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Solubility of Anthracene in Ternary Dibutyl Ether + Alcohol + 2,2,4-Trimethylpentane Solvent Mixtures

Karen J. Pribyla, Michael A. Spurgin, Ivette Chuca, 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 dibutyl ether + 1-propanol + 2,2,4-trimethylpentane, dibutyl ether + 2-propanol + 2,2,4-trimethylpentane, dibutyl ether + 1-butanol + 2,2,4-trimethylpentane, dibutyl ether + 2-butanol + 2,2,4-trimethylpentane, and dibutyl ether + 2-methyl-1-propanol + 2,2,4-trimethylpentane solvent mixtures at 25 °C and atmospheric pressure. Nineteen compositions were studied for each of the five solvent systems. Results of these measurements are used to test the predictive ability of the ternary solvent form of the combined nearly ideal multiple solvent/Redlich−Kister equation. Computations showed that the model predicted the observed solubility behavior to within an overall average absolute deviation of about 1.4%, which is comparable to the experimental uncertainty of ±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, in terms of both 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 nearly ideal binary solvent (NIBS)/Redlich−Kister equation, was found to accurately describe the observed solubility behavior in a large number of different binary solvent systems. We recently extended our solubility studies to ternary two alkane + alcohol (Deng and Acree, 1998a; Deng et al., 1999a) and alkane + two alcohol (Deng and Acree, 1998b; Deng et al., 1998, 1999b) solvent mixtures. Such systems exhibit hydrogen-bond formation, and the measured solubility data will be used in future studies to test expressions derived from both the Kretschmer−Wiebe association model and mobile order theory. Deviations from ideality arise from the self-association of each alcohol cosolvent and, in mixtures containing two alcohol cosolvents, from the formation of heterogeneous hydrogen-bonded chains between dissimilar alcohol molecules. Powell et al. (1997b) and McHale et al. (1996) showed that the aforementioned thermodynamic models provided reasonably accurate descriptions for the solubility behavior of pyrene and anthracene in binary alkane + alcohol and alcohol + alcohol solvent mixtures.

In the present study anthracene solubilities have been measured in the five ternary dibutyl ether + alcohol + 2,2,4-trimethylpentane systems at 25 °C. Nineteen ternary compositions were studied for each of the five systems. Unlike the ternary solvent mixtures studied previously, hydrogen-bond formation is terminated each time that an alcohol molecule hydrogen bonds with dibutyl ether. 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-methyl-1-propanol (Aldrich; 99.5%, anhydrous), 2,2,4-trimethylpentane (Aldrich; HPLC; 99.7+%), and dibutyl ether (Aldrich; 99.3%, anhydrous) 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., 1997a). Experimental anthracene solubilities in the five dibutyl ether + alcohol + heptane 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%.

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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 Dibutyl Ether (B) + Alcohol (C) + 2,2,4-Trimethylpentane (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}
Dibutyl Ether (B) + 1-Propanol (C) + 2,2,4-Trimethylpentane (D)					
0.2322	0.5275	0.001 614	0.1563	0.3499	0.001 432
0.0841	0.8301	0.000 976	0.5910	0.2741	0.002 829
0.1911	0.4260	0.001 530	0.3955	0.4020	0.002 143
0.1564	0.6849	0.001 292	0.0880	0.3581	0.001 265
0.6297	0.2036	0.002 825	0.0546	0.8429	0.000 866
0.5363	0.3822	0.002 608	0.1782	0.1955	0.001 538
0.0954	0.8520	0.000 987	0.0736	0.5961	0.001 128
0.0671	0.6827	0.001 028	0.3493	0.2152	0.001 955
0.2596	0.6760	0.001 633	0.4710	0.1778	0.002 308
0.3345	0.6094	0.001 956			
Dibutyl Ether (B) + 2-Propanol (C) + 2,2,4-Trimethylpentane (D)					
0.2336	0.5237	0.001 486	0.1293	0.2886	0.001 319
0.0834	0.8265	0.000 808	0.5654	0.2981	0.002 577
0.1926	0.4284	0.001 416	0.3732	0.4279	0.001 915
0.1589	0.6771	0.001 143	0.0885	0.3575	0.001 173
0.5998	0.2146	0.002 666	0.0585	0.8278	0.000 742
0.5476	0.3587	0.002 542	0.1770	0.2093	0.001 424
0.1471	0.7714	0.001 030	0.0747	0.5888	0.001 014
0.0684	0.6779	0.000 905	0.3485	0.2137	0.001 865
0.2492	0.6802	0.001 431	0.4303	0.2133	0.002 153
0.3314	0.5913	0.001 763			
Dibutyl Ether (B) + 1-Butanol (C) + 2,2,4-Trimethylpentane (D)					
0.2328	0.5360	0.001 646	0.1344	0.2940	0.001 394
0.0818	0.8368	0.001 120	0.5682	0.2998	0.002 688
0.1910	0.4336	0.001 532	0.3718	0.4350	0.002 097
0.1558	0.6862	0.001 442	0.0892	0.3637	0.001 273
0.6055	0.2124	0.002 734	0.0604	0.8286	0.001 063
0.5445	0.3634	0.002 633	0.1741	0.2157	0.001 491
0.1066	0.8334	0.001 190	0.0728	0.5952	0.001 186
0.0678	0.6881	0.001 171	0.3429	0.2238	0.001 936
0.2431	0.6884	0.001 684	0.4257	0.2215	0.002 179
0.3233	0.6021	0.001 959			
Dibutyl Ether (B) + 2-Butanol (C) + 2,2,4-Trimethylpentane (D)					
0.2599	0.4757	0.001 678	0.1363	0.2517	0.001 379
0.1216	0.7154	0.001 187	0.6043	0.2571	0.002 765
0.2101	0.3818	0.001 606	0.4049	0.3828	0.002 154
0.1797	0.6393	0.001 403	0.0936	0.3132	0.001 305
0.6286	0.1793	0.002 771	0.0635	0.7636	0.000 994
0.5848	0.3226	0.002 707	0.1801	0.1888	0.001 505
0.1260	0.8067	0.001 097	0.0825	0.5438	0.001 189
0.0783	0.6384	0.001 124	0.3591	0.1860	0.001 937
0.2797	0.6428	0.001 658	0.4449	0.1868	0.002 213
0.3701	0.5489	0.001 989			
Dibutyl Ether (B) + 2-Methyl-1-Propanol (C) + 2,2,4-Trimethylpentane (D)					
0.2585	0.4763	0.001 585	0.1332	0.2526	0.001 348
0.0982	0.7999	0.000 878	0.6055	0.2554	0.002 708
0.2043	0.3769	0.001 471	0.4056	0.3856	0.002 051
0.1784	0.6378	0.001 246	0.0922	0.3174	0.001 217
0.6270	0.1809	0.002 734	0.0646	0.8027	0.000 798
0.5870	0.3217	0.002 615	0.1823	0.1789	0.001 462
0.1664	0.7408	0.001 097	0.0775	0.5460	0.001 056
0.0766	0.6373	0.000 980	0.3585	0.1807	0.001 916
0.2818	0.6390	0.001 529	0.4490	0.1806	0.002 187
0.3696	0.5440	0.001 871			

