

Solubility of Anthracene in Ternary Dibutyl Ether + Alcohol + Cyclohexane Solvent Mixtures

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Experimental solubilities are reported for anthracene dissolved in ternary dibutyl ether + 1-propanol + cyclohexane, dibutyl ether + 2-propanol + cyclohexane, dibutyl ether + 1-butanol + cyclohexane, dibutyl ether + 2-butanol + cyclohexane, and dibutyl ether + 2-methyl-1-propanol + cyclohexane 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 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, dibenzothiofene, 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 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 and 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 + cyclohexane 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), cyclohexane (Aldrich, HPLC, 99.9+%), 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 + 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 $\pm 1.5\%$.

Results and Discussion

Expressions for predicting the thermodynamic properties of ternary nonelectrolyte systems have served as the point

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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 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

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

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 $(x_A^{\text{sat}})_i$ 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 and 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 ($x_A^{\text{sat}} = 0.000\ 591$), 2-propanol ($x_A^{\text{sat}} = 0.000\ 411$), 1-butanol ($x_A^{\text{sat}} = 0.000\ 801$), 2-butanol ($x_A^{\text{sat}} = 0.000\ 585$), 2-methyl-1-propanol ($x_A^{\text{sat}} = 0.000\ 470$), cyclohexane ($x_A^{\text{sat}} = 0.001\ 553$), and dibutyl ether ($x_A^{\text{sat}} = 0.003\ 615$). Solubility data for the eleventh 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 + cyclohexane 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.

Table 1. Experimental Mole Fraction Solubilities of Anthracene (x_A^{sat}) in Ternary Dibutyl Ether (B) + Alcohol (C) + Cyclohexane (D) Solvent Mixtures at 298.15 K

x_B^o	x_C^o	x_A^{sat}	x_B^o	x_C^o	x_A^{sat}
Dibutyl Ether (B) + 1-Propanol (C) + Cyclohexane (D)					
0.2048	0.4725	0.001 883	0.1013	0.2196	0.001 817
0.0829	0.7919	0.001 078	0.5267	0.2862	0.002 812
0.1571	0.3599	0.001 868	0.3307	0.4042	0.002 260
0.1444	0.6322	0.001 477	0.0673	0.2755	0.001 700
0.5557	0.1911	0.002 866	0.0581	0.7822	0.001 021
0.5146	0.3534	0.002 707	0.1353	0.1581	0.001 946
0.1064	0.8015	0.001 114	0.0636	0.5051	0.001 432
0.0611	0.6006	0.001 285	0.2819	0.1716	0.002 258
0.2761	0.6272	0.001 783	0.3502	0.1940	0.002 409
0.3104	0.5792	0.002 007			
Dibutyl Ether (B) + 2-Propanol (C) + Cyclohexane (D)					
0.2085	0.4629	0.001 764	0.0876	0.2459	0.001 783
0.0804	0.7946	0.000 901	0.5322	0.2793	0.002 725
0.1595	0.3583	0.001 829	0.3408	0.3834	0.002 166
0.1423	0.6291	0.001 337	0.0659	0.2768	0.001 631
0.5532	0.1930	0.002 866	0.0581	0.7789	0.000 876
0.5205	0.3386	0.002 609	0.1342	0.1578	0.001 903
0.1095	0.8006	0.000 943	0.0649	0.5031	0.001 330
0.0624	0.5968	0.001 176	0.2799	0.1784	0.002 287
0.2398	0.6594	0.001 487	0.3611	0.1831	0.002 434
0.3150	0.5723	0.001 816			
Dibutyl Ether (B) + 1-Butanol (C) + Cyclohexane (D)					
0.2276	0.4225	0.002 015	0.1032	0.1886	0.001 889
0.0932	0.7567	0.001 310	0.5607	0.2398	0.002 908
0.1718	0.3132	0.001 956	0.3549	0.3531	0.002 347
0.1623	0.5790	0.001 718	0.0699	0.2412	0.001 794
0.5686	0.1685	0.002 936	0.0642	0.7467	0.001 244
0.5536	0.3029	0.002 840	0.1354	0.1357	0.001 999
0.1237	0.7723	0.001 370	0.0721	0.4500	0.001 604
0.0683	0.5553	0.001 499	0.2926	0.1472	0.002 290
0.2684	0.6125	0.001 967	0.3690	0.1587	0.002 408
0.3477	0.5235	0.002 233			
Dibutyl Ether (B) + 2-Butanol (C) + Cyclohexane (D)					
0.2263	0.4202	0.001 953	0.1068	0.1852	0.001 888
0.0883	0.7556	0.001 118	0.5520	0.2327	0.002 876
0.1620	0.3218	0.001 915	0.3553	0.3571	0.002 334
0.1639	0.5791	0.001 594	0.0688	0.2384	0.001 750
0.5718	0.1685	0.002 910	0.0623	0.7482	0.001 074
0.5549	0.3047	0.002 764	0.1353	0.1363	0.001 971
0.1227	0.7703	0.001 184	0.0646	0.4555	0.001 513
0.0692	0.5495	0.001 399	0.2894	0.1478	0.002 339
0.2677	0.6133	0.001 779	0.3818	0.1541	0.002 541
0.3530	0.5220	0.002 112			
Dibutyl Ether (B) + 2-Methyl-1-Propanol (C) + Cyclohexane (D)					
0.2279	0.4132	0.001 816	0.1058	0.1875	0.001 818
0.0943	0.7510	0.000 991	0.5620	0.2305	0.002 810
0.1766	0.3052	0.001 848	0.3639	0.3433	0.002 222
0.1634	0.5744	0.001 414	0.0740	0.2402	0.001 653
0.5694	0.1686	0.002 811	0.0696	0.7413	0.000 939
0.5573	0.3059	0.002 740	0.1400	0.1377	0.001 941
0.1268	0.7694	0.001 032	0.0703	0.4527	0.001 375
0.0697	0.5503	0.001 229	0.2902	0.1523	0.002 268
0.2681	0.6128	0.001 594	0.3756	0.1556	0.002 402
0.3527	0.5251	0.001 946			

