

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

Taihe Deng, Sabrina D. Childress, Karina M. De Fina, Tina L. Sharp, 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 + 1-butanol + 2,2,4-trimethylpentane, 1-propanol + 2-butanol + 2,2,4-trimethylpentane, 2-propanol + 1-butanol + 2,2,4-trimethylpentane, and 2-propanol + 2-butanol + 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 0.9%.

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, 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 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 propanol + butanol + 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 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 2,2,4-trimethylpentane (Aldrich, HPLC, 99.7+%) 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. Excess solute and solvent were placed in sealed amber glass bottles and allowed to equilibrate with periodic agitation in a constant-temperature bath for at least 3 days. Attainment of equilibrium was verified both by repetitive measurements after a minimum of three additional days and by approaching equilibrium from supersaturation by pre-equilibrating the solutions at higher temperature.

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 method of spectrophotometric analysis is discussed in an earlier paper (Powell et al., 1997). Experimental anthracene solubilities in the four propanol + butanol + 2,2,4-trimethylpentane 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

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

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

x_B^o	x_C^o	$x_A^{(sat)}$	x_B^o	x_C^o	$x_A^{(sat)}$
1-Propanol (B) + 1-Butanol (C) + 2,2,4-Trimethylpentane (D)					
0.4435	0.3595	0.000 859	0.2645	0.2247	0.001 035
0.1929	0.7217	0.000 834	0.7877	0.1379	0.000 701
0.3694	0.2952	0.000 943	0.6094	0.2510	0.000 787
0.3254	0.5270	0.000 848	0.1729	0.2882	0.001 056
0.8169	0.0894	0.000 707	0.1350	0.7436	0.000 869
0.7674	0.1803	0.000 687	0.3431	0.1416	0.001 022
0.2459	0.6932	0.000 804	0.1534	0.4995	0.000 998
0.1458	0.5880	0.000 937	0.5683	0.1189	0.000 878
0.4571	0.4883	0.000 746	0.6548	0.1104	0.000 825
0.5695	0.3721	0.000 727			
1-Propanol (B) + 2-Butanol (C) + 2,2,4-Trimethylpentane (D)					
0.4377	0.3595	0.000 781	0.2494	0.2078	0.001 017
0.1928	0.7220	0.000 675	0.7883	0.1377	0.000 665
0.3684	0.3005	0.000 881	0.6149	0.2466	0.000 721
0.3263	0.5277	0.000 725	0.1720	0.2865	0.001 009
0.7996	0.0900	0.000 697	0.1287	0.7485	0.000 718
0.7771	0.1745	0.000 636	0.4497	0.1113	0.000 949
0.2464	0.6966	0.000 646	0.1553	0.4965	0.000 911
0.1480	0.5903	0.000 845	0.5660	0.1153	0.000 874
0.4701	0.4770	0.000 637	0.6568	0.1052	0.000 805
0.5729	0.3736	0.000 630			
2-Propanol (B) + 1-Butanol (C) + 2,2,4-Trimethylpentane (D)					
0.4292	0.3609	0.000 790	0.2482	0.2120	0.001 015
0.1910	0.7235	0.000 794	0.7791	0.1406	0.000 562
0.3641	0.2998	0.000 883	0.6034	0.2523	0.000 678
0.3170	0.5335	0.000 786	0.1717	0.2768	0.001 051
0.7964	0.0964	0.000 579	0.1247	0.7546	0.000 850
0.7636	0.1840	0.000 545	0.3424	0.1350	0.000 967
0.2375	0.7068	0.000 758	0.1508	0.5030	0.000 979
0.1400	0.5964	0.000 933	0.5590	0.1166	0.000 802
0.4599	0.4855	0.000 661	0.6495	0.1082	0.000 720
0.5662	0.3817	0.000 623			
2-Propanol (B) + 2-Butanol (C) + 2,2,4-Trimethylpentane (D)					
0.4326	0.3660	0.000 709	0.2566	0.2110	0.000 977
0.1880	0.7267	0.000 651	0.7813	0.1414	0.000 532
0.3650	0.3021	0.000 833	0.6075	0.2552	0.000 621
0.3222	0.5324	0.000 674	0.1760	0.2841	0.001 016
0.7965	0.0989	0.000 557	0.1317	0.7471	0.000 702
0.7607	0.1861	0.000 514	0.3232	0.1402	0.000 966
0.2462	0.6990	0.000 611	0.1516	0.4991	0.000 904
0.1475	0.5947	0.000 822	0.5605	0.1256	0.000 778
0.4665	0.4786	0.000 561	0.6477	0.1152	0.000 703
0.5636	0.3803	0.000 552			

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. The parameters are denoted by the symbols A_{ABC} , $B_{AB}^{(i)}$, $B_{AC}^{(j)}$, and $B_{BC}^{(k)}$. In eqs 1 and 2 x_i is the mole fraction of component i .

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

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
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
2-propanol (B) + 1-butanol (C)	0.243 0.011
2-propanol (B) + 2,2,4-trimethylpentane (C)	1.193 0.369 0.333
1-propanol (B) + 2-butanol (C)	0.000 0.000
2-propanol (B) + 2-butanol (C)	0.097 0.013
2-butanol (B) + 2,2,4-trimethylpentane (C)	1.070 0.213

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

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

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

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 $(x_A^{(sat)})_i$ 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; Acree and Zvaigzne, 1994) 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 ($x_A^{(sat)} = 0.000 591$), 2-propanol ($x_A^{(sat)} = 0.000 411$), 1-butanol ($x_A^{(sat)} = 0.000 801$), 2-butanol ($x_A^{(sat)} = 0.000 585$) and 2,2,4-trimethylpentane ($x_A^{(sat)} = 0.001 074$). 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 $x_B^o \ln(x_A^{(sat)})_B + x_C^o \ln(x_A^{(sat)})_C$ arithmetic average, in terms of the Redlich–Kister equation. For a ternary solvent system, the mathematical representation takes the form of

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

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

ternary solvent mixture	% dev. ^a
1-propanol (B) + 1-butanol (C) + 2,2,4-trimethylpentane (D)	0.77
1-propanol (B) + 2-butanol (C) + 2,2,4-trimethylpentane (D)	0.52
2-propanol (B) + 1-butanol (C) + 2,2,4-trimethylpentane (D)	1.11
2-propanol (B) + 2-butanol (C) + 2,2,4-trimethylpentane (D)	1.27

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

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

$$\ln x_A^{(\text{sat})} = \sum x_i^0 \ln(x_A^{(\text{sat})})_i + \sum \sum [x_i^0 x_j^0 \sum S_{k,ij} (x_i^0 - x_j^0)^k] \quad (5)$$

will be referred to hereafter as the combined nearly ideal multiple solvent (NIMS)/Redlich–Kister expression. The double summation extends over all binary combinations of solvents. 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 propanol + butanol + 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 0.92%, 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.

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