(19) Benson, G. C.; Kiyohara, O. J. Chem. Thermodn. 1979, 11, 1061.
(20) Acree, Jr. E. W. J. Chem. Eng. Data. 1983, 28, 215.
(21) Desnoyers, J. E.; Quirion, F.; Hetu, D.; Perron, G. Can. J. Chem. Eng. 1983, 61, 672.
(22) Desnoyers, J. E.; Beaudoin, R.; Perron, G.; Roux, G. ACS Symp. Ser. 1978, No. 90.
(23) Kell, G. C. J. Chem. Eng. Data 1975, 20, 97.
(24) Roux, G.; Perron, G.; Desnoyers, J. E. J. Solution Chem. 1978, 7, 839.
(25) International Critical Tables; McGraw-Hill: New York, 1926.
(26) Fortier, J. L.; Benson, G. C.; Picker, P. J. Chem. Thermodyn. 1976, 8, 289.
(27) Zlochower, I. A.; Schulman, J. H. J. Colloid Interface Sci. 1967, 24, 115.
(28) Gillberg, G.; Lehtinen, H.; Friberg, S. J. Colloid Interface Sci. 1970, 40, 33.

(29) Shah, D. O.; Hamlin, Jr. R. M. Science 1971, 171, 483.
(30) Hansen, J. R. J. Phys. Chem. 1974, 78, 256.
(31) Desroslers, O.; Van Dinter, T.; Saunders, J. K. Can. J. Chem. 1984, 62, 56.

Solubility of Anthracene in Binary Solvent Mixtures Containing Dibutyl Ether

Mary V. Marthandan and William E. Acree, Jr.*

Department of Chemistry, Kent State University, Kent, Ohio 44242

Experimental solubilities are reported for anthracene in binary solvent mixtures containing dibutyl ether with n-hexane, cyclohexane, n-heptane, methylcyclohexane, n-octane, isooctane, and cyclooctane at 25 °C. Results of these measurements, combined with estimates for the excess Gibbs free energies of the binary solvents, are used to test predictive expressions derived from the nearly ideal binary solvent (NIBS) model. Expressions based on a volume fraction average of solute properties in the two pure solvents predict anthracene solubilities to within a maximum deviation of 5.1% and an overall average deviation of 2.1%.

Introduction

This work continues (1–8) a systematic search for mixing models and equations which will provide predictions for thermochemical properties of a solute at high dilution in binary solvent mixtures. In two earlier papers, Acree and Rytting (5, 6) reported solubilities for benzil and p-benzoquinone in binary solvent mixtures containing carbon tetrachloride, in which the mole fraction solubility of benzil and p-benzoquinone cover a 14-fold and 6-fold range, respectively. The experimental data were interpreted with solution models developed previously for solubility in systems containing specific solute–solvent interactions and with models of purely nonspecific solute–solvent interactions and with models of purely nonspecific interactions. A stoichiometric complexation model based entirely on specific interactions (nonspecific interactions ignored) required several equilibrium constants to mathematically describe the experimental results, while the nearly ideal binary solvent (NIBS) model based on nonspecific interactions described adequately the observed solubilities without introducing a single equilibrium constant.

The success of the NIBS approach in predicting the binary solvent effect on benzil and p-benzoquinone solubilities suggested the possibility that this solution model may provide a foundation for approximations of physical interactions even in a system known to contain chemical interactions. To pursue this idea further, the basic NIBS model was extended to systems containing association between the solute (component A) and a complexing cosolvent (component C)
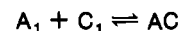
$$A_1 + C_1 \rightleftharpoons AC$$

$$K_{AC}^{\phi} = \frac{\phi_{AC}}{\phi_{A_1}\phi_{C_1}}$$

A relatively simple expression was developed (8) for the determination of solute–solvent equilibrium constants from the measured solubility as a function of solvent composition and the excess Gibbs free energy of the binary solvent mixture

$$RT\left[\ln(a_A^{solid}/\phi_{A_1}^{sat}) - 1 + \bar{V}_A\left(\frac{\phi_{A_1}^{sat}}{\bar{V}_A} + \frac{\phi_B}{\bar{V}_B} + \frac{\phi_C}{\bar{V}_C}\right)\right] = (1 - \phi_A^{sat})^2[\phi_B^0(\Delta\bar{G}_A^{fh})_B^* + \phi_C^0(\Delta\bar{G}_A^{fh})_C^* - \bar{V}_A(X_B^0\bar{V}_B + X_C^0\bar{V}_C)^{-1}\Delta\bar{G}_{BC}^{fh}] \quad (1)$$

