INFINITE DILUTION ACTIVITY COEFFICIENTS FOR MEASUREMENT OF ENVIRONMENTAL PARAMETERS

By

MOHAMMAD MEHDI MONTAZER-RAHMATI

Bachelor of Science
Michigan State University
East Lansing, Michigan
1983

Bachelor of Arts
Michigan State University
East Lansing, Michigan
1983

Master of Arts
Michigan State University
East Lansing, Michigan
1984

Master of Science
Oklahoma State University
Stillwater, Oklahoma
1985

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Thesis Approved:

Jan Wagner
Thesis Adviser

Robert Robinson Jr.

Arland H. Johannes

John Chandler

Norman N. Durham
Dean of the Graduate College

PREFACE

Experimental values of infinite dilution activity coefficients were obtained from the literature and through an experimental program so that binary interaction parameters for the UNIFAC group contribution model could be calculated. This group contribution model has thus been tuned for aqueous systems containing pollutants such as aromatic and halogenated hydrocarbons which are of environmental significance because of the health hazards they pose to living organisms.

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LIST OF SYMBOLS

Symbol	
C	concentration
f	fugacity
H	Henry's law constant
k	equilibrium constant
m	mass
n	number of moles
P	pressure
R	universal gas constant
t	time
T	temperature
v	molar volume
V	volume
x	liquid composition
y	vapor composition
Greek symbols	
γ	activity coefficient
ϕ	fugacity coefficient
δ	differential
σ	standard deviation

Σ	summation

Subscripts

1	solvent
2	solute
i	component number

Superscript

E	excess property
L	liquid property
V	vapor property
s	saturation condition
∞	infinite dilution property
$\circ$	pure component property

CHAPTER I

INTRODUCTION

Environmental parameters such as Henry's law constants, aqueous solubilities, and octanol-water partition coefficients are often required to describe the rates and directions of organic chemical mass transfer in the environment. These parameters can be obtained from experimental data. However, a more utilitarian approach is based on the calculation of these parameters from activity coefficients correlated in terms of molecular structure. Using group contribution methods, the physical properties of a fluid can be formulated in terms of the functional groups of a molecule, and a very large number of aqueous organic solutions can be described in terms of a relatively small number of groups. In addition, no specific experimental data or correlations are required for new chemicals.

The objective of this work is to determine the extent of the available equilibrium data for aqueous systems of environmental significance in the literature. These data are used to determine missing interaction parameters for the UNIFAC group contribution activity coefficient model or to obtain new parameters which will improve the performance of the model as compared to the available parameters. An experimental facility is also to be developed to measure activity coefficients. The performance of the experimental setup will be checked by comparing the obtained experimental data to the well-established literature values. This setup can further be used to obtain new data, as needed, to complete the correlation framework of the particular activity coefficient model selected for this work. The experimental facility will make possible the determination of UNIFAC parameters for specific application to dilute aqueous solutions of organic chemicals. New parameters are required, since existing activity coefficient model parameters have been obtained from data at high concentrations and are often inaccurate for environmental applications.

Objectives

The objectives of this work can be achieved by performing the following specific tasks.

Compilation and Evaluation of Published Data

Data from the literature will be compiled on those properties from which activity coefficients can be determined, i.e., directly measured activity coefficient values, Henry's constants, etc. These data will be evaluated to assess their quality in terms of estimated errors in the results and the suitability for use in model testing.

Evaluation of the performance of the UNIFAC model

The data from the literature and from this project will be used to evaluate the performance of the UNIFAC model with current parameters in determination of activity coefficients of dilute aqueous solutions. If existing model parameters prove inadequate, they will be modified to provide improved representation. In particular, parameters from the UNIFAC model will be derived from data restricted to low solute concentrations to the extent possible. Activity coefficient predictions with the new parameters will be compared with predictions made with current UNIFAC parameters. This comparison will provide a basis for assessing the capability of this group contribution method for estimating environmental parameters.

Development of Experimental Facility

The experimental techniques for measurement of activity coefficients in the systems of interest will be reviewed and evaluated. The aqueous organic systems present unique problems as a result of their very low mutual solubilities, and the high level of nonideality in these systems. The various potential experimental techniques will be evaluated in terms of the accuracy of the method and available analytical capabilities. These evaluations will provide the framework for an experimental program to measure activity coefficients for those systems considered to be of highest priority. Extensive data collection will not be the emphasis of this work. However, enough data will be collected to ensure the validity of the experimental procedure.

CHAPTER II

LITERATURE REVIEW

The literature review will consist of two segments. In the first segment, the experimental methods that have been used to measure activity coefficients at infinite dilution will be reviewed. Attention will be focused on methods that have been successful in measuring the infinite dilution activity coefficient or related thermodynamic parameters in aqueous solutions. In the second segment, the theory behind the UNIFAC group contribution model which is the newest, and most successful general model for prediction of activity coefficients, will be reviewed.

Experimental Methods

There are several methods of measuring activity coefficients at infinite dilution. Each method has certain advantages and drawbacks. The following descriptions of each method should help determine which one is the most appropriate for the case at hand.

The Gas Stripping Method

Leroi et al. (77) who introduced this technique describe the principles of the method in the following way. A binary system contained in an equilibrium cell is placed in a constant temperature bath. A constant carrier gas flow is introduced into the still and strips the solute and solvent components into the vapor phase. The outlet gas flow, which is in equilibrium with the liquid phase in the still, is periodically introduced into a gas chromatograph through a gas sampling valve which is maintained at a higher temperature in order to avoid any condensation of the vapor. The total pressure at equilibrium, the carrier gas flow rate, and the total amount of solvent are the quantities that are measured. For a nonvolatile solvent and concentrations in the linearity range of the GC detector, it is shown that the variation with time of the peak area of the solute can be simply derived from these measurements only. No calibration is necessary, and there is no need for the initial concentration of the solute in the liquid phase to be known. The method can also be extended to multicomponent systems, the only condition required being a good chromatographic separation. Using an electronic integrator for the determination of peak areas yields accurate and reliable values of the infinite dilution activity coefficient.

The equations that are used to calculate the infinite dilution activity coefficient (γ^{∞}) are as follows:

for non-volatile solvents:

$$\ln \frac{S_{sol}}{(S_{sol})_{t=0}} = - \frac{DP_{sol}}{RTN} \gamma^{\infty} t \qquad (1)$$

and for volatile solvents:

$$\ln \frac{S_{sol}}{(S_{sol})_{t=0}} = (\frac{\gamma^{\infty} P^{\circ}_{sol}}{P^{\circ}_{s}}) \ln(1 - \frac{P\, DP^{\circ}_{s} t}{(P-P^{\circ}_{s}) N_{\circ} RT}) \qquad (2)$$

where:

D = carrier gas flow rate

N = amount of solvent in the still

P = pressure

P°_{j} = vapor pressure

P_{j} = partial pressure

R = gas constant

S = peak area

t = time

T = temperature

and subscripts:

i, j = component

sol = solute

s = solvent

$\circ$ = initial value

Duhem et al. (46) have used the above experimental method to measure large value activity coefficients. They call this method the 'exponential diluter method' because of the exponential variation of the solute concentration with respect to time. They have modified Eq. (2) above by introducing a corrective term consisting of the ratio of the total number of moles of solute to the total number of moles of the solvent, which was neglected before. They also take the volatility of the solvent into account and correct for it by using the ratio of the solvent vapor pressure to the total system pressure. Their final equation is:

$$\ln \frac{S}{S_o} = - \frac{D\, P^{\circ}_{sol}\, \gamma^{\infty}\, t\, (1 - P^{\circ}_{s}/P)}{RTN \left(1 + \dfrac{V P^{\circ}_{sol} \gamma^{\infty}}{R\,T\,N}\right) \left(1 - \dfrac{\tilde{\bar{n}}\, \gamma^{\infty}\, P^{\circ}_{sol}}{N\left(1 + \dfrac{V\, P^{\circ}_{sol}\, \gamma^{\infty}}{R\,T\,N}\right) P}\right)} \qquad (3)$$

where:

$\tilde{\bar{n}} = (n-n_o) / \ln(n/n_o)$ = logarithmic mean of n

n = amount of solute in the still

n_o = initial n

V = volume of the vapor space in the still

and all the other terms are as defined before.

Using this equation, Duhem et al. (46) have measured the activity coefficient of benzene in water to be 1700. They obtained a value of 1910 using Eq. (2) and a value of

2420 using Eq. (3) without the volatility correction term, ($[1-P_s^\circ/P]$) in a simulated run. They state that the value based on solubility measurements is 2415 at 24°C.

Richon et al. (123) have determined limiting activity coefficients and Henry's law constants by the inert gas stripping method proposed by Leroi et al. (77) for a wide range of normal and branched alkanes in n-hexadecane. They have improved the original apparatus design and have determined the limits of validity of the experimental method. They suggest the construction of a special cell for high values of Henry's constants. The Henry's constants can be found from limiting or infinite dilution activity coefficients in the following fashion:

$$\gamma_i^\infty P_i^s = H_i^\infty \qquad (4)$$

where:

γ_i^∞ = infinite dilution activity coefficient of the solute
P_i^s = solute vapor pressure
H_i^∞ = Henry's law constant of the solute

Richon et al. (123) state that their experiments with the series of normal alkanes give lower and lower slopes, a, of the elution law, $\ln[(S_i)/(S_i)_{t=0}]=-at$, with increasing carbon number of the solute molecule. For the system n-octane - n-hexadecane, the experiment takes several hours to produce a sufficient variation of S_i. The experiment with n-nonane lasts about four times longer than for n-octane in order to obtain a significant change in S_i which remains very small in magnitude. The dispersion in S_i values in time does not allow a precise determination of the slope and the activity coefficient.

The difficulty in measuring the activity coefficient of nonane and other high carbon number alkanes is attributed by Richon et al. (123) to the very small amount of the solute in the vapor phase. Therefore, they have extended the original method to measurement of high values of Henry's constants by taking into account the influence of the volume of the vapor phase in the equilibrium cell. Their considerations of some mass transfer models result in the following conclusion. The bubbles of the carrier gas must have a diameter less than 2 mm and a path length in solution higher than 3 cm in order to entrain the solute molecules from the solution and carry them effectively into the vapor phase at equilibrium. Fritted glass discs through which the gas enter the equilibrium cell are deemed insufficient for this purpose and well spaced capillaries have therefore been used instead.

In another study, Richon et al. (124) have extended the use of the inert gas stripping method for measurement of infinite dilution activity coefficients to the study of viscous and foaming mixtures with viscosities up to 1000 cP. They have developed a new device that breaks foams without disturbing phase equilibrium inside the equilibrium cell. This new apparatus is well suited to investigations of aqueous mixtures of polyols, glucides, and proteins. The main application of this method is in the measurement of aroma retention in food so that the best sensory qualities could be provided to the consumer at the lowest prices.

Mackay et al. (90) have determined Henry's law constants for hydrophobic pollutants with a novel system capable of providing an accuracy of about 5%. The method consists of measuring the compound concentration in only the water phase while being stripped isothermally from solution at a known gas flow rate. They have determined Henry's law constants for benzene, toluene, ethylbenzene, chlorobenzene, naphthalene, biphenyl, and phenanthrene and have found good agreement with literature values. They state that since the three quantities -- Henry's law constant, aqueous solubility, and vapor pressure -- are interrelated, if any two of these three parameters are known the third can be calculated. This method can be used for obtaining accurate solubility and vapor pressure data or for verifying existing data. Their method can also be used to determine the extent of sorption of volatilizing compounds in aqueous environments and quantifying the role of sorption in the reduction of the volatilization rates.

A brief description of the experimental procedure follows. A concentrated solution of the hydrocarbon in the water is formed and then the hydrocarbon is stripped using the carrier gas. The initial hydrocarbon solution is obtained by equilibrating some hydrocarbon with water in a separate vessel, then transferring it to the column. The solution could also be obtained by by-passing the nitrogen stream after saturation with water through a vessel containing the hydrocarbon solution. The hydrocarbon then evaporates into the nitrogen stream and desorbs into the water. Desorption and dissolution into water cause the solute to achieve its equilibrium solubility in water. The volume of the water in the stripping vessel is measured and the nitrogen flow rate is set at 50 to 500 cc/min. Flow rates are measured at 5-min intervals. The pump carrying the sample into the spectrophotometer is turned on only for sampling and is run at 5 cc/s for about 1 minute. The sampling frequency ranges between once every minute to once every 20 minutes, depending on the rate of volatilization. The absorbance of the hydrocarbon and time are recorded for each sample. A semi log plot of absorbance versus time is linear and the Henry's law constant can be obtained from the slope of this plot.

Mackay et al. (90) used an ultraviolet spectrophotometer containing a 1-cm path length flow cell for their analysis and concluded that this analytical method is suited only for compounds with solubilities greater than 5 g m^{-3}. They have also used fluorescence but they suggest radio labeling compounds and measuring concentration by liquid scintillation counting. The major advantage of this method is its applicability in the low solubility range. In order to obtain an experimental value for the Henry's law constant, one needs to measure the concentration of the solute in both the liquid and the vapor in equilibrium preferably at several concentrations. This kind of measurement would be accurate if the concentrations are high, but for many pollutants this is not the case, because the solutes are only sparingly soluble in water and have low vapor pressures. Therefore, one needs concentration measurements at very low concentrations. The data of Mackay et al. (90) will be used for comparative purposes in this work. Of course the accuracy of these data is primarily dependent on the degree of approach to equilibrium, i.e., the extent to which the vapor and the liquid at the column exit are in equilibrium. Mackay et al. (90) have quantified this approach to equilibrium by operating the system at 11 liquid depths ranging from 0.9 to 38.5 cm. They then fitted the data to a mass transfer equation that they derived. They compared the experimental data with data calculated from vapor pressure and solubility data and reached the conclusion that for benzene each 10-cm depth yielded an 80% approach to equilibrium. They then concluded that this indicated an approach to equilibrium of more than 90% in their system which had a height of 38.5 cm. The 5% accuracy that they claim for their method is an average value.

A sub category of the stripping method is stripping in combination with a purge and trap step. When the concentration of the solute in the vapor phase in equilibrium with the liquid phase is not large enough to allow its analysis by the available analytical methods, as is the case with low vapor pressure organic chemicals such as polynuclear aromatic hydrocarbons, the vapor sample needs to be concentrated before being sent forward to the analysis step. Junk et al. (68) mention that the best documented and most frequently employed analytical procedure for measuring low levels of organic compounds in water involve solvent extraction and charcoal adsorption. They also point out that recently an increasing number of reports have described an additional analytical method which uses porous polymer resins as the sorbing agent. The most widely used resins are XAD-2 and Tenax. XAD-2 is a low-polarity styrene-divinylbenzene copolymer which possesses the macroreticular characteristics essential for high sorptive capacity (68). Tenax, poly(p-2, 6-diphenylphenyleneoxide), is another porous polymer used for high temperature applications in the 400-450 °C temperature range (68).

The analytical procedure involves the extraction of organic solutes by passing the contaminated water through a column of clean sorbent resin. The contaminants are then desorbed by elution with a solvent. The eluate is then concentrated by evaporation and the components in an aliquot of this concentrate are separated by gas chromatography

(68). The GC data provide the information that is necessary for quantification. If the solutes need to be identified, a separate aliquot is subjected to GC-MS analysis. Junk et al. (68) claim that an accurate quantitative estimation of organics in water at parts per million to trillion level is possible, if great care is taken in applying the analytical technique correctly. The resins, however, are 100% efficient only in removing alkanes. For other organic chemicals the adsorption efficiency is considerably less, with an average efficiency of about 78% with an average deviation of 6.1% and a standard deviation of 6.3% for the XAD-2 resin obtained for 110 individual determinations (68). Van Rossum et al. (162) have investigated the recovery efficiencies of different kinds of XAD resins. These resins were found to be applicable to a broad range of materials found in drinking waters and industrial effluents. However, their range of application is not as wide as that of carbon.

Leighton et al. (73) have measured the distribution coefficients of 21 chlorinated hydrocarbons plus benzene and toluene in dilute air-water systems for groundwater contamination applications using the above method which is described in more detail below.

Air-water distribution coefficients are measured by comparing the response of a gas chromatograph for a known quantity of air to its response for a known quantity of water. The experimental procedure follows. A liquid solution is prepared in a 2.3 L equilibration cell by first pouring the water in and then injecting about 5 μL of the compound of interest. There is some headspace left for better mixing which is achieved by shaking the cell vigorously for about 5 minutes. The head space is then reduced to 10 cc by filling the cell with distilled water before the experimental run. Homogeneity of the mixture is achieved by mechanical agitation and by the passing of air bubbles through the solution. The temperature is maintained at a desired set point using a constant temperature bath.

A known quantity of air is filtered through the activated charcoal trap and is then admitted to the equilibration cell through a glass frit. The air passes through an equilibration height of about 40 cm. The effluent gases pass through a concentrator trap and a soap film flowmeter; 15 to 20 cc of sample is used at a flow rate of 3-4 cc/min. The chlorinated hydrocarbons extracted from the air by the trap are then desorbed into the gas chromatograph carrier gas stream at 100°C.

Relative concentrations in the liquid sample are determined by the withdrawal of a 5 cc aliquot and stripping the dissolved volatiles into the concentrator trap. Ten minutes of purging is deemed sufficient for stripping the compounds of interest. The contents of the concentrator trap are then sent to the gas chromatograph for analysis. A correction factor is applied if all of the compound cannot be stripped out.

Distribution coefficients are calculated using:

$$K_i = y_i/x_i = (A_{air}v_{air}/V_{air})Q/(A_{water}v_{water}/V_{water}) \qquad (5)$$

where A refers to the integrated peak area, v is the specific volume, V the total volume and Q is the correction factor applied for incomplete purging and can be determined from successive purge data using:

$$Q = 1 - \{1-[1-4R(1-R)]^{0.5}\} / 2R \qquad (6)$$

where

$$R = A_1/(A_1 + A_2) \qquad (7)$$

A_1 and A_2 refer to the first and second 10-min purges, respectively.

Therefore, the distribution coefficients can be obtained from the GC-integrator data only and no calibration is necessary. Thus better accuracy is achieved by eliminating the calibration errors. The inclusion of the correction term ensures that incomplete stripping of the compounds with low distribution coefficients does not affect the final value of this coefficient.

Another technique known as spray volatilization has been proposed by Chriswell (31). This technique is a variation of the inert gas stripping technique which instead of using an adsorbing trap atomizes water into a high-velocity gas stream using a nebulizer of the type used on perfume bottles and throat sprayers. The very fine water mist which is thus produced is then directed to impact on a glass surface; there it condenses and coalesces on impact and drains into a reservoir. Gas chromatographable organic impurities in the water are carried out of the system in the gas stream. The advantage of this technique according to Chriswell (31) is that larger volumes of water can be handled and that the inconvenient and difficult trap desorbing step is eliminated.

De Bortoli et al. (36) have used a graphitized carbon black sorbent in their purge and trap method to adsorb perfluorocarbon tracers in air. Because of the low concentrations they used a GC equipped with a capillary column and an electron capture detector which is especially sensitive to halogenated hydrocarbons.

Avoiding water adsorption in the trap is important. Termonia et al. (150) used the following method to avoid this problem. Using the common stripping method, nitrogen is first passed through a purifying charcoal filter and then over the sample contained in a pyrex cylindrical purging vessel. An electrically heated oven assures a temperature of 85 ± 5 °C around the 7 cm part of the Pyrex line immediately preceding the adsorbing cartridge, thus preventing the water aerosol generated in the purging vessel from reaching the adsorbing bed. The adsorbing cartridge itself consists of a pyrex tube filled with Tenax T.A.. When the sampling is completed, the Tenax cartridge is disconnected from the sampling system and fixed in the desorber. Overnight conditioning consists of purging with deoxygenated nitrogen.

A modification of the purge and trap method is the purge and cold trap technique suggested by Badings et al. (13). Their work resulted in the fabrication of a commercial unit in the Netherlands which is now available from Chrompack International. Their description of the system follows. The purge gas is led through the sample flask via a glass tube provided with a glass frit to ensure highly dispersed purge flow. The purge flow, containing volatiles and water vapor, passes the first cold trap, kept at -15 °C by a cryostat. In this trap the bulk of the water vapor is frozen out in order to avoid the blockage of the second cold trap. The flow is led through the second cold trap of fused silica capillary tubing by means of a glass tube in the oven compartment of the purge and cold trap injector. This second cold trap is cooled by an air stream which is itself cooled by liquid nitrogen from a dewar flask. The volatiles from the sample, present in the purge flow, are trapped in the second cold trap at temperatures of at most -120°C. The trapped sample is now heated by resistance heating a surrounding metal capillary. The sample is then swept with carrier gas and injected into the GC. The condensed water collected in the first trap is flushed from the system. All of the many steps involved including the closing and opening of the valves, heating and cooling are controlled by an automatic control unit.

Multiple Phase Equilibration.

McAuliffe proposes the use of the multiple phase equilbration method for the estimation of distribution coefficients, Henry's law constants, vapor pressure, solubility, and several related thermodynamic parameters. The method is based on the demonstration that analysis of only one phase after two successive phase equilibrations yields all necessary data.

The experimental aspect of the multiple equilibration method is described by McAuliffe (97). Typically, a 50 ml glass hypodermic syringe with a Luer-Lok fitting is flushed several times with the aqueous sample. 25 ml of the sample is finally retained. 25 ml of an inert gas such as helium or nitrogen is added and the syringe is capped. The syringe is shaken vigorously for 3 to 5 minutes in order to establish equilibrium between the phases. 20 to 23 ml of the gas phase is allowed to flow through a previously evacuated sample loop of a gas chromatograph. A measured volume of between 1 to 10 ml of the gas is introduced into the GC column for analysis. The remainder of the gas in the syringe is carefully discharged by moving the solution to the syringe tip and 25 ml of fresh inert gas is added. The equilibration process is repeated as many times as needed for the specific application. If water is lost from the syringe, a correspondingly smaller volume of inert gas is added. The only condition is that the ratio of the volume of the gas phase to the aqueous phase must remain constant. The temperature must also be kept constant during the analysis.

The mathematics of the model are given below.

Let

X_i = quantity of compound x in the system during ith equilibration

G_i = quantity of x in the gas phase, of volume V_G, during ith equilibration

L_i = quantity of x in the liquid phase, of volume V_L, during ith equilibration

Then

$$X_i = G_i + L_i \qquad (8)$$

and

$$Hx_i = (G_i V_G / L_i V_L) \qquad (9)$$

where Hx is the Henry's law constant or distribution coefficient.

But if $V_G = V_L$ and and $Hx_i = Hx$, a constant, then

$$G_i = Hx\ X_i/(Hx+1) \qquad (10)$$

$$L_i = X_i/(Hx+1) \qquad (11)$$

and the fraction f, of the total x in each phase is

$$f_G = Hx/(Hx+1) \qquad (12)$$

$$f_L = 1/(Hx+1) = 1-f_G \qquad (13)$$

Furthermore,

$$G_{i+1} = Hx(X_i-G_i)/(Hx+1) \qquad (14)$$

and substituting for G_i

$$G_{i+1} = Hx\ X_i/(Hx+1)^2 \qquad (15)$$

Dividing the equation for G_i by the equation for G_{i+1}

$$Hx = (G_i/G_{i+1})-1 \tag{16}$$

Thus Hx can be determined from gas composition of two adjacent equilibrations only. Upon generalization of the equation for G_{i+1}, one gets:

$$G_n = Hx\ X_\circ/(Hx+1)^n \tag{17}$$

or

$$\log G_n = an+b \tag{18}$$

where

$$a = -\log(Hx+1) \tag{19}$$

$$b = \log Hx\ X_\circ \tag{20}$$

Thus, a semi log plot of G_n versus n is linear with the slope only a function of Hx and the intercept a function of initial sample composition, $X_\circ$.

From the straight line obtained by plotting the log of the hydrocarbon concentration in the gas phase versus the number of equilibrations, one could read any two adjacent gas phase concentrations, divide the greater value by the lower value and subtract 1 to obtain the Henry's law constant. One could average all Henry's constants thus obtained and get a mean value.

McAuliffe (97) has compared the gas equilibration and the gas stripping methods. He states that gas stripping and gas equilibration are similar in that both methods depend on volatile compounds diffusing from the water into a gas phase. Gas Stripping involves bubbling a nonreactive gas through the aqueous phase to remove volatile compounds and then adsorbing these compounds on a solid adsorbent or in a cold trap. The compounds are subsequently desorbed from the adsorbent or evaporated from the cold trap and analyzed.

Gas equilibration involves mixing a given volume of nonreactive gas with the liquid sample, thus establishing equilibrium of the organic solute between water and the gas phase. The gas is then analyzed in order to determine its concentration.

There are also differences between the two methods. Gas stripping is a partial equilibrium method, whereas gas equilibration allows for true equilibrium. Each method has advantages and disadvantages. The principal advantage of the gas equilibration method is that all volatile hydrocarbons will be present in the vapor phase. Their proportion in the vapor phase depends on their vapor pressure and solubility in the aqueous phase. Thus, all volatile hydrocarbons can be determined regardless of their molecular weight.

The multiple gas-phase aspect (repeated equilibration with a second volume of pure gas) provides for the separation of a given class of organic compounds from others, e.g., aromatic hydrocarbons from paraffinic and naphthenic hydrocarbons.

Because gas stripping is a partial equilibrium method, lower-molecular-weight organic compounds are stripped first.

Therefore, the amount removed is proportional to vapor pressure and inversely proportional to solubility . This results in complete removal of lower-molecular-weight organic compounds. Different classes of compounds also strip with different speeds, for hydrocarbons, alkanes > cycloalkanes > aromatics. As an example, cyclohexane strips faster than benzene despite their having similar molecular weight. Thus careful calibration of the stripping conditions is essential. If the stripping method analyzes a mixture containing compounds of different molecular weights in a single gas chromatographic run, the analysis lacks information obtainable by the gas equilibration method.

The use of an adsorbent or cold trap introduces another step and another potential source of error into the gas-stripping method. If stripping is carried out long enough to quantitatively remove the most difficult to strip organic compounds from the aqueous phase, the easiest to strip compounds start to be lost from the solid adsorbent, or cold trap. As an example, McAuliffe (97) cites the case of removing benzene and trimethylbenzenes from a Tenax solid adsorbent. It is difficult to remove the trimethylbenzenes from water and still retain benzene.

A principle advantage of the gas stripping method is high sensitivity. Gas stripping is capable of removing volatile organic materials from 10 μL to 2.0 L of aqueous samples. Gas equilibration, on the other hand, typically introduces the organic compounds from 1- to 50-mL samples. However, the higher sensitivity is often balanced by presence of contaminants in the stripping gas, air contamination, water interference, adsorption losses in recovering volatile organics from the solid adsorbent, and production of artifacts by heating organic polymer adsorbents (97).

Groups of compounds, such as hydrocarbons and chlorinated hydrocarbons have different distribution coefficients. Each class of hydrocarbons (alkanes, alkenes, cycloalkanes, and aromatics) has different distribution coefficients. For instance, McAuliffe (97) found that for his experimental conditions, the alkanes partition 95+% into the gas when equal volumes of gas and water are equilibrated. For this reason two or three equilibrations will transfer all the alkanes present into the gas phase. Aromatic hydrocarbons, however, partition less favorably to the gas phase, about 20%. Therefore, many equilibrations will be needed to obtain an analysis by summing successive gas phases. Because different classes of hydrocarbons partition differently, successive equilibrations remove alkanes, alkenes, and cycloalkanes, leaving only aromatic hydrocarbons in solution. This makes identification of compounds in a chromatogram easy.

McAuliffe (97) describes the accuracy and sensitivity of the gas equilbration method as follows. The standard deviation of replicates is less than 1% for most compounds. The method is capable of detecting alkane, alkene, and cycloalkane hydrocarbons down to 1-3 parts in 10^{12} parts of water by weight (ppt). Aromatic hydrocarbons, because of their lower partitioning into the gas phase, can be detected at 4-12 ppt. Reasonable accuracy requires concentrations 20-30 times higher.

Head Space Analysis

The head space analysis method is a static equilibrium method, as opposed to gas stripping which is a dynamic method. The method involves contacting the vapor and the liquid phase in an equilibrium cell and then taking a vapor sample for analysis. Milanova et al. (102) have determined the activity coefficient of several solutes in dilute binary solutions of nonelectrolytes at 20°C from vapor-liquid equilibria in a novel static equilibrium apparatus by gas chromatographic analysis of the equilibrium vapor phase. The glass cell was capped with a rotating metal head. This rotating head was fitted with three calibrated vapor-sampling loops that could be sequentially filled with equilibrium vapor over the solution, then switched directly into the carrier gas stream of a gas chromatograph. This design made possible repetitive measurements of the concentrations of components present in a true sample of the equilibrium vapor over a multicomponent liquid mixture.