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

$$\ln x_A^{\text{sat}} = x_B^o \ln(x_A^{\text{sat}})_B + x_C^o \ln(x_A^{\text{sat}})_C + x_D^o \ln(x_A^{\text{sat}})_D + x_B^o x_C^o \sum_{i=0}^r S_{i,BC} (x_B^o - x_C^o)^i + x_B^o x_D^o \sum_{j=1}^n S_{j,BD} (x_B^o - x_D^o)^j + x_C^o x_D^o \sum_{k=1}^t S_{k,CD} (x_C^o - x_D^o)^k \quad (4)$$

Table 2. Combined NIBS/Redlich–Kister Parameters (Eq 3) Calculated from Anthracene Solubilities in the Subbinary Solvent Systems

solvent B + solvent C	S_0^a	solvent B + solvent C	S_1^a
2-methyl-1-propanol (B) + cyclohexane (C)	1.116	dibutyl ether (B) + 2-propanol (C)	2.588
	-0.172		-1.235
	0.341		0.866
2-propanol (B) + cyclohexane (C)	1.589	dibutyl ether (B) + 1-butanol (C)	1.736
	0.143		-0.488
	0.248		0.574
2-butanol (B) + cyclohexane (C)	1.260	dibutyl ether (B) + 2-butanol (C)	2.109
	-0.206		-0.849
	1.121		0.726
1-propanol (B) + cyclohexane (C)	-0.040	dibutyl ether (B) + 2-methyl-1-propanol (C)	2.231
	0.256		-0.932
	0.741		0.927
1-butanol (B) + cyclohexane (C)	-0.345	dibutyl ether (B) + cyclohexane (C)	0.467
	0.223		-0.190
	2.167		
dibutyl ether (B) + 1-propanol (C)	-0.931		
	0.891		

^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 + Cyclohexane Solvent Mixtures and Predicted Values Based upon the Combined NIBS/Redlich–Kister eq 4

ternary solvent mixture	% dev ^a
dibutyl ether (B) + 1-propanol (C) + cyclohexane (D)	1.68
dibutyl ether (B) + 2-propanol (C) + cyclohexane (D)	1.16
dibutyl ether (B) + 1-butanol (C) + cyclohexane (D)	1.94
dibutyl ether (B) + 2-butanol (C) + cyclohexane (D)	1.07
dibutyl ether (B) + 2-methyl-1-propanol (C) + cyclohexane (D)	1.77

^a Deviation (%) = $(100/N)\sum_i |(x_A^{\text{sat}})^{\text{calc}} - (x_A^{\text{sat}})^{\text{exp}}| / (x_A^{\text{sat}})^{\text{exp}}$, 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.

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

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

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 (solv) 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 + 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 1.5%, which is comparable to the experimental uncertainty of $\pm 1.5\%$. For the five systems studied, eq 4 was found to provide very accurate predictions of the observed solubility behavior.

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