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Solubility in Binary Solvent Mixtures: Anthracene Dissolved in Alcohol + 2-Methyl-1-butanol Mixtures at 298.2 K

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Experimental solubilities are reported for anthracene dissolved in seven binary alcohol + 2-methyl-1-butanol solvent mixtures at 25 °C. The alcohol cosolvents studied were 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 3-methyl-1-butanol, and 2-pentanol. Results of these measurements are used to test a mathematical representation based upon the combined nearly ideal binary solvent (NIBS)/ Redlich−Kister equation. For the seven systems studied, the combined NIBS/Redlich−Kister equation was found to mathematically describe the experimental data to within an overall average absolute deviation of approximately ±0.4%.

Introduction

Solid−liquid equilibrium data of organic nonelectrolyte systems are becoming increasingly important in the petroleum industry, particularly in light of present trends toward heavier feedstocks and known carcinogenicity/ mutagenicity of many of the larger polycyclic aromatic compounds. Solubility data for a number of polycyclic aromatic hydrocarbons (i.e., anthracene and pyrene) and heteroatom polynuclear aromatics (i.e., carbazole, dibenzothiophene, and xanthene) have been published in the recent chemical literature (for a listing of references, see refs 1−3). Despite efforts by experimentalists and scientific organizations, both in terms of new experimental measurements and critically evaluated data compilations, it is not feasible to experimentally measure solubilities in every possible binary and ternary solvent mixture that might be encountered in pharmaceutical and engineering applications.

Recognizing this fact, researchers have turned to predictive methods as a means to generate desired quantities. Numerous equations have been suggested for predicting solute solubilities in binary solvent mixtures. For the most part, the predictive methods do provide fairly reasonable estimates for noncomplexing systems. There still remains, however, the need to develop better predictive expressions and mixing models to describe the more nonideal complexing systems believed to contain hydrogen bonding solvent components. Continued development of solution models for describing the thermodynamic properties of a solute in binary solvent systems requires that a large database be available for assessing the applications and limitations of derived expressions. Currently, only a limited database exists for crystalline nonelectrolyte solubility in binary solvent mixtures. For this reason, anthracene solubilities were determined in seven binary alcohol + 2-methyl-1-butanol solvent mixtures. Results of these measurements are used to further test the descriptive ability of the combined nearly ideal binary solvent (NIBS)/Redlich−Kister equation.

Experimental Methods

Anthracene (Aldrich, 99%) was recrystallized three times from acetone. 1-Propanol (Aldrich, 99+%, anhydrous), 2-propanol (Aldrich, 99+%, anhydrous), 1-butanol (Aldrich, HPLC, 99.8+%), 2-butanol (Aldrich, 99+%, anhydrous), 2-methyl-1-propanol (Aldrich, 99.5%, anhydrous), 3-methyl-1-butanol (Aldrich, 99+%, anhydrous), 2-pentanol (Acros, 99+%), and 2-methyl-1-butanol (Aldrich, 99+%) were stored over molecular sieves and distilled shortly before use. Gas chromatographic analysis showed solvent purities to be 99.7 mol % or better. Binary solvent mixtures were prepared by mass 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 water bath at (25.0 ± 0.1) °C with periodic shaking for at least 3 days (often longer). Attainment of equilibrium was verified both by repetitive measurements after a minimum of 3 additional days and by approaching equilibrium from supersaturation by pre-equilibrating the solutions 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 for spectrophotometric analysis at 356 nm on a Bausch and Lomb Spectronic 2000. Concentrations of the dilute solutions were determined from a Beer−Lambert law absorbance versus concentration working curve derived from measured absorbances of standard solutions of known molar concentrations. Apparent molar absorptivities, ϵ, of the nine standard solutions varied systematically with molar concentration and ranged from approximately $\epsilon/(\text{L mol}^{-1}\text{ cm}^{-1}) = 7450$ to $\epsilon/(\text{L mol}^{-1}\text{ cm}^{-1}) = 7150$ for anthracene concentrations ranging from $C/M = 6.75 \times 10^{-5}$ to $C/M = 2.25 \times 10^{-4}$. Identical molar absorptivities were obtained for select anthracene standard solutions that contained up to 5 vol % of the neat alcohol cosolvents. Experimental anthracene solubilities in the seven binary alcohol + 2-methyl-1-butanol solvent mixtures are listed in Table 1. Numerical values represent the average of between four and eight independent determinations, with the measured values being reproducible to within ±1.0%.

