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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Table I. Concentrations of Naphthalene in Ethanol/Water Mixtures at Various Stirring and Temperature-Equilibration Times

solute-free vol fracn ethanol	stirring time, h	temp equlibration time, h	concn of naphthalene, mg/L (SD)[a]
0.0	36	36	31.3 (0.62)
0.0	36	36	31.3 (0.36)
0.25	24	24	134.3 (3.57)
0.25	24	48	140.8 (0.99)
0.25	48	24	136.0 (1.21)
0.25	48	48	139.7 (1.34)
0.50	36	36	2634.0 (12.7)
0.50	36	36	2665.0 (14.3)
0.75	24	24	19020.0 (539)
0.75	24	48	18840.0 (185)
0.75	48	24	18920.0 (75)
0.75	48	48	18373.0 (66)
1.0	36	36	83983.0 (512)
1.0	36	36	83250.0 (330)

[a] SD = standard deviation based on three samples.

tures are reported. Information is presented to establish the precision and accuracy of the measurements. The solubility data are summarized and compared to previously published values to expand the mixed solvent solubility data base and establish confidence intervals for the solubility of hydrophobic aromatic chemicals in organic solvent/water mixtures. This information will assist the development of predictive methods for determining solubility in organic solvent/water mixtures.

Experimental Section

Chemicals. The naphthalene used was scintillation grade and reported to be 99% pure. The organic solvents used had the following purities: methanol (99.9%), ethanol (200 proof), 1-propanol (99.5%), 1-butanol (99.9%), 1-pentanol (99%), acetone (99.5%), methyl ethyl ketone (2-butanone, 99.7%), diethyl ketone (3-pentanone, 97.7%), benzene (99.9%), and toluene (99%), as reported by the manufacturers. Acetonitrile, which was used as an HPLC eluent, was reported to be 99.9% pure. The water used was pretreated by distillation and passage through a Milli-Q water purification system affixed with a 0.22-μm Organex-Q filter. Preliminary studies showed no significant difference between aqueous solubilities of naphthalene measured in Organex-Q filtered Milli-Q water and Milli-Q water that was also UV oxidized for 3 h prior to use.

Preparation of Saturated Solutions. Saturated solutions were prepared by adding an excess of naphthalene to glass bottles affixed with ground glass tops, containing either pure solvents or a premixed combination of solvents. The flasks were then mixed at room temperature for 24 h on magnetic stirrers and temperature equilibrated for an additional 24 h in a water bath at 25 ± 0.5 °C. This combination of stirring and equilibration times was determined experimentally to be adequate for attaining equilibrium. Both times were systematically varied, and the concentrations of naphthalene in ethanol/water mixtures, ranging from 0 to 1.0 solute-free volume fraction ethanol, were measured (Table I). Equilibrium was established on the basis of no significant change in naphthalene concentration with an increase in stirring or temperature-equilibration time (Table I) and by comparison of the measured naphthalene solubility in pure water to previously determined solubility values (*30–33*).

Analysis. Samples from the alcohol/water mixtures were filtered through glass wool (previously extracted with methylene chloride), and absorbance in a 50/50 mixture of methanol and aqueous sample was measured at 254 nm by use of a Varian UV spectrophotometer. Samples from the ketone/water and aromatic solvent/water mixtures were filtered through 0.2-μm Nylon 66 filters, and absorbance of a constant sample volume (50 μL), in a 50/50 mixture of methanol/aqueous sample was measured at 254 nm by use of a Waters high-pressure liquid chromatograph (HPLC). A reversed-phase (spherisorb S-5-ODS, 5-μm particle size) 4.6-mm-i.d. × 250-mm-long column and a 50/50 mixture of acetonitrile and water were used as the HPLC stationary and mobile phases, respectively. To minimize sample loss during filtration, filters were preequilibrated by passing two sample volumes (10 mL) through the filters prior to sample collection. Naphthalene concentrations were quantified from calibration curves of UV detector response at 254 nm versus concentration determined from standard solutions for both UV spectrophotometry and HPLC analysis.

