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Solubility of Anthracene in Ternary Propanol + 2,2,4-Trimethylpentane + Cyclohexane and Butanol + 2,2,4-Trimethylpentane + Cyclohexane Solvent Mixtures

Taihe Deng and William E. Acree, Jr.*

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

Experimental solubilities are reported for anthracene dissolved in ternary 1-propanol + 2,2,4-trimethylpentane + cyclohexane, 2-propanol + 2,2,4-trimethylpentane + cyclohexane, 1-butanol + 2,2,4-trimethylpentane + cyclohexane, and 2-butanol + 2,2,4-trimethylpentane + cyclohexane 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 1.6%.

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 two ternary propanol + 2,2,4-trimethylpentane + cyclohexane systems and two ternary butanol + 2,2,4-trimethylpentane + cyclohexane 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 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+ %, anhydrous), 2-propanol (Aldrich, 99%, anhydrous), 1-butanol (Aldrich, HPLC, 99.8+ %), 2-butanol (Aldrich, 99+ %, anhydrous), 2,2,4-trimethylpentane (Aldrich, HPLC, 99.7+ %), 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. Karl Fischer titrations performed on select samples both prior to and after equilibration gave, to within experimental uncertainty, identical water contents (mass/mass %) of <0.01%. The methods of sample equilibration and spectrophotometric analysis are discussed in an earlier paper (Powell et al., 1997). Experimental anthracene solubilities in the two propanol + 2,2,4-trimethylpentane + cyclohexane and two butanol + 2,2,4-trimethylpentane + cyclohexane 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%.

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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* To whom correspondence should be addressed. E-mail: acree@unt.edu. FAX: (940) 565-4318.

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Table 1. Experimental Mole Fraction Solubilities of Anthracene (x_A^{sat}) in Ternary Propanol (B) + 2,2,4-Trimethylpentane (C) + Cyclohexane (D) and Butanol (B) + 2,2,4-Trimethylpentane (C) + Cyclohexane (D) Solvent Mixtures at 298.15 K

x_B°	x_C°	x_A^{sat}	x_B°	x_C°	x_A^{sat}
1-Propanol (B) + 2,2,4-Trimethylpentane (C) + Cyclohexane (D)					
0.4603	0.2145	0.001 175	0.2112	0.0975	0.001 515
0.2597	0.5536	0.001 180	0.7983	0.0792	0.000 831
0.3512	0.1606	0.001 346	0.6334	0.1443	0.001 033
0.3826	0.3479	0.001 190	0.1517	0.1336	0.001 515
0.7937	0.0500	0.000 875	0.1860	0.5644	0.001 235
0.8129	0.1052	0.000 815	0.2748	0.0615	0.001 504
0.3443	0.5356	0.001 133	0.1643	0.2855	0.001 405
0.1695	0.3739	0.001 351	0.5069	0.0570	0.001 236
0.5746	0.3232	0.001 027	0.6086	0.0551	0.001 119
0.6654	0.2401	0.000 952			
2-Propanol (B) + 2,2,4-Trimethylpentane (C) + Cyclohexane (D)					
0.4621	0.2148	0.001 108	0.2199	0.0982	0.001 433
0.2607	0.5549	0.001 117	0.8023	0.0799	0.000 675
0.3516	0.1612	0.001 267	0.6340	0.1468	0.000 899
0.3847	0.3501	0.001 114	0.1468	0.1350	0.001 446
0.7899	0.0533	0.000 695	0.1808	0.5706	0.001 189
0.8115	0.1065	0.000 637	0.2747	0.0633	0.001 428
0.3441	0.5378	0.001 069	0.1557	0.2927	0.001 364
0.1696	0.3764	0.001 310	0.4998	0.0585	0.001 147
0.5718	0.3340	0.000 906	0.6017	0.0566	0.000 983
0.6621	0.2447	0.000 815			
1-Butanol (B) + 2,2,4-Trimethylpentane (C) + Cyclohexane (D)					
0.4339	0.2251	0.001 287	0.1823	0.1027	0.0015 20
0.2242	0.5821	0.001 224	0.7655	0.0928	0.001 018
0.3060	0.1717	0.001 414	0.5852	0.1639	0.001 175
0.3335	0.3762	0.001 269	0.1193	0.1401	0.001 497
0.7539	0.0612	0.001 045	0.1510	0.5933	0.001 244
0.7812	0.1246	0.000 988	0.2374	0.0655	0.001 536
0.2982	0.5749	0.001 192	0.1360	0.2984	0.001 407
0.1429	0.3869	0.001 370	0.4554	0.0648	0.001 364
0.5252	0.3620	0.001 135	0.5589	0.0625	0.001 269
0.6185	0.2737	0.001 098			
2-Butanol (B) + 2,2,4-Trimethylpentane (C) + Cyclohexane (D)					
0.4142	0.2428	0.001 242	0.1792	0.1028	0.001 499
0.2231	0.5841	0.001 198	0.7706	0.0884	0.000 858
0.3036	0.1715	0.001 392	0.5869	0.1609	0.001 086
0.3359	0.3758	0.001 236	0.1120	0.1352	0.001 493
0.7570	0.0583	0.000 893	0.1569	0.5842	0.001 223
0.7810	0.1233	0.000 840	0.2346	0.0664	0.001 495
0.2937	0.5768	0.001 164	0.1268	0.2983	0.001 380
0.1387	0.3866	0.001 338	0.4186	0.0574	0.001 358
0.5293	0.3591	0.001 041	0.5570	0.0609	0.001 151
0.6182	0.2727	0.000 976			

