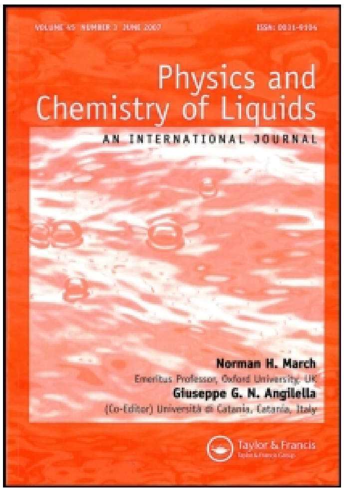

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Solubility of Anthracene in Binary Toluene + Alkane Solvent Mixtures

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Experimental solubilities are reported for anthracene in binary solvent mixtures containing toluene with *n*-hexane, cyclohexane, *n*-heptane, methylcyclohexane, *n*-octane, cyclooctane and isooctane at 25°C. Results of these measurements are used to test five predictive expressions derived from the Nearly Ideal Binary Solvent (NIBS) model. The most successful equation in terms of goodness of fit involved a surface fraction average of the excess partial molar Gibbs free energy of the solute relative to Raoult's law and predicted the experimental anthracene solubilities in the 7 systems studied to within an average absolute deviation of 4.5%.

Key Words: Anthracene solubility—binary solvents, solid-liquid equilibria, binary solvents—predictive expressions for solubility, solubility—binary solvents.

INTRODUCTION

Solid-liquid equilibria data of organic systems are becoming increasingly important in the petroleum industry, particularly in light of present trends towards heavier feed stocks and coal-derived fuels. Solubility data for a number of polycyclic aromatic hydrocarbons[1-5] (*i.e.*, pyrene and anthracene) and heterocyclic polynuclear aromatics[6,7] (*i.e.*, carbazole) have been published in recent chemical literature. Despite the increased experimental efforts, there still exists numerous systems for which actual solubility data are not readily available.

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To address this problem, researchers have turned to semiempirical and semi-theoretical methods to predict the desired quantities. The Nearly Ideal Binary Solvent (NIBS) model developed previously[8,9] provides a relatively simple method for estimating the excess partial molar Gibbs free energies of a solute, $\bar{G}_3^{ex}$, at infinite dilution in a binary solvent (components 1 and 2):

$$\bar{G}_3^{ex} = f_1^0(\bar{G}_3^{ex})_1 + f_2^0(\bar{G}_3^{ex})_2 - \Gamma_3(X_1^0\Gamma_1 + X_2^0\Gamma_2)^{-1}\bar{G}_{12}^{ex} \qquad (1)$$

and

$$f_1^0 = 1 - f_2^0 = X_1^0\Gamma_1/(X_1^0\Gamma_1 + X_2^0\Gamma_2) \qquad (2)$$

in terms of a weighted mole fraction average of the properties of the solute in the two pure solvents $[(\bar{G}_3^{ex})_1$ and $(\bar{G}_3^{ex})_2]$ and a contribution due to the unmixing of the solvent pair by the presence of the solute. Equation (1) gives accurate predictions for naphthalene, iodine, *p*-dibromobenzene, benzil, *p*-benzoquinone, benzoic acid and phenylacetic acid in systems of non-specific interactions when molar volumes are used as weighting factors (Γ_i).[10] Approximation of weighting factors with molecular surface areas enables Eq. (1) to provide accurate predictions for both anthracene[1] and pyrene[3] solubilities in binary solvent mixtures containing benzene.

Continued development of solution models for predicting the thermodynamic properties of a solute in binary solvent systems requires that a large data base be available for assessing the applications and limitations of derived predictive expressions. As part of our ongoing study of solubility in binary solvents, we report anthracene solubilities in mixtures containing toluene with *n*-hexane, cyclohexane, *n*-heptane, methylcyclohexane, *n*-octane, cyclooctane and isooctane. For the seven systems studied, anthracene solubilities covered up to a sevenfold range in mole fraction. Results of these measurements are compared to predictions based on the NIBS model.

