053	0.0050
15.76	6.659	0.0588	0.0107	0.0102
20.16	6.663	0.0588	0.0160	0.0156
24.57	6.667	0.0588	0.0214	0.0211
29.05	6.671	0.0588	0.0267	0.0267
33.31	6.676	0.0588	0.0321	0.0321
37.60	6.680	0.0588	0.0374	0.0374
41.95	6.684	0.0588	0.0428	0.0429
46.21	6.688	0.0588	0.0481	0.0481
50.41	6.692	0.0588	0.0535	0.0537
10.64	6.846	0.0517	0.0055	0.0049
15.13	6.851	0.0517	0.0110	0.0104
19.68	6.855	0.0517	0.0165	0.0159
24.25	6.860	0.0517	0.0219	0.0215
28.83	6.865	0.0517	0.0274	0.0272
33.36	6.869	0.0517	0.0329	0.0328
37.87	6.874	0.0517	0.0384	0.0383
42.26	6.878	0.0517	0.0439	0.0439
46.62	6.882	0.0517	0.0494	0.0494
51.01	6.887	0.0517	0.0548	0.0549
55.36	6.891	0.0517	0.0603	0.0604
59.63	6.895	0.0517	0.0658	0.0658
63.81	6.900	0.0517	0.0713	0.0712
67.98	6.904	0.0517	0.0768	0.0765
17.38	6.823	0.0928	0.0082	0.0076
21.37	6.827	0.0928	0.0137	0.0131
25.44	6.831	0.0928	0.0191	0.0187
29.53	6.835	0.0928	0.0246	0.0243
33.64	6.839	0.0928	0.0300	0.0299
37.79	6.843	0.0928	0.0355	0.0357
41.77	6.847	0.0928	0.0410	0.0411
45.88	6.851	0.0928	0.0464	0.0468
49.85	6.855	0.0928	0.0519	0.0523
53.80	6.859	0.0928	0.0573	0.0578

TABLE 69

Vapor Pressure Data for the System Methanol-Diethylamine in Diphenylmethane at 25°

P_T	R_{VS}	f_A*	f_M*	f_M*(calcd.)
6.88	6.790	0.06199	0.0120	0.0126
9.66	6.790	0.06196	0.0239	0.0246
12.44	6.790	0.06193	0.0359	0.0368
15.15	6.790	0.06191	0.0478	0.0490
17.83	6.789	0.06188	0.0597	0.0619
20.43	6.789	0.06185	0.0716	0.0733
23.04	6.788	0.06183	0.0835	0.0856
25.43	6.788	0.06180	0.0954	0.0971
27.75	6.687	0.06177	0.1073	0.1084
30.13	6.787	0.06175	0.1191	0.1203
10.99	6.775	0.09868	0.0238	0.0235
13.20	6.774	0.09864	0.0357	0.0348
15.53	6.772	0.09860	0.0476	0.0469
17.82	6.771	0.09855	0.0595	0.0589
20.01	6.770	0.09851	0.0713	0.0706
22.24	6.769	0.09847	0.0832	0.0826
24.41	6.767	0.09842	0.0950	0.0945
26.52	6.766	0.09838	0.1069	0.1061
28.60	6.765	0.09834	0.1187	0.1178
30.57	6.764	0.09830	0.1305	0.1289

TABLE 70

Vapor Pressure Data for the System Methanol-Diethylamine in Diphenylmethane at 35°

P_T	R_{VS}	f_A*	f_M*	f_M*(calcd.)
13.43	6.741	0.06086	0.0237	0.0237
17.24	6.742	0.06083	0.0356	0.0354
21.05	6.743	0.06080	0.0474	0.0473
24.84	6.744	0.06078	0.0592	0.0593
28.52	6.744	0.06075	0.0711	0.0711
32.08	6.745	0.06072	0.0829	0.0828
35.69	6.746	0.06070	0.0947	0.0947
39.11	6.746	0.06067	0.1064	0.1063
42.54	6.746	0.06064	0.1182	0.1180
49.19	6.746	0.06059	0.1417	0.1414
15.57	6.720	0.09353	0.0236	0.0236
18.89	6.720	0.09349	0.0355	0.0351
22.29	6.721	0.09345	0.0473	0.0469
25.76	6.721	0.09341	0.0591	0.0592
29.09	6.721	0.09337	0.0709	0.0711
32.33	6.722	0.09333	0.0827	0.0828
35.60	6.722	0.09329	0.0945	0.0948
38.72	6.722	0.09324	0.1062	0.1064
42.44	6.722	0.09320	0.1203	0.1204
48.89	6.722	0.09311	0.1437	0.1437

