MUTUAL SOLUBILITIES OF ALKYLBENZENE - WATER MIXTURES

By

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PREFACE

A liquid-liquid equilibrium apparatus has been designed, constructed and operated to acquire the liquid-liquid mutual solubility of water and organic component mixtures. A simple, reliable and efficient gas chromatographic method has been developed and successfully applied to analyze quantitatively the very low water solubility in the organic solvents and vice versa. Systematic measurements have been conducted on the mutual solubility of water and alkylbenzene mixtures with special attention to the molecular structure effects of the organic components on their water solubilities. The newly measured data, together with reliable literature data, are used to evaluate the capability of the UNIFAC (UNIQUAC Functional-group Activity Coefficients) model to represent the mutual solubilities of water and alkylbenzene mixtures.

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CHAPTER I

INTRODUCTION

Waste water and its treatment have become important issues these days. To prevent the water supply from being contaminated, increasingly stringent emission standards have been enforced here in the United States. Subject to these standards and many new regulations coming into play, many refineries and petrochemical plants are beginning to modify or totally replace their waste water treatment systems (1). Benzene and its various derivatives have been known exist in many process streams and are extremely toxic to the human health and damaging to the living environment. To remove these toxic compounds from the process waste water before it is discharged into environment or to reduce its concentration level before it is biologically treated downstream is highly desirable. There are many engineering practices which might be used to remove or to reduce organic chemicals from waste water stream, however, many of them appears energy intensive or economically costive. There is one approach which appears attractive. This is so called solvent extraction. Solvent extraction has gradually been recognized as one of best developed technology for refinery waste water treatment. To successfully design and operate a solvent extraction unit to treat refinery waste water stream, accurate and reliable liquid-liquid equilibrium data of the water and organic mixture is needed, which is not plentiful at current time.

The objective of this research are to design and operate a liquid-liquid equilibrium unit to acquire liquid-liquid equilibrium data of water and organic compound mixtures; to develop simple, reliable and affordable analytical technique to quantitatively analyze the very dilute water solubility in the organic solvents and vice versa; to conduct a series systematic measurements on the mutual solubility of water and alkylbenzene mixtures with the special attention on the molecular structure effect of the organic component on its water solubility; to evaluate the capability of the UNIFAC (UNIQUAC Functional-group Activity Coefficients) model to represent the water and alkylbenzene mixtures.

Chapter II describes the design and operation of a flow-through liquid-liquid equilibrium unit and an overall procedure to measure the mutual solubility of hydrocarbon-water systems, exemplified with the measurement results of benzene-water mixture in the temperature region 303-373K. Chapter III details an efficient and reliable gas chromatographic method for measuring mutual solubility of alkylbenzene-water mixture at very low analyte concentration, exemplified with the measurement of toluene-water mutual solubility in the same temperature region as that for benzene-water mixture. Chapter IV presents the mutual solubility data of alkylbenzene-water systems in the temperature region of 303 to 373K including ethylbenzene, p-xylene, 1,3,5-trimethylbenzene and n-butylbenzene. Chapter V reports the evaluation results on the capability of the original UNIFAC model and several its variants including the very recent one in representing the liquid-liquid mutual solubility data of alkylbenzene and water mixture. Chapter VI summarizes the results obtained in this research. Since this research actually initiates a systematic research program in the framework of the waste water treatment, recommendations are given in the Chapter VI with respect to the future research activities in this area.

CHAPTER II

AN APPARATUS AND PROCEDURE FOR MEASURING MUTUAL SOLUBILITIES OF HYDROCARBON-WATER SYSTEMS: BENZENE-WATER IN THE REGION 303-373 K

ABSTRACT

A continuous flow type liquid-liquid equilibrium apparatus has been designed, constructed and operated to measure the mutual solubility of hydrocarbon-water systems. New data for the benzene-water system has been generated in the temperature range of 303 to 373 K along the three-phase curve. The data compare favorably with the literature data in the 303 to 333 K temperature range. The solubility of benzene in water matches the lower range of high temperature data (373-473 K). The average percentage deviation in both liquid phase compositions measurements is less than 6 percent for all data points. The benzene-water mutual solubility data are correlated and used to estimate heats of solution of benzene in water and water in benzene. The results are in good agreement with literature values based on calorimetric measurements.

INTRODUCTION

Increasingly stringent emission standards are forcing many refineries and petrochemical plants to modify or totally replace waste water treatment systems (*1*). While solvent extraction has been recognized as one of the best developed available technologies (BDAT) for refinery waste water treatment, reliable liquid-liquid equilibrium data needed for the design of extraction processes are not plentiful. The very low liquid-liquid mutual solubilities of water and hydrocarbons poses significant difficulties in performing accurate and reliable measurements (*2*). Large variations, and even conflicts, are common in the data reported in the temperature range of 303 to 373 K. To resolve conflicts in the liquid-liquid mutual solubility data for hydrocarbon-water mixtures in this temperature range and to obtain reliable new data, a liquid-liquid equilibrium apparatus was constructed and operated. The flow-through unit facilitates sampling equilibrium phases and subsequent sample treatment and analysis.

The measurements were begun with the benzene-water binary system because it has been extensively studied (*3*) and could serve as a basis for testing the performance of both the equilibrium unit and overall experimental procedures. In addition, this system is of immediate practical concern with the promulgation of the *National Emission Standards for Hazardous Air Pollutants; Benzene* (*4*).

EXPERIMENTAL

Two key points had to be addressed to successfully design and operate a continuous-flow type equilibrium unit to obtain equilibrium mutual solubility for water-hydrocarbon systems. First, mass transfer between the two liquid phases must be accomplished well before the two phases are separated at equilibrium. Second, the two phases must be completely separated after equilibrium is reached. The physical properties of the aqueous systems considered are different from most of the previous vapor-liquid or liquid-liquid equilibrium systems which have been experimentally studied using flow-type equilibrium cells (*5-7*). The liquid water and liquid hydrocarbon mixtures have very high interfacial tensions in the temperature range covered here. This results in a high mass transfer resistance between the two phases. Meanwhile, the tendency to form emulsions prohibits the vigorous mixing of the two phases. The design of the experimental apparatus must provide mixing at a level to promote mass transfer while avoiding the formation of emulsions which hinders subsequent phase separation.

In vapor-liquid equilibrium measurements using a flow through type equilibrium unit, a large range of flow rates may have a relatively small effect on the phase separation. However, the situation is entirely different when liquid-liquid equilibrium measurements are being made. At the low concentrations of solute addressed in this work, the entrainment of a small droplet of one phase into another phase due to variation in flow rates can lead to very large errors. Therefore, relatively low flow rates are preferred to assure complete separation of the two liquid phases inside equilibrium cell and to minimize possible liquid entrainment.

A schematic diagram of the experimental apparatus is shown in Figure 1 and is similar to systems described by Thies and Paulatis (*5*) and Wang and Chao (*6*). A flow system is used to mix and, subsequently, to separate and sample the two liquid phases. A LDC Analytical Type NSI-33R minipump with a flow rate range of 46-460 ml/h is used to feed water and hydrocarbon continuously to the equilibrium unit. Approximately 16 feet of 1/4-in. stainless steel tubing is used to promote the mixing of the hydrocarbon and water phases. The first 4 feet of tubing is fitted a static mixer made from a band of notched and twisted stainless steel. The remaining 12 feet of tubing is packed with approximately 1.5 mm diameter glass beads. A heating tape is wrapped around the last 4 feet of tubing to provide optional preheating of the feed.

The liquid mixture from the mixing line enters a 30 ft long, 1/8-in diameter stainless steel tube. This coiled tube is immersed in a constant temperature bath and used to bring the feed mixture to equilibrium before it enters the equilibrium cell. The 12 feet of 1/8-in ID tubing used by Wang and Chao (*6*) was found to be too short for the systems studied. The 100 feet of 1/16-in ID tubing used as a preheater by Christensen (*7*) is not adequate because the interfacial area for mass transfer is inadequate for the mixture to reach equilibrium.

The two equilibrated liquids are separated inside a modified Jerguson JT-40 sight gage. The total internal volume of the cell is about 60 ml. The sight gage was modified by tapping a port for the feed and replacing the inside fiber gaskets with two layers of Union Carbide Grafoil® graphite tape. Spring washers were installed to accommodate thermal expansion. The less-dense hydrocarbon phase exits from the top of the cell and the more-dense water phase exits from the bottom.

The equilibrium cell and preheat coil are immersed in a Neslab TEV 70 constant temperature bath filled with Dow-Corning Silicon 200 heat transfer fluid. Bath temperature is measured with an iron-constantan thermocouple calibrated against a laboratory platinum resitance thermometer that is NBS traceable. The uniformity of the bath temperature is better than 0.1K. Bath temperature is controlled within ±0.2 K of the set point. The temperature inside the cell is also monitored and the difference between cell temperature and bath temperature is less than 0.1K. A Sensotec STJE-AP112 pressure transducer and 450D readout are used to measure the cell pressure at the feed port of the cell.

During the evaluation of the equilibrium apparatus, it was found that dead volume between the cell outlet and the sampling port must be minimized. The temperature and pressure in the sampling ports are lower than those in the equilibrium cell, resulting in the possibility of phase separations. If this occurs, droplets of the dispersed liquid phase can accumulate on the walls of tubing or in dead volume (such as internal volume under the diaphragms of back pressure regulators or valve bodies). This accumulated fluid periodically reenters the flow stream, and, thus, causes large concentration fluctuations in the collected samples. To minimize the dead volume, a back-pressure regulator is not used. Instead, the pressure control is accomplished by manually adjusting the two Whitey Series SS-22RS2 Micro-metering valves. These valves, together with the equilibrium cell and the preheat coil, are immersed in the constant temperature bath to minimize the potential for phase separations in the valve bodies. Capillary bore stainless steel tubing leads from the regulating valves through a water-cooled heat exchanger to the sampling ports. No significant variations in the phase compositions were observed when the combined (total) flow rate is less the 4 ml/min and the volumetric feed ratio of hydrocarbon to water is between 0.5 and 2.

Sampling Procedure. Proper sampling procedures are extremely important for accurate determination of the mutual solubility of water-hydrocarbon systems. In the 100 to 1000 ppm (by weight) concentration range, a slight evaporation of the hydrocarbon component from the aqueous phase can greatly affect the results; the measured hydrocarbon solubility tends to be lower than the true value. For water dissolved in the hydrocarbon phase, the situation is even more complicated. Water can evaporate from the sample, or water can be absorbed into the sample, depending on the humidity of the environment where the sample is taken. Thus, the sampling process must be conducted to minimize exposure to the atmosphere. The following sampling procedure has been adopted.

All samples are collected consecutively from the cell at time intervals corresponding to one-half the residence time of the organic phase in the cell. A 25-ml or 60-ml sampling vial is filled with 0.5 to 4.0 ml of dehydrated ethanol solvent depending on the concentration of the sample being collected. (The ethanol is dehydrated using 4A molecular sieve from Fisher Scientific Company.) The vial is then closed by a screw-cap fitted with a Teflon™ coated septum. The capillary tubing from the equilibrium cell passes through the septum and ends beneath the surface of the ethanol. Upon exiting the equilibrium cell, the stream to be sampled is cooled, at which point it forms a two-phase emulsion before entering the sample vial, where it is blanketed by the ethanol solvent to minimize sample loss. The septum used to cap the vial prevents any contact with the atmosphere. At the completion of sampling, the vial is carefully removed from the sampling port *without being mixed*, capped and stored at 4°C. Prior to GC analysis, the vial is shaken to provide a single phase mixture of the sample and ethanol; 2 μl of this mixture is then injected into the GC.

Gas Chromatographic Analysis. A Hewlett-Packard 5880A Gas Chromatograph equipped with a thermal conductivity detector (TCD) is used for both water and hydrocarbon phase analyses. A 1/8-in., 8-ft. long Porapak Q column from Alltech is used. Chromatographic helium is used as the carrier gas. The operating conditions for the hydrocarbon and water phase analyses are shown in Table I. The analytical procedure used in the sample treatment and analyses is outlined here. Details are described by Chen and Wagner (*8*).

Hydrocarbon solubility in water is characterized by a minimum at approximately room temperature. Direct preparation of single-phase liquid mixtures for use as GC standards with compositions comparable to those encountered at higher temperatures is not feasible. Use of single-phase vapor mixtures as GC standards can resolve this difficulty (*9*), but the results may be subject to large errors due to the technical difficulties involved. Using a cosolvent can resolve the low temperature immisibility problem. However, it is difficult to control the composition of standards to give calibration points evenly distributed over the composition range of interest. More seriously, such a procedure does not give a clear indication of the approach to the nonlinear response region of the GC. This, in turn, makes it very difficult to treat either the calibration data or sample analysis data correctly.

To resolve the low temperature immisibility problem, a very simple procedure was developed . For the benzene-water binary, two calibration curves were made to measure water solubility in benzene and benzene solubility in water: water-ethanol and benzene-ethanol.

All calibration standards were prepared gravimetrically, and all calibration curves are regressed as log(weight ratio) as a function of log(area ratio). This calibration method is both simple and straightforward. More importantly, it significantly reduces the magnitude of uncertainties and errors in the calibrations from approximately 10 % or greater (which is very common for these highly dilute systems) to less than 1 %.

Sample analysis for water solubility in the organic phase must include a correction for the water introduced by the ethanol solvent. An ethanol solvent blank is analyzed, and the water content of the ethanol solvent is obtained. This result is then used to correct the GC analysis of the hydrocarbon-phase sample . This correction is discussed elsewhere by Chen and Wagner (*8*).

MATERIALS

Spectral grade benzene with a purity of 99+ mole % from Aldrich Chemical Company and distilled/deionized water were used without further purification. Ethanol USP Absolute-200 Proof from AAPER Alcohol and Chemical Co. was dehydrated and stored over 4A molecular sieve from Fisher Chemical Co.

RESULTS AND DISCUSSION

Mutual solubility data for the benzene-water system are presented in Table II. Each measurement is the average of at least six replicate determinations. From these extensive replications, the maximum relative error for any data point is less than 6 percent. The maximum correction for water content introduced by the ethanol cosolvent is less than 15 percent.

Benzene Solubility in Water. As shown in Figure 2, the new solubility data for benzene in water agree well with values reported by Alexander (*10*), Bradley et al. (*11*), Bittrich et al. (*12*) and Tsonopoulos and Wilson (*13*). The data given by Udovenko et al. (*14*) show higher benzene solubilities, while the data given by Arnold et al. (*15*), Franks et al. (*16*), and Sanemasa et al. (*17*) are lower. The results of Arnold et al. (*15*) have essentially been reproduced by Franks et al. (*16*) The close agreement between these two sets of measurements may result from both groups using similar experimental apparatus, procedures, analytical techniques and calibration methods.

The new measurements in the temperature range from 335 to 375 K bridge a gap in the previous benzene solubility measurements and tie the published low-temperature data (less than 340 K) to high-temperature (373 to 540 K) data. The new measurements at 373.15 K agree very well with the benzene soulbilities reported for the lower range of high temperature data, as exemplified by the solubilities reported by Tsomopoulos and Wilson (*13*) at 373 K and Anderson and Prausnitz (*9*) at 374 K.

Benson and Krause (*18*) and Wilhelm et al. (*19*) have discussed the merits of different forms of empirical equations for correlating the temperature dependence of high-precision solubility data. What is used here is the following empirical relation for benzene solubility (20):

$$\ln\frac{1}{x_b} = -6.191 + 14.03\frac{1}{T_r} - 3.511\frac{1}{T_r^2} \qquad (1)$$

where x_b is the mole fraction of benzene and T_r is the reduced temperature (system temperature divided by the critical temperature of benzene, 562.2 K). This relationship is shown as the solid line in Figure 2. From the Gibbs-Duhem equation, assuming the activity coefficients for both water in the aqueous phase and for the hydrocarbon in the organic phase are equal to one, thus:

$$\left(\frac{\partial \ln x_i}{\partial T}\right)_P \cong \frac{\Delta \overline{H}_i}{RT^2} \qquad (2)$$

where the heat of solution , $\Delta \overline{H}_i$ is the difference between the partial molar enthalpy of component *i* in solution, $\overline{H}_i$, and the pure molar enthalpy, H_i, at temperature T,

$$\Delta \overline{H}_i = \overline{H}_i - H_i. \qquad (3)$$

The specific heat of mixing, $\Delta \overline{C}_{p_i}$, is defined by,

$$\left(\frac{\partial \Delta \overline{H}_i}{\partial T}\right)_P = \Delta \overline{C}_{P_i} \qquad (4)$$

where,

$$\Delta \overline{C}_{P_i} = \overline{C}_{P_i} - C_{P_i}. \qquad (5)$$

Using Equations 1, 2 and 4, the enthalpy of mixing and specific heat, $\Delta \overline{H}_i$ and $\Delta \overline{C}_{p_i}$, at 298.15 K are estimated as 3.69 kJ/mole and 208 J/mole-K, respectively. The estimated heat capacity compares well with the calorimetrically measured value of 225 J/mole-K reported by Gill et al. (*21,22*).

The temperature at which benzene reaches its minimum solubility in water is estimated from Equation 1 as 281K; Gill et al. (*21,22*) report a value of 288.9 K from calorimetric measurements.

Water Solubility in Benzene. There are many published data for this system, and the agreement among these data is fair. From the Figures 3 and 4, water solubilities measured by Berkengeim (*23*), Clifford (*24*), Rosenbaum and Walton (*25*), Bittrich et al. (*12*), and Englin et al. (*26*) are generally low. The data by Hill (*27*) show a weaker temperature dependence of solubility than the majority of other data. Tsonopoulos and Wilson (*13*) state that their "...new measurements at 373 K are unaccountably too low." Water solubilities measured by Anderson and Prausnitz (9) are also low at 373 K. Nevertheless, considering the experimental difficulty and uncertainty involved in measuring the water solubility data, the new measurements are in excellent agreement with the majority of the literature data, especially those of Moule and Thurston (*28*), Groschuff

(*29*), Staveley (*30, 31*) , Goldman (32), Karlsson (3*3*), and Tarassenkow and Poloshinzewa (34) in both the trend and absolute values.

The water solubility data in Table II can be correlated with following equation (*20*), as shown by the solid line in Figures 3 and 4:

$$\ln\frac{1}{x_w} = -1.557 - 9.415 \ln T_r \tag{6}$$

The uncertainty in the experimental data indicates this exponential correlation may be adequate, as shown in Figures 3 and 4. From Equations 2 and 6, the heat of the solution at 298.15 K is estimated as 23.3 kJ/mole from the solubility measurements. The calculated heat of solution is very close to the hydrogen bonding energy (21 kJ/mole to 29 kJ/mole). This result is in line with current theory and experimental evidence (*35*), which indicates that liquid water dissolving into a non-polar hydrocarbon liquid phase is virtually a process of breaking hydrogen bonds. The specific heat of mixing at 298.15 K is estimated as 78.3 J/mole-K from Equation 6.

SUMMARY AND CONCLUSIONS

A continuous flow type liquid-liquid equilibrium unit has been designed, constructed, and evaluated. The unit was tested thoroughly using the benzene-water binary system. A relatively simple gas chromatographic method has been developed which permits both water-phase and hydrocarbon-phase samples to be analyzed accurately and efficiently.

New mutual solubility data for the benzene-water system compares favorably with previously published data and bridges a gap which existed in the temperature range from 333 to 373 K. Estimated heats of solution from solubility measurements of benzene in water agree well with calorimetric measurements. The estimated heat of solution of water in benzene is very close to the hydrogen bonding energy, which supports the argument that water dissolves into non-polar organic solvents mainly by breaking hydrogen bonds.

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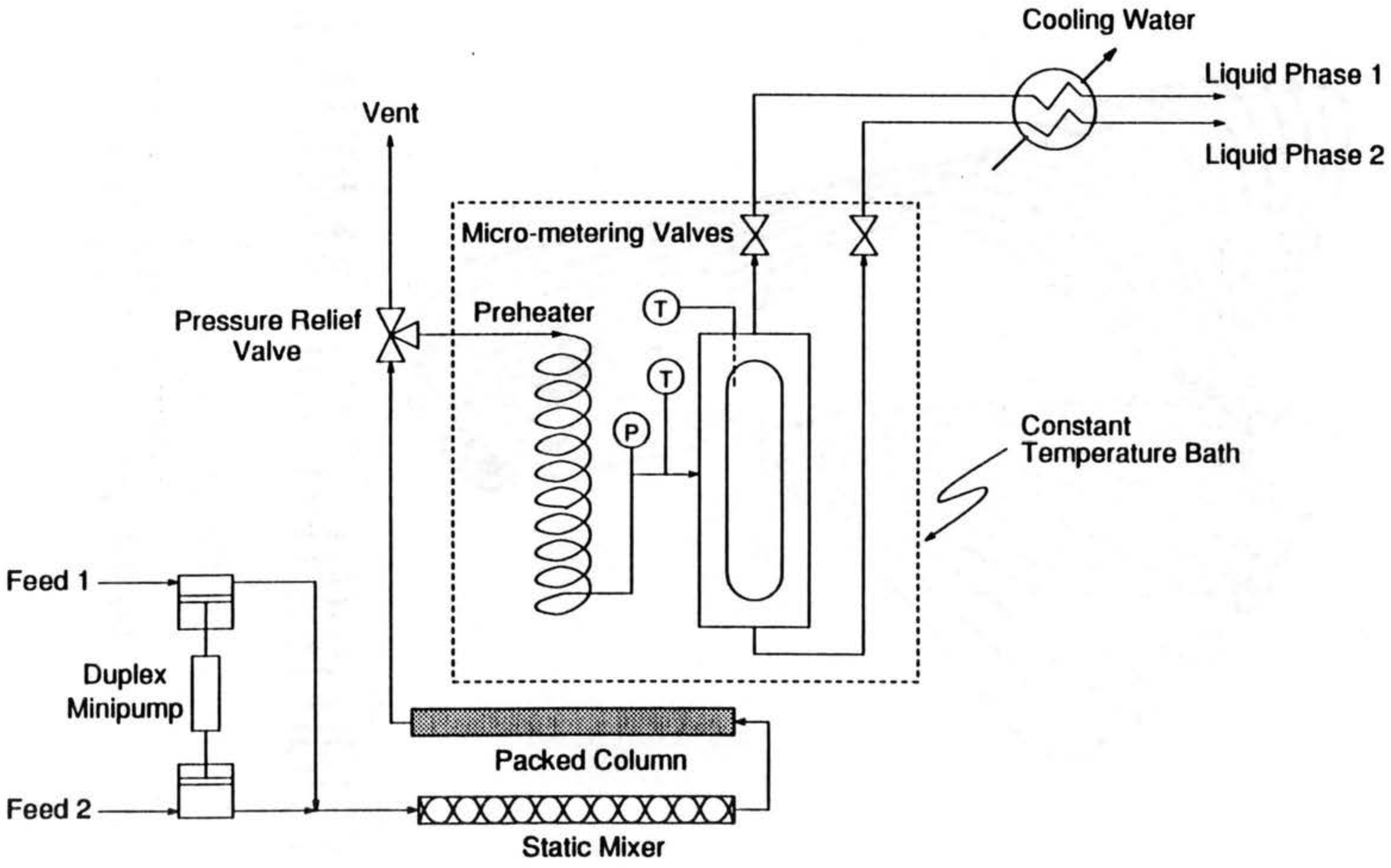
TABLE I. GAS CHROMATOGRAPH OPERATING CONDITIONS

Operating Conditions	Hydrocarbon Phase Analysis	Water Phase Analysis
Injector Temperature, °C	240	200
Column Temperature, °C	240	200
Detector Temperature, °C	240	220
Carrier/Reference Gas Flow, ml/min	30	30
Auxiliary Gas Flow, ml/min	40	40

TABLE II. MUTUAL SOLUBILITIES OF BENZENE AND WATER

Temperature	Pressure	Benzene Solubility in Water			Water Solubility in Benzene		
K	bar	$10^3 x$	10^3 S	N	$10^3 x$	10^3 S	N
303.15	1.0	0.424	0.0231	6	3.84	0.173	6
313.15	1.0	0.464	0.0231	6	4.74	0.217	6
323.15	1.0	0.510	0.0369	6	7.23	0.563	6
333.15	1.5	0.565	0.0346	6	9.5	0.260	6
343.15	2.5	0.625	0.0369	6	12.2	0.260	6
353.15	2.5	0.699	0.0185	6	15.4	0.390	6
363.15	3.5	0.800	0.0323	6	20.7	0.390	6
373.15	3.5	0.950	0.0254	6	26.5	0.303	6

x = mole fraction
S = standard deviation
N = number of measurements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Liquid Phase 2
Vent
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T
T
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Duplex Minipump
Feed 2
Packed Column
Static Mixer

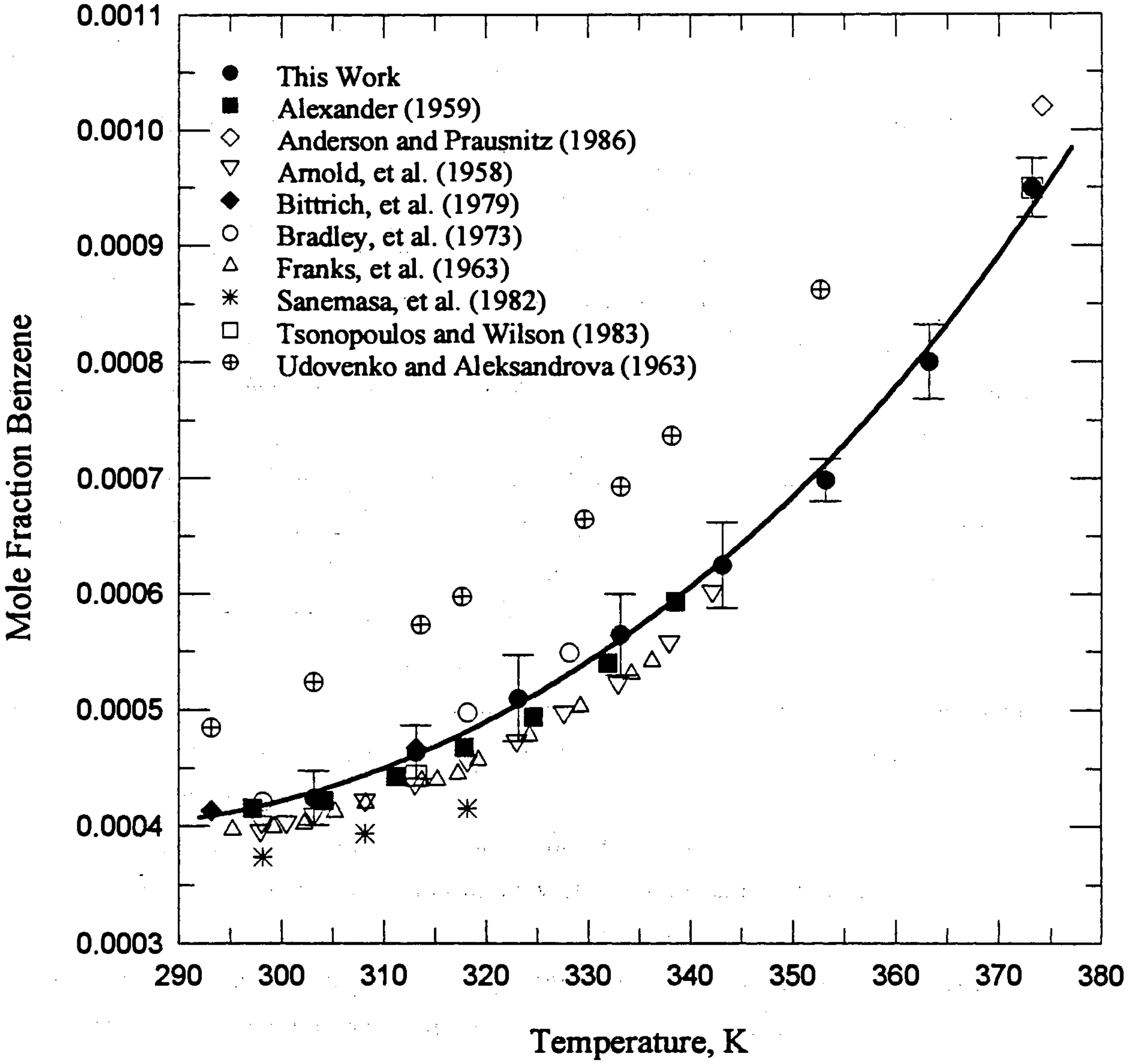

Figure 2. Solubility of Benzene in Water

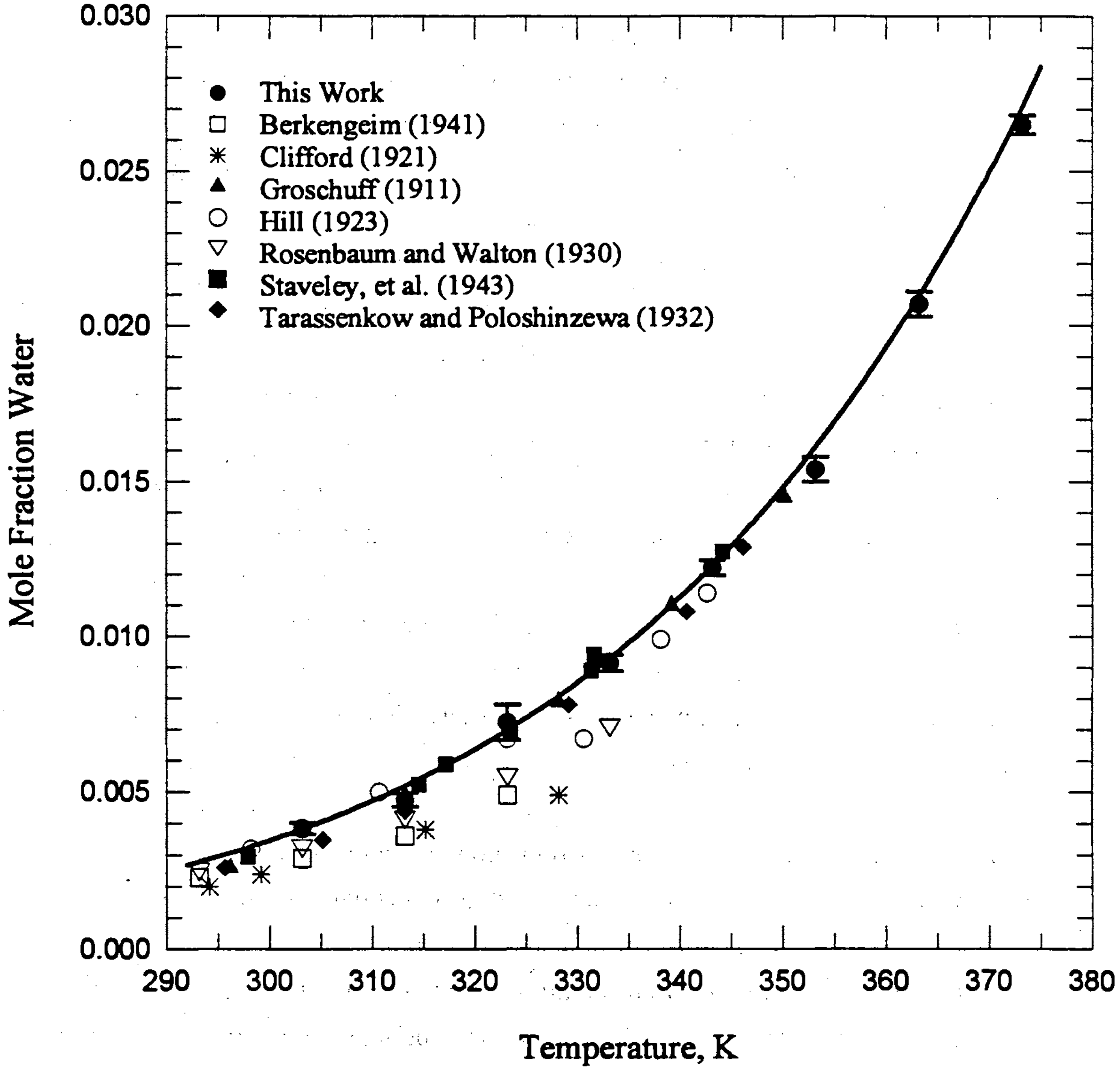

Figure 3. Solubility of Water in Benzene (Literature Data Before 1950)

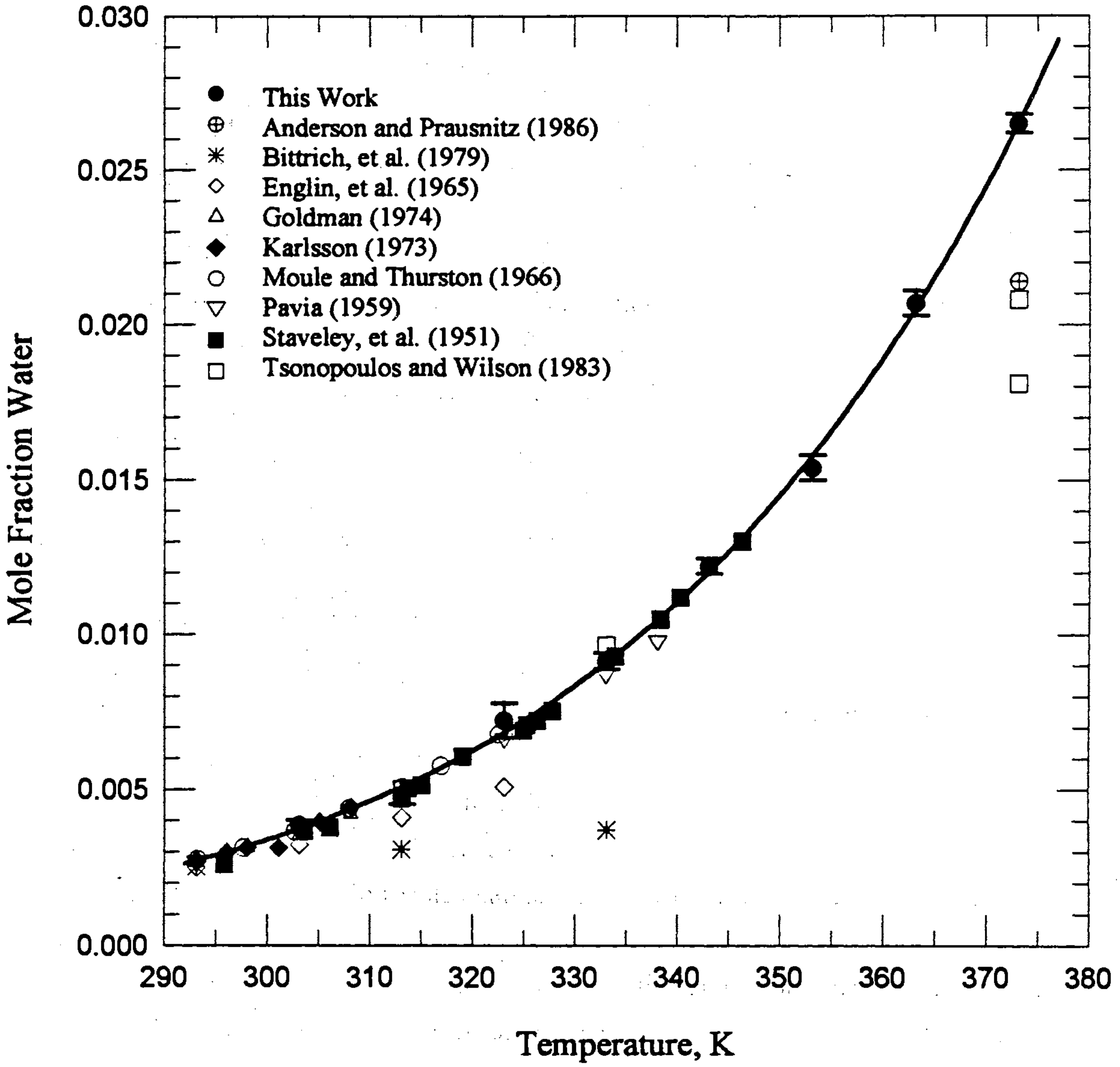

Figure 4. Solubility of Water in Benzene (Literature Data After 1950)

CHAPTER III

AN EFFICIENT AND RELIABLE GAS CHROMATOGRAPHIC METHOD FOR MEASURING LIQUID-LIQUID MUTUAL SOLUBILITIES IN ALKYLBENZENE-WATER MIXTURES: TOLUENE-WATER IN THE REGION 303-373 K

ABSTRACT

An efficient and reliable gas chromatography (GC) method has been developed for measuring mutual solubilities of alkylbenzenes and water. The reliability and precision of the method are demonstrated for toluene and water in the temperature range 303 to 373 K. The reproducibility of the GC analysis of a given sample is excellent; the absolute average percentage deviation of the analysis is consistently less than 1.0 %. The method has also been used to determine the solubility of other alkylbenzenes in water at concentrations as low as 10 ppm, by weight, and water solubility in alkylbenzenes as low as 300 ppm. The average percentage deviation of these measurements is less than 6.0 %, due largely to the high precision of the GC analysis. The method developed here minimizes the use of sophisticated analytical instrumentation, which makes it suitable for routine analysis. The method employs a GC equipped with a standard thermal conductivity detector, and a single column is used for analysis of samples of both the organic and the water phases. The overall time required for a single analysis is less than 15 minutes.