MATERIALS AND METHODS

Anthracene (Aldrich Gold Label) was used as received. Cyclohexane (Aldrich HPLC), *n*-heptane (Aldrich HPLC), *n*-hexane (Aldrich 99%), *n*-octane (Aldrich Gold Label), isooctane (Aldrich HPLC), methylcyclohexane (Aldrich Gold Label), cyclooctane (Aldrich Gold Label) and toluene (Aldrich HPLC) were stored over molecular sieves to remove trace water. Gas chromatographic analysis showed solvent purities to be 99.8% or better. 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 ±0.1 °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 solutions at a higher temperature. Aliquots of saturated 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 are listed in Table 1. Numerical values represent the average of 4–8 determinations, with measurements being reproducible to ±1 %. Solubilities in the pure alkane solvents are in excellent agreement with earlier values of Acree and Rytting.[1]

RESULTS AND DISCUSSION

The general NIBS expressions for predicting solubilities in systems of non-specific interactions depend on different models of solution ideality and weighting factor approximations:

$$RT\ln(a_3^{\text{solid}}/X_3^{\text{sat}}) = (1 - X_3^{\text{sat}})^2[X_1^0(\bar{G}_3^{\text{ex}})_1 + X_2^0(\bar{G}_3^{\text{ex}})_2 - \bar{G}_{12}^{\text{ex}}] \tag{XX}$$

$$\begin{aligned} RT\ln(a_3^{\text{solid}}/X_3^{\text{sat}}) &= (1 - \phi_3^{\text{sat}})^2[\phi_1^0(\bar{G}_3^{\text{ex}})_1 + \phi_2^0(\bar{G}_3^{\text{ex}})_2 \\ &\quad - \bar{V}_3(X_1^0\bar{V}_1 + X_2^0\bar{V}_2)^{-1}\bar{G}_{12}^{\text{ex}}] \end{aligned} \tag{XV}$$

$$\begin{aligned} RT\ln(a_3^{\text{solid}}/X_3^{\text{sat}}) &= (1 - \theta_3^{\text{sat}})^2[\theta_1^0(\bar{G}_3^{\text{ex}})_1 + \theta_2^0(\bar{G}_3^{\text{ex}})_2 \\ &\quad - \bar{A}_3(X_1^0\bar{A}_1 + X_2^0\bar{A}_2)^{-1}\bar{G}_{12}^{\text{ex}}] \end{aligned} \tag{XA}$$

$$\begin{aligned} &RT\left[\ln(a_3^{\text{solid}}/\phi_3^{\text{sat}}) - (1 - \phi_3^{\text{sat}})\left(1 - \frac{\bar{V}_3}{X_1^0\bar{V}_1 + X_2^0\bar{V}_2}\right)\right] \\ &\quad = (1 - \phi_3^{\text{sat}})[\phi_1^0(\bar{G}_3^{\text{fh}})_1 + \phi_2^0(\bar{G}_3^{\text{fh}})_2 - \bar{V}_3(X_1^0\bar{V}_1 + X_2^0\bar{V}_2)^{-1}\bar{G}_{12}^{\text{fh}}] \\ &RT\left[\ln(a_3^{\text{solid}}/\phi_3^{\text{sat}}) - (1 - \phi_3^{\text{sat}})\left(1 - \frac{\bar{V}_3}{X_1^0\bar{V}_1 + X_2^0\bar{V}_2}\right)\right] \qquad \text{(VV)} \\ &\quad = (1 - \theta_3^{\text{sat}})^2[\theta_1^0(\bar{G}_3^{\text{fh}})_1 + \theta_2^0(\bar{G}_3^{\text{fh}})_2 - \bar{A}_3(X_1^0\bar{A}_1 + X_2^0\bar{A}_2)^{-1}\bar{G}_{12}^{\text{fh}}] \end{aligned} \tag{VA}$$

Equations (XX), (XV), and (XA) are based on Raoult's law while Eqs (VV) and (VA) are based on the Flory–Huggins model. In the above expressions $\bar{V}_i$ is the molar volume of a pure liquid, $\bar{A}_i$ is the molecular surface area, X_i denotes mole fraction, ϕ_i is volume fraction, θ_i is surface

Table 1 Mole fraction solubility of anthracene in various binary alkane + toluene solvent mixtures at 25°C.