TABLE 71

Vapor Pressure Data for the System Methanol-Diethylamine in Diphenylmethane at 45°

P_T	R_{VS}	f_A*	f_M*	f_M*(calcd.)
18.37	6.694	0.05947	0.0235	0.0237
23.58	6.696	0.05944	0.0353	0.0354
28.75	6.698	0.05941	0.0471	0.0470
33.86	6.700	0.05939	0.0588	0.0587
38.98	6.702	0.05936	0.0705	0.0706
43.98	6.704	0.05930	0.0823	0.0823
48.88	6.706	0.05931	0.0940	0.0939
53.84	6.708	0.05928	0.1057	0.1058
58.71	6.709	0.05926	0.1174	0.1176
67.99	6.712	0.05920	0.1408	0.1407
20.83	6.678	0.08554	0.0235	0.0234
25.62	6.680	0.08550	0.0352	0.0349
30.45	6.681	0.08546	0.0469	0.0466
35.48	6.683	0.08542	0.0587	0.0589
40.22	6.685	0.08539	0.0704	0.0706
44.87	6.686	0.08535	0.0821	0.0822
49.49	6.688	0.08531	0.0938	0.0939
54.05	6.689	0.08527	0.1055	0.1055
58.77	6.693	0.08524	0.1172	0.1177
67.30	6.693	0.08516	0.1405	0.1401

TABLE 72

Vapor Pressure Data for the System Water-Diethylamine in Benzyl Ether at 25°

P_T	R_{VS}	f_A*	f_W*	f_W*(calcd.)
9.46	6.768	0.12034	0.0110	0.0105
12.13	6.766	0.12030	0.0275	0.0273
14.70	6.764	0.12027	0.0439	0.0441
17.15	6.762	0.12023	0.0604	0.0607
19.51	6.760	0.12020	0.0768	0.0773
21.77	6.757	0.12017	0.0933	0.0937
23.93	6.755	0.12013	0.1097	0.1099
24.62	6.754	0.12012	0.1152	0.1152
25.31	6.754	0.12011	0.1206	0.1206
25.99	6.753	0.12010	0.1261	0.1258
7.74	6.805	0.07456	0.0166	0.0158
10.71	6.803	0.07454	0.0331	0.0325
13.57	6.801	0.07452	0.0497	0.0493
16.32	6.799	0.07450	0.0662	0.0661
18.93	6.796	0.07448	0.0827	0.0827
21.43	6.794	0.07446	0.0992	0.0992
23.80	6.792	0.07444	0.1157	0.1154

TABLE 73

Vapor Pressure Data for the System Water-Diethylamine in Benzyl Ether at 35°

P_T	R_{VS}	f_A*	f_W*	f_W*(calcd.)
16.82	6.689	0.13952	0.0163	0.0164
20.64	6.687	0.13948	0.0326	0.0324
24.34	6.685	0.13945	0.0489	0.0487
27.91	6.683	0.13941	0.0652	0.0651
31.36	6.681	0.13937	0.0815	0.0816
34.67	6.679	0.13933	0.0978	0.0979
37.87	6.677	0.13930	0.1140	0.1143
40.94	6.675	0.13926	0.1303	0.1305
43.92	6.672	0.13922	0.1465	0.1466
46.75	6.670	0.13918	0.1627	0.1625
12.81	6.729	0.09075	0.0164	0.0164
17.02	6.727	0.09072	0.0328	0.0326
21.10	6.725	0.09070	0.0492	0.0490
25.05	6.723	0.09067	0.0655	0.0654
28.88	6.721	0.09065	0.0819	0.0821
32.46	6.719	0.09062	0.0983	0.0982
35.98	6.717	0.09060	0.1146	0.1146
39.38	6.715	0.09057	0.1309	0.1310
42.61	6.713	0.09055	0.1473	0.1471

