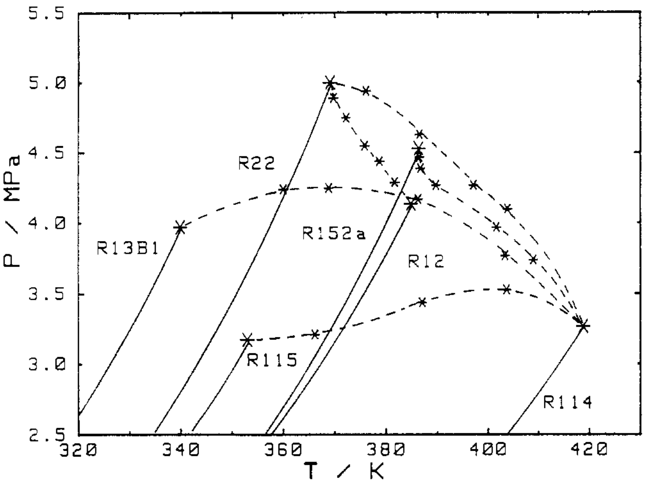

Figure 1. Critical curves of binary refrigerant mixtures.

surements cover densities from 265 to 1199 kg/m^3. The 144 *PVTx* data along 10 isochores, including 79 data in the vapor-liquid two-phase region are tabulated in Table I.

Discussion

The detailed examination and discussion of the dew- and bubble-point curves of this R 115 + R 114 system have been described in another paper (*11*). In this report we discuss the comparison of this system with other refrigerant mixtures that have also been reported by the present authors (*3*-*7*).

For the purpose of comparing some typical thermodynamic behaviors for the R 115 + R 114 system with those of the four refrigerant mixtures that we have measured previously, i.e., R 12 + R 22 (*3*), R 22 + R 114 (*4*), R 13B1 + R 114 (*5*), and R 152a + R 114 (*6*, *7*), we have prepared Figure 1. Although the critical curves usually bend near the critical points of polar substances, as discussed in ref *7*, we do not find such behavior for the present R 115 + R 114 system. We found that the behavior of the present mixture is similar to that of the system R 13B1 + R 114. Both critical curves have a tendency to be convex to the high-pressure side. The mixture of R 13B1 + R 114 is unique in the sense that its components have a large difference in the critical temperature (about 80 K) and a small difference in critical pressure (about 0.70 MPa). For the present mixture, the difference in the critical temperature of the components is also large (about 60 K), and in the critical pressure the difference is similarly small (about 0.14 MPa). Thus, the behavior of thermodynamic properties for binary refrigerant mixtures may depend rather heavily on the differences in the critical parameters of their respective components. This should be subjected to more detailed discussion with further accumulation of additional data.

Acknowledgment

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Registry No. R 115, 76-15-3; R 114, 76-14-2.

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Correlation of the Phase Equilibrium Data for the Heptane–Toluene–Sulfolane and Heptane–Xylene–Sulfolane Systems

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Liquid–liquid equilibrium data were measured for the heptane–toluene–sulfolane system at 25 °C and for the heptane–xylene–sulfolane system at 17, 25, and 50 °C. The NRTL and UNIQUAC equations were used to correlate the experimental data and to predict the phase compositions of the ternary systems. The agreement between the predicted and the experimental results was equally good with both equations.

Introduction

Because of the important industrial applications of sulfolane, several investigators have studied the liquid–liquid phase equilibria for ternary systems containing sulfolane and aromatic hydrocarbons (*1*-*4*). Due to the lack of experimental data for some ternary systems, however, thermodynamic models are frequently used for predicting phase equilibrium compositions. Some of the more widely used models are the Wilson equation for excess Gibbs energy (*5*), the nonrandomness two-liquid equation (NRTL) proposed by Renon and Prausnitz (*6*), and the UNIQUAC equation of Abrams and Prausnitz (*7*). The interaction parameters present in these equations are evaluated