Solvent (1) + Solvent (2)	X_1^0	X_3^{sat}
n-Hexane + Toluene	0.0000	0.00736
	0.1631	0.00607
	0.3540	0.00454
	0.4514	0.00388
	0.5453	0.00327
	0.7369	0.00226
	1.0000	0.00127
n-Heptane + Toluene	0.0000	0.00736
	0.1606	0.00606
	0.1692	0.00598
	0.3246	0.00480
	0.3247	0.00477
	0.4137	0.00420
	0.4254	0.00412
	0.5316	0.00344
	0.5396	0.00336
	0.7341	0.00245
	0.7413	0.00242
	1.0000	0.00157
n-Octane + Toluene	0.0000	0.00736
	0.1397	0.00623
	0.1415	0.00619
	0.2977	0.00502
	0.3014	0.00498
	0.3936	0.00434
	0.4024	0.00431
	0.4956	0.00375
	0.4988	0.00374
	0.7147	0.00271
	0.7211	0.00268
	1.0000	0.00184
Methylcyclohexane + Toluene	0.0000	0.00736
	0.1756	0.00631
	0.1817	0.00626
	0.3532	0.00516
	0.3621	0.00508
	0.4512	0.00450
	0.4634	0.00443
	0.5541	0.00384
	0.5657	0.00376
	0.7607	0.00269
	0.7720	0.00263
	1.0000	0.00165
Isooctane + Toluene	0.0000	0.00736
	0.1362	0.00593
	0.1381	0.00592

Solvent (1) + Solvent (2)	X_1^0	X_3^{sat}
	0.2926	0.00447
	0.2944	0.00446
	0.3895	0.00373
	0.3921	0.00370
	0.4862	0.00308
	0.4932	0.00304
	0.7059	0.00200
	0.7127	0.00195
	1.0000	0.00107
Cyclohexane + Toluene	0.0000	0.00736
	0.2043	0.00600
	0.3954	0.00483
	0.4964	0.00414
	0.5950	0.00356
	0.7930	0.00248
	1.0000	0.00155
Cyclooctane + Toluene	0.0000	0.00736
	0.1664	0.00658
	0.3173	0.00568
	0.4412	0.00508
	0.5401	0.00451
	0.7519	0.00337
	1.0000	0.00225

fraction, $\bar{G}_{12}^{\text{ex}}$ refers to the molar excess Gibbs free energy of the binary solvent relative to Raoult's law, and

$$\bar{G}_{12}^{\text{fh}} = \bar{G}_{12}^{\text{ex}} + RT[\ln(X_1^0\bar{V}_1 + X_2^0\bar{V}_2) - X_1^0\ln\bar{V}_1 - X_2^0\ln\bar{V}_2]$$

The superscript (0) indicates that the solvent composition is calculated as if the solute were not present. The activity of the solid solute (a_3^{solid}), relative to the supercooled liquid, can be calculated from

$$\ln a_3^{\text{solid}} = -\frac{\Delta\bar{H}_3^{\text{fus}}(T_m - T)}{RT\,T_m} + \frac{\Delta\bar{C}_p(T_m - T)}{RT} - (\Delta\bar{C}_p/R)\ln(T_m/T)$$

the molar heat of fusion ($\Delta\bar{H}_3^{\text{fus}}$) at the normal melting point (T_m) and the differences between the molar heat capacities of the liquid and solid.

The predictive ability of the five NIBS expressions are summarized in Table 2. For four of the binary systems studied, methylcyclohexane + toluene,[11] *n*-heptane + toluene,[12] cyclooctane + toluene[13] and cyclohexane + toluene,[14] experimental excess Gibbs free energies are available in the chemical literature at or near 25°C. Excess Gibbs free energies of the remaining three systems were estimated *via* the Scatchard-Hildebrand solubility parameter model

$$\bar{G}_{12}^{\text{ex}} = \phi_1^0\phi_2^0(X_1^0\bar{V}_1 + X_2^0\bar{V}_2)(\delta_1 - \delta_2)^2 \tag{3}$$

Table 2 Summarized comparison between experimental anthracene solubilities and values predicted from the NIBS equations.

Binary solvent system	% Deviations of calcd. values[a]				
	(XX)	(XV)	(VV)	(XA)	(VA)
n-Hexane + Toluene	−1.1	−5.7	−5.6	0.9	1.0
n-Heptane + Toluene	+4.6	−4.3	−4.0	1.3	+1.6
n-Octane + Toluene	+8.0	−3.6	−3.3	1.3	+1.8
Cyclohexane + Toluene	−12.7	−13.6	−13.4	−8.1	−8.1
Methylcyclohexane + Toluene	−7.4	−10.9	−10.7	−5.7	−5.6
Cyclooctane + Toluene	−2.5	−5.8	−5.6	1.1	−1.7
Isooctane + Toluene	+14.6	1.7	1.6	+12.7	+13.3