with the overall volume fraction solubility, ϕ_A^{sat}, being related to the solubility of the uncomplexed solute and the equilibrium constant by

$$\phi_A^{sat} = \phi_{A_1}^{sat}[1 + \bar{V}_A K_{AC}^{\phi}\phi_{C_1}/(\bar{V}_A + \bar{V}_C)]$$

and the quantities $(\Delta\bar{G}_A^{fh})_B^*$ and $(\Delta\bar{G}_A^{fh})_C^*$ being calculated from the appropriate binary reduction of eq 1

$$(\Delta\bar{G}_A^{fh})_B^* = (1 - \phi_A^{sat})^{-2}RT\left[\ln(a_A^{solid}/\phi_A^{sat}) - (1 - \phi_A^{sat})\left(1 - \frac{\bar{V}_A}{\bar{V}_B}\right)\right]$$

$$(\Delta\bar{G}_A^{fh})_C^* = (1 - \phi_A^{sat})^{-2}RT\left[\ln(a_A^{solid}/\phi_{A_1}^{sat}) - 1 + \bar{V}_A\left(\frac{\phi_{A_1}^{sat}}{\bar{V}_A} + \frac{\phi_C}{\bar{V}_C}\right)\right]$$

using the molar volumes of the pure components, $\bar{V}_i$, and the solubilities in the two pure solvents. The superscript (0) denotes that the solvent compositions are calculated as if the solute were not present.

Postulating the formation of a 1:1 anthracene–benzene complex, the authors demonstrated that eq 1 could describe

the solubility of anthracene in benzene + n-heptane and benzene + isooctane mixtures to within a maximum deviation of 4% using a single value of $K_{AC}{}^{\phi}$ = 1.91. More importantly, it was noted that the determination of solute–solvent equilibrium constants from solubility measurements does depend on the manner in which nonspecific interactions are incorporated into the model. In the case of anthracene solubilities, failure to include nonspecific interactions led to a calculated value of $K_{AC}{}^{\phi}$ = 4.07 for the anthracene–benzene complex in solvent mixtures containing n-heptane.

Application of eq 1 to solubility measurements does require *a prior* knowledge of $\Delta \bar{G}_{BC}{}^{fh}$, which for many systems may not be easily measurable or readily available in the chemical literature. In anticipation of calculating solute–dibutyl ether association constants from solubility measurements, we decided to first measure anthracene solubilities in several binary solvent mixtures containing dibutyl ether in hopes of estimating $\Delta \bar{G}_{BC}{}^{fh}$ values for subsequent studies. Solubilities are reported for anthracene in binary dibutyl ether + n-hexane, dibutyl ether + cyclohexane, dibutyl ether + n-heptane, dibutyl ether + methylcyclohexane, dibutyl ether + n-octane, dibutyl ether + isooctane, and dibutyl ether + cyclooctane mixtures at 25 °C. Results of these measurements, combined with estimated $\Delta \bar{G}_{BC}{}^{fh}$ (or $\Delta \bar{G}_{BC}{}^{ex}$) values, are compared to predictions based on the NIBS model.

Experimental Section

Anthracene (Aldrich Gold Label) was used as received. Cyclohexane (Aldrich HPLC), n-heptane (Aldrich HPLC), n-hexane (Aldrich 99%), isooctane (Fisher 99 mol %), n-octane (Aldrich Gold Label), methylcyclohexane (Aldrich Gold Label), cyclooctane (Aldrich Gold Label), and di-n-butyl ether (Aldrich Gold Label) were stored over molecular sieves to remove trace water. Binary solvent mixtures were prepared by weight so that compositions could be calculated to 0.0001 mole fraction.

Excess solute and solvent were placed in amber glass bottles and allowed to equilibrate in a constant temperature bath at 25.0 °C for several days. Attainment of equilibrium was verified by repetitive measurements after several additional days and in some instances by approaching equilibrium from supersaturation by preequilibrating the solution at a higher temperature. Aliquots of saturated anthracene solutions were transferred through a coarse filter into a tared volumetric flask to determine the amount of sample and diluted quantitatively with methanol. Concentrations were determined spectrophotometrically at 356 nm on a Bausch and Lomb Spectronic 2000. Experimental solubilities of anthracene in the seven binary solvent systems studied are listed in Table I. Numerical values represent the average of between 4 and 8 independent determinations, with the measurements being reproducible to within ±1%.