Selected organic solvent concentrations were monitored to assess variability during the experiments. Ketone and aromatic solvent concentrations were measured by absorbance at 254 nm during the HPLC analyses described above. Concentrations of 1-butanol and 1-pentanol in solvent blanks were determined by absorbance at 190 nm using UV spectrophotometry. Organic solvent concentrations were quantified from calibration curves of UV detector response as outlined above.

Results and Discussion

Solubility Measurements. Several experimental replicates (single flasks 212 total) were used to determine the solubility values reported here. Each replicate was sampled and analyzed a minimum of two, but generally three, times. These unsmoothed solubility data are given in Table I of the supplementary material (see paragraph at the end of the paper regarding supplementary material).

Relative deviation from the sample mean was <5% in all but six cases, and the variation did not exceed 6% in the remaining flasks. The sample variation illustrates the analytical and sampling precision and can be used to estimate the error in the solubility values due to the analytical procedures. From a propagation of error analysis (*34*) the estimated error in the solubility values attributable to the analytical and sampling method is negligible compared to other sources of uncertainty in the measurements.

Saturated solutions were prepared and analyzed in randomly arranged groups, for a minimum of three replicates of solvent mixtures containing ≤0.12 solute-free volume fraction organic solvent. The groups varied in size from 2 to 13 flasks and are detailed in Table I of the supplementary material. For each group, a control flask containing only water as a solvent was also prepared and analyzed. This experimental design was used to evaluate and eliminate variation in the solubility results associated with data collection over the extended time period of this investigation.

A one-way analysis of variance on the control flasks showed that variation in naphthalene solubility, with contiguous time periods during the study, was significant (10%) compared to analytical and sampling variance (6%) at the 95% confidence level. Therefore, the following model was used to quantitatively ajust the solubility measurements in each group:

$$\ln x_i = \ln x_{ij} - \beta_j \qquad (1)$$

where x_i = the mole fraction solubility of naphthalene in the ith solvent mixture, x_{ij} = mole fraction solubility of naphthalene in the ith solvent mixture as measured in the jth group, and β_j = the deviation in naphthalene solubility associated with its measurement in the jth group. The β_j's were calculated as the amount that the solubility of naphthalene in the control for each group deviated from the mean aqueous solubility value of naphthalene at 25 °C.

The mean aqueous solubility value for naphthalene was taken as the average for 35 individual determinations made over the course of this investigation. From these, $\ln x_w = -12.402$,

