

Solubility of Anthracene in Binary Alcohol + 3-Methoxy-1-butanol Solvent Mixtures

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Experimental solubilities are reported for anthracene dissolved in ten binary mixtures containing 3-methoxy-1-butanol with 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, 2-pentanol, 3-methyl-1-butanol, 4-methyl-2-pentanol, 1-octanol, and 2-ethyl-1-hexanol at 25 °C. Results of these measurements are used to test two mathematical representations based upon the combined nearly ideal binary solvent (NIBS)/Redlich–Kister equation and modified Wilson model. For the ten systems studied, both equations were found to provide an accurate mathematical representation of the experimental data, with an overall average absolute deviation between measured and calculated values being 0.4% and 0.5% for the combined NIBS/Redlich–Kister and modified Wilson equations, respectively.

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 listing of references see Acree, 1994, 1995a,b). 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 data base be available for assessing the applications and limitations of derived expressions. Currently, only a limited data base exists for crystalline nonelectrolyte solubility in binary solvent mixtures containing a multifunctional alcohol cosolvent. For this reason, anthracene solubilities were determined in ten binary alcohol + 3-methoxy-1-butanol solvent mixtures. Results of these measurements are used to further test the descriptive abilities of several previously derived expressions.

Experimental Methods

Anthracene (Acros, 99.9+%) was recrystallized several times from 2-propanone. 3-Methoxy-1-butanol (Aldrich

99+%), 1-propanol (Aldrich 99+%, anhydrous), 2-propanol (Aldrich 99+%, anhydrous), 1-butanol (Aldrich HPLC, 99.8+%), 2-butanol (Aldrich 99+%, anhydrous), 1-pentanol (Aldrich 99%), 2-ethyl-1-hexanol (Aldrich 99+%), 3-methyl-1-butanol (Aldrich 99+%, anhydrous), 1-octanol (Aldrich 99+%, anhydrous), 2-pentanol (Acros 99+%), and 4-methyl-2-pentanol (Acros 99+%) were stored over both anhydrous sodium sulfate and molecular sieves before use. Gas chromatographic analysis showed solvent purities to be 99.7 mol % or better. Karl Fischer titration gave water contents (mass/mass %) of <0.01% for all eleven alcohols used. 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 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 concentration. Molar absorptivities of the nine standard solutions varied systematically with molar concentration and ranged from approximately $\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1} = 7450$ to $\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1} = 7150$ for anthracene concentrations ranging from $C/\text{mol L}^{-1} = 6.75 \times 10^{-5}$ to $C/\text{mol L}^{-1} = 2.25 \times 10^{-4}$. Experimental anthracene solubilities in the ten binary alcohol + 3-methoxy-1-butanol mixtures studied 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 $\pm 1.5\%$.

Results and Discussion

Acree and co-workers (Acree and Zvaigzne, 1991; Acree *et al.*, 1991; Acree 1992) suggested possible mathematical

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Table 1. Experimental Mole Fraction Solubilities of Anthracene (x_A^{sat}) in Binary Alcohol (B) + 3-Methoxy-1-butanol (C) Solvent Mixtures at 25.0 °C