Results and Discussion

The general NIBS expressions for predicting solubilities in systems of nonspecific interactions depend on two different models of solution ideality:

$$RT \ln (a_A{}^{solid}/X_A{}^{sat}) =$$
$$(1 - X_A{}^{sat})^2 [X_B{}^0 (\Delta \bar{G}_A{}^{ex})_B{}^* + X_C{}^0 (\Delta \bar{G}_A{}^{ex})_C{}^* - \Delta \bar{G}_{BC}{}^{ex}] \quad (2)$$

$$RT \ln (a_A{}^{solid}/X_A{}^{sat}) = (1 - \phi_A{}^{sat})^2 [\phi_B{}^0 (\Delta \bar{G}_A{}^{ex})_B{}^* +$$
$$\phi_C{}^0 (\Delta \bar{G}_A{}^{ex})_C{}^* - \bar{V}_A (X_B{}^0 \bar{V}_B + X_C{}^0 \bar{V}_C)^{-1} \Delta \bar{G}_{BC}{}^{ex}] \quad (3)$$

$$RT \left[\ln (a_A{}^{solid}/\phi_A{}^{sat}) - (1 - \phi_A{}^{sat}) \times \right.$$
$$\left. \left(1 - \frac{\bar{V}_A}{X_B{}^0 \bar{V}_B + X_C{}^0 \bar{V}_C} \right) \right] = (1 - \phi_A{}^{sat})^2 [\phi_B{}^0 (\Delta \bar{G}_A{}^{fh})_B{}^* +$$
$$\phi_C{}^0 (\Delta \bar{G}_A{}^{fh})_C{}^* - \bar{V}_A (X_B{}^0 \bar{V}_B + X_C{}^0 \bar{V}_C)^{-1} \Delta \bar{G}_{BC}{}^{fh}] \quad (4)$$

Table I. Comparison of Predicted and Experimental Anthracene Solubilities in Several Binary Solvent Mixtures at 25 °C

solvent (B) + solvent (C)	$X_B{}^0$	$X_A{}^{sat}$	% dev of calcd values[a] (2)	(3)	(4)
n-hexane +	0.0000	0.003 609			
dibutyl ether	0.2515	0.002 944	−4.7	−0.1	−0.1
	0.4505	0.002 453	−6.8	−0.3	−0.3
	0.5676	0.002 177	−7.1	−0.3	−0.3
	0.6493	0.001 989	−6.6	−0.2	−0.2
	0.8402	0.001 571	−3.5	0.6	0.6
	1.0000	0.001 273			
cyclohexane +	0.0000	0.003 609			
dibutyl ether	0.2869	0.003 066	−7.1	−0.2	−0.1
	0.5080	0.002 647	−10.8	−1.4	−1.1
	0.6074	0.002 435	−10.9	−1.4	−1.1
	0.7032	0.002 230	−10.3	−1.6	−1.2
	0.8577	0.001 884	−6.8	−1.2	−1.0
	1.0000	0.001 551			
n-heptane +	0.0000	0.003 609			
dibutyl ether	0.2330	0.003 091	−3.6	−1.6	−1.6
	0.4186	0.002 676	−4.5	−1.7	−1.7
	0.5379	0.002 447	−5.5	−2.5	−2.5
	0.6243	0.002 258	−4.7	−1.8	−1.8
	0.8130	0.001 894	−3.0	−1.1	−1.1
	1.0000	0.001 568			
methylcyclohexane +	0.0000	0.003 609			
dibutyl ether	0.2544	0.003 122	−4.8	−0.9	−0.9
	0.4391	0.002 799	−8.1	−2.8	−2.8
	0.5727	0.002 520	−8.0	−2.5	−2.5
	0.6674	0.002 315	−7.0	−1.8	−1.8
	0.8201	0.002 021	−5.6	−1.9	−1.9
	1.0000	0.001 652			
n-octane +	0.0000	0.003 609			
dibutyl ether	0.2167	0.003 185	−1.9	−1.5	−1.5
	0.4059	0.002 837	−3.0	−2.4	−2.4
	0.5116	0.002 652	−3.4	−2.7	−2.7
	0.6030	0.002 478	−2.8	−2.2	−2.2
	0.7914	0.002 151	−1.5	−1.0	−1.0
	1.0000	0.001 836			
isooctane +	0.0000	0.003 609			
dibutyl ether	0.2142	0.002 942	−1.8	−1.7	−1.7
	0.4073	0.002 391	−2.9	−2.7	−2.7
	0.5008	0.002 146	−3.2	−3.1	−3.1
	0.6114	0.001 860	−2.7	−2.5	−2.5
	0.7886	0.001 469	−2.3	−2.2	−2.2
	1.0000	0.001 067			
cyclooctane +	0.0000	0.003 609			
dibutyl ether	0.2387	0.003 481	−5.2	−3.5	−3.5
	0.4663	0.003 242	−7.7	−5.1	−5.1
	0.5512	0.003 114	−7.6	−4.9	−4.9
	0.6522	0.002 961	−7.6	−5.0	−5.0
	0.8273	0.002 653	−6.1	−4.2	−4.2
	1.0000	0.002 251			