Afrashtehfar et al. (2) have modified the apparatus of Milanova et al. (102) by constructing an all-glass head space sampler. Neither of these two works deals with the measurement of the infinite dilution activity coefficient of aqueous systems. However, Sagert et al. (133) have measured the activity coefficients of some butyl alcohols in water and in two organic solvents namely, n-octane and carbon tetrachloride using the head space analysis method.

Sagert et al. (133) describe the procedure as follows. The gas chromatograph was calibrated by injecting known quantities of solute so that the peak areas were known as a function of the number of moles of solute. 50 mL samples were then prepared by weight and placed in the cell, after retaining a small amount for analysis. The glass cell was then attached to the valve and the liquid degassed by a technique known as the freeze-pump-thaw. In this technique the solution is frozen, all gases are evacuated from the cell using a vacuum pump and the frozen solution is then allowed to thaw and reach equilibrium with its vapor. A thermostat with water at 20.00 ± 0.04°C was then placed around the cell and the solution in the cell was stirred using a magnetic stirrer. Samples were taken at regular intervals until equilibrium was reached. When equilibrium was achieved, samples of the retained liquid were injected into the gas chromatograph. From the calibration curve, solute concentrations in the vapor and liquid phases were calculated. The gas chromatography measurements were reliable to within ±2%, according to Sagert et al. (133).

Schoene et al. (135) have used an automated head space-gas chromatography technique to determine Henry's law constants for the following six organic chemicals, acetone, 2,6-dichlorobenzonitrile, 2-nitrophenol, pyridine, trichloroethene, and toluene. Their study was mainly concerned with the proof of the linearity of the dependence of the Henry's law constant on temperature in the Arrehenius region. They did find that a plot of log H versus 1/T yielded a straight line.

Other Methods

Among other methods of measuring activity coefficients one could mention the non-steady-state gas chromatography method proposed by Belfer et al. (16). They describe their method as follows. In non-steady-state gas chromatography, a relatively volatile solvent at the column temperature is injected into a column packed with solid support. The solvent condenses uniformly on the solid and reaches equilibrium with the carrier gas. As the solvent slowly evaporates out of the column, several injections of a solute are made. As the total volume of solvent decreases with time, so does the retention time of the injected solute. The decrease in retention time with change in time of injection at constant temperature and flow rate is related directly to the solute limiting activity coefficient in the solvent. Belfer et al. (16) state that their measured limiting activity coefficients of a variety of solutes in acetonitrile and n-octane solvents agree satisfactorily with published data. They claim an accuracy of about 10% with their apparatus.

In non-steady-state gas chromatography, no knowledge of the weight of the solvent in the column or the retention time of a non-retained substance is necessary.

The mathematical model presented by Belfer et al. (16) for the infinite dilution activity coefficient is as follows.

$$\gamma_2^{\infty}=\frac{RTn_1\phi_2Z_m\exp(-v_2^{\infty}P/Rt)}{\phi_2^sP_2^{\circ}V_N} \tag{21}$$

where

ϕ_2 = vapor phase fugacity coefficient of solute at P

P = total system pressure

ϕ_2^s = fugacity coefficient of the solute vapor under its saturation vapor pressure

Z_m = mixture compressibility

v_2^{∞} = solute-limiting partial molar volume

R = universal gas constant

T = column temperature

n_1 = number of moles of solvent in the column

t = retention time

p_2° = solute vapor pressure

V_N = net retention volume

Thomas et al. (153) have measured the infinite dilution activity coefficient of dichloromethane, chloroform and carbon tetrachloride in water using this method. The measured activity coefficients for these three solutes were 1000, 6300 and 4500, respectively. They state that the accuracy of their data is no better than 40% for limiting activity coefficient values of greater than 100. Therefore, this method does not seem to be appropriate for aqueous systems.

Loblen et al. (84) have used differential ebulliometry to measure infinite dilution activity coefficients for four systems two of which are aqueous, namely i-butanol-water and 2,4-pentanedione-water. However, the author of the present work knows from an earlier study that this method fails for sparingly soluble solutes because extremely large quantities of solvent are needed and the temperature measuring devices available are not sensitive enough to detect the boiling point temperature elevation produced by the introduction of a minute amount of the solute into the pure solvent. It is the temperature difference between the boiling pure solvent and the boiling solution that is the basis of the infinite dilution activity coefficient measurement by differential ebulliometry.

Chian et al. (29) have used a distillation/ headspace/

gas chromatography method of analysis for measurement of volatile polar organics at the ppb level. The purpose of their study was the monitoring of trace organics in drinking and nonconsumptive water. The sensitivity of the available methods had to be increased by a factor of 10 to 100. This could be accomplished either by improving the sensitivity of the final analytical step (GC or GC/MS) or by preconcentrating the initial sample. The concentration step could be achieved by the traditional trap method or using this new method of distillation proposed by Chian et al. (29), in which a few milliliters of distillate could be obtained by the distillation of a few hundred milliliters of the sample solution. Chian et al. (27) found that the resulting concentration factor depended on the initial sample volume, the final volume of the distillate collected, and the volatility of the specific volatile polar organic relative to that of water. The desired concentration factor of 10-100 could be achieved easily. In this manner, the volatile polar organics in the distillate could be determined at the sub-ppm and ppb levels by the direct aqueous injection/GC method and the head space gas injection/GC method, respectively.

Lincoff et al. (81) have determined Henry's constants for volatile organics by a simple technique known as equilibrium partitioning in closed systems. The advantages of this method are as follows. It requires no special apparatus and obtains results from the measurement of gas concentration ratios so that the preparation of standard curves for determining exact concentrations is not required. This is a total equilibrium method and does not have the problems of determining the approach to equilibrium in the partial equilibrium dynamic methods such as gas stripping. Lincoff et al. (81) have determined Henry's constants for five priority pollutants at 10 to 30 °C and have found good agreement with other experimental data in the literature. Lincoff et al.'s description of the theory behind the method follows (81). They have used the dimensionless Henry's constant defined as: $H_c = C_g / C_l$, in their derivation.

When a volatile chemical is added to a closed system containing a liquid and a gas phase, a mass balance shows:

$$M = C_l V_l + C_g V_g \tag{22}$$

where M is the mass added (mol), C_l is the concentration in the liquid (mol/m^3), V_l is the total liquid volume (m^3), C_g is the concentration in the gas (mol/m^3) and V_g is the gas volume (m^3). At equilibrium, the ratio of gas to liquid phase concentrations can be expressed as the Henry's law constant. The mass balance can be rewritten to include the Henry's law constant:

$$M = C_g V_l / H_c + C_g V_g \tag{23}$$

if the same mass of organic is added to two identical bottles at the same temperature, but with different liquid volumes, the last equation above can be written for both bottles and solved for the Henry's law constant.

$$H = [(C_{g1}/C_{g2})V_{l1}-V_{l2}] \; / \; [V_{g2}-(C_{g1}/C_{g2})V_{g1}] \qquad (24)$$

The above equation expresses the Henry's law constant as a function of the ratio of concentrations in only the gas phase. The ratio C_{g1}/C_{g2} can be replaced by a ratio of raw concentration data, such as gas chromatograph areas-under-the curve, if there is a linear relationship between raw data and absolute concentrations. It is not necessary to know the mass of the volatile chemical added to each system. All that is required is that the added masses are equal. In the experimental procedure, this is achieved by spiking each system with the same volume of organic-saturated water.

According to Lincoff et al. (81), plots of Henry's law constant versus gas phase concentration ratio (C_{g1}/C_{g2}) for various liquid volumes show that the technique has maximum sensitivity when one system has a low liquid volume and the other has a high liquid volume. Their study shows that the technique loses utility when the dimensionless Henry's constant is greater than two or three. However, most common ground water pollutants have Henry's law constants less than one, throughout the temperature range of interest.

Activity Coefficient Theory

From the Gibbs-Duhem equation:

$$\sum_i x_i \, d \ln \gamma_i = 0 \qquad (25)$$

at constant temperature and pressure. This equation relates the activity coefficients of all of the components in a mixture. There have been many models proposed for the relation between activity coefficients and mole fractions. Simpler models such as the Margules and van Laar (one and two constant) models are easy to use but require constants to be determined for each mixture from experimental data. The Wilson equation which uses the local concentration concept is more complicated but is capable of much better predictions. In the Wilson model, the effects of differences in molecular size and intermolecular forces are incorporated by an extension of the Flory-Huggins relation. Overall solution volume fractions are replaced by local volume fractions, which are related to local molecule concentrations caused by differing energies of interaction between pairs of molecules.

The most significant advantage of the Wilson model over the Margules and van Laar models is its enhanced ability to predict activity coefficients at very high dilution (less than 0.1 mole%). It is quite easy to determine the constant of the Margules model: $\log \gamma_1 = Ax_2^2$ once the infinite dilution activity coefficient is known, i.e., when $x_1=1$ and $x_2=0$, $\log \gamma_2 = A$. The two constant Margules equation requires the solution of two simultaneous equations, which is again quite straightforward. However, the values of activity coefficients obtained using these models are not nearly as accurate as the values predicted by the more complicated Wilson equation. The constants of the Wilson model are based on energy interactions between binary pairs.

The NRTL and UNIQUAC models are similar to the Wilson equation in that they too take local concentration into account and do not take the solution concentration to be uniform throughout. However, they use a mole fraction and a surface fraction, respectively, instead of the volume fraction used in the Wilson model.

The ASOG model is quite different in its approach because it considers the solution as a solution of chemical groups which comprise the molecules instead of the molecules themselves. The major advantage of this model is that once the binary interaction parameters are obtained from experimental data, they can be used to predict the activity coefficients of other molecules in a binary or multicomponent solution for which no experimental data exist but which are composed of the same functional groups. UNIFAC which is the newest and most widely used activity coefficient model combines the concepts introduced by the Wilson and the ASOG models, namely local composition effects which include the size and the shape of the molecules and the energy interactions between them and the solution of functional groups concept which broadens the range of applicability of the binary interaction parameters in exchange for some loss in accuracy because the model is approximate and not exact unless the groups and the molecules are identical.

For broad applications in water resources, methods based on a group contribution approach are particularly attractive. The basic idea is that although there are thousands of chemical compounds of interest in chemical technology, the number of functional groups which constitute these compounds is small. Thus, if a physical property of a fluid can be formulated in terms of the sum of the contributions from the functional groups of a molecule, the properties of a very large number of fluids can be correlated in terms of a relatively small number of parameters which characterize the contributions of individual groups. This approach is fairly utilitarian since activity coefficients can be estimated from chemical structure and no specific experimental data or correlation coefficients are required. Therefore, the UNIFAC model which is the activity coefficient model selected for this study is considered in detail below.

Fredenslund et al. (53) present a group-contribution estimation method for determination of activity coefficients in non-ideal mixtures. The method combines the solution-of-functional-groups concept with a model for activity coefficients based on an extension of the quasi chemical theory of mixtures. The resulting model known as UNIFAC (UNIQUAC Functional-group Activity Coefficients) contains two adjustable parameters per pair of functional groups.

Activity coefficients in a large number of binary and multicomponent mixtures may be predicted using the UNIFAC model, once binary interaction parameters have been obtained from experimental data. These mixtures may contain any organic chemicals. According to Fredenslund et al. (53), the applicable temperature range for this model is between 275 K to 400 K. In most cases, predicted activity coefficients at infinite dilution deviate less than 20% from measured values (53). The constants in this model reflect the volume and surface areas of individual functional groups. The parameters are an indication of energy interactions between groups.

Fredenslund et al. (53) describe the basis of their proposed model (UNIFAC) as follows. UNIFAC is based on the group contribution concept which has been successful for estimating a variety of pure component properties such as liquid densities, heat capacities, and critical constants. The basic idea is that although there is a large number of chemical compounds, the number of functional groups which constitute these compounds is much smaller. Therefore, if we assume that a physical property of a fluid is the sum of the contributions made by the functional groups constituting that molecule, we obtain a method for correlating the properties of a very large number of compounds in terms of a much smaller number of parameters which represent the contribution of individual groups.

Any group contribution method can only be approximate because the contribution of a given group in one molecule will not be the same as its contribution in another molecule. The fundamental assumption of a group contribution method is additivity, i.e., contributions made by one group are assumed to be independent of the contributions made by another group in the same molecule. This assumption is valid only when the different groups comprising the molecule are very similar in nature.

The accuracy of the estimation method can be improved as more and more distinct groups are defined. In the limit, the molecule itself is defined as a group. In this case, one no longer benefits from the group contribution method. For practical purposes a compromise must be reached. A small number of distinct groups is selected but not so small that significant effects of molecular structure on physical properties would be ignored.

If the group contribution method is extended to mixtures, many multicomponent liquid mixtures can be constituted from a limited number of functional groups.

The UNIversal QUAsi-Chemical (UNIQUAC) equation, developed by Abrams and Prausnitz in 1975, is a good starting point for establishing a group contribution correlation. In this model, the important independent variables are the concentrations of the functional groups rather than those of the molecules themselves.

The basic idea of a solution-of-groups model is to use existing phase equilibrium data for predicting phase equilibria of systems for which no experimental data are available. The UNIFAC model conceptually follows the ASOG (Analytical SOlution of Groups) model developed by Derr and Deal in 1969. In the ASOG model, activity coefficients in mixtures are related to interactions between structural groups. Derr and Deal (1969) separate the activity coefficient of a molecule into two parts: one part incorporates the contribution of the differences in molecular size and the other part incorporates the contributions due to molecular interactions. The contributions due to size difference are arbitrarily estimated using the athermal Flory-Huggins equation. The Wilson equation, applied to functional groups, is selected for the estimation of the molecular interaction contributions. Much of the arbitrariness is removed by the combination of the solution-of-groups concept with the UNIQUAC equation. The UNIQUAC model contains a combinatorial part which is due to differences in size and shape of the molecules in the mixture, and a residual part which is due to energy interactions. Functional group sizes and interaction surface areas are obtained from pure component data.

UNIFAC is based on binary vapor-liquid and liquid-liquid equilibrium data from more than 200 different literature sources. No ternary data have been used. The available group interaction parameters have been tabulated by Fredenslund et al. (53) and one can quickly discover whether group interaction parameters are available in the desired temperature range.

In order to get the interaction parameters, Fredenslund et al. (53) have calculated activity coefficients using low pressure phase equilibrium data, not taking vapor phase non-idealities into account. The interaction parameters have been calculated using a non-linear, least squares data reduction scheme.

The UNIQUAC equation which was developed by Abrams and Prausnitz (1975) relates the activity coefficient to excess molar Gibbs free energy. At low or moderate pressures, the excess Gibbs free energy depends only on liquid composition and temperature. The UNIQUAC equation consists of two parts:

$$g^E = g^E \text{ (combinatorial)} + g^E \text{ (residual)} \qquad (26)$$

where for a binary mixture:

$$\frac{g^E \text{ (combinatorial)}}{RT} = x_1 \ln\frac{\phi_1}{x_1} + x_2 \ln\frac{\phi_2}{x_1} + (Z/2)\left(q\, x_1 \ln\frac{\theta_1}{\phi_1} + q_2 x_2 \ln\frac{\theta_2}{\phi_2}\right) \qquad (27)$$

$$\frac{g^E \text{ (residual)}}{RT} = -q_1^{'} x_1 \ln(\theta_1^{'} + \theta_2^{'} \tau_{21}) - q_2^{'} x_2 \ln(\theta_2^{'} + \theta_1^{'} \tau_{12}) \qquad (28)$$

Where R is the universal gas constant, Z is the coordination number set equal to 10. The segment fraction (ϕ), and the area fractions (θ and $\theta^{'}$) are given by:

$$\phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \qquad \phi_2 = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2} \qquad (29)$$

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \qquad \theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2} \qquad (30)$$

$$\theta_1^{'} = \frac{x_1 q_1^{'}}{x_1 q_1^{'} + x_2 q_2^{'}} \qquad \theta_2^{'} = \frac{x_2 q_2^{'}}{x_1 q_1^{'} + x_2 q_2^{'}} \qquad (31)$$

The parameters r, q, and $q^{'}$ are pure component molecular-structure constants depending on molecular size and external surface areas. In the original formulation by Abrams and Prausnitz (1975) $q = q^{'}$, but Anderson and Prausnitz (6) have determined $q^{'}$ empirically to find an optimum fit to a variety of systems containing water and alcohols. For alcohols, for instance, the surface of interaction (q') is smaller than the geometric external surface (q) which indicates that for alcohols, intermolecular attraction is determined mostly by the OH group. These structural parameters have been tabulated for many compounds by Anderson and Prausnitz (6).

For each binary combination in a multicomponent mixture, there are two adjustable parameters, τ_{12} and τ_{21}. These in turn are given in terms of characteristic energies Δm_{12} and Δm_{21} by:

$$\tau_{12} = \exp\left(-\frac{\Delta m_{12}}{RT}\right) = \exp\left(-\frac{a_{12}}{T}\right) \qquad (32)$$

$$\tau_{21} = \exp\left(-\frac{\Delta m_{21}}{RT}\right) = \exp\left(-\frac{a_{21}}{T}\right) \qquad (33)$$

The effect of temperature on τ_{12} and τ_{21} can be seen in the above equations. Δm_{12} and Δm_{21} are weakly dependent on temperature. Using the relationship between molar excess Gibbs free energy and the activity coefficient:

$$g = RT \sum_i x \ln \gamma \quad \text{and} \quad \left(\frac{\partial n_T g^E}{\partial n_i}\right)_{T,P,n_j} = RT \ln \gamma_i \qquad (34)$$

The activity coefficients γ_1 and γ_2 are given by:

$$\ln \gamma_1 = \ln \frac{\phi_1}{x_1} + (Z/2)\, q_1 \ln \frac{\theta_1}{\phi_1} + \phi_2 \left(l_1 - \frac{r_1}{r_2}\, l_2\right)$$

$$- q'_1 \ln (\theta'_1 + \theta'_2 \tau_{21})$$

$$+ \theta'_2\, q'_1 \left(\frac{\tau_{21}}{\theta'_1 + \theta'_2 \tau_{21}} - \frac{\tau_{12}}{\theta'_2 + \theta'_1 \tau_{12}}\right) \tag{35}$$

$$\ln \gamma_2 = \ln \frac{\phi_2}{x_2} + (Z/2)\, q_2 \ln \frac{\theta_2}{\phi_2} + \phi_1 \left(l_2 - \frac{r_2}{r_1}\, l_1\right)$$

$$- q'_2 \ln (\theta'_2 + \theta'_1 \tau_{12})$$

$$+ \theta'_1\, q'_2 \left(\frac{\tau_{12}}{\theta'_2 + \theta'_1 \tau_{12}} - \frac{\tau_{21}}{\theta'_1 + \theta'_2 \tau_{21}}\right) \tag{36}$$

where

$$l_1 = (Z/2)(r_1 - q_1) - (r_1 - 1) \tag{37}$$

and

$$l_2 = (Z/2)(r_2 - q_2) - (r_2 - 1) \tag{38}$$

For binary vapor-liquid equilibrium measurements, the optimum parameters are those that minimize the objective function given by:

$$S = \sum_{i}^{N} [\frac{(P_i^\circ - P_i^e)^2}{\sigma^2_{P_i}} + \frac{(T_i^\circ - T_i^e)^2}{\sigma^2_{T_i}} + \frac{(x_{1i}^\circ - x_{1i}^e)^2}{\sigma^2_{x_{1i}}} +$$

$$- \frac{(y_{1i}^\circ - y_{1i}^e)^2}{\sigma^2_{y_{1i}}}] \qquad (39)$$

The summation is over all N data points and the equation is subject to the equilibrium constraint:

$$\phi_i \; y_i \; P = \gamma_i \; x_i \; P_i^\circ \qquad (40)$$

Superscript e indicates an experimentally measured value, and superscript ∘ indicates the estimated value corresponding to each measured point. σ^2 is the estimated variance of each measured variable, i.e., pressure, temperature, and liquid and vapor-phase mole fractions. These variances are estimated from probable experimental uncertainties. Since all data points are used and each point has an associated error, the true value of each measured variable is also found in the course of the parameter estimation. Anderson and Prausnitz (6) have obtained binary parameters for 130 distinct binary systems.

The multicomponent versions of the above equations are given below:

$$\frac{g^E(\text{combinatorial})}{RT} = \sum_i x_i \ln \frac{\phi_i}{x_i} - \frac{Z}{2} \sum_i q_i x_i \ln \frac{\theta_i}{\phi_i} \tag{41}$$

$$\frac{g^E(\text{residual})}{RT} = -\sum_i q_i' x_i \ln\left(\sum_j \theta_j' \tau_{ji}\right) \tag{42}$$

where segment fraction (ϕ) and area fractions (θ and θ') are given by:

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \qquad \theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \qquad \theta_i' = \frac{q_i' x_i}{\sum_j q_j' x_j} \tag{43}$$

For any component i in a multicomponent mixture, the activity coefficient is given by:

$$\ln \gamma_i = \ln \frac{\phi_i}{x_i} + (Z/2)\, q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j$$

$$- q_i' \ln\left(\sum_j \theta_j' \tau_{ji}\right) + q_i' - q_i' \sum_j \frac{\theta_j' \tau_{ij}}{\sum_k \theta_k' \tau_{kj}} \tag{44}$$

where

$$l_j = (Z/2)\,(r_j - q_j) - (r_j - 1) \tag{45}$$

The above equation requires only pure component and binary parameters.

The equilibrium constraint equation is:

$$\phi_i \; y_i \; P = \gamma_i \; x_i \; P_i^\circ \tag{46}$$

where P_i° is the vapor pressure of component i in the liquid mixture, x_i is the mole fraction of component i in the liquid mixture, γ_i is the activity coefficient of component i in the mixture, P is the total system pressure, y_i is the mole fraction of component i in the vapor phase, and ϕ_i is the fugacity coefficient of component i in the vapor phase.

Extensions and modifications to the UNIFAC model and other methods of calculating activity coefficients are discussed below.

Skjold-Jorgensen et al. (143) have revised and extended the range of applicability of the UNIFAC model. They have added eight different new groups: tertiary amines, formates, iodides, methanethiol, furfural, pyridine, and glycols. They have also redefined the alcohol group as a group containing OH only. They have determined the volume and surface area parameters (r_k and q_k) empirically instead of using van der Waals volumes and surface areas.

Sorensen et al. (147) have retrieved most of the available liquid-liquid equilibrium data and have evaluated different correlations for prediction of these data. Their data base contains 884 binary, 772 ternary, and 23 quaternary data sets. Liquid-liquid equilibrium is needed to determine the distribution of the solute between or among the liquid phases present. This solute could be an environmental pollutant.

The quantity of interest in predicting liquid-liquid equilibria is the liquid phase activity coefficient. Sorensen et al. (146) conclude that UNIQUAC and NRTL (Non-Random Two Liquid) are the best predictive models available, and that in most instances, UNIQUAC is superior to NRTL. One of the main advantages of UNIQUAC is its having only two adjustable parameters per binary pair as mentioned earlier. It must be noted that UNIQUAC was originally developed for prediction of vapor-liquid equilibria and not liquid-liquid equilibria, however, its performance seems to be satisfactory for the latter case, as well (147).

Rizzi and Huber (125) use a new approach to obtain universal interaction parameters between the groups CH_2-H_2O and ACH-H_2O within the solution of groups model. This involves a careful estimation of the combinatorial part of the model which is the term not associated with groups. This method accounts for association effects in the region of infinite dilution which is based on the definition of two additional groups which occur only in alkanes and aromatic hydrocarbons. This procedure allows one to keep constant the value for the most important CH_2-H_2O and ACH-H_2O interaction parameters in all systems and gives results similar to those expected by the introduction of an additional correction term $\ln \gamma_i^{corr}$ to the combinatorial and residual parts. This approach is important because it leads to better predictions in the infinite dilution range where the group contribution model predictions are not very good. The poorer prediction in this region is of course a result of the use of vapor-liquid equilibrium data pertaining to higher concentration regions. The interest in infinite dilution predictions stems from the need to determine model parameters and also environmental applications where very low solubilities of pollutants are quite common.

From a practical standpoint liquid-liquid equilibrium data could be useful for solvent extraction. King et al. (70) discuss the extraction of organic priority pollutants from water. Referring to the list of 129 priority pollutants published by the Environmental Protection Agency, they discuss the need for the development of reliable and precise analytical techniques and evaluation of appropriate control technology. They state that solvent extraction holds good potential for removal of many organic priority pollutants from effluent water streams. Solvent extraction can be attractive in cases where the solutes are toxic or nonbiodegradable, where the solutes are present at high enough concentrations to provide economic recovery value, and when steam stripping would be complicated or precluded by low solute volatility or formation of azeotropes, according to King et al. (70). Therefore, the principal factors that they considered in choosing the particular pollutant for their experiments were solubility in water, nonbiodegradability, difficulty of stripping, and the presence of functional groups which might lead to specific interactions with certain solvents. The main piece of information that they sought was the equilibrium distribution coefficient defined as the weight fraction of the solute in the solvent phase divided by the weight fraction of the solute in the aqueous phase, at equilibrium and at high dilution.

Based on their findings, King et al. (70) concluded that equilibrium distribution coefficients for extraction of chlorinated hydrocarbons and aromatic hydrocarbons into undecane were high enough to make kerosene an attractive solvent for removing these compounds from water by solvent extraction. Undecane was used as a model for kerosene in their investigations.

Since the three quantities-- Henry's constant, vapor pressure and aqueous solubility-- are related and any one can be calculated from the other two, it is worthwhile to look at the available vapor pressure and solubility data that can be used to calculate the Henry's constant. As far as aqueous solubility is concerned, there is much published data and there are many correlations available, some of which will be considered below.

Mackay and Shiu (89) use the hydrocarbon infinite dilution activity coefficient, γ_W^∞ , to correlate aqueous solubility and obtain average deviations in log solubility of about 0.26. They base their derivation on the equality of the water and hydrocarbon fugacities at equilibrium:

$$f = x_w \gamma_w f_r = x_h \gamma_h f_r \tag{47}$$

Since the reference fugacities (f_r) cancel and the hydrocarbon mole fraction (x_h) and activity coefficient (γ_h) in the hydrocarbon phase can be assumed to be unity, it follows that γ_w^∞ is simply the reciprocal of the mole fraction solubility:

$$\gamma_w^\infty = 1/x_w \tag{48}$$

The procedure that Mackay and Shiu (89) propose for estimation of γ_w^∞ is the use of a parabolic equation for γ_w^∞ as a function of carbon number which approaches the Tsonopoulos and Prausnitz correlation at low carbon numbers:

$$\log \gamma_w^\infty = 3.5055 + 0.3417(N-6) - 0.002640(N-6)^2 \tag{49}$$

Leinonen et al. (74) have developed a correlation for the solubility of C_4 to C_{10} hydrocarbons at 25°C and atmospheric pressure. The excess Gibbs free energy is correlated in terms of an effective molar volume which is related to the actual molar volume adjusted to include the effects of the degree of branching, the number of olefinic and acetylinic bonds and the number of aromatic and cycloalkane rings. They obtained a root mean square deviation between 59 correlated and experimental solubilities of 20%. The solubilities range from 0.052 to 5150 grams of hydrocarbon per 10^6 g of water. The correlation can be used as a basis for estimation of the solubilities of halogenated hydrocarbons in water. This correlation has been developed for estimation of dynamic behavior, particularly dissolution, of oil spills in water, however, its applicability is not limited to this case only.

Hydrocarbons exhibit low solubilities in water as a result of very high activity coefficients or high excess Gibbs free energy of mixing. The excess Gibbs free energy and the activity coefficient are related to hydrocarbon solubility through a constant K:

$$g^E = x_1(1 - x_1)K \tag{50}$$

$$\gamma_1 = \exp[(1 - x_1)^2 K/RT] \tag{51}$$

The logarithm of the solubility of a homologous series is approximately a linear function of the molar volume. Since the activity coefficient is inversely related to the solubility, a plot of RT ln γ_1 versus molar volume will also be approximately linear. Leinonen et al. (74) did obtain a linear relationship between K and the molar volume. The slope obtained by least squares for normal alkane data was 58.3 cal/cm^3. Branched chain isomers generally deviate from this correlation since they usually have a higher solubility and a higher molar volume than the corresponding normal alkanes. Leinonen et al. (74) obtained similar correlations for olefinic, acetylinic and aromatic hydrocarbons, and cycloalkanes. The slopes of the K versus molar volume plot were very similar for these homologous series and a mean value of 56.11 cal/cm^3 was used in the final correlation.

Branched chain alkanes could be correlated satisfactorily by using an effective molar volume defined as the actual molar volume reduced by an increment of 3.1425 cal/cm^3 for each degree of branching. Similar increments were found to apply for olefins, acetylenes, aromatics, and cycloalkanes.