Table II. Solubilities of Naphthalene in Organic Solvent/Water Mixtures at 25 °C

organic cosolvent	solute-free vol fracn organic solvent	ln x (99% CI),[a] this work	n[b]	literature values for ln x			
				c	*d*	*e*	*f*
(water only)	0.0	-12.402 (0.041)	35	-12.358			
methanol	0.01	-12.361 (0.135)	3	-12.100			
methanol	0.03	-12.219 (0.065)	3				
methanol	0.05	-12.150 (0.219)	3	-11.879			
methanol	0.10	-11.876 (0.139)	3	-11.595			
methanol	1.00	-3.752 (0.025)	5	-3.743			-3.721
ethanol	0.01	-12.305 (0.072)	3				
ethanol	0.03	-12.246 (0.080)	3				
ethanol	0.05	-12.057 (0.095)	3			-12.047	
ethanol	0.10	-11.736 (0.143)	3			-11.703	
ethanol	0.25	-10.408 (0.051)	4				
ethanol	0.50	-7.211 (0.058)	2				-7.208
ethanol	0.75	-5.193 (0.037)	4				-4.712
ethanol	1.00	-3.223 (0.045)	2				-3.161
1-propanol	0.01	-12.297 (0.010)	3		-12.370		
1-propanol	0.03	-12.121 (0.102)	3		-12.308		
1-propanol	0.05	-11.905 (0.096)	3		-12.238		
1-propanol	0.10	-11.440 (0.022)	3		-11.873		
1-propanol	1.00	-2.985 (0.054)	3				-2.918
1-butanol	0.01	-12.300 (0.175)	3				
1-butanol	0.03	-12.003 (0.128)	3				
1-butanol	0.05	-11.964 (0.267)	3				
1-butanol	0.07	-11.558 (0.047)	3				
1-butanol	1.00	-2.709 (0.084)	3				
1-pentanol	0.005	-12.390 (0.331)	3				
1-pentanol	0.01	-12.308 (0.076)	3				
1-pentanol	0.02	-12.092 (0.130)	3				
1-pentanol	1.00	-2.512 (0.045)	3				
acetone	0.01	-12.299 (0.318)	3		-12.370		
acetone	0.03	-11.922 (0.234)	3		-12.285		
acetone	0.05	-11.719 (0.536)	3	-11.373	-12.156		
acetone	0.10	-11.090 (0.172)	3	-10.800	-11.609		
methyl ethyl ketone	0.01	-12.278 (0.163)	3		-12.354		
methyl ethyl ketone	0.03	-11.902 (0.018)	3		-12.165		
methyl ethyl ketone	0.05	-11.430 (0.411)	3		-11.826		
methyl ethyl ketone	0.10	-10.748 (0.711)	3		-10.700		
diethyl ketone	0.005	-12.278 (0.130)	3				
diethyl ketone	0.01	-12.160 (0.122)	3				
benzene	0.0005	-12.415 (0.250)	3				
benzene	0.001	-12.456 (0.083)	6				
toluene	0.00015	-12.425 (0.113)	4				
toluene	0.0003	-12.407 (0.116)	5				
methanol/1-propanol (50/50)	0.01	-12.283 (0.191)	3				
methanol/1-propanol (50/50)	0.02	-12.286 (0.304)	3				
methanol/1-propanol (50/50)	0.04	-12.126 (0.110)	3				
methanol/1-propanol (50/50)	0.10	-11.620 (0.228)	3				
methanol/1-butanol (50/50)	0.01	-12.335 (0.017)	3				
methanol/1-butanol (50/50)	0.02	-12.196 (0.160)	3				
methanol/1-butanol (50/50)	0.04	-11.995 (0.227)	3				
methanol/1-butanol (50/50)	0.10	-11.533 (0.078)	3				
methanol/1-propanol/1-butanol (50/25/25)	0.02	-12.260 (0.020)	3				
methanol/1-propanol/1-butanol (50/25/25)	0.04	-12.027 (0.137)	3				
methanol/1-propanol/1-butanol (50/25/25)	0.08	-11.758 (0.166)	3				
methanol/1-propanol/1-butanol (50/25/25)	0.12	-11.397 (0.162)	3				

[a] ln (mole fraction solubilities) and 99% confidence intervals calculated from the internal standard deviations. [b] Number of replicates. [c] Reference *29*. [d] Reference *28*. [e] Reference *27*. [f] Christiansen, in ref *25*, pp 1303–1304.

where x_w = mole fraction solubility of naphthalene in pure water at 25 °C. The accuracy of this mean aqueous solubility value for naphthalene is established by agreement to within 6% of the accepted aqueous solubility value for naphthalene at 25 °C, as determined by various methods (*30–33*).

Acceptance of the above model for smoothing the measured solubility values is based on the assumption that the variation associated with contiguous periods in time is not merely random variation, but attributable to a systematic occurrence. This assumption is supported by Figure 1 where the β values, plotted versus group number, show a nonrandom distribution about zero. β values for groups 1–15 tend to be positive, while those for groups 16–34 tend to be negative. This bimodal systematic distribution indicates the effect of some unaccounted for quantitative variable. Although the β values shown in Figure 1 are not large, they are significantly different, justifying the use of eq 1 for smoothing the data.

The corrected solubility values for naphthalene in the various solvent mixtures were averaged, and these values are reported in Table II, along with the corresponding 99% confidence intervals for each. Measured values for naphthalene solubility in various pure solvents and in ethanol/water mixtures of ≥0.25 solute-free volume fraction of ethanol are also given in Table II. These measurements were made as part of a different experiment and, hence, were not corrected for the systematic variation mentioned above.

