

# Solubility of Anthracene in Binary Alcohol + 2-Ethyl-1-hexanol Solvent Mixtures

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Experimental solubilities are reported for anthracene dissolved in seven binary mixtures containing 2-ethyl-1-hexanol with 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-octanol, 2-methyl-1-propanol, and 3-methyl-1-butanol 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 seven 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 on the order of 0.6%.

## 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 (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 group contribution methods and semiempirical expressions to predict desired quantities. Group contribution methods have proved fairly successful in estimating solid solubility in pure and binary solvent mixtures from structural information. Practical application, though, is limited to systems for which all group interaction parameters are known. Generally, interaction parameters are evaluated from solid-liquid and liquid-vapor equilibrium data. It is important that the data base contain as many different functional groups as possible, preferably with adequate representation from both mono- and multifunctional solute/solvent molecules to permit evaluation of potential synergistic effects. The data base should contain sufficient experimental values near infinite dilution in the event that one wishes to determine separate interaction parameters for finite concentration and infinite dilution activity coefficient predictions.

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. For this reason, anthracene solubilities were determined in seven binary alcohol + 2-ethyl-1-hexanol

solvent mixtures. Results of these measurements are used to further test the descriptive abilities of several previously derived expressions.

## Experimental Methods

Anthracene (Aldrich, 99.9+%) was used as received. 2-Ethyl-1-hexanol (Aldrich, 99+%), 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+%, anhydrous), 3-methyl-1-butanol (Aldrich, 99+%, anhydrous), and 1-octanol (Aldrich, 99+%, anhydrous) were stored over both anhydrous sodium sulfate and molecular sieves before being fractionally distilled. 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 seven 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 by repetitive measurements after a minimum of three additional days and by approaching equilibrium from supersaturation by preequilibrating 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. Concentrations were determined spectrophotometrically at 356 nm on a Bausch and Lomb Spectronic 2000. Experimental anthracene solubilities in the seven binary alcohol + 2-ethyl-1-hexanol 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 ±1.3%.

## Results and Discussion

Acree and co-workers (Acree and Zvaigzne, 1991; Acree *et al.*, 1991; Acree, 1992) suggested possible mathematical representations for isothermal solubility data based upon

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**Table 1. Experimental Mole Fraction Solubilities of Anthracene ( $x_A^{\text{sat}}$ ) in Binary Alcohol (B) + 2-Ethyl-1-hexanol (C) Solvent Mixtures at 25.0 °C**

$x_C^0$	$x_A^{\text{sat}}$	$x_C^0$	$x_A^{\text{sat}}$
1-Propanol (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.000 591	0.4163	0.000 924
0.0594	0.000 643	0.6438	0.001 101
0.0966	0.000 672	0.8162	0.001 232
0.2392	0.000 778	1.0000	0.001 397
0.3050	0.000 826		
2-Propanol (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.000 411	0.4326	0.000 845
0.0574	0.000 467	0.6680	0.001 072
0.1132	0.000 529	0.8076	0.001 184
0.2440	0.000 663	1.0000	0.001 397
0.3270	0.000 739		
1-Butanol (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.000 801	0.4660	0.001 074
0.0648	0.000 844	0.6914	0.001 219
0.1314	0.000 886	0.8288	0.001 310
0.2816	0.000 969	1.0000	0.001 397
0.3448	0.000 997		
2-Butanol (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.000 585	0.4726	0.000 998
0.0659	0.000 635	0.6981	0.001 168
0.1301	0.000 688	0.8550	0.001 291
0.2803	0.000 827	1.0000	0.001 397
0.3650	0.000 881		
2-Methyl-1-propanol (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.000 470	0.4535	0.000 905
0.0627	0.000 542	0.7047	0.001 135
0.1336	0.000 607	0.8015	0.001 226
0.2863	0.000 737	1.0000	0.001 397
0.3734	0.000 826		
3-Methyl-1-butanol (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.000 727	0.5144	0.001 076
0.0697	0.000 784	0.7374	0.001 228
0.1346	0.000 822	0.8105	0.001 276
0.3070	0.000 942	1.0000	0.001 397
0.3896	0.000 997		
1-Octanol (B) + 2-Ethyl-1-hexanol (C)			
0.0000	0.002 160	0.6044	0.001 694
0.1173	0.002 082	0.8006	0.001 541
0.2147	0.002 001	0.8905	0.001 468
0.3891	0.001 845	1.0000	0.001 397
0.5065	0.001 748		

either the 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 Kopećni, 1990)

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

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

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

$\Delta_{\text{fus}} H_A$  is the molar enthalpy of fusion at the normal melting point temperature of the solute,  $T_{\text{mp}}$ .

