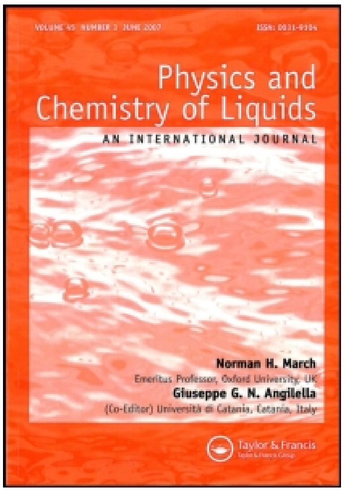

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Angel Toro[a]; William E. Acree Jr.[a]
[a] Department of Chemistry, University of North Texas, Denton, Texas, USA

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SOLUBILITY OF ANTHRACENE IN BINARY ALCOHOL+ETHYL ACETATE SOLVENT MIXTURES

ANGEL TORO and WILLIAM E. ACREE, Jr.*

Department of Chemistry, University of North Texas, Denton, Texas 76203-5070, USA

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Experimental solubilities are reported for anthracene dissolved in six binary mixtures containing ethyl acetate with 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol and 3-methyl-1-butanol at 298.15 K. Results of these measurements are used to test a mathematical representation based upon the combined Nearly Ideal Binary Solvent (NIBS)/Redlich-Kister model. For the six systems studied, the model was found to provide an accurate mathematical representation of the experimental results, with an overall average absolute deviation between measured and calculated values being on the order of 0.6% or less.

Keywords: Anthracene solubilities; Binary solvent mixtures; Alcohol cosolvents

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 the 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

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*Corresponding author. E-mail: acree@unt.edu

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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, 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 group contribution methods and semi-empirical 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 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 database should contain sufficient experimental values near infinite dilution in order to ensure that calculated interactional parameters accurately describe thermodynamic properties in this mole fraction region.

Continued development of solution models for predicting the thermodynamic properties of a solute dissolved in binary solvent systems requires that a large data base be available for assessing the applications and limitations of newly-derived expressions. Currently, only a limited database exists for crystalline nonelectrolyte solubility in binary solvent mixtures. For this reason, anthracene solubilities were determined in six binary alcohol + ethyl acetate solvent mixtures. Results of these measurements are used to test further the descriptive ability of a previously derived expression.

EXPERIMENTAL METHODS

Anthracene (Acros, 99.9+ %) was recrystallized three times from 2-propanone. 1-Propanol (Aldrich, 99+ %, anhydrous), 2-propanol (Aldrich, 99+ %, anhydrous), 1-butanol (Aldrich, HPLC, 99.8+ %), 2-butanol (Aldrich, 99+ %), 2-methyl-1-propanol (Aldrich, 99.5%

anhydrous), 3-methyl-1-butanol (Aldrich, 99+ %), anhydrous) and ethyl acetate (Aldrich, 99.8%, anhydrous) were stored over molecular sieves and distilled shortly before use. Gas chromatographic analysis showed solvent purities to be 99.8% 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 $T = (298.15 \pm 0.05)$ K for at least three days (often longer) with periodic shaking in order to facilitate dissolution of the solid. Attainment of equilibrium was verified 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 then 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. Molar absorptivities of the nine standard solutions varied systematically with molar concentration and ranged from *circa* $\epsilon/(L\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-1}) = 7450$ to $\epsilon/(L\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-1}) = 7150$ for anthracene concentrations ranging from $\mathrm{C}/(\mathrm{Molar}) = 6.75 \times 10^{-5}$ to $\mathrm{C}/(\mathrm{Molar}) = 2.25 \times 10^{-4}$. Identical molar absorptivities were obtained for select anthracene standard solutions that contained up to 5 vol.% of the neat ethyl acetate and alcohol cosolvents. Experimental molar concentrations were converted to (mass/mass) solubility fractions by multiplying by the molar mass of anthracene, volume(s) of volumetric flask(s) used, and any dilutions required to place the measured absorbances on the Beer–Lambert law absorbance versus concentration working curve and then dividing by the mass of the saturated solution analyzed. Mole fraction solubilities were computed from (mass/mass) solubility fractions using the binary solvent initial mole fraction compositions and molar masses of the solute and both cosolvents. Experimental anthracene solubilities in the six binary alcohol + ethyl acetate mixtures studied are listed in Table I. Numerical values represent the average of between four and eight independent determinations, with the measured values being reproducible to within ± 1.5%.