Leinonen et al. (74) observed, however, that for hydrocarbons with multiple olefinic or acetylinic bonds, the correlation predicted an unusually high solubility (low K). They concluded that the second bond is only fractionally as effective as the first in increasing the solubility, and presumably further bonds would be still less effective. They found a best value for this fraction of 0.589. Therefore, the effective number of olefinic bonds, D', to be used in the correlation, is equal to the actual number D for D=0 or 1, 1.589 for D=2, and 1.936 for D=3. Similarly, the effective number of acetylinic bonds E' to be used in the correlation is equal to the actual number E for E=0 or 1, 1.589 for E=2. The final correlation is:

$$K = 303.158 + 56.116\ (v - 11.9132\ A - 3.1425\ B + 6.6742\ C - 9.6734\ D' - 21.297\ E') \qquad (52)$$

where v, A, B, and C denote the actual molar volume, the number of olefinic rings, the degree of branching, and the number of cycloalkane rings, respectively. D' and E' are the effective number of olefinic and acetylinic bonds calculated from the actual numbers, D and E. The objective function minimized to obtain the optimum values of the parameters was the sum of squares of the fractional error between the experimental and correlated solubilities of 44 hydrocarbons with no weighting factor.

McAuliffe (98) has measured the solubilities in water at room temperature of 65 hydrocarbons using a gas-liquid partition chromatographic technique. He reached the following conclusions which are quite similar to the conclusions of Leinonen et al. (74). For each homologous series of hydrocarbons, the logarithm of the solubility in water is a linear function of the hydrocarbon molar volume. Branching increases water solubility for paraffin, olefin, and acetylene hydrocarbons. The increased solubilities due to branching apparently are not due to a structural feature of the molecules, but to the higher vapor pressure of the branched chain hydrocarbons compared with the corresponding paraffin or olefin hydrocarbon. The structure of water is such that, for the same hydrocarbon vapor pressure, approximately the same weight of C_2 through C_9 paraffin hydrocarbons dissolves in water. Increasing unsaturation of the hydrocarbon molecule, chain or ring, increases the solubility of the hydrocarbon in water.

Polak and Lu (118) have experimentally determined mutual solubilities of 14 paraffinic and 6 aromatic hydrocarbons and water at 0 and 25°C. The solubilities of aromatic hydrocarbons in water are smaller at 0 than at 25°C. The solubilities of paraffins in water are larger at 0 than at 25°C. The aromatics considered in their work are benzene, toluene, ethylbenzene and three isomers of xylene.

May and Wasik (94) use a dynamic coupled column liquid chromatographic technique to obtain aqueous solubility data on 11 aromatic hydrocarbons. The aqueous solubility at 25°C was determined for each compound. Their precision of replicate solubility measurements was better than 3%. They have expressed the variation of solubility of each compound with temperature in the form of either a quadratic or cubic equation based on a least squares fit of the solubility to temperature. They state that these equations can be used to interpolate the solubility to within ±2% of the experimentally measured values between 5 and 30°C. The aromatics considered here are benzene, naphthalene, fluorene, anthracene, phenanthrene, 2-methylanthracene, 1-methylphenanthrene, fluoranthene, pyrene, 1,2-benzanthracene, and chrysene, which range in molecular weight between 78 and 228. These are aromatics of great interest for environmental studies because of their toxicity and carcinogenic effects and because there is very little data available on the solubility and other properties of these compounds.

Yalkowsky and Valvani (164) propose the following equation for the estimation of the aqueous solubility of nonelectrolytic organic chemicals:

$$\log S_w = -\log PC - (1.11/1364)[\Delta S_f(MP-25)] + 0.54 \qquad (53)$$

where S_w is the aqueous solubility, PC is the octanol-water partition coefficient, ΔS_f is the entropy of fusion, and MP is the melting point. They have extended tabulations of data obtained using the above equation including data for halobenzenes, aromatics, and polycyclic hydrocarbons.

Mackay and Shiu (88) have reviewed the Henry's law constants of hydrophobic organic compounds of environmental concern. They have tabulated vapor pressure, solubility, and Henry's law constant data for a total of 150 compounds including monoaromatics, polynuclear aromatics, and halogenated alkanes.

CHAPTER III

EXPERIMENTAL SETUP AND PROCEDURE

Experimental Setup

The head space analysis method was selected over other experimental methods for the following reasons. It is a total equilibrium method as compared to the partial equilibrium gas stripping method. It is a static equilibrium method and takes longer to reach equilibrium than the dynamic equilibrium methods, however, it requires a smaller sample size than the multiple equilibration method. The sample size becomes significant for aqueous samples because of the possibility of column flooding. Another advantage of this method is that three of the four equilibrium terms are measured directly in this method. These quantities are liquid composition, vapor composition and the total system pressure. The fourth quantity, vapor pressure of the pure solute, could also be measured experimentally, if desired, however, this was not done in the present work because of the accurate vapor pressure values available in the literature for the compounds of interest in this work. The system temperature can also be controlled and measured directly for each isothermal run, whereas the multiple equilibration technique which uses a syringe as its equilibrium vessel is not amenable to accurate temperature control and one is restricted mostly to the room temperature.

A schematic diagram of the experimental setup is shown in Figure 1. The major parts and pieces of equipment used in the experimental setup are described below.

Equilibrium Cell

The equilibrium cell consists of a stainless steel container with a volume of 500 cc. This equilibrium cell is equipped with two quarter inch pipe to tube fittings at the top and the bottom.

At the bottom, the cell is connected to a tee. One leg of this tee is used for the insertion of a T-type thermocouple into the cell whereby the temperature inside the cell can be measured directly. The probe head is immersed in the liquid phase very near the vapor-liquid interface. The thermocouple read-out indicates the temperature to the nearest degree Fahrenheit. The other leg of the tee is connected to another tee, one leg of which serves as the housing for a Teflon septum through which the solution to be studied is injected into the cell. The other leg is connected through quarter inch stainless steel tubing to a Cole-Parmer gear pump which is located 3 ft below the cell. This pump is driven by a Cole-Parmer Masterflex drive

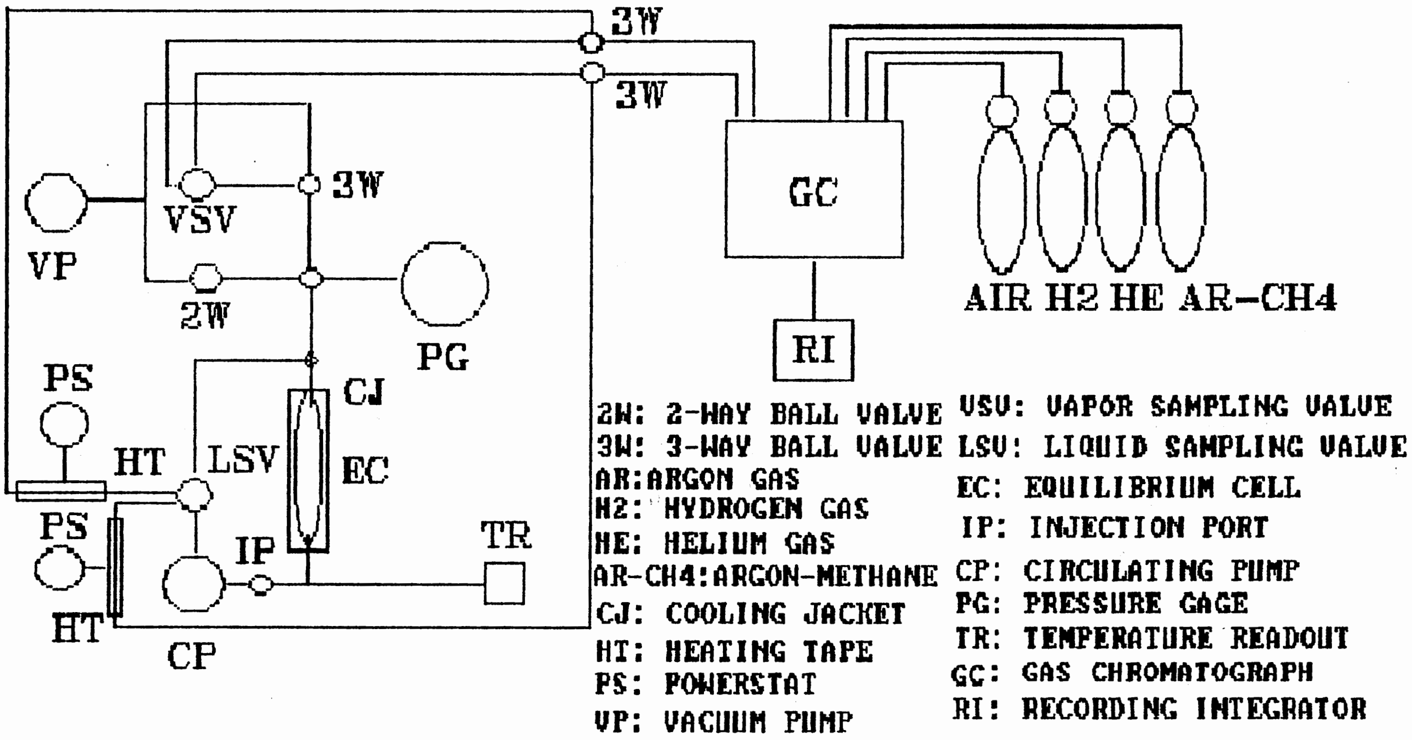


Figure 1. Schematic Diagram of the Experimental Setup.

which has a variable speed controller capable of adjusting the flow between 6 and 2800 cc/min. This pump is used for circulating the liquid solution. The outlet of the pump is connected to a Valco 1 micro-liter 6 port liquid sampling valve through one eighth inch Teflon tubing which is transparent and allows for the verification of the existence of liquid flow through the pump at low pressures (20-50 mmHg). This Teflon tubing is inserted in a quarter inch stainless steel tubing which is connected to the top of the cell via a tee. The liquid travels through the inner Teflon tubing back into the cell, passes through the vapor space of the cell thus ensuring good vapor-liquid contact which is essential for equilibrium conditions, and drips back into the liquid space at the bottom, hence eliminating the need for stirring.

The vapor travels through the annulus of the quarter inch tubing at the top into the other opening of the tee. This leg is connected to a stainless steel cross. The other three legs are connected as follows. The right leg goes to a Texas Instrument Model 141A quartz precision pressure gage capable of measuring the pressure to 0.01 mmHg.

The left leg is connected to a shut-off valve which is in turn connected to a vacuum pump. The top leg is connected through a three-way ball valve to the vapor sampling valve which is a 6 port Valco valve equipped with a sampling loop which consists of coiled one eighth inch tubing with a volume of 0.35 cc. This valve is also connected to the vacuum pump thus ending the loop.

The volume of the loop through which liquid circulation takes place is about 20 cc. This includes 12 cc for the quarter inch tubing, 4 cc for the one eighth inch tubing and 4 cc for the pump head volume.

Sampling is done on line and the carrier gas from and to the gas chromatograph is distributed to the gas sampling valve and the liquid sampling valve through two three way ball valves. The lines leading to and coming from the liquid sampling valve are wrapped with heating tape and heated to 200°C. The heating tape is covered by insulating material. This ensures that the one micro liter liquid sample is vaporized and does not condense as it is carried to the GC.

Constant Temperature Bath

In order to maintain the temperature inside the cell at a constant value, a cooling/heating jacket was used. This jacket consisted of 6 feet of quarter inch copper tubing coiled around the equilibrium cell. The jacket was connected to a Blue M constant temperature refrigerated bath with a temperature range between -15 and 100 °C. The bath is equipped with an agitator and a circulating pump. The temperature settings used in this work were between 15 and 35°C in increments of 5 °C.

Gas Chromatograph

The analytical section of the experiment is carried out using a series 3700 Varian Gas Chromatograph (GC). This GC is equipped with a flame ionization detector (FID) and an electron capture detector (ECD). The FID is capable of resolution down to the part per million range and analyzes any organic compound that can be burned. Water and air are, therefore, not detected by this detector. The carrier gas used for this detector is GC grade helium. Hydrogen and an excess of air are used to ignite and maintain the flame in the detector. A battery-run igniter is used for ignition. The carrier gas used for the ECD is a mixture of 90% argon and 10% methane with less than 1 part per million of each oxygen and water. The ECD is most sensitive to halogenated hydrocarbons and is capable of detecting them to the part per billion range.

A 6-foot glass column packed with Tenax GC which is a hydrophobic resin was selected. The inside diameter of this column is 4 mm and the column packing has a mesh size of 80/100 and a maximum temperature limit of 350°C. This column was purchased from Alltech under Catalog # C6192. This column is connected to the injection port where liquid injections are made by the insertion of a Hamilton 10 μL syringe into a septum which is Teflon on one side and rubber on the other and is 10 mm in diameter. Vapor injections are made by connecting the sampling valve to the carrier gas line, i.e., the carrier gas coming from the carrier gas tank passes through the sampling valve and then through the column via the injection port.

The GC is connected to a Hewlett-Packard model 3390A reporting integrator which is capable of directly integrating the area-under-the-curve of each GC peak that it plots.

Procedure

The system is first purged with air at moderate pressures (about 5 psig) for about 15 minutes. The system is then connected to the vacuum pump by opening the two-way ball valve. The system remains connected to the vacuum pump over night and then the valve is closed. The cell pressure is read and checked periodically for about an hour to make sure that the pressure is stable while the system is under vacuum but disconnected from the vacuum pump. If the pressure increases, one should check for leaks and any liquid that might have remained in the cell from the previous run which would now be evaporated and cause the pressure inside the cell to rise. The heating jacket could be used to vaporize any remaining liquid and the system would be evacuated once more.

The carrier gas of the GC is allowed to flow and the GC is turned on. The proper settings on the GC are selected. For the majority of these experiments the column temperature was set at 230 °C using the temperature programming option of the GC which increased the temperature from the initial room temperature of about 25°C to the final temperature of 230°C at a rate of 10°C/min. The injection port temperature and the detector temperature are set at 250°C. These temperatures were selected because they are above the boiling point of all of the solutes used in this work by at least 50°C and thus prevent any condensation in the lines or the column.

The hydrogen and air flows are also established and the flame ionization detector flame is ignited. The pressure at the tank for the carrier gas (chromatographic helium) was 30 psig and 40 psig for both air and hydrogen . These corresponded to flow rates of 210 and 400 cc/min, respectively.

The solution to be studied is prepared in a beaker by mixing the solute in 100 cc of distilled water. If the saturation limit is desired, solute is added in quantities just slightly above its solubility limit. The solution is mixed well and allowed to settle. The desired amount of solution is drawn into the syringe below the excess solute surface and injected into the cell at the septum. The solution could then be diluted below its solubility limit by injecting known amounts of pure distilled water into the cell. For this work three concentrations were usually selected between the solubility limit of the solute and the detection limit of the GC detector at minimum attenuation

(2^{-8}).

After the solution is injected into the cell, the gear pump is turned on and the circulation of the liquid phase through the vapor phase is initiated. About one hour is allowed for achieving equilibrium as indicated by the stabilization of the cell pressure at the given system temperature. Each system is run at five different temperatures (15, 20, 25, 30 and 35°C). Thus for a given binary system, fifteen samples are obtained, five temperature levels and three concentration levels. The effect of these two parameters (temperature and concentration) on the activity coefficient could thus be studied. This effect could also be mapped onto related thermodynamic properties such as Henry's law constants or equilibrium constants (k-values).

Four replicate vapor samples are taken at intervals of 20 to 30 minutes. The first sample data are usually ignored, because the sampling loop is not evacuated prior to this sampling. The area-under-the-curve of the samples is recorded on the Hewlett-Packard recorder-integrator. Several sub-micro liter injections of the pure solute are used to develop a calibration curve whereby one could determine the concentration for a given value of the integrated area-under-the-curve as recorded by the integrator reporting the GC response. The vapor space is about 420 cc and the size of the vapor sampling loop is 0.35 cc. Therefore, taking samples of this size in intervals of at least 20 minutes does not disturb equilibrium.

Liquid samples are taken in a similar manner through the 1 micro liter liquid sampling valve. The sample is vaporized through the use of the heating tape before being injected into the GC. Knowing the injection volumes of the vapor and liquid samples and also the molar volumes of the compounds in the solution in both the liquid and the vapor phase allows one to convert the area-under-the-curve data into concentration and mole fraction data using the calibration curve. Since multiple samples are taken, a measure of the reproducibility of the data is at hand. Usually the mean of the three values of the area-under-the-curve was used. These values differed from one another by less then five percent always.

CHAPTER IV

DISCUSSION AND RESULTS

The discussion and presentation of results in this chapter are divided into two sections. In the first section, the data obtained in the experimental part of this work are discussed. A sample calculation is performed, the errors are analyzed, and the results are presented and compared to the literature values. The second section deals with the correlation aspect of this work. Literature data are presented and are then used to obtain interaction parameters for aqueous systems in the very dilute range. The prediction power of these parameters is then compared to that of the original and other parameters in the literature for the UNIFAC model.

Experimental Results

Before presenting the data that have been obtained in this work using the experimental procedure outlined in the previous chapter, a sample calculation is presented to illustrate how the measured quantities of liquid and vapor composition and total system pressure along with the calculated vapor pressures are used to obtain the activity coefficient. The errors due to these measurements are first discussed and an error analysis is performed so that the accuracy of the data presented in the following sections can be known.

Error Analysis

The variance of a multivariate function is obtained as follows.

$$\sigma^2_{f(x_i)} = \sum_{i=1}^{N} (\delta f(x_i)/\delta x_i)^2 \ \sigma^2_{x_i} \qquad (54)$$

The objective function in this case is the activity coefficient which is a function of the vapor and liquid compositions, the solute vapor pressure and the total system pressure:

$$\gamma_i = (y_i \ P)/(x_i \ P_i^V) \qquad (55)$$

Therefore,

$$\sigma^2_{\gamma_i} = \sum_{i=1}^{4} (\delta \gamma_i/\delta x_i)^2 \sigma^2_{x_i} \quad (56)$$

The activity coefficient is a function of four variables:

$$\sigma^2_{\gamma} = (\delta\gamma/\delta y)^2 \sigma^2_{y} + (\delta\gamma/\delta P)^2 \sigma^2_{P} + (\delta\gamma/\delta x)^2 \sigma^2_{x} + (\delta\gamma/\delta P^V)^2 \sigma^2_{P^V} \qquad (57)$$

where the component index was eliminated for simplicity.

According to the phase rule there are two degrees of freedom in a two-phase binary system at equilibrium. Therefore, if one fixes two variables, namely temperature and liquid composition, the other three variables in the activity coefficient expression are automatically fixed.

$$\sigma_\gamma^2 = (P/xP^v)^2\sigma_y^2 + (y/xP^v)^2\sigma_P^2 + (yP/x^2P^v)^2\sigma_x^2 + (yP/xP^{v2})^2\sigma_{P^v}^2 \qquad (58)$$

factoring out γ^2:

$$\sigma_\gamma^2 = [\sigma_y^2/y^2 + \sigma_P^2/P^2 + \sigma_x^2/x^4 + \sigma_{P^v}^2/P^{v4}]\gamma^2 \qquad (59)$$

or

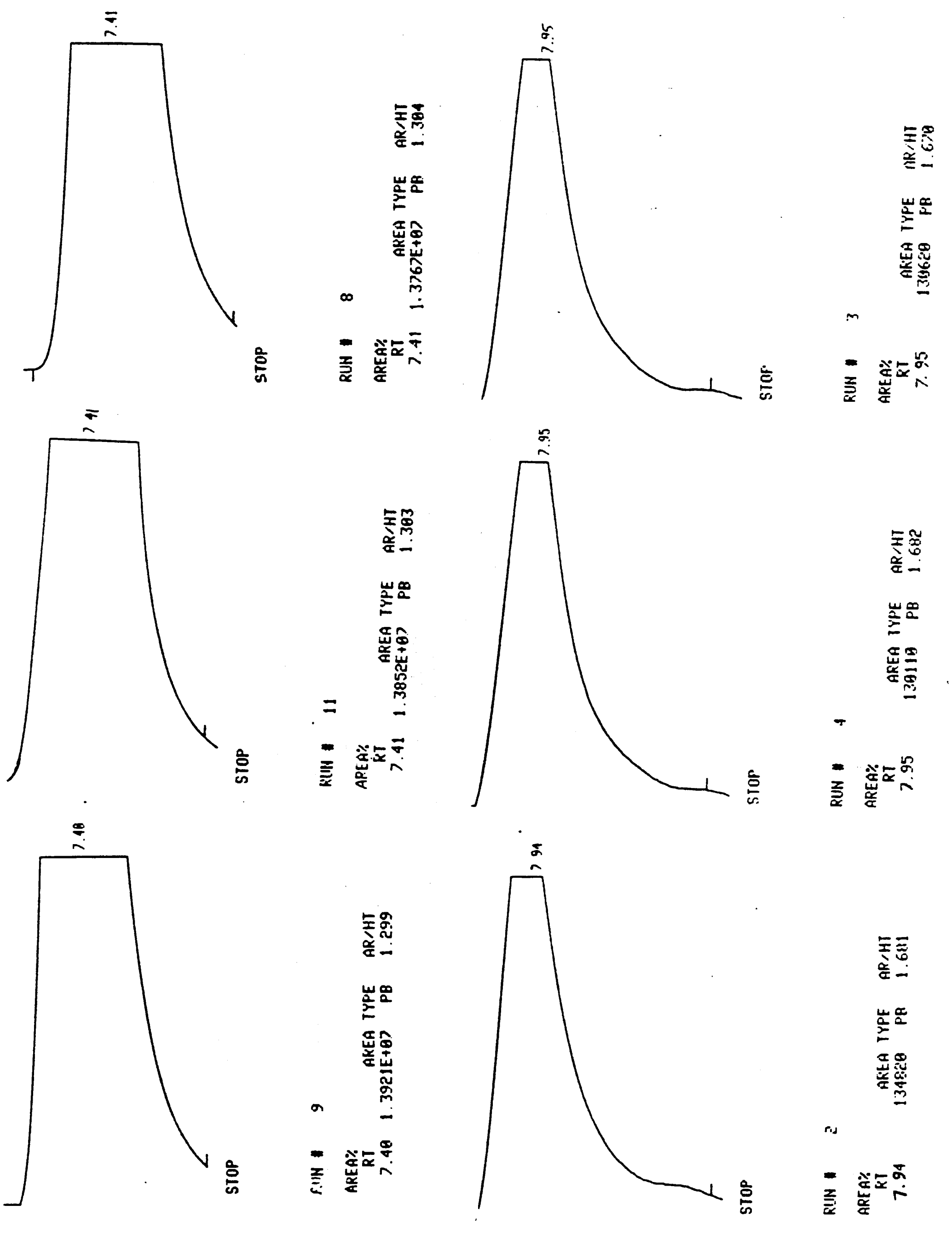
$$\sigma_\gamma{}^2 = [(\sigma_y/y)^2 + (\sigma_P/P)^2 + (\sigma_x/x^2)^2 + (\sigma_{P^v}/P^{v2})^2]\gamma^2 \qquad (60)$$

therefore, the standard deviation in the activity coefficient can be obtained using the following equation.

$$\sigma_\gamma = \gamma\,[(\sigma_y/y)^2 + (\sigma_P/P)^2 + (\sigma_x/x^2)^2 + (\sigma_{P^v}/P^{v2})^2]^{0.5} \qquad (61)$$

Sample Calculation

Several vapor and liquid samples are taken to measure the vapor and liquid concentrations. Figure 2 shows the data obtained from the GC as areas-under-the-curve for each injection. The data on the left pertain to vapor samples and the data on the right represent liquid samples. A total of



```
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AREA%
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  7.40  1.3921E+07   PB     1.299
```

```
RUN #    11

AREA%
   RT          AREA TYPE    AR/HT
  7.41  1.3852E+07   PB     1.303
```

```
RUN #    8

AREA%
   RT          AREA TYPE    AR/HT
  7.41  1.3767E+07   PB     1.304
```

```
RUN #    2

AREA%
   RT          AREA TYPE    AR/HT
  7.94      134820   PB     1.681
```

```
RUN #    4

AREA%
   RT          AREA TYPE    AR/HT
  7.95      130110   PB     1.682
```

```
RUN #    3

AREA%
   RT          AREA TYPE    AR/HT
  7.95      130620   PB     1.670
```

Figure 2. Actual Experimental Data as Reported by the Recorder-Integrator.

at least three samples was taken in each phase. The vapor peaks have been attenuated by a factor of 4. The liquid peaks have been amplified by a factor of 8.

Based on the areas-under-the-curve for liquid and vapor samples, one obtains the following statistics, where ε is the percent deviation from the mean:

x	$\varepsilon(\%)$	$y(10^{-7})$	$\varepsilon(\%)$
130110	1	1.37671	1
130620	1	1.38520	0
134820	2	1.39211	1
$\bar{x}$ = 131850	1.33	$\bar{y}$ = 1.38467	0.67

These data were taken at 25°C. The total system pressure at this temperature was 40 mmHg and the vapor pressure of the solute at this temperature is 94 mmHg. The temperature is known to within 1°C and the pressure is known to within 0.1 mmHg. Therefore, the standard error in the value of the activity coefficient is as follows.

$$\sigma_{\gamma} = \sqrt{\{[(0.0067)(1.38467)]^2/(1.38467)^2+(0.1)^2/(40)^2 +[(0.0133)(138150)]^2/(131850)^4+(1)^2/(94)^4]\}}\ \gamma$$

$$\sigma_{\gamma} / \gamma = 0.007 = 0.7\ \%$$

where the standard deviation in the value of the vapor pressure calculated from the Antoine equation was assumed to be 1 mmHg. Figure 3 shows the calibration curve for benzene as obtained by injecting various amounts of benzene in

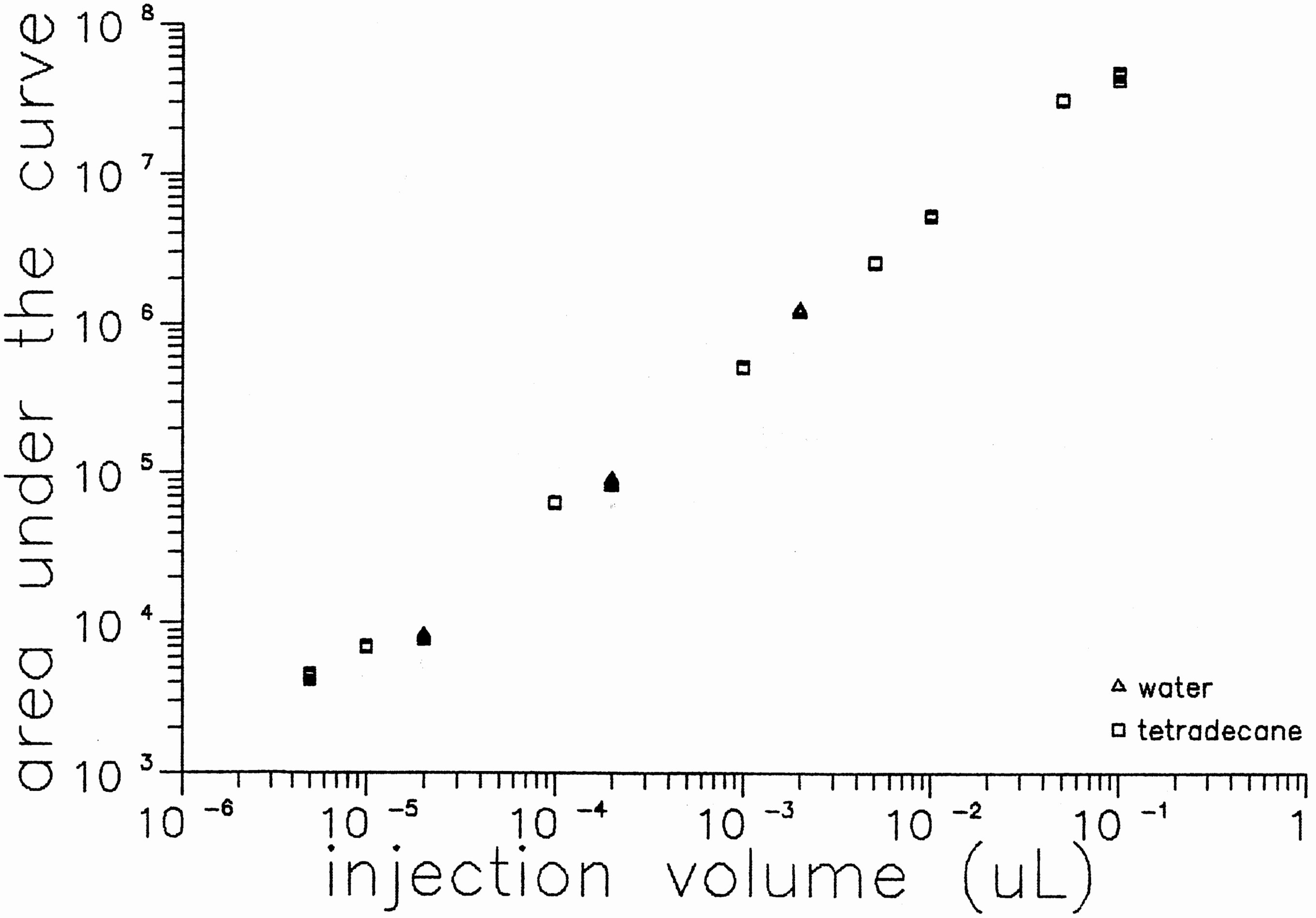

Figure 3. GC Calibration Curve for Benzene.

solution into the GC. The solutions were prepared by injecting 100 μl of benzene into an empty 10 ml volumetric flask. The solvent was then added until the liquid level reached the 10 ml mark on the flask. Several 1 μl injections of this solution were made into the GC so that the accuracy could be determined through replication. Subsequently, 1 ml of the above solution was injected into another empty flask and enough solvent was poured into the flask to bring the liquid level to the 10 ml mark. Several 1μl injections of this solution were then made into the GC. Several 10μl injections of this solution were also made and the results compared to the 1 μl injections of the previous solution. The results were identical within the accuracy of the GC. This procedure, known as serial dilution, was repeated until calibration data were obtained for the entire experimental data range.