To establish the accuracies of the solubility values in Table II, the 99% confidence intervals were calculated from the replicate solubility determinations. Of the 48 solubility values, 38 are accurate within 28% (0.25 ln unit), most of these values

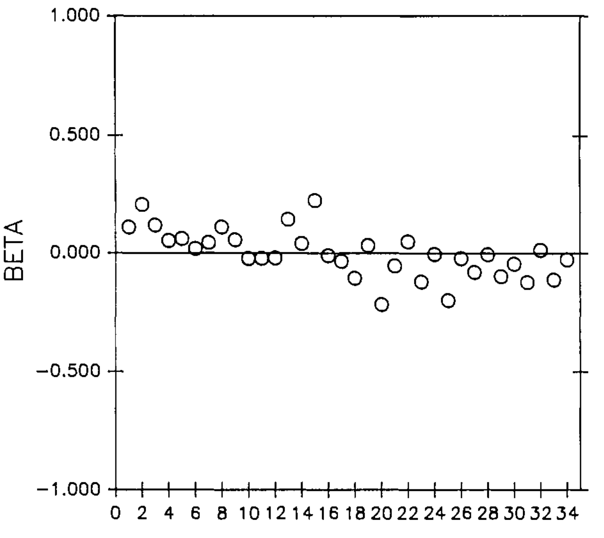

Figure 1. β as a function of group number.

being accurate to within 16% (0.15 ln unit). Six of the solubility values have associated uncertainties between 28% and 49% (0.25–0.4 ln unit). Only two of the solubility values have larger uncertainties (>65% or 0.5 ln unit).

A propagation of error analysis (*34*) showed the expected uncertainty to be 20.5% and that almost all of this uncertainty (99%) is associated with variability in organic solvent concentration. This variable was not quantitatively determined for all of the solvent mixtures and thus was used only to describe the uncertainties of the presented values. Careful attention to maintaining constant volatile component concentrations should significantly reduce uncertainties in these types of measurements.

Comparisons of the solubility values determined in this study to those measured previously show some interesting trends. While the solubilities in pure solvents are very consistent over the various investigations (±10% or 0.1 ln unit), the remaining data are not, indicating experimental deviations that are associated with the mixed solvent solubility measurements alone.

The data of Fu and Luthy (*29*), for naphthalene solubility in organic solvent/water mixtures, are consistently higher than those measured here by 35% (0.3 ln unit), although their values are not significantly outside of the ranges of the calculated uncertainties for our experimental data. This indicates the existence of a constant error, most likely associated with only one set of data.

With the exception of their value for naphthalene solubility in a mixture of 0.1 solute-free volume fraction methyl ethyl ketone in water, the solubility data of Sarker and Wilson (*28*) are all lower than those determined in this investigation. The disagreement increases as the solubility, or concentration of organic solvent, increases. This indicates the existence of a proportional error associated with one of these groups of solubility measurements.

Comparison of the data of Sarker and Wilson (*28*) to those of Fu and Luthy (*29*) also indicates a proportional error associated with one set of these data. It is extremely unlikely that two independent sets of data would exhibit a similar proportional error. Therefore, the discrepancy is probably associated with the Sarker and Wilson (*28*) data. These data were obtained from fitted equations to the original data, since no original measurements were reported (*28*). Thus, the error may be in the equations used to obtain the smoothed solubility values (*28*) rather than in the measured values.

The few data of Bennett and Canady (*27*) for naphthalene solubility in ethanol/water mixtures show the best quantitative agreement with our values. The data of Christiansen (*25*) for organic solvent concentrated mixtures also show good agreement with our values.

