

Solubility of Anthracene in Ternary 2-Butoxyethanol + Propanol + Butanol Solvent Mixtures

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Experimental solubilities are reported for anthracene dissolved in ternary 2-butoxyethanol + 1-propanol + 1-butanol, 2-butoxyethanol + 1-propanol + 2-butanol, 2-butoxyethanol + 2-propanol + 1-butanol, and 2-butoxyethanol + 2-propanol + 2-butanol solvent mixtures at 25 °C and atmospheric pressure. For each of the four solvent systems, 19 compositions were studied. Results of these measurements are used to test the predictive ability of the ternary solvent form of the Combined NIMS/Redlich–Kister equation. Computations showed that the model predicted the observed solubility behavior to within an overall average absolute deviation of about 1.5%, which is comparable to the experimental uncertainty of $\pm 1.5\%$.

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 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 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, 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 semiempirical equations to predict desired quantities from either pure component properties or measured binary data. In earlier studies, we have used the binary solvent reduction of a predictive expression derived from a combined two- and three-body interactional mixing model as a mathematical representation for describing how the measured isothermal solubility of a crystalline solute varies with binary solvent composition. The binary reduction, referred to as the combined NIBS/Redlich–Kister equation, was found to accurately describe the observed solubility behavior in a large number of different binary solvent systems. We now extend our solubility studies to ternary solvent mixtures. Anthracene solubilities have been measured in the four ternary 2-butoxyethanol + propanol + butanol systems at 25 °C. For each of the four systems, 19 ternary compositions were studied. Results of these measurements are used to test the predictive ability of expressions based upon the general mixing model used in deriving the combined NIBS/Redlich–Kister equation.

Experimental Methods

Anthracene (Acros, 99.9+%) was recrystallized three times from 2-propanone. 1-Propanol (Aldrich, 99+%, an-

hydrous), 2-propanol (Aldrich, 99+%, anhydrous), 1-butanol (Aldrich, HPLC, 99.8+%), 2-butanol (Aldrich, 99+%, anhydrous), and 2-butoxyethanol (Acros, 99+%) were stored over molecular sieves and distilled shortly before use. Gas chromatographic analysis showed solvent purities to be 99.7 mole percent or better. Ternary solvent mixtures were prepared by mass so that compositions could be calculated to 0.0001 mole fraction. The methods of sample equilibration and spectrophotometric analysis are discussed in an earlier paper (Powell et al., 1997). Experimental anthracene solubilities in the four 2-butoxyethanol + propanol + 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 $\pm 1.5\%$.

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 volume data. Differences between predicted and observed values are expressed as

$$(Z_{ABC}^E)^{\text{exp}} - (Z_{ABC}^E)^{\text{calc}} = x_A x_B x_C Q_{ABC} \quad (1)$$

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

$$Q_{ABC} = A_{ABC} + \sum_{i=1}^r B_{AB}^{(i)} (x_A - x_B)^i + \sum_{j=1}^s B_{AC}^{(j)} (x_A - x_C)^j + \sum_{k=1}^t B_{BC}^{(k)} (x_B - x_C)^k \quad (2)$$

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 database to warrant computerized storage in

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Table 1. Experimental Mole Fraction Solubilities of Anthracene (x_A^{sat}) in Ternary 2-Butoxyethanol (B) + Propanol (C) + Butanol (D) Solvent Mixtures at 298.15 K

