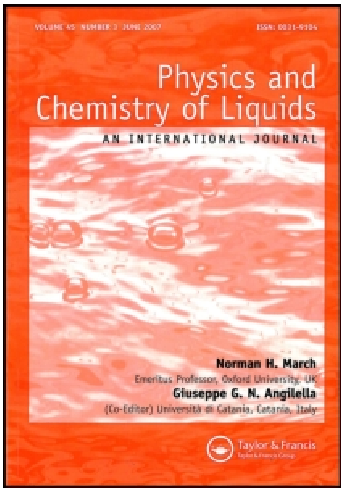

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Carmen E. Hernández[a]; Lindsay E. Roy[a]; Gaddum D. Reddy[a]; Tammie L. Borders[a]; Jessica T. Sanders[a]; William E. Acree JR.[a]
[a] Department of Chemistry, University of North Texas, Denton, Texas, U.S.A.

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SOLUBILITY OF ANTHRACENE IN BINARY ALKANE + 3–METHOXY-1-BUTANOL SOLVENT MIXTURES AT 298.2 K

CARMEN E. HERNÁNDEZ, LINDSAY E. ROY,
GADDUM D. REDDY, TAMMIE L. BORDERS,
JESSICA T. SANDERS and WILLIAM E. ACREE, JR.*

Department of Chemistry, University of North Texas, Denton, Texas 76203-5070 (U. S. A.)

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Experimental solubilities are reported for anthracene dissolved in seven binary alkane + 3-methoxy-1-butanol solvent mixtures at 25°C. The alkane cosolvents studied were hexane, heptane, octane, cyclohexane, methylcyclohexane, 2,2,4-trimethylpentane and *tert*-butylcyclohexane (also called (1,1-dimethylcyclohexane). Results of these measurements are used to test two mathematical representations based upon the combined Nearly Ideal Binary Solvent (NIBS)/Redlich-Kister and Modified Wilson equations. 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 being 0.6% and 0.9% for the Combined NIBS/Redlich-Kister and Modified Wilson equations, respectively.

Keywords and Phrases: Anthracene solubilities; binary solvent mixtures; alcohols

1. INTRODUCTION

Solid-liquid equilibrium data of organic nonelectrolyte systems are becoming increasingly important in the petroleum industry, particularly in light of present trends towards heavier feedstocks and known carcinogenicity/mutagenicity of many of the larger polycyclic aromatic compounds. Solubility data for a number of polycyclic aromatic

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*To whom correspondence should be addressed.

hydrocarbons (*i.e.*, anthracene and pyrene) and hetero-atom polynuclear aromatics (*i.e.*, carbazole, dibenzothiophene and xanthene) have been published in the recent chemical literature (for listing of references see Acree [1–3]). 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 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 non-complexing 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. For this reason, anthracene solubilities were determined in seven binary alkane + 3-methoxy-1-butanol solvent mixtures. Results of these measurements are used to further test the descriptive abilities of two previously derived expressions.

2. EXPERIMENTAL METHODS

Anthracene (Acros, 99.9+%) was recrystallized three times from 2 propanone. 3-Methoxy-1-butanol (Aldrich, 99%), hexane (Aldrich, 99+%), heptane (Aldrich, HPLC), octane (Aldrich, 99+%, anhydrous), cyclohexane (Aldrich, HPLC), methylcyclohexand (Aldrich, 99+%, anhydrous), 2,2,4-trimethylpentane (Aldrich, HPLC) and *tert*-butylcyclohexane (Aldrich, 99%, alco called (1,1-dimethylethyl) cyclohedxane) were stored over molecular sieves and distilled shortly before use. Gas chromatographic analysis showed solvent purities to be 99.7 mole percent 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 $(25.0 \pm 0.1)^{\circ}C$ with periodic agitation for at last three days (often longer). Attainment of equilibrium was verified both by repetitive measurements after a minimum of three 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. Apparent molar absorptivities of the nine standard solutions varied systematically with molar concentration, and ranged from approximately $\varepsilon/(\text{Liter mol}^{-1}\text{cm}^{-1}) = 7450$ to $\varepsilon/(\text{Liter mol}^{-1}\text{cm}^{-1}) = 7150$ for athracene concentrations ranging from $C/(\text{mol L}^{-1}) = 6.75 \times 10^{-5}$ to $C/(\text{mol L}^{-1}) = 2.25 \times 10^{-4}$. Identical molar absorptivities were obtained for select anthracene standard solutions that contained up to 5 volume percent of the neat alkane and 3-methoxy-1-butanol cosolvents. Experimental anthracene solubilities in the seven binary alkane + 3-methoxy-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 ± 1.5%.