TABLE 74

Vapor Pressure Data for the System Water-Diethylamine in Benzyl Ether at 45°

P_T	R_{VS}	f_A*	f_W*	f_W*(calcd.)
22.05	6.641	0.12279	0.0162	0.0158
27.76	6.639	0.12276	0.0325	0.0322
33.32	6.637	0.12273	0.0487	0.0486
38.71	6.635	0.12269	0.0649	0.0650
43.95	6.633	0.12266	0.0811	0.0814
48.94	6.631	0.12263	0.0973	0.0973
53.92	6.629	0.12260	0.1134	0.1137
58.69	6.627	0.12256	0.1296	0.1297
63.32	6.625	0.12253	0.1457	0.1457
67.78	6.623	0.12250	0.1619	0.1615
18.74	6.652	0.11112	0.0108	0.0106
24.58	6.650	0.11109	0.0271	0.0269
30.29	6.648	0.11106	0.0433	0.0433
35.69	6.646	0.11103	0.0595	0.0592
41.11	6.644	0.11100	0.0757	0.0756
46.35	6.642	0.11098	0.0919	0.0920
51.43	6.640	0.11095	0.1081	0.1082
56.39	6.638	0.11092	0.1242	0.1244
61.15	6.636	0.11089	0.1404	0.1405
65.72	6.634	0.11086	0.1566	0.1563

TABLE 75

Vapor Pressure Data for the System Methanol-Diethylamine in Benzyl Ether at 25°

P_T	R_{VS}	f_A*	f_M*	f_M*(calcd.)
9.05	6.791	0.08094	0.0364	0.0326
13.24	6.780	0.08082	0.0727	0.0698
17.26	6.769	0.08071	0.1089	0.1067
21.10	6.758	0.08059	0.1450	0.1434
24.77	6.747	0.08048	0.1811	0.1798
28.27	6.736	0.08036	0.2170	0.2160
31.60	6.725	0.08025	0.2528	0.2517
34.77	6.714	0.08014	0.2884	0.2872
37.79	6.703	0.08002	0.3240	0.3223
40.67	6.692	0.07991	0.3595	0.3572
11.56	6.756	0.12342	0.0363	0.0353
15.24	6.745	0.12324	0.0724	0.0725
18.75	6.734	0.12307	0.1085	0.1092
22.15	6.723	0.12289	0.1444	0.1457
25.43	6.712	0.12272	0.1802	0.1821
28.60	6.701	0.12254	0.2160	0.2181
31.63	6.690	0.12237	0.2516	0.2536
34.52	6.679	0.12220	0.2872	0.2886
37.31	6.668	0.12202	0.3226	0.3232
40.00	6.657	0.12185	0.3580	0.3578

TABLE 76

Vapor Pressure Data for the System Methanol-Diethylamine in Benzyl Ether at 35°

P_T	R_{VS}	f_A*	f_M*	f_M*(calcd.)
17.28	6.688	0.12984	0.0359	0.0341
22.89	6.678	0.12966	0.0718	0.0708
28.34	6.667	0.12948	0.1075	0.1073
33.57	6.656	0.12930	0.1431	0.1435
38.64	6.645	0.12911	0.1787	0.1795
43.51	6.635	0.12893	0.2141	0.2150
48.21	6.624	0.12875	0.2495	0.2503
52.71	6.613	0.12857	0.2847	0.2852
57.03	6.603	0.12839	0.3198	0.3196
61.21	6.592	0.12821	0.3549	0.3538
13.96	6.707	0.11186	0.0240	0.0222
19.84	6.696	0.11170	0.0600	0.0587
25.58	6.685	0.11155	0.0958	0.0953
31.13	6.675	0.11139	0.1315	0.1317
36.45	6.664	0.11123	0.1672	0.1677
41.56	6.653	0.11108	0.2027	0.2033
46.47	6.642	0.11092	0.2381	0.2387
51.18	6.632	0.11077	0.2734	0.2737
55.70	6.621	0.11061	0.3087	0.3084
60.01	6.610	0.11045	0.3439	0.3426

TABLE 77

Vapor Pressure Data for the System Methanol-Diethylamine in Benzyl Ether at 45°

P_T	R_{VS}	f_A*	f_M*	f_M*(calcd.)
24.40	6.616	0.14691	0.0237	0.0213
29.76	6.609	0.14677	0.0474	0.0454
35.10	6.602	0.14664	0.0711	0.0697
39.83	6.596	0.14652	0.0923	0.0916
45.11	6.589	0.14638	0.1159	0.1163
50.55	6.582	0.14624	0.1418	0.1421
55.48	6.575	0.14610	0.1652	0.1659
60.31	6.568	0.14600	0.1887	0.1895
65.00	6.561	0.14583	0.2120	0.2129
69.60	6.554	0.14570	0.2354	0.2362
74.08	6.547	0.14557	0.2587	0.2593
78.47	6.540	0.14543	0.2819	0.2822
82.74	6.533	0.14530	0.3052	0.3050
86.89	6.526	0.14516	0.3283	0.3275
91.01	6.519	0.14503	0.3515	0.3503

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