x_B^0	x_C^0	x_A^{sat}	x_B^0	x_C^0	x_A^{sat}
2-Butoxyethanol (B) + 1-Propanol (C) + 1-Butanol (D)					
0.2408	0.4227	0.001 293	0.1077	0.1887	0.001 003
0.0966	0.7688	0.000 853	0.5947	0.2240	0.002 333
0.1805	0.3140	0.001 141	0.3817	0.3407	0.001 696
0.1713	0.5866	0.001 061	0.0719	0.2390	0.000 915
0.6026	0.1473	0.002 376	0.0641	0.7572	0.000 778
0.5871	0.2886	0.002 305	0.1453	0.1274	0.001 109
0.1294	0.7796	0.000 918	0.0677	0.4630	0.000 887
0.0647	0.5681	0.000 853	0.3062	0.1403	0.001 544
0.2802	0.6189	0.001 387	0.4004	0.1413	0.001 805
0.3734	0.5212	0.001 651			
2-Butoxyethanol (B) + 1-Propanol (C) + 2-Butanol (D)					
0.2394	0.4230	0.001 192	0.1058	0.1889	0.000 840
0.0950	0.7728	0.000 820	0.5924	0.2268	0.002 283
0.1790	0.3143	0.001 027	0.3858	0.3386	0.001 612
0.1698	0.5914	0.001 018	0.0697	0.2415	0.000 751
0.6047	0.1541	0.002 330	0.0638	0.7612	0.000 745
0.5833	0.2959	0.002 304	0.1492	0.1300	0.000 960
0.1282	0.7818	0.000 905	0.0682	0.4614	0.000 741
0.0657	0.5665	0.000 738	0.3104	0.1375	0.001 401
0.2816	0.6186	0.001 326	0.4016	0.1411	0.001 684
0.3723	0.5234	0.001 602			
2-Butoxyethanol (B) + 2-Propanol (C) + 1-Butanol (D)					
0.2420	0.4100	0.001 193	0.1079	0.1800	0.000 987
0.0968	0.7641	0.000 695	0.5985	0.2177	0.002 210
0.1807	0.3042	0.001 059	0.3888	0.3312	0.001 626
0.1716	0.5813	0.000 940	0.0714	0.2412	0.000 869
0.6011	0.1519	0.002 359	0.0644	0.7557	0.000 633
0.5887	0.2894	0.002 248	0.1474	0.1263	0.001 106
0.1301	0.7780	0.000 766	0.0677	0.4570	0.000 753
0.0657	0.5599	0.000 706	0.3110	0.1349	0.001 523
0.2848	0.6128	0.001 210	0.4032	0.1378	0.001 765
0.3765	0.5170	0.001 507			
2-Butoxyethanol (B) + 2-Propanol (C) + 2-Butanol (D)					
0.2397	0.4116	0.001 088	0.1081	0.1813	0.000 802
0.0985	0.7613	0.000 664	0.5944	0.2181	0.002 215
0.1799	0.3082	0.000 938	0.3857	0.3340	0.001 507
0.1717	0.5850	0.000 873	0.0701	0.2362	0.000 712
0.6039	0.1487	0.002 280	0.0605	0.7591	0.000 590
0.5870	0.2887	0.002 202	0.1483	0.1265	0.000 917
0.1299	0.7772	0.000 750	0.0674	0.4599	0.000 651
0.0659	0.5594	0.000 628	0.3120	0.1341	0.001 360
0.2853	0.6114	0.001 189	0.4016	0.1440	0.001 627
0.3768	0.5166	0.001 448			

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 co-workers (Acree, 1992; Acree and Zvaigzne, 1991; Acree et al., 1991) suggested a possible mathematical representation for isothermal solubility data based upon the combined NIBS/Redlich–Kister model

$$\ln x_A^{\text{sat}} = x_B^0 \ln(x_A^{\text{sat}})_B + x_C^0 \ln(x_A^{\text{sat}})_C + x_B^0 x_C^0 \sum_{i=0}^n S_i (x_B^0 - x_C^0)^i \quad (3)$$

where 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, and $(x_A^{\text{sat}})_i$ denotes the measured solute solu-

Table 2. Combined NIBS/Redlich–Kister Parameters Calculated from Anthracene Solubilities in the Subbinary Solvent Systems

solvent (B) + solvent (C)	S_i^a
1-propanol (B) + 1-butanol (C)	0.117
	-0.015
2-butoxyethanol (B) + 1-propanol (C)	1.222
	-0.572
	0.255
2-butoxyethanol (B) + 1-butanol (C)	0.800
	-0.319
	0.185
2-propanol (B) + 1-butanol (C)	0.243
	0.011
2-butoxyethanol (B) + 2-propanol (C)	1.550
	-0.790
	0.726
1-propanol (B) + 2-butanol (C)	0.000
	0.000
2-propanol (B) + 2-butanol (C)	0.097
	0.013
2-butoxyethanol (B) + 2-butanol (C)	1.155
	-0.609
	0.267

^a Combined NIBS/Redlich–Kister curve-fit parameters are ordered as S_0 , S_1 , and S_2 .

bility in pure solvent i . The various S_i curve-fit parameters can be evaluated with a least-squares analysis. Published papers (Zvaigzne and Acree, 1994; McHale et al., 1996) have reported the calculated S_i parameters for anthracene dissolved in the eight subbinary solvent systems, as well as the measured mole fraction solubilities in 1-propanol ($x_A^{\text{sat}} = 0.000 591$), 2-propanol ($x_A^{\text{sat}} = 0.000 411$), 1-butanol ($x_A^{\text{sat}} = 0.000 801$), 2-butanol ($x_A^{\text{sat}} = 0.000 585$), and 2-butoxyethanol ($x_A^{\text{sat}} = 0.003 785$). Numerical values of the S_i parameters have been tabulated in Table 2 for convenience.