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Table I. Tie-Line Data for the Heptane (1)–Toluene (2)–Sulfolane (3) System at 25 °C, wt %

sulfolane-rich phase			heptane-rich phase		
1	2	3	1	2	3
0.80	3.30	95.9	90.4	8.30	1.30
1.00	8.30	90.7	75.6	23.0	1.40
1.20	12.7	86.1	67.5	30.9	1.60
1.40	15.4	83.2	59.7	37.5	2.80
2.00	20.3	77.7	51.3	45.5	3.20
2.60	27.3	70.1	39.9	54.8	5.30
3.90	32.3	63.8	29.8	60.3	9.90

from experimental data of the binaries of the systems (*8*). The purpose of the present study was to obtain liquid–liquid equilibrium data for the heptane–toluene–sulfolane and heptane–xylene–sulfolane systems and to correlate these data with the NRTL and UNIQUAC equations.

Experimental Section

***Materials*.** All of the chemicals used were high purity grade reagents. Sulfolane was obtained from Alfa Products with a stated purity of 99%. It was further purified by repeated crystallization, heating it to a temperature of 50 °C, then allowing it to cool slowly until approximately 90% had solidified; the remaining 10% was discarded. Toluene and xylene were obtained from the J. T. Baker Chemical Company, and heptane was obtained from Mallinkrodt, Inc. Although all of the chemicals had a stated minimum purity of 99%, they were further purified with a Bughi-R rotary evaporator operated near atmospheric pressure. A heart cut was collected by discarding approximately the first 10% of the distillate and the last 10% residue. The purities of all the chemicals were greater than 99.9% after purification.

***Procedure*.** The experimental measurements were carried out in the two-phase region. Sample mixtures were prepared and placed in Supelco sample bottles and then sealed with Teflon lined septum caps. In each experiment, the ternary mixture was shaken vigorously in a Magin Whirl Blue M shaker bath, controlled at the desired temperature (±0.2 °C). After equilibrium was attained, the phases were allowed to separate and small samples of approximately 25 μL were taken from each phase. The samples were then diluted with 1.5 mL of carbon disulfide solvent to prepare them for analysis. The sample analysis was performed by using a Hewlett-Packard Model 5793 chromatograph equipped with a single-channel flame ionization detector and a Hewlett-Packard integrator Model 3390. A stainless steel column 1.5 m long × 3.2 mm diameter packed with 2% OV-101 methylsilicone fluid on a W-HP 100/120 Hewlett-Packard packing was used. A capillary column chromatograph (Hewlett-Packard Model 5792) employing a 12 m × 6 mm cross-linked methylsilicone column constructed of fused silica along with an integrator was used to analyze for the extremely low concentrations. The compositions of the liquid phases were determined by using an area analysis of the peak size of each component produced from the gas chromatograph. The procedure was repeated in each experiment for different temperatures.

Results and Discussion

***Experimental Data*.** The experimental tie-line data for the heptane–toluene–sulfolane and the heptane–xylene–sulfolane systems are shown in Tables I and II. The solubility data obtained for the heptane–toluene–sulfolane system together with those published by Tripathi et al. (*4*) and Rawat and Gulati (*9*) are shown in Figure 1. The present data compare well with those of Tripathi et al. and Rawat and Gulati for the entire region except near the plait point. Figure 2 shows a comparison of the selectivity of sulfolane as a function of the solvent-free mole

Table II. Tie-Line Data for the Heptane (1)–Xylene (2)–Sulfolane (3) System at 17, 25, and 50 °C, wt %