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

solvent (B) + solvent (C)	S_i[a]
1-propanol (B) + 2,2,4-trimethylpentane (C)	0.825 0.103 0.291
1-propanol (B) + cyclohexane (C)	1.121 −0.040 0.256
1-butanol (B) + 2,2,4-trimethylpentane (C)	0.536 −0.151 0.142
1-butanol (B) + cyclohexane (C)	0.741 −0.345 0.223
2-propanol (B) + 2,2,4-trimethylpentane (C)	1.193 0.369 0.333
2-propanol (B) + cyclohexane (C)	1.589 0.143 0.248
2-butanol (C) + 2,2,4-trimethylpentane (C)	1.070 0.213
2-butanol (B) + cyclohexane (C)	1.260 −0.206
2,2,4-trimethylpentane (B) + cyclohexane (C)	−0.011 0.021

[a] Combined NIBS/Redlich−Kister curve-fit parameters are ordered as S_0, S_1, and S_2.

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 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 not only provide 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

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

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 and $(x_A^{sat})_i$ denotes the measured solute solubility in pure solvent *i*. The various S_i "curve-fit" parameters can be evaluated via least-squares analysis. Published papers (Zvaigzne et al., 1993; Zvaigzne and Acree, 1994; Acree et al., 1994) have reported the calculated S_i parameters for anthracene dissolved in eight of the nine sub-binary solvent systems, as well as the measured mole fraction solubilities in 1-propanol (x_A^{sat} = 0.000 591), 2-propanol (x_A^{sat} = 0.000 411), 1-butanol (x_A^{sat} = 0.000 801), 2-butanol (x_A^{sat} = 0.000 585), 2,2,4-trimethylpentane (x_A^{sat} = 0.001 074), and cyclohexane (x_A^{sat} = 0.001 553). Solubility data for the ninth binary solvent system was 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) solvent system 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 $x_B^\circ \ln(x_A^{sat})_B + x_C^\circ \ln(x_A^{sat})_C$ arithmetic average, in terms of the Redlich−Kister equation. For a ternary solvent system, the

Table 3. Summarized Comparison between Observed Anthracene Solubilities in Ternary Alcohol + 2,2,4-Trimethylpentane + Cyclohexane Solvent Mixtures and Predicted Values Based upon the Combined NIBS/Redlich−Kister Equation 4

ternary solvent mixture	% dev.[a]
1-propanol (B) + 2,2,4-trimethylpentane (C) + cyclohexane (D)	1.60
2-propanol (B) + 2,2,4-trimethylpentane (C) + cyclohexane (D)	1.40
1-butanol (B) + 2,2,4-trimethylpentane (C) + cyclohexane (D)	1.70
2-butanol (B) + 2,2,4-trimethylpentane (C) + cyclohexane (D)	1.71

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

mathematical representation takes the form of

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

The three solvents, designated as B, C, and D, are different. 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 propanol + 2,2,4-trimethylpentane + cyclohexane and two ternary butanol + 2,2,4-trimethylpentane + cyclohexane 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 1.60%, which is comparable to the experimental uncertainty of ±1.5%. For the four systems studied, eq 4 was found to provide very accurate predictions of the observed solubility behavior.

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