**Table 2. Mathematical Representation of Anthracene Solubilities in Several Binary Alcohol (B) + 2-Ethyl-1-hexanol (C) Solvent Mixtures**

binary solvent system (component B + component C)	eq 1		eq 2	
	$S_1^a$	% dev <sup>b</sup>	$\Lambda_{ij}^{\text{adj}c}$	% dev <sup>b</sup>
1-propanol + 2-ethyl-1-hexanol	0.315	0.7	1.485	0.7
	0.241		0.677	
2-propanol + 2-ethyl-1-hexanol	0.737	0.6	1.881	1.1
	0.427		0.537	
1-butanol + 2-ethyl-1-hexanol	0.126	0.2	1.065	0.5
	-0.010		1.069	
	0.206			
2-butanol + 2-ethyl-1-hexanol	0.484	0.4	2.201	0.6
	0.053		0.349	
	-0.170			
2-methyl-1-propanol + 2-ethyl-1-hexanol	0.558	0.9	1.805	0.8
	0.278		0.553	
	0.494			
3-methyl-1-butanol + 2-ethyl-1-hexanol	0.261	0.6	1.473	0.3
	0.122		0.677	
1-octanol + 2-ethyl-1-hexanol	0.072	0.5	1.853	0.4
	0.052		0.749	

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

The ability of eqs 1 and 2 to mathematically represent the experimental solubility of anthracene in the seven binary alcohol + 2-ethyl-1-hexanol 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 seven anthracene systems studied, the overall average absolute deviation between the experimental and calculated values is 0.6%, which is less than the experimental uncertainty.

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 that the future presentation of experimental isothermal solubility data for slightly soluble solid solutes dissolved in binary solvent mixtures include a tabulation of the actual observed values but if possible that 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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## Literature Cited

- Acree, W. E., Jr. Mathematical Representation of Thermodynamic Properties. Part 2. Derivation of the Combined Nearly Ideal Binary Solvent (NIBS)/Redlich–Kister Mathematical Representation from a Two-Body and Three-Body Interactional Mixing Model. *Thermochim. Acta* **1992**, *198*, 71–79.
- Acree, W. E., Jr. *Polycyclic Aromatic Hydrocarbons in Pure and Binary Solvents*; IUPAC Solubility Data Series; Oxford University Press: Oxford, U.K., 1994; Vol. 54.
- Acree, W. E., Jr. *Polycyclic Aromatic Hydrocarbons: Binary Non-aqueous Systems: Part 1 (Solutes A–E)*; IUPAC Solubility Data Series; Oxford University Press: Oxford, U.K., 1995a; Vol. 58.

- Acree, W. E., Jr. *Polycyclic Aromatic Hydrocarbons: Binary Non-aqueous Systems: Part 2 (Solutes F-Z)*; IUPAC Solubility Data Series; Oxford University Press: Oxford, U.K., 1995b; Vol. 59.
- Acree, W. E., Jr.; Rytting, J. H. Solubility in Binary Solvent Systems III: Predictive Expressions Based on Molecular Surface Areas. *J. Pharm. Sci.* **1983**, *72*, 292-296.
- Acree, W. E., Jr.; Zvaigzne, A. I. Thermodynamic Properties of Nonelectrolyte Solutions. Part 4. Estimation and Mathematical Representation of Solute Activity Coefficients and Solubilities in Binary Solvents Using the NIBS and Modified Wilson Equations. *Thermochim. Acta* **1991**, *178*, 151-167.
- Acree, W. E. Jr.; McCargar, J. W.; Zvaigzne, A. I.; Teng, I.-L. Mathematical Representation of Thermodynamic Properties. Car-

- bazole Solubilities in Binary Alkane + Dibutyl Ether and Alkane + Tetrahydropyran Solvent Mixtures. *Phys. Chem. Liq.* **1991**, *23*, 27-35.
- Comer, J. F.; Kopečni, M. M. Prediction of Gas Chromatography Solute Activity Coefficients in Mixed Stationary Phases Based on the Wilson Equation. *Anal. Chem.* **1990**, *62*, 991-994.

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