	sulfolane-rich phase			heptane-rich phase		
temp, °C	1	2	3	1	2	3
17	0.92	2.92	96.2	88.2	11.4	0.31
	0.87	5.33	93.8	77.3	22.2	0.53
	1.01	8.13	90.9	66.4	32.8	0.90
	1.09	10.7	88.2	58.4	40.4	1.28
	1.08	13.9	85.1	48.5	49.4	2.15
	1.08	17.0	81.9	38.2	57.5	4.33
	1.24	20.2	78.6	31.8	62.2	6.02
	1.49	24.2	74.3	25.3	66.0	8.72
	1.58	27.4	71.0	22.0	38.9	9.11
25	0.77	0.00	99.2	99.8	00.0	0.17
	0.93	2.82	96.3	88.2	11.5	0.35
	1.03	5.50	93.5	77.3	22.1	0.60
	1.10	10.9	88.0	38.2	40.1	1.72
	1.16	13.8	85.1	48.1	49.1	2.87
	1.30	16.7	82.0	39.1	56.6	4.29
	1.42	20.5	78.1	35.4	60.2	4.47
	1.51	24.0	74.5	27.8	65.0	7.20
	2.03	31.0	66.9	22.0	68.9	9.11
50	0.96	0.00	99.0	99.6	0.00	0.37
	1.53	2.77	95.7	88.0	11.4	0.62
	1.46	5.47	93.1	77.3	21.7	1.07
	2.00	8.61	89.4	66.7	31.6	1.71
	1.81	11.0	87.2	47.6	47.5	4.90
	2.18	19.9	77.9	38.9	55.0	6.18
	2.41	23.4	74.2	34.4	48.5	7.10
	2.80	28.7	68.5	26.1	63.6	10.3
	3.38	33.8	62.8	21.8	65.5	12.8

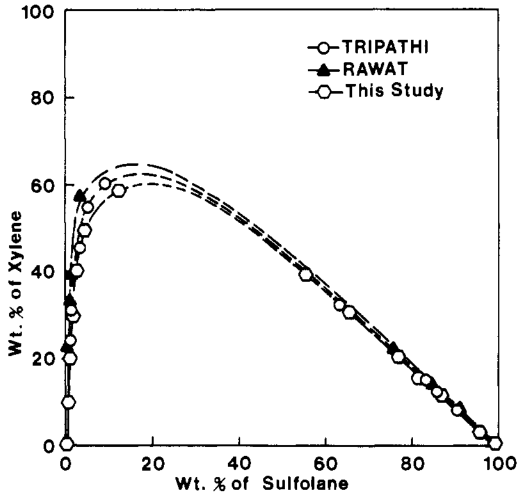

Figure 1. Solubility data for the heptane (1)–toluene (2)–sulfolane (3) system at 25 °C.

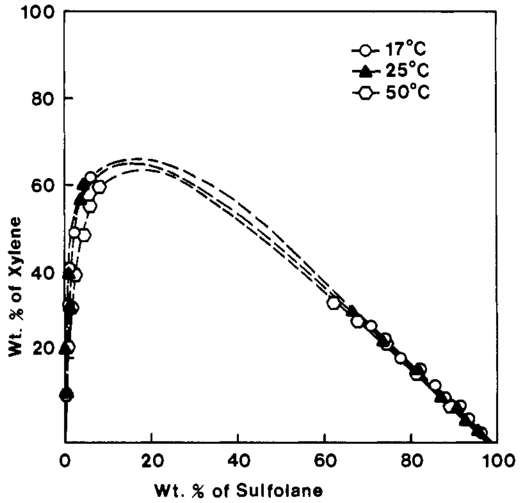

Figure 2. Effect of temperature on the solubility of the heptane (1)–xylene (2)–sulfolane (3) system.

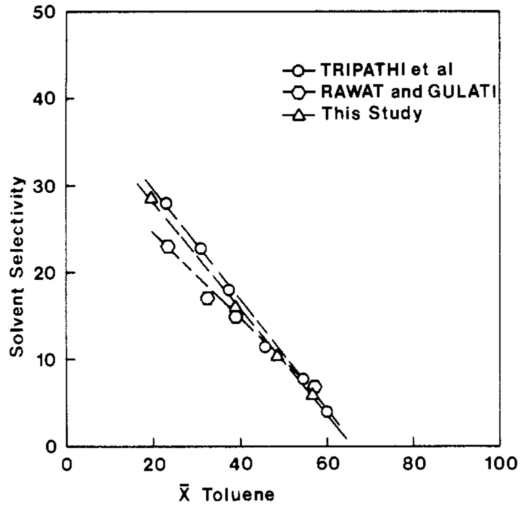

Figure 3. Solvent selectivity of sulfolane as a function of solvent-free mole fraction of toluene for the heptane (1)-toluene (2)-sulfolane system at 25 °C.