INTRODUCTION

Many alkylbenzenes are considered toxic or hazardous to human health and must be removed from wastewater streams before the effluent can be discharged into the environment. The design of appropriate processing units requires information on alkylbenzene solubilities in water. Accurate and reliable mutual solubility data for water and hydrocarbons are vital to a better understanding of the liquid water structure and its solution behavior. Although many measurements have been reported in the literature since the beginning of the century, agreement among different investigators is poor. This lack of consistency in measurements can be attributed to many factors. However, the main difficulty appears to be measuring solubilities in the low concentration range, from 1 to 1000 ppm. With the introduction of the GC, the analytical technique has realized a significant improvement, and the difficulty of analysis at low analyte concentrations has been largely resolved, though not completely eliminated. The remaining key factors are sample treatment prior the GC analysis and appropriate columns.

Many recommendations concerning sample treatment and proper instrumentation for the analysis of trace organic compounds in water have appeared in the literature. Poole et al (*1*); Namiesnik et al, (*2*); and Jennings and Rapp (*3*) present good reviews. Some of their recommendations have been used in the routine analysis of trace organics in water (*4*). There are also many suggestions for the GC analysis of trace water in an organic solvent (*5-22*). However, none of these has been widely accepted in practice, presumably for the following reasons: (1) the Karl Fischer titration method has become a *defacto* standard method for water content determination, and highly specialized and automated commercial units are readily available, (2) the reliability and accuracy of GC methods have not been well demonstrated for routine applications, (3) some GC methods are complicated and require both specialized personnel and analytical equipment which may not be readily available, and (4) some GC methods are tedious and inefficient and do not have general applicability.

In this study, a detailed GC method is presented for the determination of mutual solubilities of alkylbenzenes and water in the very low concentration range. The precision and reliability of the method is demonstrated by applying it to the determination of toluene-water mutual solubilities. A single column is used for both the toluene and the water analyses, and the time required for a single run is less than 15 minutes. The method is reliable and accurate down to 10 ppm level of the analyte concentration for both the organic and the water phases, provided appropriate sample preconcentration and solvent purification techniques are adopted.

EXPERIMENTAL

In the discussion which follows, demonstration will be presented on the GC method by applying it to the determination of the liquid-liquid mutual solubilities of water and toluene. The equilibrium measurement unit and sampling technique have been described elsewhere (*23*).

Materials and Apparatus. The 25 ml sampling vials and the 60 ml and 125 ml sampling bottles with open-hole caps and Teflon™ lined silicon septa are from Alltech. The 99.9%+ grade iso-octane, toluene, and methylenechloride are from Aldrich Chemical Co. Ethanol, USP Absolute -200 Proof from AAPER Alcohol and Chemical Co. was dehydrated and stored over 4A molecular sieve from Fisher Chemical Co.

A Hewlett-Packard 5880A gas chromatograph equipped with a thermal conductivity detector (TCD) and a Hewlett-Packard Level-4 integrator were used. A Porapak® Q GC column (packed, 80-100 mesh, 6 feet, 1/8 inch stainless steel coil) from Alltech Chemical Co. was used for preliminary analyses. This was replaced with a GasChrom® 254 column (packed, 80-100 mesh, 6 feet, 1/8 inch stainless steel coil) to achieve better resolution for organic components. The drying oven was a VWR Scientific Model 1410. Chromatographic helium was obtained from Sooner Gas Supply, Inc.

Glassware for Sample Transfer or Storage. The sampling vials and bottles were meticulously cleaned using the following procedure: (1) soak in Micro Clean™ solution for 24 hours, (2) wash and rinse with tap water, (3) rinse with methylenechloride, (4) rinse with methanol, (5) rinse with distilled water, and (6) dry at 100 °C under vacuum overnight. The cleaned vials or bottles were removed from the oven, and when cool enough to handle, loosely capped and stored in a desiccator.

The septa for vials and bottles were cleaned by soaking in ethanol for 24 hours and, subsequently, soaked in distilled water for 2 hours. After a final rinse with distilled water, the septa were oven dried at 50 °C under vacuum.

The cleanness of the sampling vials and bottles is extremely important for reproducibility in sample analysis; extreme care should be excised for this part of the overall analytical procedure.

Standard Preparation and Calibration. Serial dilution techniques were used to prepare the standard solutions for toluene diluted in iso-octane (methylenechloride can also be used) and for water diluted in dehydrated ethanol. The standard solutions were prepared gravimetrically over the range in which actual analysis will be conducted, with an approximately constant solution concentration ratio maintained between consecutive dilutions. All standards were analyzed immediately to establish calibration curves.

A "monitoring solution" containing the mixed analytes in the concentration range of the standards was also prepared during the course of calibration. This solution was then analyzed, and the area ratios of the analytes to the respective standards were recorded. These area ratios were then used to monitor the stability of the GC system on a daily bases.

Sample Analysis Procedure. A dry, clean sampling bottle is removed from the dessicator and the cap tightened. The sampling bottle is weighted to ±0.1 mg before and after iso-octane or dehydrated ethanol is added. The difference in weight gives the amount of solvent added. The bottle is then cooled to 4 °C in a refrigerator before it is used to collect the sample. After the sample is collected, the sampling bottle is weighed again. The difference in weight before and after sample collection gives the actual amount of the sample collected.

The known amount of iso-octane added to the sample bottle before the water phase is sampled serves as both an internal standard and an extractant. The known amount of dehydrated ethanol added before the organic phase is sampled serves as an internal standard and as the homogenizing cosolvent.

The water phase samples are shaken vigorously to extract the dissolved organics from the water into the iso-octane phase. The sample is then stabilized for at least 4 hours before any of the iso-octane phase is injected into the GC.

After a water phase sample is extracted with iso-octane and the iso-octane phase is analyzed, 2 μl of water in contact with the iso-octane phase is injected at the lowest GC attenuation to check for any response from the analyte being analyzed. This step serves to monitor the actual recovery of the extraction process used to concentrate the analyte. If the recovery of the analyte is less than 100 %, a second extraction may be necessary. However, recovery was always greater than 99.9% throughout this study, when the weight ratio of iso-octane to water phase is 0.20 to 0.30. Therefore, a second extraction was not required to correct for possible analyte losses during the sample concentration step.

The organic phase samples are also vigorously shaken to homogenize the mixture and are analyzed immediately. The dehydrated ethanol is also analyzed to obtain the area ratio of the water to ethanol. This ratio is used to correct for the small amount of water introduced into the organic phase sample by the dehydrated ethanol.

Operating conditions for the GC are given in Table I. The injection sample size for both phase samples is 2 μl. For routine analysis, a 2 μl monitoring sample (usually prepared while standard solutions are being made) is injected prior to the sample analysis at the beginning of each working day to monitoring the GC stability. If the resulting chromatogram indicates a significant (more than 1 percent) change in the area ratios of analytes to respective standards , the whole system is recalibrated. Sample analysis begins only after system stability is confirmed. Recalibration is required after approximately 60 sample injections.

RESULTS AND DISCUSSION

Calibration. All of the analyses reported here are obtained with a GasChrom® 254 column. The calibration curves for the toluene /iso-octane mixture and the water /ethanol mixture are shown in Figures 1 and 2, respectively. The reproducibility of all points on the calibration curves is within 1.0 %. The following calibration curves were obtained by linear regression: For toluene and iso-octane

$$\log_{10} W_{R(toluene/octane)} = 1.08389 \log_{10} A_{R(toluene/octane)} - 0.01200 \tag{1}$$

and for water and ethanol

$$\log_{10}\left(W_{R(Water/Ethanol)} + C\right) = 1.01518 \log_{10} A_{R(Water/Ethanol)} - 0.05573 \tag{2}$$

where W_R and A_R are the weight and area ratios, respectively, of analyte to solvent and C is a constant.

The constant C in the water and ethanol calibration curve represents the combined effects of trace water in the dehydrated ethanol and the limit of the GC response. Because the calibration results indicate a nonlinear relation between W_R and A_R on log-log coordinates, the conventional blanking method cannot be used, especially at the low analyte concentrations. Also, the thermal conductivity detector gives no response below the detection limits of the analyte. The effects from the blank and the detection limit can be represented better by introducing a constant into the regression based on multiple point (as compared to single point blanking) calibration. The value of the constant is approximately $2.5\text{x}10^{-4}$ and can change whenever a new batch of dehydrated ethanol is used in the analysis. There is little variation when the analyses use the same batch of dehydrated ethanol solvent. Since the GC detection limit for water under the conditions listed in Table I appears to be around $1.0\text{x}10^{-5}$, or approximately 4.0% of the value of the constant C, a new value can be easily estimated by the running a dehydrated ethanol blank.

The calculated value of W_R is sensitive to the value of C *at low values of* W_R ($<1.0\text{x}10^{-4}$). Therefore, the injected sample should have a water concentration at least one order of magnitude higher than the constant C. This can be accomplished in three ways. The first is to further dehydrate the ethanol solvent, which can be very difficulty in practice. The second is to concentrate the water in the sample before it is homogenized by ethanol. Brady (1982) used ethylene glycol to concentrate the water before the sample was analyzed using Karl Fischer titration. A similar procedure can be used with GC analysis. The third is to minimize the amount of ethanol, and thus maximize the water to ethanol weight ratio. Certainly, the third method may not be feasible all the time, especially when there is a thermodynamic miscibility limit imposed on such ratio tuning. Since the ethanol used here serves as both the reference compound and the cosolvent to homogenize the sample, the quantity used can be minimized to the limit at which the sample can be homogenized. This point is further illustrated in the following section.

Example Calculation. The example given here is from the measurement of the mutual solubility of toluene and water at 303 K near the three-phase liquid-liquid-vapor equilibrium curve. For the organic phase sample there are six replicates as shown in Table II.

Since $A_R = 2.700\text{x}10^{-4}$ for the dehydrated ethanol, one obtains $C = 2.10\text{x}10^{-4}$ from the calibration curve for water and ethanol by nonlinear regression. For each of the Samples 1 to 6, A_R (water/ethanol) can be used to calculate W_R (water/ethanol) from Equation 1 rewritten as

$$W_{R(water/ethanol)} = 10^{\left(1.015\log_{10} A_{R(water/ethanol)} - 0.05573\right)} - C \qquad (3)$$

The actual amount of water in toluene is then calculated from

$$W_{R(water/toluene)} = W_{R(water/ethanol)} W_{R(ethanol/toluene)} \qquad (4)$$

Note that the weight of organic phase sample is approximated as the weight of toluene. This is a reasonable approximation considering the low water solubility in the sample. Also note that the correction, C, amounts to about 5.0 percent of the value of W_R for water and ethanol. The magnitude of this correction can be decreased, if less ethanol solvent is used to homogenize the sample. However, since good reproducibility is clearly achieved, no further efforts were made in this direction.

For solubility of toluene in water, the calculation is similar to that shown above but no correction is required. A correction may be required for the loss of isooctane into the water phase during the extraction procedure. Because the solubility of isooctane in water is small at room temperature (0.35 ppm at 25 °C), and the isooctane to sample weight ratio is controlled; a correction was not required in this work. Therefore, the calculation procedure has not presented here.

Comparison of Measured Mutual Solubility Data of Toluene and Water With Literature Data. The liquid-liquid mutual solubility of benzene and water have been presented previously (*23*) using essentially the same analytical technique given above. Here, the mutual solubility data of toluene and water will be presented in the temperature range 303 to 373 K to demonstrate the reliability of the proposed GC method. Results are summarized in Table III.

Toluene Solubility in Water. The new toluene solubility in water data are shown in Figure 3 together with data from the literature (*24-30*). The solubilities reported by Bohon and Claussen (*26*) and Pierotti and Liabastre (*28*) appear too high. Hefter (*31*) reached the same conclusion. Sanemasa et al. (29, 30) reported two sets of measurements obtained in 1981 and 1982. The 1982 solubilities were approximately 8 percent lower than the 1981 values. The new data are in excellent agreement with the Sanemasa et al. (*29*) 1981 measurements and the solubility reported by Gross and Saylor (*27*) at 298 K.

The new toluene solubility measurements were correlated with temperature by the following equation:

$$\ln\frac{1}{x_T} = -12.21 + 21.39\frac{1}{T_r} - 5.372\frac{1}{T_r^2} \qquad (5)$$

where x_T is the mole fraction of toluene and T_r is the reduced temperature (system temperature divided by the critical temperature of toluene, 591.8 K). This relationship can be used to estimate the heat of solution by assuming the activity coefficients for water in the water phase and for toluene in the toluene phase are unity. From the Gibbs-Duhem equation

$$\left(\frac{\partial \ln x_i}{\partial T}\right)_P = \frac{\Delta\overline{H}_i}{RT^2} \qquad (6)$$

where $\Delta\overline{H}_i$ is the difference between the partial molar enthalpy of component *i* in solution and the molar enthalpy of pure *i*. The specific heat of solution, $\Delta\overline{C}_p$ in defined as

$$\Delta\overline{C}_p = \left(\frac{\partial \Delta \overline{H}_i}{\partial T}\right)_P \qquad (7)$$

From Equations 5, 6, and 7, the specific heat of solution at 298 K is estimated as 351 J/mole-K. Gill et al. (*32*) report a value of 363 J/mole-K based on calorimetric measurements. Also, the minimum solubility temperature obtained by extrapolation of Equation 5 is 297.3 K. This is in excellent agreement with the value of 291.6 K from calorimetric measurement (*32*)

Water Solubility in Toluene. The water solubility in toluene measurements together with data reported in the literature (*24, 33-36*) are plotted as a function of temperature in Figure 4. Tarassenkow and Poloshinzewa (*36*) have covered the same temperature range, and there is some disagreement between the two sets of measurements, particularly in the temperature dependence of the water solubility. the new data are correlated with the following equation

$$\ln\frac{1}{x_w} = -1.483 - 9.647\ln T_r \qquad (8)$$

where x_w is the mole fraction of water and T_r is the reduced temperature for water (critical temperature of 647.3 K). From this relationship, the estimated heat of solution is 23.9 kJ/mole. This is close to the value of 23.3 kJ/mole for benzene (*23*) and close to the hydrogen bonding energy of water (21 to 29 kJ/mole). Current theory and experimental evidence (*37*) indicates that liquid water dissolving into a liquid hydrocarbon phase is essentially a process of breaking hydrogen bonds. Since the Tarassenkow and Poloshinzewa (*36*) data are lower than the most of the new measurements when temperature is lower than 313 K, and the calculated heat of solution using their data (correlated with Equation 8) is 97.9 kJ/mole; Tarassenkow and Poloshinzewa's data may not be reliable. The new data appear very consistent with the majority data at temperatures below 323.15 K The datum given by Anderson and Prausnitz (*24*) near 373 K is somewhat lower than ours.

Efficiency of Analysis. Typical chromatograms are shown in Figure 5 and Figure 6 for the analysis of toluene in water and water in toluene, respectively. The required time for a single run is less than 7 minutes for water and less than 2 minutes for toluene. This is significantly less than the time required by other methods (*10*). The peak shape is symmetrical for both toluene and water and does not exhibit the tailing reported by Oguchi et al. (*19*). This good separation efficiency is achieved on a standard 6 ft x 1/8 in packed stainless steel coiled column which is available commercially (GasChrom® from Alltech). The early methods using large customer packed columns and injection of large-sized samples (*13*) is avoided.

Limits of the Method. In addition to the toluene-water system data reported here, the method has been used for water and benzene (*23*), *para*xylene, *1,3,5*-trimethylbenzene, ethylbenzene and butylbenzene (*38*). For these organic compounds dissolved in water, the method appears reliable and accurate down to 10 ppm, for butylbenzene in water (*38*). The combined precision (equilibrium measurement and GC analysis) is always better than 6.0% for hydrocarbon solubility in water. For water solubility in the alkylbenzenes, the method is used down to about 300 ppm. Further sample treatment methods are needed to extend the range of application, as pointed out in the section on calibration. Nevertheless, water solubility in liquid organic solvents is always above 100 ppm when the equilibrium temperature is above 273.15 K, and the method proposed here can be applied to determine the water solubility in various liquid organic solvents.

The method does not have an apparent upper limit on the water concentration. The dilution method can easily be used to bring high water concentration of the sample to the concentration range best suited for the GC analysis. From the experience gained, it is believed that the method can be used directly with confidence to determine the water content in an organic sample when concentrations are above 300 ppm.

CONCLUSIONS

An efficient and reliable gas chromatographic (GC) method is developed for measuring liquid-liquid mutual solubilities in alkylbenzene-water mixtures. The reliability, precision and efficiency is demonstrated by applying it in the determination of the liquid-liquid mutual solubility of toluene and water. The method has also been applied in the determination of the hydrocarbon solubility in water down to 10 ppm (by weight) with good precision (average percentage deviation is about 6.0). Water solubility in hydrocarbons has been determined down to 300 ppm (by weight) with an average percentage deviation about 8.0. The required instrumentation is a GC equipped with a thermal conductivity detector and an integrator. A standard commercially available column is used for both water and organic solute analysis. The GC method presented here can be useful for routine analysis of water content in organic solvents.

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TABLE I. GAS CHROMATOGRAPHIC OPERATING CONDITIONS

Porapak® Q Column

Operating Conditions	Hydrocarbon Phase Analysis	Water Phase Analysis
Injector Temperature, °C	240	200
Column Temperature, °C	240	200
Detector Temperature, °C	240	220
Carrier/Reference Gas Flow, ml/min	30	30
Auxiliary Gas Flow, ml/min	40	40

GasChrom® 254 Column

Operating Conditions	Hydrocarbon Phase Analysis	Water Phase Analysis
Injector Temperature, °C	270	270
Column Temperature, °C	250-270	150-270
Detector Temperature, °C	300	300
Carrier/Reference Gas Flow, ml/min	30	30
Auxiliary Gas Flow, ml/min	40	40

TABLE II. CHROMATOGRAPHIC ANALYSIS OF TOLUENE PHASE SAMPLES COLLECTED AT 303 K

Replicate	W_R [a] (ethanol/toluene)	A_R [b] (water/ethanol)	W_R [c] (water/ethanol)	W_R [d] (water/toluene)	Mole Fraction Water [e]
1	0.01040	0.007753	0.006064	0.000613	0.000312
2	0.10444	0.006600	0.005109	0.000534	0.000272
3	0.09407	0.007123	0.005542	0.000521	0.000266
4	0.10109	0.007796	0.006100	0.000617	0.000314
5	0.09983	0.007099	0.005522	0.000551	0.000281
6	0.09966	0.007585	0.005868	0.000585	0.000298
Dehydrated Ethanol		0.000270			

[a] From gravimetric analysis
[b] From chromatographic analysis
[c] Calculated using Equation 3
[d] Calculated using Equation 4

[e] $$x_{H_2O} = \frac{1}{1+\frac{18}{92}\frac{1}{W_R}}$$

TABLE III. MUTUAL SOLUBILITIES OF TOLUENE AND WATER

Temperature	Pressure	Toluene Solubility in Water			Water Solubility in Toluene		
K	bar	$10^3\, x$	10^3 S	N	$10^3\, x$	10^3 S	N
303.15	1.0	0.117	0.0261	6	2.91	0.189	6
313.15	1.0	0.119	0.0357	6	4.16	0.065	6
323.15	1.0	0.127	0.0144	6	5.30	0.394	6
333.15	1.5	0.144	0.0365	6	7.11	0.204	6
343.15	2.5	0.171	0.0547	5	9.46	0.261	5
353.15	2.5	0.198	0.0561	5	12.8	0.646	5
363.15	3.5	0.232	0.0239	5	16.2	0.495	5
373.15	3.5	0.268	0.0595	5	22.6	1.02	5

x = mole fraction
S = standard deviation
N = number of measurements

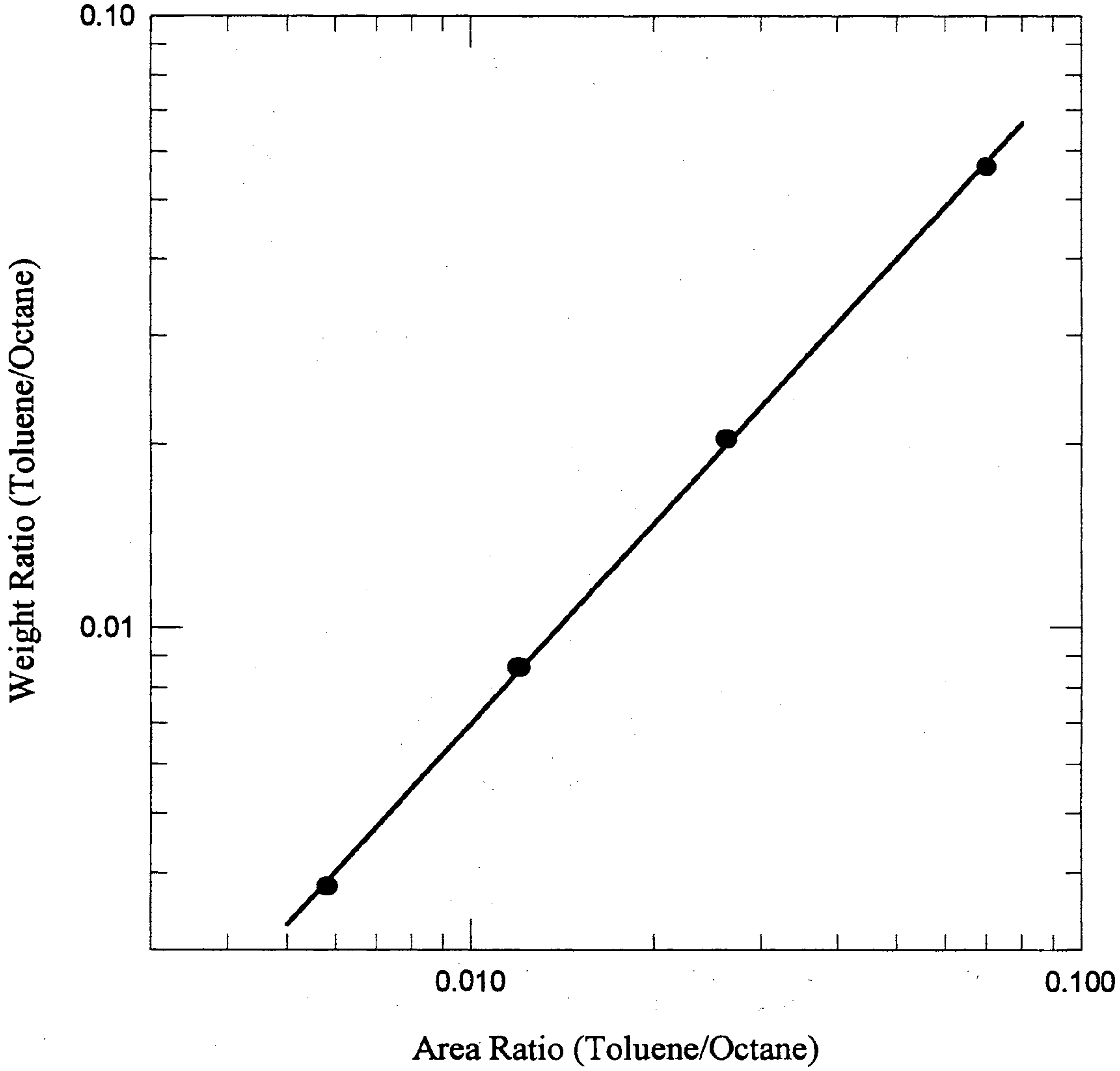


Figure 1. Calibration Curve for Toluene in iso-Octane

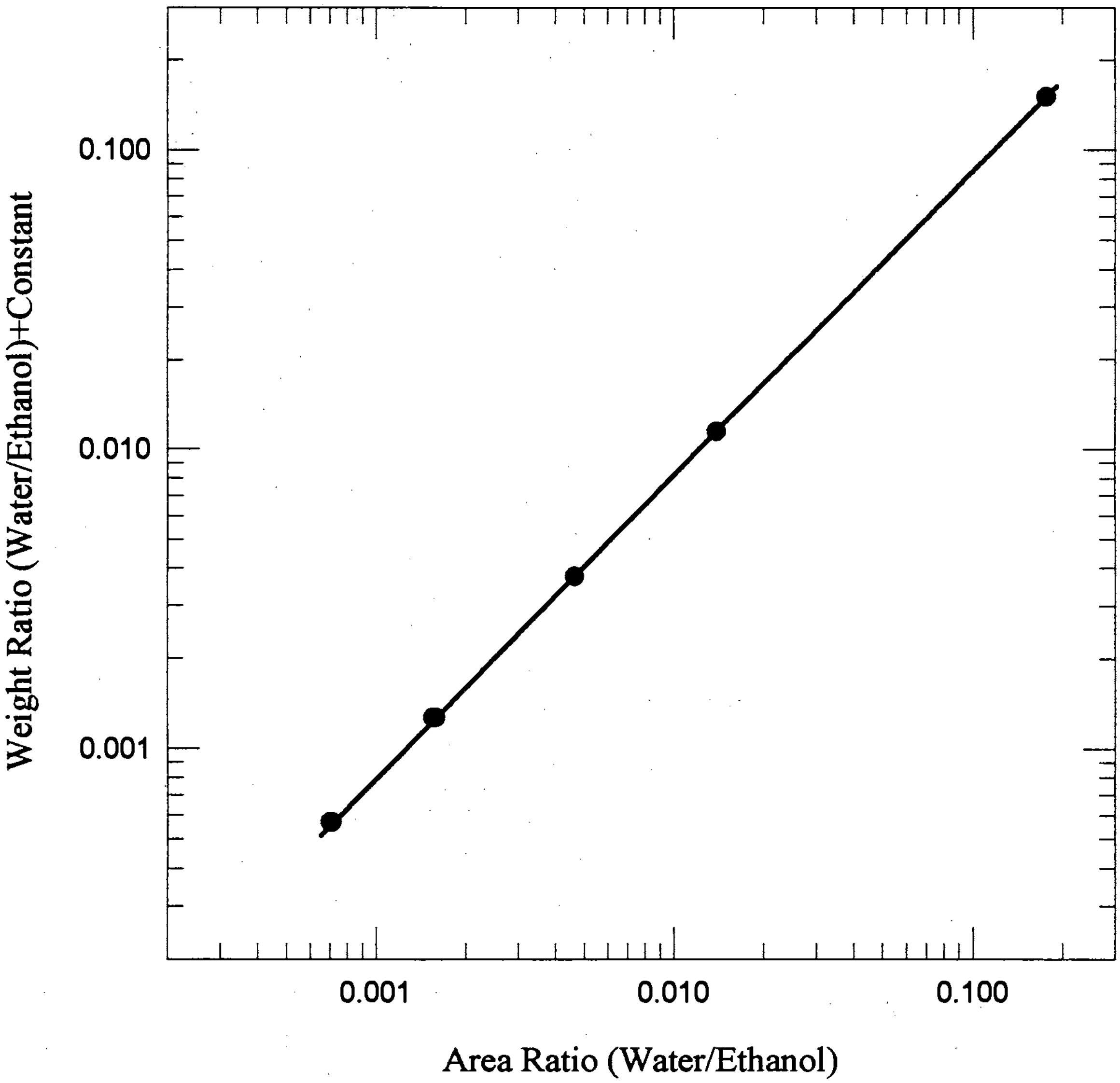


Figure 2. Calibration Curve for Water in Ethanol

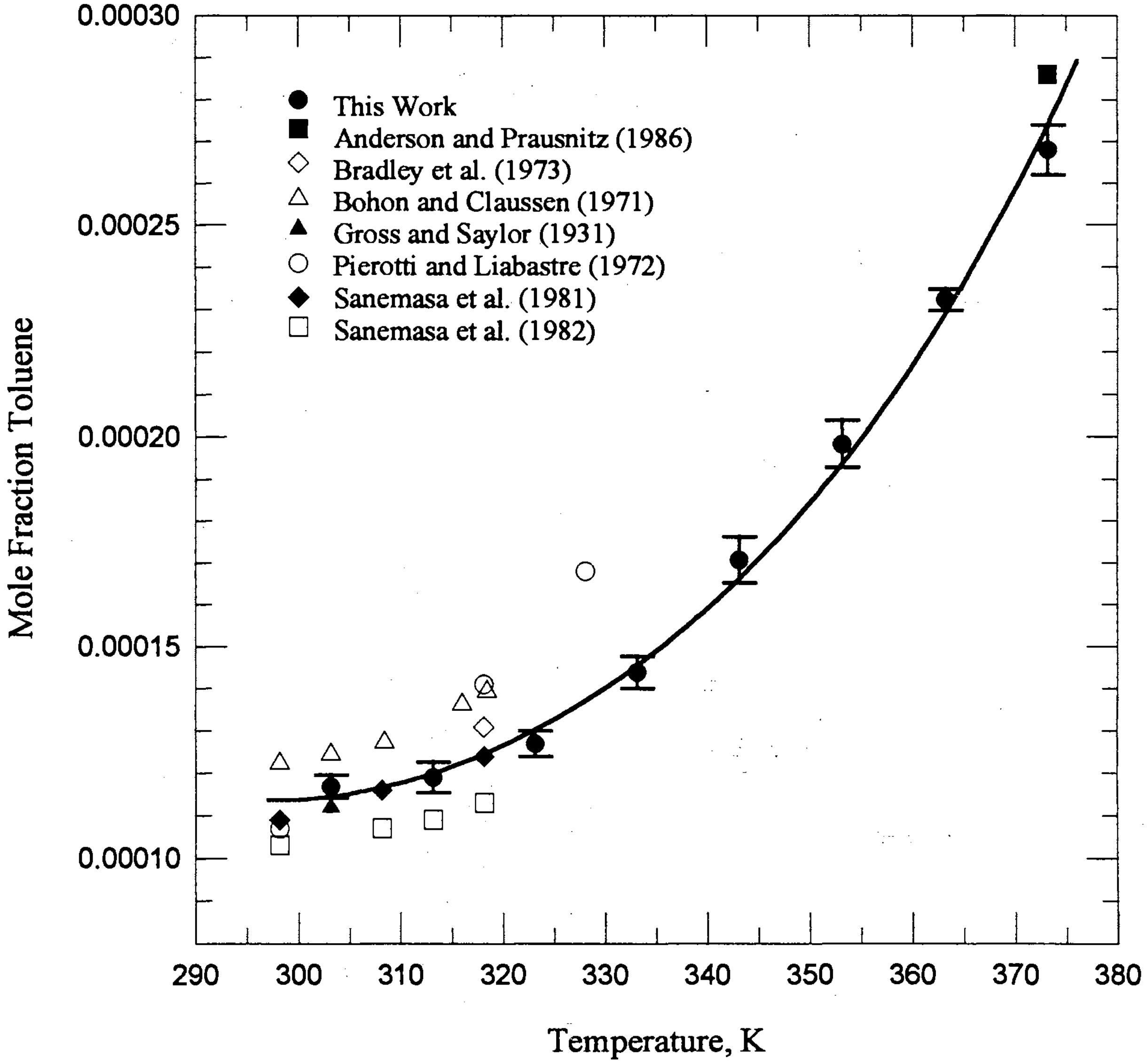


Figure 3. Solubility of Toluene in Water

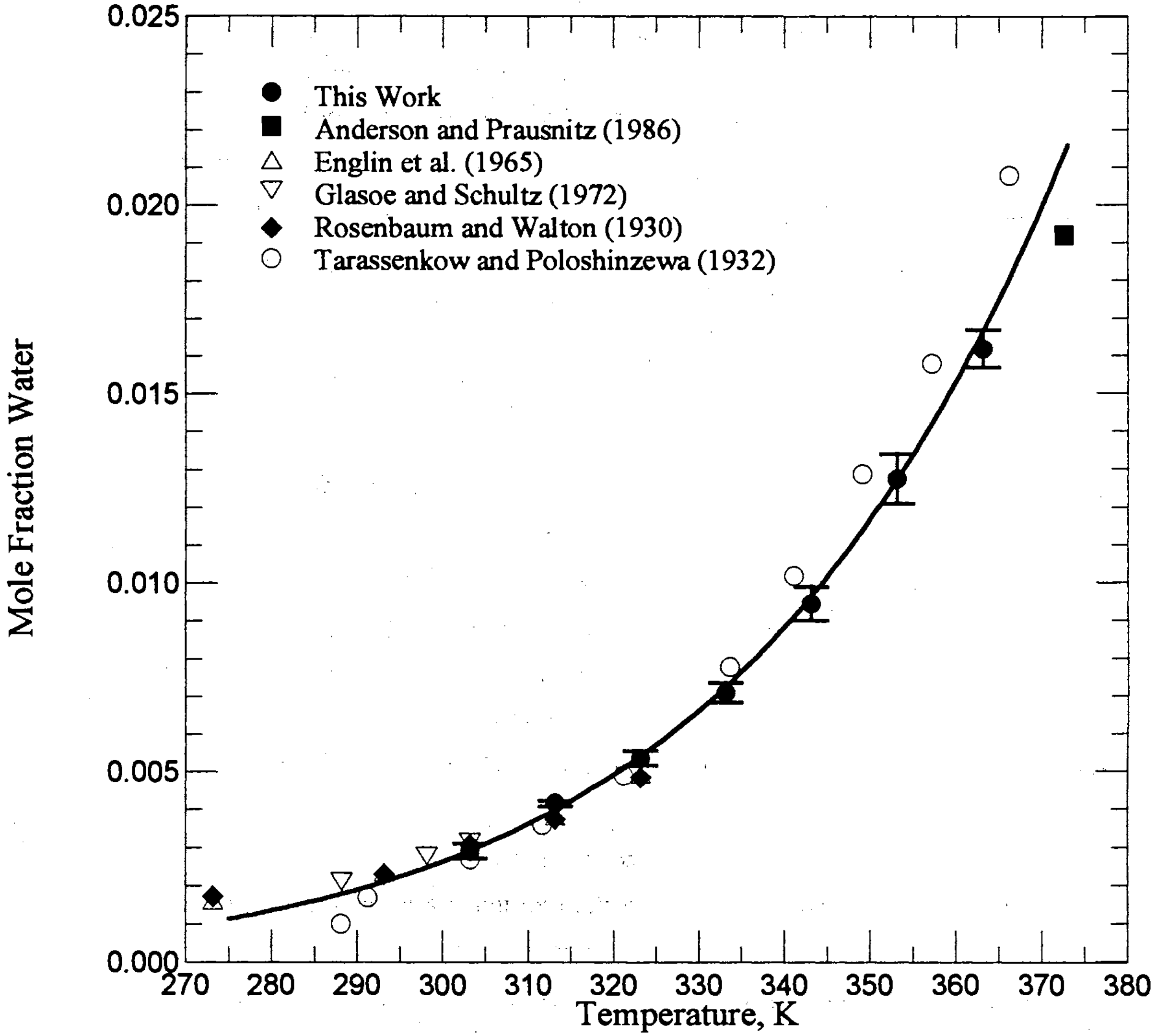
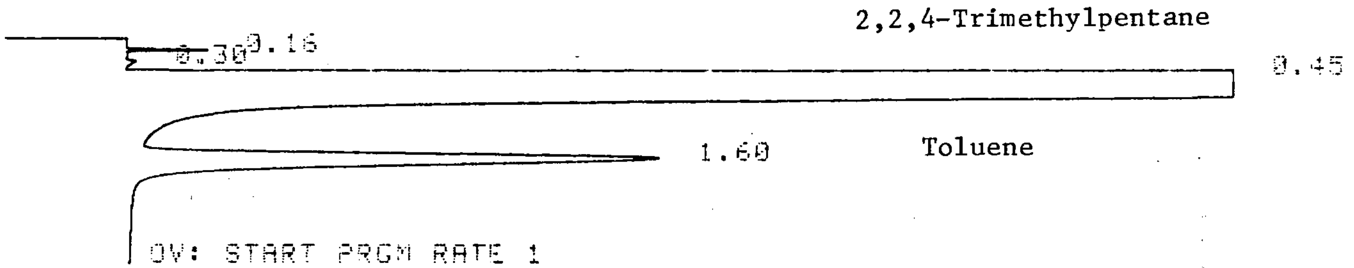


