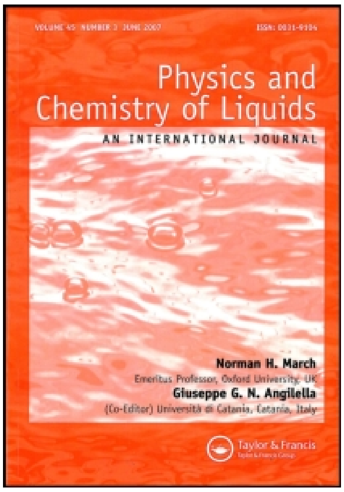

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Polycyclic Aromatic Nitrogen Heterocycles. Solubility of Carbazole in Binary Solvent Mixtures Containing Cyclohexane

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POLYCYCLIC AROMATIC NITROGEN HETEROCYCLES. SOLUBILITY OF CARBAZOLE IN BINARY SOLVENT MIXTURES CONTAINING CYCLOHEXANE

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Experimental solubilities are reported for carbazole 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 carbazole solubilities. Deviations between calculated and observed values were less than 3% for most of the mixtures studied.

KEY WORDS: Binary solvent mixtures, activity, carbazole solubilities.

INTRODUCTION

Most fossil fuels contain some sulfur and nitrogen, the latter believed to be present exclusively in the organic portion of the crude materials. Jewell and Hartung[1] tentatively identified hydroxyhexahydrocarbazoles and hydroxyindolines in hydrogenated furnace oil *via* combined gas–liquid chromatographic, UV spectrophotometric and mass spectrometric methods. More recently, Bodzek and Marzec[2] extracted a high-volatile bituminous coal with various organic solvents, and reported high-resolution mass spectrometric data consistent with hydroxyquinolines, hydroxycarbazoles, hydroxyacridines and hydroxyazapyrenes. While nitrogen levels generally vary from approximately 0.5% in crude petroleum samples to 1–2% in shale oils and coal, there is a growing interest in the petroleum industry to develop methods for characterizing and removing the various polycyclic aromatic nitrogen heterocycles (PANHs) because of their association with color, odor, corrosive power and the formation of gums and deposits during storage.[3] PANHs deactivate catalysts during the cracking and re-forming process,[4] and numerous basic nitrogen-containing substances are toxic. Several azaarenes and primary aromatic amines are reported to be tumorigenic in experimental animals,[5–7] and other neutral nitrogen aromatics, such as dibenzocarbazoles, showed carcinogenic activity.[8]

Design of efficient processes for the removal of organo-nitrogen 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 PANH compounds. Even group contribution methods, such as UNIFAC[9–12] and DISQUAC[13–16] are of limited use for predicting desired liquid–vapor, liquid–liquid and solid–liquid equilibrium properties. The inputted group 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, I have initiated a study to measure solubilities of solid PANH solutes in binary solvent mixtures. In this paper I report carbazole solubilities in binary solvent mixtures containing cyclohexane with *n*-hexane, *n*-heptane, *n*-octane, methylcyclohexane, cyclooctane and isooctane. Results of these measurements are compared to predictions based on the Nearly Ideal Binary Solvent (NIBS) model.

MATERIALS AND METHODS

Carbazole (Aldrich 99%) was recrystallized several times from absolute ethanol, giving a melting point of 246.5 ± 0.5°C (literature value 247–248°C[17]). Cyclohexane (Aldrich HPLC grade), *n*-hexane (Aldrich 99%), *n*-heptane (Aldrich HPLC grade), *n*-octane (Aldrich 99% anhydrous), methylcyclohexane (Aldrich 99+% anhydrous) cyclooctane (Aldrich Gold Label) and isooctane (Aldrich HPLC grade) were stored over molecular sieves (Type 4A) to remove trace amounts of water. Binary solvent