x_C^0	x_A^{sat}	x_C^0	x_A^{sat}
1-Propanol (B) + 3-Methoxy-1-butanol (C)			
0.0000	0.000 591	0.4442	0.001 483
0.0756	0.000 724	0.7246	0.002 092
0.1453	0.000 859	0.8578	0.002 382
0.3091	0.001 200	1.0000	0.002 702
0.3996	0.001 389		
2-Propanol (B) + 3-Methoxy-1-butanol (C)			
0.0000	0.000 411	0.5119	0.001 529
0.0792	0.000 570	0.7182	0.002 059
0.1492	0.000 705	0.8687	0.002 408
0.3079	0.001 053	1.0000	0.002 702
0.3921	0.001 258		
1-Butanol (B) + 3-Methoxy-1-butanol (C)			
0.0000	0.000 801	0.5384	0.001 806
0.0869	0.000 955	0.7641	0.002 220
0.1708	0.001 113	0.8660	0.002 424
0.3534	0.001 474	1.0000	0.002 702
0.4257	0.001 596		
2-Butanol (B) + 3-Methoxy-1-butanol (C)			
0.0000	0.000 585	0.5787	0.001 745
0.0900	0.000 748	0.7583	0.002 143
0.1763	0.000 912	0.8621	0.002 345
0.3518	0.001 276	1.0000	0.002 702
0.4653	0.001 503		
1-Pentanol (B) + 3-Methoxy-1-butanol (C)			
0.0000	0.001 097	0.5946	0.002 135
0.1027	0.001 300	0.8129	0.002 471
0.1966	0.001 484	0.8835	0.002 560
0.4260	0.001 896	1.0000	0.002 702
0.4935	0.001 980		
2-Pentanol (B) + 3-Methoxy-1-butanol (C)			
0.0000	0.000 800	0.5970	0.001 999
0.1016	0.000 992	0.7902	0.002 373
0.1998	0.001 184	0.8873	0.002 533
0.3826	0.001 567	1.0000	0.002 702
0.4891	0.001 778		
3-Methyl-1-butanol (B) + 3-Methoxy-1-butanol (C)			
0.0000	0.000 727	0.5973	0.001 890
0.1066	0.000 920	0.7843	0.002 281
0.1951	0.001 083	0.8828	0.002 454
0.3847	0.001 456	1.0000	0.002 702
0.4925	0.001 669		
4-Methyl-2-pentanol (B) + 3-Methoxy-1-butanol (C)			
0.0000	0.000 779	0.6035	0.001 937
0.1207	0.000 970	0.8069	0.002 335
0.2089	0.001 124	0.9032	0.002 531
0.4263	0.001 537	1.0000	0.002 702
0.5282	0.001 775		
1-Octanol (B) + 3-Methoxy-1-butanol (C)			
0.0000	0.002 160	0.6730	0.002 786
0.1499	0.002 400	0.8426	0.002 779
0.2591	0.002 518	0.9182	0.002 749
0.4806	0.002 692	1.0000	0.002 702
0.5817	0.002 747		
2-Ethyl-1-hexanol (B) + 3-Methoxy-1-butanol (C)			
0.0000	0.001 397	0.6751	0.002 414
0.1432	0.001 586	0.8432	0.002 611
0.2603	0.001 770	0.9231	0.002 662
0.4770	0.002 118	1.0000	0.002 702
0.5773	0.002 283		

representations for isothermal solubility data based upon either a combined NIBS/Redlich–Kister model

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

or modified Wilson equation (Comer and Kopecni, 1990)

Table 2. Mathematical Representation of Anthracene Solubilities in Several Binary Alcohol (B) + 3-Methoxy-1-butanol (C) Solvent Mixtures

binary solvent system component (B) + component (C)	eq 1		eq 2	
	S_i^a	% dev ^b	$\Lambda_{ij}^{\text{adj}c}$	% dev ^b
1-propanol + 3-methoxy-1-butanol	0.973	0.2	1.956	0.3
2-propanol + 3-methoxy-1-butanol	1.405	0.8	2.217	0.7
1-butanol + 3-methoxy-1-butanol	0.667	0.3	1.753	0.7
2-butanol + 3-methoxy-1-butanol	0.929	0.4	1.840	0.9
1-pentanol + 3-methoxy-1-butanol	0.600	0.5	2.188	0.4
2-pentanol + 3-methoxy-1-butanol	0.818	0.2	1.608	0.2
3-methyl-1-butanol + 3-methoxy-1-butanol	0.766	0.6	1.811	0.5
4-methyl-2-pentanol + 3-methoxy-1-butanol	0.644	0.4	1.318	0.4
1-octanol + 3-methoxy-1-butanol	0.475	0.4	1.666	0.5
2-ethyl-1-hexanol + 3-methoxy-1-butanol	0.423	0.2	1.115	0.4
	-0.167		2.449	
	-0.069			

