Solubility in Binary Solvent Mixtures: Pyrene Dissolved in Alcohol + Acetonitrile Mixtures at 299.2 K

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Experimental solubilities are reported for pyrene dissolved in seven binary alcohol + acetonitrile solvent mixtures at 26 °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 ±1.0%.

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 Acree[1−3]). Despite efforts by experimentalists and scientific organizations, in terms of both new experimental measurements and critically evaluated data compilations, there still exist numerous systems for which solubility data are not readily available.

To address this problem, 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, pyrene solubilities were determined in seven binary alcohol + acetonitrile 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. This marks the first time that we have used acetonitrile as a binary cosolvent in our pyrene solubility studies.

Experimental Methods

Pyrene (Aldrich, 98%) was recrystallized three times from anhydrous methanol. 1-Propanol (Aldrich, 99.9+%, 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 acetonitrile (Aldrich, 99.8%, anhydrous) 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 (26.0 ± 0.1) °C with periodic agitation 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 pyrene 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 372 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 of the nine standard solutions varied systematically with molar concentration and ranged from approximately $\epsilon/(\mathrm{L\ mol^{-1}\ cm^{-1}}) = 237$ to $\epsilon/(\mathrm{L\ mol^{-1}\ cm^{-1}}) = 220$ for pyrene concentrations ranging from $C/\mathrm{M} = 8.31 \times 10^{-4}$ to $C/\mathrm{M} = 4.15 \times 10^{-3}$. Identical molar absorptivities were obtained for select pyrene standard solutions that contained up to 5 vol % of the neat alcohol and acetonitrile cosolvents. Experimental pyrene solubilities in the seven binary alcohol + acetonitrile 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 ±1.5%.

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Table 1. Experimental Mole Fraction Solubilities of Pyrene (x_A^{sat}) in Binary Alcohol (B) + Acetonitrile (C) Solvent Mixtures at 26.0 °C

x_C^0	x_A^{sat}	x_C^0	x_A^{sat}
1-Propanol + Acetonitrile		2-Methyl-1-propanol + Acetonitrile	
0.0000	0.004 26	0.0000	0.003 26
0.1499	0.007 02	0.1714	0.006 42
0.2732	0.008 65	0.3074	0.008 72
0.4927	0.009 90	0.5382	0.010 72
0.5924	0.009 84	0.6341	0.010 58
0.6906	0.009 29	0.7241	0.009 92
0.8323	0.007 94	0.8686	0.008 02
0.9245	0.006 89	0.9331	0.006 99
1.0000	0.006 14	1.0000	0.006 14
2-Propanol + Acetonitrile		3-Methyl-1-butanol + Acetonitrile	
0.0000	0.002 90	0.0000	0.005 46
0.1619	0.005 55	0.1981	0.009 95
0.2662	0.006 86	0.3709	0.012 23
0.4903	0.008 45	0.5829	0.012 96
0.5636	0.008 62	0.6600	0.012 55
0.6684	0.008 28	0.7605	0.011 32
0.8408	0.007 25	0.8929	0.008 49
0.9241	0.006 63	0.9461	0.007 34
1.0000	0.006 14	1.0000	0.006 14
1-Butanol + Acetonitrile		2-Pentanol + Acetonitrile	
0.0000	0.006 22	0.0000	0.006 40
0.1806	0.010 34	0.2222	0.012 74
0.3037	0.012 17	0.3733	0.015 17
0.5242	0.013 63	0.5690	0.015 84
0.6349	0.012 80	0.6652	0.014 95
0.7332	0.011 79	0.7626	0.012 83
0.8770	0.008 86	0.8900	0.009 25
0.9377	0.007 48	0.9494	0.007 51
1.0000	0.006 14	1.0000	0.006 14
2-Butanol + Acetonitrile			
0.0000	0.004 39		
0.1711	0.008 39		
0.3252	0.011 18		
0.5339	0.012 25		
0.6346	0.011 63		
0.7300	0.010 50		
0.8762	0.008 07		
0.9412	0.006 93		
1.0000	0.006 14		

Results and Discussion

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

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

as a possible mathematical representation for describing how experimental isothermal solubility of a crystalline solute dissolved in a binary solvent mixture varies with binary solvent composition. In eq 1, x_B^0 and x_C^0 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.

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[7−10] successfully used the volume fraction, ϕ_i, modification of eq 1,

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

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.[10] More recently, Deng et al.[11−13] and Pribyla et al.[14−16] 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

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

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 literature, different mathematical expressions can be found for describing how the measured solute solubility varies with binary solvent composition (see Jouyban-Gharamaleki and co-workers[7−10]). 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. Pyrene solubilities have been measured at 299.2 K, rather than 298.2 K, because all of our earlier solubility studies involving pyrene were performed at 299.2 K. The curve-fit coefficients of eq 1 will be used in subsequent solubility studies involving pyrene dissolved in ternary solvent systems.

The ability of eq 1 to mathematically represent the experimental solubility of pyrene in the seven binary alcohol + acetonitrile mixtures is summarized in Table 2 in the form of curve-fit parameters and percent deviations in back-calculated solubilities. Each percent deviation is based upon the measured pyrene solubility data at the seven different binary solvent compositions. Careful examination of Table 2 reveals that eq 1 provided a fairly accurate mathematical representation for how the solubility of pyrene varies with solvent composition. Deviations between the experimental mole fraction solubilities and back-calculated values based upon eq 1 differed by an

Table 2. Mathematical Representation of Pyrene Solubilities in Several Binary Alcohol (B) + Acetonitrile (C) Solvent Mixtures by Equation 1

binary solvent system component B + component C	eq 1	
	S_i[a]	% dev[b]
1-propanol + acetonitrile	2.698 0.860 0.217	1.0
2-propanol + acetonitrile	2.822 1.273 0.294	1.0
1-butanol + acetonitrile	3.158 0.062 0.515	0.8
2-butanol + acetonitrile	3.539 0.908 −0.088	1.1
2-methyl-1-propanol + acetonitrile	3.537 0.708 −0.136	1.0
3-methyl-1-butanol + acetonitrile	3.285 0.079 0.701	1.0
2-pentanol + acetonitrile	3.822 −0.011 0.476	1.0

[a] Combined NIBS/Redlich−Kister curve-fit parameters are ordered as S_0, S_1, and S_2. [b] Deviation (%) = $(100/N)\sum|[(x_A^{sat})^{calc} - (x_A^{sat})^{exp}]/(x_A^{sat})^{exp}|$.

overall average absolute deviation of about ±1.0%, which is less than the experimental uncertainty of ±1.5% based upon replicate measurements. Equation 1 correctly describes the maximum pyrene mole fraction solubility that is observed in each solubility versus acetonitrile composition curve. The solubility of pyrene passes through a maximum at approximately $x_C^0 = 0.5$.

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