TABLE I Experimental mole fraction solubilities of anthracene (x_A^{sat}) in binary alcohol (B) + ethyl acetate (C) solvent mixtures at $T = 298.15\,K$

x_C^o	x_A^{sat}
1-Propanol (B) + Ethyl Acetate (C)	
0.0000	0.000591
0.0813	0.000874
0.1607	0.001185
0.3340	0.001936
0.4303	0.002337
0.5441	0.002886
0.7484	0.003870
0.8557	0.004293
1.0000	0.004842
2-Propanol (B) + Ethyl Acetate (C)	
0.0000	0.000411
0.1024	0.000742
0.1756	0.000994
0.3478	0.001691
0.4462	0.002149
0.5394	0.002554
0.7502	0.003669
0.8694	0.004250
1.0000	0.004842
1-Butanol (B) + Ethyl Acetate (C)	
0.0000	0.000801
0.1045	0.001191
0.1874	0.001537
0.3802	0.002389
0.4713	0.002804
0.5821	0.003325
0.7878	0.004097
0.8820	0.004391
1.0000	0.004842
2-Butanol (B) + Ethyl Acetate (C)	
0.0000	0.000585
0.1022	0.000950
0.1966	0.001362
0.3851	0.002238
0.4869	0.002698
0.5851	0.003137
0.7876	0.004013
0.8867	0.004414
1.0000	0.004842
2-Methyl-1-propanol (B) + Ethyl Acetate (C)	
0.0000	0.000470
0.0978	0.000757
0.1920	0.001099
0.3787	0.001863
0.4926	0.002397
0.5773	0.002801

Continued

TABLE I (Continued)

x_C^o	x_A^{sat}
0.7953	0.003823
0.8959	0.004310
1.0000	0.004842
3-Methyl-1-butanol (B) + Ethyl Acetate (C)	
0.0000	0.000727
0.1184	0.001145
0.2225	0.001554
0.4240	0.002424
0.5238	0.002913
0.6244	0.003392
0.8130	0.004205
0.9022	0.004512
1.0000	0.004842

RESULTS AND DISCUSSION

Expressions for predicting the thermodynamic properties of ternary nonelectrolyte systems have served as the point of departure for mathematical representation of experimental excess molar Gibbs energy, excess molar heat capacity, excess molar enthalpy and excess molar valume data. Differences between predicted and observed values are expressed as

$$\left(Z_{ABC}^{E}\right)^{obs} - \left(Z_{ABC}^{E}\right)^{calc} = x_A x_B x_C \, Q_{ABC} \tag{1}$$

with Q-functions of varying complexity. For most systems encountered, the experimental data can be adequately represented by a power series expansion

$$\begin{aligned} Q_{ABC} = A_{ABC} &+ \sum_{i=0}^{r} B_{AB}^{(i)}(x_A - x_B)^i + \sum_{j=0}^{s} B_{AC}^{(j)}(x_A - x_C)^j \\ &+ \sum_{k=0}^{t} B_{BC}^{(k)}(x_B - x_C)^k \end{aligned} \tag{2}$$

though rarely are experimental data determined with sufficient precision to justify more than a few parameters.

Conceptually, these ideas can be extended to solute solubilities in binary solvent mixtures, however, there has never been up until recently a sufficiently large solid solute solubility data base to warrant computerized storage in equational form. With computerized data storage and retrieval becoming increasingly popular, it seems appropriate to discuss the various mathematical expressions that have been proposed in the chemical literature for describing the variation of solute solubility with binary solvent composition. Mathematical representations provide not only a means to screen experimental data sets for possible outliers in need of redetermination, but also facilitate interpolation at solvent compositions falling between measured data points.

Acree and Zvaigzne [4] suggested possible mathematical representations for isothermal solubility data in binary solvent mixtures based upon either a Combined Nearly Ideal Binary Solvent (NIBS)/Redlich-Kister model

$$\ln x_A^{sat} = x_B^o \ln(x_A^{sat})_B + x_C^o \ln(x_A^{sat})_C + x_B^o x_C^o \sum_{i=0}^{N} S_i (x_B^o - x_C^o)^i \tag{3}$$

where 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, and $(x_A^{sat})_i$ is the saturated mole fraction solubility of the solute in pure solvent i. The above expression can be derived from published solution models that assume either two-body and/or three-body interactions between molecules in the fluid solution.