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Table 1. Experimental Mole Fraction Solubilities of Anthracene (x_A^{sat}) in Binary Alcohol (B) + 2-Methyl-1-butanol (C) Solvent Mixtures at 25.0 °C

x_C°	x_A^{sat}	x_C°	x_A^{sat}
1-Propanol + 2-Methyl-1-butanol			
0.0000	0.000 591	0.5214	0.000 689
0.0901	0.000 623	0.7294	0.000 715
0.1537	0.000 646	0.8209	0.000 742
0.3090	0.000 666	1.0000	0.000 786
0.4030	0.000 679		
2-Propanol + 2-Methyl-1-butanol			
0.0000	0.000 411	0.5216	0.000 601
0.0931	0.000 467	0.7443	0.000 662
0.1659	0.000 491	0.8572	0.000 701
0.3264	0.000 545	1.0000	0.000 786
0.4298	0.000 576		
1-Butanol + 2-Methyl-1-butanol			
0.0000	0.000 801	0.5861	0.000 793
0.0885	0.000 801	0.7789	0.000 791
0.1869	0.000 803	0.8742	0.000 789
0.3816	0.000 795	1.0000	0.000 786
0.4621	0.000 795		
2-Butanol + 2-Methyl-1-butanol			
0.0000	0.000 585	0.5584	0.000 683
0.0862	0.000 618	0.7708	0.000 709
0.1784	0.000 637	0.8895	0.000 730
0.3684	0.000 659	1.0000	0.000 786
0.4613	0.000 667		
2-Methyl-1-propanol + 2-Methyl-1-butanol			
0.0000	0.000 470	0.5616	0.000 617
0.1074	0.000 512	0.7692	0.000 673
0.1916	0.000 541	0.8860	0.000 714
0.3689	0.000 574	1.0000	0.000 786
0.4513	0.000 593		
3-Methyl-1-butanol + 2-Methyl-1-butanol			
0.0000	0.000 727	0.6169	0.000 756
0.1215	0.000 733	0.7935	0.000 766
0.2037	0.000 739	0.8880	0.000 775
0.3955	0.000 743	1.0000	0.000 786
0.5057	0.000 748		
2-Pentanol + 2-Methyl-1-butanol			
0.0000	0.000 800	0.6114	0.000 792
0.1032	0.000 808	0.7899	0.000 790
0.2144	0.000 800	0.9010	0.000 789
0.4011	0.000 795	1.0000	0.000 786
0.5105	0.000 795		

Results and Discussion

Acree and co-workers[4−6] suggested the combined NIBS/Redlich−Kister model

$$\ln x_A^{sat} = x_B^\circ \ln(x_A^{sat})_B + x_C^\circ \ln(x_A^{sat})_C + x_B^\circ x_C^\circ \sum_{i=0}^{N} S_i (x_B^\circ - x_C^\circ)^i \tag{1}$$

as a possible mathematical representation for describing how the experimental isothermal solubility of a crystalline solute dissolved in a binary solvent mixture varies with binary solvent composition. In eq 1 x_B° and x_C° refer to the initial mole fraction composition of the binary solvent calculated as if solute (A) were not present, N is the number of curve-fit parameters used, and $(x_A^{sat})_i$ is the saturated mole fraction solubility of the solute in pure solvent i. The various S_i "curve-fit" parameters can be evaluated via least-squares analysis as discussed elsewhere.[7]

The combined NIBS/Redlich−Kister equation has been shown to provide very accurate mathematical representations of anthracene, pyrene, and carbazole solubilities in a large number of both complexing and noncomplexing solvent mixtures.[1−3] Jouyban-Gharamaleki and co-workers[8−11] successfully used the volume fraction, ϕ_i, modification of eq 1

$$\ln x_A^{sat} = \phi_B^\circ \ln(x_A^{sat})_B + \phi_C^\circ \ln(x_A^{sat})_C + \phi_B^\circ \phi_C^\circ \sum_{i=0}^{N} S_i (\phi_B^\circ - \phi_C^\circ)^i \tag{2}$$