Two solvents were used: water and tetradecane. Since the solubility of benzene in water is limited, this solvent could not be used for the entire range of interest. Water is not detected by the flame ionization detector, and there are no peak separation problems. Tetradecane was selected as the second solvent because it was the lightest hydrocarbon that gave a good separation of the solute and solvent peaks for the particular column and column conditions in use.

Figure 3 is a log-log representation of the calibration data. The curve obtained is linear and is used to calculate compositions based on area-under-the-curve data. The amount of the solute in the sample was always less than 0.11 μl in both the liquid and the vapor phase. The area-under-the-curve for the liquid samples fall on the low end of the curve; vapor samples fall on the upper end of the curve. The triangles in Figure 3 represent calibration data obtained with water as the solvent and the squares represent tetradecane as the solvent.

The liquid density of benzene at room temperature is 0.879 g/cc. A 1 μl injection of pure benzene results in an area-under-the-curve of 1.40×10^{8}. On a mass basis this volume corresponds to 0.00088 g and on a mole basis to 1.13×10^{-5} gmol.

The vapor molar volume of benzene at the low system pressure can be obtained from the ideal gas law ($v_B=RT/P$) to be 47076 cc/gmol which is the inverse of the vapor density at 25°C. One can calculate the number of moles corresponding to the areas-under-the-curve for the liquid and the vapor sample using the calibration curve. These values are:
$n_2^L = 3.23\times10^{-10}$ gmol and $n_2^V = 9.61\times10^{-7}$ gmol

The size of the liquid sampling loop is 1 μl. Therefore, one can obtain the mole fraction of benzene through a simple mass balance. The area-under-the-curve for the liquid sample represents the volume of benzene in the liquid sample. One can subtract this volume from the total sample volume to obtain the volume of water in the sample and thus obtain the mole fraction by converting the volume fractions to mole fractions.

The volume of the vapor sampling loop is 0.35 cc. If this loop were filled with pure benzene vapor at the system temperature, it would have 9.13×10^{-6}gmol of benzene according to the ideal gas law. The ratio of the number of moles of benzene in the vapor sample to this value will give the vapor mole fraction. The vapor composition is the ratio of the partial pressure of benzene to the total system pressure.

The values obtained for x and y according to the above discussion are: $x_2 = 8.08\times10^{-6}$ and $y_2 = 0.154$

Substituting these values along with the measured system pressure and calculated solute vapor pressure, one obtains the following value for γ_2:

$\gamma_2 = (0.154)(40)/(8.08\times10^{-6})(94.1) = 8100$

Data Obtained and Comparison with Literature Values

The experimental values of the activity coefficient obtained in this work for the water-benzene system are shown in Table I. These data have also been plotted in Figure 4. These values have been obtained at five different temperatures and at least 3 different liquid compositions. The error listed in this Table is defined as the ratio of the standard deviation to the mean multiplied by 100:

TABLE I

EXPERIMENTAL ACTIVITY COEFFICIENTS OBTAINED FOR THE WATER (1)- BENZENE(2) SYSTEM.

T (C)	x	y	P (mmHg)	pv (mmHg)	gamma	error(%)
15	7.49E-6	0.141	33	58.42	10679	0.169
15	6.54E-6	0.108	33	58.42	9354	0.169
15	5.01E-6	0.090	33	58.42	10194	0.049
20	7.35E-6	0.107	35	74.45	6904	0.048
20	3.84E-6	0.091	35	74.45	11247	0.168
20	3.61E-6	0.064	35	74.45	8317	0.168
25	8.08E-6	0.154	40	94.10	8084	0.646
25	5.82E-6	0.129	40	94.10	9451	0.096
25	4.38E-6	0.105	40	94.10	10242	0.096
25	5.91E-6	0.158	40	94.10	11385	0.016
25	3.61E-6	0.999	40	94.10	11767	0.016
25	1.89E-6	0.089	40	94.10	20145	0.016
25	8.26E-6	0.155	40	94.10	7966	0.166
25	1.42E-6	0.080	40	94.10	24143	0.166
25	1.06E-6	0.048	40	94.10	19256	0.166
25	8.37E-7	0.042	40	94.10	21464	0.050
30	3.30E-6	0.145	46	118.91	16990	0.165
30	2.85E-6	0.106	46	118.91	14404	0.365
30	2.04E-6	0.072	46	118.91	13641	0.045
35	1.97E-6	0.137	50	146.83	23675	0.014
35	8.15E-7	0.092	50	146.83	38244	0.014
35	4.38E-7	0.063	50	146.83	48981	0.094

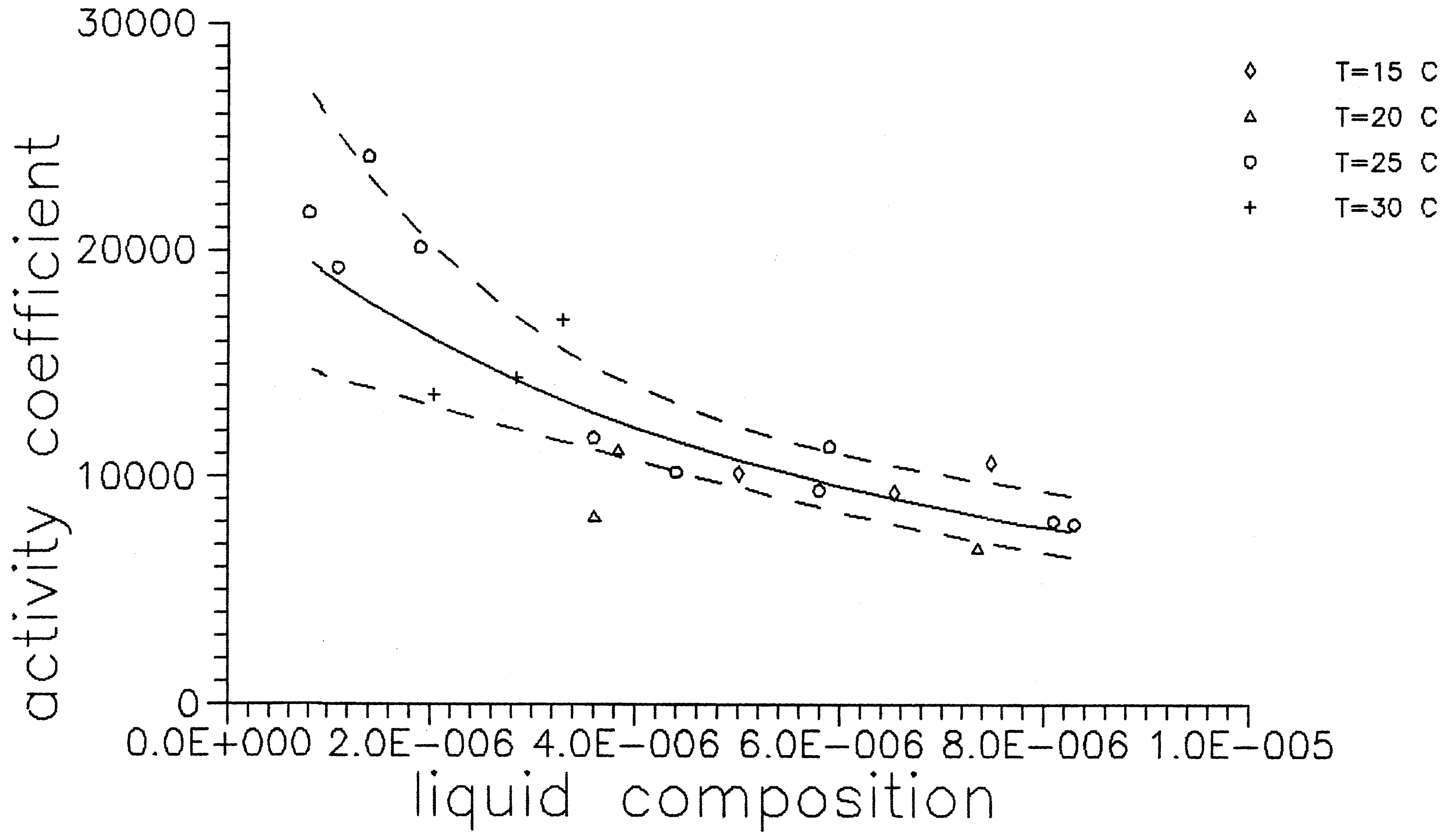

Figure 4. Experimental Values of the Activity Coefficient of Benzene as a Function of Liquid Composition.

$\varepsilon = 100(\sigma_\gamma/\bar{\gamma})$.

In each experimental run a saturated solution was prepared and then serial dilution was performed by adding pure distilled water to the system in order to obtain the activity coefficient at different liquid compositions and study the trend. In some cases, however, the range of liquid composition for which the activity coefficient was determined was so limited that prescribing a trend might not have been justified for that particular isotherm. All data have been plotted in Figure 4 to determine the effect of composition on the activity coefficient.

The data in Figure 4 seem to indicate that the activity coefficient decreases with increasing liquid composition. However, the curve becomes asymptotic near the saturation limit.

Using the ten 25°C data points in the composition range between 1×10^{-6} and 1×10^{-5} and the activity coefficient value of Tsonopoulos at saturation (4×10^{-4}), an empirical curve fit has been obtained which relates the activity coefficient to the liquid composition in the following manner:

$$\ln(\gamma/\gamma_s) = 2.195\ [(x_s-x)/x_s)]^{32.278}$$

where the subscript s refers to the saturation property. The liquid composition has been normalized and varies between 0 at saturation ($x=x_s$) and 1 at infinite dilution ($x=0$). The predicted curve is shown in Figure 4 as the solid line. The dashed lines on the two sides of the predicted curve indicate the 99% confidence envelop which includes most experimental data. The activity coefficient can be obtained at any composition using this approach.

Tsonopoulos et al. (155) have measured the aqueous solubility and the Henry's law constant of benzene, cyclohexane and hexane. These data are presented in Table II. One can see that the aqueous solubility decreases by an order of magnitude and the activity coefficient increases by an order of magnitude as one moves step wise from the benzene column to the cyclohexane column and the hexane column representing aromatic, naphthenic and paraffinic organic compounds all of which have the same number of carbon atoms (six). The temperature seems to have a small effect on the value of the aqueous solubility and the value of the activity coefficient, although these properties go through a minimum and a maximum respectively in the range of temperatures indicated. The Henry's law constant is a much stronger function of temperature. In the case of benzene, the Henry's law constant increases drastically with increasing temperature so that the Henry's law constant at 40°C is almost 6 times larger than the Henry's law constant at 0°C. Cyclohexane exhibits a similar increase in the Henry's law constant. Hexane temperature dependency is even higher, and the value of the Henry's law constant increases ten fold between the two temperatures mentioned above. This seems to indicate that the solute vapor pressure increases

TABLE II

TSONOPOULOS' EXPERIMENTAL SOLUBILITY, HENRY'S LAW CONSTANT AND ACTIVITY COEFFICIENT DATA (15).

	benzene			cyclohexane			hexane		
T(C)	X	H	GAMMA	X	H	GAMMA	X	H	GAMMA
0	4.00E-4	1358	2658	1.20E-5	44902	83307	3.34E-6	2.60E5	2.97E5
5	3.97E-4	1788	2652	1.19E-5	59151	83547	3.01E-6	3.73E5	3.29E5
10	3.95E-4	2313	2634	1.20E-5	76322	83049	2.77E-6	5.21E5	3.58E5
15	3.96E-4	2943	2600	1.21E-5	96579	81916	2.60E-6	7.05E5	3.81E5
20	4.00E-4	3688	2566	1.24E-5	119995	80104	2.48E-6	9.28E5	3.99E5
25	4.10E-4	4554	2497	1.27E-5	146543	77700	2.41E-6	1.19E6	4.10E5
30	4.20E-4	5546	2428	1.32E-5	176086	74867	2.37E-6	1.49E6	4.15E5
35	4.30E-4	6666	2351	1.37E-5	208377	71656	2.37E-6	1.82E6	4.14E5
40	4.40E-4	7913	2266	1.44E-5	243061	68142	2.41E-6	2.18E6	4.07E5

much faster with temperature than does the aqueous solubility of the solute.

The activity coefficient has been plotted as a function of temperature for benzene, cyclohexane and hexane and the plots are shown in Figures 5 through 7. In all of these figures, the activity coefficient increases with increasing temperature until it reaches a maximum where it starts a downward trend.

Duhem et al (46) and Mackay et al. (90) have obtained the activity coefficient of the saturated aqueous solution of benzene at 25 °C. Their values at a total system pressure of 1 atm are 1700 and 2470, respectively. These two data points at a single temperature and the data of Tsonopoulos et al. (155) for benzene in the range of 0°C to 40°C have been plotted in Figure 8 along with the experimental activity coefficients of Leighton et al. (73). The activity coefficient has been obtained by Tsonopoulos et al. (155) as the inverse of the experimental value of the maximum solute solubility in water under atmospheric pressure. This is the definition of Raoult's law in liquid-liquid equilibrium which states that the activity coefficient of the solvent is equal to unity as its composition approaches unity and hence the activity coefficient of the solute is equal to the inverse of its solubility. In this definition, the criterion for equilibrium is the equality of fugacities of the solvent and solute which are defined as the product of the activity

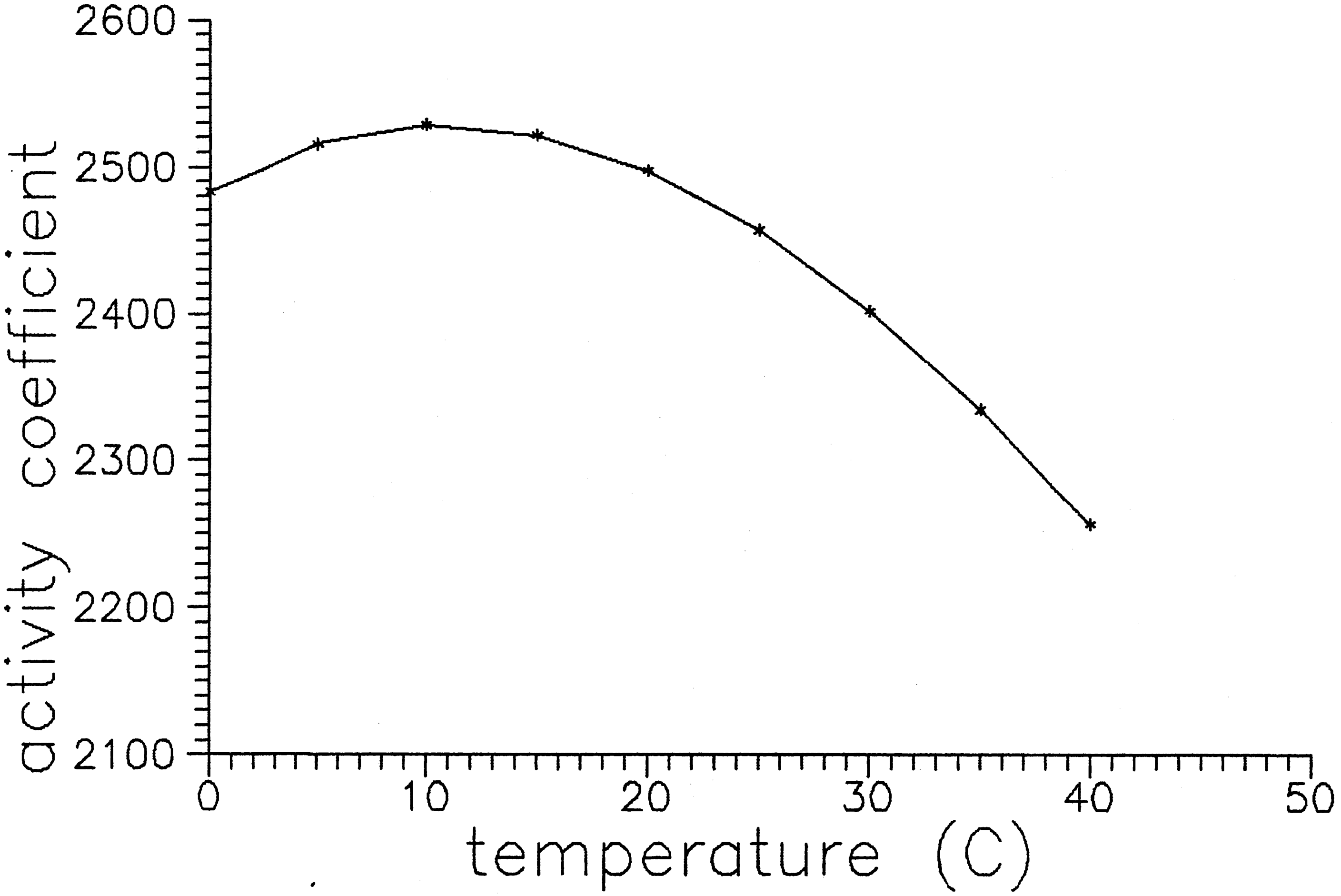

Figure 5. Activity Coefficient of Benzene as a Function of Temperature.

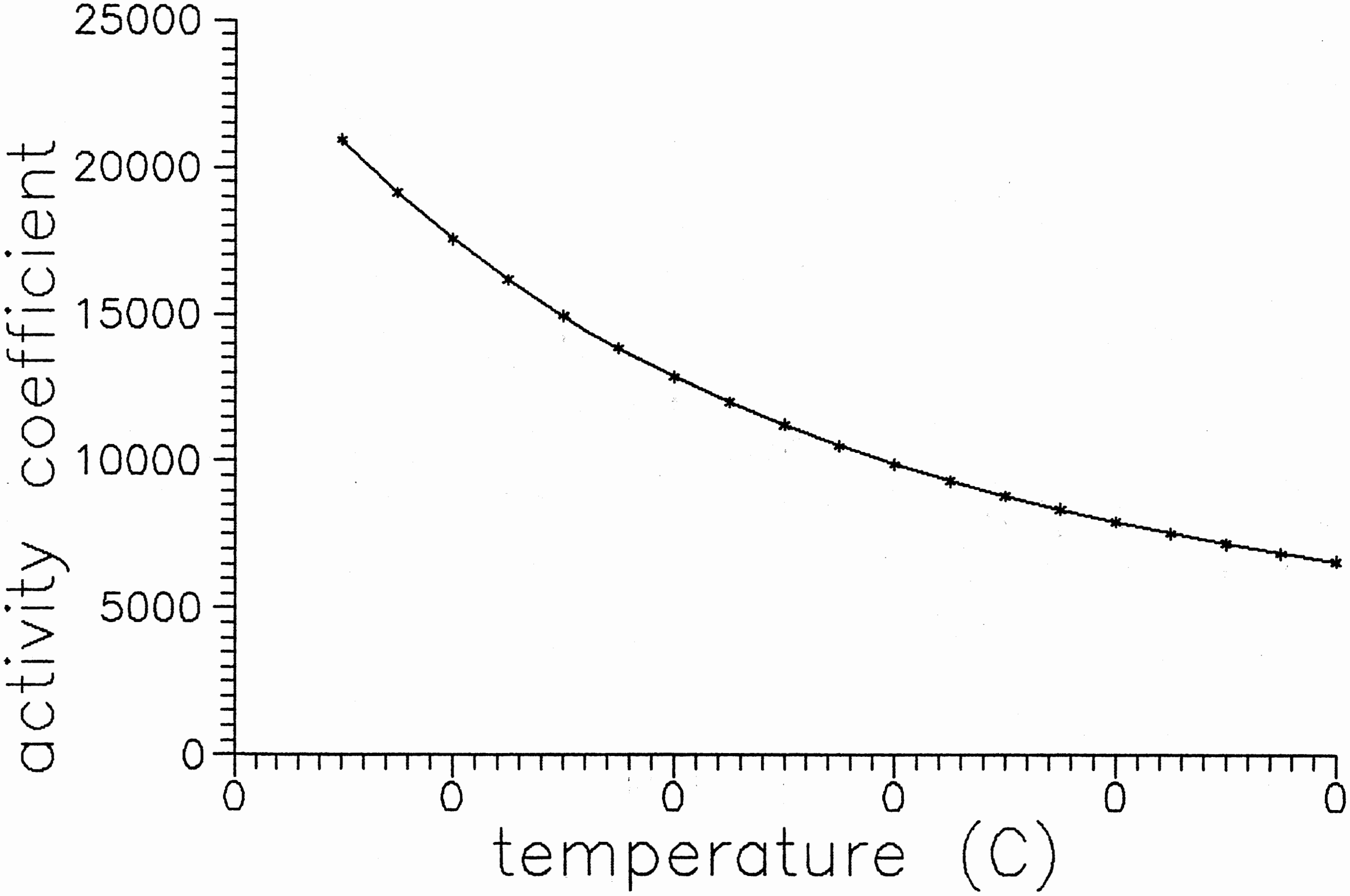

Figure 6. Activity Coefficient of Cyclohexane as a Function of Temperature.

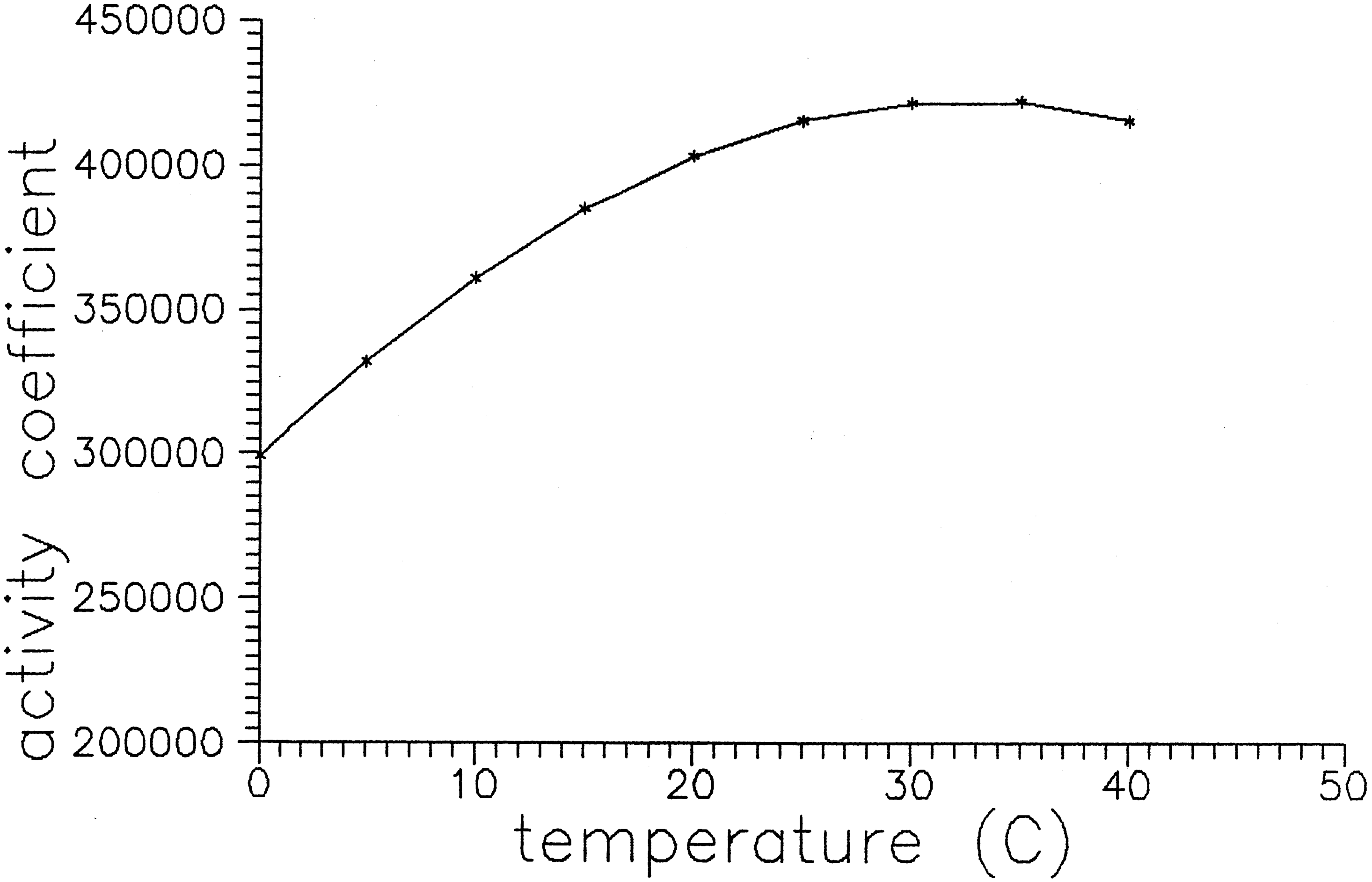

Figure 7. Activity Coefficient of Hexane as a Function of Temperature.

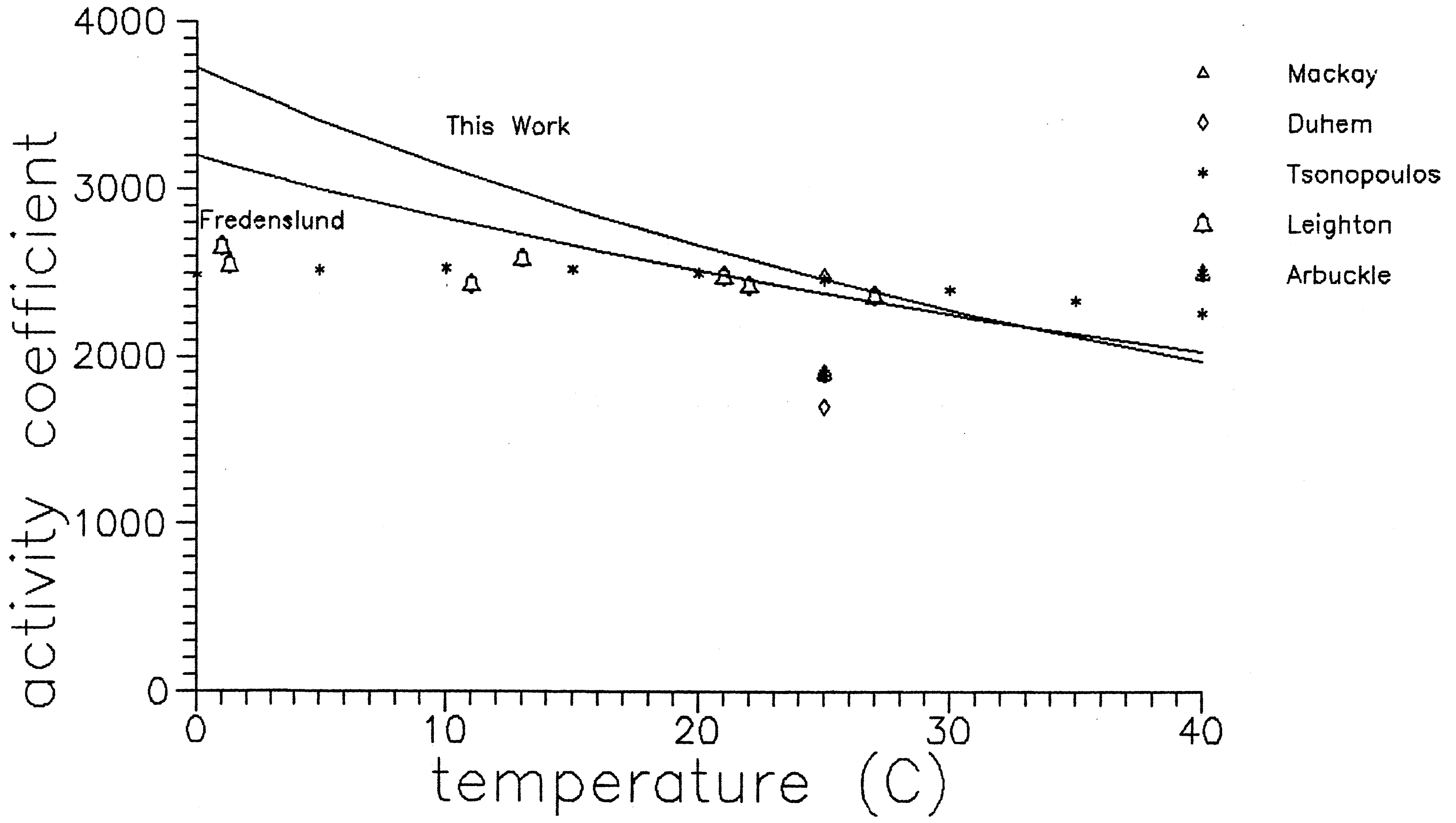

Figure 8. Comparison of the Experimental and Predicted values of the Activity Coefficient for Benzene.

coefficient and the solubility for each of the two liquid phases in equilibrium (aqueous and hydrocarbon): $x_h\gamma_h = x_w\gamma_w$. Leighton's data have been obtained from vapor-liquid equilibrium in an experimental setup using the stripping method and subsequent concentration of the sample. These values have also been obtained under atmospheric pressure. There is good agreement between the data obtained from liquid-liquid and vapor-liquid equilibrium experiments as indicated by the activity coefficient curves of Figure 8 for the data of Tsonopoulos and Leighton for the entire temperature range.