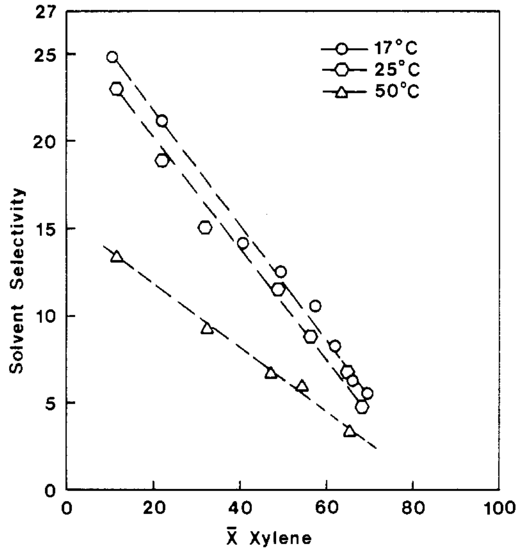

Figure 4. Solvent selectivity of sulfolane as a function of solvent-free mole fraction of xylene for the heptane (1)-xylene (2)-sulfolane (3) system at 17, 25, and 50 °C.

fraction of toluene in the heptane-rich phase at 25 °C with the selectivities given by Tripathi et al. and Rawat and Gulati at the same temperature. The three data sets are in fair agreement. The solubility data for the heptane-xylene-sulfolane system (Figure 3) show that the area of the two-phase region decreases slightly as temperature rises. The selectivity of sulfolane is shown in Figure 4 as a function of the solvent-free mole fraction of xylene in the heptane-rich phase. The solvent selectivity was defined in terms of mole fractions as

$$S = \frac{[x(2)/x(3)]_{\text{sulfolane-rich phase}}}{[x(2)/x(3)]_{\text{heptane-rich phase}}} \qquad (1)$$

where the index 2 can represent either toluene or xylene and index 3 represents heptane.

Data Correlation and Prediction. The prediction and correlation of phase equilibrium data for ternary systems are based on the excess Gibbs energy and related activity coefficients. The regular-solution theory of Hildebrand and Scott (*10*) provides a method for calculating the activity coefficient for simple, nonpolar molecules. Also, Pierotti et al. (*11*) used a method to correlate the infinite dilution activity coefficient with the molecular structure of binary systems. The activity coefficients at infinite dilution are considered to be useful data sources for evaluating the group contribution parameters, especially for the H_2–sulfolane pair. Group contribution models, such as ASOG and UNIFAC, were developed to predict phase equilibria of vapor–liquid systems by Derr and Deal (*12*) and by Fredenslund et al. (*13*), respectively. However, a large number of group interaction parameters obtained from vapor–liquid equilibrium data have been used by others to predict liquid–liquid equilibria for ternary systems composed of alcohols, ketones, *n*-paraffins, and water (*14*).

Wilson (*5*) developed a semiempirical expression based on the local composition concept of liquid mixtures. Although considerable progress has been made by using the Wilson equation to predict the excess properties of multicomponent mixtures of electrolytes, the original form of the equation was unable to handle the liquid-phase immiscibility. A nonrandom two-liquid equation (NRTL) was developed by Renon and Prausnitz (*6*), which for multicomponent mixtures is given by

$$\frac{g^E}{RT} = \sum_{i=1}^{M} x_i \frac{\sum_{j=1}^{M} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{M} G_{ki} x_k} \qquad (2)$$

where M is the number of components. The parameter τ_{ij} depends on the interaction energy, g_{ji}, between the molecules i and j according to the relations

$$\tau_{ji} = (g_{ji} - g_{ii})/RT \qquad (3)$$

and

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \qquad (4)$$

Renon and Prausnitz (*6*) introduced a parameter, α_{ij}, to characterize the binary mixture nonrandomness. The NRTL equation, like the Wilson equation, involves two energy parameters (τ_{ij} and τ_{ji}) for each binary. In addition, the nonrandomness parameter, α_{ij}, can be set to a predetermined value ranging from 0.2 to 0.5, according to the recommendations of Renon and Prausnitz (*6*).