[a] Deviations (%) = $(100/N^{1/2})\{\Sigma[\ln(X_3^{calc}/X_3^{exp})]^2\}^{1/2}$; an algebraic sign indicates that all deviations were of the same sign.

where δ_i is solubility parameter of component *i*. Table 3 lists numerical values of solubility parameters, molar volumes and surface areas used in the NIBS predictions. Surface areas of the individual molecules are taken from tabulated values presented in previous reports.[15–18] In all cases, the surface areas exclude solvent molecules which may be located within the solvation sphere surrounding the solute molecule.

Inspection of Table 2 reveals that Eq. (XA), based on surface areas as weighting factors for the excess Gibbs free energies relative to Raoult's law, is found to be the "best" predictive expression with an overall average (RMS) deviation of 4.5% and a maximum error for a single data point of 16%. Deviations between observed and predicted solubilities for anthracene are larger than experimental uncertainties. It must be remembered, however, that three measured values are needed for each NIBS prediction. Anthracene solubility in each pure solvent was reproducible to within 1%, and experimental $\bar{G}_{12}^{ex}$ values are believed to be accurate to at least ±6 cal/mole. Ratios of $\Gamma_3/(X_1^0\Gamma_1 + X_2^0\Gamma_2)$ greater than unity magnify the effect that errors in the unmixing term has on the solubility predictions. A 6 cal/mole error in $\Gamma_3(X_1^0\Gamma_1 + X_2^0\Gamma_2)^{-1}\ \bar{G}_{12}^{ex}$ corresponds to an error of 1% in the predicted value. Based on these observations, "uncertainties" in the NIBS predictions are estimated to be on the order of 2–3% which in part explains deviations between observed and predicted values. The much larger deviations noted in the isooctane + toluene system are probably attributed to errors in the $\bar{G}_{12}^{ex}$ values. For the isooctane + toluene system the excess Gibbs free energies were not available in the literature and thus were estimated *via* Eq. (3).

Table 3 Solute and solvent properties used in the NIBS predictions.

Component	$\bar{V}_i$, cm^3/mole	$\bar{A}_i$, Å^2/mole	δ_i, cal$^{1/2}$ cm$^{-3/2,a}$
n-Hexane	131.51	142.1	7.27
n-Heptane	147.48	160.3	
n-Octane	163.46	178.4	7.54
Cyclohexane	108.76	120.8	
Methylcyclohexane	128.32	137.7	
Cyclooctane	134.88	148.8	
Isooctane	166.09	163.1	6.86
Toluene	106.84	126.5	8.93
Anthracene	150.00	202.2	$a_3^{\text{solid}} = 0.01049$

[a] Solubility parameters are taken from Hoy.[20]

An important consequence of this research involves earlier contentions that the failure of Eq. (1) may be taken as an indication of specific solute-solvent or solvent-solvent interactions. While this concept is relatively straightforward in principle, its practical applications can be complicated by the various weighting factor approximations. For example, does the failure of Eqs (XV) and (VV) to predict anthracene solubilities in binary mixtures containing toluene indicate specific solute-solvent ($\pi - \pi$) interactions, or does the success of Eq. (XA) (and (VA)) indicate that surface areas provide a better approximation of weighting factors in systems containing both a planar aromatic hydrocarbon solute and solvent molecule.

Price and Stone[19] have recently suggested that benzene forms weak van der Waals complexes with anthracene and perylene. Using quantum mechanical calculations, the authors located minima in the electrostatic energy surfaces. Electrostatic interactions favor two types of structures for the anthracene-benzene complex. The first set corresponds to approximately displaced parallel plate structures, with the edge of the benzene molecule roughly parallel to the long axis of anthracene. T-shaped complexes represent the second set of structures and the edge of the benzene molecule points to either the central or end ring of anthracene. A toluene-anthracene complex could be argued on the basis of structural similarities between benzene and toluene.

Readers are reminded that quantum mechanical calculations do not conclusively prove that such complexes actually exist in solution. The presence of molecular complexes should be supported by a number of independent measurements involving spectroscopy, calorimetry, etc. Irrespective of whether complexation does occur in these systems, results of the present study show that the best expressions for predicting anthracene solubilities in binary alkane + toluene solvent mixtures approximate weighting factors with molecular surface areas.

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