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MODELING INFINITE DILUTION ACTIVITY COEFFICIENTS OF ENVIRONMENTAL POLLUTANTS IN WATER USING CONFORMAL SOLUTION THEORY

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ABSTRACT

The fate of organic pollutants in the environment and in wastewater treatment processes is commonly modeled using a Henry's law constant approach. By definition, Henry's law constant is the product of a compound's vapor pressure and infinite dilution activity coefficient. For many organic compounds in water solution, the infinite dilution activity coefficients are very large and are not adequately modeled by conventional methods such as UNIFAC. In this work, infinite dilution activity coefficients were determined for phenol, pyridine, aniline, p-toluidine, and o-toluidine in water by differential ebulliometry. An equation rigorously derived from conformal solution theory and van der Waals one-fluid mixing

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rules was used to model the temperature dependency of the infinite dilution activity coefficients. No corrections other than the introduction of two adjustable parameters were incorporated into the model to account for the strong interactions between molecules. Relationships derived from corresponding states theory were used to relate molecular parameters for size and energy interaction to the critical properties. Arithmetic mean combining rules and geometric mean combining rules were used to calculate size and interaction parameters, respectively.

INTRODUCTION

Accurate vapor-liquid equilibrium data of organic-aqueous systems are needed when designing wastewater purification processes and modeling the fate of organics in the environment. Models have been proposed for air stripping in aerobic biological waste treatment processes (1-4), separation processes for water-organic mixtures (4,5), and fate analysis of organic compounds in the environment (6,7). In all of these models, a major parameter is Henry's law constant. By definition, Henry's law constant is the product of a compounds vapor pressure and infinite dilution activity coefficient. Vapor pressures for many organic pollutants are available in the literature or can be easily measured. Therefore, the problem of determining Henry's law constant reduces to evaluating the infinite dilution activity coefficient.

Several experimental techniques are available for determining infinite dilution activity coefficients of organics in water including classical vapor-liquid equilibrium measurements (9), gas chromatography (10,11), and differential ebulliometry (12,13). Theoretical models for infinite dilution activity coefficients have not been successful at representing organics in water. Popular models include the modified cohesive energy density model (MOSCED) (14), the

analytical solution of groups model (ASOG) (15), and the UNIFAC model (16). The MOSCED and ASOG models are not applicable to systems with aqueous solvents. The UNIFAC method is possibly the best known and most widely used model because of its ability to predict activity coefficients in the absence of experimental data. However, the UNIFAC model has been criticized as inaccurate when predicting certain organic-water activity coefficients (17,18). UNIFAC is most accurate for systems with activity coefficients less than approximately 10 (19). Organics in water can have activity coefficients in excess of 100. Based on regular solution theory, several researchers have modeled the temperature dependency of infinite dilution activity coefficients by plotting the natural log of the infinite dilution activity coefficient verses the reciprocal of temperature (13,19). Although this approach may provide approximations over small temperature intervals, it cannot be used over any substantial temperature range or for extrapolation with any certainty.

In this study, infinite dilution activity coefficients of five organic pollutants (pyridine, aniline, phenol, o-toluidune, p-toluidine) in water were determined by differential ebulliometry. This technique is based on accurately measuring the boiling point difference between pure solvent and solvent with dissolved organic. The data were modeled using equations based on conformal solution theory. These compounds exhibit large infinite dilution activity coefficients in water and are all environmentally significant. The model requires fugacity coefficients and compressibility factors for the solvent and reduced properties for the solute and solvent and utilizes only two adjustable parameters per binary mixture.

BACKGROUND AND THEORY

The theory of corresponding states can be extended to mixtures by assuming the existence of a hypothetical fluid with

the same configurational thermodynamic properties as the mixture. If the intermolecular potential energy for any pair of molecules i and j depends only on the distance between the molecules, the potential energy can be expressed as:

$$\Gamma_{ij} = \varepsilon_{ij} F(r_{ij} / \sigma_{ij}) \qquad (1)$$

where, in the conformal solution approximation, F is the same function for all pair interactions, and ε_{ij} and σ_{ij} are the characteristic energy and size factors, respectively (19, 20).

