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Solubility of Anthracene in Ternary 2-Alkoxyethanol + Cyclohexane + Heptane and 2-Alkoxyethanol + Cyclohexane + 2,2,4-Trimethylpentane Solvent Mixtures

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Experimental solubilities are reported for anthracene dissolved in ternary 2-ethoxyethanol + cyclohexane + heptane, 2-ethoxyethanol + cyclohexane + 2,2,4-trimethylpentane, 2-butoxyethanol + cyclohexane + heptane, and 2-butoxyethanol + cyclohexane + 2,2,4-trimethylpentane solvent mixtures at 25 °C. Nineteen compositions were studied for each of the four solvent systems. 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 1.42%.

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 ternary 2-ethoxyethanol + cyclohexane + heptane, 2-ethoxyethanol + cyclohexane + 2,2,4-trimethylpentane, 2-butoxyethanol + cyclohexane + heptane, and 2-butoxyethanol + cyclohexane + 2,2,4-trimethylpentane systems at 25 °C. Nineteen ternary compositions were studied for each of the four systems. Results of these measurements are used to test the predictive ability of expressions based on 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. 2-Butoxyethanol (Acros, 99+ %), 2-ethoxyethanol (Aldrich, 99%), 2,2,4-trimethylpentane (Aldrich, HPLC, 99.7+ %), heptane (Aldrich, HPLC, 99+ %), and cyclohexane (Aldrich, HPLC, 99.9+ %) were stored over molecular sieves and distilled shortly before use. Gas chromatographic analysis showed solvent purities to be 99.7 mol % 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 ternary solvent systems 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 ±1.7%.

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

$$(Z^{E}_{ABC})^{exp} - (Z^{E}_{ABC})^{calc} = x_A x_B x_C Q_{ABC} \qquad (1)$$

with Q functions of varying complexity. For most systems encountered, the experimental data can be adequately

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

x_B°	x_C°	x_A^{sat}	x_B°	x_C°	x_A^{sat}
2-Ethoxyethanol (B) + Cyclohexane (C) + Heptane (D)					
0.3938	0.3505	0.002892	0.2028	0.1774	0.002297
0.1742	0.7122	0.002319	0.7536	0.1408	0.003301
0.3113	0.2773	0.002617	0.5575	0.2558	0.003142
0.2919	0.5167	0.002589	0.1366	0.2412	0.002072
0.7590	0.0982	0.003310	0.1170	0.7309	0.002108
0.7391	0.1898	0.003337	0.2665	0.1167	0.002402
0.2226	0.7008	0.002437	0.1358	0.4481	0.002131
0.1275	0.5498	0.002110	0.4867	0.1123	0.002894
0.4380	0.4905	0.003064	0.5839	0.1085	0.003140
0.5417	0.3868	0.003242			
2-Ethoxyethanol (B) + Cyclohexane (C) + 2,2,4-Trimethylpentane (D)					
0.4026	0.3604	0.002614	0.2183	0.1914	0.001821
0.1747	0.7223	0.002240	0.7585	0.1461	0.003190
0.3268	0.2930	0.002262	0.5739	0.2574	0.002963
0.2976	0.5293	0.002470	0.1402	0.2619	0.001613
0.7683	0.1010	0.003173	0.1182	0.7428	0.001946
0.7498	0.1890	0.003333	0.2889	0.1289	0.001947
0.2269	0.7079	0.002436	0.1297	0.4810	0.001768
0.1315	0.5702	0.001846	0.5128	0.1169	0.002549
0.4415	0.4944	0.002953	0.6075	0.1080	0.002739
0.5460	0.3923	0.003110			
2-Butoxyethanol (B) + Cyclohexane (C) + Heptane (D)					
0.3226	0.3877	0.002669	0.1572	0.1889	0.002150
0.1332	0.7450	0.002227	0.6915	0.1745	0.003417
0.2521	0.3028	0.002429	0.4873	0.2944	0.003064
0.2324	0.5579	0.002487	0.1052	0.2485	0.002015
0.7006	0.1207	0.003491	0.0890	0.7553	0.002029
0.6783	0.2368	0.003414	0.2089	0.1302	0.002317
0.1750	0.7492	0.002373	0.0966	0.4699	0.001975
0.0922	0.5734	0.002019	0.4116	0.1287	0.002882
0.3636	0.5559	0.002903	0.5109	0.1243	0.003068
0.4648	0.4525	0.003026			
2-Butoxyethanol (B) + Cyclohexane (C) + 2,2,4-Trimethylpentane (D)					
0.3300	0.4025	0.002415	0.1718	0.2036	0.001726
0.1357	0.7585	0.002099	0.6986	0.1814	0.003283
0.2686	0.3146	0.002113	0.4965	0.3059	0.002823
0.2386	0.5732	0.002314	0.1153	0.2664	0.001601
0.7169	0.1220	0.003227	0.0935	0.7656	0.001863
0.6873	0.2348	0.003313	0.2308	0.1388	0.001860
0.1766	0.7500	0.002304	0.1027	0.4913	0.001702
0.0997	0.5913	0.001739	0.4376	0.1323	0.002436
0.3692	0.5568	0.002813	0.5343	0.1280	0.002729
0.4706	0.4506	0.003019			

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, until recently, there has never been a sufficiently large solid solute solubility database to warrant computerized storage in equation 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.