The Combined NIBS/Redlich-Kister model 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 coworkers [5–8] successfully used the volume fraction, ϕ_i, modification of Eq. (3)

$$\ln x_A^{sat} = \phi_B^o \ln(x_A^{sat})_B + \phi_C^o \ln(x_A^{sat})_C + \phi_B^o \phi_C^o \sum_{i=0}^{N} S_i (\phi_B^o - \phi_C^o)^i \tag{4}$$

to describe the solubility behavior of various drug molecules in binary aqueous-organic solvent mixtures. 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 [8]. More recently, Deng *et al.* [9–12] and Pribyla *et al.* [13–18] have shown that the S_i coefficients determined by regressing experimental anthracene solubility data in binary alkane + alkane, alkane + alcohol, alcohol + alcohol, alcohol + ether and alkane + ether solvent mixtures allows 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

$$\begin{aligned}\ln x_{\mathrm{A}}^{\mathrm{sat}} = {} & x_{\mathrm{B}}^{\mathrm{o}} \ln(x_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{B}} + x_{\mathrm{C}}^{\mathrm{o}} \ln(x_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{C}} + x_{\mathrm{D}}^{\mathrm{o}} \ln(x_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{D}} \\ & + x_{\mathrm{B}}^{\mathrm{o}} x_{\mathrm{C}}^{\mathrm{o}} \sum_{i=0}^{r} S_{i,\mathrm{BC}}(x_{\mathrm{B}}^{\mathrm{o}} - x_{\mathrm{C}}^{\mathrm{o}})^i + x_{\mathrm{B}}^{\mathrm{o}} x_{\mathrm{D}}^{\mathrm{o}} \sum_{j=0}^{s} S_{j,\mathrm{BD}}(x_{\mathrm{B}}^{\mathrm{o}} - x_{\mathrm{D}}^{\mathrm{o}})^j \\ & + x_{\mathrm{C}}^{\mathrm{o}} x_{\mathrm{D}}^{\mathrm{o}} \sum_{k=0}^{t} S_{k,\mathrm{CD}}(x_{\mathrm{C}}^{\mathrm{o}} - X_{\mathrm{D}}^{\mathrm{o}})^k \qquad (5)\end{aligned}$$

a mole fraction average of the logarithmic solute solubilities in the three pure solvents plus a Redlich-Kister summation term for each solvent pair.

The ability of Eq. (3) to represent mathematically the experimental solubility of anthracene in the six binary alcohol + ethyl acetate solvent systems is summarized in Table II in the form of "curve-fit" parameters and average absolute and maximum per cent deviations in back-calculated solubilities. The parameters S_i were computed from a polynomial least squares analysis of

$$\begin{aligned}\left[\ln x_{\mathrm{A}}^{\mathrm{sat}} - x_{\mathrm{B}}^{\mathrm{o}} \ln(x_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{B}} - x_{\mathrm{C}}^{\mathrm{o}} \ln(x_{\mathrm{A}}^{\mathrm{sat}})_{\mathrm{C}}\right]/(x_{\mathrm{B}}^{\mathrm{o}} x_{\mathrm{C}}^{\mathrm{o}}) = {} & S_0 + S_1(x_{\mathrm{B}}^{\mathrm{o}} - x_{\mathrm{C}}^{\mathrm{o}}) \\ & + S_2(x_{\mathrm{B}}^{\mathrm{o}} - x_{\mathrm{C}}^{\mathrm{o}})^2 \qquad (6)\end{aligned}$$

using the commercial software TableCurve (Jandel Scientific, Corte Madera, California). Careful examination of Table II reveals that the Combined NIBS/Redlich-Kister equations does provide an accurate mathematical representation for how the solubility of anthracene varies with solvent composition. The overall average absolute deviation between back-calculated and experimental values is 0.6%,

TABLE II Mathematical representation of anthracene solubilities in several binary alcohol (B) + ethyl acetate (C) solvent mixtures

Binary solvent system	*Eq. 3*		
Component (B) + Component (C)	S_i[a]	*Dev.*[b]	*Max. Dev.*
1-Propanol + Ethyl Acetate	1.837	0.5	1.2
	0.828		
	0.572		
2-Propanol + Ethyl Acetate	2.085	0.9	1.6
	1.162		
	0.900		
1-Butanol + Ethyl Acetate	1.634	0.7	1.6
	0.686		
	0.041		
2-Butanol + Ethyl Acetate	1.987	0.2	0.5
	0.945		
	0.341		
2-Methyl-1-propanol + Ethyl Acetate	1.914	0.5	1.2
	0.904		
	0.268		
3-Methyl-1-butanol + Ethyl Acetate	1.599	0.6	1.2
	0.539		
	0.272		

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

which is less than the uncertainty associated with the measured mole fraction solubilites.

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