Solubility of Anthracene in Ternary 2,2,4-Trimethylpentane + Propanol + 1-Pentanol and 2,2,4-Trimethylpentane + Butanol + 1-Pentanol Mixtures

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Experimental solubilities are reported for anthracene dissolved in ternary 2,2,4-trimethylpentane + 1-propanol + 1-pentanol, 2,2,4-trimethylpentane + 2-propanol + 1-pentanol, 2,2,4-trimethylpentane + 1-butanol + 1-pentanol, and 2,2,4-trimethylpentane + 2-butanol + 1-pentanol solvent mixtures at 298.15 K and atmospheric pressure. For each of the four ternary solvent systems, 19 compositions were studied. Results of these measurements are used to test the predictive ability of the ternary solvent form of the Jouyban−Acree model (also referred to in the literature as the combined NIBS/Redlich–Kister model). Computations showed that the model predicted the observed solubility behavior to within an overall average absolute relative percentage deviation of about 1.5.

Introduction

Recrystallization is a purification process used widely throughout the chemical and pharmaceutical industry during the synthesis of organic compounds. Purification by recrystallization generally follows one of two approaches. The first approach involves dissolving the impure solid material in a "good" solvent and then slowly adding a "non-solvent" to precipitate the solute from solution. In the second approach, an appreciable amount of the solid material is dissolved in a hot solution, and upon cooling, purified crystals of the solute form. Solvent selection is important in both cases, and considerable effort has been given in recent years to developing mathematical equations that accurately predict how solute solubility varies with both temperature and solvent composition.

Over the past 20 years, we have reported experimental solubility data for anthracene and pyrene dissolved in numerous binary solvents. As part of our solubility studies, we have developed a simple predictive method for estimating the solubility of crystalline organic compounds in ternary[1–4]

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

and higher-order multicomponent solvent mixtures[5]

$$
\ln x_A^{\text{sat}} = \sum_I x_I^{\circ} \ln(x_A^{\text{sat}})_I + \sum_I \sum_{J>I} \left(x_I^{\circ} x_J^{\circ} \sum_{i=0}^{r} S_{IJ,i}(x_I^{\circ} - x_J^{\circ})^i \right) \quad (2)
$$

based on the extended form of the combined nearly ideal binary solvent (NIBS)/Redlich–Kister solution model. Predictions are based on the measured solubility data in all of the contributing sub-binary solvent mixtures. In eqs 1 and 2, x_I°'s refer to the initial mole fraction solvent composition of component *i*

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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 $S_{IJ,i}$ parameters can be evaluated with a least-squares regression analysis. Modified versions of eqs 1 and 2 have been developed to include temperature dependence. Currently, the most generalized version of the model is referred to as the Jouyban−Acree model (JAM).[6,7]

In the present study, we report the solubility of anthracene in four ternary solvent mixtures containing 2,2,4-trimethylpentane and 1-pentanol with either 1-propanol, 2-propanol, 1-butanol, or 2-butanol at 298.15 K. These measurements were performed to provide the scientific community with additional solubility data for solutes dissolved in ternary solvent mixtures. The published literature contains experimental solubility data for solutes dissolved in a large number of binary solvent mixtures; however, solubility data for ternary and higher-order multicomponent solvent mixtures are not very abundant. Results of our measurements are used to test the predictive ability of eq 1.

Experimental Methods

Anthracene (Aldrich, 99+ %) was recrystallized several times from 2-propanone to yield a purified sample having a melting point temperature of $T/K = 489$. 2,2,4-Trimethylpentane (Aldrich, 99.8 %, anhydrous), 1-propanol (Aldrich, 99+ %, anhydrous), 2-propanol (Aldrich, 99+ %, anhydrous), 1-butanol (Aldrich, 99+ %, anhydrous), 2-butanol (Aldrich, 99+ %, anydrous), and 1-pentanol (Aldrich, 99 %) were stored over molecular sieves and distilled shortly before use. Gas chromatographic analysis showed the solvent mole fraction purities to be 99.7 % or better. Binary solvent mixtures were prepared by mass (Mettler AE100 balance, precision of 0.0002 g) so that composition could be calculated to 0.0001 mol fraction.