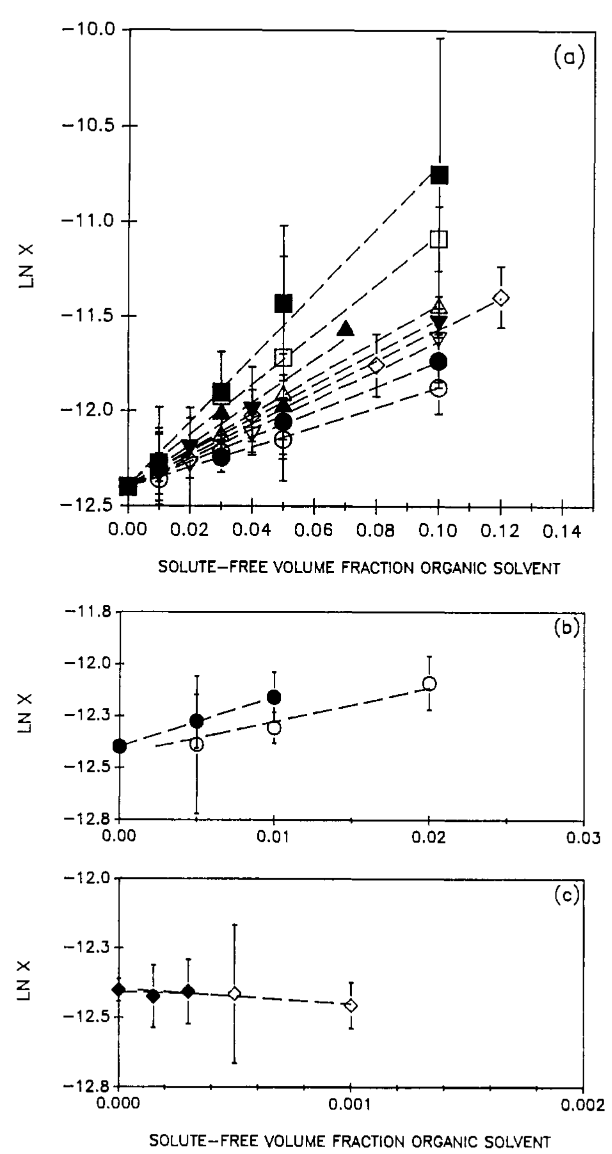

Figure 2. Natural logarithm of mole fraction solubility of naphthalene as a function of solute-free volume fraction organic solvent in selected organic solvent/water mixtures at 25 °C. (a) (○) Methanol/water; (●) ethanol/water; (▽) methanol/1-propanol (50/50)/water; (◇) methanol/1-propanol/1-butanol (50/25/25)/water; (▼) methanol/1-butanol (50/50)/water; (△) 1-propanol/water; (▲) 1-butanol/water; (□) acetone/water; (■) methyl ethyl ketone/water. (b) (○) 1-Pentanol/water; (●) diethyl ketone/water. (c) (◇) Benzene/water; (◆) toluene/water.

Solubility—Organic Solvent Dependence. Figure 2 illustrates the influence of organic cosolvents on the aqueous-phase solubility of a hydrophobic aromatic solute. In general, the solubility of naphthalene is observed to increase as the organic cosolvent concentration increases. The increase in ln x with organic solvent concentration is linear up to a solute-free organic solvent volume fraction of 0.12 (Figure 2a,b).

With the associated uncertainties, the naphthalene solubility values in the benzene/water and toluene/water mixtures do not differ significantly from naphthalene solubility in pure water at 25 °C. Although naphthalene solubility in benzene/water mixtures appears to decrease with an increase in aromatic solvent concentration (Figure 2c), establishment of a trend will require a reduction in the uncertainty associated with the measured values. Nonetheless, this finding is supported by the data of Akiyoshi et al. (*35*), who report a naphthalene solubility in a benzene/water mixture, with a benzene concentration near