A similar expression for the excess Gibbs free energy for a multicomponent mixture was proposed by Abrams and Prausnitz (*7*) to provide an accurate correlation and prediction of liquid–liquid equilibria. Their universal quasichemical equation (UNIQUAC) was derived by introducing the local composition concept into the quasichemical theory of Guggenheim (*15*). The UNIQUAC equation is given by

$$\frac{g^E}{RT} = \sum_{i=1}^{M} x_i \ln\frac{\phi_i}{x_i} + \frac{w}{2}\sum_{i=1}^{M} q_i x_i \ln\frac{\theta_i}{\phi_i} - \sum_{i=1}^{M} q_i x_i \ln\left[\sum_{j=1}^{M} \theta_j \tau_{ji}\right] \qquad (5)$$

where

$$\theta_i = q_i N_i / \sum_{j=1}^{M} q_j N_j \qquad (6)$$

and

$$\phi_i = r_i N_i / \sum_{j=1}^{M} r_j N_j \qquad (7)$$

The τ_{ij} parameter is related to the adjustable parameters u_{ji} and u_{ii} according to the expression

$$\tau_{ji} = \exp\left(-\frac{u_{ji} - u_{ii}}{RT}\right) \qquad (8)$$

Pure component parameters r and q are measures of molecular

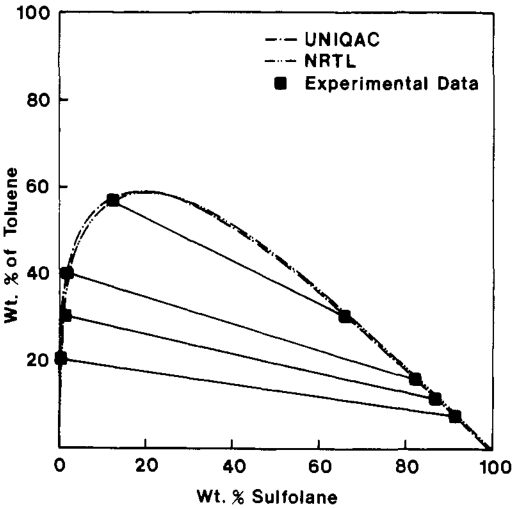

Figure 5. Liquid-liquid equilibria for the heptane (1)-toluene (2)-sulfolane (3) system at 25 °C.

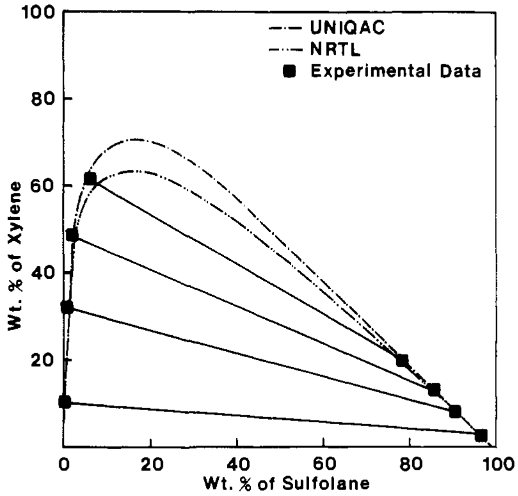

Figure 6. Liquid-liquid equilibria for the heptane (1)-xylene (2)-sulfolane (3) system at 17 °C.

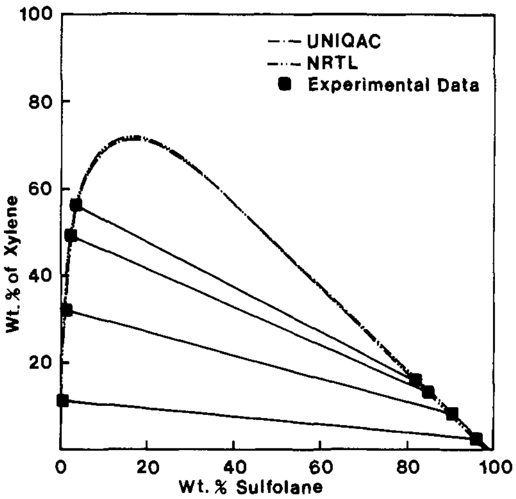

Figure 7. Liquid-liquid equilibria for the heptane (1)-xylene (2)-sulfolane (3) system at 25 °C.