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

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

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

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

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 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

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

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

solvent (B) + solvent (C)	S_i[a]
2-methyl-1-propanol (B) + 2,2,4-trimethylpentane (C)	0.972
	0.100
	0.462
2-propanol (B) + 2,2,4-trimethylpentane (C)	1.193
	0.369
	0.333
2-butanol (B) + 2,2,4-trimethylpentane (C)	1.070
	0.213
1-propanol (B) + 2,2,4-trimethylpentane (C)	0.825
	0.103
	0.291
1-butanol (B) + 2,2,4-trimethylpentane (C)	0.536
	−0.151
	0.142
dibutyl ether (B) + 1-propanol (C)	2.167
	−0.931
	0.891
dibutyl ether (B) + 2-propanol (C)	2.588
	−1.235
	0.866
dibutyl ether (B) + 1-butanol (C)	1.736
	−0.488
	0.574
dibutyl ether (B) + 2-butanol (C)	2.109
	−0.849
	0.726
dibutyl ether (B) + 2-methyl-1-propanol (C)	2.231
	−0.932
	0.927
dibutyl ether (B) + 2,2,4-trimethylpentane (C)	0.353
	−0.026

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

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

ternary solvent mixture	% dev[a]
dibutyl ether (B) + 1-propanol (C) + 2,2,4-trimethylpentane (D)	1.71
dibutyl ether (B) + 2-propanol (C) + 2,2,4-trimethylpentane (D)	1.08
dibutyl ether (B) + 1-butanol (C) + 2,2,4-trimethylpentane (D)	1.39
dibutyl ether (B) + 2-butanol (C) + 2,2,4-trimethylpentane (D)	1.29
dibutyl ether (B) + 2-methyl-1-propanol (C) + 2,2,4-trimethylpentane (D)	1.45

[a] Deviation (%) = $(100/N)\sum|[(x_A^{sat})^{calc} - (x_A^{sat})^{exp}]/(x_A^{sat})^{exp}|$, where N corresponds to the number of data points for each ternary system. In the present study, solubilities were determined at 19 different ternary solvent compositions.

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 $(x_A^{sat})_i$ denotes the measured solute solubility in pure solvent *i*. The various S_i curve-fit parameters can be evaluated with a least-squares analysis. Published papers (Zvaigzne et al., 1993, 1994; Zvaigzne and Acree, 1994; Powell and Acree, 1995; Acree et al., 1994) have reported the calculated S_i parameters for anthracene dissolved in 10 of the 11 subbinary 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-methyl-1-propanol ($x_A^{sat} = 0.000\,470$), 2,2,4-trimethylpentane ($x_A^{sat} = 0.001\,074$), and dibutyl ether ($x_A^{sat} = 0.003\,615$). Solubility data for the 11th binary solvent system 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 dibutyl ether + 2,2,4-trimethylpentane solvent system by curve fitting the experimental anthracene mole fraction solubility data of Marthandan and Acree (1987) 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 $x_B^0 \ln(x_A^{sat})_B + x_C^0 \ln(x_A^{sat})_C$ arithmetic average, in terms of the Redlich−Kister equation. For a ternary solvent system, the mathematical representation takes the form of

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

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

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

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 five dibutyl ether + alcohol + 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 1.4%, which is comparable to the experimental uncertainty of ±1.5%. For the five systems studied, eq 4 was found to provide very accurate predictions of the observed solubility behavior.

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