Figure 4. Solubility of Water in Toluene



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  0.00                        THRESHOLD @ START RUN =  4
  0.00                        PEAK WIDTH @ START RUN = 0.04
  0.16          1249.94  BV    0.018        1098.67      2066.74      0.052
  0.30           427.38  VP    -----*        150.38      2064.92      0.018
  2.45        2337670.00 PV    0.16 *     234485.00      2064.69     96.628
  1.60          79895.26 VB    0.17 *       7160.38      2095.24      3.302

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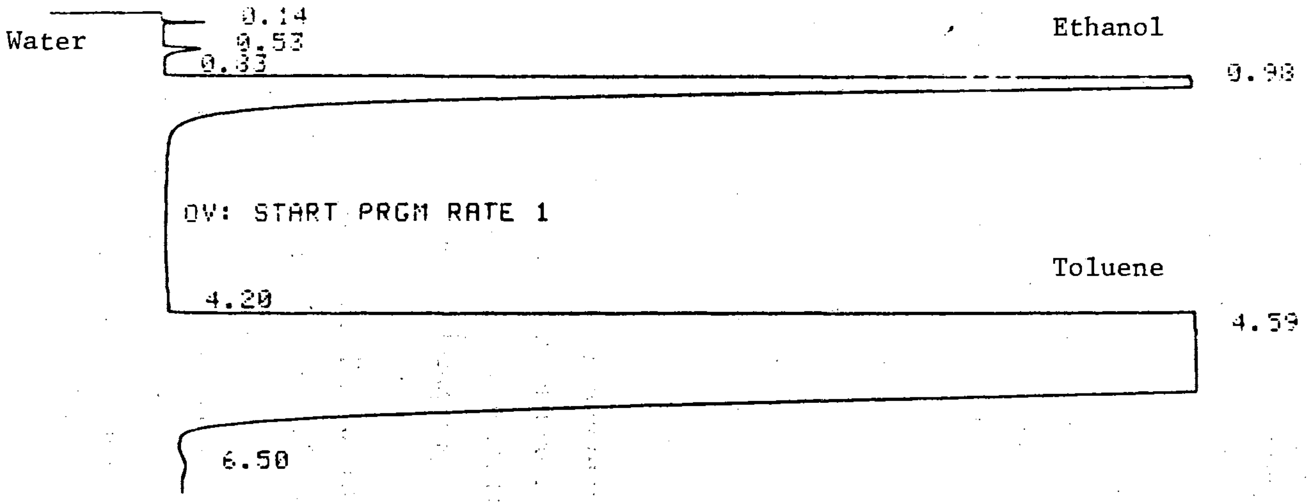

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 0.98          322161.00   VB    0.18 *     27634.30     2009.43     10.283
 4.20             670.04   BH   *------        40.50     2017.84      0.021
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CHAPTER IV

MUTUAL SOLUBILITIES OF ALKYLBENZENE-WATER SYSTEMS AT TEMPERATURES FROM 303 to 373 K: ETHYLBENZENE, *P*-XYLENE, *1,3,5*-TRIMETHYLBENZENE, AND *N*-BUTYLBENZENE

ABSTRACT

Mutual solubilities of a series of alkylbenzenes have been measured near the three-phase curve from 303 to 373 K. Data for *p*-xylene, *1,3,5*-trimethylbenzene, ethylbenzene and butylbenzene demonstrate the effects of molecular size, molecular structure and temperature on the solubility of hydrocarbons in water. Calculated heats of solution of hydrocarbons into water compare well with published calorimetric measurements. Estimated minimum solubility temperatures agree well with those estimated from calorimetric measurements. The data also provide insight into the mechanism of water dissolving into liquid hydrocarbons. The calculated heats of solution of water into hydrocarbons are approximately equal to the molar hydrogen bonding energy of water. Both the enthalpy and entropy of mixing can be considered constant for this series of alkylbenzenes from 303 to 373 K.

INTRODUCTION

Mutual solubility measurements have been reported earlier for benzene-water (*1*) and toluene-water (*2*) over the temperature range of 303 to 373 K. In an effort to gain some insight into the effects of molecular size and structure, as well as temperature, to provide guidance in the development and evaluation of equations of state and activity coefficient models for hydrocarbon-water systems, the experimental data base has been extended to other alkylbenzene-water mixtures. *p*-Xylene and *1,3,5*-trimethylbenzene were selected to determine the effects of molecular size. Together with benzene, this series represents fairly symmetrical compounds of increasing molecular volume.

Ethylbenzene and n-butylbenzene, together with toluene form a homologous series of increasing length of the side chain on the substituted benzene structure. The length of the side chain should tend to make the molecule more asymmetrical and induce a larger dipole moment relative to a more symmetrical component of the same molecular weight, i.e. ethylbenzene compared to *p*-xylene.

In addition to representing a range of molecular size and structure, alkylbenzene-water systems are important in the chemical process industry. They also represent a class of environmentally important chemicals. Emissions of benzene are currently regulated (*3*) and other aromatic hydrocarbons are among the U. S. Environmental Protection Agency priority pollutants (*4*).

EXPERIMENTAL

The detailed design and operation of a continuous flow equilibrium apparatus for mutual solubility measurements have been described by Chen and Wagner (*1*). Temperatures are controlled to within 0.2 K over the temperature range of 303 to 383 K. The hydrocarbon and water phases are sampled simultaneously. Sample preparation and analysis procedures described by Chen and Wagner (*2*) were followed. The solvents used as an extractants and internal standards for each of the hydrocarbons dissolved in the aqueous samples are listed in Table 1, together with the type of column used in the gas chromatographic analyses.

The procedure described by Chen and Wagner (*2*) was modified to monitor analyte left in the aqueous phase after solvent extraction. When methylene chloride serves as extractant and internal standard, the solubility of methylene chloride in water must be accounted for in the calibration procedure. To correct for the slight solubility of methylene chloride in water, the solubility at room temperature (1.9 weight percent) is used to calculate the amount of methylene chloride remaining in the organic phase. This quantity of methylene chloride is subtracted from the amount added to the water phase sample. The difference is the actual amount of the internal standard.

Ethanol was used as a cosolvent and an internal standard for all organic phase samples. Water solubility in hydrocarbon was corrected for the concentration of water in the ethanol cosolvent following the method described by Chen and Wagner (*2*).

MATERIALS

Ethylbenzene, *p*-xylene, *n*-butylbenzene, *iso*-octane, and methylene chloride of 99+ percent purity were used as received from Alderich Chemical Company. The *1,3,5*-trimethylbenzene was also obtained from Alderich Chemical Company, but with a purity of 98.5 percent. Distilled/deionized water was used without further purification. Ethanol USP Absolute-200 Proof from AAPER Alcohol and Chemical Co. was dehydrated and stored over 4A molecular sieve from Fisher Chemical Company.

RESULTS AND DISCUSSION

The mutual solubilities of *p*-xylene, *1,3,5*-trimethylbenzene, ethylbenzene, and *n*-butylbenzene are presented in Tables II, III, IV, and V, respectively. Each measurement was replicated as shown and the mean values are reported together with the standard deviations. The maximum correction for water content introduced by the ethanol cosolvent is about 15 percent, while the maximum correction introduced by the methylene chloride is about 18 percent. The maximum coefficient of variation is less than 6 percent for hydrocarbon solubility in water and less than 9 percent for water solubility in hydrocarbons.

Alkylbenzene Solubility in Water

The measured solubility data are correlated with following empirical relation:

$$\ln\frac{1}{x_i} = A + B\frac{1}{T_{r,i}} + C\frac{1}{(T_{r,i})^2} \qquad (1)$$

Where x_i is the mole fraction of hydrocarbon *i*, and $T_{r,i}$ is the reduced temperature of the hydrocarbon (system temperature divided by the critical temperature of the hydrocarbon as reported by Reid et al. (*5*)). The coefficients of this equation for each of the systems, as well as those from previous studies on benzene (*1*) and toluene (*2*), are summarized in Table VIII. These correlations are plotted as solid lines in Figures 1 through 4 for each of the systems discussed below.

Ethylbenzene Solubility in Water. Few data are available in the temperature range covered in this study. There are about twelve independent measurements at 298 K. These data are summarized in Table VI, with the average and standard deviations plotted in Figure 1. The data of Bohon and Claussen (*17*) are too high. There is fairly good agreement between the new data with the earlier data reported by Sanemasa et al. (*14*), and excellent agreement with their latter measurements (*15*). At higher temperatures, the measurements tend to be lower that those of Heidman et al. (*18*), but the difference is within the combined experimental errors.

***p*-Xylene Solubility in Water.** There are limited data published for this system. The measurements at 298 K are listed in Table VII, and the average and standard deviation (as an error bar) are plotted in Figure 2. The solubilities measured in this work are consistent with the published values at 298 K. The data of Bohon and Claussen (*17*) are more than one standard deviation above the average of the other data at 298 K, and are considered to be too high. The *p*-xylene solubility reported by Pryor and Jentoft (*21*) is higher than the value of Bohon and Claussen (*17*) at 216 K. Because the IUPAC-recommended solubility values of *p*-xylene in water (*22*) are strongly influenced by the data of Pryor and Jentoft (*21*) and Bohon and Claussen (*17*), the IUPAC recommended solubilities are too high.

1,3,5-Trimethylbenzene Solubility in Water. The measurements for this system are summarized in Table IV and plotted in Figure 3. There are no published data for this system, but as discussed later, the temperature dependence of *1,3,5*-trimethylbenzene is consistent with the other alkylbenzenes.

***n*-Butylbenzene Solubility in Water.** There are four published measurements on *n*-butylbenzene solubility in water at 298 K by Andrews and Keefer (*6*), Klevens (*7*), Massaldi and King (*21*) and Sutton and Calder (*12*). Of these measurements, the datum of Andrews and Keefer (*6*) has been judged as too low by Hefter (*22*), while the datum of Klevens (*7*) is too high (*20*). As shown in Figure 4, the current measurements are in good agreement with the datum of Massaldi and King (*23*). From the trend of the solubility measurements with temperature, the minimum solubility temperature should be near 300 K. Thus the datum of Sutton and Calder (*12*) may be low.

The alkylbenzene solubility measurements reported in this study, and previously published data for benzene and toluene are cross-plotted as a function of the hydrocarbon molecular weight in Figure 5. The least-squares regression lines through the data are shown to indicate trends in the data, not to correlate solubility or to interpret physical solution processes. Figure 5 indicates a systematic decrease in solubility with increasing molecular weight (size) and decreasing temperature (down to the minimum solubility temperature) for this series of hydrocarbons. Figure 5 illustrates the overall consistency of this series of alkylbenzene solubility measurements.

Equation 1 can be used to estimate the heat of solution of hydrocarbons in water. From the Gibbs-Duhem equation, assuming both the activity coefficient for water in the water phase and for the hydrocarbon component in the hydrocarbon phase are equal to one, thus:

$$\left(\frac{\partial \ln x_i}{\partial T}\right)_P = \frac{\Delta \overline{H}_i}{RT^2} \qquad (2)$$

where, $\Delta \overline{H}_i$ is the difference between the partial molar enthalpy of component *i* in solution and the molar enthalpy of pure *i*. The specific heat of mixing, $\Delta \overline{C}_{Pi}$,, is defined as

$$\Delta \overline{C}_{Pi} = \left(\frac{\partial \Delta \overline{H}_i}{\partial T}\right)_P \qquad (3)$$

Heats of solution at 298.15 K calculated using Equations 1 and 2 are presented in Table VIII. The calorimetric measurements of Gill et al. (*24*) are included for comparison. The disagreement between heats of solution estimated from solubility data and those obtained from calorimetric measurements is expected. Franks (*25*) points out the pitfalls of differentiating solubility data, and the functional form of Equation 1 may not represent the actual solution behavior of these apolar species in water. The comparisons of calculated and experimental of heats of solution and specific heats of solution presented in Table VII are intended to provide a general indication of the quality of the solubility data; not for comparison of heat effects from calorimetric and solubility measurements. In this context, calorimetric measurements tend to validate the general temperature dependence of the measured alkylbenzene solubilities in water.

The minimum solubility temperature obtained by extrapolation of Equation 1 and Gill et al's (*24*) estimates from calorimetric data are also presented in Table VII. These estimates from solubility and calorimetric measurements are of comparable magnitude.

Water Solubility in Alkylbenzenes

The solubility of water in each of the alkylbenzene solvents was correlated with an equation of the form:

$$\ln\left(\frac{1}{x_w}\right) = A + B\ln(T_{r,w}) \qquad (4)$$

where x_w in the mole fraction of water and $T_{r,w}$ is the reduced temperature of water (system temperature divided by the critical temperature of water, 647.3 K). The coefficients of Equation 4 for each of the alkylbenzene-water systems appear in Table IX. The correlating equations are plotted as solid lines in Figures 6 through 9.

Water Solubility in Ethylbenzene. A total four data sets have been published for water solubility in ethylbenzene. Most consist of measurements at two or three temperatures, except those by Filippov (*26*). Filippov's data (shown in Figure 6) exhibit a steep, linear temperature dependence as noted by Heidman (*18*). The linear temperature dependence is not consistent with water solubilities in the homologous series of alkylbenzenes. The data by Heidman (*18*) are higher than the new data and the measurements of Englin et al. (*27*). The new data are in good agreement with those of Polak and Lu (*11*) and Englin et al. (*27*).

Water Solubility in *p*-Xylene. There are only three measurements reported in the literature; all at 298.15 K. As shown in Figure 7, the extrapolated data appear slightly lower than these three measurements. The difference is probably within experimental error, and the temperature dependence is similar to that for ethylbenzene (Figure 6), as well as benzene (*1*) and toluene (*2*).

Water Solubility in 1,3,5-Trimethylbenzene. There are no data reported for the solubility of water in *1,3,5*-trimethylbenzene in the temperature range covered here. The solubility data summarized in Table IV and plotted in Figure 8 exhibit a temperature dependence similar to the other alkylbenzenes in this series of mixtures.

Water Solubility in n-Butylbenzene. No published data are available for the solubility of water in *n*-butylbenzene in the temperature range covered here. Once again the temperature dependence shown in Figure 9 is reasonable. The consistency of the solubility measurements among the mixtures is discussed below.

The entropy of mixing for these dilute systems can be approximated as:

$$\left(\frac{\partial \ln x_i}{\partial T}\right)_P = \frac{\Delta \overline{S}_i}{RT} \tag{5}$$

where, $\Delta \overline{S}_i$ is the difference between the partial molar entropy of component i in solution and molar entropy of pure i. Equation 4 is obtained by integrating Equation 5, and assuming the entropy of mixing for water dissolving in the hydrocarbon is constant. An analysis of variance to compare the slopes of the correlations for water solubility in each of the hydrocarbons indicates that, with respect to these data, the deviation removed by using individual least squares lines for each hydrocarbon solvent over that removed using a pooled slope is only slightly significant (*28*). The approximately equal slopes for each system indicate that the heat of solution is primarily dependent on the properties of water, with an average value of 24.2 kJ/mole based on the pooled slope from Table VIII. This result and other theoretical and experimental studies (*25*) support the argument that liquid water dissolving into a liquid hydrocarbon phase is essentially a process of breaking hydrogen bonds. The heat of solution of water estimated from the solubility data compares well with typical hydrogen bonding energies of 21 to 29 kJ/mole (*29*). Both the enthalpy and entropy of solution of water into these liquid hydrocarbons can be considered constant in the temperature range of 303 to 373 K.

SUMMARY AND CONCLUSIONS

Mutual solubilities for binary aqueous mixtures of ethylbenzene, *p*-xylene, *1,3,5*-trimethylbenzene and *n*-butylbenzene were measured at temperatures from 303 to 373 K near the three phase locus. Together with previous measurements for benzene and toluene, these measurements provide liquid-liquid equilibrium data for a series of alkylbenzenes which include the effects of molecular size and structure. The new measurements compare well with the limited reliable data in the literature.

Heats of mixing for the hydrocarbons dissolving in water estimated from solubility measurements compare favorably with published calorimetric measurements. For water dissolving in these liquid hydrocarbons, the heat of mixing is essentially constant and equal to typical hydrogen bonding energies. These heat effects provide a general indication of consistency in the mutual solubility measurements for this series of alkylbenzene-water mixtures.

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TABLE I. COSOLVENTS AND GC COLUMNS FOR WATER - PHASE ANALYSIS

Solute	Solvent	GC Column
Ethylbenzene	Methylenechloride	Porapac®
n-Butylbenzene	*iso*-Octane	Gas Chrom®
p-Xylene	Methylenechloride	Porapac®
1,3,5-Trimethylbenzene	*iso*-Octane	Gas Chrom®

TABLE II. MUTUAL SOLUBILITIES OF ETHYLBENZENE AND WATER

Temperature K	Pressure bar	Ethylbenzene Solubility in Water			Water Solubility in Ethylbenzene		
		$10^6 x$	10^6 S	N	$10^3 x$	10^3 S	N
303.15	1.36	28.8	0.4	6	2.71	0.18	6
313.15	1.36	29.2	0.4	4	3.66	0.23	6
323.15	1.36	33.5	0.9	6	4.57	0.25	6
333.15	1.36	40.7	2.3	5	5.73	0.26	6
343.15	1.36	49.3	2.1	6	8.30	0.66	5
353.15	1.36	59.9	2.4	6	10.7	0.47	5
363.15	1.70	69.5	1.7	6	15.4	1.34	5
373.15	2.24	85.4	3.4	6	20.2	0.64	6

x = mole fraction
S = standard deviation
N = number of measurements

TABLE III. MUTUAL SOLUBILITIES OF *p*-XYLENE AND WATER

Temperature	Pressure	*p*-Xylene Solubility in Water			Water Solubility in Paraxylene		
K	bar	$10^6 x$	10^6 S	N	$10^3 x$	10^3 S	N
303.15	1.36	28.6	0.6	5	2.71	0.09	4
313.15	1.36	31.8	1.5	6	3.48	0.20	4
323.15	1.36	34.4	0.7	6	4.75	0.16	4
333.15	1.36	40.4	0.5	6	6.51	0.47	4
343.15	1.36	48.3	0.6	6	8.70	0.75	6
353.15	1.36	57.1	0.7	6	11.5	0.73	6
363.15	1.70	67.0	1.0	6	15.7	0.63	6
373.15	2.04	87.4	2.2	6	20.2	1.07	6

x = mole fraction
S = standard deviation
N = number of measurements

TABLE IV. MUTUAL SOLUBILITIES OF *1,3,5*-TRIMETHYLBENZENE AND WATER

Temperature K	Pressure bar	Trimethylbenzene Solubility in Water			Water Solubility in Trimethylbenzene		
		$10^6 x$	10^6 S	N	$10^3 x$	10^3 S	N
303.15	1.36	9.58	0.53	6	2.47	0.09	6
313.15	1.36	10.0	0.5	6	3.50	0.19	6
323.15	1.36	11.1	0.6	6	4.88	0.18	6
333.15	1.36	13.6	0.7	6	6.09	0.17	6
343.15	1.36	16.6	1.2	6	7.97	0.28	6
353.15	1.36	20.9	0.6	6	10.6	0.30	6
363.15	2.04	24.5	0.6	6	14.0	0.70	6
373.15	2.38	29.1	0.6	6	19.0	0.40	6

x = mole fraction
S = standard deviation
N = number of measurements

TABLE V. MUTUAL SOLUBILITIES OF *n*-BUTYLBENZENE AND WATER

Temperature	Pressure	*n*-Butylbenzene Solubility in Water			Water Solubility in n-Butylbenzene		
K	bar	$10^6 x$	10^6 S	N	$10^3 x$	10^3 S	N
303.15	1.36	2.24	0.12	5	2.36	0.10	5
313.15	1.36	2.39	0.17	6	3.15	0.06	6
323.15	1.36	2.73	0.10	6	4.13	0.07	6
333.15	1.36	3.61	0.10	6	5.95	0.27	6
343.15	1.36	4.30	0.11	4	8.37	0.33	5
353.15	1.36	6.40	0.20	6	10.7	0.5	6
363.15	2.04	8.20	0.43	6	14.8	0.3	6
373.15	2.38	11.2	0.10	6	19.9	0.8	6

x = mole fraction
S = standard deviation
N = number of measurements

TABLE VI. SOLUBILITY OF ETHYLBENZENE IN WATER AT 298 K

$10^3 x$	Reference	
0.0285	Andrews and Keefer, 1950	(*6*)
0.0297	Klevans, 1950	(*7*)
0.0280	Morrison and Billett, 1952	(*8*)
0.0270	McAuliffe, 1963	(*9*)
0.0258	McAuliffe, 1966	(*10*)
0.0301	Polak and Lu, 1973	(*11*)
0.0273	Sutton and Calder, 1975	(*12*)
0.0306	Korenman and Aref'eva, 1978	(*13*)
0.0307	Sanemasa et al. 1981	(*14*)
0.0287	Sanemasa et al., 1982	(*15*)
0.0292	Sanemasa et al., 1984	(*16*)
0.0287	**Average**	
0.0016	**Standard Deviation**	

x = mole fraction ethylbenzene

TABLE VII. SOLUBILITY OF *p*-XYLENE IN WATER AT 298 K

$10^3 x$	Reference	
0.0340	Andrews and Keefer, 1949	(*19*)
0.0336	Bohon and Claussen, 1951	(*17*)
0.0314	Polak and Lu, 1973	(*11*)
0.0265	Sutton and Calder, 1975	(*12*)
0.0267	Price, 1976	(*20*)
0.0277	Sanemasa et al., 1982	(*15*)
0.0299	**Average**	
0.0034	**Standard Deviation**	

x = mole fraction *p*-xylene

TABLE VIII. AQUEOUS ALKYLBENZENE SOLUBILITY CORRELATIONS AND DERIVED ENTHALPIES OF SOLUTION

Solute	Coefficients in Equation 1 $\ln(1/x) = A + BT_r^{-1} + CT_r^{-2}$			Minimum Solubility Temperature, K	$\Delta\overline{H}_l$ kJ/mole at 298.15 K	$\Delta\overline{C}_{Pl}$ kJ/mole-K at 298.15 K
	A	B	C	Equation 1 / (*24*)	Equation 1 / (*24*)	Equation 1 / (*24*)
Benzene	-6.2	14.0332	-3.5112	281 / 288.9	3.69 /2.08	207 / 225
Toluene	-6.4	14.4014	-3.2639	268 / 291.6	7.11 / 1.73	213 / 263
Ethylbenzene	-11.6	20.4964	-4.7440	285 / 292.0	4.39 / 2.02	338 / 318
p-Xylene	-11.8	20.8923	-4.8914	288 / --	3.45 / --	347 / --
1,3,5-Trimethylbenzene	-11.3	20.6353	-4.6295	286 / --	4.47 / --	352 / --
n-Propylbenzene				-- / 292.3	-- / 2.3	-- / 391
n-Butylbenzene	-26.3	35.2564	-7.9052	296 / --	1.27 / --	645 / --

TABLE IX. WATER SOLUBILITY CORRELATIONS AND DERIVED ENTHALPIES OF SOLUTION

Solvent	Coefficients in $\ln(1/x) = A + B\ln(T_r)$		$\Delta\overline{H}_l$ at 298.15 K	$\Delta\overline{C}_{Pl}$ at 298.15 K
	A	B	kJ/mole	kJ/mole-K
Benzene	-1.5717	-9.4385	23.4	78.5
Toluene	-1.4407	-9.5978	23.8	79.8
Ethylbenzene	-1.3718	-9.6807	24.0	80.5
p-Xylene	-1.5623	-9.9133	24.6	82.4
1,3,5-Trimethylbenzene	-1.2465	-9.5312	23.6	79.2
n-Butylbenzene	-1.7441	-10.3404	25.6	86.0