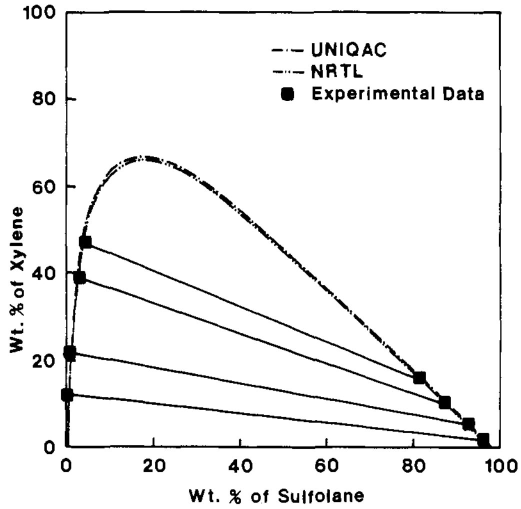

Figure 8. Liquid-liquid equilibria for the heptane (1)-xylene (2)-sulfolane (3) system at 50 °C.

van der Waals volumes and molecular surface areas, respectively. The UNIQUAC equation has two adjustable parameters for each binary and provides a method for predicting phase properties based on pure component data.

The NRTL and UNIQUAC equations were both fitted to the experimental data for the heptane-toluene-sulfolane and the heptane-xylene-sulfolane ternary systems. For each set of data, the specific parameters τ_{ji} and τ_{ij} for the NRTL and the UNIQUAC equations were obtained by using an iterative computer program developed by Sorensen (*16*) to minimize the value of the objective function

$$F = \sum_{i=1}^{N} \sum_{l=1}^{2} \sum_{m=1}^{M} (x_{ilm} - \hat{x}_{ilm})^2 \tag{9}$$

In the above expression the indices i, l, and m represent the number of components, the phases, and the tie lines, respectively. The composition x is calculated from an appropriate model. A proper value for the third nonrandomness parameter, α_{ij}, can be chosen independently.

Figures 5-8 show good agreement between the experimental points corresponding to the tie-line data and the theoretical curves (dashed lines) obtained by using the NRTL and the UNIQUAC equations. The two-phase region predicted by using the UNIQUAC equation for the heptane-xylene-sulfolane system at 17 °C was larger than that predicted by using the NRTL equation. However, the slopes of the tie lines are satisfactorily described by both equations. The specific parameters for the NRTL and the UNIQUAC equations are listed in Tables III and IV. The specific parameters for the heptane-xylene-sulfolane system vary randomly and appear to be insensitive to temperature. The experimental data, on the other hand, exhibit a

Table III. UNIQUAC and NRTL Parameters for the Heptane (1)-Toluene (2)-Sulfolane (3) System at 25 °C

	UNIQUAC parameters		NRTL parameters	
i-j	$(u_{ij} - u_{ji})/R$	$(u_{ji} - u_{jj})/R$	$(g_{ij} - g_{jj})/R$	$(g_{ji} - g_{ii})/R$
1-2	304.80	−186.15	103.30	−31.94
1-3	914.70	50.79	1934.30	1032.60
2-3	39.15	91.99	380.11	67.46

Table IV. UNIQUAC and NRTL Parameters for the Heptane (1)-Xylene (2)-Sulfolane (3) System at 17, 25, and 50 °C

temp, °C		UNIQUAC parameters		NRTL parameters	
	i-j	$(u_{ij} - u_{jj})/R$	$(u_{ji} - u_{ii})/R$	$(g_{ij} - g_{jj})/R$	$(g_{ji} - g_{ii})/R$
	1-2	134.72	−106.59	385.06	−267.24
17	1-3	555.44	67.18	1802.80	1050.00
	2-3	185.16	−8.00	562.80	65.37
	1-2	103.77	−104.01	343.44	−308.12
25	1-3	504.28	68.77	1621.80	966.12
	2-3	225.74	−38.01	638.32	10.39
	1-2	102.16	−110.21	353.22	−353.18
50	1-3	500.81	50.55	1468.60	840.33
	2-3	224.93	−42.23	649.66	−10.47

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definite temperature dependence.