Based on conformal solution theory, Jonah (21) rigorously derived expressions for infinite dilution activity coefficients. Beginning with the expression for the residual Helmholtz energy of a mixture:

$$A_{rm} (T,\rho,N_1...N_c)/T = A_{ro}^* (T^*,\rho^*,N)/T^*. \qquad (2)$$

Taking the derivative of expression (2) with respect to the mole numbers, using standard equations from thermodynamics, and van der Waals one- fluid mixing rules (22), we obtain the expressions of Jonah (21):

$$\ln (\gamma^\infty f_a / f_b) = F_u U_{br}/k_B T + F_z (1-Z_{br'}), \qquad (5)$$

$$F_u = 2.0 (\sigma_{ab} / \sigma_{bb}) (\varepsilon_{ab} / \varepsilon_{bb} - 1.0), \text{ and} \qquad (6)$$

$$F_z = 2.0 ((\sigma_{ab} / \sigma_{bb})^3 - 1.0). \qquad (7)$$

In Eq. 5, $Z_{br'}$ is the compressibility of the solvent, and has a value of approximately -1 at liquid densities.

Jonah used these equation for modeling γ^∞ by plotting $\ln (\gamma^\infty f_a / f_b))/(1-Z_{br'})$ versus $U_b/RT(1-Z_{br'})$ for several organic compounds in organic and aqueous solvents (21,23).

From corresponding states theory (19), the molecular parameters in Eqs. (6) and (7) are related to a compounds

critical properties by the equations:

$$\sigma = (3 c_1 V_c / 2 N_A \pi)^{1/3} \quad (8)$$

$$\varepsilon = c_2 k_B T_c \quad (9)$$

From Eqs. (8) and (9), the ratios of molecular parameters are given by:

$$(\sigma_{ab} / \sigma_{bb})^{1/3} = ((V_{ac} + V_{bc}) /2)/V_{bc} (1-k) \text{ and} \quad (10)$$

$$\varepsilon_{ab} / \varepsilon_{bb} = (T_{ac} T_{bc})^{1/2}/T_{bc} (1-\eta), \quad (11)$$

where an arithmetic mean combining rule has been assumed for the ratio of size parameters, and a geometric mean combining rule has been assumed for the ratio of energy parameters. The parameters k and η are binary interaction parameters and depend on the accuracy of the data and deviation of the compounds from behavior consistent with theory. Equations (10) and (11) along with (5) through (7) form the model for γ^{∞}.

EXPERIMENTAL

Experimental Apparatus

The organic compounds were purchased from Aldrich Chemical Co., Milwaukee, WI. All compounds were >99% pure. The water used in the experiments was purified with a Corning MP-3A Megapure water system.

Figure 1 is a schematic diagram of the experimental apparatus. The system consisted of two ebulliometers connected to a common manifold. The ebulliometers are identical to those used by Thomas and Eckert(14). Teflon joint

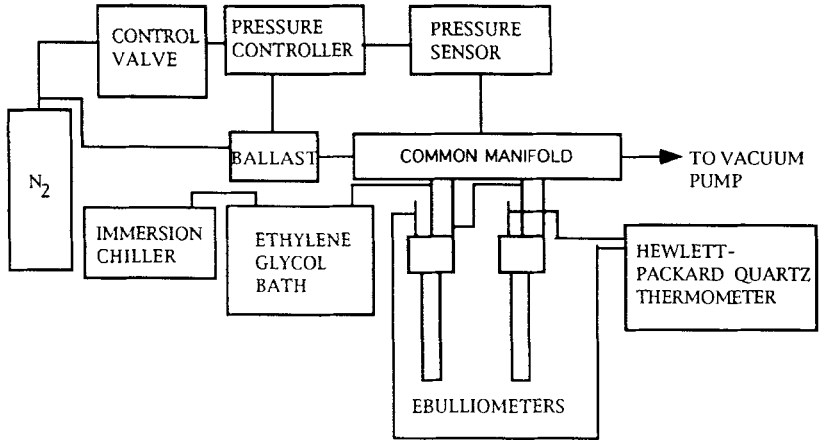

FIGURE 1. Differential ebulliometry apparatus for determining infinite dilution activity coefficients.

sleeves and clamps were used to seal the connections. Stainless steel tubing and vacuum hose were used to connect the equipment.