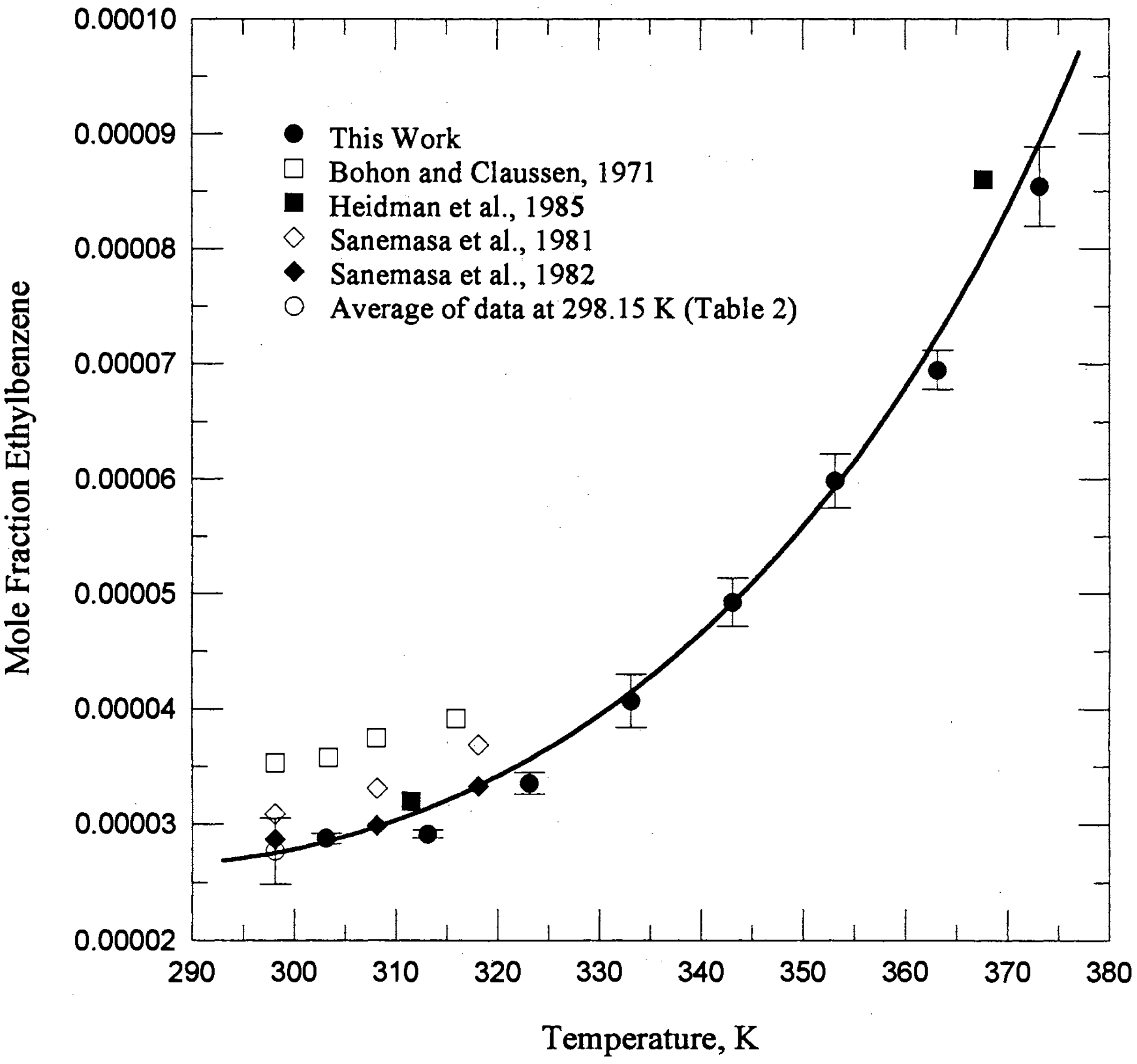

Figure 1. Solubility of Ethylbenzene in Water

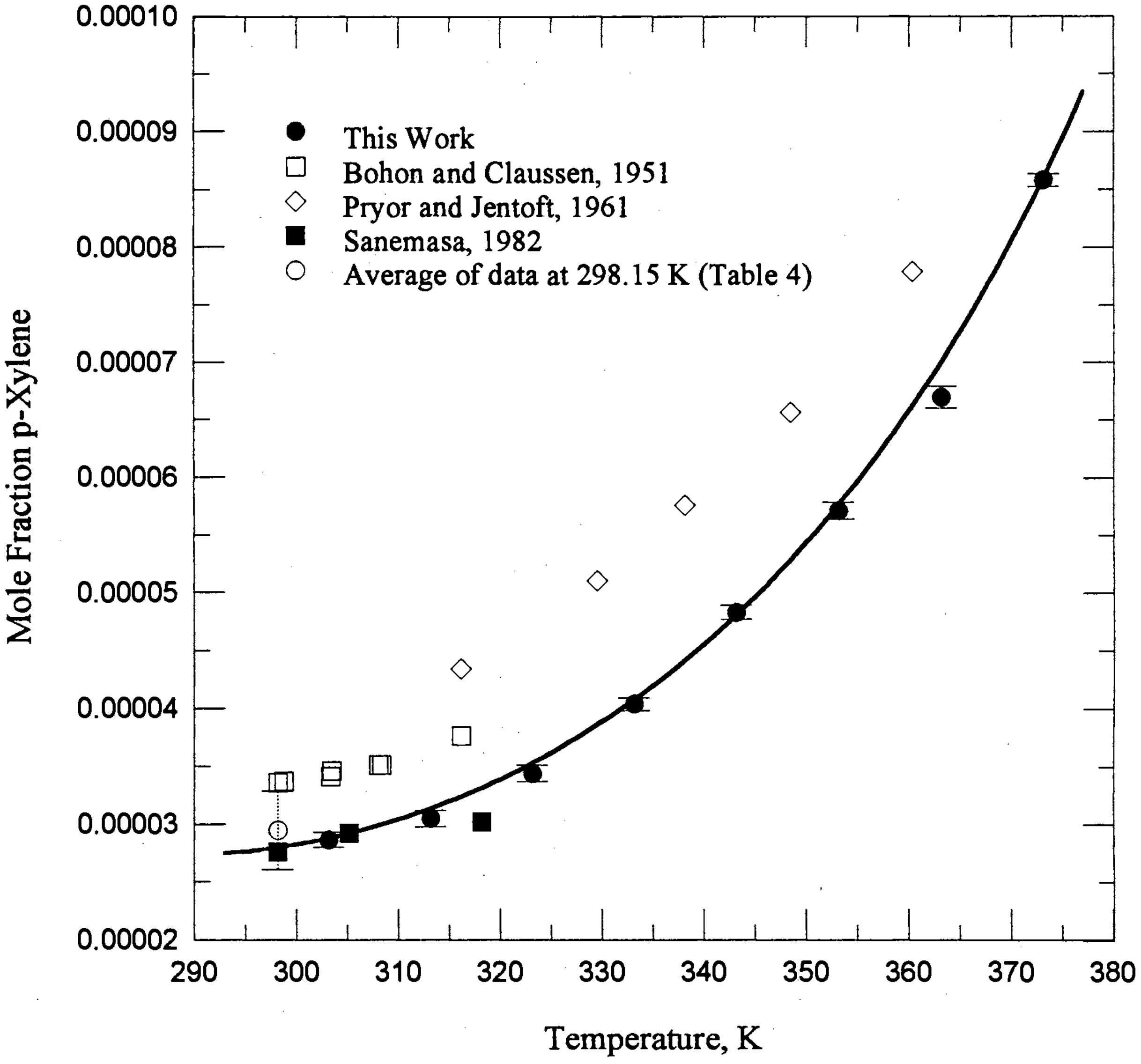

Figure 2. Solubility of p-Xylene in Water

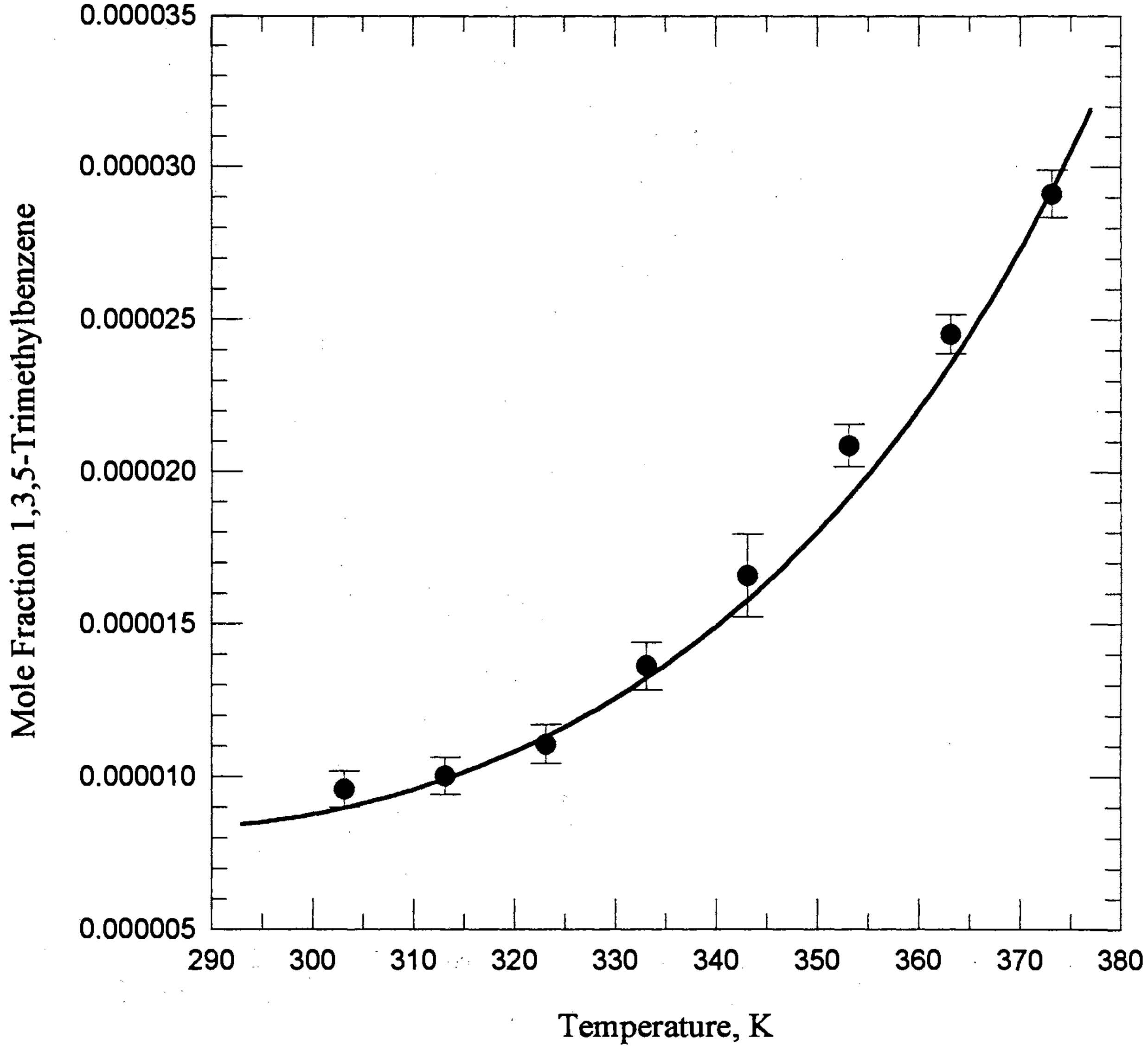

Figure 3. Solubility of 1,3,5-Trimethylbenzene in Water

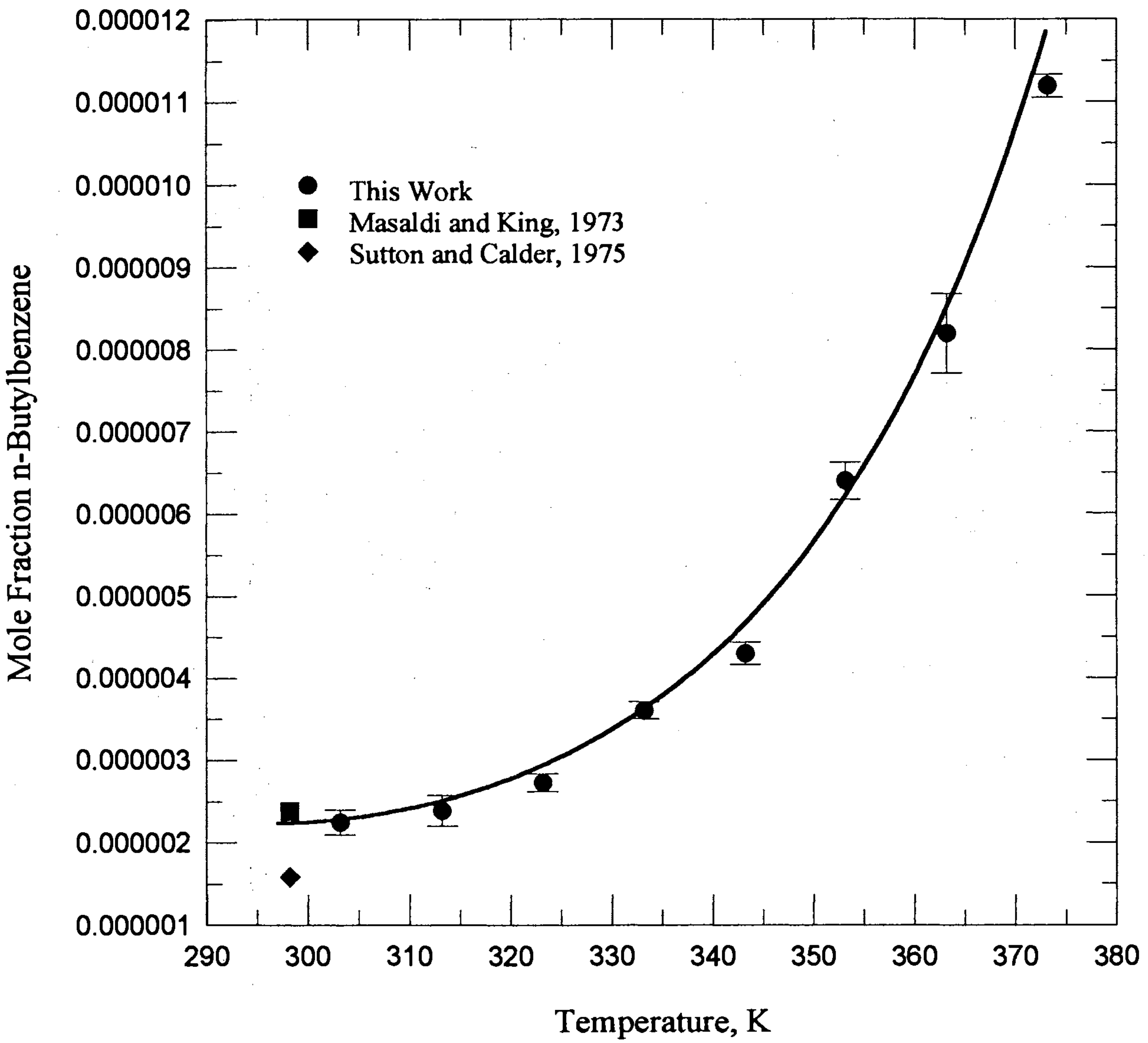

Figure 4. Solubility of n-Butylbenzene in Water

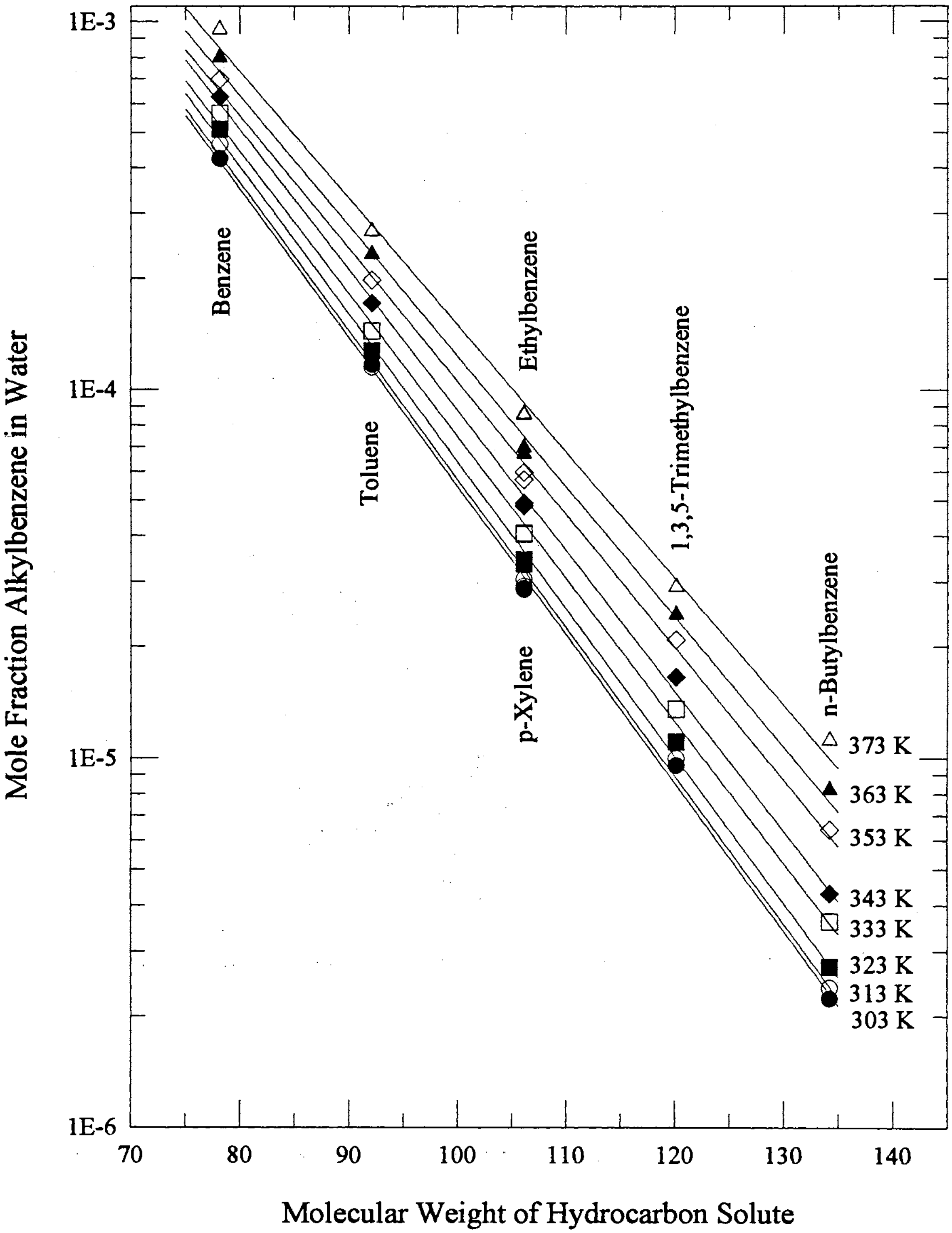

Figure 5. Solubility of Alkylbenzenes as a Function of Hydrocarbon Molecular Weight

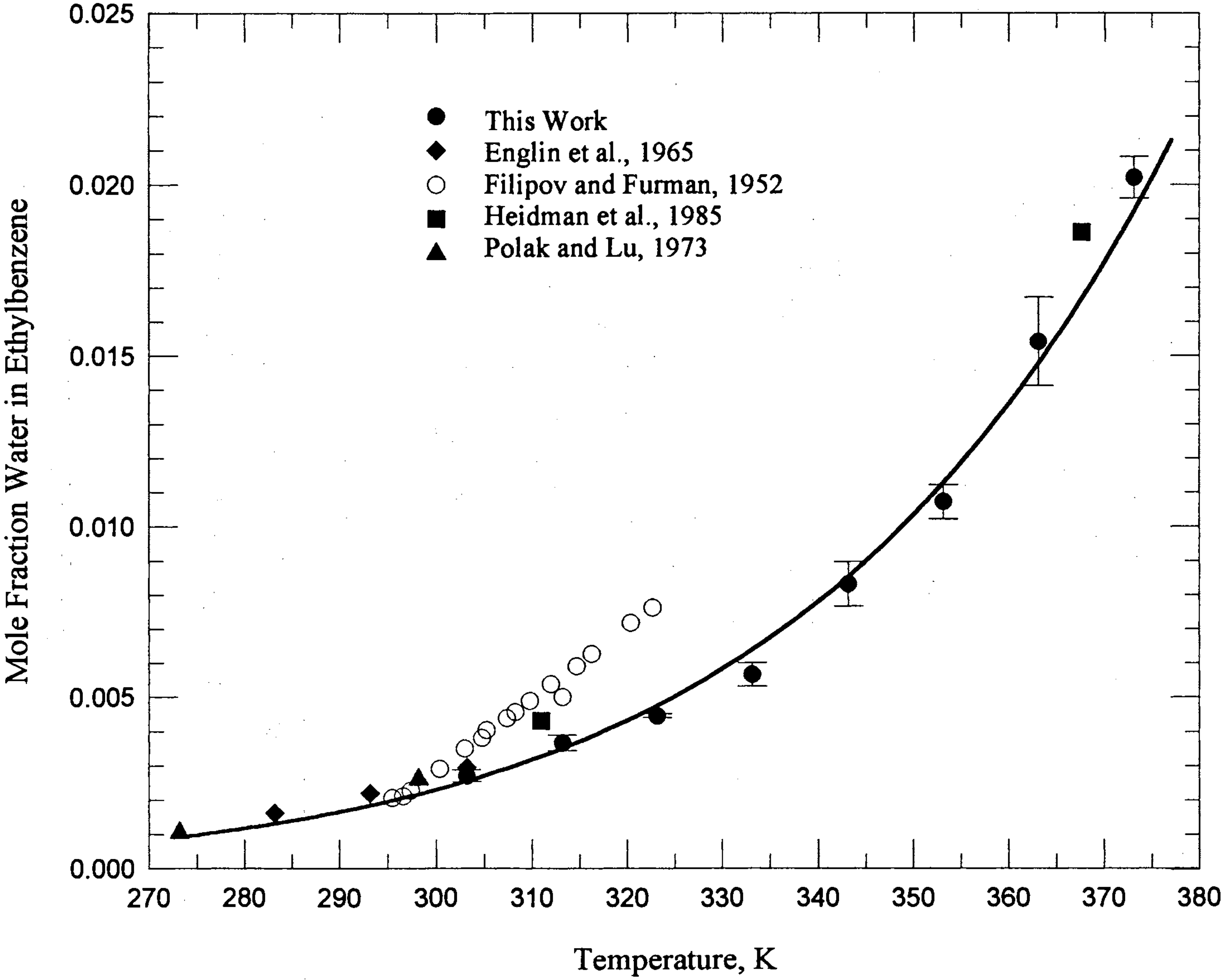

Figure 6. Solubility of Water in Ethylbenzene

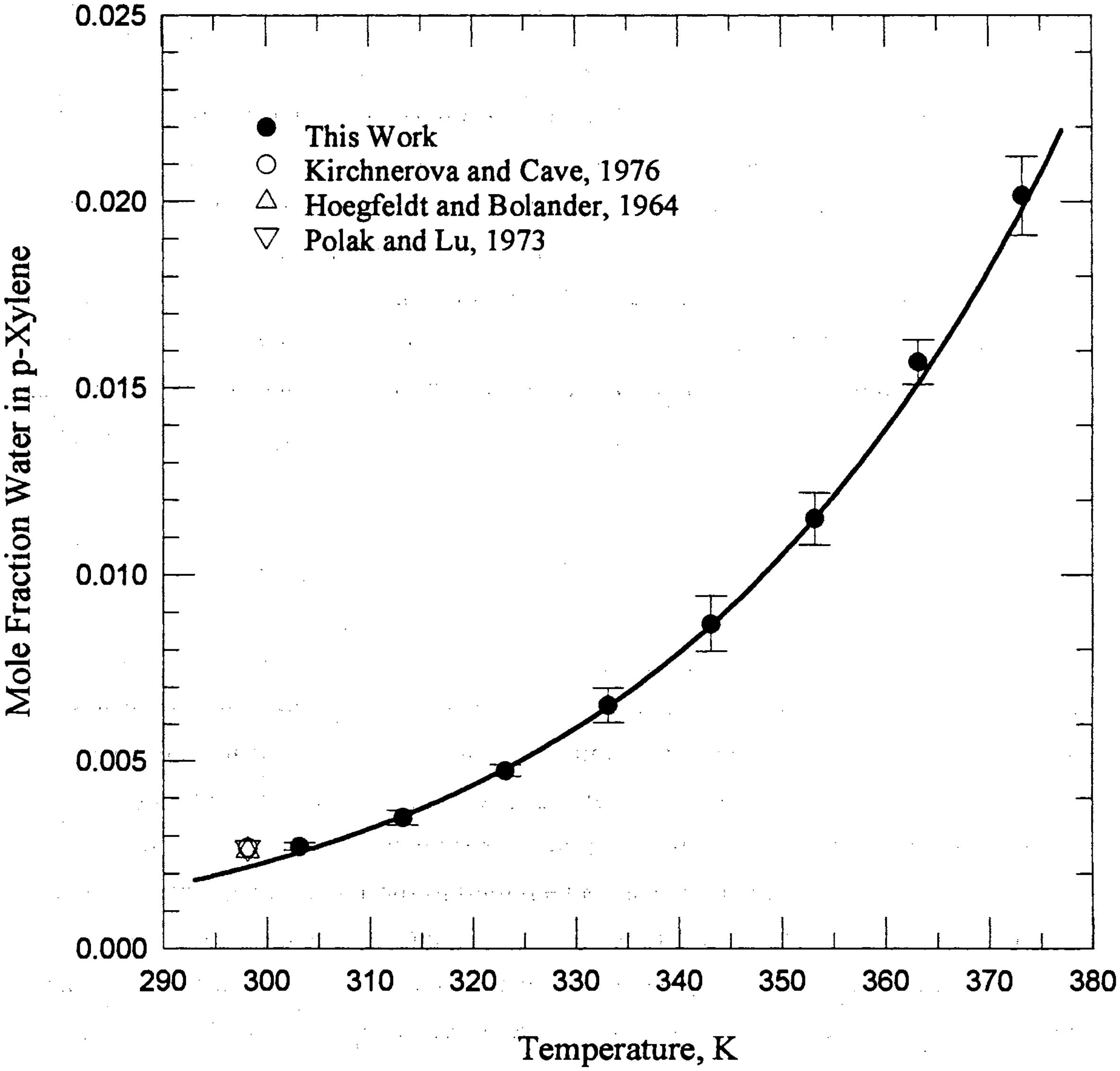

Figure 7. Solubility of Water in p-Xylene

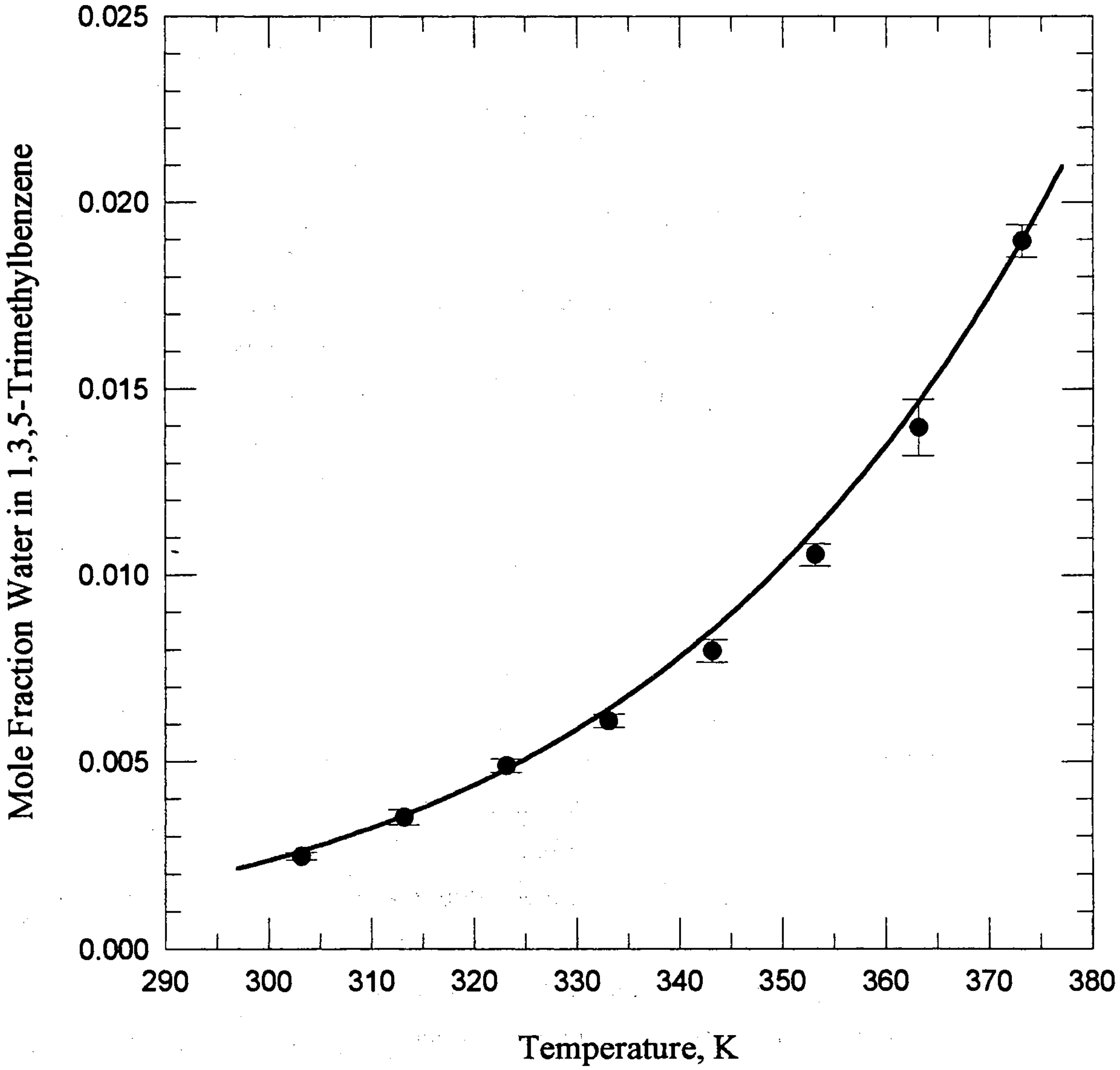

Figure 8. Solubility of Water in 1,3,5-Trimethylbenzene

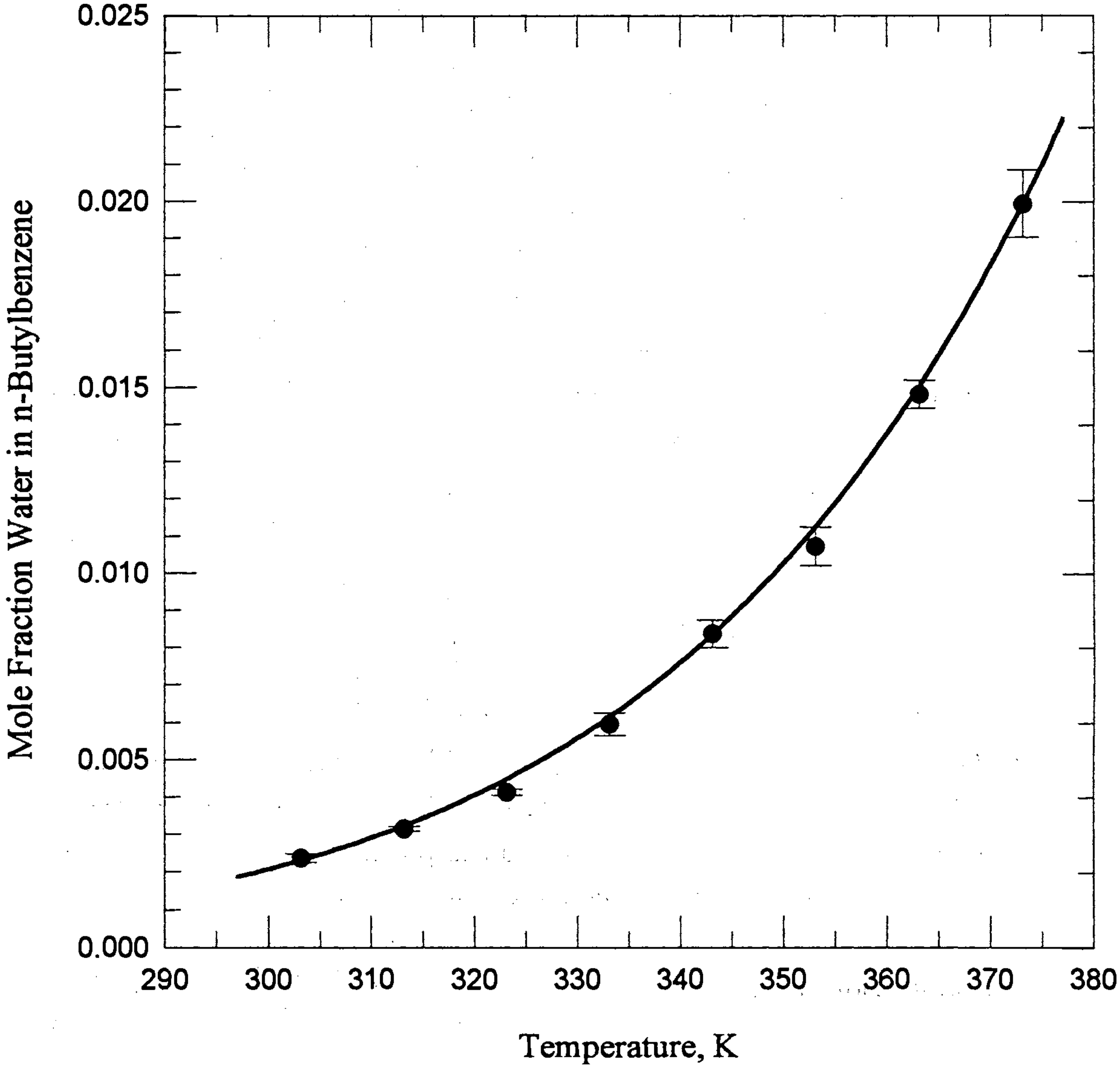

Figure 9. Solubility of Water in n-Butylbenzene

CHAPTER V

EVALUATION OF UNIFAC MODELS FOR REPRESENTING LIQUID-LIQUID EQUILIBRIA OF ALKYLBENZENE-WATER MIXTURES

ABSTRACT

Several variants of UNIFAC (UNIQUAC Functional-group Activity Coefficients) models have been evaluated for their capability to represent liquid-liquid equilibria of alkylbenzene-water systems. These water-hydrocarbon mixtures exhibit large miscibility gaps, and for design purposes, activity-coefficient models must describe mutual solubility behavior in very dilute regions. With temperature-dependent group interaction parameters, a UNIFAC activity coefficient model can correlate mutual solubility data for these systems reasonably well at temperatures above the minimum solubility temperature of the alkylbenzene in water. However, UNIFAC models with parameters derived from large data bases and intended for general application can not be used for calculating liquid-liquid equilibria for these water-hydrocarbon mixtures with an accuracy comparable to experimental data.

INTRODUCTION

The capability to correlate and predict the mutual solubility of hydrocarbon-water systems is important in the design of emission control systems and alternative processes which eliminate or minimize waste water. Aromatic hydrocarbons represent a group of compounds which, in general, pose a threat to human health and the environment at aqueous concentrations in the part per million range. From the environmental viewpoint, the primary focus is on the solubility of hydrocarbons in water. If activity coefficient models are used to describe these systems, they must also capture the thermodynamic behavior of a very nonideal solvent - water.

Group contribution models are particularly attractive for describing fluid phase equilibria. In principle, model parameters can be derived from molecular structure. The thermodynamic properties of a whole class of compounds can be estimated from the experimental measurements of a small number of model systems which contain all of the functional groups of interest. One of the most serious limitations of the approach is the inability to distinguish between isomers without introducing additional parameters to describe molecular structure in more detail. With these advantages and limitation in mind, a brief quantitative assessment of the UNIFAC model (Fredenslund et al., 1975) and several variants was conducted to determine (1) the capability of the method to correlate mutual solubility data for a single group of hydrocarbons, alkylbenzenes, and water mixtures and to extrapolate the results to higher/lower temperatures, and (2) the general applicability of a group contribution approach to describing liquid-liquid equilibria of these systems.

UNIFAC MODELS

The UNIFAC (UNIQUAC Functional-group Activity Coefficients) model developed by Fredenslund et al. (1975) is one of the most popular and successful activity coefficient models based on the group contribution concept. Various modifications have been proposed to improve the accuracy and extend the application range. Fredenslund and Rasmussen (1985), Gmehling (1986), and Fredenslund (1989) presented reviews and pointed out the major limitations of both the model and the numerical aspects of the model parameters fitted from experimental data. We limit ourselves in this discussion to the major modifications directed toward correlating liquid-liquid phase equilibria.

The original UNIFAC model (Fredenslund et al., 1975) does not describe liquid-liquid phase equilibria quantitatively, or in some cases qualitatively. Fredenslund (1989) noted the inability of UNIFAC to quantitatively predict liquid-liquid equilibrium with parameters derived from vapor-liquid equilibrium as a fundamental deficiency of the group-contribution approach. Magnussen et al. (1981) fitted group interaction parameters to available liquid-liquid equilibrium data to obtain UNIFAC parameters tailored to liquid-liquid equilibria. Due to the limited temperature range of the data, the recommended range of application of the Magnussen et al. UNIFAC-LLE model is restricted to the 283 to 313 K range. Subsequently, Gupte and Danner (1987) published a critical evaluation of UNIFAC-LLE using data for binary and ternary systems. They concluded that the model predicted phase compositions for systems not used in parameter development with approximately the same precision as those systems used in development. However the model does not represent phase behavior over small temperature ranges because an additional parameter is required to account for the temperature dependence.

Major modifications over the last decade have focused on the combinatorial contribution to the excess Gibbs free energy and the temperature dependence of the group interaction parameters. The most comprehensive and generally applicable models are UNIFAC-Lyngby (Larsen et al., 1987) and UNIFAC-Dortmund (Weidlich and Gmehling, 1987; Gmehling et al., 1993). Parameters in these models are developed from data bases which included experimental data for vapor-liquid equilibria, liquid-liquid equilibria, enthalpies of mixing, and (for UNIFAC-Dortmund) infinite dilute activity coefficients. The UNIFAC-Lyngby and UNIFAC-Dortmund models are intended for application to a broad range of hydrocarbon and organic mixtures. For liquid-liquid equilibrium, UNIFAC-Lyngby is reported to perform as well as UNIFAC-LLE. The UNIFAC-Dortmund model is claimed to be superior to the UNIFAC-Lyngby formulation, "partly because more reliable γ^{∞} [infinite dilution activity coefficient] results were obtained (Gmehling et al., 1993)." Assessments based on differences between model calculations and data must be interpreted very carefully when the results have been averaged over a large number of data and several classes of systems. Like other models with empirical parameters, there is usually a compromise between generality and accuracy. In any specific application, the real question is whether the balance has been tipped so far in favor of generality that the accuracy is no longer satisfactory for the problem at hand.

To correlate liquid-liquid equilibria specifically for hydrocarbon-water systems, Hooper et al. (1988) adopted the UNIFAC-Lyngby combinatorial expression and introduced an empirical temperature dependence for group interaction parameters. By restricting application to a single thermodynamic property (liquid-liquid equilibria) for a single class of systems (water-hydrocarbon mixtures), they obtained reasonable agreement with experimental data over a wide temperature range and for liquids exhibiting a wide range of mutual solubilities with water. We have narrowed the scope of application even further by focusing on a series of alkylbenzene-water mixtures.

CORRELATION OF ALKYLBENZENE-WATER MUTUAL SOLUBILITIES

The UNIFAC model used in this work is the formulation presented by Hooper et al. (1988) and summarized in the Appendix C. The water-organic group temperature-dependent interaction parameters were fitted to the mutual solubility data reported by Chen and Wagner (1994a, 1994b, 1994c) in the temperature range of 303 to 373 K. The objective function is given as

$$\sum_{n}\sum_{m}\left(\frac{x_{\text{model}} - x_{\text{experimental}}}{x_{\text{experimental}}}\right)^2 \tag{1}$$

where x is the mole fraction of solute and for each of the n measurements of the m binary systems. Following the usual approach in specifying UNIFAC group interactions, we do not distinguish between CH_3-H2O and CH_2-H_2O or $ACCH_3$-H_2O and $ACCH_2$-H2O group interaction parameters. Thus, there were a total of 15 coefficients in Equations 13c and 14c simultaneously fit to a total of 96 experimental data points (8 isotherms for each of 6 binary alkylbenzene-water systems). These parameters are summarized in Table I, together with the parameters recommended by Hooper et al. (1988). The only differences between the UNIFAC correlations presented by Hooper et al. and the one used in this work are the values of the coefficients in Table I.

The empirical nature of UNIFAC models is evident from the coefficients in Table I. Group interaction parameters calculated at three temperatures using the correlations obtained in this work and those of Hooper et al. (1988) are listed in Table II. The values of group interaction parameters are not constrained by either qualitative or quantitative descriptions of molecular or group interactions. Model parameters are very sensitive to the database used in the fitting procedure. As matter fact, parameters can also depend on the initial estimates and the optimization algorithm, since there may be no unique solution to the optimization problem (Prausnitz et al., 1980).

The deviations between experimental and calculated mutual solubilities of the six binary systems used to fit the UNIFAC model parameters are summarized in Tables III and IV. Results corresponding to individual experimental measurements are tabulated in Appendix D. Errors in calculated hydrocarbon solubilities in water demonstrate that the UNIFAC model proposed by Hooper et al., with temperature-dependent parameters developed for liquid-liquid equilibria, represents a significant improvement over the temperature-independent interaction parameter formulation of Magnussen et al. (1981) or the more general UNIFAC-Lyngby (Larsen et al., 1987) and UNIFAC-Dortmund (Weidlich and Gmehling, 1987; Gmehling et al., 1993) models. For these systems, the

UNIFAC-Lyngby model is superior to the UNIFAC-Dortmund, but neither provide satisfactory results.

