

# Solubility of Anthracene in Binary Alcohol + Dibutyl Ether Solvent Mixtures

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Experimental solubilities are reported for anthracene dissolved in seven binary mixtures containing dibutyl ether 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 systems studied, the combined NIBS/Redlich-Kister provided the better mathematical representations, with deviations between experimental and back-calculated values being on the order of  $\pm 1.5\%$  or less in the case of the three-parameter form. Slightly larger deviations were noted for the modified Wilson mathematical representation.

## 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, 1995, and in press). Despite efforts by experimentalists and scientific organizations, both in terms of new experimental measurements and critically-evaluated data compilations, there still exist numerous systems for which actual 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 equilibria data. It is important that measurements be made on compounds containing 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. It is essential to make measurements 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 the solubility of crystalline nonelectrolyte in binary solvent mixtures. For this reason, anthracene solubilities were determined in seven binary alcohol + dibutyl ether solvent mixtures. Results of these measurements are used to

**Table 1. Experimental Mole Fraction Solubilities of Anthracene (A) in Binary Alcohol (B) + Dibutyl Ether (C) Solvent Mixtures at 25.0 °C**

$x_C^o$	$x_A^{sat}$	$x_C^o$	$x_A^{sat}$
1-Propanol (B) + Dibutyl Ether (C)			
0.0000	0.000 591	0.3948	0.002 175
0.0532	0.000 787	0.6368	0.003 018
0.0984	0.000 961	0.8042	0.003 409
0.2230	0.001 463	1.0000	0.003 615
0.3074	0.001 784		
2-Propanol (B) + Dibutyl Ether (C)			
0.0000	0.000 411	0.4112	0.001 989
0.0517	0.000 570	0.6286	0.002 827
0.1011	0.000 750	0.7938	0.003 267
0.2268	0.001 226	1.0000	0.003 615
0.3126	0.001 609		
1-Butanol (B) + Dibutyl Ether (C)			
0.0000	0.000 801	0.4627	0.002 513
0.0564	0.001 004	0.6851	0.003 259
0.1215	0.001 246	0.8369	0.003 526
0.2719	0.001 822	1.0000	0.003 615
0.3541	0.002 085		
2-Butanol (B) + Dibutyl Ether (C)			
0.0000	0.000 585	0.3916	0.002 085
0.0642	0.000 807	0.6777	0.003 067
0.1203	0.001 019	0.7413	0.003 211
0.2536	0.001 544	1.0000	0.003 615
0.3457	0.001 901		
2-Methyl-1-propanol (B) + Dibutyl Ether (C)			
0.0000	0.000 470	0.4450	0.002 093
0.0627	0.000 668	0.6767	0.002 936
0.1127	0.000 837	0.8164	0.003 345
0.2427	0.001 323	1.0000	0.003 615
0.3429	0.001 693		
3-Methyl-1-butanol (B) + Dibutyl Ether (C)			
0.0000	0.000 727	0.4656	0.002 350
0.0753	0.000 964	0.6713	0.003 026
0.1270	0.001 142	0.7950	0.003 343
0.2884	0.001 737	1.0000	0.003 615
0.3892	0.002 076		
1-Octanol (B) + Dibutyl Ether (C)			
0.0000	0.002 160	0.5892	0.003 459
0.0964	0.002 415	0.7847	0.003 792
0.1982	0.002 665	0.8897	0.003 722
0.3832	0.003 114	1.0000	0.003 615
0.4861	0.003 299		

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further test the descriptive abilities of several previously derived expressions.

**Table 2. Mathematical Representation of Anthracene Solubilities in Several Binary Alcohol (B) + Dibutyl Ether (C) Solvent Mixtures**

binary solvent system component (B) + component (C)	2-Par eq 1		3-Par eq 1		eq 2	
	$S_1^a$	% dev <sup>b</sup>	$S_1^a$	% dev <sup>b</sup>	$\Lambda_{ij}^{adj\ c}$	% dev <sup>b</sup>
1-propanol + dibutyl ether	2.396 0.986	2.3	2.167 0.931 0.891	1.1	3.268 10.096	1.6
2-propanol + dibutyl ether	2.796 1.519	2.8	2.588 1.235 0.866	0.8	3.436 10.096	1.6
1-butanol + dibutyl ether	1.894 0.616	2.2	1.736 0.488 0.574	0.9	2.948 10.096	1.9
2-butanol + dibutyl ether	2.259 1.103	2.2	2.109 0.849 0.726	0.3	3.172 10.096	1.3
2-methyl-1-propanol + dibutyl ether	2.477 1.170	3.0	2.231 0.932 0.927	0.6	3.028 10.096	1.0
3-methyl-1-butanol + dibutyl ether	1.771 0.560	1.1	1.694 0.464 0.338	0.3	2.708 10.096	1.3
1-octanol + dibutyl ether	0.761 0.138	2.2	0.712 -0.143 0.169	0.6	2.824 10.096	2.0

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

## Experimental Methods

Anthracene (Aldrich 99.9+%) was used as received. Dibutyl ether (Aldrich 99+%, anhydrous) was stored over molecular sieves before use. 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  $25.0 \pm 0.1$  °C for several days. Attainment of equilibrium was verified by repetitive measurements after several 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 + dibutyl ether 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  $\pm 1.3\%$ .

## 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

either a combined NIBS/Redlich–Kister model

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

or modified Wilson equation (Comer and Kopečni, 1990)

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

where the various  $S_i$  and  $\Lambda_{ij}^{adj}$  "curve-fit" parameters can be evaluated via least squares analysis. In eqs 1 and 2  $x_B^o$  and  $x_C^o$  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  $(x_A^{sat})_i$  is the saturated mole fraction solubility of the solute in pure solvent  $i$ . The numerical value of  $a_A(s) = 0.01049$  (Acree and Rytting, 1983) used in the modified Wilson computations was calculated from

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

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

The ability of eqs 1 and 2 to mathematically represent the experimental solubility of anthracene in the seven binary alcohol + dibutyl ether 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 the three-parameter form of the combined NIBS/Redlich–Kister equation provided the better mathematical description for how the solubility of anthracene varies with solvent composition. For the most part, back-calculated and experimental values differ by less than  $\pm 1.5\%$ , which is comparable to the experimental uncertainty. Slightly larger deviations were noted in the case of the modified Wilson equation.

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 that the future presentation of experimental isothermal solubility data for slightly soluble solid solutes dissolved in binary solvent mixtures include not only 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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