The pressure in the manifold was controlled with a MKS 250 pressure controller and an MKS 0248A control valve. Dry nitrogen was bled into one side of the manifold and removed at the other end with a vacuum pump. A needle valve between the manifold and vacuum pump was used to control the flow rate of the nitrogen being removed from the system. The system pressure was measured with a MKS 390H sensor and an MKS 200 signal conditioner. Pressure fluctuations were minimized by connecting a 10 liter ballast tank between the nitrogen source and the manifold.

Temperature measurements were made with a Hewlett Packard 2804A Digital Quartz Thermometer. This instrument has a resolution of 10^{-4} °C. A triple point of water cell was constructed and used to calibrate the instrument.

To prevent escape of any volatile compounds, a 50% ethylene glycol solution was continuously cycled through the ebulliometer condensers with a Cole-Parmer model 7553-20 pump. This solution was cooled and maintained at 1 °C with a Polyscience immersion chiller and a Haake E3 circulating heater. Coolant temperatures below 0 °C resulted in ice formation in the ebulliometer condensers and occasional breakage.

The ebulliometer boilers were wrapped with approximately 8 ft of nichrome ribbon and insulated with glass wool covered with closed cell insulation. Power was supplied to each ebulliometer with Staco Energy Products variacs. An Omega HHM59 clamp meter was used to monitor the power supplied to each boiler.

Experimental Procedure

The ebulliometers were first tested by measuring the boiling point of pure water and acetone. Over the temperature range of 50 to 100 °C all values were within 1% of values reported in the literature. Infinite dilution activity coefficients measurements were initiated by filling both ebulliometers with 60 ml of water. The system pressure was then set, and sufficient power was supplied to each ebulliometer to induce boiling. The system was allowed to run for approximately 1 h to reach steady state. A small amount of organic was then injected into one of the ebulliometers with a Hamilton model CR700-200 constant-rate syringe, which has an accuracy of ±1%. Typical injections were between 20 and 100 μL. All of the compounds investigated in this study are liquids at ambient temperature except phenol and p-toluidine. These compounds were heated above their melting points before injection. After the system reached equilibrium, typically 15-30 min, the boiling point difference between the ebulliometer containing the organic-aqueous solution and the reference ebulliometer

containing pure water was recorded. Additional injections were then made, and the boiling point differences were measured.

RESULTS AND DISCUSSION

The boiling point-composition data were used to calculate infinite dilution activity coefficients as described by Moore (24). The results are presented in Table 1 along with the relative standard deviation in the measurements. As indicated by the data, all of these compounds exhibit large deviation from ideal behavior. With the exception of pyridine, no literature values were available for comparison at the temperatures of this work. For pyridine, the values differ by approximately 10% with the values reported by Loben and Prausnitz (25).

The data were fit to the above equations by nonlinear regression. Vapor-phase fugacity coefficients for each organic were estimated using the method of Hayden and O'Connell (26). The procedure requires critical properties, dipole moments, and the mean radius of gyration for each compound. Most of these properties can be found in the literature. For o-toluidine and p-toluidine, the mean radius of gyration was not available and was estimated from the parachor (15).

The residual internal energy of vaporization was calculated using the expression:

$$U_{br} / RT = - \Delta h^{vap} / RT - (Z_{br}-1). \qquad (12)$$

The results of fitting the data are presented graphically in Figures 2 through 6. The model gave a good fit of the data for all of the systems except p-toluidine. However, only three data points were available for this compound. Table 2 lists the resulting empirical parameters k and η. The large values for

Table 1. Infinite dilution activity coefficients of organics in water.