Tables II, III and IV clearly demonstrate the trade off between generality and accuracy of UNIFAC models for a specific class of mixtures. If the scope of application is restricted to the series of alkylbenzenes, Hooper et al.'s model with group interactions fit to the experimental data of Chen and Wagner (1994a, b, c) can be used to correlate mutual solubilities with deviations of the same magnitude as experimental errors. Results for toluene-water, a representative system, are shown in Figures 1 and 2. As Hooper et al. (1988) pointed out, the UNIFAC framework cannot describe the solubility minimum near room temperature for these systems. Above the minimum solubility temperature, their model using our parameters correlates toluene solubility in water and water solubility in toluene very well. Most of the results for UNIFAC-Lyngby and UNIFAC-Dortmund lie outside the range of Figure 1. The results for the original UNIFAC model (Fredenslund et al., 1975) are included for reference since this model is commonly used in commercial simulation software. The limitation of UNIFAC-LLE is a result of the lack of an additional parameter to incorporate temperature dependence of group-interaction parameters.

To gain some insight into the predictive capability of UNIFAC models in representing liquid-liquid equilibria, the mutual solubilities of the benzene-, toluene-, *p*-xylene and ethylbenzene-water systems were calculated in the high temperature region (373 to ~500 K). Although pressure is neglected in the calculations, the effect of pressure on aqueous solubility of alkylbenzenes is very small (Sawamura, et al., 1989). The results are summarized in Figures 3 through 9 together with the experimental data used by Hooper et. al. (1988) to fit their model parameters.

Figures 3-5 and 7-9 illustrate once again the capability of a UNIFAC model to correlate water-hydrocarbon mutual solubilities if the range of application is restricted to these mixtures, i.e. Hooper et al.'s formulation. Results using the same model with parameters fit to low temperature data (this work) exemplify the capability, and the need for caution, in extrapolating the correlations beyond the temperature range of the database used to determine model parameters. For benzene and toluene our UNIFAC correlations predict higher temperature data very well, but not for ethylbenzene and *p*-xylene.

Results for ethylbenzene, Figures 5 and 9, and *p*-xylene, Figure 6, demonstrate the capability of the UNIFAC group contribution framework to interpolate among components. Hooper et. al (1988) used only four data points in the temperature range of 368 to 536 K for the ethylbenzene-water system. However, low temperature data were available for water-*m*-xylene and other water-alkylbenzene systems to fit water-hydrocarbon group interaction parameters around 273 K. They did not use data for the *p*-xylene-water system; but this system is represented reasonably well (compared to other UNIFAC models) as shown in Figure 6 and Tables II and III. The group-contribution approach is discussed later.

EXCESS PROPERTIES

Excess Gibbs energy, enthalpy and entropy of mixing can provide insight into the effects of molecular structure and size on phase equilibria. These properties can also indicate limitations of activity coefficient models used to represent these thermodynamic quantities. The molar excess Gibbs energy, G^E, can be expressed as

$$G^E = RT\sum x_i \ln \gamma_i \qquad (1)$$

where γ_i is the activity coefficient of component i in solution. For the dilute systems considered here,

$$\gamma_i \approx \frac{1}{x_i} \qquad (2)$$

for the solute, and $\gamma_i \approx 1$ for the solvent. The partial excess Gibbs energy can be approximated as

$$\overline{G}_i^E = RT \ln \frac{1}{x_i} \qquad (3)$$

The excess Gibbs energy for the toluene-water system is plotted as a function of reciprocal temperature in Figures 10 and 11. The experimental values have been estimated using Equation 3; predicted values are calculated using Equation 1 and the model results for γ_i and x_i. From thermodynamics

$$\frac{G^E}{RT} = \frac{H^E}{RT} - \frac{S^E}{R} \qquad (4)$$

where H^E and S^E are the excess enthalpy and entropy of mixing, respectively. The shape of the curves in Figures 10 and 11 indicates the capability of the models to represent the enthalpy and entropy of mixing. With the exception of the model formulation of Hooper et al. (1988), which is also used in this work, none of the UNIFAC models adequately represent H^E or S^E, or both.

Consider the toluene-water system. At the minimum solubility temperature, $H^E = 0$ and $G^E \approx -TS^E$. As the temperature increases, H^E becomes more negative and may take on absolute values which are orders of magnitude larger than G^E. From Equation 4, S^E must also take on large negative values, and large cancellations between H^E and S^E are indicated. Referring to Figure 8 for example, at temperature 363 K, or 0.00227 K^{-1}, the excess Gibbs energy parameter, G^E/RT, of an aqueous solution of toluene is about 0.00215. The slope at this point, H^E/RT, is approximately -4.1 or about three orders of magnitude magnitudes larger than G^E/RT in absolute value. According to Equation 4, $S^E/R = -4.10215$. The cancellations in large absolute values of H^E and S^E tend to mask these properties for relatively small values of G^E. Thus, using empirical models to simultaneously describe G^E, H^E, and S^E is understandably difficult and prone to error, especially when UNIFAC model parameters are fit to vapor-liquid equilibria or G^E information alone. The functionality Gibbs energy is fairly insensitive to vapor-liquid equilibrium data. Enthalpy and liquid-liquid equilibrium actually represent first and second derivatives, respectively, of the Gibbs energy and are very sensitive to inadequacies in excess Gibbs energy expressions (Lafyatis et al., 1989).

GROUP CONTRIBUTION METHODS

The generally poor performance of UNIFAC models in describing alkylbenzene-water mutual solubilities raises the question of whether the phase equilibria of these types of mixtures can be described properly by group contribution methods. Figure 12 shows the effect of molecular structure on partial excess Gibbs free energy of the solute. This figure indicates that the effect of adding a CH3 (or CH2) group is nearly the same regardless of the specific molecular component involved, although the slope is slightly temperature dependent. Thus, an activity coefficient model based on the group contribution concept should be applicable to these systems. The limitations of the UNIFAC model should be then due to inadequacy of the model formulation rather than the group-contribution concept, at least for the systems considered here.

The UNIFAC model is based on the UNIQUAC model, which is known to over-correct for deviations from random mixing (Prausnitz et al., 1986). Therefore, significant modification of the UNIFAC model may appear to be warranted. However, modifications within the current framework may not be fruitful, as evidenced by almost twenty years of continuous efforts along this line. Recent developments in statistical mechanics (Wertheim, 1984a, 1984b, 1986a, 1986b) suggest promising routes to the development of a theoretically sound and mathematically tractable thermodynamic model within the framework of group-contribution method. We are currently working in this direction.

SUMMARY

UNIFAC and it variants have been evaluated for their capability to represent the mutual solubility of alkylbenzene-water systems. A UNIFAC activity coefficient with temperature dependent group interaction parameters can correlate these with deviation on the order of experimental errors. As the range of application is broadened by expanding the database use to fit model parameters to other types of systems, model performance deteriorates. The user must carefully evaluate the tradeoffs between generality and accuracy for the systems of interest. The UNIFAC correlation framework can be used to interpolate mutual solubility among alkylbenzene-water mixtures, provided the model parameters are fit to this class of mixtures. Due to the empirical nature of model parameters, the type of data selected to fit model parameters must be critically evaluated in terms of the intended application. This is particularly important in calculating Gibbs free energy and enthalpy and entropy of mixing. Group-contribution methods should be capable of describing the systems considered here, at least in principle. To attain generality for broad classes of mixtures alternative thermodynamic correlation frameworks are required.

NOMENCLATURE

$a_{nm,1}$	UNIFAC group interaction parameter between groups *n* and *m* (K)
$a_{nm,2}$	UNIFAC group interaction parameter between groups *n* and *m*
$a_{nm,3}$	UNIFAC group interaction parameter between groups *n* and *m* (K^{-1})
G^E	molar excess Gibbs free energy
$\overline{G}^E$	partial molal excess Gibbs free energy
H	molar enthalpy
H^E	molar excess enthalpy of mixing
q_i	relative van der Waals surface area of component *i*
Q_k	relative van der Waals surface area of subgroup *k*
r_i	relative van der Waals volume of component *i*
R_k	relative van der Waals volume of subgroup *k*
S	molar entropy
S^E	molar excess entropy of mixing
T	absolute temperature, K
x_i	mole fraction of component *i* in the liquid phase
X_m	group mole fraction of group *m* in the liquid phase

$\Gamma_k^{(i)}$	group activity coefficient of group *k* in the pure component *i*
Γ_k	group activity coefficient *k* in the mixture
γ_i	activity coefficient of component *i*
Θ_m	surface fraction of group m in the liquid phase
$\gamma_k^{(i)}$	number of structural groups of type *k* in molecule *i*
Ψ_{nm}	UNIFAC group interaction parameter between groups *n* and *m*

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Table I. Coefficients for Temperature-Dependent Water(1)-Hydrocarbon Group(j) Interaction Parameters a_{1j} and a_{j1}: Hooper et al. (1988) / This Work

	m		
	CH3	ACCH3	ACH
$a_{1m}^{(0)}$	-40.72 / -2157.1	-50.19 / -790.32	-39.04 / -707.03
$a_{1m}^{(1)}$	3.286 / 16.558	3.673 / 7.7489	3.928 / 7.6957
$a_{1m}^{(2)}$	-0.004110 / -0.024912	-0.005061 / -0.010412	-0.004370 / -0.0094561
$a_{m1}^{(0)}$	3060.6 / 3115.6	2143.9 / 2265.2	2026.5 / 2080.0
$a_{m1}^{(1)}$	-5.374 / -5.3298	-3.076 / -3.3594	-3.267 / -3.4397

Table II. Water(1)-Hydrocarbon(m) Interaction Paramerers

		This Work			Hooper et al (1988)		
	Temp., K	CH3	ACCH3	ACH	CH3	ACCH3	ACH
$a_{1,m}$	273	506	549	1393	550	575	707
	373	553	6516	2163	613	615	818
	473	101	5454	2933	594	554	841
$a_{m,1}$	273	1660	1348	114	1593	1304	1134
	373	1127	1012	796	1056	996	807
	473	594	676	453	518	688	481

Table III. Average Errors Between Experimental and Calculated Alkylbenzene Solubility in Water

System (Chen and Wagner, 1994a, 1994b, 1994c)	This Work		Hooper et al., 1988		Magnussen et al., 1981		UNIFAC (Lyngby)		UNIFAC (Dortmund)	
	Bias %	AAD %	Bias %	AAD %	Bias %	AAD %	Bias %	AAD %	Bias %	AAD %
Benzene	-1.73	3.41	14.0	12.7	4.82	6.03	-0.33	9.93	61.7	55.5
Toluene	4.11	4.20	29.2	26.5	35.1	32.6	-27.9	34.5	60.9	55.3
Ethylbenzene	15.4	14.1	15.9	17.6	31.3	28.7	11.4	18.7	79.5	69.8
p-Xylene	10.7	9.85	45.1	39.3	91.2	82.5	-47.0	54.0	62.7	55.3
1,3,5-Trimethylbenzene	-3.55	3.44	34.7	30.0	135.	121.	-66.8	72.3	37.0	33.1
n-Butylbenzene	-1.87	3.76	-60.2	61.5	42.9	39.6	40.6	50.7	91.2	74.8

$$\text{Bias}\,\% = 100\frac{\sum_{n}\left(x_{calc}-x_{\exp}\right)/x_{\exp}}{n}; \qquad \text{AAD}\,\% = 100\frac{\sum_{n}\left|x_{calc}-x_{\exp}\right|/x_{\exp}}{n}.$$

Table IV. Average Errors Between Experimental and Calculated Water Solubility in Alkylbenzene

System (Chen and Wagner, 1994a, 1994b, 1994c)	This Work		Hooper et al (1988)		UNIFAC-LLE		UNIFAC-Lyngby		UNIFAC-Dortmund	
	Bias %	AAD %	Bias %	AAD %	Bias %	AAD %	Bias %	AAD %	Bias %	AAD %
Benzene	1.84	2.77	0.87	3.26	-49.1	44.2	9.85	6.86	173	133
Toluene	12.3	8.98	15.3	11.4	-52.3	43.7	61.5	42.2	144	110
Ethylbenzene	16.8	10.8	18.7	12.5	-38.1	35.7	36.9	25.2	267	201
p-Xylene	107	180	235	307	-37.1	59.4	235	307	182	242
1,3,5-Trimethylbenzene	4.79	3.54	14.1	9.47	-83.1	71.6	118	81.2	66.3	51.1
n-Butylbenzene	4.95	3.10	8.39	5.04	-37.2	34.8	5.48	3.58	324	234

$$\text{Bias \%} = 100\frac{\sum_{n}\left(x_{calc}-x_{\exp}\right)/x_{\exp}}{n}; \qquad \text{AAD \%} = 100\frac{\sum_{n}\left|x_{calc}-x_{\exp}\right|/x_{\exp}}{n}$$