The predicted values of the activity coefficient corresponding to the temperatures for which experimental data are available have been obtained using the interaction parameters obtained in this work based on our experimental data, and the original UNIFAC interaction parameters as published by Fredenslund et al (53). The results of these predictions are also plotted in Figure 8. The predictions based on the original parameters start at a higher value than the experimental value, intersect the experimental value curves and end at a lower value than the experimental value. The predictions based on the interaction parameters obtained from the experimental data of this work are quite similar but are in more error than the predictions based on Fredenslund's parameters. This could be due to the fact that the interaction parameters of this work have been obtained from only one binary system (benzene-water) at one temperature (25°C) for which activity coefficients at ten compositions were measured, whereas Fredenslund data are based on several systems and several isotherms. The prediction of the interaction parameters based on the experimental data of this work is good for 25°C where data were obtained and coincides with the literature experimental data.

The prediction curve has been obtained at compositions equal to the saturation limit for the given temperature so that the predicted values could be compared to the experimental values from the literature sources which have all been measured at the saturation point. The experimental data of this work have been obtained at various compositions but not at the saturation point, therefore, these data could not be compared directly to the other data in Figure 8, and that is why the interaction parameters obtained from the experimental data of this work have been used to predict values at the saturation limit.

Since liquid composition is so low, one should be in the linear Henry's law region where the Henry's law constant does not change with decreasing liquid composition. However, the data obtained in this work seem to indicate that for these low solubility compounds this is not the case and activity coefficient changes with composition even in the very dilute region. Therefore, these saturation limit activity coefficients are not the same as the infinite dilution activity coefficients which can be obtained by extrapolation to x=0 in the dilute region.

Although the experimental activity coefficients collected from the literature were obtained at atmospheric pressure and the experimental activity coefficients in this work were measured at system pressures ranging between 33 and 50 mmHg, the data could be compared because the activity coefficient is a liquid property and a very weak function of pressure. Therefore, the difference in pressure should have a negligible effect on the measured value of the activity coefficient.

Limitations of Experiment

The aqueous solubility of hexane is about 170 times lower than that of benzene. The aqueous solubility of benzene has been reported as 1.78 g/L in the literature and the aqueous solubility of hexane has been reported in the range between 0.0095 to 0.0183 g/L. This prevented the experimental determination of the activity coefficient for hexane in this work. The vapor composition could be measured for this compound but the liquid composition was outside the detection range of the gas chromatograph. Both a flame ionization detector and an electron capture detector were used but neither yielded satisfactory results.

Therefore, it is suggested that another detection method such as spectrophotometry be used for the measurement of liquid compositions.

Correlation Framework

The literature experimental data are used in this section to modify the UNIFAC group contribution method so that this model can predict the activity coefficient of aqueous systems better. Therefore, some of the flexibility and generality of the model will be sacrificed for better accuracy for specific systems in a narrow composition range. The modifications to the UNIFAC model include obtaining new interaction parameters and discovering how the new parameters compare with the original parameters. If there is a temperature dependency in the interaction parameters, the model will be rendered more rigid for the sake of better prediction power by developing correlations for the temperature dependency of these parameters.

New Parameters

The interaction parameters between the methyl and aromatic methyl groups and water obtained in this work based on the experimental data of Tsonopoulos (155) have been listed in Table III. These values can be compared with the

TABLE III

COMPARISON OF Aij WITH LITERATURE VALUES.

pair	Fredenslund	Bastos	This work
CH2-H2O	1318	1.44	5696
H2O-CH2	300	354.53	547
ACH-H2O	903.8	n. a.	6441
H2O-ACH	362.3	n. a.	312

original UNIFAC interaction parameters as reported by Fredenslund et al. (53) based on vapor-liquid equilibrium data and the interaction parameters reported by Bastos et al. (15) based on infinite dilution activity coefficients mostly.

The interaction parameters of this work have been used to predict the activity coefficients of benzene, cyclohexane and hexane. These predicted values have been compared to the experimental values of Tsonopoulos et al. (155). The results of this comparison are presented in Table IV as percentage errors defined as the ratio of the difference of the calculated and experimental values of the activity coefficient to the experimental value of the activity coefficient: $(\gamma^c - \gamma^e)/\gamma^e$. The prediction errors are an indication of the correlation power of the UNIFAC model with the new interaction parameters. These errors range between 1 and 75% for the temperature-independent interaction parameters in Table IV.

The interaction parameters used for the above predictions were overall values obtained for the range of temperatures between 0°C and 40°C. These parameters have also been obtained for specific temperatures and are listed in Table V. Here, a distinction has been made between a paraffinic methyl group and a naphthenic methyl group as they appear in hexane and cyclohexane, whereas in the original classification these two are taken to be the same

TABLE IV

PERCENTAGE ERRORS IN THE CORRELATION OF ACTIVITY COEFFICIENTS USING THE GENERAL BINARY INTERACTION PARAMETERS OBTAINED IN THIS WORK

BENZENE

		T-INDEPENDENT		T-DEPENDENT	
T(C)	EXPERIMENTAL	CALCULATED	ERRROR(%)	CALCULATED	ERROR(%)
0	2658	3015	13	2644	-0.52
5	2652	2855	8	2647	-0.17
10	2634	2709	3	2619	-0.56
15	2600	2575	-1	2580	-0.74
20	2566	2452	-4	2557	-0.33
25	2497	2338	-6	2492	-0.18
30	2428	2233	-8	2411	-0.67
35	2351	2135	-9	2347	-0.13
40	2266	2045	-10	2261	-0.21

CYCLOHEXANE

		T-INDEPENDENT		T-DEPENDENT	
T(C)	EXPERIMENTAL	CALCULATED	ERRROR(%)	CALCULATED	
0	83307	107567	29	82943	-0.44
5	83547	96432	15	83317	-0.27
10	83049	86782	5	82605	-0.54
15	81916	78384	-4	80968	-1.16
20	80104	71044	-11	79238	-1.08
25	77700	64604	-17	77102	-0.77
30	74867	58931	-21	74438	-0.57
35	71656	53916	-25	71497	-0.22
40	68142	49469	-27	67929	-0.31

HEXANE

		T-INDEPENDENT		T-DEPENDENT	
T(C)	EXPERIMENTAL	CALCULATED	ERRROR(%)	CALCULATED	ERROR(%)
0	296959	518639	75	295128	-0.62
5	329311	451672	37	325736	-1.09
10	357820	395216	11	355505	-0.65
15	381108	347382	-9	380060	-0.27

TABLE IV (CONTINUED)

T(C)	EXPERIMENTAL	T-INDEPENDENT CALCULATED	 ERRROR(%)	T-DEPENDENT CALCULATED	 ERROR(%)
20	398812	306659	-23	402022	0.81
25	410103	271824	-34	405574	-1.10
30	415069	241895	-41	413282	-0.43
35	414081	216066	-48	409610	-1.08
40	406626	193683	-52	401904	-1.16

TABLE V

INTERACTION PARAMETERS AS A FUNCTION OF TEMPERATURE.

	aromatic CH2		naphthenic CH2		paraffinic CH2	
T (C)	A12	A21	A12	A21	A12	A21
0	280	429	429	547	433	563
5	291	435	434	558	458	577
10	301	440	448	566	481	591
15	303	447	457	574	503	604
20	313	452	465	582	534	615
25	314	458	475	589	538	627
30	321	461	481	596	547	639
35	324	466	504	599	555	649
40	320	472	506	605	564	658
temperature-independent	5039	346	4470	512	5697	547

group.

These interaction parameters have been plotted as a function of temperature in Figures 9 and 10 for comparison. Quadratic fits of the type:

$A_{12} = a_1 + b_1T + c_1T^2$ and $A_{21} = a_2 + b_2T + c_2T^2$ (T in K)

have been obtained for these groups and the coefficients are listed in Table VI. An analysis of variance study was used to determine the significance of adding more terms to the polynomial expression used for fitting. It was based on this analysis that a quadratic fit was selected. Using the temperature-dependent interaction parameters results in a vast improvement in the correlation power of the model such that the absolute percentage errors are in no case larger than 1.16% as indicated in Table IV for the temperature -dependent interaction parameters.

The experimental data in the literature that deal with aqueous systems have been gathered and are presented in Tables A-I through A-IX in the Appendix. These include activity coefficients, Henry's law constants and distribution coefficients. Whenever the liquid composition has been specified, this value is included in Tables A-I through A-IX. Otherwise, the equilibrium value is assumed to be at the saturation limit. Since infinite dilution activity coefficients are used to determine the UNIFAC interaction coefficients, other forms of equilibrium data have been converted to activity coefficients. Therefore, in Tables A-I

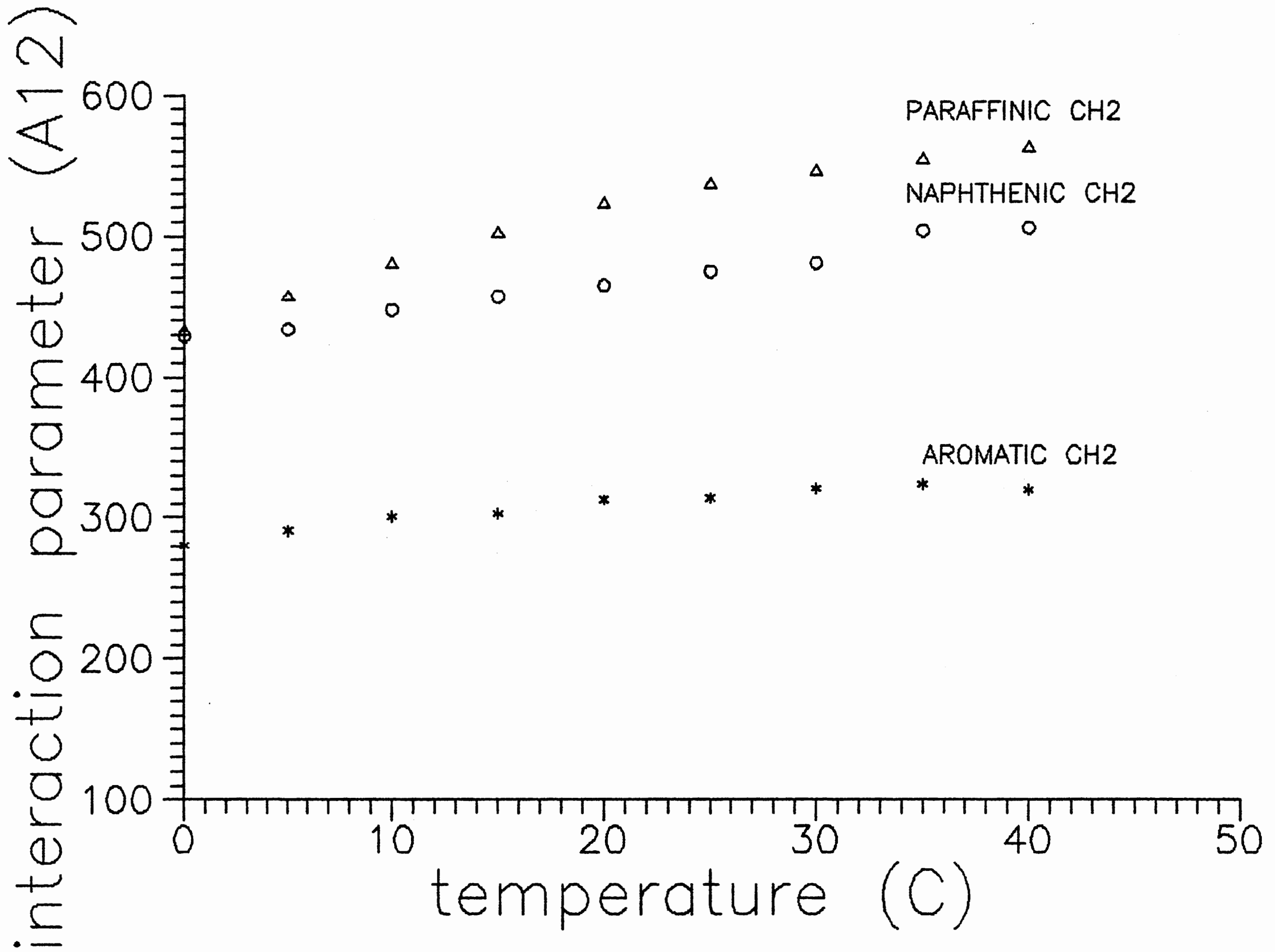

Figure 9. Interaction Parameters (A12) for Aromatic CH2, Naphthenic CH2 and Paraffinic CH2 as a Function of Temperature.

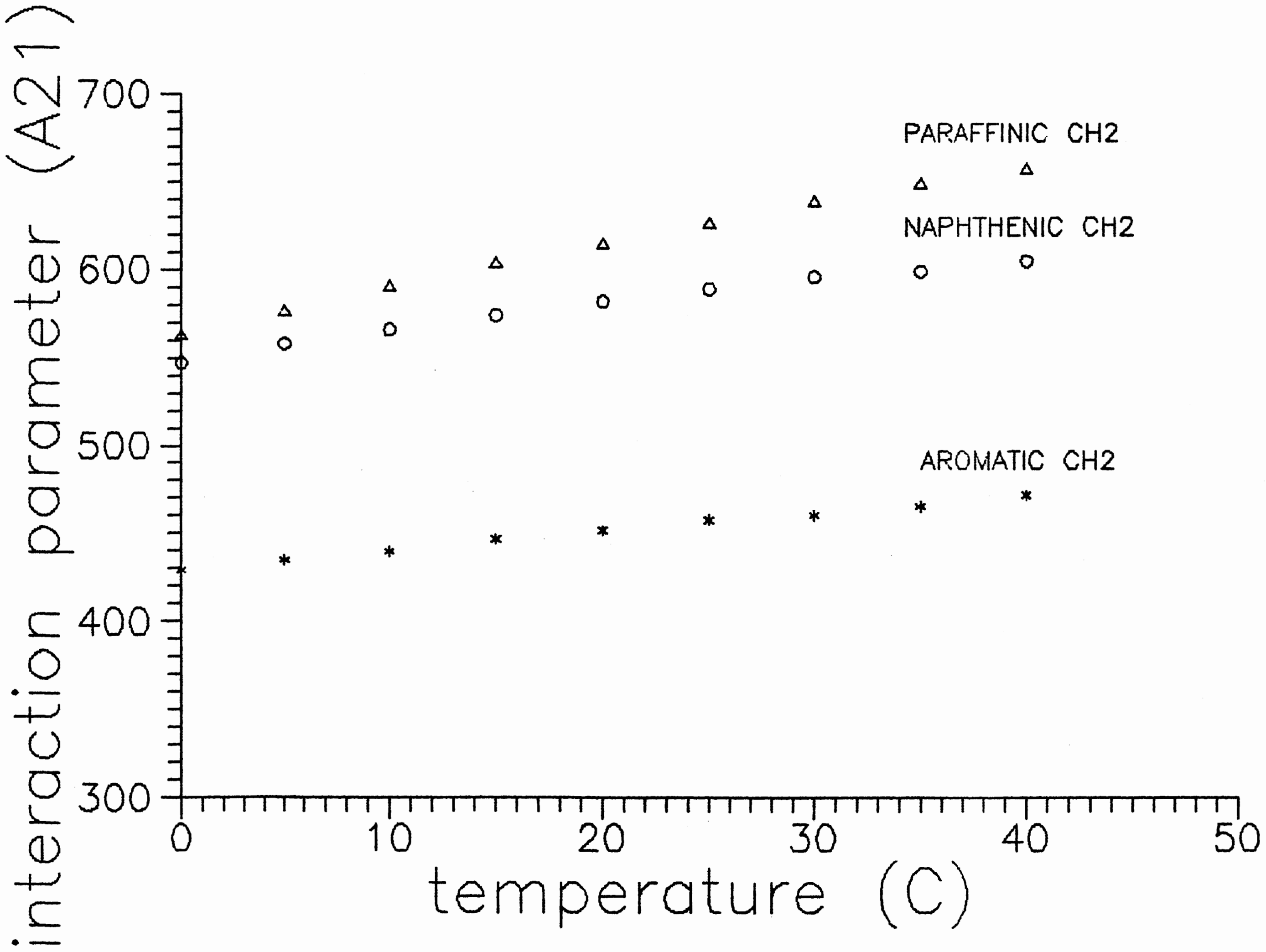

Figure 10. Interaction Parameters (A21) for Aromatic CH2, Naphthenic CH2 and Paraffinic CH2 as a Function of Temperature.

TABLE VI

COEFFICIENTS FOR THE QUADRATIC FIT OF THE INTERACTION PARAMETERS AS A FUNCTION OF TEMPERATURE.

binary pair	a1	b1	c1	a2	b2	c2
aromatic CH2	280.515	2.107	-0.027	428.921	1.230	-0.004
naphthenic CH2	428.139	1.712	-0.007	547.333	2.043	-0.015
paraffinic CH2	431.897	5.687	-0.060	563.000	2.898	-0.013

through A-IX where there is a column with values other than activity coefficients, the activity coefficient values have been calculated in this work and are not by the original authors. Most data are at either 20 or 25°C, as specified in the headings of Tables A-I through A-IX. Otherwise, the temperature has been specified in another column.

Henry's law constants are presented in three different ways: dimensionless, with units of pressure, and with units of pressure over concentration. These originate from the definition of the Henry's law constant as the ratio of the fugacity over the liquid composition as liquid composition approaches zero. Sometimes this parameter is defined as the ratio of the vapor and liquid phase compositions, sometimes as partial pressure over liquid composition and sometimes as partial pressure over liquid concentration.

The experimental error or accuracy has been reported in some of the original sources. In Table A-I the error in the activity coefficients has been reported as ±2%. Mackay et al. (87) report an accuracy of 5% for their data in Table A-II. Arbuckle (10) reports that his Henry's law constants have an average absolute error of 0.112. He defines the absolute error as the difference between the logarithms of predicted and observed values. His data are presented in Table A-III. An accuracy of 5% is reported by Mackay et al. (90) for the data in Table A-V. Finally, the data in Table A-IX are the least reliable because they include both experimental and calculated values based on estimated properties such as the vapor pressure.

Table A-I presents the activity coefficients of four C_4 alcohols at various compositions. All four of these alcohols are made up of only five distinct groups, namely, CH_3, CH_2, CH, C and OH. There is a difference in the group surface areas and the group volumes among the CH_3, CH_2, CH and C groups. However, as far as energy interactions are concerned, these four groups are treated alike; and one pair of binary interaction parameters represents all four groups. This demonstrates the approximate nature of the group contribution models such as UNIFAC. For example, 2-butanol and 2-methyl-1-propanol which are composed of the same groups have widely varying values of activity coefficients. The values for 2-butanol range between 19.1 and 22 whereas the values for 2-methyl-1-propanol range between 11.7 and 44.2 in the same composition range. The activity coefficient of these compounds has been plotted as a function of liquid composition in Figures 11 and 12. Since the composition range of 2-methyl-2-propanol is larger than the other three compounds, these data have not been superimposed on Figure 12.

The interaction parameters of Bastos et al. (15) for the H_2O - OH binary pair were used to predict activity coefficients for the four alcohols above which have very similar structures. The predicted activity coefficients were

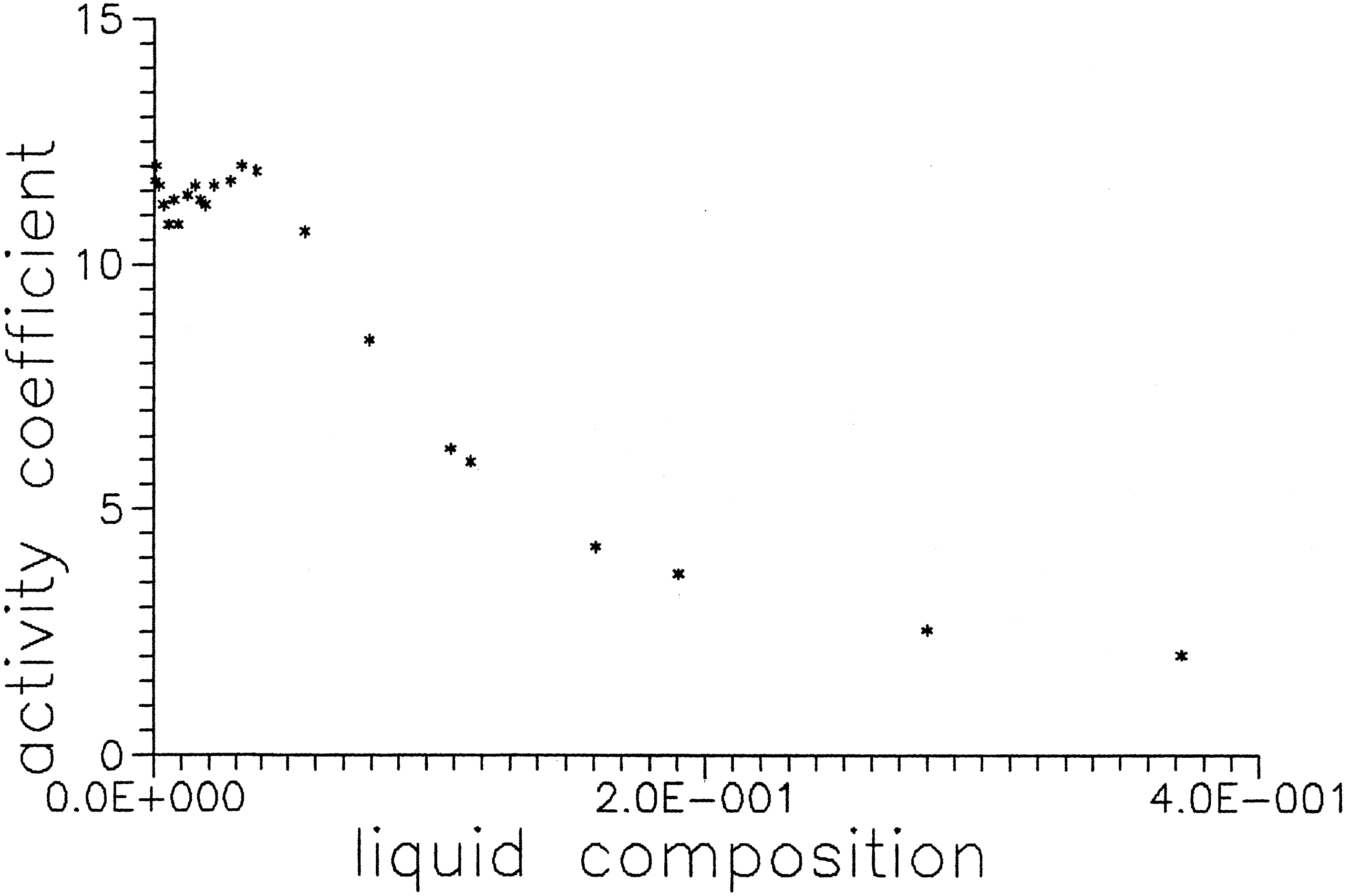

Figure 11. Activity Coefficient as a Function of Composition for 2−methyl−2−propanol.

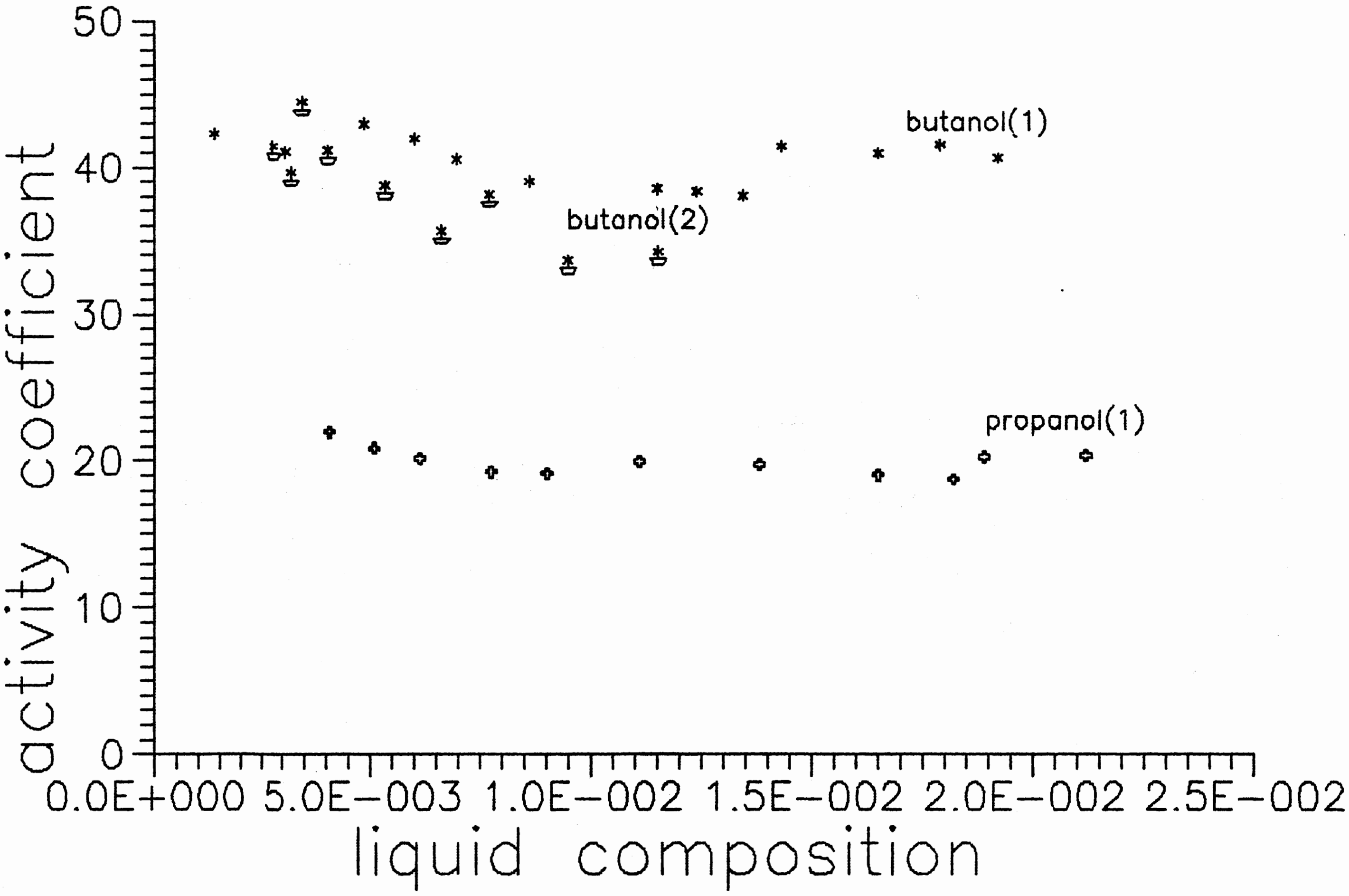

Figure 12. Activity Coefficient as a Function of Composition for 1−butanol, 2−butanol and 2−methy−1−propanol.

best for 2-methyl-2-propanol where the prediction errors did not exceed 2% and were worst for 2-butanol where the prediction errors ranged between 42% and 49 % when compared to the experimental values of Table A-I. This illustrates the inability of group contribution methods to predict the activity coefficient of compounds with similar structures but widely varying activity coefficients accurately.

Once the experimental activity coefficient values are known, these values are used to determine the interaction parameters between the solvent (water) and the solute. The experimental activity coefficients, those found in the literature and those obtained in this work, are compared with the values obtained using the UNIFAC model which was presented in Chapter II. The simplex method (149) is used to determine the interaction parameters based on this comparison.

Bastos et al. (15) have proposed using only infinite dilution activity coefficient data for obtaining the binary interaction parameters needed in the UNIFAC model. Data based on infinite dilution activity coefficients are preferred because they entail no extrapolation from high concentration to low concentration regions, thereby avoiding some inherent errors in prediction.

The group volumes and surface areas that have been used in this work are presented in Table VII.

The experimental activity coefficients listed in Tables

TABLE VII

GROUP SURFACE AREAS AND VOLUMES USED IN THIS WORK (15).