[a] Deviations (%) = $100 \ln (X_{calcd}{}^{sat}/X_{exptl}{}^{sat})$.

Equations 2 and 3 are based on Raoult's law and eq 4 is based on the Flory–Huggins model. In the above expressions $a_A{}^{solid}$ is the activity of the solid solute relative to the pure subcooled liquid, X_i is mole fraction, and ϕ_i is volume fraction. Binary solvent properties $\Delta \bar{G}_{BC}{}^{ex}$ and $\Delta \bar{G}_{BC}{}^{fh}$ refer to the excess Gibbs free energies relative to Raoult's law and the Flory–Huggins model, respectively. Solubility data measured in each pure solvent can be used to calculate the excess partial molar Gibbs free energy of the solute $(\Delta \bar{G}_A{}^{ex})_i{}^*$ and $(\Delta \bar{G}_A{}^{fh})_i{}^*$. These quantities are then combined with the free energy of the binary solvent mixture to predict solubility in mixed solvents.

To date, testing of the limitations and applications of the NIBS model has been restricted to binary solvent systems for which experimental $\Delta \bar{G}_{BC}{}^{ex}$ values could be found in the literature. There are a number of systems, such as binary dibutyl ether + alkane systems, that have not been studied thermodynamically. Excess Gibbs free energies of such systems can

Table II. Properties Used in the NIBS Predictions

component (i)	$\bar{V}_i$, cm³/mol	$\delta_i,^a$ (cal/cm³)$^{1/2}$
n-hexane	131.51	7.27
n-heptane	147.48	7.50
n-octane	163.46	7.54
cyclohexane	108.76	8.19
cyclooctane	134.88	8.51[b]
dibutyl ether	170.41	7.76
isooctane	166.09	6.86
methylcyclohexane	128.32	7.83[c]
anthracene	150.00[d]	0.01049[e]

[a] Unless otherwise noted, solubility parameters are taken from ref 9. [b] Calculated from the calorimetric data from ref 10. [c] Calculated from data in ref 11. [d] Value from ref 7. [e] Value of a_A^{solid} from ref 7.

be estimated from the Scatchard–Hildebrand solubility parameter model

$$\Delta\bar{G}_{BC}^{ex} = \phi_B^0\phi_C^0(X_B^0\bar{V}_B + X_C^0\bar{V}_C)(\delta_B - \delta_C)^2 \quad (5)$$

where δ_i refers to the solubility parameter of component i.

Comparisons between experimental and predicted anthracene solubilities are tabulated in the last three columns of Table I. Solvent properties used in the NIBS predictions are listed in Table II. In general, eq 3 and 4 are comparable with identical overall average deviations of 2.1% and are superior to eq 2 which has an overall average (rms) deviation of 5.5%. More importantly, deviations for eq 3 and 4 fall almost within the experimental uncertainty of 1%. This indicates that approximation of dibutyl ether + alkane $\Delta\bar{G}_{BC}^{ex}$ values via eq 5 introduces only a relatively small error in the NIBS predictions and makes possible the calculation of presumed solute–dibutyl ether association constants from future solubility measurements.