^a Combined NIBS/Redlich–Kister curve-fit parameters are ordered as S_0 , S_1 and S_2 . ^b Deviation (%) = $(100/7) \sum |[(x_A^{\text{sat}})^{\text{calc}} - (x_A^{\text{sat}})^{\text{exp}}]/(x_A^{\text{sat}})^{\text{exp}}|$. ^c Adjustable parameters for the modified Wilson equation are ordered as $\Lambda_{BC}^{\text{adj}}$ and $\Lambda_{CB}^{\text{adj}}$.

$$\ln[a_A(s)/x_A^{\text{sat}}] = 1 - x_B^0 \{1 - \ln[a_A(s)/(x_A^{\text{sat}})_B]\}/(x_B^0 + x_C^0 \Lambda_{BC}^{\text{adj}}) - x_C^0 \{1 - \ln[a_A(s)/(x_A^{\text{sat}})_C]\}/(x_B^0 \Lambda_{CB}^{\text{adj}} + x_C^0) \quad (2)$$

where the various S_i and $\Lambda_{ij}^{\text{adj}}$ “curve-fit” parameters can be evaluated via least squares analysis. In eqs 1 and 2 x_B^0 and x_C^0 refer to the initial mole fraction composition of the binary solvent calculated as if the solute were not present, $a_A(s)$ is the activity of the solid solute, and $(x_A^{\text{sat}})_i$ is the saturated mole fraction solubility of the solute in pure solvent i . The numerical value of $a_A(s) = 0.010 49$ (Acree and Rytting, 1983) used in the modified Wilson computations was calculated from

$$\ln a_A(s) = -\Delta_{\text{fus}} H_A (T_{\text{mp}} - T)/(RTT_{\text{mp}}) \quad (3)$$

the molar enthalpy of fusion, $\Delta_{\text{fus}} H_A/\text{J mol}^{-1} = 28 860$ (Weast, 1983), at the normal melting point temperature of the solute, $T_{\text{mp}}/\text{K} = 490.0$.

The ability of eqs 1 and 2 to mathematically represent the experimental solubility of anthracene in the ten binary alcohol 3-methoxy-1-butanol solvent systems is summarized in Table 2 in the form of “curve-fit” parameters and percent deviations in back-calculated solubilities. Careful examination of Table 2 reveals that both equations provide an accurate mathematical representation for how the solubility of anthracene varies with solvent composition. For the ten anthracene systems studied, the overall average absolute deviation between the experimental and calculated values is 0.4% and 0.5% for eqs 1 and 2, respectively, which is less than the experimental uncertainty. Both expressions describe the synergistic solubility behavior evidenced by the maxima in the anthracene mole fraction solubility versus solvent composition curve for the 1-octanol + 3-methoxy-1-butanol system. Synergistic behavior has been noted in published studies involving nonpolar and stable intramolecularly hydrogen-bonded

solutes dissolved in binary hydrocarbon + alcohol, halo-hydrocarbon + alcohol, and cyclohexane + methylene iodide mixtures (Buchowski *et al.*, 1979; Coon *et al.*, 1988; Domanska, 1981, 1987, 1990a,b; Domanska and Hofman, 1985).

From a computational standpoint, eq 1 will likely be preferred because most research groups involved in reporting thermodynamic properties have computer programs for evaluating the Redlich–Kister coefficients. With this idea in mind, we recommend not only that the future presentation of experimental isothermal solubility data for slightly soluble solid solutes dissolved in binary solvent mixtures include not a tabulation of the actual observed values but also that, if possible, the solubility data be mathematically represented by eq 1. Realizing that a single equation will not be applicable to all systems encountered, we further suggest eq 2 as an alternative mathematical representation for systems having extremely large solubility ranges and/or highly asymmetrical $\ln x_A^{\text{sat}}$ versus x_B^0 curves, such as the carbazole + alkane + tetrahydropyran systems reported previously (Acree *et al.*, 1991).

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