to describe the solubility behavior of various drug molecules in binary aqueous−organic solvent mixtures. In the pharmaceutical industry, researchers often express the solvent composition in terms of volume fractions, rather than in terms of mole fractions. In the case of structurally similar drug molecules, the numerical values of the S_i coefficients were found to be nearly constant in a given binary solvent mixture.[11] More recently, Deng et al.[12−14] and Pribyla et al.[15−17] have shown that the S_i coefficients determined by regressing experimental anthracene data in binary alkane + alkane, alkane + alcohol, alcohol + alcohol, alcohol + ether, and alkane + ether solvent mixtures allow one to predict anthracene solubilities in ternary alkane + alkane + alcohol, alkane + alcohol + alcohol, and alkane + alcohol + ether solvent mixtures. The predictive expression for the ternary solvent mixture is

$$\ln x_A^{sat} = x_B^\circ \ln(x_A^{sat})_B + x_C^\circ \ln(x_A^{sat})_C + x_D^\circ \ln(x_A^{sat})_D + x_B^\circ x_C^\circ \sum_{i=0}^{r} S_{i,BC}(x_B^\circ - x_C^\circ)^i + x_B^\circ x_D^\circ \sum_{j=0}^{S} S_{j,BD}(x_B^\circ - x_D^\circ)^j + x_C^\circ x_D^\circ \sum_{k=0}^{t} S_{k,CD}(x_C^\circ - x_D^\circ)^k \tag{3}$$

a mole fraction average of the logarithmic solute solubilities in the three pure solvents [$(x_A^{sat})_B$, $(x_A^{sat})_C$, and $(x_A^{sat})_D$] plus a Redlich−Kister summation term for each solvent pair. The documented success[11−16] of eq 3 in predicting anthracene solubilities in more than 60 different ternary solvent systems illustrates the need for measured solute solubilities in binary solvent mixtures.

In the chemical and pharmaceutical literature, different mathematical expressions can be found for describing how the measured solute solubility varies with binary solvent composition (see refs 8−11). For many of the published mathematical representations the equations are limited to binary solvent systems. The calculated equation coefficients cannot be used to predict the solubility of the solute in ternary solvent mixtures. This is not the case with the combined NIBS/Redlich−Kister equation. Equation coefficients determined by curve-fitting the measured solute solubility data in accordance with eq 1 can be used to predict solubilities in ternary solvent mixtures through eq 3. It is hoped that as additional solubility data become available for solutes dissolved in ternary solvent mixtures, researchers will apply many of the previously published equations for describing solute solubilities in binary solvent systems to ternary and higher-order multicomponent solvent systems.

The ability of eq 1 to mathematically represent the experimental solubility of anthracene in the seven binary alcohol + 2-methyl-1-butanol mixtures is summarized in Table 2 in the form of "curve-fit" parameters, that were obtained by regressing the measured mole fraction solubility data (see Table 1) in accordance with eq 1, and the percent deviations in back-calculated solubilities. Two of the binary solvent systems, 1-butanol + 2-methyl-1-butanol and 2-pentanol + 2-methyl-1-butanol, did not require any curve-fit parameters. Each percent deviation is based upon the measured anthracene solubility data at the seven different binary solvent compositions. Careful examination

Table 2. Mathematical Representation of Anthracene Solubilities in Several Binary Alcohol (B) + 2-Methyl-1-butanol (C) Solvent Mixtures by Eq 1

binary solvent system (B + C)	eq 1 S_i[a]	 % dev[b]
1-propanol + 2-methyl-1-butanol	0.031	0.3
	0.267	
	0.174	
2-propanol + 2-methyl-1-butanol	0.154	0.7
	0.509	
	0.162	
1-butanol + 2-methyl-1-butanol[c]		0.2
2-butanol + 2-methyl-1-butanol	−0.040	0.7
	0.433	
	0.021	
2-methyl-1-propanol + 2-methyl-1-butanol	−0.024	0.4
	0.423	
3-methyl-1-butanol + 2-methyl-1-butanol	−0.034	0.2
	0.035	
2-pentanol + 2-methyl-1-butanol[c]		0.4

[a] The combined NIBS/Redlich−Kister curve-fit parameters are ordered as S_0, S_1, and S_2. [b] Deviation (%) = $(100/N)\sum|[(x_A^{sat})^{calc} - (x_A^{sat})^{exp}]/(x_A^{sat})^{exp}|$. [c] Equation 1 accurately described the measured anthracene solubility data without the use of curve-fit parameters.

of Table 2 reveals that eq 1 provided a fairly accurate mathematical representation for how the solubility of anthracene varies with solvent composition. Deviations between the experimental mole fraction solubilities and back-calculated values based upon eq 1 differed by an overall average absolute deviation of about ±0.4%.

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