GROUP	R	Q
AC	0.3652	0.1200
ACH	0.5313	0.4000
ACCH3	1.2663	0.9680
ACCL	1.1562	0.8440
BR	0.9492	0.8320
C=C	0.6605	0.4850
CH=CH	1.1167	0.8670
CCL	1.0060	0.7240
CCL2	1.8016	1.4480
CCL3	2.8700	2.4100
CCL4	3.3900	2.9100
CH2COO	1.9031	1.7280
CH	0.4469	0.2280
CH2	0.6744	0.5400
CH3	0.9011	0.8480
CH2O	0.9183	0.7800
CL	0.7910	0.7240
H2O	0.9200	1.4000

A-I through A-IX in the Appendix have been used to obtain interaction parameters between the binary pairs listed in Table VIII. The reference column in Table VIII indicates which experimental data were used to obtain the interaction parameters. Vapor pressure data were taken from Lange's Handbook of Chemistry and Physics where coefficients for the Antoine equation are listed. Vapor pressures were used when it was necessary to convert Henry's constant data to activity coefficients.

The results of applying the UNIEST program (52) which estimates UNIFAC interaction parameters with the simplex optimization method to the available experimental data are presented in Table VIII as binary interaction parameters. The component listed first is designated by 1. In the majority of cases the solvent which is water is this first component, although interactions between other binary pairs have also been obtained.

The procedure was as follows. The interaction parameters were obtained sequentially. For instance, benzene is composed of the aromatic methyl group (ACH_2) only. Therefore, this compound was used as the first building block and the binary interaction parameters between the ACH_2 and the H_2O groups were determined. Toluene which is composed of five aromatic methyl groups and an $ACCH_3$ group was selected for the next step. The interaction parameters obtained in the previous step were used to obtain the binary

TABLE VIII

BINARY INTERACTION PARAMETERS OBTAINED IN THIS WORK.

			REFERENCES						
BINARY PAIR	A12	A21	1	2	3	4	5	6	7
H2O-ACH2	5335	349	10	34	90				
H2O-CCL	5091	547	42	73					
H2O-C=C	-12	178	34	89	90	135			
H2O-CCL3	4077	494	10	34	42	89	90	109	135
H2O-ACCL	67	247	10	34	90				
H2O-ACCH3	345	473	10	34	90				
H2O-CCL4	2031	704	10	34	42	89	90		
H2O-CL	1545	1492	34	42					
H2O-CCL2	68	868	34	42	81	90			
CCL2-CCL	5271	4597	34	42					
H2O-Br	426	544	34	109					
H2O-CH2O	103	222	34						
CH2O-CCL	-193	103	34						
H2O-CCOO	66	242	34						

interaction parameter between the $ACCH_3$ and the H_2O groups. One would then move on to a compound like chlorotoluene and so on.

In all of these determinations the data from different sources were pooled. For example, for benzene data were taken from three different sources, namely, the data in Tables A-I, A-II and A-V. All of these data are at 25°C and they range in value between 1910 to 6200. However, the data in Tables A-I and A-II are obtained at the maximum (saturation) solubility of benzene in water which is 1780 mg/L and range between 1910 and 2470, whereas the one data point for benzene in Table A-V has been obtained at a concentration of 700 mg/L and is much larger in magnitude (6200). The data for toluene in Tables A-I, A-II and A-V have all been measured at maximum solubility and range between 9050 and 9900. Therefore, it seems to matter a great deal at which concentration the activity coefficient has been measured. Similarly, the activity coefficient of chlorobenzene varies between 11000 and 13400 in the same three Tables.

One needs experimental data to evaluate the prediction capability of the interaction parameters obtained above as a result of pooling the data in Tables A-I through A-IX.

Leighton et al (73) have obtained distribution coefficients for 21 chlorinated hydrocarbons in addition to benzene and toluene in dilute air-water systems in the temperature range between 0°C and 30°C. They have obtained these data for the purpose of ground water contamination applications. Their experimental method was discussed in Chapter II. They used a simple equilibration cell, a trap for concentration purposes, and a gas chromatograph for analysis in their experimental measurements. They state that their technique has a random error of less than ±1% and a systematic error due to gas chromatograph peak separation and integration error of less than 5% for compounds whose distribution coefficients range between 100 and 1000. Vapor pressure data were used to convert distribution coefficients to activity coefficients. These activity coefficients which are listed in Table IX at various temperatures were used to evaluate the performance of the interaction parameters listed in Table VIII. Of course these interaction parameters are independent of temperature and are not expected to perform well, if the activity coefficient is a strong function of temperature.

Table X shows the result of this comparison. The column labeled original in this Table refers to the interaction parameters originally proposed by Fredenslund et al.(53). Both Fredenslund's interaction parameters and the interaction parameters obtained from the experimental data of Tables A-I through A-IX are independent of temperature. For the case of chlorobutane, the interaction parameters of this work give better results which are 20 to 46 percent

TABLE IX

LEIGHTON'S DISTRIBUTION COEFFICIENT DATA AS A FUNCTION OF TEMPERATURE (73).

SOLUTE	TEMPERATURE (C)	K	GAMMA
DICHLOROMETHANE	1.90	61.40	294
	13.50	111.50	317
	15.70	121.50	314
	17.10	141.60	345
	22.00	157.10	313
	24.90	161.90	287
TRICHLOROMETHANE	1.90	68.90	834
	13.50	128.70	856
	15.70	146.70	878
	17.10	155.00	868
	22.00	194.50	869
	24.90	204.80	804
CHLOROBUTANE(2)	1.90	358.20	5096
	13.50	773.60	6232
	15.70	847.20	6165
	17.10	891.00	6084
	22.00	1109.30	6095
	24.90	1243.30	6030
DICHLOROPROPANE(1,2)	1.90	45.80	2412
	13.50	90.20	2460
	15.70	101.60	2464
	17.10	108.60	2446
	22.00	131.40	2302
	24.90	153.50	2329
DICHLOROPROPANE(1,3)	1.90	17.71	
	13.50	31.70	
	15.70	36.21	
	17.10	37.14	
	22.00	44.97	
	24.90	53.57	
TRICHLOROPROPANE(1,2,3)	1.90	11.66	
	13.50	11.46	
	15.70	13.55	
	17.10	14.18	
	22.00	15.12	
	24.90	19.81	
DICHLOROBUTANE(1,4)	13.50	15.27	
	15.70	20.05	
	17.10	21.35	
	22.00	24.76	
	24.90	26.61	
CHLOROBUTANE(1)	1.00	325.50	8184
	3.00	375.30	8441
	12.40	536.90	7336
	12.50	569.20	7738
	17.90	693.40	7209

TABLE IX (CONTINUED)

SOLUTE	TEMPERATURE (C)	K	GAMMA
	19.10	738.00	7243
	22.70	833.00	6901
	23.00	839.00	6847
TOLUENE	1.00	121.80	12919
	3.00	129.20	12078
	12.40	204.60	10880
	12.50	198.10	10473
	17.90	251.50	9814
	19.10	278.70	10185
	22.70	309.80	9335
	23.00	342.70	10165
CHLOROBENZENE	1.00	68.00	19194
	3.00	68.80	16938
	12.40	104.10	13915
	12.50	112.80	14984
	17.90	133.20	12740
	19.10	153.30	13658
	22.70	148.70	10753
	23.00	175.90	12504
CHLOROHEXANE(1)	1.00	399.50	151489
	3.00	365.50	120224
	12.40	668.30	116498
	12.50	728.40	126156
	17.90	873.20	107501
	19.10	969.70	110897
	22.70	1161.40	106943
	23.00	1267.70	114677
DICHLOROPENTANE(1,5)	1.00	16.36	
	3.00	23.10	
	12.40	21.41	
	12.50	22.87	
	17.90	26.96	
	19.10	36.69	
	22.70	79.33	
CHLOROTOLUENE	1.00	87.40	93033
	3.00	66.90	61384
	12.40	97.85	46186
	12.50	118.50	55526
	17.90	133.50	43685
	19.10	175.30	53077
	22.70	176.70	42569
	23.00	202.70	47925
TRICHLOROETHANE(1,1,1)	1.00	297.00	5534
	1.00	297.90	5551
	1.20	307.00	5660
	2.50	327.80	5641
	7.00	418.50	5699
	10.00	504.00	5893
	12.00	556.80	5892

TABLE IX (CONTINUED)

SOLUTE	TEMPERATURE (C)	K	GAMMA
	12.00	569.60	6027
	12.90	586.20	5933
	14.00	652.70	6258
	18.00	766.70	6057
	18.00	793.40	6268
	18.00	802.90	6343
	19.00	828.30	6239
	19.20	836.70	6242
	19.50	788.10	5797
	24.30	1027.60	6042
	25.20	1094.30	6174
	25.30	1110.70	6238
	26.00	1090.20	5930
	26.00	1131.40	6154
	26.10	1073.80	5814
TRICHLOROETHENE	1.00	131.60	5500
	1.00	139.50	5830
	1.20	138.80	5729
	2.50	168.40	6413
	7.00	200.90	5836
	10.00	232.70	5681
	12.00	254.80	5556
	12.00	265.80	5796
	12.90	287.00	5952
	14.00	309.90	6048
	18.00	375.00	5900
	18.00	379.60	5973
	18.00	375.00	5900
	19.00	393.50	5874
	19.20	417.30	6165
	19.50	396.50	5766
	24.30	537.10	6117
	25.20	539.90	5880
	25.30	545.70	5914
	26.00	551.10	5771
	26.00	563.80	5904
	26.10	558.10	5815
TETRACHLOROETHENE	1.00	206.90	36841
	1.00	226.70	40366
	1.20	236.10	41482
	2.50	260.40	41970
	7.00	314.10	37848
	10.00	370.20	36980
	12.00	401.00	35445
	12.00	473.30	38654
	12.90	452.90	37915
	14.00	501.50	39309
	18.00	615.10	38144
	18.00	627.20	38895

TABLE IX (CONTINUED)

SOLUTE	TEMPERATURE (C)	K	GAMMA
	18.00	627.50	38913
	19.00	644.90	37764
	19.20	633.90	36699
	19.50	647.90	36875
	24.30	868.10	37814
	25.20	889.80	36907
	25.30	905.40	37351
	26.00	896.80	35624
	26.00	938.80	37292
	26.10	920.70	36377
DICHLOROETHANE	1.00	30.62	1045
	1.30	30.89	1036
	11.00	46.56	909
	21.00	68.89	805
	22.00	76.59	852
	27.20	95.46	828
CARBONTETRACHLORIDE	1.00	412.10	8835
	1.30	412.40	8700
	11.00	719.50	9199
	13.00	859.50	9961
	21.00	1280.30	10178
	22.00	1319.40	10024
	27.20	1571.40	9482
BENZENE	1.00	97.50	2657
	1.30	95.20	2550
	11.00	153.70	2435
	13.00	181.00	2587
	21.00	257.70	2482
	22.00	264.30	2427
	27.20	327.60	2365
TETRACHLOROETHANE	11.00	10.94	5264
	13.00	12.52	5166
	21.00	17.03	3920
	22.00	19.40	4165
	27.20	20.94	3162
DICHLOROETHENE(1,1)	2.50	533.50	5023
	7.00	780.10	5879
	12.90	1161.80	6623
	18.00	1336.40	6049
	19.50	1752.00	7423
	24.30	1714.50	5912
	26.10	2146.80	6866
DICHLOROETHENE(1,1)	2.50	16.67	2289
	7.00	20.96	2137
	12.90	26.91	1892
	18.00	34.14	1768
	19.50	33.64	1596
	24.30	44.61	1612
	26.10	48.47	1586

TABLE IX (CONTINUED)

SOLUTE	TEMPERATURE (C)	K	GAMMA
CHLOROPENTANE	2.50	362.40	
	7.00	464.20	
	12.90	683.00	
	18.00	906.60	
	19.50	955.20	
	24.30	1302.60	
	26.10	1318.20	

TABLE X

COMPARISON OF EXPERIMENTAL AND CALCULATED ACTIVITY COEFFICIENTS USING TWO SETS OF TEMPERATURE-INDEPENDENT BINARY INTERACTON PARAMETERS

CHLOROBUTANE

T(K)	EXPERIMENTAL	THIS WORK	E(%)	ORIGINAL	E(%)
274	8184	12072	47	2694	-67
286	7738	9993	29	2325	-70
291	7209	9187	27	2176	-70
296	6847	8512	24	2048	-70

CHLOROHEXANE

T(K)	EXPERIMENTAL	THIS WORK	E(%)	ORIGINAL	E(%)
274	151489	169524	11	30804	-80
286	126156	132989	14	25341	-80
291	107501	119445	11	23228	-78
296	114677	108335	-5	21451	-81

CHLOROTOLUENE

T(K)	EXPERIMENTAL	THIS WORK	E(%)	ORIGINAL	E(%)
274	93033	236957	154	1628771	1650
286	55526	168340	203	1116618	1910
291	43685	144803	231	945140	2063
296	47925	126335	163	812733	1595

TABLE X (CONTINUED)

TETRACHLOROETHYLENE

T(K)	EXPERIMENTAL	THIS WORK	E(%)	ORIGINAL	E(%)
274	36841	67394	82	19	100
286	37915	49884	31	18	100
291	38913	44197	13	18	100
299	36377	36779	1	17	100

DICHLOROETHANE

T(K)	EXPERIMENTAL	THIS WORK	E(%)	ORIGINAL	E(%)
274	1045	7746	641	860	-18
284	909	6895	658	782	-14
294	805	5447	576	670	-17
300	828	4966	499	627	-24

BENZENE

T(K)	EXPERIMENTAL	THIS WORK	E(%)	ORIGINAL	E(%)
274	2657	3044	14	3156	18
284	2435	2734	12	2726	5
294	2482	2473	-1	2458	-1
300	2365	2331	-1	2321	-2

DICHLOROETHYLENE

T(K)	EXPERIMENTAL	THIS WORK	E(%)	ORIGINAL	E(%)
275	5023	28569	468	83	-98
286	6623	21529	225	76	-99
291	6049	18732	209	73	-99
299	6866	15281	122	69	-99

closer to experimental values. Fredenslund's parameters underestimate and the parameters of this work overestimate the activity coefficients. The errors in prediction are almost constant for Fredenslund's parameters but they decrease with increasing temperature for the parameters of this work. For chlorohexane, the interaction parameters of this work give better results which are closer to experimental values by 67 to 76 percent. Fredenslund's interaction parameters grossly overestimate the activity coefficients of chlorotoluene in water as do the interaction parameters of this work. However, the estimates of the parameters of this work are closer to the experimental values by a factor of 10. The errors in Fredenslund's predictions range between 1595 and 2063 percent and are random as are the prediction errors obtained from the parameters of this work, i.e., there is no decreasing or increasing pattern with temperature. In the case of tetrachloroethylene, Fredenslund's parameters grossly underestimate the experimental data and the parameters of this work give much better results. However, a pattern of decreasing error with increasing temperature for the parameters of this work is evident. Fredenslund's parameters do a much better job in the case of dichloroethane. However the same pattern of decreasing error with increasing temperature occurs for the parameters of this work. For benzene, the prediction results are quite similar and there does not seem to be a distinct advantage in either set of parameters. The predictions are quite good in both cases. Finally, both sets of parameters fail quite badly in the case of dichloroethylene. Fredenslund's parameters grossly underestimate and the parameters of this work grossly overestimate the experimental data. The decreasing pattern of errors with increasing temperature continues to hold for the parameters of this work.

In view of the temperature-dependent pattern of the errors for five of the seven compounds in Table X, it was decided to use Leighton's experimental activity coefficients which have been obtained at various temperatures, to obtain temperature-dependent interaction parameters. Thus, that portion of Leighton's data that had not been used for comparison with predicted values was used to obtain temperature-dependent interaction parameters.

A polynomial fit was considered for the sake of simplicity and an analysis of variance showed that a quadratic fit was sufficient and adding extra terms in the polynomial did not improve the correlation power significantly. Interaction parameters for nine binary pairs were obtained as a function of temperature. These were used to fit polynomials of the form:

$A_{12} = A_1 + B_1T + C_1T^2$ and $A_{21} = A_2 + B_2T + C_2T^2$ (T in K)

Coefficients for each binary pair are presented in Table XI.

The above coefficients have been used to obtain

TABLE XI

COEFFICIENTS FOR A QUADRATIC FIT OF BINARY INTERACTION PARAMETERS AS A FUNCTION OF TEMPERATURE

A12

BINARY PAIR	A1	B1	C1
H2O-CCL	-4575.01	32.336	-0.0566
H2O-CCL2	-3177.60	23.831	-0.0410
H2O-CCL3	-4370.86	32.575	-0.0525
H2O-CCL4	-338.93	3.175	-0.0020
H2O-ACCH3	12967.47	-89.273	0.1564
H2O-ACCL	7311.68	-50.578	0.0864
H2O-C=C	1724.67	-12.406	0.0208
H2O-CL	23829.35	-161.692	0.2791
CCL-CCL2	4963.53	-35.399	0.0632

A21

BINARY PAIR	A2	B2	C2
H2O-CCL	-4944.27	36.463	-0.0642
H2O-CCL2	-5022.25	37.722	-0.0652
H2O-CCL3	-6238.21	47.300	-0.0800
H2O-CCL4	-4543.89	33.429	-0.0547
H2O-ACCH3	13296.44	-90.032	0.1570
H2O-ACCL	3929.96	-25.402	0.0422
H2O-C=C	-4753.01	33.640	-0.0547
H2O-CL	-5371.79	39.165	-0.0647
CCL-CCL2	120553.55	-854.702	1.5166

temperature-dependent interaction parameters which have in turn been used to predict activity coefficients for the same compounds as in Table X. The results of the comparison of these predicted values with the experimental values and the predicted values using the original parameters of Fredenslund et al. (53) are shown in Table XII.

The temperature-dependent parameters of this work predict the activity coefficients of chlorobutane better than Fredenslund's original parameters by 1 to 17 percent. In the case of chlorohexane, the temperature-dependent parameters give lower prediction errors which are 28 to 63 percent closer to the actual experimental values. There is a significant change in the prediction ability of UNIFAC with the new temperature-dependent interaction parameters in the case of chlorotoluene where the errors ranging between 1595 and 2063 percent have been cut down to between -10 and -18 percent. There is also a notable improvement in the case of tetrachloroethylene especially when the actual values of the activity coefficients are considered which is a better indication of the prediction power when predicted values of the activity coefficient are lower than the experimental values because the maximum possible error in these cases is 100% due to the definition of error as: $(\gamma^c-\gamma^e)/\gamma^e$. In the case of dichloroethane, however, the original UNIFAC parameters due to Fredenslund et al. (53) give better results. This is the only case where the temperature-

TABLE XII

COMPARISON OF EXPERIMENTAL AND CALCULATED ACTIVITY COEFFICIENTS USING TWO SETS OF BINARY INTERACTION PARAMETERS

CHLOROBUTANE

		CALCULATED			
T(K)	EXPERIMENTAL	THIS WORK	E(%)	ORIGINAL	E(%)
274	8184	2787	-66	2694	-67
286	7738	3349	-56	2325	-70
291	7209	3098	-57	2176	-70
296	6847	3162	-53	2048	-70

CHLOROHEXANE

		CALCULATED			
T(K)	EXPERIMENTAL	THIS WORK	E(%)	ORIGINAL	E(%)
274	151489	73151	-52	30804	-80
286	126156	95540	-24	25341	-80
291	107501	88107	-18	23228	-78
296	114677	93631	-18	21451	-81

CHLOROTOLUENE

		CALCULATED			
T(K)	EXPERIMENTAL	THIS WORK	E(%)	ORIGINAL	E(%)
274	93033	75826	-18	1628771	1650
286	55526	48716	-12	1116618	1910
291	43685	39105	-10	945140	2063
296	47925	40700	-15	812733	1595

TABLE XII (CONTINUED)

TETRACHLOROETHYLENE

T(K)	EXPERIMENTAL	CALCULATED THIS WORK	E(%)	ORIGINAL	E(%)
274	36841	19988	-46	19	-100
286	37915	22589	-40	18	-100
291	38895	22837	-41	18	-100
299	37292	22998	-38	17	-100

DICHLOROETHANE

T(K)	EXPERIMENTAL	CALCULATED THIS WORK	E(%)	ORIGINAL	E(%)
274	1045	46	-96	860	-18
284	909	51	-94	782	-14
294	805	41	-95	670	-17
300	828	37	-96	627	-24

BENZENE

T(K)	EXPERIMENTAL	CALCULATED THIS WORK	E(%)	ORIGINAL	E(%)
274	2657	2600	-2	3156	18
286	2587	2570	-1	2726	5
295	2427	2565	6	2458	1
300	2365	2472	5	2321	-2

DICHLOROETHYLENE

T(K)	EXPERIMENTAL	CALCULATED THIS WORK	E(%)	ORIGINAL	E(%)
276	5023	1606	-68	83	-98
286	6623	1543	-77	76	-99
291	6049	1573	-74	73	-99
299	6866	1446	-79	69	-99

dependent interaction parameters of this work do a worse job than the original parameters. For benzene, the prediction results are quite similar. Finally, for the case of dichloroethylene, the parameters of this work result in better predictions which are closer to experimental values by 20 to 30 percent.

Therefore, the temperature-dependent interaction parameters obtained in this work using the experimental data of Leighton et al. (73) result in a marked improvement in the predictive power of the UNIFAC group contribution model as demonstrated by the above comparisons with experimental data and the predicted values obtained using the original interaction parameters as suggested by Fredenslund et al. (53). It is also noteworthy that the temperature-dependent parameters obtained in this work underestimate the experimental values in all cases for all but two data points. However, the errors are no longer dependent on the temperature and the pattern of decreasing error with increasing temperature which was observed in five of the seven cases for the temperature-independent parameters has been eliminated. It must also be noted that the improvements have been achieved for aqueous systems in the very dilute composition range and in the limited temperature range between 0 and 40 °C. However, these are the ranges of temperature and composition which are of interest in environmental applications.

Comparison with Predictions of other Binary Parameters

The temperature-dependent interaction parameters obtained in this work for paraffinic, naphthenic and aromatic methyl groups with water were used to predict activity coefficients for cyclopentane, pentane, heptane and toluene. These predicted values were compared with the experimental values of Sorensen et al. (146) based on liquid-liquid equilibrium (solubility data). The interaction parameters of Fredenslund et al. (53) and Bastos et al. (15) have also been used for the same prediction. The results of these comparisons are shown in Table XIII.

The interaction parameters obtained in this work result in a moderate improvement in predicted values of activity coefficients using the UNIFAC method. The errors listed in Table XIII are defined as the absolute value of the ratio of the difference of the predicted and experimental values of the activity coefficient to the experimental value.

The best results are obtained for pentane for all three sets of interaction parameters. The parameters of this work give the best results and the parameters of Bastos et al. (15) give the worst results, in all cases. Some values predicted by the parameters of Bastos are off by as much as two orders of magnitude from the experimental values as in the case of the water-heptane system. The maximum error

TABLE XIII

COMPARISON OF PREDICTED ACTIVITY COEFFICIENTS WITH EXPERIMENTAL VALUES USING THREE SETS OF BINARY INTERACTION PARAMETERS

CYCLOPENTANE

T(C)	EXP	ORIG	E(%)	BASTOS	E(%)	THIS WORK	E(%)
25	25000	1819	-93	209	-99	6303	-74

PENTANE

T(C)	EXP	ORIG	E(%)	BASTOS	E(%)	THIS WORK	E(%)
0	70400	4427	-93	326	-100	14994	-79
10	93400	3874	-95	280	-100	22092	-76
20	99000	3417	-97	243	-100	33348	-66
25	99000	3219	-97	227	-100	31569	-68

HEPTANE

T(C)	EXP	ORIG	E(%)	BASTOS	E(%)	THIS WORK	E(%)
0	1636700	52706	-97	1657	-100	265737	-84
10	1792100	44145	-98	1353	-100	444133	-75
20	1901100	37384	-98	1120	-100	766670	-60
25	2000000	34532	-98	1024	-100	712915	-64
30	2114200	31972	-99	940	-100	714503	-66
40	2314800	27587	-99	797	-100	701511	-70

TOLUENE

T(C)	EXP	ORIG	E(%)	BASTOS	E(%)	THIS WORK	E(%)
0	7000	14972	114	154	-98	5828	-17
10	7800	12457	60	142	-98	5754	-26
20	8800	10493	19	132	-99	5360	-39
25	9400	9670	3	127	-99	5012	-47

obtained using the parameters of this work is 84%. Except for the original parameters in the case of toluene, all three sets of interaction parameters underestimate the experimental values.

In a case by case study, one can see that for cyclohexane, the parameters of this work result in predictions which are 19% better than the predictions of Fredenslund's parameters (53). In the case of pentane, the predictions using the parameters obtained in this work are in less error than the original parameters by 14 to 31 percent. The predictions for heptane are between 13 and 38 percent better when using the temperature-dependent interaction parameters obtained in this work instead of the original parameters. Finally, in the case of toluene, the original parameters result in errors which decrease from 114% to 3% with the temperature increasing from 0 to 25°C. The errors using the temperature-dependent interaction parameters range between 17 to 39 percent which is better than the original parameter predictions for two points and worse for the other two. However, the range of errors using the parameters of this work is much smaller.

Comparing the magnitude of the predicted activity coefficient is a better means of comparison as far as the predictions using the parameters of Bastos are concerned. The values obtained using the parameters of Bastos are smaller than the actual experimental values by an order of magnitude but because of the definition of the error term, the error cannot surpass 100% in such cases. The same is true for all four compounds in Table XIII as far as predictions using the parameters of Bastos are concerned and the parameters of this work yield better results in all cases.

There is no temperature dependency in the prediction errors using the temperature-dependent interaction parameters obtained in this work except for the case of toluene where the prediction errors are not constant or random but increase with increasing temperature and follow a trend opposite to that of the original parameter prediction errors although the rate of change is not as rapid.

Hooper, Michel and Prausnitz (63) have recently obtained temperature-dependent interaction parameters for several water-organic binary groups in the range of 20-250 °C for the purpose of engineering design in the processing of fossil fuels. They have obtained temperature-dependent interaction parameters for seven water-organic groups, three of which are binary groups for which temperature-dependent interaction parameters have also been obtained in this work. They have also used a polynomial fit for their temperature-dependent interaction parameters, however, they have used a quadratic fit for the A_{12} term and a linear fit for the A_{21} term. Moreover, the coefficients of the polynomial expressions cannot be compared directly because Hooper et al. (63) have used a different expression for the combinatorial part of the activity coefficient expression in the UNIFAC model.

The combinatorial expression that they have used is a modification of the Flory-Huggins expression in which the volume fractions have been replaced by surface fractions. Thus, the expression used in their work for the combinatorial part of the activity coefficient expression is:

$$\ln \gamma^{C} = \ln (\phi_i/x_i) + 1 - (\phi_i/x_i) \quad (62)$$

where

$$\phi_i = x_i r_i^{2/3} / \sum_j x_j r_j^{2/3} \quad (63)$$

The molecular volume parameter, r_i, is calculated by summing over Bondi group volumes as in the original UNIFAC model.

In order to compare the parameters obtained in this work with the parameters of Hooper et al. (63) in terms of predictive capability, the UNIEST program was modified so that the combinatorial part of the activity coefficient would be calculated according to the above expression. This was the only modification, since the residual part had not been changed by Hooper et al. (63) as pointed out in their work. This modified UNIEST program was then used to predict activity coefficients using Hooper's temperature-dependent interaction parameters for three compounds, namely, toluene, chlorotoluene and heptane for which activity coefficients have also been obtained using the original UNIEST program and the temperature-dependent interaction parameters obtained in this work. These predicted values are compared to the experimental values of Sorensen et al. (146) in Table XIV.

The predictions using the temperature-dependent binary interaction parameters of this work are 10 to 12 percent better in the case of toluene. The prediction results of the parameters of this work are also better for chlorotoluene where they are closer to the experimental values by 38 to 51 percent. In the case of heptane, however, Hooper's interaction parameters give better results which are closer to the experimental values by 17 to 72 percent.

In conclusion, one can say that the temperature-dependent binary interaction parameters obtained in this work result in much better predictions as compared with the original UNIFAC parameters and the parameters of Bastos (15) which are independent of the temperature, and are comparable in their prediction power to the temperature-dependent interaction parameters of Hooper et al. (63).