3. RESULTS AND DISCUSSION

Acree and Zvaigzne [4] suggested possible mathematical representations for isothermal solubility data based upon either a combined NIBS/Redlich-Kister model

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

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

x_C^0	x_A^{sat}
Hexane (B) + 3-Methoxy-1-butanol (C)	
0.0000	0.001274
0.1175	0.001696
0.2440	0.002079
0.4481	0.002576
0.5596	0.002785
0.6554	0.002893
0.8271	0.002889
0.9141	0.002803
1.0000	0.002702
Heptane (B) + 3-Methoxy-1-butanol (C)	
0.0000	0.001571
0.1216	0.002009
0.2596	0.002337
0.4640	0.002705
0.5653	0.002878
0.6659	0.002964
0.8421	0.002933
0.9125	0.002863
1.0000	0.002702
Octane (B) + 3-Methoxy-1-butanol (C)	
0.0000	0.001838
0.1406	0.002288
0.2681	0.002542
0.4926	0.002921
0.5954	0.003045
0.6860	0.003079
0.8435	0.003040
0.9102	0.002936
0.9287	0.002905
1.0000	0.002702
Cyclohexane (B) + 3-Methoxy-1-butanol (C)	
0.0000	0.001553
0.0919	0.001991
0.2033	0.002407
0.3865	0.002817
0.4914	0.002978
0.5915	0.003021
0.7926	0.002969
0.8827	0.002870
1.0000	0.002702

TABLE I (Continued)

x_C^o	x_A^{sat}
Methylcyclohexane (B) + 3-Methoxy-1-butanol (C)	
0.0000	0.001649
0.1251	0.002234
0.2244	0.002522
0.4239	0.002911
0.5353	0.003104
0.6258	0.003156
0.8104	0.003112
0.9039	0.002950
1.0000	0.002702
2,2,4-Trimethylpentane (B) + 3-Methoxy-1-butanol (C)	
0.0000	0.001074
0.1346	0.001465
0.2734	0.001780
0.4997	0.002238
0.5963	0.002414
0.6901	0.002578
0.8541	0.002741
0.9268	0.002739
1.0000	0.002702
tert-Butylcyclohexane (B) + 3-Methoxy-1-butanol (C)	
0.0000	0.001978
0.1745	0.002564
0.2876	0.002808
0.5072	0.003116
0.6071	0.003179
0.7027	0.003200
0.8581	0.003039
0.9262	0.002899
1.0000	0.002702

or Modified Wilson equation

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

where the various S_i and Λ_{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 solute (A) were not present, $a_A(S)$ is the activity of the solid solute, 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 numerical value of $a_A(s)$ used in the Modified Wilson computations was $a_A(s) = 0.00984$ [5].

The ability of eqs 1 and 2 to mathematically represent the experimental solubility of anthracene in the seven binary alkane + 3-methoxy-1-butanol mixtures is summarized in Table II in the form of "curve-fit" parameters and percent deviations in back-calculated solubilities. Each percent deviation is based upon the measured anthracene solubility data at the seven different binary solvent compostions. In the case of the octane + 3-methoxy-1-butanol system, anthracene solubility data was measured at eight binary solvent compositions. Careful examination of Table II 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

TABLE II Mathematical Representation of Anthracene Solubilities in Several Binary Alkane (B) + 3-Methoxy-1-butanol (C) Solvent Mixtures

Binary Solvent System	*Eq 1*		*Eq 2*	
Component (B) + Component (C)	S_i^a	*% Dev.*[b]	$\Lambda_{ij}^{adj,c}$	*% Dev.*[b]
Hexane + 3-Methoxy-1-butanol	1.489	0.7	2.960	1.1
	0.344		4.160	
	0.189			
Heptane + 3-Methoxy-1-butanol	1.196	0.8	3.170	0.7
	0.217		4.190	
	0.476			
Octane + 3-Methoxy-1-butanol	1.088	0.4	3.070	0.5
	−0.032		6.100	
	0.516			
Cyclohexane + 3-Methoxy-1-butanol	1.480	0.6	4.623	1.0
	0.670		3.506	
	0.465			
Methylcyclohexane + 3-Methoxy-1- butanol	1.459	1.0	4.550	0.9
	0.377		6.470	
	0.692			
2,2,4-Trimethylpentane + 3-Methoxy-1-butanol	1.108	0.5	2.101	0.9
	0.265		2.970	
	0.487			
tert-Butylcyclohexane + 3-Methoxy-1-butanol	1.199	0.3	3.890	1.0
	0.084		5.870	
	0.353			

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

deviation between the experimental and calculated values is 0.6 and 0.9% for eqs. 1 and 2, respectively, which is less than the experimental uncertainty.

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