Table III. Equations Describing Naphthalene Solubility in Organic Solvent/Water Mixtures

solvent mixture	organic solvent concn range[a]	equation coefficients[b] A	B	C	D	r^2
methanol/water	0.0–0.10	-12.401	5.26			0.997
ethanol/water	0.0–0.10	-12.400	6.60			0.995
ethanol/water	0.0–1.00	-12.437	6.84	9.61	7.30	0.999
1-propanol/water	0.0–0.10	-12.399	9.62			1.000
1-butanol/water	0.0–0.07	-12.406	11.25			0.974
1-pentanol/water	0.0–0.02	-12.440	16.27			0.968
acetone/water	0.0–0.10	-12.388	13.19			0.997
methyl ethyl ketone/water	0.0–0.10	-12.398	17.00			0.995
diethyl ketone/water	0.0–0.01	-12.401	24.20			1.000
methanol/1-propanol (50/50)/water	0.0–0.10	-12.406	7.72			0.994
methanol/1-butanol (50/50)/water	0.0–0.10	-12.390	8.75			0.996
methanol/1-propanol/1-butanol (50/25/25)/water	0.0–0.12	-12.402	8.33			0.998

[a] Solute-free volume fraction organic solvent. [b] $\ln x = A + Bz + Cz^2 - Dz^3$, where z = solute-free volume fraction organic solvent.

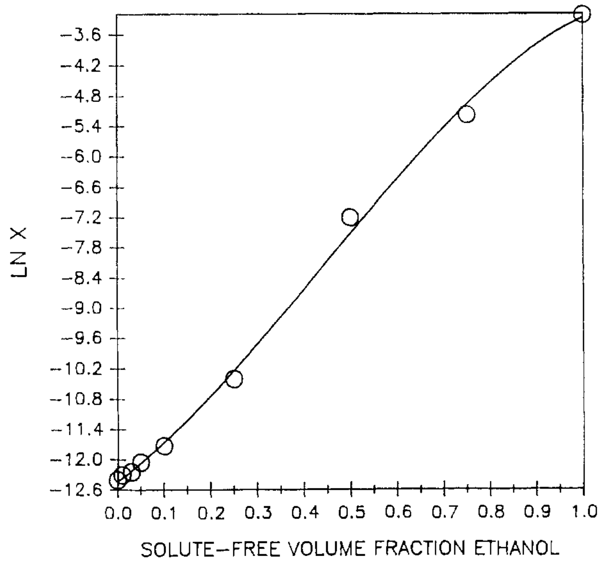

Figure 3. Natural logarithm of mole fraction solubility of naphthalene as a function of solute-free volume fraction ethanol in ethanol/water mixtures at 25 °C.

saturation, which is lower than its solubility in pure water at 25 °C.

Linear equations, which can be used to interpolate naphthalene solubilities within the ranges of the experimental data in the alcohol/water and ketone/water mixtures, are given in Table III. All the predicted solubilities obtained by using these equations fall within 10% of the observed values and, thus, well within the determined accuracy of the data.

Figure 3 shows the equation of best fit for the variation in naphthalene solubility over the entire range of organic solvent concentrations in ethanol/water mixtures. The equation is for a third-order polynomial, indicating that the linear equations given in Table III should not be extrapolated for predicting solubilities outside of the ranges of the experimental data. The cubic equation (Table III) can be used to interpolate naphthalene solubility values over the entire range of ethanol concentrations in ethanol/water mixtures. Solubilities predicted with this equation are as accurate as those predicted with the linear equation up to 0.1 solute-free volume fraction ethanol. Predicted values are somewhat less accurate, within 15–30% of the observed values for higher ethanol concentrations.

Solubilizing Power of Organic Cosolvents. Solubilizing power is defined as the slope of a plot of ln x versus solute-free volume fraction of organic solvent (*10*, *11*). The solubilizing power of the alcohols and ketones for naphthalene in water, increased as follows (Figure 2 and Table III): 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 was observed to increase as the hydrogen-bonding capability per unit size of the organic cosolvent decreased. However, this observation is restricted to organic cosolvents that are completely miscible with water at a solute-free organic solvent volume fraction of ≥0.01 (i.e., alcohols and ketones). By definition, benzene and toluene possess no solubilizing power for naphthalene in water.

