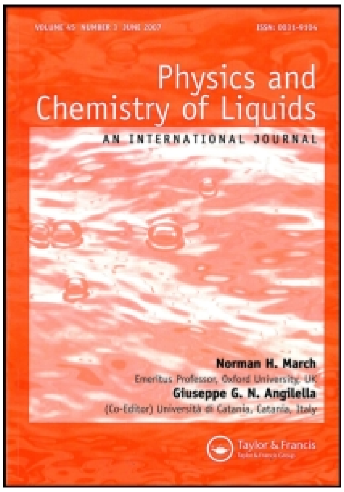

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Polycyclic Aromatic Sulfur Heterocycles. Solubility of Thianthrene in Binary Solvent Mixtures Containing Cyclohexane

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POLYCYCLIC AROMATIC SULFUR HETEROCYCLES. SOLUBILITY OF THIANTHRENE IN BINARY SOLVENT MIXTURES CONTAINING CYCLOHEXANE

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Experimental solubilities are reported for thianthrene in binary solvent mixtures containing cyclohexane with *n*-hexane, *n*-heptane, *n*-octane, methylcyclohexane, cyclooctane and isooctane at 25°C. Results of these measurements are used to test three predictive expressions derived from the Nearly Ideal Binary Solvent (NIBS) model. All three predictive expressions provided very reasonable estimates of the thianthrene solubilities. Deviations between calculated and observed values were less than 4 % for most of the mixtures studied.

INTRODUCTION

Polycyclic aromatic sulfur heterocycles (PASHs) are found in coal liquids, coal tars and heavy crude oil feedstocks derived from fossil fuels. There is a growing interest in the petroleum industry to develop methods for characterizing and removing the various sulfur heterocycles, particularly in light of the health risks posed by PASH compounds. Many of the different isomers are suspected mutagens/carcinogens, and several PASHs are known to be more toxic and to exhibit greater aquatic bioaccumulation than their polycyclic aromatic hydrocarbon counterparts. Removal of sulfur compounds from coals and oil products is also important from processing and environmental standpoints. Large PASHs poison catalysts used in desulfurization and catalytic cracking processes, and their combustion produces sulfur dioxide along with other sulfur-containing pollutants.

Design of efficient processes for the removal of organo-sulfur compounds from coal tars and crude oils requires that thermodynamic and physical property data bases be readily available for design calculations. Unfortunately, very little experimental data has been published on PASH compounds. Even group contribution methods, such as UNIFAC[1–4] and DISQUAC,[5–8] are of limited use for predicting desired liquid-vapor, liquid-liquid and solid-liquid equilibrium properties. The inputted group

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contribution parameters cannot be evaluated from the existing data bases. Development of group contribution methods for predicting thermodynamic properties of binary and higher-order multicomponent mixtures from molecular structure requires large data bases with all functional groups being adequately represented. For this reason, we have initiated a study to measure solubilities of solid PASH solutes in binary solvent mixtures. In this paper we report thianthrene solubilities in binary solvent mixtures containing cyclohexane with *n*-hexane, *n*-heptane, *n*-octane, methylcyclohexane, isooctane and cyclooctane. Results of these measurements are compared to predictions based on the Nearly Ideal Binary Solvent (NIBS) model.

MATERIALS AND METHODS

Thianthrene (Aldrich, 99 + %) was recrystallized three times from absolute ethanol, giving a melting point temperature of 159.2 ± 0.5°C (literature value of 158–159°C[9]). Cyclohexane (Aldrich, HPLC), *n*-heptane (Aldrich, HPLC), methylcyclohexane (Aldrich, 99 + % anhydrous), *n*-hexane (Aldrich, 99 %), isooctane (Aldrich, HPLC), *n*-octane (Aldrich, 99 + % anhydrous) and cyclooctane (Aldrich, 99 + %) were stored over molecular sieves to remove trace amounts of water and distilled shortly before use. 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 thianthrene and the 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 pre-equilibrating 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 255 nm (molar absorptivity of about 3.6×10^4 liter mol^{-1} cm^{-1}) on a Bausch and Lomb Spectronic 2000. Experimental solubilities are listed in Table 1. Numerical values represent the average of 4–8 determinations, with the measurement being reproducible to ± 1 %.

RESULTS AND DISCUSSION

The general NIBS expressions for predicting solubilities in systems of nonspecific interactions depend on two different models of ideality:[10–14]

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

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

Table 1 Comparison between experimental thianthrene solubilities and values calculated from the NIBS equations.