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

Solvent (B) + Solvent (C)			*Dev (%) of calcd values*[a]			$\Delta\bar{G}_{BC}^{ex}$
	X_B^0	X_A^{sat}	*Eq.(1)*	*Eq.(2)*	*Eq.(3)*	*Ref.*
Cyclohexane + *n*-Hexane	0.0000	0.000139	—	—	—	25
	0.1316	0.000147	−0.5	−0.9	−0.8	
	0.2887	0.000154	0.5	−0.1	0.0	
	0.3942	0.000161	−0.5	−1.0	−0.9	
	0.4631	0.000165	−0.8	−1.2	−1.2	
	0.6030	0.000171	−0.4	−0.6	−0.5	
	0.7289	0.000176	−0.2	−0.3	−0.2	
	0.8724	0.000181	−0.3	−0.3	−0.2	
	1.0000	0.000183	—	—	—	
Cyclohexane + *n*-Heptane	0.0000	0.000173	—	—	—	26
	0.1538	0.000178	−0.5	−0.6	−0.5	
	0.2877	0.000180	0.0	−0.1	0.1	
	0.4165	0.000182	0.1	0.1	0.3	
	0.5381	0.000185	−0.8	−0.8	−0.5	
	0.6574	0.000186	−1.0	−0.8	−0.5	
	0.7619	0.000184	0.2	0.4	0.6	
	0.8738	0.000184	0.0	0.2	0.4	
	1.0000	0.000183	—	—	—	

(*continued*)

Table 1 (*Continued*)

Solvent (B) + Solvent (C)			*Dev (%) of calcd values*[a]			$\Delta\bar{G}^{ex}_{BC}$
	X^0_B	X^{sat}_A	*Eq.(1)*	*Eq.(2)*	*Eq.(3)*	*Ref.*
Cyclohexane + *n*-Octane	0.0000	0.000198	—	—	—	27
	0.1449	0.000200	−0.7	−0.4	−0.3	
	0.2861	0.000201	−1.5	−0.9	−0.7	
	0.4315	0.000198	−0.9	0.0	0.3	
	0.5637	0.000194	−0.1	1.0	1.3	
	0.6890	0.000192	−0.4	0.7	1.0	
	0.7732	0.000190	−0.4	0.5	0.8	
	0.8826	0.000187	−0.4	0.3	0.5	
	1.0000	0.000183	—	—	—	
Cyclohexane + Methylcyclohexane	0.0000	0.000196	—	—	—	28
	0.1463	0.000195	−0.3	−0.2	−0.2	
	0.2738	0.000193	−0.1	0.2	0.2	
	0.4366	0.000191	−0.1	0.3	0.4	
	0.5744	0.000189	0.0	0.4	0.5	
	0.6903	0.000188	−0.3	0.1	0.2	
	0.7639	0.000187	−0.3	0.0	0.0	
	0.8576	0.000185	0.1	0.3	0.3	
	1.0000	0.000183	—	—	—	
Cyclohexane + Cyclooctane	0.0000	0.000309	—	—	—	29
	0.1715	0.000289	−1.7	−0.1	0.0	
	0.2948	0.000274	−2.6	−0.2	−0.1	
	0.4369	0.000256	−3.1	−0.1	0.0	
	0.5671	0.000241	−3.8	−0.7	−0.6	
	0.6839	0.000226	−3.6	−0.8	−0.7	
	0.7605	0.000213	−1.8	0.5	0.7	
	0.8760	0.000198	−0.9	0.6	0.7	
	1.0000	0.000183	—	—	—	
Cyclohexane + Isooctane	0.0000	0.000126	—	—	—	30
	0.1478	0.000133	1.0	−0.8	−0.8	
	0.2743	0.000140	1.3	−1.5	−1.4	
	0.3768	0.000145	1.9	−1.5	−1.4	
	0.5069	0.000152	2.1	−1.6	−1.4	
	0.6029	0.000158	1.8	−1.8	−1.5	
	0.7065	0.000164	1.7	−1.5	−1.2	
	0.8537	0.000173	1.3	−0.6	−0.4	
	1.0000	0.000183	—	—	—	

Deviations (%) = 100 $\ln(X^{calcd}_A/X^{exp}_A)$.

mixtures were prepared by weight so that solvent compositions could be calculated to 0.0001 mole fraction.