Equation 3 expresses the excess logarithmic mole fraction solubility, relative to the simple $x_B^0 \ln(x_A^{\text{sat}})_B + x_C^0 \ln(x_A^{\text{sat}})_C$ arithmetic average, in terms of the Redlich–Kister equation. For a ternary solvent system, the mathematical representation takes the form of

$$\ln x_A^{\text{sat}} = x_B^0 \ln(x_A^{\text{sat}})_B + x_C^0 \ln(x_A^{\text{sat}})_C + x_D^0 \ln(x_A^{\text{sat}})_D + x_B^0 x_C^0 \sum_{i=0}^r S_{i,BC} (x_B^0 - x_C^0)^i + x_B^0 x_D^0 \sum_{j=0}^s S_{j,BD} (x_B^0 - x_D^0)^j + x_C^0 x_D^0 \sum_{k=0}^t S_{k,CD} (x_C^0 - x_D^0)^k \quad (4)$$

In keeping with our established terminology, the generalized mathematical representation given below

$$\ln x_A^{\text{sat}} = \sum_I x_I^0 \ln(x_A^{\text{sat}})_I + \sum_I \sum_J [x_I^0 x_J^0 \sum S_{k,IJ} (x_I^0 - x_J^0)^k] \quad (5)$$

will be referred to hereafter as the combined nearly ideal multiple solvent (NIMS)/Redlich–Kister expression. The first summation in eq 5 extends over all solvents in the multicomponent mixture, whereas the double summation extends over all binary combinations of solvents. In a ternary solvent mixture, as is the case here, there are three binary solvent combinations (BC, BD, and CD). Equation 4 can be used to predict the solubility as a function of ternary solvent composition, provided that all of the various curve-fit parameters are known. The predictive ability of eq 4 is summarized in Table 3 for anthracene dissolved in the four 2-butoxyethanol + propanol + butanol systems.

Table 3. Summarized Comparison between Observed Anthracene Solubilities in Ternary 2-Butoxyethanol + Propanol + Butanol Solvent Mixtures and Predicted Values Based upon the Combined NIMS/Redlich–Kister Equation 4

ternary solvent mixture	% dev ^a
2-butoxyethanol (B) + 1-propanol (C) + 1-butanol (D)	1.20
2-butoxyethanol (B) + 1-propanol (C) + 2-butanol (D)	1.69
2-butoxyethanol (B) + 2-propanol (C) + 1-butanol (D)	1.42
2-butoxyethanol (B) + 2-propanol (C) + 2-butanol (D)	1.75

^a Deviation (%) = (100/N) $\sum | [(x_A^{\text{sat}})^{\text{calc}} - (x_A^{\text{sat}})^{\text{exp}}] / (x_A^{\text{sat}})^{\text{exp}} |$, where $N = 19$.

Examination of the numerical entries in Table 3 reveals that eq 4 predicts the solubility of anthracene to within an overall average absolute deviation of 1.5%, which is comparable to the experimental uncertainty of $\pm 1.5\%$. For the four systems studied, eq 4 was found to provide very accurate predictions of the observed solubility behavior.

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 54; Oxford University Press: Oxford, U.K., 1994.
- Acree, W. E., Jr. *Polycyclic Aromatic Hydrocarbons: Binary Nonaqueous Systems: Part 1 (Solutes A–E)*; IUPAC Solubility Data Series 58; Oxford University Press: Oxford, U.K., 1995a.
- Acree, W. E., Jr. *Polycyclic Aromatic Hydrocarbons: Binary Nonaqueous Systems: Part 2 (Solutes F–Z)*; IUPAC Solubility Data Series 59; Oxford University Press: Oxford, U.K., 1995b.
- Acree, W. E., Jr.; McCargar, J. W.; Zvaigzne, A. I.; Teng, I.-L. Mathematical Representation of Thermodynamic Properties. Carbazole Solubilities in Binary Alkane + Dibutyl Ether and Alkane + Tetrahydropyran Solvent Mixtures. *Phys. Chem. Liq.* **1991**, *23*, 27–35.
- 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.; Zvaigzne, A. I. Thermochemical Investigations of Hydrogen-Bonded Solutions. Part 5. Development of Predictive Equations for the Solubility of Anthracene in Binary Alcohol + Alcohol Mixtures Based Upon Mobile Order Theory. *Fluid Phase Equilib.* **1994**, *99*, 167–183.
- McHale, M. E. R.; Kauppila, A.-S. M.; Powell, J. R.; Acree, W. E., Jr. Solubility of anthracene in (binary alcohol + 2-butoxyethanol) solvent mixtures. *J. Chem. Thermodyn.* **1996**, *28*, 209–214.
- Powell, J. R.; Coym, K. S.; Acree, W. E., Jr. Solubility of Anthracene in Binary Alcohol + 2-Methoxyethyl Ether Solvent Mixtures. *J. Chem. Eng. Data* **1997**, *42*, 395–397.

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