Compound	Temperature (K)	Number of Determinations	Infinite Dilution Activity Coefficient	Standard Deviation
Pyridine	356.32	3	23.4	2.97
	362.06	3	20.7	1.86
	366.87	3	19.7	1.78
Phenol	349.25	3	42.3	0.6
	356.34	3	38.7	0.4
	361.99	3	34.8	0.6
	366.86	3	32.8	0.4
	370.99	3	30.3	0.6
Aniline	356.33	4	135	25.5
	361.97	4	128	11.0
	366.84	4	119	9.68
	371.03	2	113	0.29
o-Toluidine	349.11	1	775	-
	356.36	2	500	1
	366.84	2	268	13.5
p-Toluidine	356.36	3	388	55.2
	362.03	3	316	23.2
	366.84	3	311	17.4

some systems is not unexpected since the compounds in this study and the solvent are polar and form highly nonideal solutions. No corrections other than the introduction of the adjustable parameters have been incorporated into the model to account for the strong interactions between molecules. In general, the values of k and η deviate further from zero for systems that have higher infinite dilution activity coefficients,

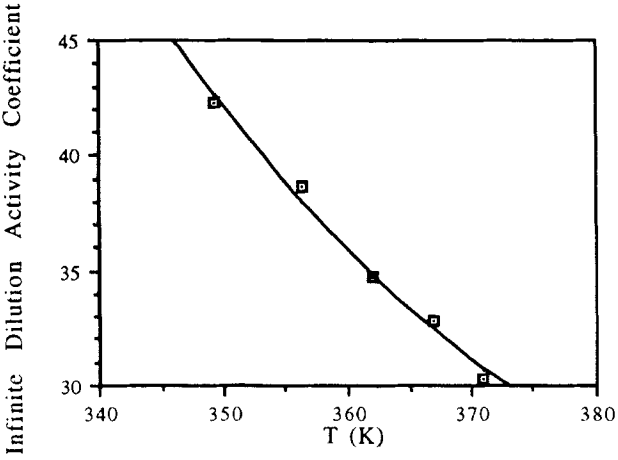

FIGURE 2. Infinite dilution activity coefficient of phenol in water.

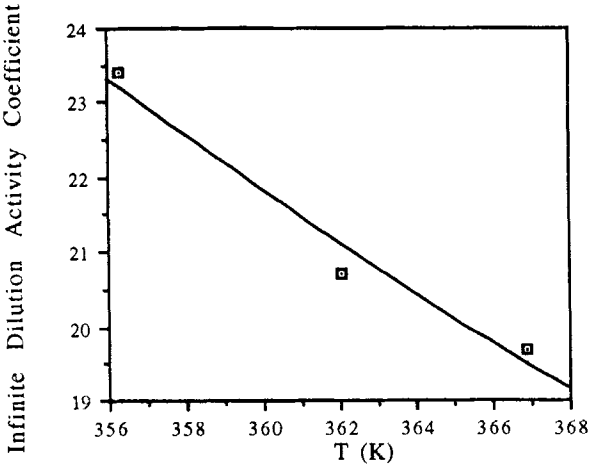

FIGURE 3. Infinite dilution activity coefficient of pyridine in water.

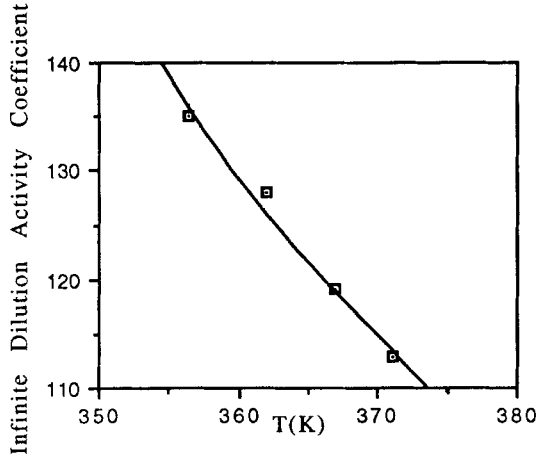

FIGURE 4. Infinite dilution activity coefficient of aniline in water.

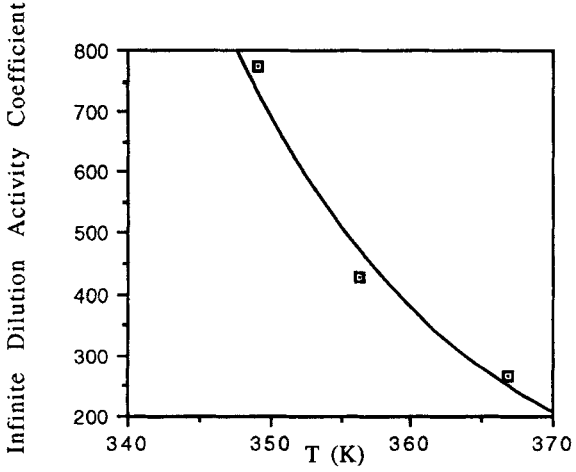

FIGURE 5. Infinite dilution activity coefficient of o-toluidine in water.