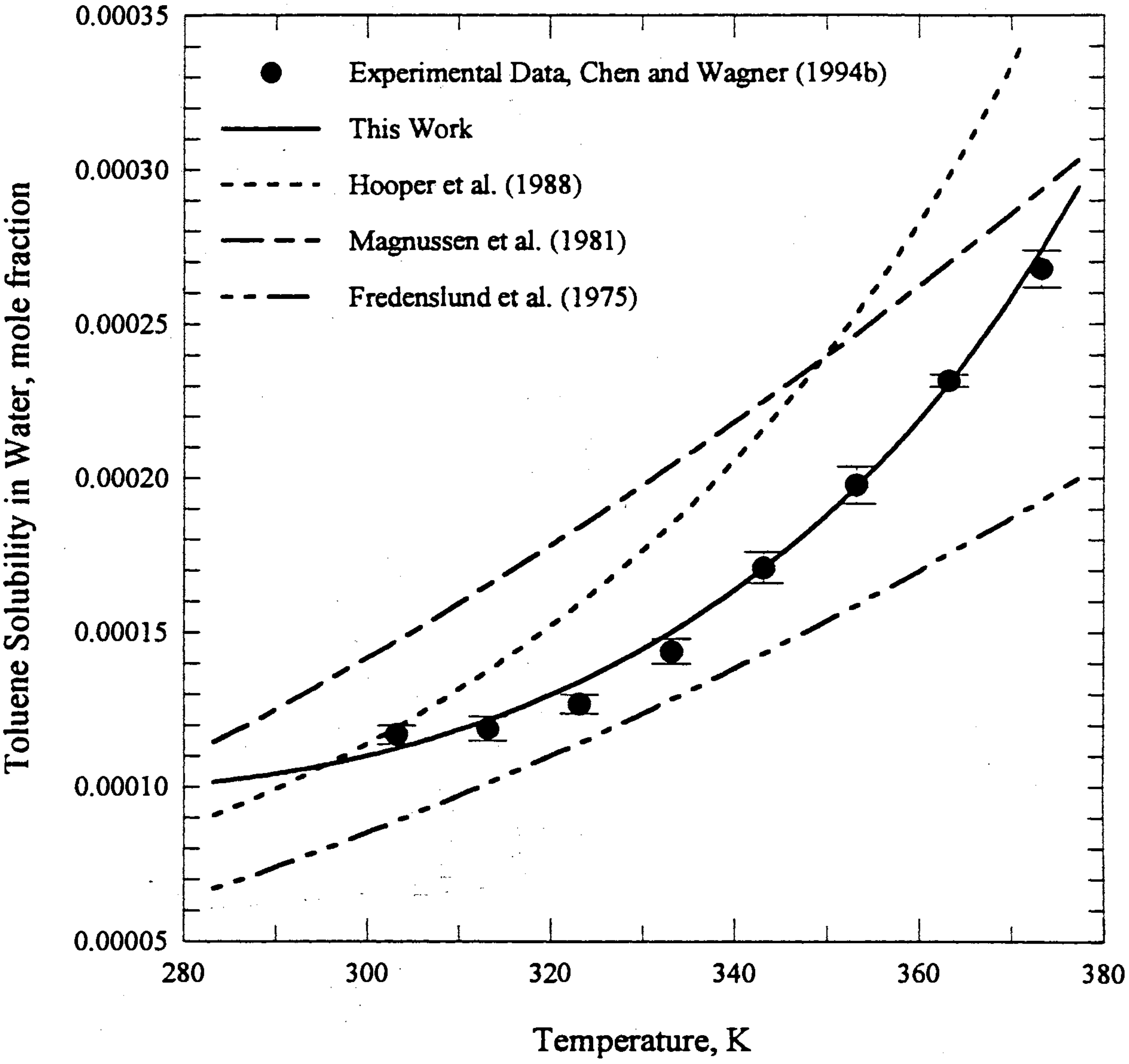

Figure 1. Toluene Solubility in Water: Low Temperature Range

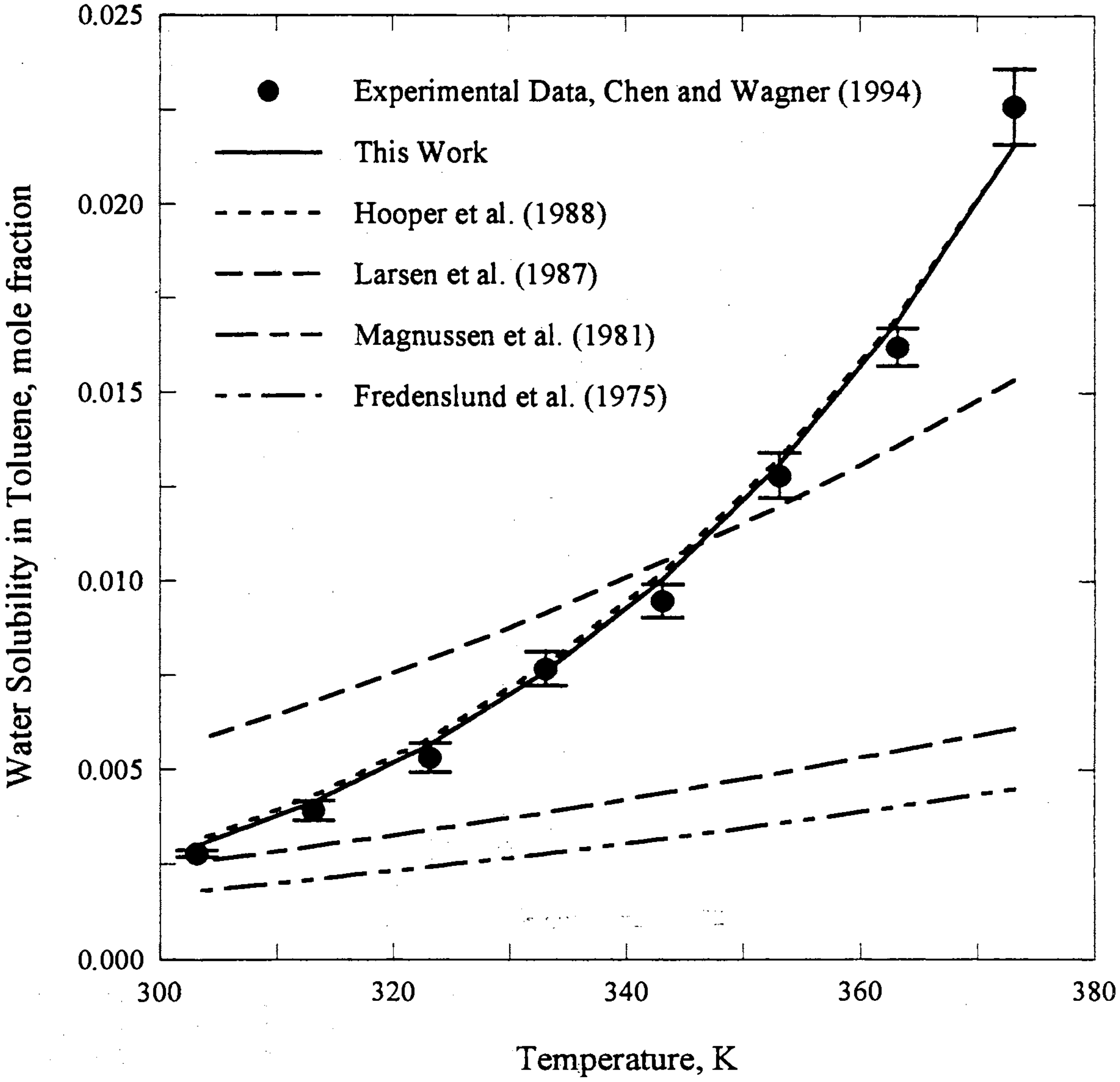

Figure 2. Water Solubility in Toluene: Low-Temperature Range

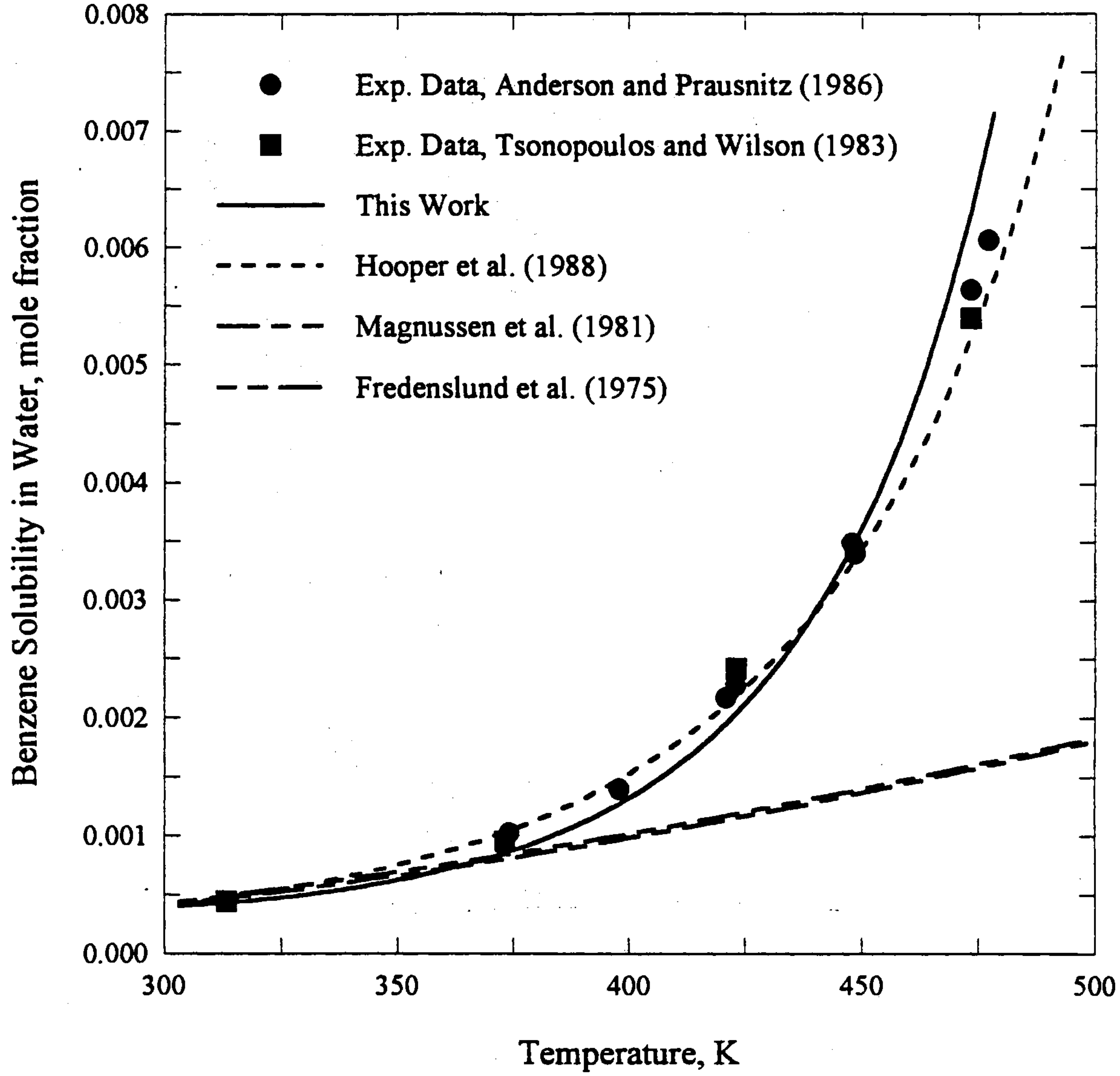

Figure 3. Benzene Solubility in Water: High-Temperature Range

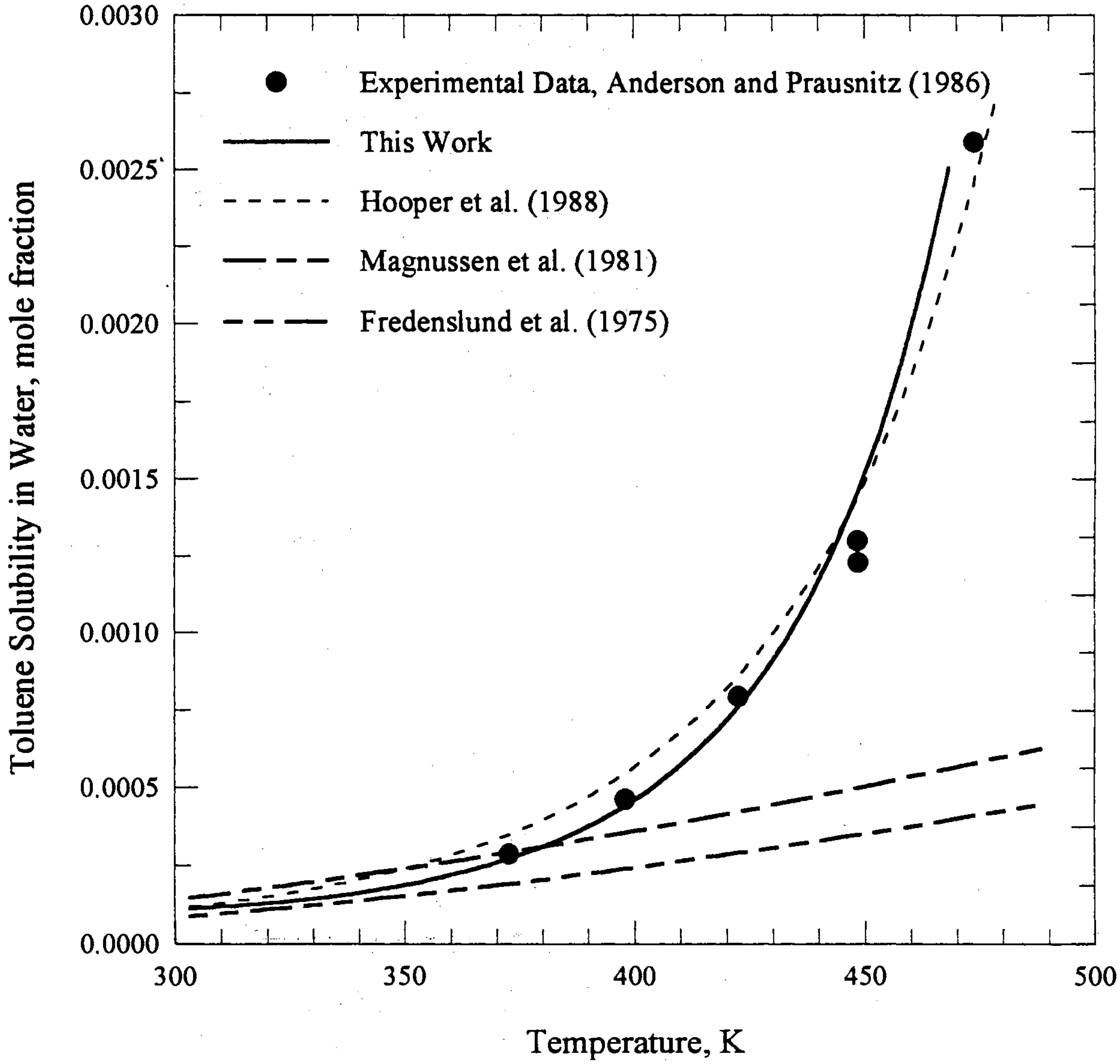

Figure 4. Toluene Solubility in Water: High Temperature Range

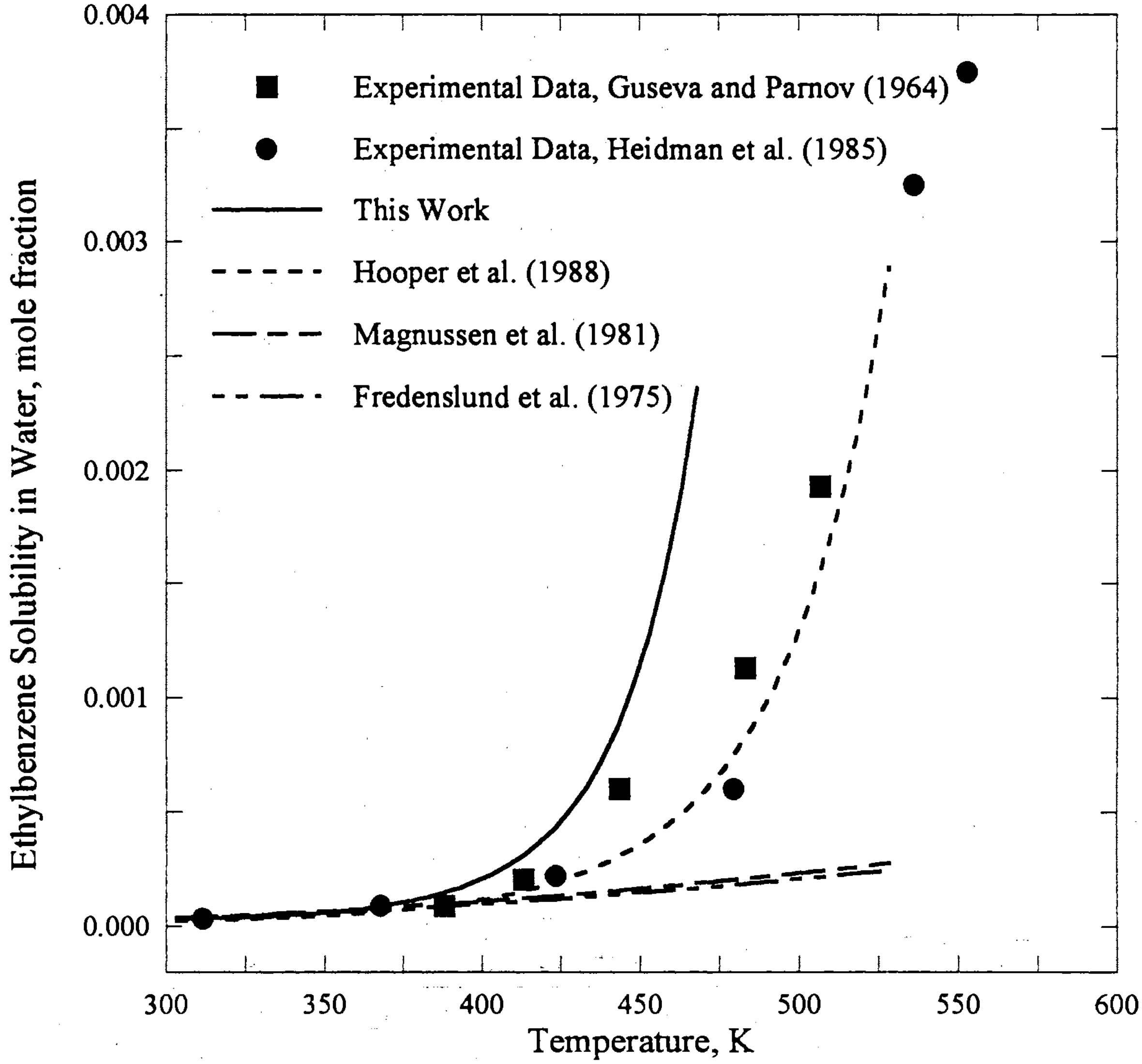

Figure 5. Ethylbenzene Solubility in Water: High-Temperature Range

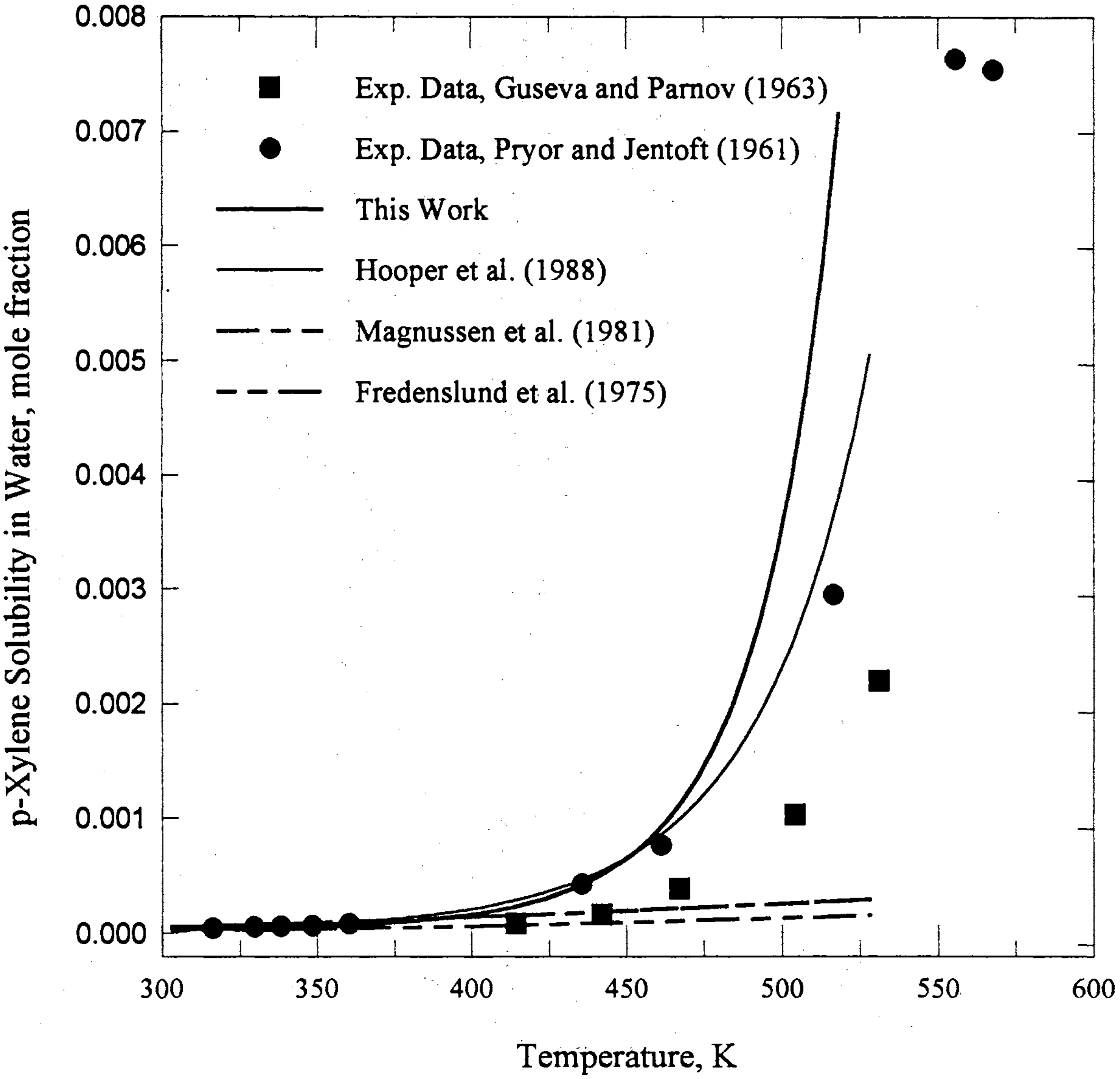

Figure 6. p-Xylene Solubility in Water: High-Temperature Range

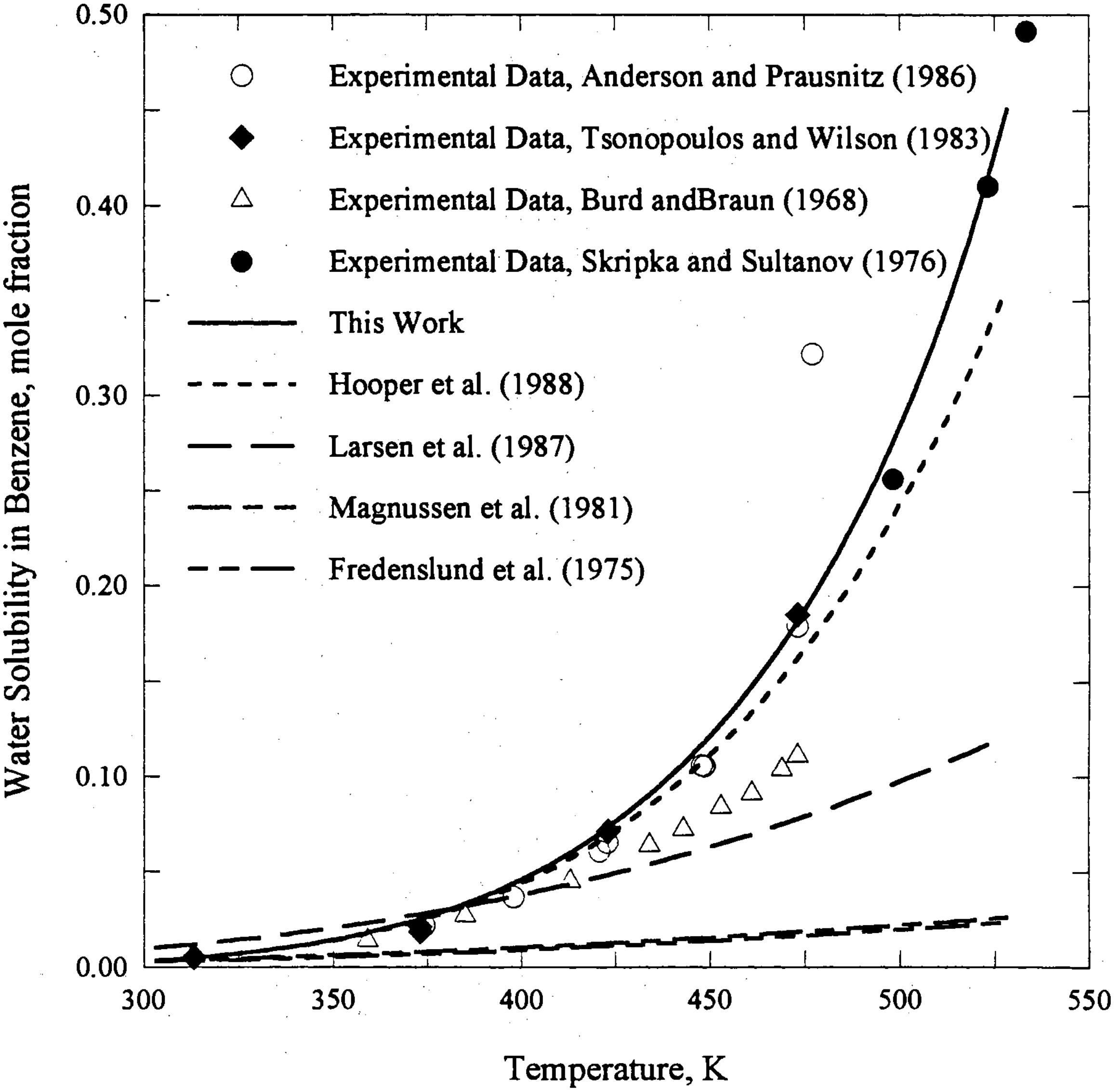

Figure 7. Water Solubility in Benzene: High-Temperature Range

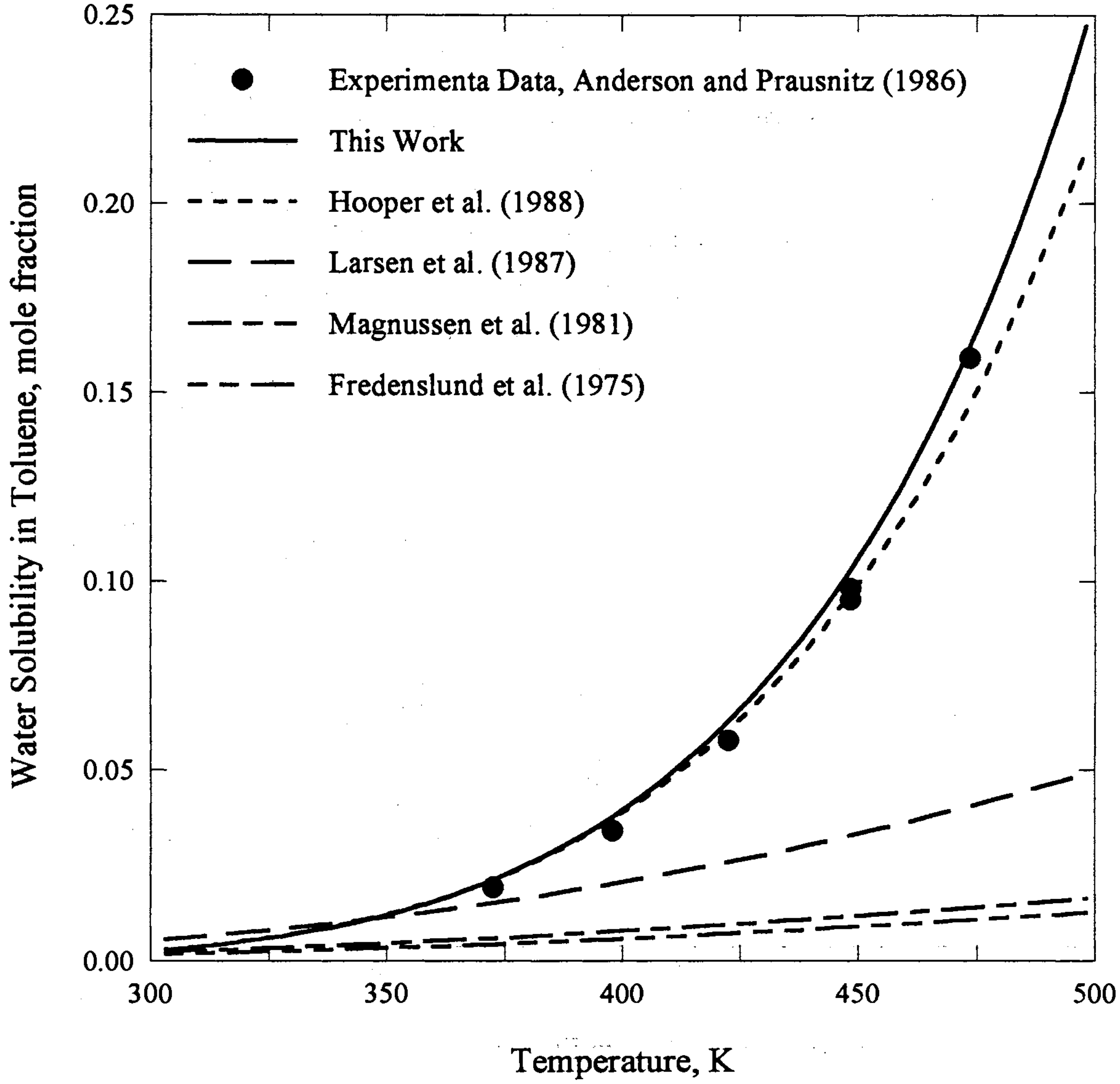

Figure 8. Water Solubility in Toluene: High-Temperature Range

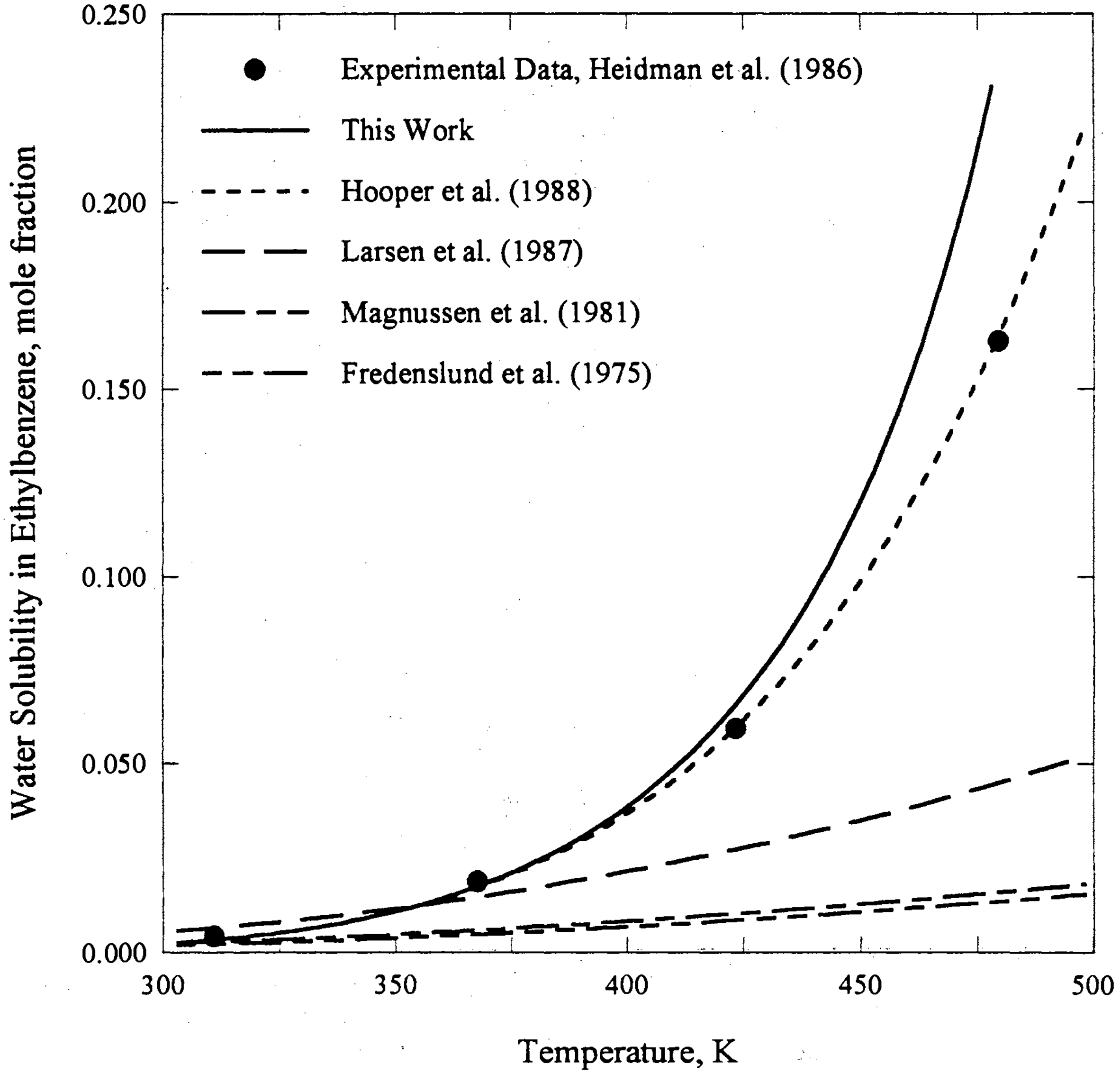

Figure 9. Water Solubility in Ethylbenzene: High-Temperature Range

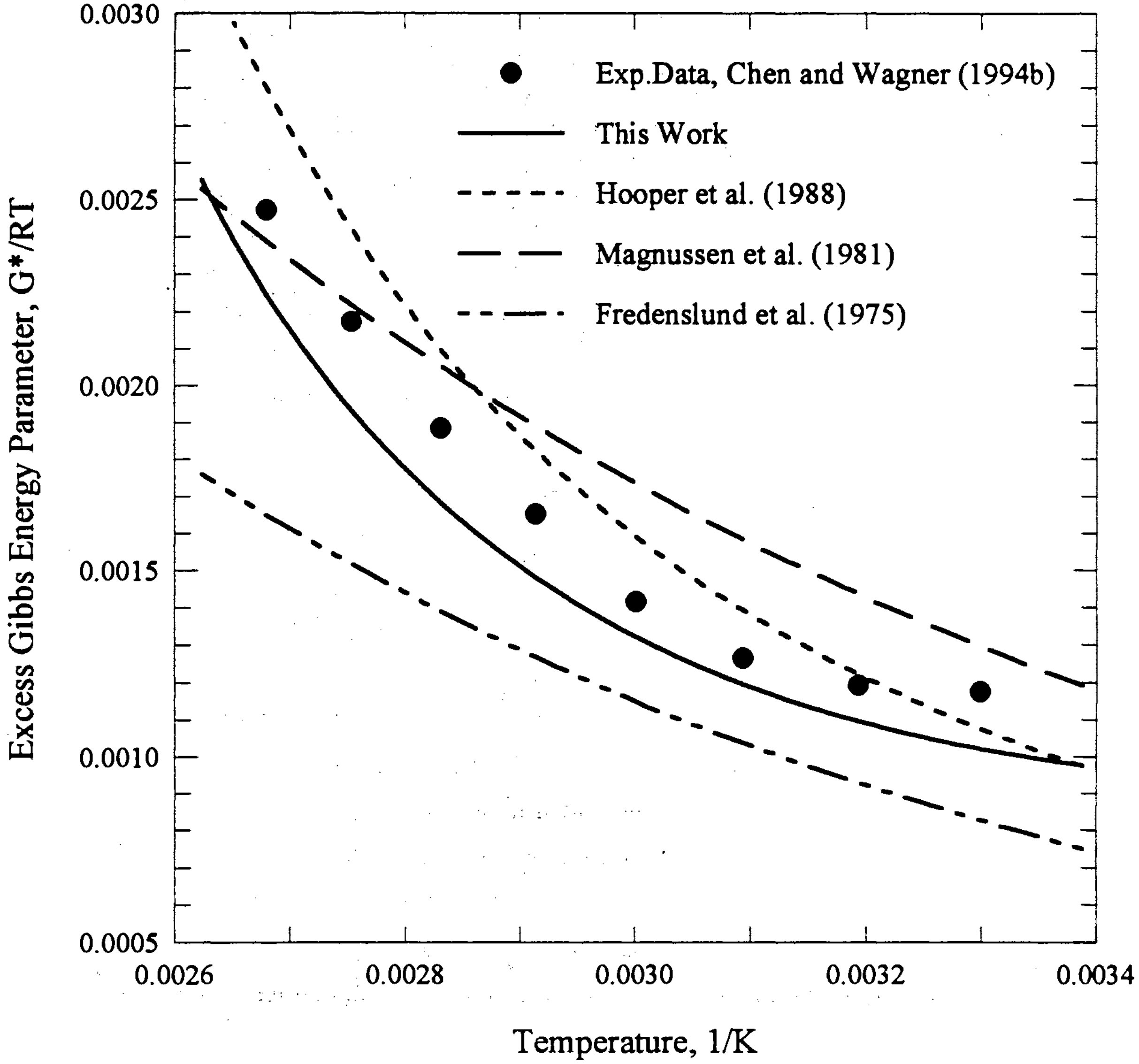

Figure 10. Excess Gibbs Energy of Toluene Saturated Water

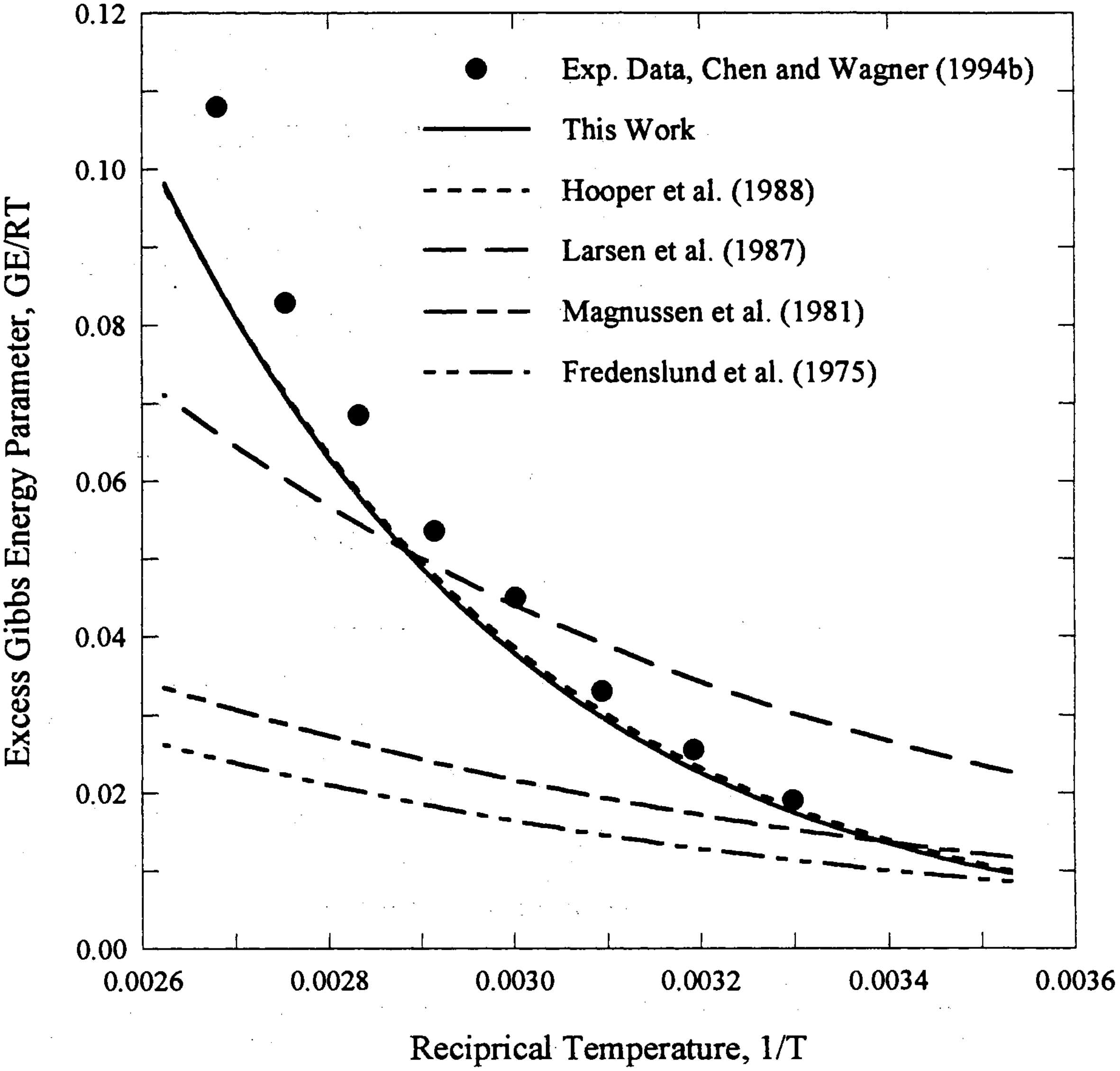

Figure 11. Excess Gibbs Energy of Water Saturated Toluene

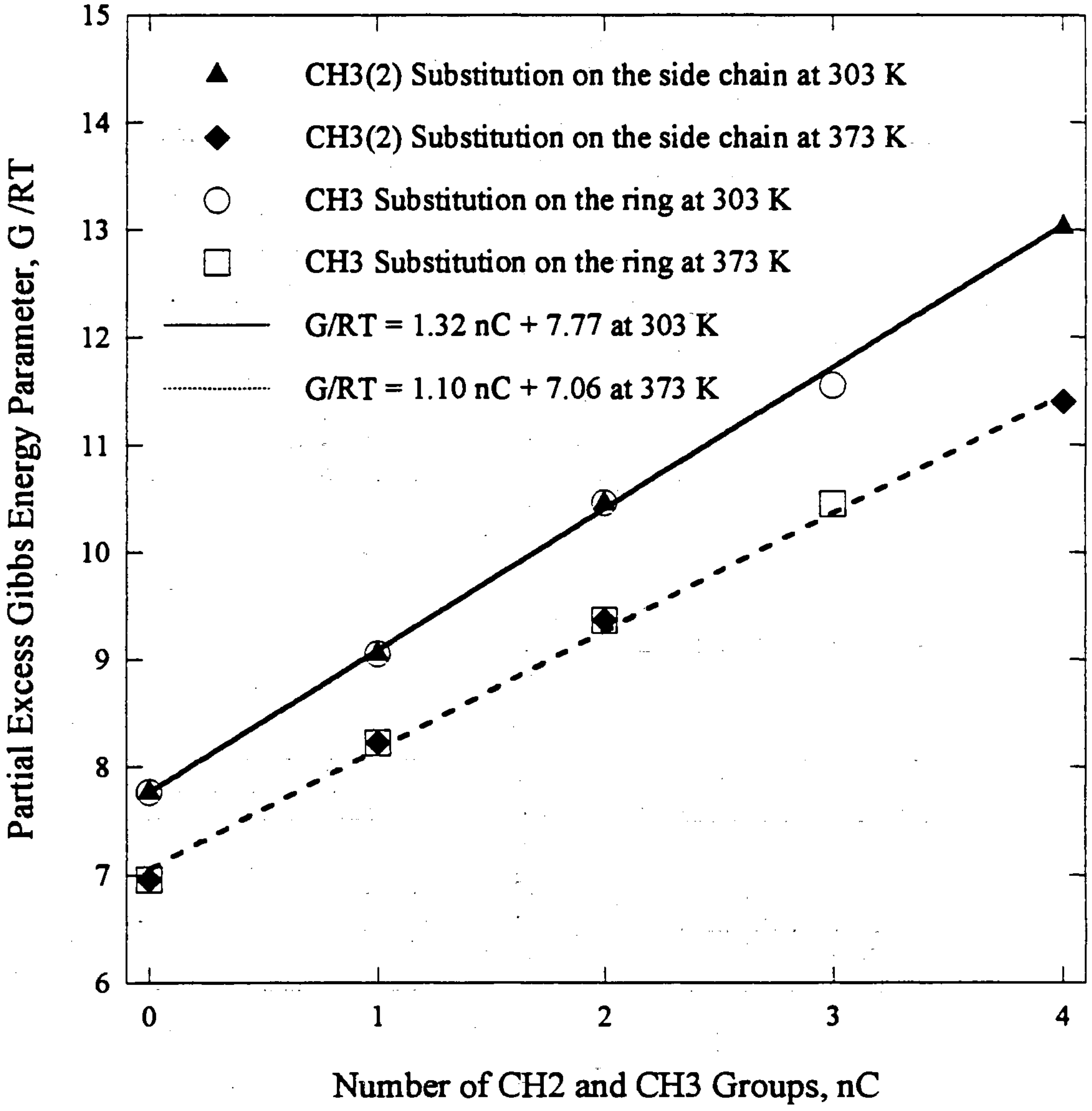

Figure 12. Effect of Molecular Structure on Partial Excess Gibbs Energy of Alkylbenzene Saturated Water

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

To summarize the work accomplished in this research, following conclusions can be made:

1. A continuous flow type liquid-liquid equilibrium apparatus has been designed, constructed and operated to measure the mutual solubility of alkylbenzene-water systems. Because large samples can be collected during equilibrium operation of the unit, it is especially attractive for the solubility measurements of the systems exhibiting very low liquid-liquid mutual solubility.

2. An accurate, efficient and reliable gas chromatographic method has been developed to perform solubility analysis in the very low analyte concentration range of either water in organic solvents or organic solvent in water. The method developed in this work minimizes the use of sophisticated analytical instrumentation, which makes it well suitable for routine analysis.

3. The mutual solubility of alkylbenzene and water has been measured in the temperature region 303-373K with good quality. The mutual solubility measured in this work can serve a basis for the technological development of refinery waste water processing. It also can be used in future theoretical development on the solubility behavior of hydrocarbon in water and its relationship with toxicity of the water solution containing these hydrocarbons on a molecular level.

4. The original UNIFAC as well as it major variants have been evaluated for their capability to represent the mutual solubility of alkylbenzene-water mixtures. A UNIFAC activity coefficient model with temperature dependent group interaction parameters can correlate these data with the deviations on the order of experimental error. As the range of application is broadened by expanding the data base used to model parameters to other types of systems, model performance deteriorates. The UNIFAC correlation framework can be used to interpolate mutual solubility among alkylbenzene-water mixtures, provided the model parameters are fit to this class of mixtures.

Since this work represents the beginning of a systematic research program on the waste water treatment, much work lies ahead. It is the author opinion that following works should be conducted to achieve the ultimate goal of successful treatment of waste water.

1. The liquid-liquid equilibrium unit should be modified to extend it to wider temperature and pressure operation range.
2. The analytical method needs further improvement. One may need to substitute the packed column with capillary column to enhance the separation power of the gas chromatographic method. One may need also looking for the possibility of on-column concentration technique, which can greatly reduce the uncertainty caused by sampling.
3. The possibility of using HPLC (High Performance Liquid Chromatography) technique in the analysis of aqueous hydrocarbon solution should be investigated.
4. More binary hydrocarbon and water mixtures should be investigated for their liquid-liquid mutual solubility behavior with respect to their individual molecular structure.
5. Some multicomponent aqueous liquid-liquid equilibrium measurements will be valuable to provide a solid base for technical development of the refinery waste water treatment and theoretical model development.
6. Since the process waste water usually contains some ionic species, and ionic specie usually tends to salt out the organic components from the aqueous solution, there will be of interest to investigate the liquid-liquid mutual solubility of hydrocarbon-water mixtures in the presence of the ionic species.
7. Future work should also include search for or develop of a thermodynamic model capable of treating aqueous solution with a sound theoretical basis and yet tractable mathematics.

APPENDIX A

RAW EXPERIMENTAL DATA

TABLE A1 BENZENE SOLUBILITY IN WATER (MOLE FRACTION)

T (K)	P (BAR)	# 1	# 2	# 3	# 4	# 5	# 6
303.15	1.0	4.43E-4	4.46E-4	4.29E-4	4.01E-4	3.97E-4	4.29E-4
313.15	1.0	4.33E-4	5.00E-4	4.78E-4	4.67E-4	4.35E-4	4.69E-4
323.15	1.0	5.57E-4	5.60E-4	5.18E-4	5.00E-4	4.44E-4	4.78E-4
333.15	1.5	6.16E-4	6.02E-4	5.29E-4	5.77E-4	5.31E-4	5.32E-4
343.15	2.5	5.55E-4	6.07E-4	6.58E-4	6.19E-4	6.67E-4	6.44E-4
353.15	2.5	6.98E-4	6.85E-4	7.12E-4	7.23E-4	6.76E-4	7.01E-4
363.15	3.5	8.54E-4	7.94E-4	8.34E-4	7.73E-4	7.85E-4	7.60E-4
373.15	3.5	9.71E-4	9.10E-4	9.58E-4	9.78E-4	9.55E-4	9.25E-4

TABLE A2 WATER SOLUBILITY IN BENZENE (MOLE FRACTION)

T (K)	P (BAR)	# 1	# 2	# 3	# 4	# 5	# 6
303.15	1.0	3.83E-3	3.82E-3	3.84E-3	3.81E-3	3.85E-3	3.82E-3
313.15	1.0	4.79-E3	4.49E-3	4.70E-3	4.83E-3	4.87E-3	4.70E-3
323.15	1.0	7.18E-3	6.84E-3	7.40E-3	7.10E-3	7.74E-3	7.14E-3
333.15	1.5	9.32E-3	9.02E-3	8.81E-3	9.32E-3	9.32E-3	9.06E-3
343.15	2.5	1.22E-2	1.20E-2	1.22E-2	1.27E-2	1.22E-2	1.23E-2
353.15	2.5	1.51E-2	1.51E-2	1.54E-2	1.52E-2	1.59E-2	1.53E-2
363.15	3.5	2.10E-2	2.03E-2	2.05E-2	2.05E-2	2.11E-2	2.06E-2
373.15	3.5	2.67E-2	2.65E-2	2.69E-2	2.64E-2	2.65E-2	2.66E-2

TABLE A3 TOLUENE SOLUBILITY IN WATER (MOLE FRACTION)

T (K)	P (BAR)	# 1	# 2	# 3	# 4	# 5	# 6
303.15	1.0	1.12E-4	1.15E-4	1.18E-4	1.18E-4	1.19E-4	1.19E-4
313.15	1.0	1.12E-4	1.19E-4	1.23E-4	1.20E-4	1.20E-4	1.20E-4
323.15	1.0	1.24E-4	1.24E-4	1.24E-4	1.29E-4	1.31E-4	1.30E-4
333.15	1.5	1.41E-4	1.39E-4	1.49E-4	1.43E-4	1.46E-4	9.69E-5
343.15	2.5	1.60E-4	1.73E-4	1.74E-4	1.72E-4	1.75E-4	--------
353.15	2.5	1.94E-4	2.07E-4	2.00E-4	2.01E-4	1.90E-4	--------
363.15	3.5	2.34E-4	2.32E-4	2.34E-4	2.28E-4	2.33E-4	--------
373.15	3.5	2.57E-4	2.72E-4	2.70E-4	2.69E-4	2.73E-4	--------

TABLE A4 WATER SOLUBILITY IN TOLUENE (MOLE FRACTION)

T (K)	P (BAR)	# 1	# 2	# 3	# 4	# 5	# 6
303.15	1.0	2.72E-3	2.66E-3	2.81E-3	2.98E-3	3.12E-3	3.14E-3
313.15	1.0	4.21E-3	4.09E-3	4.09E-3	4.25E-3	4.13E-3	4.21E-3
323.15	1.0	5.23E-3	5.52E-3	5.27E-3	5.17E-3	5.21E-3	5.74E-3
333.15	1.5	7.20E-3	6.68E-3	6.87E-3	7.47E-3	7.26E-3	7.21E-3
343.15	2.5	9.24E-3	9.67E-3	8.73E-3	1.00E-2	7.97E-3	7.91E-3
353.15	2.5	1.34E-2	1.25E-2	1.32E-2	1.17E-2	1.32E-2	--------
363.15	3.5	1.69E-2	1.66E-2	1.60E-2	1.56E-2	1.58E-2	--------
373.15	3.5	2.17E-2	2.39E-2	2.12E-2	2.27E-2	2.34E-2	--------

TABLE A5 ETHYLBENZENE SOLUBILITY IN WATER (MOLE FRACTION)

T (K)	P (BAR)	# 1	# 2	# 3	# 4	# 5	# 6
303.15	1.4	2.82E-5	2.86E-5	2.95E-5	2.87E-5	2.90E-5	2.85E-5
313.15	1.4	2.88E-5	2.89E-5	2.95E-5	2.95E-5	--------	--------
323.15	1.4	3.38E-5	3.15E-5	3.41E-5	3.40E-5	3.42E-5	3.37E-5
333.15	1.4	4.51E-5	4.09E-5	3.93E-5	3.92E-5	3.89E-5	--------
343.15	1.4	5.04E-5	4.89E-5	4.50E-5	5.15E-5	4.97E-5	5.05E-5
353.15	1.4	6.14E-5	5.87E-5	6.60E-5	6.20E-5	6.39E-5	6.34E-5
363.15	1.7	6.19E-5	6.77E-5	6.81E-5	6.86E-5	7.10E-5	7.21E-5
373.15	2.2	7.85E-5	8.92E-5	8.80E-5	8.64E-5	8.59E-5	8.45E-5

TABLE A6 WATER SOLUBILITY IN ETHYLBENZENE (MOLE FRACTION)

T (K)	P (BAR)	# 1	# 2	# 3	# 4	# 5	# 6
303.15	1.4	2.86E-3	3.03E-3	2.59E-3	2.55E-3	2.63E-3	2.58E-3
313.15	1.4	3.97E-3	3.96E-3	3.43E-3	3.52E-3	3.66E-3	3.42E-3
323.15	1.4	5.12E-3	4.46E-3	4.45E-3	4.45E-3	4.37E-3	4.54E-3
333.15	1.4	5.54E-3	5.79E-3	5.54E-3	6.25E-3	5.77E-3	5.47E-3
343.15	1.4	7.70E-3	7.97E-3	7.74E-3	8.71E-3	9.41E-3	--------
353.15	1.4	1.11E-2	1.01E-2	1.13E-2	1.07E-2	1.02E-2	--------
363.15	1.7	1.45E-2	1.69E-2	1.72E-2	1.44E-2	1.40E-2	--------
373.15	2.2	1.96E-2	2.14E-2	2.00E-2	1.96E-2	2.07E-2	1.99E-2

TABLE A7 P-XYLENE SOLUBILITY IN WATER (MOLE FRACTION)

T (K)	P (BAR)	# 1	# 2	# 3	# 4	# 5	# 6
303.15	1.4	2.86E-5	2.95E-5	2.91E-5	2.83E-5	2.77E-5	--------
313.15	1.4	2.98E-5	3.03E-5	3.40E-5	3.29E-5	3.24E-5	3.15E-5
323.15	1.4	3.39E-5	3.60E-5	3.42E-5	3.38E-5	3.42E-5	3.42E-5
333.15	1.4	4.01E-5	4.04E-5	4.07E-5	3.98E-5	3.99E-5	4.14E-5
343.15	1.4	4.77E-5	4.75E-5	4.87E-5	4.81E-5	4.84E-5	4.93E-5
353.15	1.4	5.70E-5	5.80E-5	5.57E-5	5.69E-5	5.78E-5	5.74E-5
363.15	1.7	6.75E-5	6.77E-5	6.80E-5	6.74E-5	6.56E-5	6.56E-5
373.15	2.0	8.98E-5	9.11E-5	8.61E-5	8.60E-5	8.63E-5	8.50E-5

TABLE A8 WATER SOLUBILITY IN P-XYLENE (MOLE FRACTION)