Glossary

F	objective function
g^E	molar excess Gibbs energy
g_{ij}	energy parameter in the NRTL equation, K
G	UNIQUAC binary parameter related to τ
M	numbers of components
N	number of molecules
q	pure component surface area parameter
r	pure component volume parameter
R	gas constant, cal/(mol·K)
S	solvent selectivity
T	temperature, K
u_{ij}	energy parameter in the UNIQUAC equation, K
w	lattice coordination number
x_i	mole fraction of component i
$\bar{X}$	solvent-free composition (wt %)

Greek Letters

τ	interaction parameter in the UNIQUAC and NRTL equations
ϕ_i	segment fraction of component i
θ_i	area fraction of component i

Subscripts

i, j, k	components
l	phases
m	tie lines

Superscripts

E	excess
$\hat{}$	calculated

Registry No. Sulfolane, 126-33-0; heptane, 142-82-5; xylene, 1330-20-7; toluene, 108-88-3.

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Naphthalene Solubility in Selected Organic Solvent/Water Mixtures

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In order to characterize the solubility of hydrophobic aromatic chemicals in organic solvent/water mixtures, the solubility of a model compound, naphthalene, in binary, ternary, and quaternary alcohol/water (methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol) mixtures and binary ketone/water (acetone, methyl ethyl ketone, diethyl ketone) and aromatic organic solvent/water (benzene, toluene) mixtures has been measured. In the range of their miscibilities with water, the alcohols and ketones significantly increase naphthalene solubility while benzene and toluene show no significant effect on naphthalene solubility. Plots of ln x, where x is mole fraction solubility, versus z (solute-free organic solvent volume fraction) were linear in the range z = 0–0.12, with slopes increasing for organic cosolvents in the following order: methanol < ethanol < methanol/1-propanol (50/50) < methanol/1-propanol/1-butanol (50/25/25) < methanol/1-butanol (50/50) < 1-propanol < 1-butanol < acetone < 1-pentanol < methyl ethyl ketone < diethyl ketone. The solubilizing power, defined as the slope of the line of a plot of ln x vs z, of the alcohols and ketones was observed to increase as the hydrogen-bonding capability per unit size of the organic solvent decreases.

Introduction

The solubilization of hydrophobic substances in water by cosolvents is of both fundamental and practical importance to such disciplines as chemical engineering, pharmacology, toxicology, and environmental science. A review of the present literature indicates that the solubilization of semipolar drugs by polar cosolvents in water (*1–17*) has been widely studied but few measurements of the solubility of nonpolar hydrocarbon solutes in organic/aqueous cosolvent systems have been reported (*18–24*). Solubility data for hydrophobic aromatic chemicals in aqueous mixed solvents is sparse (*25–29*). In order to thoroughly understand the solubilization process for hydrophobic chemicals in organic solvent/water mixtures, an accurate data base must be established.

This work was undertaken to characterize the solubility of hydrophobic aromatic chemicals in organic solvent/water mixtures. A typical hydrophobic aromatic chemical, naphthalene, was studied and its solubility measured in a variety of organic solvent/water mixtures. The organic cosolvents investigated were selected to permit systematic variation of hydrogen-bonding capability and molecular size and to evaluate the effect of cosolvent characteristics on the solubilization of hydrophobic aromatic chemicals.

In this paper we present solubility data for naphthalene in several organic solvent/water mixtures. Naphthalene solubility in binary, ternary, and quaternary alcohol/water mixtures and binary ketone/water and aromatic organic solvent/water mix-

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