TABLE XIV

COMPARISON OF EXPERIMENTAL AND CALCULATED ACTIVITY COEFFICIENTS USING TWO SETS OF TEMPERATURE-DEPENDENT BINARY INTERACTION PARAMETERS

TOLUENE

		CALCULATED			
T(K)	EXPEIMENTAL	THIS WORK	E(%)	HOOPER	E(%)
273	7000	5827	-16	5831	-16
283	7800	5754	-26	4979	-36
293	8800	5359	-39	4232	-51
298	9400	5012	-46	3887	-58

CHLOROTOLUENE

		CALCULATED			
T(K)	EXPERIMENTAL	THIS WORK	E(%)	HOOPER	E(%)
274	93033	75827	-18	31143	-66
285	55526	48716	-12	21469	-61
291	43685	39103	-10	17001	-61
296	47925	40700	-15	16014	-66

HEPTANE

		CALCULATED			
T(K)	EXPERIMENTAL	THIS WORK	E(%)	HOOPER	E(%)
273	1636700	265736	-83	2153795	31
283	1792100	444133	-75	1845975	3
293	1901100	766670	-59	1547350	-18
298	2000000	712915	-64	1421212	-28
303	2114200	714503	-66	1307760	-38
313	2314800	701511	-69	1097173	-52

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

An experimental setup based on the headspace analysis method was developed to measure the activity coefficient of aqueous systems at low liquid compositions. Measurement of the activity coefficient at low liquid compositions allows one to avoid extrapolation from the high concentration region. Activity coefficients were measured for the water(1)-benzene(2) system at at least three compositions levels for five isotherms. An error analysis showed that the accuracy of the activity coefficients was better than 1 percent. The experimental results were compared to literature values obtained from both liquid-liquid and vapor-liquid equilibrium measurements. The experimental results were not directly comparable because unlike the literature values, our values were not measured at the saturation composition. Therefore, interaction parameters were backed out from our experimental data and these parameters were used to predict the activity coefficients at saturation. There was poor agreement with literature values at temperatures other than the temperature at which our experimental data had been obtained (25°).

The second part of this work consisted of modifying the UNIFAC group contribution method so that it could predict the activity coefficient of aqueous-organic systems better. In order to achieve this, it was necessary to sacrifice some of the generality of the model by obtaining binary interaction parameters which are specific to aqueous-organic solutions in the very dilute region and near ambient temperatures. Based on the experimental vapor-liquid equilibrium data in the literature such as Henry's law constants, distribution coefficients and activity coefficients, binary interaction parameters were developed for the UNIFAC group contribution activity coefficient model. Most of these interaction parameters consist of the interaction between water and groups in aromatic and halogenated hydrocarbons which are classified as environmentally hazardous materials. These interaction parameters resulted in better predictions when compared to the original UNIFAC parameters of Fredenslund et al. (53). However, a temperature dependence was observed in the prediction errors. Therefore, binary interaction parameters were obtained for specific temperatures based on the available experimental data in the literature. Correlations were developed for interaction parameters as a function of temperature. The temperature-dependent interaction parameters resulted in much better predictions using the UNIFAC model as compared with the original parameters and the general parameters of this work.

The prediction capability of the temperature-dependent parameters of this work was similar to the prediction power of the one set of temperature-dependent interaction parameters available in the literature for aqueous systems.

Recommendations

Since extensive data collection was not the objective of this work, it is recommended that the new experimental setup whose performance as far as reproducibility has been proven satisfactory, be used to develop binary interaction parameters between water and other environmentally significant groups such as chlorine, and paraffinic and naphthenic groups.

Since successful measurement of the liquid composition was not possible for compounds with low aqueous solubility due to the detection limitation of the gas chromatograph, it is recommended that a more powerful means of detection such as an ultraviolet spectrophotometer be used for this purpose. Gas chromatography should continue to be used for vapor phase analysis. Another possible alternative is the use of a concentration step where the liquid sample is trapped and concentrated through the removal of the bulk of the water, and the concentrated solution is subsequently sent to the GC for analysis. Because of the inherent inaccuracies of this method such as the loss of sample in the cold trap or on the surface of the adsorbent, the former improvement is preferable.

The multiple equilibration method should also be seriously considered as an alternative and perhaps a better method than the head space analysis method. The simplicity of this procedure makes it attractive and the present experimental setup could be modified easily to test the multiple equilibration method as well.

It can also further be recommended that the activity coefficients be measured at the saturation limit in solubility so that the obtained data could be compared directly with the available experimental data in the literature. The effects of temperature and composition should also be studied in more detail by studying the same binary system at several temperatures and compositions. This procedure could be carried out for a few systems and once the effect of temperature and composition and their interdependence is well-established, data could be obtained only at selected temperatures and compositions.

SELECTED BIBLIOGRAPHY

1. Aboul-Fotouh, K. H. and K. E. Starling, 'Use of a Generalized Modified BWR Equation of State for Halogenated Hydrocarbon Saturated Thermodynamic Properties,' Proc. Oklah. Acad. Sci., Vol. 58, 77-80 (1978).

2. Afrashtehfar, S. and G. C. B. Cave, 'Limiting activity coefficients in dilute solutions of nonelectrolytes. II. Determination for polar-nonpolar and polar-polar binary mixtures, and the application of some solubility-parameter treatments,' Can. J. Chem., Vol. 64, 198-203 (1985).

3. Alessi, P., Kikic, I., Fredenslund, A. and P. Rasmussen, 'UNIFAC and Infinite Dilution Activity Coefficients,' Can. J. Chem. Eng., Vol. 60, 300-304 (1982).

4. Alessi, P., Kikic, I., Alessandrini, A. and M. Fermeglia, 'Activity Coefficients at Infinite Dilution by Gas-Liquid Chromatography. 1. Hydrocarbons and n-Chloroparaffins in Organic Solvents,' J. Chem. Eng. Data, Vol. 27, 445-448 (1982).

5. Alessi, P., Kikic, I., Nonino, C. and M. Orlandini Visalberghi, 'Activity Coefficients at Infinite Dilution by Gas-Liquid Chromatography. 2. Polar Compounds in Organic Solvents,' J. Chem. Eng. Data, Vol. 27, 448-450 (1982).

6. Anderson, T. F. and J. M. Prausnitz, 'Application of the UNIQUAC Equation to Calculation of Multicomponent Phase Equilibria. 1. Vapor-Liquid Equilibria,' Ind. Eng. Chem. Process Des. Dev., Vol. 17, No.4, 552-561 (1978).

7. Anderson, T. F. and J. M. Prausnitz, 'Application of the UNIQUAC Equation to Calculation of Multicomponent Phase Equilibria. 2. Liquid-Liquid Equilibria,' Ind. Eng. Chem. Process Des. Dev., Vol. 17, No.4, 561-567, (1978).

8. Antezana, F. J. and H. Y. Cheh, 'Component Fugacities in Hydrogen-Ammonia-Propane Mixtures. I. The Fugacity of Hydrogen,' Ind. Eng. Chem. Fundam., Vol. 14, No. 3, 224-231 (1975).

9. Antezana, F. J. and H. Y. Cheh, 'Component Fugacities in Hydrogen-Ammonia-Propane Mixtures. II. The Fugacity of Ammonia,' Ind. Eng. Chem. Fundam., Vol. 15, No. 2, 95-99 (1976).

10. Arbuckle, W. B., 'Estimating Activity Coefficients for Use in Calculating Environmental Parameters,' Environ. Sci. Technol., Vol. 17, 537-542 (1983).

11. Arnold, D. W., Greenkorn, R. A. and Kwang-Chu Chao, 'Infinite Dilution Activity Coefficients for Alkanals, Alkanoates, Alkanes, and Alkanones in n-Octane,' J. Chem. Eng. Data, Vol. 27, 123-125 (1982).

12. Ashworth, A. J., Chien, C. F., Furio, D. L., Hooker, D. M., Kopecni, M. M., Laub, R. J. and G. J. Price, 'Comparison of Static with Gas Chromatographic Solute Infinite-Dilution Activity Coefficients with Poly(dimethylsiloxane) Solvent,' Macromolecules, Vol. 17, 1090-1094 (1984).

13. Badings, H. T., De Jong, C., Dooper, R. P. M. and R. C. M. De Nijs, 'Pure Analysis of Volatile Compounds in Food Products by Purge-and-Cold-Trapping/Capillary Gas Chromatography,' Proc. of the 4th Weurman Flavour Research Symposium, 523-532 (1985).

14. Balakrishnan, S., Krishnan, V. and H. E. Eduljee, 'Prediction of Activity Coefficients from the Properties of Pure Components,' Ind. J. Chem Eng., 49-52 (1969).

15. Bastos, J. C., Soares, M. E. and A. G. Medina, 'Infinite Dilution Activity Coefficients Predicted by UNIFAC Group Contribution,' Ind. Eng. Chem. Res., Vol. 27, No. 7, 1269-1277 (1988).

16. Belfer, A. J. and D. C. Locke, 'Non-Steady-State Gas Chromatography for Activity Coefficient Measurements,' Anal. Chem., Vol. 58, 2485-2489 (1984).

17. Bonner, D. C. and N. F. Brockmeier, 'Infinite-Dilution Activity Coefficients of Ethylene in Solvent-High-Density Polyethylene,' Ind. Eng. Chem Process Des. Dev., Vol. 16, No. 2 180-186 (1977).

18. Black, C., Joris, G. G. and Hugh S. Taylor, 'The Solubility of Water in Hydrocarbons,' J. Chem. Phys., Vol. 16, No. 5, 537-543 (1948).

19. Bonner, O. D., Kim, S. J. and A. L. Torres. 'A Comparison of the Osmotic and Activity Coefficients of Some Solutes in Structured Solvents,' J. Phys. Chem., Vol. 73, No. 6, 1968-1974 (1969).

20. Boublik, T. and B. C.-Y. Lu, 'Solubility of Gases in Liquids from First-Order Perturbation Theory of Convex Molecules,' J. Phys. Chem., Vol. 82, No. 26, 2801- 2805 (1978).

21. Bozzelli, J. W. and B. B. Kebbekus, 'A Study of Some Aromatic and Halocarbon Vapors in the Ambient Atmosphere of New Jersey,' J. Environ. Sci. Health, Vol. A17, No. 5, 693-711 (1982).

22. Burris, D. R. and W. G. MacIntyre, 'Solution of Hydrocarbon-Water System with Changing Phase Composition due to Evaporation,' Environ. Sci. Technol., Vol. 20, 296-299 (1986).

23. Burkhard, L. P., Armstrong, D. E. and A. W. Andren, 'Henry's Law Constants for the Polychlorinated Biphenyls,' Environ. Sci. Technol., Vol. 19, 590-598, (1985).

24. Burkhard L. P., Andren, A. W. and D. E. Armstrong, 'Estimation of Vapor Pressures for Polychlorinated Biphenyls: A Comparison of Eleven Predictive Methods,' Environ. Sci. Technol., Vol. 19, 500-507 (1985).

25. Burks, S. L., 'Evaluation of the Effectiveness of Granular Activated Carbon Adsorption and Aquaculture for Removing Toxic Compounds from Treated Petroleum Refinery Effluents,' NTIS Report No. EPA-600/2-81-067 (1980).

26. Campbell, J. R., Luthy, R. G. and M. J. T. Carrondo, 'Measurement and Prediction of Distribution Coefficients for Wastewater Aromatic Solutes,' Environ. Sci. Technol., Vol. 17, 582-590 (1983).

27. Campbell, J. R. and R. G. Luthy, 'Prediction of Aromatic Solute Partition Coefficients Using the UNIFAC Group Contribution Model,' Environ. Sci. Technol., Vol. 19, No. 10, 980-985 (1985).

28. Carta, R., Dernini, D. and G. Tola, 'A Comparative Analysis of the Derivation of Infinite Dilution Activity Coefficients from ΔT-x and ΔP-x Data,' Chem. Eng. Commun., Vol. 33, 231-236 (1985).

29. Chian, E. S. K. and P. P. K. Kuo, 'Distillation/Headspace/Gas Chromatographic Analysis for Volatile Polar Organics at ppb Level,' Environ. Sci. Tech. Vol. 11, No. 3, 282-285 (1977).

30. Christiansen, L. J. and A Fredenslund, 'Thermodynamic Consistency Using Orthogonal Collocation or Computation of Equilibrium Vapor Compositions at High Pressures,' A.I.Ch.E. J., Vol. 21, No. 1, 49-57 (1975).

31. Chriswell, C. D., 'Removal of gas chromatographable organic compounds from water by a spray vaporization technique,' J. Chrom., Vol. 132, 537-542 (1977).

32. Cohen, Y., 'Organic Pollutant Transport,' Environ. Sci. Technol., Vol. 20, No. 6, 538-544 (1986).

33. Cori, L. and P. Delogu, 'Infinite Dilution Activity Coefficients of Ethanol-n-Alkanes Mixtures,' Fluid Phase Equilibria, Vol. 27, 103-118 (1986).

34. Cowen, W. F. and R. K. Baynes, 'Estimated Application of Gas Chromatographic Headspace Analysis to Priority Pollutants,' J. Environ. Sci. Health, Vol. A15, No. 5, 413-427 (1980).

35. Daemen, J. M., Dankelman, W. and M. E. Hendriks, 'Properties and Applications of TENAX GC as a Column Packing Material in Gas Chromatography,' J. Chrom. Sci., Vol. 80, 79-83 (1975).

36. De Bortoli, M. and E. Pecchio, 'Sensitive Determination of Perfluorocarbon Tracers in Air by Intermediate Trapping and GC-ECD Analysis,' Commission of the European Communities, Joint Research Center, 21020 Ispra, Italy (1986).

37. Deiters, U., 'A New Semiempirical Equation of State for Fluids: Application to Pure Substances,' Chem. Eng. Sci., Vol. 36, 1147-1151 (1981).

38. Derr, E. L. and C. H. Deal, 'Analytical Solutions of Groups: Correlation of Activity Coefficients through Structural Group Parameters,' Ind. Eng. Chem. Ind., Vol. 61, 37-47 (1969).

39. De Zeeuw, J.,de Nijs, R. C. M. and L. T. Henrich, 'Adsorption Chromatography on PLOT (Porous-Layer Open-Tubular) Columns: A new Look at the Future of Capillary GC,' J. Chrom. Sci., Vol.25, 71-83 (1987).

40. Dickhut, R. M., Andren, A. W. and D. E. Armstrong, 'Aqueous Solubilities of Six Polychlorinated Biphenyl Cogeners at Four Temperature,' Environ. Sci. Technol., Vol. 20, No. 8, 807-810 (1986).

41. Dietz, E. A., Jr. and K. F. Singley, 'Determination of Chlorinated Hydrocarbons in Water by Headspace Gas Chromatography,' Anal. Chem., Vol. 51, No. 11, 1809-1814 (1979).

42. Dilling, W. L., 'Interphase Transfer Processes. II.

Evaporation Rates of Chloro Methanes, Ethanes, Ethylenes, Propanes, and Propylenes from Dilute Aqueous Solutions: Comparison with Theoretical Predictions,'Environ. Sci. Tech. Vol. 11, No. 4, 405-409 (1977).

43. Dohnal, V. and M. Novotna, 'Infinite-Dilution Activity Coefficients by Comparative Ebulliometry: A Model of Ebulliometer and the Experimental Equipment and Procedure,' Collection Czechoslovak Chem. Commun. Vol. 51 1393-1402 (1986).

44. Dohnal, V. and M. Novotna, 'Infinite-Dilution Activity Coefficients by Comparative Ebulliometry: The Mixtures of Freon 112 with Oxygenated Solvents and Hydrocarbons,' Fluid Phase Equilibria, Vol. 23, 303-313 (1985).

45. Donohue, M. D. and J. M. Prausnitz, 'Perturbed Hard Chain Theory for Fluid Mixtures: Thermodynamic Properties for Mixtures in Natural Gas and Petroleum Technology,' A.I.Ch.E. J., Vol. 24, No. 5, 849-860 (1978).

46. Duhem, P. and J. Vidal, 'Extension of the Dilutor Method to Measurement of High Activity Coefficients at Infinite Dilution,' Fluid Phase Equilibria, Vol. 2, 231-235 (1978).

47. Dupont, R. R. and J. A. Reineman, 'Evaluation of Volatilization of Hazardous Constituents at Hazardous Waste Land Treatment Site,' EPA Report No. EPA/600/S2-86/071 (1986).

48. Eckert, C. A., Newman, B. A., Nicolaides, G. L. and T. C. Long, 'Measurement and Application of Limiting Activity Coefficients,' A.I.Ch.E. J., Vol. 27, No. 1, 33-40 (1981).

49. Ellington, J. J., Stancil, F. E. and W. D. Payne, 'Measurement of Hydrolysis Rate Constants for Evaluation of Hazardous Waste Land Disposal: Volume 1. Data on 32 Chemicals,' EPA Report No. EPA/600/S3-86/043 (1987).

50. Ellis, S. R. M. and D. A. Jonah, 'Prediction of activity coefficients at infinite dilution,' Chem Eng. Sci., Vol. 17, 971-976 (1962).

51. Ferreira, P. O., Bastos, J. C. and A. G. Medina, 'Infinite Dilution Activity Coefficients for Aromatic and Nonaromatic Compounds in n-Methylpyrrolidone, Ethylene Glycol, and Mixtures of the Two Solvents,' J. Chem. Eng. Data, Vol. 32, 25-31 (1987).

52. Fredenslund, A., Gmehling, J. and P. Rasmussen, 'Vapor-liquid equilibria using UNIFAC: a group contribution method,' Elsevier, New York (1977).

53. Fredenslund, A., Jones, R. L. and J. M. Prausnitz, 'Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures,' A.I.Ch.E. J., Vol.21, No. 6, 1086-1099 (1975).

54. Fu, J.-K. and R. G. Luthy, 'Aromatic Compound Solubility in Solvent/Water Mixtures,' J. Environ. Eng., Vol. 112, No.2, 328-345 (1986).

55. Fu, J.-K. and R. G. Luthy, 'Effect of Organic Solvent on Sorption of Aromatic Solutes onto Soils,' J. Environ. Eng., Vol. 112, No. 2, 346-367 (1986).

56. Gainey, B. W. and R. L. Pecsok, 'Nonelectrolyte Liquid Mixture Studies by Medium Pressure Gas-Liquid Chromatography. Infinite Dilution Activity Coefficients of C_5-C_8 Hydrocarbons in 1-n-Alkylbenzenes,' J. Phys. Chem., Vol. 74, No. 12, 2548-2558 (1970).

57. Gautreaux, Jr., M. F. and J. Coates, 'Activity Coefficients at Infinite Dilution,' A.I.Ch.E. J., Vol. 1, No. 4, 496-499 (1955).

58. Grob, K. and G. Grob, 'Organic Substances in Potable Water and in its Precursor, Part II. Applications in the Area of Zürich,' J. Chrom., Vol. 90, 303-313 (1974).

59. Heideman, J. L., Tsonopoulos, C., Brady, C. J. and G. M. Wilson, 'High-Temperature Mutual Solubilities of Hydrocarbons and Water,' A.I.Ch.E. J., Vol. 31, No. 3, 376-384 (1985).

60. Helpinstill, J. G. and M. Van Winkle, 'Prediction of Infinite Dilution Activity Coefficients for Polar-Polar Binary Systems,' Ind. Eng. Process Des. Dev., Vol. 7, No. 2, 213-220 (1968).

61. Henley, E. J. and J. D. Seader, 'Equilibrium Stage Separation Operations in Chemical Engineering,' John Wiley & Sons (1981).

62. Hiler, G. V. and S. D. Cameron, 'Liquid-Liquid Extraction of Trace Level Pesticides from Process Streams,' EPA Report No. EPA-600/S2-84-195 (1985).

63. Hooper, H. H., Michel, S. and M. Prausnitz, 'Correlation of Liquid-Liquid Equilibria for Some Water-Organic Liquid Systems in the Region 20-250 C,' Ind. Eng. Chem. Res., Vol. 27, No. 11, 2182-2187 (1988).

64. Howard, P. E., Sage, G. W., Lamacchia, A. and A. Colb, 'The Development of an Environmental Fate Data Base,' J. Chem. Inf. Comput. Sci., Vol. 22, 38-44 (1982).

65. Howe, G. B., Mullins, M. E. and T. N. Rogers, 'Evaluation and Prediction of Henry's Law Constants and Aqueous Solubilities for Solvents and Hydrocarbon Fuel Components. Vol III: Experimental Solubility Datat,' NTIS Publication No.: ESL-TR-86-66 (1987).

66. Ioff, B. V. and A. J. Vitenberg, 'Headspace Analysis and Related Methods in Gas Chromatography,' New York, John Wiley & Sons (1984).

67. Jonah, D. A., 'On a Method of Numerical Differentiation and its Application to the Evaluation of Limiting Activity Coefficients and Their First Derivatives,' Chem. Eng. Sci., Vol. 41, No. 9, 2261-2271 (1986).

68. Junk, G. A., Richard, J. J., Grieser, M. D., Witiak, D., Witiak, J. L., Vick, A. R., Svec, H. J., Fritz, J. S. and G. V. Calder, 'Use of Macroreticular Resins in the Analysis of Water for Trace Organic Contaminants,' J. Chrom., Vol. 99, 745-762 (1974).

69. Kaiser, R., 'Ultra Trace Analysis of Volatile Substances with GC Methods in the Sub ppm and ppb Range Down to 10^{-10}%,' J. Chrom. Sci., Vol. 9, 227-234 (1971).

70. King, C. J., Barbari, T. A., Joshi, D. K., Bell, N. E. and J. Senetar, 'Equilibrium Distribution Coefficients for Extraction of Organic Priority Pollutants from Water,' EPA Project No. EPA-600/S2-84-060 (1984).

71. Kruus, P. and C. A. Hayes, 'Solubility of carbon dioxide in water-t-butanol solutions,' Can. J. Chem., Vol. 63, 3403-3410, (1985).

72. Lebert, A. and D. Richon, 'Infinite Dilution Activity Coefficients of n-Alcohols as a Function of Dextrin Concentration in Water-Dextrin Systems,' J. Agric. Food Chem., Vol. 32, 1156-1161 (1984).

73. Leighton, D. T. and J. M. Calo, 'Distribution Coefficients of Chlorinated Hydrocarbons in Dilute Air-Water Systems for Groundwater Contamination Applications,' J. Chem. Engr. Data, Vol. 26, 382-385 (1981).

74. Leinonen, P. J., Mackay, D. and C. R. Phillips, 'A Correlation for the Solubility of Hydrocarbons in Water,' Can. J. Chem. Eng., Vol. 49, 288-290 (1971).

75. Leo, A., Hansch, C. and D. Elkins, ' Partition Coefficients and Their Uses,' Chemical Reviews, Vol. 71, No. 6, 525-616 (1971).

76. Lenoir, J.-Y., Renault, P. and H. Renon, 'Gas Chromatographic Determination of Henry's Constants of 12 Gases in 19 Solvents,' J. Chem. Eng. Data, Vol. 16, No.3, 340-342 (1971).

77. Leroi, J.-C., Masson, J.-C., Renon, H., Fabries, J.-F. and H. Sannier, 'Accurate Measurement of Activity Coefficients at Infinite Dilution by Inert Gas Stripping and Gas Chromatography,' Ind. Eng. Chem. Process Des. Dev., Vol. 16, No. 1, 139-144 (1977).

78. Leveen, L. and W. H. Abraham, ' Multicomponent Vapor-Liquid Equilibrium: Direct Integration of the Gibbs-Duhem Equation,' Chem. Eng. Sci., Vol. 33, 1191-1199, (1978).

79. Lichtenbelt, J. H. and B. J. Schram, 'Vapor-Liquid Equilibrium of Water-Acetone-Air at Ambient Temperatures and Pressures. An Analysis of different VLE-Fitting Methods,' Ind. Engr. Chem. Proc. Des. Dev., Vol. 24, 391-397 (1985).

80. Lin, P. J. and J. Parcher, 'Direct Gas Chromatographic Determination of the Solubility of Light Gases in Liquids. Henry's Law Constants for Eleven Gases in n-Hexadecane, n-Octacosane, and n-hexatriacontane,' J. Chrom. Sci., Vol. 20, 33-38 (1982).

81. Lincoff, A. H. and J. M. Gossett, 'The Determination of Henry's Constants for Volatile Organics by Equilibrium Partitioning in Closed Systems. In: Gas Transfer at Water Surfaces,' Reidel Publishing Company, 17-25 (1984).

82. Liu, H., Wang, S., Tien, W. and J. Shi, 'UNIFAC Parameters from Gas Liquid Chromatography,' Journal of Chemical Industry and Engineering (China), Vol. 2, No. 1, 43-54 (1987).

83. Loblen, G. M. and J. M. Prausnitz, 'Correlation for the Ratio of Limiting Activity Coefficients for Binary Liquid Mixtures,' Fluid Phase Equilibria, Vol. 8, 149-160 (1982).

84. Loblen, G. M. and J. M. Prausnitz, ' Infinite-Dilution Activity Coefficients from Differential Ebulliometry,' Ind. Eng. Chem. Fund., Vol. 21, 109-113 (1982).

85. Mackay, D., 'Finding fugacity feasible,' Environ. Sci. Technol., Vol.13, No. 10, 1218-1223 (1979).

86. Mackay, D. and P. J. Leinonen, 'Rate of Evaporation of

Low-Solubility Contaminants from Water Bodies to Atmosphere,' Environ. Sci. Technol., Vol.9., No. 13, 1179-1180 (1975).

87. Mackay, D. and S. Paterson,' Model Describing the Rates of Transfer Processes of Organic Chemicals between Atmosphere and Water,' Environ. Sci. Technol., Vol. 20, No. 8, 810-816 (1986).

88. Mackay, D. and W. Y. Shiu, 'A Critical Review of Henry's Law Constants for Chemicals of Environmental Interest,'J. Phys. Chem. Ref. Data, Vol. 10, No. 4, 1175-1199 (1981).

89. Mackay, D. and W. Y. Shiu, 'Aqueous Solubility of Polynuclear Aromatic Hydrocarbons,' J. Chem. Eng. Data, Vol. 22, No. 4, 399-402 (1977).

90. Mackay, D. Shiu, W. Y. and R. P. Sutherland, 'Determination of Air-Water Henry's Law Constants for Hydrophobic Pollutants, ' Environ. Sci. Technol., Vol. 13, No. 3, 333-337 (1979).

91. Mackay, D. and A. W. Wolkoff, 'Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmosphere,' Environ. Sci. Technol., Vol. 7, No. 7, 611- 614 (1973).

92. Maher, P. J. and B. D. Smith, 'Infinite Dilution Activity Coefficient Values from Total Pressure VLE Data. Effect of Equation of State Used,' Ind. Eng. Chem. Fundam., Vol. 18, No. 4, (1979).

93. Martin, W. R. and M E. Paulaitis, 'Direct Measurement of Infinite-Dilution Activity Coefficients from Knudsen Cell-Mass Spectrometry,' Ind. Eng. Chem. Fundam., Vol. 18, No. 4, 423-425 (1979).

94. May, W. E., Wasik, S. P. and D. H. Freeman, 'Determination of the Solubility Behavior of Some Polycyclic Aromatic Hydrocarbons in Water,' Analytical Chemistry, Vol. 50, No. 7, 997-1000 (1978).

95. McAuliffe, C., 'GC determination of solutes by multiple phase equilibration,' Chem. Tech., 46-51 (Jan., 1971).

96. McAuliffe, C., 'Measuring Hydrocarbons in Water,' Chem Eng. Progress, 40-45 (Nov., 1987).

97. McAuliffe, C. D., 'The Multiple Gas-Phase Equilibration Method and Its Application to Environmental Studies,' Petroleum in the Marine Environment, Chapter 8, 193-218, American Chemical Society (1980).

98. McAuliffe, C., 'Solubility in Water of Paraffin, Cycloparaffin, Olefin, Acetylene, Cyloolefin, and Aromatic Hydrocarbons,' J. Phys. Chem., Vol. 70, No. 4, 1267-1275 (1966).

99. McCreery, R. L. and D. T. Sawyer, 'Gas-Solid Chromatography Using Various Salt-Modified Activated Aluminas and Magnesium Silicates,' J. Chrom. Sci., Vol.8, 122-127 (1970).

100. McNally, M. E. and R. L. Grob, 'A Review: Current Applications of Static and Dynamic Headspace Analysis. Part One: Environmental Applications,' Am. Lab., 20-33 (1985).

101. Mesnage, J. and A. A. Marsan, 'Vapor-Liquid Equilibrium at Atmospheric Pressure,' J. Chem. Engr. Data, Vol. 16, No. 4, 434-439 (1971).

102. Milanova, E. and G. C. B. Cave, 'Limiting activity coefficients in dilute solutions of nonelectrolytes. I. Determination for polar-nonpolar binary mixtures by a novel apparatus, and a solubility-parameter treatment of results,' Can. J. Chem., Vol. 60, 2697-2706 (1982).

103. Monfort, J. P. and J. L. Perez, 'Henry's Constants for Normal Mixtures Calculated with a Modified Pierotti Theory Using Temperature-dependent Hard Core Diameters,' Chem. Eng. J., Vol. 16, 205-209 (1978).

104. Mousa, A. H. N., 'Prediction of Henry's Constant by Gas Chromatography,' J. Chem. Engr. Japan, Vol. 17, No. 2, 206-208 (1984).

105. Mukhopadhyay, M and A. S. Pathak, 'Infinite-Dilution Activity Coefficients from Ebulliometric Isobaric Bubble Point-Composition Data of Hydrocarbon-Sulfolane Systems,' J. Chem. Eng. Data, Vol. 31, 148-152 (1986).