Excess solute and solvent were placed in amber glass bottles and allowed to equilibrate in a constant temperature water bath at $T/K = 298.15 \pm 0.05$ for at least three days (often longer) with periodic shaking in order to facilitate dissolution of the solid. Attainment of equilibrium was verified by repetitive measurements after a minimum of three

Table 1. Experimental Mole Fraction Solubilities of Anthracene, x_A^{sat}, in Ternary 2,2,4-Trimethylpentane (B) + Propanol (C) + 1-Pentanol (D) and 2,2,4-Trimethylpentane (B) + Butanol (C) + 1-Pentanol (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}
2,2,4-Trimethylpentane (B) + 1-Propanol (C) + 1-Pentanol (D)					
0.2062	0.4675	0.000975	0.5304	0.3426	0.001082
0.0995	0.2209	0.001044	0.1330	0.1575	0.001084
0.0889	0.7856	0.000756	0.1035	0.8105	0.000752
0.5354	0.2836	0.001106	0.0720	0.4995	0.000898
0.1602	0.3608	0.001001	0.0633	0.5970	0.000841
0.3472	0.3838	0.001032	0.2967	0.1588	0.001140
0.1410	0.6330	0.000859	0.2383	0.6691	0.000870
0.0631	0.2794	0.000996	0.3707	0.1823	0.001152
0.5647	0.1917	0.001140	0.3336	0.5642	0.000941
0.0621	0.7839	0.000736			
2,2,4-Trimethylpentane (B) + 2-Propanol (C) + 1-Pentanol (D)					
0.2129	0.4662	0.000887	0.5281	0.3511	0.001027
0.0763	0.2307	0.000983	0.1317	0.1484	0.001058
0.0903	0.7414	0.000618	0.1080	0.8053	0.000604
0.5654	0.2600	0.001062	0.0581	0.4958	0.000795
0.1634	0.3432	0.000943	0.0611	0.5983	0.000726
0.3453	0.3684	0.000991	0.2812	0.1550	0.001113
0.1437	0.6294	0.000746	0.2375	0.6561	0.000761
0.0592	0.2747	0.000943	0.3571	0.1912	0.001115
0.5535	0.2047	0.001122	0.3197	0.5670	0.000843
0.0595	0.7832	0.000590			
2,2,4-Trimethylpentane (B) + 1-Butanol (C) + 1-Pentanol (D)					
0.2318	0.4236	0.001069	0.5745	0.2912	0.001167
0.1092	0.1894	0.001107	0.1455	0.1277	0.001128
0.0894	0.7683	0.000919	0.1337	0.7689	0.000931
0.5754	0.2307	0.001183	0.0747	0.4475	0.001007
0.1679	0.3258	0.001080	0.0748	0.5490	0.000983
0.3728	0.3505	0.001133	0.2977	0.1361	0.001176
0.1641	0.5876	0.001001	0.2799	0.6186	0.001013
0.0769	0.2522	0.001071	0.3827	0.1435	0.001202
0.5933	0.1446	0.001231	0.3694	0.5121	0.001069
0.1288	0.7067	0.000956			
2,2,4-Trimethylpentane (B) + 2-Butanol (C) + 1-Pentanol (D)					
0.2273	0.4253	0.000995	0.5731	0.3149	0.001124
0.1036	0.1896	0.001051	0.1368	0.1326	0.001107
0.0831	0.7698	0.000749	0.1290	0.7816	0.000779
0.5590	0.2369	0.001145	0.0709	0.4424	0.000910
0.1736	0.3061	0.001026	0.0664	0.5627	0.000842
0.3658	0.3502	0.001079	0.2949	0.1525	0.001153
0.1670	0.5880	0.000896	0.2792	0.6110	0.000942
0.0744	0.2269	0.001021	0.3640	0.1629	0.001128
0.5874	0.1584	0.001200	0.3643	0.5234	0.001012
0.0635	0.7470	0.000748			

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

solvent (I) + solvent (J)	S_{IJ}^a
2,2,4-Trimethylpentane (I) + 1-Propanol (J)	0.825
	−0.103
	0.291
2,2,4-Trimethylpentane (I) + 2-Propanol (J)	1.193
	−0.369
	0.333
2,2,4-Trimethylpentane (I) + 1-Butanol (J)	0.536
	0.151
	0.142
2,2,4-Trimethylpentane (I) + 2-Butanol (J)	1.070
	−0.213
	0.000
2,2,4-Trimethylpentane (I) + 1-Pentanol (J)	0.530
	0.242
	−0.011
1-Propanol (I) + 1-Pentanol (J)	0.216
	0.089
	−0.104
2-Propanol (I) + 1-Pentanol (J)	0.445
	0.111
	0.033
1-Butanol (I) + 1-Pentanol (J)	0.055
	0.033
	−0.016
2-Butanol (I) + 1-Pentanol (J)	0.106
	−0.054
	−0.035

^{a} Combined NIBS/Redlich–Kister curve-fit parameters are ordered as $S_{IJ,0}$, $S_{IJ,1}$, $S_{IJ,2}$.