Excess carbazole 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. The attainment of equilibrium was verified by repetitive measurements after several additional days and in some cases by approaching equilibrium from supersaturation by pre-equilibrating the solution at a higher temperature. Aliquots of saturated carbazole solutions were transferred through a course filter into a tared volumetric flask to determine the amount of sample and diluted quantitatively with methanol. Concentrations were determined spectrophotometrically at 292 nm on a Bausch and Lomb Spectronic 2000. Experimental solubilities of carbazole in the six binary solvent systems studied are listed in Table 1. Numerical values represent the average of between 6 and 8 independent determinations, with the measurements being reproducible to better than ±1%. In pure isooctane the measured carbazole solubility is in excellent agreement with a previously reported value of $X_A^{\text{sat}} = 0.000128$.[18]

RESULTS AND DISCUSSION

The general NIBS expressions for predicting solubilities in systems of nonspecific interactions depend on two different models of ideality:[19–23]

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

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

and

$$\begin{aligned} RT\left[\ln(a_A^{\text{solid}}/\phi_A^{\text{sat}}) - (1 - \phi_A^{\text{sat}})\left(1 - \frac{\bar{V}_A}{X_C^0\bar{V}_C + X_B^0\bar{V}_B}\right)\right] \\ = (1 - \phi_A^{\text{sat}})^2[\phi_B^0(\Delta\bar{G}_A^{\text{fh}})_B^* + \phi_C^0(\Delta\bar{G}_A^{\text{fh}})_C^* - \bar{V}_A(X_B^0\bar{V}_B + X_C^0\bar{V}_C)^{-1}\Delta\bar{G}_{BC}^{\text{fh}}] \end{aligned} \tag{3}$$

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, ϕ_i denotes volume fraction and $\bar{V}_i$ is the molar volume of pure component i. 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 carbazole solubilities are shown in the last three columns of Table 1 for the six binary solvent systems studied. Properties used in the calculations include $\bar{V}_A = 150$ cm^3/mole[18] and the activity of the solute, $a_A^{\text{solid}} = 0.009354$, which was calculated from

$$\ln a_A^{\text{solid}} = -\frac{\Delta\bar{H}_A^{\text{fus}}(T_{\text{mp}} - T)}{RTT_{\text{mp}}} \tag{4}$$

the molar enthalpy of fusion, $\Delta\bar{H}_A^{\text{fus}} = 27.20$ kJ/mole,[24] at the normal melting point temperature of the solute, $T_{\text{mp}} = 519.2$ K. For the systems used in this investigation, the NIBS predictions are not very sensitive to the solute's activity or molar volume. Calculational errors incurred by assuming that $\Delta\bar{H}_A^{\text{fus}}$ is independent of temperature

Table 2 Solvent properties used in the NIBS predictions.

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

are negligible since it is possible to mathematically eliminate a_A^{solid} from the NIBS predictive expressions, provided that the solute is sufficiently insoluble so that both $(1 - X_A^{\text{sat}})^2 = 1$ and $(1 - \phi_A^{\text{sat}})^2 = 1$ as is the case with carbazole. Remember a_A^{solid} is used in computing numerical values of $(\Delta\bar{G}_A^{\text{ex}})_i^*$ and $(\Delta\bar{G}_A^{\text{fh}})_i^*$. Similarly, a 10% error in the numerical value of $\bar{V}_A$ affects the predicted carbazole 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 carbazole in binary cyclohexane + alkane solvent mixtures. For the most part, the predicted and observed values differ by less than 3%. Readers are reminded that three measured values are needed for each NIBS prediction. Carbazole solubility in each pure solvent was reproducible to within 1% and $\Delta\bar{G}_{BC}^{\text{ex}}$ values taken from the literature are believed to be accurate to at least 24 J/mole. A 24 J/mole error in the $\Delta\bar{G}_{BC}^{\text{ex}}$ (or $\Delta\bar{G}_{BC}^{\text{fh}}$) 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 corresponds to observed deviations between the experimental and predicted carbazole solubilities from Eqs. (1)–(3).

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