106. Munz, C. and P. V. Roberts, 'Effects of Solute Concentration and Cosolvents on the Aqueous Activity Coefficient of Halogenated Hydrocarbons,' Environ. Sci. Technol., Vol. 20, 830-836 (1986).

107. Munz, C. and P. V. Roberts, 'Transfer of Volatile Organic Contaminants into a Gas Phase during Bubble Aeration,' EPA Technical Report No. 262 under Grant No. EPA R-806631 (1982).

108. Neff, J. M., 'Biological Effects of Oil in the Marine Environment,' Chemical Engineering Progress, 27-33 (Nov., 1987).

109. Nicholson, B. C., Maguire, B. P. and D. B. Bursill,

'Henry's Law Constants for Trihalomethanes: Effects of Water Composition and Temperature,' Environ. Sci. Tech., Vol. 18, 518-521 (1984).

110. Nitta, T., Morinaga, K. and T. Katayama, 'Gas Chromatographic Study of Limiting Activity Coefficients of Organic Solutes in Squalane,' Ind. Eng. Chem. Fundam., Vol. 21, 396-401 (1982).

111. Novotna, M., Dohnal, V. and R. Holub, 'Infinite-Dilution Activity Coefficients by Comparative Ebulliometry: Five Systems Containing Bromide or Chloride Group,' Fluid Phase Equilibria, Vol. 27, 373-381 (1986).

112. Ohta, T., Koyabu, J. and I. Nagata, 'Vapor-Liquid Equilibria for the Ternary Ethanol-2-Butanone-Benzene System at 298.15 K,' Fluid Phase Equilibria, Vol. 7, 65-73 (1981).

113. Orye, R. V. and J. M. Prausnitz, 'Multicomponent Equilibria with the Wilson Equation,' Ind. Eng. Chem., Vol. 57, No. 5, 18-26 (1965).

114. Palmer, D., 'A Practical Synthesis of Experimental and Correlation Techniques for Modeling Highly Nonideal Systems with Many Components,' Ind. Eng. Chem. Process. Des. Dev., Vol. 23, 259-266 (1984).

115. Parcher, J. F., Weiner, P. H., Hussey, C. L. and T. N. Westlake, 'Specific Retention Volumes and Limiting Activity Coefficients of C_4-C_8 Alkane Solutes in C_{22}-C_{36} n-Alkane Solvents,' J. Chem. Eng. Data, Vol. 20, No. 2, 145- 151 (1975).

116. Pellizzari, E. D., 'Volatile Organics in Aeration Gases at Municipal Treatment Plants,' EPA Report No. EPA-600/S2-82-056 (1982).

117. Pierotti, G. J., Deal, C. H. and E. I. Derr, 'Activity Coefficients and Molecular Structure,' Ind. Eng. Chem., Vol. 51, No.1, 95-102 (1959).

118. Polak, J. and B. C.-Y. Lu, 'Mutual Solubilities of Hydrocarbons and Water at 0 and 25 C,' Can. J. Chem., Vol. 51, 4018-4023 (1973).

119. Ponder, L. H., 'Gas chromatography of higher polyamines on Tenax-GC columns,' J. Chrom., Vol. 97, 77-78 (1974).

120. Ray, A. K., Davis, E. J. and P. Ravindran, 'Determination of ultra-low vapor pressures by submicron droplet evaporation,' J. Chem. Phys., Vol. 71, No. 2,

582-587 (1979).

121. Rebert, C. J. and K. E. Hayworth, 'The Gas and Liquid Solubility Relations in Hydrocarbon-Water Systems,' A.I.Ch.E. J., Vol. 13, No. 1, 118-121 (1967).

122. Rebert, C.J. and W. B. Kay, 'The Phase Behavior and Solubility Relations of the Benzene-Water System,' A.I.Ch.E. J., Vol. 5, No. 3, 285-289 (1959).

123. Richon, D. Antoine, P. and H. Renon, 'Infinite Dilution Activity Coefficients of Linear and Branched Alkanes from C_1 to C_9 in n-Hexadecane by Inert Gas Stripping,' Ind. Eng. Chem. Process Des. Dev., Vol. 19, 144-147 (1980).

124. Richon, D., Sorrentino, F. and A. Volley, 'Infinite Dilution Activity Coefficients by Inert Gas Stripping Method: Extension to the Study of Viscous and Foaming Mixtures,' Ind. Eng. Chem. Process Des. Dev., Vol. 24, 1160-1165 (1985).

125. Rizzi, A. and J. F. K. Huber, 'Improved Calculation of Infinite Dilution Activity Coefficients by the Solution of Groups Model for Nonpolar Compounds in Water Introducing an Additional Group Type,' Ind. Eng. Chem. Process Des. Dev., Vol. 23, 251-268 (1984).

126. Roberts, P. V. and P. G. Dändliker, 'Mass Transfer of Volatile Organic Contaminants from Aqueous Solution to the Atmosphere during Surface Aeration,' Environ. Sci. Technol., Vol. 17, No. 8, 484-489 (1983).

127. Roberts, P. V., Hopkins, G. D., Munz, C. and A. H. Riojas, 'Evaluating Two-Resistance Models for Air Stripping of Volatile Organic Contaminants in a Countercurrent Packed Column,' Environ. Sci. Technol., Vol. 19, No. 2, 164-173 (1985).

128. Roberts, P. V., Munz, C. and P. Dändliker, 'Modeling volatile organic solute removal by surface and bubble aeration,' J. Water Pollution Control Federation, Vol. 56, No. 2, 157-163 (1984).

129. Roberts, P. V., Munz, C., Dändliker, P. a,d C. Matter-Müller, 'Volatilization of Organic Pollutants in Wastewater Treatment- Model Studies,' EPA Report No. EPA-600/S2-84-047 (1984).

130. Rodriguez, A. T. and D. Patterson, 'Prediction of Activity Coefficients and Henry's Constants at Infinite Dilution for Mixtures of n-Alkanes,' Fluid Phase Equilibria, Vol. 17, 265-279 (1984).

131. Rytting, J. H., McHan, D. R., Higuchi, T. and D. J. W. Grant, 'Importance of the Debye Interaction in Organic Solutions: Henry's Law Constants for Polar Liquids in Nonpolar Solvents and Vice Versa,' J. Solution Chemistry, Vol. 15, No. 8, 693-703 (1986).

132. Sada, E., Kito, S. and Y. Ito, 'Solubility of Nitrous Oxide in the Mixtures of Alcohols and Water: Comparison with Pierotti's Gas Solubility Theory,' Ind. Eng. Chem. Fundam., Vol. 14, No. 3, 232-237 (1975).

133. Sagert, N. H. and W. P. Lau, 'Limiting Activity Coefficients for Butyl Alcohols in Water, n-Octane, and Carbon Tetrachloride,' J. Chem. Eng. Data, Vol. 31, 475-478 (1986).

134. Sakodynskii, K., Panina, L. and N. Klinskaya, 'A Study of Some Properties of Tenax, a Porous Polymer Sorbent,' Chromatographia, Vol. 7, No. 7, 339-344 (1974).

135. Schoene, K. and J. Steinhanses, ' Determination of Henry's Law Constant by Automated Head Space-Gas Chromatography: Determination of Dissolved Gases,' Anal. Chem., Vol. 321 538-543 (1985).

136. Schreiber, L. B. and C. A. Eckert, 'Use of Infinite Dilution Activity Coefficients with Wilson's Equation,' Ind. Eng. Chem. Process Des. Dev., Vol. 10, No. 4, 572-576 (1971).

137. Scott, L. S., 'Determination of Activity Coefficients by Accurate Measurement of Boiling Point Diagram,' Fluid Phase Equilibria, Vol. 26, 149-163 (1986).

138. Shaw, D. A. and T. F. Anderson, 'Use of Gas Chromatographic Headspace Analysis in Vapor-Liquid Equilibrium Data Collection,' Ind. Engr. Chem. Fundam., Vol. 22, 79-83 (1983).

139. Shing, K. S., 'Infinite-Dilution Activity Coefficients from Computer Simulation,' Chem. Phys. Letters, Vol. 119, No. 2,3, 149-151 (1985).

140. Shing, K. S., 'Infinite dilution activity coefficients of quadrupolar Lennard-Jones mixtures from computer simulation,' J. Chem. Phys., Vol. 85, No. 8, 4633-4637 (1986).

141. Srandani, V., 'Use of Infinite-Dilution Activity Coefficients for Predicting Azeotrope Formation at Constant Temperature and Partial Miscibility in Binary Liquid Mixtures,' Ind. Eng. Chem. Fundam., Vol. 13, No. 2, 154-156

(1974).

142. Shukla, H. M. and R. E. Hicks, 'Process Design Manual for Stripping of Organics,' EPA Report No. EPA-600/S2-84-139 (1984).

143. Skjold-Jorgensen, S., Kolbe, B., Gmehling, J. and P. Rasmussen, 'Vapor-Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension,' Ind. Eng. Chem. Process Des. Dev., Vol. 18, No. 4, 714-722 (1979).

144. Smiley, H. M., 'Limiting Activity Coefficients of C_5 Hydrocarbons in Various Amides,' J. Chem. Eng. Data, Vol. 15, No. 3, 413-416 (1970).

145. Soklow, R., 'Organic Chemical Producers Data Base Development and Update,' EPA Project No. EPA-600/S2-84-034 (1984).

146. Sorensen, J. M. and W. Arlt, 'Liquid-Liquid Equilibrium Data Collection: Binary Systems,'Chemistry Data Series, Vol. V, Part 1, DECHEMA (1979).

147. Sorensen, J. M., Magnussen, T., Rasmussen, P. and A. Fredenslund, 'Liquid-Liquid Equilibrium Data: Their Retrieval, Correlation and Prediction. Part I: Retrieval,' Fluid Phase Equilibria, Vol. 2, 297-309 (1979).

148. Stein, V. B. and R. S. Narang, 'Determination of Vinyl Chloride by Headspace Analysis by Photoionization Detection,' Bull. Environ. Contam. Toxicol., Vol. 27, 582-587 (1981).

149. Tao, B. Y., 'Optimization via the Simplex Method,' Chemical Engineering, Vol. 95, No. 2, 85-89 (1988).

150. Termonia, M. and G. Alaerts, 'Dynamic Headspace Enrichment System for CGC Analysis of Volatiles Released by Plants,' I.R.C., Ministry of Agriculture, Museumlaan 5, B-1980 Tervuren, Belgium (1980).

151. Thibodeaux, L. J., Parker, D. G. and H. H. Heck, 'Measurement of Volatile Chemical Emissions from Wastewater Basins,' EPA Project No. EPA-600/S2-82-095 (1983).

152. Thomas, E. R. and C. A. Eckert, 'Prediction of Limiting Activity Coefficients by a Modified Separation of Cohesive Energy Density Model and UNIFAC,' Ind. Eng. Chem. Process Des. Dev., Vol. 23, 194-209 (1984).

153. Thomas, E. R., Newman, B. A., Nicolaides, G. L. and C. A. Eckert, 'Limiting Activity Coefficients from Differential Ebulliometry,' J. Chem. Eng. Data, Vol. 27, 233-240 (1982).

154. Thomas, E. R., Newman, B. A., Wood, D. A. and C. A. Eckert, 'Limiting Activity Coefficients of Nonpolar and Polar Solutes in both Volatile and Nonvolatile Solvents by Gas Chromatography,' J. Chem. Eng. Data, Vol. 27, 399-405 (1982).

155. Tsonopoulos, C. and G. M. Wilson, 'High-Temperature Mutual Solubilities of Hydrocarbons and Water,' A.I.Ch.E. J., Vol. 29, No. 6, 990-999 (1983).

156. Tsonopoulos, C., 'Second Virial Coefficients of Polar Haloalkanes,' A.I.Ch.E. J., Vol. 21, No. 4, 827-829 (1975).

157. Tsonopoulos, C., 'Second Virial Coefficients of Water Pollutants,' A.I.Ch.E. J., Vol. 24, No. 6, 1112-1115 (1978).

158. Turek, E. A., Arnold, D. W., Greenkorn, R. A. and K.-C. Chao, 'A Gas-Liquid Partition Chromatograph for the Accurate Determination of Infinite Dilution Activity Coefficients,' Ind. Eng. Chem. Fundam., Vol. 18, No. 4, 426-429 (1979).

159. Turek, E. A., Greenkorn, R. A. and K. C. Chao, 'Infinite Dilution Activity Coefficients for Selected Binary Mixtures of Hydrocarbons, Alcohols, and Ketones,' J. Chem. Eng. Data, Vol. 24, No. 4, 296 298 (1979).

160. Umbreit, G. R. and R. L. Grob, 'Experimental Application of Gas Chromatographic Headspace Analysis to Priority Pollutants,' J. Environ. Sci. Health, Vol. A15, No. 5, 429-466 (1980).

161. Van Ness, H. C., Byer, S. M. and R. E. Gibbs, 'Vapor-Liquid Equilibrium: An Appraisal of Data Reduction Methods,' AIChE J., Vol. 19, No. 2, 238-244 (1973).

162. Van Rossum, P. and R. G. Webb, 'Isolation of Organic Water Pollutants by XAD Resins and Carbon,' J. Chrom., Vol. 150, 381-392 (1978).

163. Wilson, A. and E. L. Simons, 'Vapor-Liquid Equilibria. 2-Propanol-Water System,' Ind. Eng. Chem., Vol. 44, 2214-2219 (1952).

164. Yalkowsky, S. H. and S. C. Valvani, 'Solubility and Partitioning I: Solubility of Nonelectrolytes in Water,' J. Pharm. Sci., Vol. 69, No. 8, 912-922 (1980).

APPENDIX

EXPERIMENTAL DATA FROM LITERATURE

Table A-I contains activity coefficient data on C_4 alcohols. Table A-II contains Henry's constants and calculated activity coefficients for aromatic and chlorinated hydrocarbons. Table A-III deals with aromatic compounds only. Table A-IV has data on a ketone and on a chlorinated hydrocarbon. Table A-V deals with heavy polynuclear aromatic hydrocarbons. Table A-VI contains data on aromatic and halogenated compounds. Table A-VII deals with data on three halogenated methanes only. Table A-VIII has data on chlorinated C_1 and C_2 hydrocarbons. Table A-IX contains data on chlorinated compounds, especially multi-chlorinated light hydrocarbons.

TABLE A-I

ACTIVITY COEFFICIENTS FOR BUTYL ALCOHOLS IN WATER AT 20 C. (133)

SOLUTE	COMPOSITION	ACTIVITY COEFF
BUTANOL(1)	0.00137	42.30
BUTANOL(1)	0.00308	41.10
BUTANOL(1)	0.00487	43.00
BUTANOL(1)	0.00603	42.00
BUTANOL(1)	0.00697	40.60
BUTANOL(1)	0.00861	39.10
BUTANOL(1)	0.01150	38.60
BUTANOL(1)	0.01240	38.40
BUTANOL(1)	0.01340	38.10
BUTANOL(1)	0.01430	41.50
BUTANOL(1)	0.01650	41.00
BUTANOL(1)	0.01790	41.60
BUTANOL(1)	0.01920	40.70
BUTANOL(2)	0.00407	22.00
BUTANOL(2)	0.00510	20.90
BUTANOL(2)	0.00614	20.20
BUTANOL(2)	0.00775	19.30
BUTANOL(2)	0.00901	19.20
BUTANOL(2)	0.01110	20.00
BUTANOL(2)	0.01380	19.80
BUTANOL(2)	0.01650	19.10
BUTANOL(2)	0.01810	18.80
BUTANOL(2)	0.01890	20.30
BUTANOL(2)	0.02120	20.40
METHYL(2)PROPANOL(1)	0.00278	41.20
METHYL(2)PROPANOL(1)	0.00321	39.40
METHYL(2)PROPANOL(1)	0.00345	44.20
METHYL(2)PROPANOL(1)	0.00404	40.90
METHYL(2)PROPANOL(1)	0.00534	38.50
METHYL(2)PROPANOL(1)	0.00662	35.40
METHYL(2)PROPANOL(1)	0.00771	37.90
METHYL(2)PROPANOL(1)	0.00948	33.40
METHYL(2)PROPANOL(1)	0.01153	34.00
METHYL(2)PROPANOL(2)	0.00028	11.70
METHYL(2)PROPANOL(2)	0.00175	11.60
METHYL(2)PROPANOL(2)	0.00520	10.80
METHYL(2)PROPANOL(2)	0.00717	11.30
METHYL(2)PROPANOL(2)	0.00877	10.80
METHYL(2)PROPANOL(2)	0.01200	11.40
METHYL(2)PROPANOL(2)	0.01490	11.60
METHYL(2)PROPANOL(2)	0.01670	11.30
METHYL(2)PROPANOL(2)	0.01860	11.20
METHYL(2)PROPANOL(2)	0.02170	11.60
METHYL(2)PROPANOL(2)	0.02780	11.70
METHYL(2)PROPANOL(2)	0.03190	12.00
METHYL(2)PROPANOL(2)	0.05600	10.67

TABLE A-I (CONTINUED)

SOLUTE	COMPOSITION	ACTIVITY COEFF
METHYL(2)PROPANOL(2)	0.07900	8.47
METHYL(2)PROPANOL(2)	0.10860	6.26
METHYL(2)PROPANOL(2)	0.11580	5.99
METHYL(2)PROPANOL(2)	0.16050	4.24
METHYL(2)PROPANOL(2)	0.19040	3.70
METHYL(2)PROPANOL(2)	0.28000	2.56
METHYL(2)PROPANOL(2)	0.37200	2.04

TABLE A-II

MACKAY'S HENRY'S CONSTANT DATA IN M3ATM/GMOL AT 25 C. (90)

SOLUTE	H	ACTIVITY COEFF
ACENAPHTHENE	0.0157	2.84E5
ACENAPHTHENE	0.0148	2.68E5
ANTHRACENE	0.0676	2.61E9
ANTHRACENE	0.0730	2.82E9
BENZENE	0.5620	2.46E3
BIPHENYL	0.0413	1.76E6
BIPHENYL	0.0304	1.30E6
BROMOBENZENE	0.2470	2.49E4
CARBON TETRACHLORIDE	2.1600	7.97E3
CARBON TETRACHLORIDE	2.2100	1.02E4
CHLORO(1)NAPHTHALENE	0.3550	
CHLORO(2)NAPHTHALENE	0.0319	
CHLOROBENZENE	0.3140	1.10E4
CHLOROBENZENE	0.3820	1.34E4
CHLOROMETHANE	0.7310	8.46E1
DICHLOROBENZENE(O)	0.1930	5.47E4
DICHLOROBENZENE(P)	0.2400	1.48E5
DICHLOROETHANE(1,2)	0.0990	5.03E2
DICHLOROETHENE(1,1)	15.6100	1.09E4
DICHLOROMETHANE	0.2720	2.59E2
DICHLOROMETHANE	0.3010	3.59E2
DIFLUORODICHLOROMETHANE	40.6000	3.94E3
ETHYLBENZENE	0.8540	3.74E4
FLUORENE	0.0101	6.33E6
FLUOROTRICHLOROMETHANE	81.2000	5.10E4
LEPTOPHOS	0.0003	4.87E9
METHYL(1)NAPHTHALENE	0.0263	1.65E5
NAPHTHALENE	0.0489	2.49E5
PHENANTHRENE	0.0037	7.59E6
PHENANTHRENE	0.0040	8.28E6
PYRENE	0.0011	6.90E7
RONNEL	0.0021	1.67E7
TETRACHLOROBENZENE(1,2,3,	0.1590	4.75E5
TETRACHLOROETHENE	2.0300	5.94E4
TETRACHLOROETHENE	1.2390	2.78E4
TOLUENE	0.6730	9.84E3
TRICHLOROBENZENE(1,2,3)	0.1270	1.33E5
TRICHLOROETHANE(1,1,1)	3.4700	2.60E3
TRICHLOROETHENE(1,1,2)	0.9040	6.39E3
TRICHLOROMETHANE	0.2830	7.84E2
TRICHLOROMETHANE	0.3220	6.99E2
VINYLCHLORIDE	117.6000	2.12E4

TABLE A-III

ARBUCKLE'S HENRY'S CONSTANT DATA IN M3ATM/GMOL AT 25 C (10).

SOLUTE	H	ACTIVITY COEFF
ACENAPHTHALENE	1.46E-4	2.17E6
BENZENE	5.55E-3	2.47E3
BENZENE	4.30E-3	1.91E3
BIPHENYL	4.08E-4	1.22E6
CARBON TETRACHLORIDE	2.32E-2	1.10E4
CHLOROBENZENE	3.77E-3	1.34E4
CHLOROFORM	3.10E-3	6.70E3
DICHLOROBENZENE(1,4)	3.40E-3	1.43E5
ETHYLBENZENE	8.43E-3	3.75E4
NAPHTHALENE	4.83E-4	2.31E5
PHENANTHRENE	3.93E-5	7.65E6
TOLUENE	6.64E-3	9.86E3
TOLUENE	6.10E-3	9.05E3
TRICHLOROETHANE(1,1,1)	7.19E-3	3.03E3
TRICHLOROETHANE(1,1,2)	7.69E-4	1.71E3
TRIMETHYLBENZENE(1,2,4)	6.35E-3	1.34E5

TABLE A-IV

SHOENE'S DIMENSIONLESS HENRY'S CONSTANT DATA. (135)

SOLUTE	ACTIVITY COEFF	H	T (K)
ACETONE	15.42	0.02550	361
ACETONE	10.13	0.00750	332
ACETONE	8.57	0.00460	322
ACETONE	7.20	0.00280	313
ACETONE	5.77	0.00130	298
ACETONE	5.16	0.00095	293
TRICHLOROETHENE	8670.00	1.41000	319
TRICHLOROETHENE	7900.00	1.08000	315
TRICHLOROETHENE	7750.00	0.88000	310
TRICHLOROETHENE	6300.00	0.34000	293

TABLE A-V

MACKAY'S ACTIVITY COEFFICIENT DATA AT 25 C (91).

SOLUTE	COMPOSITION X10E9	ACTIVITY COEFF
ACENAPHTHALENE	459.00000	433000
ANTHRACENE	7.57000	1720000
BENZANTHRACENE(1,2)	1.10000	42400000
BENZOFLUORENE(1,2)	3.75000	6730000
BENZOFLUORENE(2,3)	0.95600	16000000
BENZOPERYLENE	0.01730	189000000
BENZOPYRENE(3,4)	0.27300	121000000
BIPHENYL	815.00000	433000
CHRYSENE	0.15800	34100000
CORONENE	0.00856	9820000
DIMETHYLANTHRACENE(9,10)	4.90000	5770000
DIMETHYLBENZANTHRACENE(1,2)	4.26000	26000000
DIMETHYLNAPHTHALENE(1,3)	920.00000	1090000
DIMETHYLNAPHTHALENE(1,4)	1310.00000	763000
DIMETHYLNAPHTHALENE(1,5)	377.00000	745000
DIMETHYLNAPHTHALENE(2,3)	347.00000	502000
DIMETHYLNAPHTHALENE(2,6)	233.00000	653000
ETHYLNAPHTHALENE(1)	1240.00000	806000
FLUORANTHENE	22.80000	6020000
FLUORENE	214.00000	593000
INDAN	16650.00000	60000
METHYLANTHRACENE(2)	3.67000	4170000
METHYLANTHRACENE(9)	24.40000	11400000
METHYLCOLANTHRENE(3)	0.19200	161000000
METHYLNAPHTHALENE(1)	3550.00000	282000
METHYLNAPHTHALENE(2)	3220.00000	265000
NAPHTHACENE	0.03700	14300000
NAPHTHALENE	4460.00000	64200
PERYLENE	0.02830	115000000
PHENANTHRENE	130.00000	1500000
PYRENE	12.00000	3870000
TRIPHENYLENE	3.39000	5650000

TABLE A-VI

COWEN'S ACTIVITY COEFFICIENT DATA AT 25 C (34).

SOLUTE	SOLUBILITY (MG/L)	ACTIVITY COEFF
BENZENE	700	6200
BIS(2-CHLOROETHYL) ETHER	10200	780
BROMOFORM	3190	4400
CARBON TETRACHLORIDE	1160	7400
CHLOROBENZENE	500	12000
CHLOROFORM	9300	710
DICHLOROBENZENE(1,2)	145	56000
DICHLOROBENZENE(1,3)	123	66000
DICHLOROBENZENE(1,4)	79	100000
DICHLOROETHANE(1,1)	5500	1000
DICHLOROETHANE(1,2)	8690	630
DICHLOROETHYLENE(1,1)	400	13000
DICHLOROETHYLENE(1,2)	600	9000
DICHLOROPROPANE(1,2)	2700	2300
DIMETHYL PHTHALATE	5000	2200
ETHYLBENZENE	152	39000
HEXACHLOROETHANE	50	260000
METHYLENECHLORIDE	16700	280
NAPHTHALENE	30	240000
NITROBENZENE	1900	3600
TETRACHLOROETHANE(1,1,2,2)	2900	3200
TETRACHLOROETHYLENE	150	61000
TOLUENE	515	9900
TRICHLOROETHANE(1,1,1)	4400	1700
TRICHLOROETHANE(1,1,2)	4500	1600
TRICHLOROETHYLENE	1100	6600

TABLE A-VII

NICHOLSON'S HENRY'S CONSTANT DATA IN M3ATM/GMOL AT 20 C (109).

SOLUTE	H	ACTIVITY COEFF
BROMODICHLOROMETHANE	0.00160	16
TRIBROMOMETHANE	0.00046	3200
TRICHLOROMETHANE	0.00300	660

TABLE A-VIII

LINCOFF'S HENRY'S CONSTANT DATA IN M3ATM/GMOL AT 20 C (89).

SOLUTE	H	ACTIVITY COEFF
CHLOROFORM	0.00333	720
METHYLENE CHLORIDE	0.00225	220
TETRACHLOROETHYLENE	0.01300	29100
TRICHLOROETHANE(1,1,1)	0.01320	5550
TRICHLOROETHYLENE	0.00764	4300

TABLE A-IX

DILLING'S DIMENSIONLESS HENRY'S CONSTANT DATA AT 25 C (42).

SOLUTE	H	ACTIVITY COEFF
CHLOROETHANE	0.460	2200
CHLOROETHENE	50.000	228000
CHLOROMETHANE	0.300	1100
CHLOROPROPENE(3)	0.440	5200
CIS-DICHLOROETHENE(1,2)	0.310	8100
CIS-DICHLOROPROPENE(1,3)	0.095	13600
DICHLOROETHANE(1,1)	0.240	5800
DICHLOROETHANE(1,2)	0.040	2700
DICHLOROETHENE(1,1)	6.300	72000
DICHLOROMETHANE	0.110	1200
DICHLOROPROPENE(2,3)	0.150	17500
HEXACHLOROETHANE	0.050	2000000
PENTACHLOROETHANE(1,1,1,2,2)	0.100	250000
TETRACHLOROETHANE(1,1,1,2)	0.110	74000
TETRACHLOROETHANE(1,1,2,2)	0.019	27000
TETRACHLOROETHENE	0.820	532000
TETRACHLOROMETHANE	0.870	65800
TRANS-DICHLOROETHENE(1,2)	0.270	4500
TRANS-DICHLOROPROPENE(1,3)	0.072	13000
TRICHLOROETHANE(1,1,1)	1.400	105000
TRICHLOROETHANE(1,1,2)	0.038	12200
TRICHLOROETHENE(1,1,2)	0.490	48000
TRICHLOROMETHANE	0.130	4500
TRICHLOROPROPANE(1,2,3)	0.013	34000

2

VITA

Mohammad Mehdi Montazer-Rahmati

Candidate for the degree of

Doctor of Philosophy

Thesis: INFINITE DILUTION ACTIVITY COEFFICIENTS FOR MEASUREMENT OF ENVIRONMENTAL PARAMETERS

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Tehran, Iran, April 23, 1961. The son of Jaafar and Khadijeh.

Education: Graduated from Forest Hills Northern High School, Grand Rapids, Michigan in May 1979; received Bachelor of Science degree in Chemical Engineering from Michigan State University in June, 1983; received Bachelor of Arts in French from Michigan State University in June, 1983; received Master of Arts in French from Michigan State University in August, 1984; received Master of Science in Chemical Engineering from Oklahoma State University in December, 1985; completed requirements for the Doctor of Philosophy degree from Oklahoma State University in December, 1989.

Professional Experience: Teaching Assistant, Department of Romance and Classical Languages, Michigan State University, September, 1983 to August 1984; Research Assistant, Department of Chemical Engineering, Oklahoma State University, November, 1984 to August, 1985; Teaching Assistant, Department of Chemical Engineering, Oklahoma State University, September, 1985 to December, 1985; Research Associate, Department of Chemical Engineering, Oklahoma State University, January, 1986 to May, 1987; Teaching Assistant, Department of Chemical Engineering, Oklahoma State University, June, 1987 to December, 1989.