Glossary

a_A^{solid}	activity of the solid solute, defined as the ratio of the fugacity of the solid to the fugacity of the pure subcooled liquid
$(\Delta\bar{G}_A^{ex})^*$	partial molar Gibbs free energy of the solute (Raoult's law), extrapolated back to infinite dilution
$(\Delta\bar{G}_A^{fh})^*$	partial molar Gibbs free energy of the solute (Flory–Huggins model), extrapolated back to infinite dilution
$\Delta\bar{G}_{BC}^{ex}$	excess Gibbs free energy of the binary solvent mixture based on Raoult's law
$\Delta\bar{G}_{BC}^{fh}$	excess Gibbs free energy of the binary solvent mixture based on Flory–Huggins model, calculated from $\Delta\bar{G}_{BC}^{ex}$ values as $\Delta\bar{G}_{BC}^{fh} = \Delta\bar{G}_{BC}^{ex} + RT[\ln(X_B^0\bar{V}_B + X_C^0\bar{V}_C) - X_B^0\ln\bar{V}_B - X_C^0\ln\bar{V}_C]$
$\bar{V}_i$	molar volume of component i
X_B^0, X_C^0	mole fraction compositions of solvent mixture, calculated as if the solute were not present
X_A^{sat}	mole fraction solubility of solute
ϕ_B^0, ϕ_C^0	ideal volume fraction composition of the solvent mixture, calculated as if the solute were not present
ϕ_A^{sat}	ideal volume fraction solubility of solute
δ_i	solubility parameter of component i
rms deviation	$(100/N^{1/2})\{\sum^N[\ln(X_{calcd}^{sat}/X_{exptl}^{sat})]^2\}^{1/2}$, %

Literature Cited

(1) Acree, W. E., Jr.; Bertrand, G. L. J. Phys. Chem. 1977, 81, 1170-3.
(2) Acree, W. E., Jr.; Bertrand, G. L. J. Phys. Chem. 1979, 83, 2355-8.
(3) Acree, W. E., Jr.; Bertrand, G. L. J. Pharm. Sci. 1981, 70, 1033-6.
(4) Acree, W. E., Jr.; Bertrand, G. L. J. Solution Chem. 1983, 12, 101-13.
(5) Acree, W. E., Jr.; Rytting, J. H. J. Pharm. Sci. 1982, 71, 201-5.
(6) Acree, W. E., Jr.; Rytting, J. H. Int. J. Pharm. 1982, 10, 231-8.
(7) Acree, W. E., Jr.; Rytting, J. H. J. Pharm. Sci. 1983, 72, 292-6.
(8) Acree, W. E., Jr.; McHan, D. R.; Rytting, J. H. J. Pharm. Sci. 1983, 72, 929-34.
(9) Hoy, K. L. J. Paint Technol. 1970, 42, 76-118.
(10) Cox, J. D.; Pilcher, G. Thermochemistry of Organic and Organometallic Compounds; Academic: New York, 1970.
(11) Majer, V.; Svoboda, V.; Hala, S.; Pick, J. Collect. Czech. Chem. Commun. 1979, 44, 637-51.

Thermodynamic and Spectroscopic Properties of 2-Pyrrolidinones. 1. Excess Molar Volumes of 2-Pyrrolidinone + Dichloromethane, + Dimethyl Sulfoxide, + Acetone, + 2-Propanol, and + Water

Pälvi L. Pirilä-Honkanen and Pirkko A. Ruostesuo*

Department of Chemistry, University of Oulu, 90570 Oulu, Finland

Negative excess molar volumes were measured for the binary liquid mixtures of 2-pyrrolidinone with acetone, dimethyl sulfoxide, dichloromethane, 2-propanol, and water at 303.15 and 323.15 K over the entire composition range. The results are discussed in terms of the possible interactions between like and unlike molecules.

Introduction

As part of a study on thermodynamic and physical properties of binary liquid mixtures containing amide as one of the components, we report here the excess molar volumes for five 2-pyrrolidinone liquid mixtures. Excess molar volumes at 303.15 and 323.15 K have earlier been measured for N-methylmethanesulfinamide, N,N-dimethylmethanesulfinamide, N,N-dimethylbenzenesulfinamide, and dimethyl sulfoxide with the solvents carbon tetrachloride, 1,4-dioxane, and benzyl alcohol, and the molecular interactions in these systems have been discussed (1–3). The systems have been selected with a view to studying the molecular interactions occurring in binary mixtures of N-monosubstituted and N,N-disubstituted sulfinamides and related sulfoxides (e.g. dimethyl sulfoxide) as one compo-