Table 3. Summarized Comparison between Observed Anthracene Solubilities in Ternary 2,2,4-Trimethylpentane + Propanol + 1-Pentanol and 2,2,4-Trimethylpentane + Butanol + 1-Pentanol Solvent Mixtures and Predicted Values Based on Equation 1

ternary solvent mixture	$100 \cdot RD^a$
2,2,4-Trimethylpentane (B) + 1-Propanol (C) + 1-Pentanol (D)	1.31
2,2,4-Trimethylpentane (B) + 2-Propanol (C) + 1-Pentanol (D)	1.30
2,2,4-Trimethylpentane (B) + 1-Butanol (C) + 1-Pentanol (D)	1.74
2,2,4-Trimethylpentane (B) + 2-Butanol (C) + 1-Pentanol (D)	1.56

^{a} RD = $(1/N) \Sigma[(x_A^{sat})^{calcd} - (x_A^{sat})^{exptl}]/(x_A^{sat})^{exptl}$; where $N = 19$.

additional days and by approaching equilibrium from super-saturation by pre-equilibrating the solutions at a slightly higher temperature. Aliquots of saturated anthracene solutions were transferred through a coarse filter into a tared volumetric flask to determine the amount of sample and then diluted quantitatively with methanol for spectrophotometric analysis at 356 nm on a Bausch and Lomb Spectronic 2000 (photometric accuracy of 0.002A). Concentrations of the dilute solutions were determined from a Beer–Lambert law absorbance versus concentration working curve. Molar absorptivities of the nine standard solutions varied systematically with molar concentration and ranged from $\epsilon/(L \cdot mol^{-1} \cdot cm^{-1}) = 7450$ to $\epsilon/(L \cdot mol^{-1} \cdot cm^{-1}) = 7150$ for anthracene compositions ranging from $C/(mol \cdot L^{-1}) = 6.75 \cdot 10^{-5}$ to $C/(mol \cdot L^{-1}) = 2.25 \cdot 10^{-4}$. Identical molar absorptivities were obtained for select anthracene standard solutions that contained volume fractions up to 5 % of the neat 2,2,4-trimethylpentane and alcohol cosolvents. Experimental molar concentrations were converted to mass fraction solubility by multiplying by the molar mass of anthracene, volume(s) of the volumetric flask(s) used, and any dilutions required to

place the measured absorbances on the Beer–Lambert law absorbance versus concentration working curve and then dividing by the mass of the saturated solution analyzed. Mole fraction solubilities were computed from mass fraction solubility using the binary solvent initial mole fraction compositions and molar masses of the solute and both cosolvents. Experimental anthracene solubilities in the four ternary 2,2,4-trimethylpentane + propanol/butanol + 1-pentanol mixtures studied are listed in Table 1. Numerical values represent the average of between four and eight independent determinations, with the reproducibility of the solubilities of the solute being 1.5 %.

Results and Discussion

Equation 1 expresses the "excess" logarithmic mole fraction solubility, relative to the simple $x_B^o \ln(x_A^{sat})_B + x_C^o \ln(x_A^{sat})_C + x_D^o \ln(x_A^{sat})_D$ arithmetic average, in terms of the Redlich–Kister equation. Published papers[1,8,9] have reported the calculated S_{IJ} parameters dissolved in the nine sub-binary systems, as well as the measured mole fraction solubilities in 2,2,4-trimethylpentane ($x_A^{sat} = 0.001074$), 1-propanol ($x_A^{sat} = 0.000591$), 2-propanol ($x_A^{sat} = 0.000411$), 1-butanol ($x_A^{sat} = $

0.000801), 2-butanol ($x_A^{sat} = 0.000585$), and 1-pentanol ($x_A^{sat} = 0.001097$). Numerical values of the S_{IJ} parameters have been tabulated in Table 2 for convenience.

The predictive ability of eq 1 is summarized in Table 3 for anthracene dissolved in the four 2,2,4-trimethylpentane + propanol/butanol + 1-pentanol solvent systems. Examination of the numerical entries in Table 3 reveals that eq 1 predicts the solubility of anthracene to within an overall average absolute relative percent deviation of 1.5, which is comparable to the experimental uncertainty of ± 1.5 %. For the four systems studied, eq 1 was found to provide very accurate predictions of the observed solubility behavior.

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