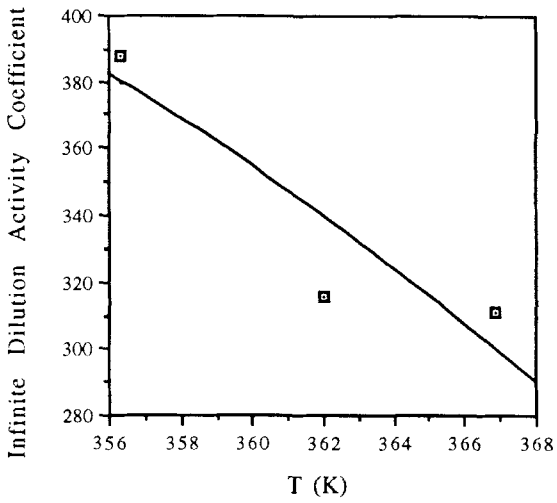

FIGURE 6. Infinite dilution activity coefficient of p-toluidine in water.

Table 2. Adjustable binary interaction parameters.

Compound	k	η
Pyridine	0.18425	0.06968
Phenol	0.57695	-0.04264
Aniline	0.76217	0.10836
o-Toluidine	-0.39840	0.11827
p-Toluidine	0.62518	0.12606

indicating behavior consistent with theory. Values of the adjustable parameter k, the binary size parameter, are much larger than values of η, the binary energy parameter. It was expected that the values of k would be much less than η. For all of the systems, the empirical constants, k and η, were highly correlated indicating the possibility of reducing the number of adjustable parameters to a single value.

Mixing rules based on a square well potential energy function were also tested. The equations are given by:

$$F_u = 2\,\sigma^3_{ab}/\sigma\; T^*\{\exp((\tau-1/T^*)-1\}, \quad (13)$$

$$T^* = kT/\varepsilon, \text{ and} \quad (14)$$

$$\tau = \varepsilon_{ab}/\varepsilon; \quad (15)$$

F_z is the same as before, as given by Eq. (7). A significantly better fit of the data using these equations was not attained.

Future work will concentrate on reducing the number of adjustable parameters to a single value. This will require fitting the model to a much larger data set.

CONCLUSIONS

No models exist that accurately represent the temperature dependency of infinite dilution activity coefficients of organic compounds in water. A model based on conformal solution theory and equations from corresponding states has been developed and used to model infinite dilution activity coefficients of five highly nonideal organic-aqueous mixtures. The data were determined by differential ebulliometry. The model provides accurate means for correlating data on organics in water by utilizing thermodynamic properties of the solvent and solute and two adjustable binary interaction parameters. Additionally, it may be possible to reduce the number of adjustable parameters to a single value. This will involve testing the model with a much larger data set that covers a larger temperature range.

NOMENCLATURE

A_{rm}	residual Helmholtz free energy of a mixture
A_{ro}^*	residual Helmholtz free energy for a reference scaled substance at the state of the mixture

c_i	universal constant
f_i	fugacity of pure component i
Δh^{vap}	enthalpy of vaporization of the solvent
k	binary size interaction parameter
kB	Boltzmann constant
N_i	mole numbers of component i
r	distance between molecules
R	ideal gas constant
T	temperature
T*	scaled temperature
U_{br}	residual internal energy of vaporization of component b
V	critical volume
$Z_{br'}$	compressibility factor for solvent

subscripts and superscripts

a	component a, solute
b	component b, solvent
c	critical property
*	reference scaled substance at state of the mixture
m	mixture

Greek letters

γ^{∞}	infinite dilution activity coefficient
ε_{ij}	characteristic energy factor
σ_{ij}	characteristic size factor
η	binary energy interaction parameter
Γ_{ij}	potential energy function for molecules i and j
ρ	density of mixture
ρ^*	scaled density

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