Solvent (B) + Solvent (C)	X_B°	X_A^{sat}	*Dev (%) of calcd values*[a]			$\Delta\bar{G}_{BC}^{ex}$
			(1)	*(2)*	*(3)*	*Ref.*
n-Hexane + Cyclohexane	0.0000	0.00587	—	—	—	18
	0.1754	0.00543	−0.3	−1.3	−1.0	
	0.3094	0.00505	−0.2	−1.7	−1.4	
	0.4494	0.00464	−0.1	−2.4	−2.1	
	0.5538	0.00432	+0.5	−1.4	−1.2	
	0.7567	0.00380	−0.2	−1.7	−1.5	
	0.8677	0.00351	+0.2	−0.7	−0.7	
	1.0000	0.00320	—	—	—	
n-Heptane + Cyclohexane	0.0000	0.00587	—	—	—	19
	0.1593	0.00550	−0.4	−2.5	−2.1	
	0.3263	0.00508	−0.3	−3.5	−3.1	
	0.4260	0.00485	−0.5	−3.9	−3.6	
	0.5284	0.00455	+0.4	−3.1	−2.7	
	0.7478	0.00400	+1.1	−1.5	−1.3	
	0.8658	0.00375	+0.6	−1.0	−0.9	
	1.0000	0.00346	—	—	—	
n-Octane + Cyclohexane	0.0000	0.00587	—	—	—	20
	0.1444	0.00552	+1.3	−0.9	−0.4	
	0.3019	0.00517	+2.5	−1.0	−0.5	
	0.4010	0.00498	+2.5	−1.3	−0.8	
	0.5006	0.00478	+2.7	−1.1	−0.7	
	0.6683	0.00447	+2.6	−0.7	−0.4	
	0.7228	0.00439	+2.1	−0.9	−0.7	
	0.8528	0.00416	+1.5	−0.3	−0.2	
	1.0000	0.00392	—	—	—	
Methylcyclohexane + Cyclohexane	0.0000	0.00587	—	—	—	21
	0.1789	0.00591	+0.7	+0.8	+1.1	
	0.3552	0.00601	+0.5	+0.7	+1.0	
	0.4599	0.00610	−0.2	+0.1	+0.5	
	0.5625	0.00616	−0.5	−0.2	0.0	
	0.7633	0.00623	−0.2	0.0	+0.1	
	0.8816	0.00626	+0.1	+0.2	+0.3	
	1.0000	0.00631	—	—	—	
Cyclooctane + Cyclohexane	0.0000	0.00587	—	—	—	22
	0.1705	0.00701	−4.5	−2.0	−1.7	
	0.3522	0.00815	−5.8	−1.8	−1.5	
	0.4506	0.00881	−6.1	−1.9	−1.6	
	0.5564	0.00950	−5.8	−1.7	−1.4	
	0.6318	0.00994	−4.8	−1.0	−0.8	
	0.7568	0.01080	−4.1	−1.1	−1.0	
	0.8455	0.01133	−2.5	−0.5	−0.4	
	1.0000	0.01232	—	—	—	
Isooctane + Cyclohexane	0.0000	0.00587	—	—	—	23
	0.1472	0.00516	+2.8	−1.8	−1.3	
	0.3035	0.00452	+4.4	−2.6	−2.1	
	0.3973	0.00420	+4.9	−2.9	−2.4	
	0.4961	0.00391	+4.6	−3.3	−2.9	
	0.6314	0.00353	+4.3	−2.9	−2.4	
	0.7157	0.00332	+3.8	−2.1	−1.8	
	0.8528	0.00301	+2.5	−1.1	−0.9	
	1.0000	0.00273	—	—	—	

[a] Deviations (%) = 100 ln (X_A^{calcd}/X_A^{exp}).

and

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

Equations (1) and (2) are based on Raoult's law and Eq. (3) is based on the Flory-Huggins model for the combinatorial entropic contribution. In the above three 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 refers to volume fraction. Binary solvent properties $\Delta\bar{G}_{BC}^{\text{ex}}$ and $\Delta\bar{G}_{BC}^{\text{fh}}$ denote 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 $(\Delta\bar{G}_A^{\text{ex}})_i^*$ and $(\Delta\bar{G}_A^{\text{fh}})_i^*$. These quantities are then combined with the free energy of the binary solvent mixture to predict solubility in mixed solvents.

Comparison between experimental and predicted thianthrene solubilities are shown in the last three columns of Table 1 for the six binary solvent systems studied. Properties used in the calculations include $\bar{V}_A = 156$ cm^3/mole, based on estimated molar volumes for anthracene ($\bar{V}_A = 150$ cm^3/mole[15]) and dibenzothiophene ($\bar{V}_A = 148.50$ cm^3/mole[16]), and the activity of the solute, $a_A^{\text{solid}} = 0.04411$, calculated from

$$\ln a_A^{\text{solid}} = -\frac{\Delta\bar{H}_A^{\text{fus}}\left(T_{\text{mp}} - T\right)}{RT\,T_{\text{mp}}} \quad (4)$$

the molar enthalpy of fusion, $\Delta\bar{H}_A^{\text{fus}} = 25.44$ kJ/mole[17], at the normal melting point temperature of the solute, $T_{\text{mp}} = 428.4$ K. For the systems used in this investigation, the NIBS predictions are not very sensitive to the solute's molar volume. A 10 % error in the numerical value of $\bar{V}_A$ affects the predicted thianthrene solubilities by less than 2 %. Solvent properties used in the calculations are tabulated in Table 2.

Examination of Table 1 reveals that all three NIBS expressions provide very reasonable estimates for the solubility of thianthrene in binary cyclohexane + alkane solvent mixtures. For the most part, the predicted and observed values differ by less than 4 %. Readers are reminded that three measured values are needed for each NIBS prediction. Thianthrene solubility in each pure solvent was reproducible to within 1 %

Table 2 Solvent properties used in the NIBS predictions.

Component	$\bar{V}_i$ *(cm^3/mole)*
n-Hexane	131.51
n-Heptane	147.48
n-Octane	163.46
Methylcyclohexane	128.32
Isooctane	166.09
Cyclooctane	134.88
Cyclohexane	108.76

and $\Delta\bar{G}_{BC}^{ex}$ values taken from the literature are believed to be accurate to at least 6 cal/mole. A 6 cal/mole error in the $\Delta\bar{G}_{BC}^{ex}$ or $\Delta\bar{G}_{BC}^{fh}$ term 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 is comparable to observed deviations between the experimental and predicted thianthrene solubilities from Eqs (1)–(3).

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