Table 2. Combined NIBS/Redlich−Kister Parameters Calculated from Anthracene Solubilities in the Sub-binary Solvent Systems

Solvent B + Solvent C	S_i [a]
2-ethoxyethanol (B) + cyclohexane (C)	1.606 −0.354 0.374
2-butoxyethanol (B) + cyclohexane (C)	1.081 −0.863 0.565
2-ethoxyethanol (B) + 2,2,4-trimethylpentane (C)	1.101 0.134 0.475
2-butoxyethanol (B) + 2,2,4-trimethylpentane (C)	0.883 −0.548 0.198
2-ethoxyethanol (B) + heptane (C)	1.220 0.168 0.594
2-butoxyethanol (B) + heptane (C)	0.928 −0.488 0.123
cyclohexane (B) + heptane (C)	0.153 0.089 −0.084
cyclohexane (B) + 2,2,4-trimethylpentane (C)	−0.011 −0.021

[a] Combined NIBS/Redlich−Kister curve-fit parameters are ordered as S_0, S_1, and S_2. The percent deviations for the mathematical representation of the solubility data for anthracene dissolved in the binary solvent mixtures are given in two earlier papaers (Hernández et al., 1997, 1998).

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

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

where x_B° and x_C° refer to the initial mole fraction composition of the binary solvent calculated as if the solute were not present, $(x_A^{sat})_i$ denotes the measured solute solubility in pure solvent i, and n indicates the number of curve-fit parameters used in the mathematical representation. The various S_i "curve-fit" parameters can be evaluated via least-squares analysis. Published papers (Hernández et al., 1997, 1998) have reported the calculated S_i parameters for anthracene dissolved in six of the eight sub-binary solvent systems, as well as the measured mole fraction solubilities in 2-butoxyethanol ($x_A^{sat} = 0.003\,785$), 2-ethoxyethanol ($x_A^{sat} = 0.002\,921$), 2,2,4-trimethylpentane ($x_A^{sat} = 0.001\,074$), heptane ($x_A^{sat} = 0.001\,571$) and cyclohexane ($x_A^{sat} = 0.001\,553$). Solubility data for two of the sub-binary solvent systems were reported several years prior to the development of the combined NIBS/Redlich−Kister equation. We have determined the numerical values of the S_i parameters for the binary 2,2,4-trimethylpentane + cyclohexane and heptane + cyclohexane solvent systems by curve-fitting the experimental anthracene mole fraction solubility data of Acree and Rytting (1983) in accordance with eq 3. 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 $x_B^\circ \ln(x_A^{sat})_B + x_C^\circ$

Table 3. Summarized Comparison between Observed Anthracene Solubilities in Ternary 2-Alkoxyethanol + Alkane + Alkane Solvent Mixtures and Predicted Values Based on the Combined NIMS/Redlich−Kister Eq 4

ternary solvent mixture	% dev[a]
2-ethoxyethanol (B) + cyclohexane (C) + heptane (D)	1.30
2-ethoxyethanol (B) + cyclohexane (C) + 2,2,4-trimethylpentane (D)	1.53
2-butoxyethanol (B) + cyclohexane (C) + heptane (D)	1.26
2-butoxyethanol (B) + cyclohexane (C) + 2,2,4-trimethylpentane (D)	1.60

[a] Deviation (%) = $(100/N)\sum|[(x_A^{sat})^{calc} - (x_A^{sat})^{exp}]/(x_A^{sat})^{exp}|$, where the number of data points in each ternary system, N, equals 19.

$\ln(x_A^{sat})_C$ arithmetic average, in terms of the Redlich−Kister equation. For a ternary solvent system, the mathematical representation takes the form of

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

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

$$\ln x_A^{sat} = \sum_{I}^{solv} x_I^\circ \ln(x_A^{sat})_I + \sum_{I}^{solv} \sum_{J}^{solv} [x_I^\circ x_J^\circ \sum_{k=0}^{n} S_{k,IJ}(x_I^\circ - x_J^\circ)^k] \quad (5)$$

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 two ternary 2-alkoxyethanol + cyclohexane + heptane and two ternary 2-alkoxyethanol + cyclohexane + 2,2,4-trimethylpentane systems. 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 1.42%, which is comparable to an experimental uncertainty of ±1.7%. For the four systems studied, eq 4 was found to provide very accurate predictions of the observed solubility behavior.

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