Summary

Several solubility data for naphthalene in organic solvent/water mixtures at 25 °C are presented and evaluated. Equations that can be used to interpolate solubility values within the ranges of the experimental data are also presented and evaluated. The experimentally determined solubilities are in good agreement with most literature values, and observed deviations are accounted for. Solubility values for hydrophobic aromatic chemicals in organic solvent/water mixtures are estimated to be accurate to within 30%. The largest source of error for the mixed solvent solubility measurements was determined to be variation in organic cosolvent concentration. Improved experimental techniques should decrease uncertainty in the data; nonetheless, the degree of accuracy is typical for aqueous solubility measurements of hydrophobic chemicals.

Alcohols (methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol) and ketones (acetone, methyl ethyl ketone, diethyl ketone) were found to significantly increase naphthalene solubility over the range of their miscibilities with water. The solubilizing power of these cosolvents tended to increase as the hydrogen-bonding capability per unit size of the organic solvent decreased. At the very low levels of benzene and toluene miscibility with water no significant effect on naphthalene solubility was observed.

Registry No. Naphthalene, 91-20-3.

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Supplementary Material Available: Table I listing unsmoothed solubility data for naphthalene in water, organic solvents, and solvent mixtures at 25 °C (9 pages). Ordering information is given on any current masthead page.

Thermodynamics of Binary Mixtures Containing Organic Carbonates. 3. Isothermal Vapor–Liquid Equilibria for Diethyl Carbonate + Cyclohexane, + Benzene, or + Tetrachloromethane†

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Vapor and liquid equilibrium phase compositions were determined at 298.65 K for binary systems containing diethyl carbonate and cyclohexane, benzene, or tetrachloromethane. The diethyl carbonate + cyclohexane system shows large positive deviations from Raoult's law. By contrast, the diethyl carbonate + benzene or + tetrachloromethane systems are almost ideal.

Introduction

In part 1 of this series (*2*) we reported excess enthalpies for dimethyl carbonate + some *n*-alkanes, + cyclohexane, + methylcyclohexane, + benzene, + toluene, and + tetrachloromethane. In part 2, the isothermal vapor–liquid equilibrium (VLE) for dimethyl carbonate + cyclohexane, + benzene, or + tetrachloromethane (*3*) were reported. In this paper isothermal VLE data are presented for the binary systems diethyl carbonate (1) + cyclohexane (2), + benzene (2), or + tetrachloromethane (2) at 298.65 K. Excess enthalpies for these systems have been published previously (*4*). All these data will serve for estimating interaction parameters for group contribution activity coefficient models. No VLE data are available for diethyl carbonate with any of the above-mentioned solvents.

Experimental Section

Materials. All the chemicals used were from Fluka. Diethyl carbonate (puriss p.a., >99.5%) was used without further purification after gas chromatographic analysis failed to show any significant impurities. Source, purity, purification, and physical constants of cyclohexane, benzene, and tetrachloromethane were found to be the same as in our previous paper (*2*). The density and refractive index at 298.15 K, ρ = 969.4 kg m^{-3} and n_D = 1.3824, were in good agreement with literature values (*5*, *6*). Prior to the actual measurements, the liquids were dried over a molecular sieve (Union Carbide Type 4A from Fluka).

Apparatus and Procedure. A detailed description of the experimental equipment and operating procedure can be found in our previous papers (*3*, *7*).

The equilibrium temperature, *T*, was measured accurate to 0.05 K with a certified PROTON mercury thermometer (Model BER-MAN) previously calibrated with a Hewlett-Packard, Model 2804A, quartz thermometer.

The composition of the vapor phase was determined by use of a Hewlett-Packard, Model 5980, gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard, Model 3390, electronic integrator. The column, 200 cm long and $^1/_4$ in. in diameter, was packed with Carbowax 1500 and was operated isothermally within the range from 80 to 130 °C depending on the nature of the analyzed materials. The chromatograph was calibrated with synthetic mixtures. The mole fraction of the vapor phase, *y*, accurate to within 0.0002 for

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† This paper is a contribution to the TOM Project (*1*).

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