T (K)	P (BAR)	# 1	# 2	# 3	# 4	# 5	# 6
303.15	1.4	2.79E-3	2.55E-3	2.75E-3	2.76E-3	--------	--------
313.15	1.4	3.53E-3	3.38E-3	3.23E-3	3.77E-3	--------	--------
323.15	1.4	4.78E-3	4.50E-3	4.94E-3	4.77E-3	--------	--------
333.15	1.4	5.85E-3	6.37E-3	7.13E-3	6.70E-3	--------	--------
343.15	1.4	8.14E-3	8.41E-3	8.65E-3	9.93E-3	7.69E-3	9.35E-3
353.15	1.4	1.23E-2	1.12E-2	1.57E-2	1.06E-2	1.10E-2	1.24E-2
363.15	1.7	1.50E-2	1.58E-2	1.47E-2	1.65E-2	1.62E-2	1.59E-2
373.15	2.0	1.81E-2	1.98E-2	2.03E-2	2.15E-2	2.06E-2	2.07E-2

TABLE A9 1,3,5-TRIMETHYLBENZENE SOLUBILITY IN WATER (MOLE FRACTION)

T (K)	P (BAR)	# 1	# 2	# 3	# 4	# 5	# 6
303.15	1.4	1.03E-5	9.94E-6	9.13E-6	9.04E-6	9.24E-6	1.01E-5
313.15	1.4	9.28E-6	1.10E-5	1.11E-5	8.91E-6	1.01E-5	9.62E-6
323.15	1.4	8.96E-6	8.97E-6	8.02E-6	8.72E-6	1.06E-5	1.05E-5
333.15	1.4	1.59E-5	1.32E-5	1.60E-5	1.40E-5	1.50E-5	1.99E-5
343.15	1.4	1.84E-5	1.81E-5	1.96E-5	1.71E-5	1.70E-5	1.82E-5
353.15	1.4	2.11E-5	2.16E-5	2.16E-5	2.17E-5	2.02E-5	2.16E-5
363.15	2.0	2.39E-5	2.51E-5	2.43E-5	2.38E-5	2.49E-5	2.54E-5
373.15	2.4	5.32E-5	2.88E-5	2.95E-5	3.00E-5	2.83E-5	3.71E-5

TABLE A10 WATER SOLUBILITY IN 1,3,5-TRIMETHYLBENZENE (MOLE FRACTION)

T (K)	P (BAR)	# 1	# 2	# 3	# 4	# 5	# 6
303.15	1.4	2.38E-3	2.50E-3	2.64E-3	2.46E-3	2.51E-3	2.35E-3
313.15	1.4	3.61E-3	3.82E-3	3.19E-3	3.53E-3	3.48E-3	3.40E-3
323.15	1.4	4.73E-3	4.86E-3	4.63E-3	4.91E-3	5.14E-3	5.05E-3
333.15	1.4	6.00E-3	6.06E-3	5.73E-3	6.18E-3	6.09E-3	6.25E-3
343.15	1.4	7.83E-3	8.42E-3	7.73E-3	8.33E-3	7.70E-3	7.86E-3
353.15	1.4	1.01E-2	1.03E-2	1.08E-2	1.07E-2	1.09E-2	1.03E-2
363.15	2.0	1.28E-2	1.51E-2	1.37E-2	1.36E-2	1.44E-2	1.41E-2
373.15	2.4	1.84E-2	1.95E-2	1.94E-2	1.89E-2	1.85E-2	1.91E-2

TABLE A11 N-BUTYLBENZENE SOLUBILITY IN WATER (MOLE FRACTION)

T (K)	P (BAR)	# 1	# 2	# 3	# 4	# 5	# 6
303.15	1.4	2.85E-6	2.33E-6	2.32E-6	2.06E-6	2.64E-6	--------
313.15	1.4	2.53E-6	2.22E-6	2.55E-6	2.57E-6	2.28E-6	2.16E-6
323.15	1.4	2.69E-6	2.68E-6	2.91E-6	2.67E-6	2.66E-6	3.31E-6
333.15	1.4	3.53E-6	4.02E-6	3.54E-6	3.77E-6	3.53E-6	3.61E-6
343.15	1.4	4.40E-6	4.86E-6	2.73E-6	4.14E-6	4.32E-6	--------
353.15	1.4	6.65E-6	6.54E-6	4.96E-6	6.15E-6	6.15E-6	6.41E-6
363.15	2.0	7.82E-6	8.31E-6	7.55E-6	6.55E-6	8.70E-6	8.53E-6
373.15	2.4	1.06E-5	1.11E-5	1.11E-5	1.10E-5	1.13E-5	1.20E-5

TABLE A12 WATER SOLUBILITY IN N-BUTYLBENZENE (MOLE FRACTION)

T (K)	P (BAR)	# 1	# 2	# 3	# 4	# 5	# 6
303.15	1.4	2.40E-3	2.50E-3	2.29E-3	2.20E-3	2.28E-3	--------
313.15	1.4	3.20E-3	3.13E-3	3.05E-3	3.15E-3	3.02E-3	3.07E-3
323.15	1.4	4.17E-3	4.08E-3	4.16E-3	4.21E-3	4.02E-3	4.72E-3
333.15	1.4	5.78E-3	5.53E-3	5.67E-3	5.99E-3	6.33E-3	6.10E-3
343.15	1.4	7.42E-3	7.97E-3	8.72E-3	8.32E-3	8.79E-3	--------
353.15	1.4	1.02E-2	1.17E-2	1.05E-2	1.05E-2	1.09E-2	1.06E-2
363.15	2.0	1.26E-2	1.49E-2	1.31E-2	1.57E-2	1.30E-2	1.88E-2
373.15	2.4	2.01E-2	1.92E-2	1.87E-2	2.03E-2	2.11E-2	1.83E-2

APPENDIX B ANALYSIS OF VARIANCE OF THE SLOPES OF WATER SOLUBILITY CORRELATIONS

TABLE B1 ANALYSIS OF VARIANCE WITH INDIVIDUAL SLOPES

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F Ratio
Means	5.33606	4	1.33402	299.25
Between means slope and pooled slope	0.88969	1	0.88969	199.58
Between individual slopes and pooled slope	0.13285	5	0.02657	5.96
Error	1.24820	280	0.00446	
Total	7.60681	290		

TABLE B2 ANALYSIS OF VARIANCE WITH POOLED SLOPE (= 9.7507)

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F Ratio
Means	5.33606	3	1.77869	368.35
Between means slope and pooled slope	0.88969	1	0.88969	184.25
Error	1.38105	286	0.00483	
Total	7.60681	290		

APPENDIX C

UNIFAC MODEL

The UNIFAC model used in this work is that presented by Hooper et al. (1988), and is summarized here for completeness and to avoid confusion with the many other variations of the original model developed by Fredenslund et al. (1975). The activity coefficient for component *i* is expressed as the sum of a combinatorial contribution and a residual contribution

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \tag{1c}$$

Combinatory Contribution:

$$\ln\gamma_i^C = \ln\left(\frac{\omega_i}{x_i}\right) + 1 - \frac{\omega_i}{x_i} \tag{2c}$$

Residual Contribution:

$$\ln\gamma_i^R = \Sigma_k\, \nu_k^{(i)}\left(\ln\Gamma_k - \ln\Gamma_k^{(i)}\right) \tag{3c}$$

where,

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \tag{4c}$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \tag{5c}$$

$$r_i = \sum_k \nu_k^{(i)} R_k \tag{6c}$$

$$q_i = \sum_k \nu_k^{(i)} Q_k \tag{7c}$$

$$\omega_i = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}} \tag{8c}$$

$$\ln\Gamma_k = Q_k\left[1-\ln\left(\sum_m \Theta_m \Psi_{mk}\right)-\sum_m\left(\frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}}\right)\right] \tag{9c}$$

$$\Psi_{nm} = \exp\left(-\frac{a_{nm}}{T}\right) \tag{10c}$$

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{11c}$$

$$X_m = \frac{\sum_J \nu_m^{(J)} x_J}{\sum_J \sum_n \nu_n^{(J)} x_J} \tag{12c}$$

The group surface area, Q_k, and volume, R_k, parameters are identical to those in the original UNIFAC (Fredenslund et al., 1975). Water (1) - hydrocarbon group (2) interaction parameters are given by

$$a_{1m} = a_{1m}^{(0)} + a_{1m}^{(1)}T + a_{1m}^{(2)}T^2 \tag{13c}$$

$$a_{m1} = a_{m1}^{(0)} + a_{m1}^{(1)}T \tag{14c}$$

where T is in Kelvin. Hydrocarbon-hydrocarbon group interaction parameters, a_{mn} are taken from Table III of Hooper et al. (1988).

APPENDIX D

SUPPLEMENTAL MATERIAL OF THE UNIFAC MODEL EVALUATION

Table D1. Experimental and Calculated Benzene Solubility in Water (mole fraction x 10^6)

Temperature K	Experiment.	This Work	Hooper et al., 1988	Magnussen et al., 1981	UNIFAC (Lyngby)	UNIFAC (Dortmund)	Fredenslund et al., 1975
303.15	401	402	425	416	437	480	444
313.15	441	431	477	463	463	577	493
323.15	473	468	537	514	491	692	544
333.15	530	514	608	567	522	826	598
343.15	588	573	689	622	557	983	655
353.15	685	647	785	680	596	1165	713
363.15	770	738	898	741	642	1378	775
373.15	930	852	1031	804	696	1624	838
Bias %		-1.73	14.0	4.82	-0.33	61.7	9.91
AAD %		3.41	12.7	6.03	9.93	55.5	9.54

Table D2. Experimental and Calculated Toluene Solubility in Water (mole fraction x 10^6)

Temperature K	Experiment.	This Work	Hooper et al., 1988	Magnussen et al., 1981	UNIFAC (Lyngby)	UNIFAC (Dortmund)	Fredenslund et al., 1975
303.15	114.	112.	119.	147.	74.1	137.	88.9
313.15	115.	122.	138.	165.	80.2	163.	101.
323.15	124.	134.	159.	184.	87.6	193.	114.
333.15	140.	150.	185.	204.	96.6	229.	128.
343.15	166.	171.	216.	225.	108.	270.	143.
353.15	192.	197.	253.	247.	121.	319.	159.
363.15	230.	231.	298.	270.	138.	375.	176.
373.15	262.	274.	353.	294.	160.	441.	193.
Bias (%)		4.11	29.2	35.1	-27.9	60.9	-11.2
AAD %		4.20	26.5	32.6	34.5	55.3	16.4

Table D3. Experimental and Calculated Ethylbenzene Solubility in Water (mole fraction x 10^6)

Temperature K	Experiment.	This Work	Hooper et al., 1988	Magnussen et al., 1981	UNIFAC (Lyngby)	UNIFAC (Dortmund)	Fredenslund et al., 1975
303.15	28.3	30.7	20.3	36.5	37.7	38.3	31.8
313.15	28.8	33.7	23.8	42.0	38.8	46.4	36.6
323.15	32.6	37.9	28.0	48.0	40.7	56.3	41.9
333.15	38.4	43.9	33.1	54.4	43.4	68.3	47.6
343.15	47.2	52.0	39.4	61.4	47.1	82.9	53.7
353.15	57.5	63.2	47.1	68.8	51.9	101.	60.3
363.15	67.8	78.4	56.7	76.6	58.1	122.	67.3
373.15	81.9	99.3	68.5	85.0	66.1	148.	74.7
Bias (%)		15.4	-15.9	31.3	11.4	79.5	15.4
AAD %		14.1	17.6	28.7	18.7	69.8	15.0

Table D4. Experimental and Calculated p-Xylene Solubility in Water (mole fraction x 10^6)

Temperature K	Experiment.	This Work	Hooper et al., 1988	Magnussen et al., 1981	UNIFAC (Lyngby)	UNIFAC (Dortmund)	Fredenslund et al., 1975
303.15	28.0	31.3	33.4	56.0	12.9	39.1	19.2
313.15	29.8	34.3	39.6	63.1	14.2	46.2	22.4
323.15	33.6	38.4	47.2	70.5	16.0	54.6	25.8
333.15	39.9	43.9	56.5	78.4	18.4	64.4	29.5
343.15	47.7	51.0	67.9	86.7	21.4	75.9	33.5
353.15	56.4	60.3	82.0	95.3	25.4	89.5	37.8
363.15	66.0	72.5	99.5	104	30.7	106	42.4
373.15	85.3	88.6	121	114	37.8	124	47.3
Bias (%)		10.7	45.1	91.2	-47.0	62.7	-24.1
AAD %		9.85	39.3	82.5	54.0	55.3	31.1

Table D5. Experimental and Calculated 1,3,5-Trimethylbenzene Solubility in Water (mole fraction $x\ 10^6$)

Temperature K	Experiment.	This Work	Hooper et al., 1988	Magnussen et al., 1981	UNIFAC (Lyngby)	UNIFAC (Dortmund)	Fredenslund et al., 1975
303.15	9.00	8.65	9.26	22.3	2.25	11.1	4.33
313.15	9.50	9.60	11.3	25.1	2.54	13.1	5.15
323.15	10.5	10.9	13.9	28.1	2.95	15.4	6.05
333.15	12.9	12.7	17.1	31.3	3.52	18.2	7.05
343.15	15.4	15.1	21.2	34.7	4.29	21.5	8.14
353.15	20.3	18.3	26.4	38.2	5.36	25.4	9.33
363.15	23.9	22.7	33.1	41.8	6.86	30.1	10.6
373.15	28.4	28.5	41.6	45.6	9.00	35.6	12.0
Bias (%)		-3.55	34.7	135	-66.8	37.0	-44.0
AAD %		3.44	30.0	121	72.3	33.1	50.0

Table D6. Experimental and Calculated n-Butylbenzene Solubility in Water (mole fraction $x\ 10^6$)

Temperature K	Experiment.	This Work	Hooper et al., 1988	Magnussen et al., 1981	UNIFAC (Lyngby)	UNIFAC (Dortmund)	Fredenslund et al., 1975
303.15	2.10	2.08	0.76	3.10	4.49	3.21	3.30
313.15	2.20	2.34	0.93	3.73	4.42	4.03	3.94
323.15	2.60	2.75	1.14	4.43	4.48	5.07	4.66
333.15	3.50	3.37	1.41	5.21	4.68	6.42	5.47
343.15	4.20	4.28	1.76	6.08	5.02	8.14	6.35
353.15	6.20	5.64	2.20	7.04	5.53	10.4	7.32
363.15	7.70	7.70	2.79	8.10	6.23	13.2	8.39
373.15	11.1	10.8	3.55	9.26	7.19	16.9	9.55
Bias (%)		-1.87	-60.2	42.9	40.6	91.2	49.9
AAD %		3.76	61.5	39.6	50.7	74.8	45.5

Table D7. Experimental and Calculated Water Solubility in Benzene (mole fraction $x\ 10^3$)

Temperature K	Experiment.	This Work	Hooper et al., 1988	Magnussen et al., 1981	UNIFAC (Lyngby)	UNIFAC (Dortmund)	Fredenslund et al., 1975
303.15	3.67	3.54	3.57	3.25	3.51	11.0	2.67
313.15	4.52	4.90	4.91	3.76	4.83	13.8	3.12
323.15	6.67	6.67	6.65	4.33	6.62	17.1	3.61
333.15	8.89	8.93	8.87	4.94	9.03	21.0	4.14
343.15	11.9	11.8	11.6	5.60	12.3	25.5	4.72
353.15	15.0	15.4	15.1	6.31	16.7	30.7	5.34
363.15	20.3	19.8	19.3	7.06	22.5	36.6	6.01
373.15	26.1	25.1	24.4	7.86	30.3	43.3	6.73
Bias %		1.84	0.87	-49.1	9.85	173	-59.6
AAD %		2.77	3.26	44.2	6.86	133	53.4

Table D8. Experimental and Calculated Water Solubility in Toluene (mole fraction $x\ 10^3$)

Temperature K	Experiment.	This Work	Hooper et al., 1988	Magnussen et al., 1981	UNIFAC (Lyngby)	UNIFAC (Dortmund)	Fredenslund et al., 1975
303.15	2.68	2.98	3.11	2.55	3.72	7.58	1.79
313.15	3.64	4.14	4.29	2.95	5.11	9.57	2.09
323.15	4.91	5.65	5.82	3.39	6.99	11.9	2.41
333.15	7.22	7.59	7.78	3.86	9.53	14.7	2.77
343.15	9.02	10.0	10.2	4.36	12.9	18.0	3.15
353.15	12.2	13.1	13.3	4.90	17.5	21.7	3.57
363.15	15.7	16.9	17.0	5.48	23.6	26.0	4.01
373.15	21.6	21.6	21.6	6.09	31.7	30.8	4.48
Bias %		12.3	15.3	-52.3	61.5	144	-71.3
AAD %		8.98	11.4	43.7	42.2	110	59.7

Table D9. Experimental and Calculated Water Solubility in Ethylbenzene (mole fraction x 10^3)

Temperature K	Experiment.	This Work	Hooper et al., 1988	Magnussen et al., 1981	UNIFAC (Lyngby)	UNIFAC (Dortmund)	Fredenslund et al., 1975
303.15	2.53	2.55	2.64	2.52	2.90	9.01	1.96
313.15	3.43	3.57	3.68	2.93	3.96	11.6	2.30
323.15	4.41	4.92	5.04	3.39	5.40	14.7	2.68
333.15	5.31	6.67	6.81	3.88	7.33	18.5	3.09
343.15	7.60	8.93	9.05	4.42	9.91	22.9	3.54
353.15	10.2	11.8	11.9	5.00	13.4	28.1	4.03
363.15	14.1	15.4	15.4	5.62	17.9	34.1	4.55
373.15	19.6	20.0	19.8	6.29	24.0	41.1	5.12
Bias %		16.8	18.7	-38.1	36.9	267	-53.4
AAD %		10.8	12.5	35.7	25.2	201	49.0

Table D10. Experimental and Calculated Water Solubility in p-Xylene (mole fraction x 10^3)

Temperature K	Experiment.	This Work	Hooper et al., 1988	Magnussen et al., 1981	UNIFAC (Lyngby)	UNIFAC (Dortmund)	Fredenslund et al., 1975
303.15	2.61	1.17	2.82	1.79	3.95	5.71	1.17
313.15	3.28	1.36	3.91	2.07	5.41	7.28	1.36
323.15	4.59	1.57	5.31	2.38	7.38	9.14	1.57
333.15	6.04	1.80	7.10	2.70	10.0	11.4	1.80
343.15	7.95	2.05	9.36	3.05	13.6	13.9	2.05
353.15	10.8	2.31	12.2	3.43	18.4	16.9	2.31
363.15	15.1	2.60	15.6	3.83	24.8	20.4	2.60
373.15	19.1	2.90	19.8	4.25	33.3	24.3	2.90
Bias %		-80.8	17.4	-63.9	93.2	100	-80.8
AAD %		71.3	12.3	56.7	65.5	77.8	71.3

Table D11. Experimental and Calculated Water Solubility in 1,3,5-Trimethylbenzene (mole fraction x 10^3)

Temperature K	Experiment.	This Work	Hooper et al., 1988	Magnussen et al., 1981	UNIFAC (Lyngby)	UNIFAC (Dortmund)	Fredenslund et al., 1975
303.15	2.38	2.38	2.63	1.14	4.17	4.57	0.71
313.15	3.31	3.33	3.65	1.31	5.71	5.87	0.83
323.15	4.71	4.57	4.97	1.50	7.78	7.44	0.95
333.15	5.92	6.18	6.66	1.71	10.6	9.31	1.09
343.15	7.69	8.22	8.79	1.93	14.3	11.5	1.24
353.15	10.3	10.8	11.4	2.17	19.3	14.1	1.40
363.15	13.3	14.0	14.7	2.42	26.0	17.0	1.57
373.15	18.6	17.9	18.7	2.68	34.9	20.4	1.76
Bias %		4.79	14.1	-83.1	118	66.3	-95.3
AAD %		3.54	9.47	71.6	81.2	51.1	81.9

Table D12. Experimental and Calculated Water Solubility in n-Butylbenzene (mole fraction x 10^3)

Temperature K	Experiment.	This Work	Hooper et al., 1988	Magnussen et al., 1981	UNIFAC (Lyngby)	UNIFAC (Dortmund)	Fredenslund et al., 1975
303.15	2.26	2.21	2.31	2.53	2.37	9.35	2.07
313.15	3.09	3.13	3.25	2.97	3.23	12.2	2.45
323.15	4.06	4.35	4.52	3.45	4.39	15.8	2.86
333.15	5.68	5.98	6.17	3.98	5.94	20.0	3.32
343.15	8.04	8.09	8.30	4.56	8.01	25.1	3.83
353.15	10.2	10.8	11.0	5.18	10.7	31.1	4.37
363.15	14.5	14.4	14.4	5.86	14.4	38.1	4.97
373.15	19.1	18.8	18.7	6.58	19.1	46.2	5.61
Bias %		4.95	8.39	-37.2	5.48	324	-50.8
AAD %		3.10	5.04	34.8	3.58	234	43.2

APPENDIX E

COMPUTER CODES USED IN UNIFAC MODEL EVALUATION

```
      IMPLICIT REAL*8(A-H,O-Z)

      PARAMETER(NN=20)
      PARAMETER(MM=600)
C
C      MARQ COMMONS
C
      COMMON /CSTEP/ X(NN),XMAX(NN),XMIN(NN),DELTX(NN),DELMN(NN),
     *         ERR(NN,NN+1),FOBJ,NV,NTRAC,MATRX,MASK(NN),
     *         NFMAX,NFLAT,JVARY,NXTRA,KFLAG,NOREP,KERFL,KW
      COMMON /NLLS4/ FLAMB,FNU,RELDF,RELMN,METHD,KALCP,KORDF,MAXIT,
     *         LEQU,MXSUB,MXUPD
      COMMON /CDAT/ FIT(MM),Y(MM),YSIG(MM),NPTS
C
C      PROGRAMM COMMONS
C
      COMMON /FIT/ NSYS, NPT(10),ERRREL,ITMAX,
     *              NCGRP(10,10,10), T(10,50), XL(10,50,10),
     *              DXL(10,50,10), YL(10,50,10), DYL(10,50,10),
     *              GAMAXL(10,50,10), GAMAYL(10,50,10),FITMC(MM),
     *              FITMR(MM), FITMS(MM)

      COMMON/DSET/ AH1(10,10),AH2(10,10),AH3(10,10), AM(10,10),
     *              AF(10,10), RKDB(10), QKDB(10),
     *              MODEL, NCOMP, NGRP, IDGRP(10),
     *              AL1(10,10),AL2(10,10),AL3(10,10),
     *              AW1(10,10),AW2(10,10),AW3(10,10),
     *              RKDBW(10), QKDBW(10)

      DIMENSION XLMIN(10,50,10), XLMAX(10,50,10), YLMIN(10,50,10),
     *           YLMAX(10,50,10), FITM(MM), TE(50), BIASX1(10),
     *           BIASY2(10), AAPDX1(10), AAPDY2(10), ERRX1(10,50),
     *           ERRY2(10,50)

      CHARACTER*50 INPUT, OUTPUT, SYSTEM

      EXTERNAL FCN

******************************************************************************
*                                                                            *
*               MODEL  =          1     HOOPER, H. H.                        *
*                      =          2     LARSEN, B.                           *
*                      =          3     MAGNUSSEN, T.                        *
*                      =          4     FREDENSLUND, A.                      *
*                      =          5     THIS WORK                            *
*                      =          6     GMEHLING,J.                          *
*                                                                            *
*               NOPT   =          1     FITTING                              *
*                      =          2     COMPARISON                           *
*                      =          3     EXTRAPOLATION                        *
*                                                                            *
*               GRP 1  =          CH3                                        *
*               GRP 2  =          CH2                                        *
*               GRP 3  =          ACH                                        *
*               GRP 4  =          H2O                                        *
*               GRP 5  =          ACCH3                                      *
*               GRP 6  =          ACCH2                                      *
*                                                                            *
******************************************************************************

      DATA  RKDB(1),RKDB(2),RKDB(3),RKDB(4),RKDB(5),RKDB(6)/0.9011,
     *       0.6744,0.5313,0.92,1.2663, 1.0396/
      DATA  QKDB(1),QKDB(2),QKDB(3),QKDB(4),QKDB(5),QKDB(6)/0.848,
     *       0.540,0.400,1.400,0.968,0.660/
      DATA  RKDBW(1),RKDBW(2),RKDBW(3),RKDBW(4),RKDBW(5),RKDBW(6)
     *       /0.6325,0.6325,0.3763,1.7334,0.9100,0.9100/
      DATA  QKDBW(1),QKDBW(2),QKDBW(3),QKDBW(4),QKDBW(5),QKDBW(6)
     *       /1.0608,0.7081,0.4321,2.4561,0.9490,0.7962/

      DATA  AH1(1,1),AH1(1,2),AH1(1,3),AH1(1,4),AH1(1,5),AH1(1,6)/
     *       2*0.0,131.30,3060.6,-1.613,-1.613/
```

```
  DATA  AH1(2,1),AH1(2,2),AH1(2,3),AH1(2,4),AH1(2,5),AH1(2,6)/
*        2*0.0,131.30,3060.6,-1.613,-1.613/
  DATA  AH1(3,1),AH1(3,2),AH1(3,3),AH1(3,4),AH1(3,5),AH1(3,6)/
*        -71.4,-71.4,0.0,2026.5,-27.67,-27.67/
  DATA  AH1(4,1),AH1(4,2),AH1(4,3),AH1(4,4),AH1(4,5),AH1(4,6)/
*        -40.72,-40.72,-39.04,0.0,-50.19,-50.19/
  DATA  AH1(5,1),AH1(5,2),AH1(5,3),AH1(5,4),AH1(5,5),AH1(5,6)/
*        15.27,15.27,47.31,2143.9,2*0.0/
  DATA  AH1(6,1),AH1(6,2),AH1(6,3),AH1(6,4),AH1(6,5),AH1(6,6)/
*        15.27,15.27,47.31,2143.9,2*0.0/

  DATA  AH2(1,1),AH2(1,2),AH2(1,3),AH2(1,4),AH2(1,5),AH2(1,6)/
*        3*0.0,-5.374,2*0.0/
  DATA  AH2(2,1),AH2(2,2),AH2(2,3),AH2(2,4),AH2(2,5),AH2(2,6)/
*        3*0.0,-5.374,2*0.0/
  DATA  AH2(3,1),AH2(3,2),AH2(3,3),AH2(3,4),AH2(3,5),AH2(3,6)/
*        3*0.0,-3.267,2*0.0/
  DATA  AH2(4,1),AH2(4,2),AH2(4,3),AH2(4,4),AH2(4,5),AH2(4,6)/
*        3.826,3.826,3.928,0.0,3.673,3.673/
  DATA  AH2(5,1),AH2(5,2),AH2(5,3),AH2(5,4),AH2(5,5),AH2(5,6)/
*        3*0.0,-3.076,2*0.0/
  DATA  AH2(6,1),AH2(6,2),AH2(6,3),AH2(6,4),AH2(6,5),AH2(6,6)/
*        3*0.0,-3.076,2*0.0/

  DATA  AH3(4,1),AH3(4,2),AH3(4,3),AH3(4,4),AH3(4,5),AH3(4,6)/
*        -0.00411,-0.00411,-0.00437,0.0,-0.005061,-0.005061/

  DATA  AL1(1,1),AL1(1,2),AL1(1,3),AL1(1,4),AL1(1,5),AL1(1,6)/
*        2*0.0,62.88,1857.0,62.88,62.88/
  DATA  AL1(2,1),AL1(2,2),AL1(2,3),AL1(2,4),AL1(2,5),AL1(2,6)/
*        2*0.0,62.88,1857.0,62.88,62.88/
  DATA  AL1(3,1),AL1(3,2),AL1(3,3),AL1(3,4),AL1(3,5),AL1(3,6)/
*        -1.447,-1.447,0.0,1055.0,2*0.0/
  DATA  AL1(4,1),AL1(4,2),AL1(4,3),AL1(4,4),AL1(4,5),AL1(4,6)/
*        410.7,410.7,736.7,0.0,736.7,736.7/
  DATA  AL1(5,1),AL1(5,2),AL1(5,3),AL1(5,4),AL1(5,5),AL1(5,6)/
*        -1.447,-1.447,0.0,1055.0,2*0.0/
  DATA  AL1(6,1),AL1(6,2),AL1(6,3),AL1(6,4),AL1(6,5),AL1(6,6)/
*        -1.447,-1.447,0.0,1055.0,2*0.0/

  DATA  AL2(1,1),AL2(1,2),AL2(1,3),AL2(1,4),AL2(1,5),AL2(1,6)/
*        2*0.0,-0.2493,-3.322,2*0.0/
  DATA  AL2(2,1),AL2(2,2),AL2(2,3),AL2(2,4),AL2(2,5),AL2(2,6)/
*        2*0.0,-0.2493,-3.322,2*0.0/
  DATA  AL2(3,1),AL2(3,2),AL2(3,3),AL2(3,4),AL2(3,5),AL2(3,6)/
*        -0.05638,-0.05638,0,-2.968,2*0.0/
  DATA  AL2(4,1),AL2(4,2),AL2(4,3),AL2(4,4),AL2(4,5),AL2(4,6)/
*        2.868,2.868,1.965,0.0,1.965,1.965/
  DATA  AL2(5,1),AL2(5,2),AL2(5,3),AL2(5,4),AL2(5,5),AL2(5,6)/
*        -0.05638,-0.05638,0,-2.968,2*0.0/
  DATA  AL2(6,1),AL2(6,2),AL2(6,3),AL2(6,4),AL2(6,5),AL2(6,6)/
*        -0.05638,-0.05638,0,-2.968,2*0.0/

  DATA  AL3(1,1),AL3(1,2),AL3(1,3),AL3(1,4),AL3(1,5),AL3(1,6)/
*        2*0.0,1.103,-9.0,2*0.0/
  DATA  AL3(2,1),AL3(2,2),AL3(2,3),AL3(2,4),AL3(2,5),AL3(2,6)/
*        2*0.0,1.103,-9.0,2*0.0/
  DATA  AL3(3,1),AL3(3,2),AL3(3,3),AL3(3,4),AL3(3,5),AL3(3,6)/
*        -1.612,-1.612,0.0,9.854,2*0.0/
  DATA  AL3(4,1),AL3(4,2),AL3(4,3),AL3(4,4),AL3(4,5),AL3(4,6)/
*        9.0,9.0,2*0.0,9.0,9.0/
  DATA  AL3(5,1),AL3(5,2),AL3(5,3),AL3(5,4),AL3(5,5),AL3(5,6)/
*        -1.612,-1.612,0.0,9.854,2*0.0/
  DATA  AL3(6,1),AL3(6,2),AL3(6,3),AL3(6,4),AL3(6,5),AL3(6,6)/
*        -1.612,-1.612,0.0,9.854,2*0.0/

  DATA AF(1,1), AF(1,2), AF(1,3), AF(1,4), AF(1,5), AF(1,6)/
*       2*0.0,61.13,1318.0,76.50,76.50/
  DATA AF(2,1), AF(2,2), AF(2,3), AF(2,4), AF(2,5), AF(2,6)/
*       2*0.0,61.13,1318.0,76.50,76.50/
  DATA AF(3,1), AF(3,2), AF(3,3), AF(3,4), AF(3,5), AF(3,6)/
```

```
     *      -11.12,-11.12,0.0,903.8,167.0,167.0/
      DATA AF(4,1), AF(4,2), AF(4,3), AF(4,4), AF(4,5), AF(4,6)/
     *      300.0,300.0,362.3,0.0,377.6,377.6/
      DATA AF(5,1), AF(5,2), AF(5,3), AF(5,4), AF(5,5), AF(5,6)/
     *      -69.70,-69.70,-146.8,5695.0,2*0.0/
      DATA AF(6,1), AF(6,2), AF(6,3), AF(6,4), AF(6,5), AF(6,6)/
     *      -69.70,-69.70,-146.8,5695.0,2*0.0/

      DATA AM(1,1), AM(1,2), AM(1,3), AM(1,4), AM(1,5), AM(1,6)/
     *      0.0,0.0,-114.8,1300.0,-115.7,-115.7/
      DATA AM(2,1), AM(2,2), AM(2,3), AM(2,4), AM(2,5), AM(2,6)/
     *      0.0,0.0,-114.8,1300.0,-115.7,-115.7/
      DATA AM(3,1), AM(3,2), AM(3,3), AM(3,4), AM(3,5), AM(3,6)/
     *      156.5,156.5,0.0,859.4,167.0,167.0/
      DATA AM(4,1), AM(4,2), AM(4,3), AM(4,4), AM(4,5), AM(4,6)/
     *      342.4,342.4,372.8,0.0,203.7,203.7/
      DATA AM(5,1), AM(5,2), AM(5,3), AM(5,4), AM(5,5), AM(5,6)/
     *      104.4,104.4,-146.8,5695.0,2*0.0/
      DATA AM(6,1), AM(6,2), AM(6,3), AM(6,4), AM(6,5), AM(6,6)/
     *      104.4,104.4,-146.8,5695.0,2*0.0/

      DATA  AW1(1,1),AW1(1,2),AW1(1,3),AW1(1,4),AW1(1,5),AW1(1,6)/
     *       2*0.0,114.2,1391.3,7.339,7.339/
      DATA  AW1(2,1),AW1(2,2),AW1(2,3),AW1(2,4),AW1(2,5),AW1(2,6)/
     *       2*0.0,114.2,1391.3,7.339,7.339/
      DATA  AW1(3,1),AW1(3,2),AW1(3,3),AW1(3,4),AW1(3,5),AW1(3,6)/
     *       16.07,16.07,0.0,792.0,139.2,139.2/
      DATA  AW1(4,1),AW1(4,2),AW1(4,3),AW1(4,4),AW1(4,5),AW1(4,6)/
     *       -17.253,-17.253,332.3,0.0,24.144,24.144/
      DATA  AW1(5,1),AW1(5,2),AW1(5,3),AW1(5,4),AW1(5,5),AW1(5,6)/
     *       47.2,47.2,-45.33,1050.2,0.0,0.0/
      DATA  AW1(6,1),AW1(6,2),AW1(6,3),AW1(6,4),AW1(6,5),AW1(6,6)/
     *       47.2,47.2,-45.33,1050.2,0.0,0.0/

      DATA  AW2(1,1),AW2(1,2),AW2(1,3),AW2(1,4),AW2(1,5),AW2(1,6)/
     *       2*0.0,0.0933,-3.6155,-0.4538,-0.4538/
      DATA  AW2(2,1),AW2(2,2),AW2(2,3),AW2(2,4),AW2(2,5),AW2(2,6)/
     *       2*0.0,0.0933,-3.6155,-0.4538,-0.4538/
      DATA  AW2(3,1),AW2(3,2),AW2(3,3),AW2(3,4),AW2(3,5),AW2(3,6)/
     *       -0.2998,-0.2998,0.0,-1.726,-0.65,-0.65/
      DATA  AW2(4,1),AW2(4,2),AW2(4,3),AW2(4,4),AW2(4,5),AW2(4,6)/
     *       0.8389,0.8389,1.158,0.0,1.6504,1.6504/
      DATA  AW2(5,1),AW2(5,2),AW2(5,3),AW2(5,4),AW2(5,5),AW2(5,6)/
     *       0.3575,0.3575,0.4223,-1.9939,0.0,0.0/
      DATA  AW2(6,1),AW2(6,2),AW2(6,3),AW2(6,4),AW2(6,5),AW2(6,6)/
     *       0.3575,0.3575,0.4223,-1.9939,0.0,0.0/

      DATA  AW3(1,1),AW3(1,2),AW3(1,3),AW3(1,4),AW3(1,5),AW3(1,6)/
     *       2*0.0,0.0,0.001144,2*0.0/
      DATA  AW3(2,1),AW3(2,2),AW3(2,3),AW3(2,4),AW3(2,5),AW3(2,6)/
     *       2*0.0,0.0,0.001144,2*0.0/
      DATA  AW3(3,1),AW3(3,2),AW3(3,3),AW3(3,4),AW3(3,5),AW3(3,6)/
     *       6*0.0/
      DATA  AW3(4,1),AW3(4,2),AW3(4,3),AW3(4,4),AW3(4,5),AW3(4,6)/
     *       0.0009021,0.0009021,0.0,0.0,0.0,0.0/
      DATA  AW3(5,1),AW3(5,2),AW3(5,3),AW3(5,4),AW3(5,5),AW3(5,6)/
     *       6*0.0/
      DATA  AW3(6,1),AW3(6,2),AW3(6,3),AW3(6,4),AW3(6,5),AW3(6,6)/
     *       6*0.0/

      WRITE(*,'(''READ SYSTEM NAMES'')')
      READ(*,100) SYSTEM

      WRITE(*,'(''READ IN INPUT DATA FILE NAMES'')')
      READ ( *,100) INPUT

      WRITE(*,'(''READ IN OUTPUT DATA FILE NAME'')')
      READ ( *,100) OUTPUT

100    FORMAT(50A)
```

```
      OPEN (UNIT=7, FILE=INPUT,  STATUS='UNKNOWN')
      OPEN (UNIT=10, FILE=OUTPUT, STATUS='UNKNOWN')

      READ(7,*) MODEL, NCOMP, NGRP, NSYS, NPARA,
     :          NOPT, ITMAX, ERRREL
      write(*,*)model,ncomp,ngrp,nsys,npara,nopt,ITMAX,ERRREL
      READ(7,*) (IDGRP(I), I=1,NGRP)
      write(*,*)(idgrp(i),i=1,ngrp)
      READ(7,*) (NPT(I),I=1,NSYS)
      write(*,*)(npt(i),i=1,nsys)

      DO I=1,NSYS
       DO J=1,NCOMP
       READ(7,*) (NCGRP(I,J,K), K=1,NGRP)
       write(*,*) (ncgrp(i,j,k),k=1,ngrp)
       END DO
      END DO

      READ(7,*) (MASK(I),I=1,20)
      write(*,*) (mask(i),i=1,20)

      IF(MODEL.EQ.5) THEN
      AH1(1,4)=3115.6
      AH1(2,4)=3115.6
      AH1(3,4)=2080.0
      AH1(5,4)=2265.2
      AH1(6,4)=2265.2

      AH2(1,4)=-5.3298
      AH2(2,4)=-5.3298
      AH2(3,4)=-3.4397
      AH2(5,4)=-3.3594
      AH2(6,4)=-3.3594

      AH1(4,1)=-2157.1
      AH1(4,2)=-2157.1
      AH1(4,3)=-707.03
      AH1(4,5)=-790.32
      AH1(4,6)=-790.32

      AH2(4,1)=16.558
      AH2(4,2)=16.558
      AH2(4,3)=7.6957
      AH2(4,5)=7.7489
      AH2(4,6)=7.7489

      AH3(4,1)=-0.024912
      AH3(4,2)=-0.024912
      AH3(4,3)=-0.0094561
      AH3(4,5)=-0.010412
      AH3(4,6)=-0.010412
      END IF

      IF(NOPT.EQ.3) THEN
      READ(7,*) TSTART,DELT,TEND
      CLOSE(UNIT=7)
      GO TO 105
      END IF

      DO I=1,NSYS
      K=NPT(I)
       DO J=1,K
       READ(7,*) T(I,J), XL(I,J,1), DXL(I,J,1)
       write(*,*)t(i,j), xl(i,j,1), dxl(i,j,1)
       END DO
      END DO

      DO I=1,NSYS
      K=NPT(I)
       DO J=1,K
       READ(7,*) T(I,J), YL(I,J,2), DYL(I,J,2)
```

```
       write(*,*)t(i,j), yl(i,j,2), dyl(i,j,2)
       END DO
      END DO

      CLOSE(UNIT=7)

      GO TO 120

105    NPTS=0
210    NPTS=NPTS+1
      IF(NPTS.GT.50) GO TO 220
      TE(NPTS)=TSTART+(NPTS-1)*DELT
      IF(TE(NPTS).LT.TEND) GO TO 210
220    NPTS=NPTS-1

      DO J=1,NSYS
       DO I=1,NPTS
       TR1=TE(I)/562.2
       TR2=TE(I)/647.3
       XX1=DEXP(6.2-14.0322/TR1+3.5112/TR1/TR1)
       XX2=DEXP(1.6+9.4164*DLOG(TR2))
C               IF(TE(I).GT.423.15) XX1=0.1
C               IF(TE(I).GT.423.15) XX2=0.1
       XX1=0.001
       XX2=0.01
       XL(J,I,1)=XX1
       YL(J,I,2)=XX2
       XL(J,I,2)=1.0-XX1
       YL(J,I,1)=1.0-XX2
       T(J,I)=TE(I)
       END DO
      NPT(J)=NPTS
      END DO
      NPTS=NPTS*NSYS*2
      GO TO 140

120    NPTS=0
      DO I=1,NSYS
      NPTS=NPTS+NPT(I)
      K=NPT(I)
       DO J=1,K
       XLMIN(I,J,1)=XL(I,J,1)-DXL(I,J,1)
       XLMAX(I,J,1)=XL(I,J,1)+DXL(I,J,1)
       YLMIN(I,J,2)=YL(I,J,2)-DYL(I,J,2)
       YLMAX(I,J,2)=YL(I,J,2)+DYL(I,J,2)
       XL(I,J,2)=1.0-XL(I,J,1)
       YL(I,J,1)=1.0-YL(I,J,2)
       END DO
      END DO

      NPTS=2*NPTS

140    IF(NOPT.NE.1) THEN
      CALL FCN(FITM)
      GOTO 110
      END IF

      CALL STSET
      NV=NPARA
      KW=10
      MXSUB=10
      MAXIT=40

C      IF(MODEL.EQ.3) XMAX(1)=10000.0
C      IF(MODEL.EQ.3) XMIN(1)=-10000.0

C       DO I=1,4
C       XMAX(I)=BOUND
C       XMIN(I)=-BOUND
C       END DO
C       DO I=9,12
```

```
C       XMAX(I)=BOUND
C       XMIN(I)=-BOUND
C       END DO
C       DO I=17,20
C       XMAX(I)=BOUND
C       XMIN(I)=-BOUND
C       END DO


      CALL STEPT(FCN)
      CALL FCN(FITM)

      KOUNT=0
110    IF(NOPT.NE.3) THEN
      DO I=1,NSYS
      BIASX1(I)=0.0
      AAPDX1(I)=0.0
      BIASY2(I)=0.0
      AAPDY2(I)=0.0
       DO J=1,NPT(I)
       KOUNT=KOUNT+1
       ERRX1(I,J)=(FITM(KOUNT)-XL(I,J,1))/XL(I,J,1)
       BIASX1(I)=BIASX1(I)+ERRX1(I,J)
       AAPDX1(I)=AAPDX1(I)+DABS(ERRX1(I,J))
       ERRY2(I,J)=(FITM(KOUNT+NPTS/2)-YL(I,J,2))/YL(I,J,2)
       BIASY2(I)=BIASX1(I)+ERRX1(I,J)
       AAPDY2(I)=AAPDX1(I)+DABS(ERRX1(I,J))
       END DO
      BIASX1(I)=BIASX1(I)/NPT(I)
      AAPDX1(I)=AAPDX1(I)/NPT(I)
      BIASY2(I)=BIASY2(I)/NPT(I)
      AAPDY2(I)=AAPDY2(I)/NPT(I)
      END DO
      END IF

      WRITE(10,20) MODEL
      write(*,20)  model
      WRITE(10,30) NCOMP
      write(*,30)  ncomp
      WRITE(10,40) NGRP
      write(*,40)  ngrp
      WRITE(10,50) NSYS
      write(*,50)  nsys
      WRITE(10,60) NPARA
      write(*,60)  npara
      WRITE(10,70) (IDGRP(I),I=1,NGRP)
      write(*,70)  (idgrp(i),i=1,ngrp)
      WRITE(10,80) (NPT(I),I=1,NSYS)
      write(*,80)  (npt(i),i=1,nsys)

      KOUNT=0
      WRITE(10,89)
      write(*,89)
      DO I=1,NSYS
      K=NPT(I)
       DO J=1,K
       KOUNT=KOUNT+1
       GEEX=-XL(I,J,1)*DLOG(XL(I,J,1))-XL(I,J,2)*DLOG(XL(I,J,2))
       XL(I,J,1)=1000000.0*XL(I,J,1)
       FITM(KOUNT)=1000000.0*FITM(KOUNT)
       GEEX=GEEX*1000000.0
       FITMS(KOUNT)=FITMS(KOUNT)*1000000.0
       FITMC(KOUNT)=FITMC(KOUNT)*1000000.0
       FITMR(KOUNT)=FITMR(KOUNT)*1000000.0
       WRITE(10,90) T(I,J), XL(I,J,1), FITM(KOUNT), GEEX,
     *                      FITMS(KOUNT), FITMC(KOUNT), FITMR(KOUNT)
       END DO
      END DO
      WRITE(10,91)
      DO I=1,NSYS
      K=NPT(I)
```

```
       DO J=1,K
       KOUNT=KOUNT+1
       GEEX=-YL(I,J,1)*DLOG(YL(I,J,1))-YL(I,J,2)*DLOG(YL(I,J,2))
       GEEX=GEEX*1000000.0
       YL(I,J,2)=YL(I,J,2)*1000000.0
       FITM(KOUNT)=FITM(KOUNT)*1000000.0
       FITMS(KOUNT)=FITMS(KOUNT)*1000000.0
       FITMC(KOUNT)=FITMC(KOUNT)*1000000.0
       FITMR(KOUNT)=FITMR(KOUNT)*1000000.0
       WRITE(10,90) T(I,J), YL(I,J,2), FITM(KOUNT), GEEX,
     *                    FITMS(KOUNT), FITMC(KOUNT), FITMR(KOUNT)
       END DO
      END DO
      STOP
10     FORMAT(2X,50A)
20     FORMAT(2X,'MODEL =',2X,I5)
30     FORMAT(2X,'NCOMP =',2X,I5)
40     FORMAT(2X,'NGRP  =',2X,I5)
50     FORMAT(2X,'NSYS  =',2X,I5)
60     FORMAT(2X,'NPARA =',2X,I5)
70     FORMAT(2X,'IDGRP =',2X,/
     *         2X,'        ',2X,6(I5,2X))
80     FORMAT(2X,'NPT    =',2X,6(I5,2X))
89     FORMAT(2X,'TEMP    ',4X,'XL-EXP',4X,'XL-CAL',4X,'GE-EXP',4X,
     *      'GE-CAL',4X,'GE-COMB-CAL',4X,'GE-RES-CAL')
91     FORMAT(2X,'TEMP    ',4X,'YL-EXP',4X,'YL-CAL',4X,'GE-EXP',4X,
     *      'GE-CAL',4X,'GE-COMB-CAL',4X,'GE-RES-CAL')
90     FORMAT(2X,F7.2,6(2X,F14.2))
      END

***********************************************************************
*                        SUBROUTINE SECTION                           *
***********************************************************************

      SUBROUTINE FCN(FITM)

      IMPLICIT REAL*8(A-H,O-Z)

      PARAMETER(NN=20)
      PARAMETER(MM=600)

C
C      MARQ COMMONS
C
      COMMON /CSTEP/ X(NN),XMAX(NN),XMIN(NN),DELTX(NN),DELMN(NN),
     *        ERR(NN,NN+1),FOBJ,NV,NTRAC,MATRX,MASK(NN),
     *        NFMAX,NFLAT,JVARY,NXTRA,KFLAG,NOREP,KERFL,KW
      COMMON /NLLS4/ FLAMB,FNU,RELDF,RELMN,METHD,KALCP,KORDF,MAXIT,
     *        LEQU,MXSUB,MXUPD
      COMMON /CDAT/ FIT(MM),Y(MM),YSIG(MM),NPTS
C
C      PROGRAMM COMMONS

      COMMON /FIT/ NSYS, NPT(10),ERRREL,ITMAX,
     *             NCGRP(10,10,10), T(10,50), XL(10,50,10),
     *             DXL(10,50,10), YL(10,50,10), DYL(10,50,10),
     *             GAMAXL(10,50,10), GAMAYL(10,50,10),FITMC(MM),
     *             FITMR(MM), FITMS(MM)

      COMMON/DSET/ AH1(10,10),AH2(10,10),AH3(10,10), AM(10,10),
     *             AF(10,10), RKDB(10), QKDB(10),
     *             MODEL, NCOMP, NGRP, IDGRP(10),
     *             AL1(10,10),AL2(10,10),AL3(10,10),
     *             AW1(10,10),AW2(10,10),AW3(10,10),
     *             RKDBW(10), QKDBW(10)

      COMMON/NEQ/ TWK, NCGRPWK(10,10), GAMAWOK1(10),GAMAWOK2(10),
     :            GAMAWOKC1(10), GAMAWOKC2(10), GAMAWOKR1(10),
     :            GAMAWOKR2(10)

      DIMENSION XWK(10),FITM(MM), FNORM(10), X1(10), X2(10),
```

```
:          XCAL(10)

  EXTERNAL UNIFAC, DNEQNF, FEQ

  LL=LL+1

  IF(LL.NE.1) GO TO 50

  KOUNT=0
  DO I=1,NSYS
  K=NPT(I)
   DO J=1,K
   KOUNT=KOUNT+1
   Y(KOUNT)=XL(I,J,1)
   YSIG(KOUNT)=Y(KOUNT)
   END DO
  END DO

  DO I=1,NSYS
  K=NPT(I)
   DO J=1,K
   KOUNT=KOUNT+1
   Y(KOUNT)=YL(I,J,2)
   YSIG(KOUNT)=Y(KOUNT)
   END DO
  END DO
  KOUNT=0

  IF(MODEL.EQ.1.OR.MODEL.EQ.5) THEN
  X(1)=AH1(1,4)
  X(1)=AH1(2,4)
  X(2)=AH1(3,4)
  X(3)=AH1(5,4)
  X(3)=AH1(6,4)

  X(4)=AH2(1,4)
  X(4)=AH2(2,4)
  X(5)=AH2(3,4)
  X(6)=AH2(5,4)
  X(6)=AH2(6,4)

  X(7)=AH1(4,1)
  X(7)=AH1(4,2)
  X(8)=AH1(4,3)
  X(9)=AH1(4,5)
  X(9)=AH1(4,6)

  X(10)=AH2(4,1)
  X(10)=AH2(4,2)
  X(11)=AH2(4,3)
  X(12)=AH2(4,5)
  X(12)=AH2(4,6)

  X(13)=AH3(4,1)
  X(13)=AH3(4,2)
  X(14)=AH3(4,3)
  X(15)=AH3(4,5)
  X(15)=AH3(4,6)
  END IF

  IF(MODEL.EQ.2.OR.MODEL.EQ.4) THEN
  X(1)=AF(1,4)
  X(1)=AF(2,4)
  X(2)=AF(3,4)
  X(3)=AF(4,1)
  X(3)=AF(4,2)
  X(4)=AF(4,3)
  END IF

  IF(MODEL.EQ.3) THEN
  X(1)=AM(1,3)
```

```
        X(2)=AM(1,4)
        X(1)=AM(2,3)
        X(2)=AM(2,4)
        X(3)=AM(3,1)
        X(3)=AM(3,2)
        X(4)=AM(3,4)
        X(5)=AM(4,1)
        X(5)=AM(4,2)
        X(6)=AM(4,3)
        END IF

50       CONTINUE

        IF(MODEL.EQ.1.OR.MODEL.EQ.5) THEN
        AH1(1,4)=X(1)
        AH1(2,4)=X(1)
        AH1(3,4)=X(2)
        AH1(5,4)=X(3)
        AH1(6,4)=X(3)

        AH2(1,4)=X(4)
        AH2(2,4)=X(4)
        AH2(3,4)=X(5)
        AH2(5,4)=X(6)
        AH2(6,4)=X(6)

        AH1(4,1)=X(7)
        AH1(4,2)=X(7)
        AH1(4,3)=X(8)
        AH1(4,5)=X(9)
        AH1(4,6)=X(9)

        AH2(4,1)=X(10)
        AH2(4,2)=X(10)
        AH2(4,3)=X(11)
        AH2(4,5)=X(12)
        AH2(4,6)=X(12)

        AH3(4,1)=X(13)
        AH3(4,2)=X(13)
        AH3(4,3)=X(14)
        AH3(4,5)=X(15)
        AH3(4,6)=X(15)
        END IF

        IF(MODEL.EQ.2.OR.MODEL.EQ.4) THEN
        AF(1,4)=X(1)
        AF(2,4)=X(1)
        AF(3,4)=X(2)
        AF(4,1)=X(3)
        AF(4,2)=X(3)
        AF(4,3)=X(4)
        END IF

        IF(MODEL.EQ.3) THEN
        AM(1,3)=X(1)
        AM(1,4)=X(2)
        AM(2,3)=X(1)
        AM(2,4)=X(2)
        AM(3,1)=X(3)
        AM(3,2)=X(3)
        AM(3,4)=X(4)
        AM(4,1)=X(5)
        AM(4,2)=X(5)
        AM(4,3)=X(6)
        END IF

        NROOT=2*NCOMP
        KOUNT=0
        DO I=1,NSYS
         DO K=1,NCOMP
```

```
       DO L=1,NGRP
       NCGRPWK(K,L)=NCGRP(I,K,L)
       END DO
       END DO

C              DO K=1,NCOMP
C              WRITE(*,*) K,(NCGRPWK(K,L),L=1,NGRP)
C              END DO

       KK=NPT(I)
       DO K=1,KK
               DO L=1,NCOMP
               XWK(L)=XL(I,K,L)
               XWK(L+NCOMP)=YL(I,K,L)
               END DO

       KOUNT=KOUNT+1
       TWK=T(I,K)

C              WRITE(*,*) KOUNT, TWK, XWK(1), XWK(4)

       CALL DNEQNF(FEQ,ERRREL,NROOT,ITMAX,
     :                     XWK,XCAL,FNORM)

C              WRITE(*,*) KOUNT, TWK, XCAL(1), XCAL(4)
       WRITE(*,*) I,K,XCAL(1),XCAL(4)
       DO L=1,NCOMP
       X1(L)=XCAL(L)
       X2(L)=XCAL(L+NCOMP)
       END DO


       FIT(KOUNT)  = X1(1)
       FITM(KOUNT) = X1(1)
       FITMC(KOUNT)= X1(1)*GAMAWOKC1(1)+X1(2)*GAMAWOKC1(2)
       FITMR(KOUNT)= X1(1)*GAMAWOKR1(1)+X1(2)*GAMAWOKR1(2)
       FITMS(KOUNT)= FITMC(KOUNT)+FITMR(KOUNT)
       FIT(KOUNT+NPTS/2)  = X2(2)
       FITM(KOUNT+NPTS/2) = X2(2)
       FITMC(KOUNT+NPTS/2)= X2(1)*GAMAWOKC2(1)+
     *                              X2(2)*GAMAWOKC2(2)
       FITMR(KOUNT+NPTS/2)= X2(1)*GAMAWOKR2(1)+
     *                              X2(2)*GAMAWOKR2(2)
       FITMS(KOUNT+NPTS/2)= FITMC(KOUNT+NPTS/2)+
     *                              FITMR(KOUNT+NPTS/2)

       END DO
      END DO

      RETURN
      END

      SUBROUTINE FEQ(X, F, NV)

      IMPLICIT REAL*8(A-H,O-Z)

      PARAMETER (N=10)

      COMMON/DSET/ AH1(10,10),AH2(10,10),AH3(10,10), AM(10,10),
     *              AF(10,10), RKDB(10), QKDB(10),
     *              MODEL, NCOMP, NGRP, IDGRP(10),
     *              AL1(10,10),AL2(10,10),AL3(10,10),
     *              AW1(10,10),AW2(10,10),AW3(10,10),
     *              RKDBW(10), QKDBW(10)

      COMMON/NEQ/ TWK, NCGRPWK(10,10), GAMAWOK1(10),GAMAWOK2(10),
     :             GAMAWOKC1(10), GAMAWOKC2(10), GAMAWOKR1(10),
     :             GAMAWOKR2(10)

      DIMENSION X(N), F(N), XWOK1(N), XWOK2(N)
```

```
       EXTERNAL UNIFAC

       ICHK=(NV)/2
       IF(ICHK.NE.NCOMP) THEN
       WRITE( *,'('' *** ITERATIVE VECTOR SIZE DOESNOT MATCH *** '')')
       END IF

       DO I=1,2*NCOMP
       IF(X(I).LT.1.0D-14) X(I)=1.0D-8
       IF(X(I).GT.1.0)     X(I)=1.0
       END DO

       DO I=1,NCOMP
       XWOK1(I)=X(I)
       XWOK2(I)=X(I+NCOMP)
       END DO

       CALL UNIFAC(NCGRPWK,TWK,XWOK1,GAMAWOK1,GAMAWOKC1,GAMAWOKR1)
       CALL UNIFAC(NCGRPWK,TWK,XWOK2,GAMAWOK2,GAMAWOKC2,GAMAWOKR2)

       DO I=1,NCOMP
       F(I)=GAMAWOK1(I)*XWOK1(I)-GAMAWOK2(I)*XWOK2(I)
       END DO

       SUMX1=0.0
       SUMX2=0.0

       DO I=1,NCOMP
       SUMX1=SUMX1+XWOK1(I)
       SUMX2=SUMX2+XWOK2(I)
       END DO

       F(NCOMP+1)=SUMX1-1.0
       F(NCOMP+2)=SUMX2-1.0

       RETURN
       END

       SUBROUTINE UNIFAC(NCGRP, T, X, GAMA, GAMAC, GAMAR)
******************************************************************************
*       PROGRAMM USAGE:                                                      *
*               THIS SUBROUTINE IS DESIGNED TO CALCULATE THE ACTIVITY        *
*       COEFFICIENT OF A NONELECTROLYTE COMPONENT IN THE FLUID PHASE         *
*       USING FOUR DIFFERENT VERSION OF UNIFAC METHODS                       *
*                                                                            *
*       MAIN ARGUMENTS:                                                      *
*                                                                            *
*               MODEL  =          DIFFERENT UNIFAC VERSIONS                  *
*               NCOMP  =          NUNBER OF COMPONENTS                       *
*               NGRP   =          NUNBER OF FUNCTIONAL GROUPS                *
*               NCGRP  =          NUMBER OF GROUPS IN A COMPONENT            *
*               T      =          TEMPERATURE (KELVIN)                       *
*               X      =          MOLE FRACTION                              *
*                                                                            *
*               MODEL  =          1     HOOPER, H. H.                        *
*                      =          2     LARSEN, B.                           *
*                      =          3     MAGNUSSEN, T.                        *
*                      =          4     FREDENSLUND, A.                      *
*                      =          5     THIS WORK                            *
*                                                                            *
*               GRP 1  =          CH3                                        *
*               GRP 2  =          CH2                                        *
*               GRP 3  =          ACH                                        *
*               GRP 4  =          H2O                                        *
*               GRP 5  =          ACCH3                                      *
*               GRP 6  =          ACCH2                                      *
*                                                                            *
*       REFERENCE     :           HOOPER, H. H.; MICHEL, S.; PRAUSNITZ, J. P.*
*                                 IND. ENG. CHEM. RES. 1988,27,2182-2187     *
*                                 LARSEN, B.; RASMUSSEN, P.; FREDENSLUND, A. *
*                                 IND. ENG. CHEM. RES. 1987, 26, 2274-2286   *
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*                                MAGNUSSEN, T.;  RASMUSSEN, P.;            *
*                                FREDENSLUND, A.                           *
*                                IND. ENG. CHEM. PROCESS. DES. DEV. 1981,  *
*                                20, 331-339                               *
*                                FREDENSLUND, A.; JONES, R. L.;            *
*                                PRAUSNITZ, J. P.                          *
*                                AICHE J. 1975, 21, 1086-1099              *
****************************************************************************

      IMPLICIT REAL*8(A-H,O-Z)

      PARAMETER (N=10)

      COMMON/DSET/ AH1(10,10),AH2(10,10),AH3(10,10), AM(10,10),
     *             AF(10,10), RKDB(10), QKDB(10),
     *             MODEL, NCOMP, NGRP, IDGRP(10),
     *             AL1(10,10),AL2(10,10),AL3(10,10),
     *             AW1(10,10),AW2(10,10),AW3(10,10),
     *             RKDBW(10), QKDBW(10)

      DIMENSION  NCGRP(10,10), X(10), GAMA(10)

      DIMENSION  RK(N), QK(N), A(N,N)

      DIMENSION  R(N), Q(N), XR(N), XQ(N), FI(N), SITA(N),
     :           CL(N), GAMAC(N)

      DIMENSION  U(N,N), GRPM(N), SFM(N), SFR(N,N), TSR(N),
     :           TSEM(N), TSER(N,N), SUMEFM(N), SUMEFR(N,N),
     :           GLNM(N), GLNP(N,N), GAMAR(N)

      IF(MODEL.NE.6) THEN
      DO I=1,NGRP
      RK(I)=RKDB(IDGRP(I))
      QK(I)=QKDB(IDGRP(I))
      END DO
      ELSE
      DO I=1,NGRP
      RK(I)=RKDBW(IDGRP(I))
      QK(I)=QKDBW(IDGRP(I))
      END DO
      END IF

C      write(*,*) (rk(i),i=1,ngrp)
C      write(*,*) (qk(i),i=1,ngrp)

      DO I=1,NGRP
       DO J=1,NGRP
       IF(MODEL.EQ.1.OR.MODEL.EQ.5) THEN
       A(I,J)=AH1(IDGRP(I),IDGRP(J))+AH2(IDGRP(I),IDGRP(J))*T+
     :              AH3(IDGRP(I),IDGRP(J))*T*T
       END IF
       IF(MODEL.EQ.2) THEN
       A(I,J)=AL1(IDGRP(I),IDGRP(J))+AL2(IDGRP(I),IDGRP(J))*
     :              (T-298.15)+AL3(IDGRP(I),IDGRP(J))*
     :              (T*DLOG(298.15/T)+T-298.15)
       END IF
       IF(MODEL.EQ.3) THEN
       A(I,J)=AM(I,J)
       END IF
       IF(MODEL.EQ.4) THEN
       A(I,J)=AF(I,J)
       END IF
       IF(MODEL.EQ.6) THEN
       A(I,J)=AW1(IDGRP(I),IDGRP(J))+AW2(IDGRP(I),IDGRP(J))*T+
     :              AW3(IDGRP(I),IDGRP(J))*T*T
       END IF
       END DO
      END DO

      IF(MODEL.EQ.3.OR.MODEL.EQ.4) GO TO 100
```

```
       IF(MODEL.EQ.6) GO TO 150
C
C       COMBINATORY PART OF MODEL 1,2 AND 5
C
       DO I=1,NCOMP
       R(I)=0.0
        DO J=1,NGRP
        R(I)=R(I)+NCGRP(I,J)*RK(J)
       END DO
       END DO
C       do i=1,ncomp
C       write(*,*) (ncgrp(i,j),j=1,ngrp)
C       end do
C       write(*,*) (x(i),i=1,ncomp)
C       write(*,*) (r(i),i=1,ncomp)
C       pause

       SUMXR=0.0
       DO I=1,NCOMP
       SUMXR=SUMXR+X(I)*(R(I)**(2.0/3.0))
       END DO


       IF(DABS(SUMXR).LT.1.0D-14) SUMXR=1.0D-10

       DO I=1,NCOMP
       FI(I)=(R(I)**(2.0/3.0))/SUMXR
       END DO

       DO I=1,NCOMP
       GAMAC(I)=DLOG(FI(I))+1.0-FI(I)
       END DO
       GO TO 200
C
C       END OF COMBINATORY PART OF MODEL 1,2 AND 5
C
C
C       COMBINATORY PART OF MODEL 3 AND 4
C
100     DO I=1,NCOMP
       R(I)=0.0
       Q(I)=0.0
        DO J=1,NGRP
        R(I)=R(I)+NCGRP(I,J)*RK(J)
        Q(I)=Q(I)+NCGRP(I,J)*QK(J)
        END DO
       END DO

       SUMXR=0.0
       SUMXQ=0.0
       DO I=1,NCOMP
        XRTEM=X(I)*R(I)
        XQTEM=X(I)*Q(I)
        SUMXR=SUMXR+XRTEM
        SUMXQ=SUMXQ+XQTEM
        XR(I)=XRTEM
        XQ(I)=XQTEM
       END DO

       IF(DABS(SUMXR).LT.1.0D-14) SUMXR=1.0D-10
       IF(DABS(SUMXQ).LT.1.0D-14) SUMXQ=1.0D-10

       DO I=1,NCOMP
       FI(I)=XR(I)/SUMXR
       SITA(I)=XQ(I)/SUMXQ
       END DO
       DO I=1,NCOMP
       CL(I)=5.0*(R(I)-Q(I))-(R(I)-1.0)
       END DO
       TCL=0.0
       DO I=1,NCOMP
```

```
       TCL=TCL+X(I)*CL(I)
       END DO

       DO I=1,NCOMP
       GAMAC(I)=DLOG(FI(I)/X(I))+5.0*Q(I)*DLOG(SITA(I)/FI(I))+
     :          CL(I)-FI(I)*TCL/X(I)
       END DO
       GO TO 200
C
C       END OF COMBINATORY PART OF MODEL 3 AND 4
C
C       COMBINATORY PART OF MODEL 6
C
150     DO I=1,NCOMP
       R(I)=0.0
       Q(I)=0.0
        DO J=1,NGRP
        R(I)=R(I)+NCGRP(I,J)*RK(J)
        Q(I)=Q(I)+NCGRP(I,J)*QK(J)
        END DO
       END DO

       SUMXR=0.0
       DO I=1,NCOMP
       SUMXR=SUMXR+X(I)*(R(I)**(3.0/4.0))
       END DO

       IF(DABS(SUMXR).LT.1.0D-14) SUMXR=1.0D-10

       DO I=1,NCOMP
       FI(I)=(R(I)**(3.0/4.0))/SUMXR
       END DO

       DO I=1,NCOMP
       GAMAC(I)=DLOG(FI(I))+1.0-FI(I)
       END DO


       SUMXR=0.0
       SUMXQ=0.0
       DO I=1,NCOMP
        XRTEM=X(I)*R(I)
        XQTEM=X(I)*Q(I)
        SUMXR=SUMXR+XRTEM
        SUMXQ=SUMXQ+XQTEM
        XR(I)=XRTEM
        XQ(I)=XQTEM
       END DO

       IF(DABS(SUMXR).LT.1.0D-14) SUMXR=1.0D-10
       IF(DABS(SUMXQ).LT.1.0D-14) SUMXQ=1.0D-10

       DO I=1,NCOMP
       FI(I)=R(I)/SUMXR
       SITA(I)=Q(I)/SUMXQ
       END DO

       DO I=1,NCOMP
       GAMAC(I)=GAMAC(I)-5.0*Q(I)*
     :          (1.0-FI(I)/SITA(I)+DLOG(FI(I)/SITA(I)))
       END DO
C
C       END OF COMBINATORY PART OF MODEL 6
C
C       RESIDUAL PART
C
200     DO I=1,NGRP
        DO J=1,NGRP
        U(I,J)=DEXP(-(A(I,J)/T))
        END DO
       END DO
```

```
DO M=1,NGRP
GRPM(M)=0.0
 DO I=1,NCOMP
 GRPM(M)=GRPM(M)+NCGRP(I,M)*X(I)
 END DO
END DO

TGRPM=0.0
DO I=1,NGRP
TGRPM=TGRPM+GRPM(I)
END DO
DO I=1,NGRP
GRPM(I)=GRPM(I)/TGRPM
END DO
TSM=0.0
DO I=1,NGRP
TSM=TSM+QK(I)*GRPM(I)
END DO
DO I=1,NGRP
SFM(I)=QK(I)*GRPM(I)/TSM
END DO
DO I=1,NCOMP
TSR(I)=0.0
 DO J=1,NGRP
 TSR(I)=TSR(I)+NCGRP(I,J)*QK(J)
 END DO
END DO
DO I=1,NCOMP
 DO J=1,NGRP
 SFR(I,J)=NCGRP(I,J)*QK(J)/TSR(I)
 END DO
END DO
DO I=1,NGRP
TSEM(I)=0.0
 DO J=1,NGRP
 TSEM(I)=TSEM(I)+SFM(J)*U(J,I)
 END DO
END DO
DO I=1,NGRP
SUMEFM(I)=0.0
 DO J=1,NGRP
 SUMEFM(I)=SUMEFM(I)+SFM(J)*U(I,J)/TSEM(J)
 END DO
END DO
DO K=1,NCOMP
 DO I=1,NGRP
 TSER(K,I)=0.0
          DO J=1,NGRP
          TSER(K,I)=TSER(K,I)+SFR(K,J)*U(J,I)
          END DO
 END DO
END DO
DO K=1,NCOMP
 DO I=1,NGRP
 SUMEFR(K,I)=0.0
          DO J=1,NGRP
 SUMEFR(K,I)=SUMEFR(K,I)+SFR(K,J)*U(I,J)/TSER(K,J)
          END DO
 END DO
END DO
DO K=1,NCOMP
 DO I=1,NGRP
 GLNM(I)=QK(I)*(1.0-DLOG(TSEM(I))-SUMEFM(I))
 GLNP(K,I)=QK(I)*(1.0-DLOG(TSER(K,I))-SUMEFR(K,I))
 END DO
END DO
DO I=1,NCOMP
GAMAR(I)=0.0
 DO J=1,NGRP
 GAMAR(I)=GAMAR(I)+NCGRP(I,J)*(GLNM(J)-GLNP(I,J))
```

```
         END DO
        END DO
C
C        END OF RESIDUAL PART
C
        DO I=1,NCOMP
        GAMA(I)=DEXP(GAMAC(I)+GAMAR(I))
        END DO

        RETURN
        END
```

VITA 2

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