Solubility of Anthracene in Binary Propyl Acetate + Alcohol Solvent Mixtures at 298.15 K

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Experimental solubilities are reported for anthracene in six binary propyl acetate + alcohol solvent mixtures at 298.15 K. The alcohol solvents studied were 1-propanol, 1-butanol, 2-propanol, 2-butanol, 2-methyl-1-propanol, and 3-methyl-1-butanol. Results of these measurements were used to test a mathematical representation based on the combined nearly ideal binary solvent (NIBS)/Redlich–Kister equation. For the six systems studied, the combined NIBS/Redlich–Kister equation was found to accurately describe the experimental data, with an average absolute deviation between measured and back-calculated values being approximately ± 0.8 %.

Introduction

Solubility plays an essential role in many manufacturing processes, especially in the purification of organic compounds through recrystallization and liquid extraction. Over the past 20 years, we have reported experimental solubility data for anthracene and pyrene dissolved in numerous binary solvents and have developed a fairly simple predictive method for estimating the solubility of crystalline organic compounds in ternary mixtures[1–4]

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

and higher-order multicomponent solvent mixtures[5]

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

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^{o} refers to the initial mole fraction–solvent composition of component i calculated as if the solute were not present, and $(x_A)_I$ denotes the measured solute solubility in pure solvent i. The various $S_{IJ,i}$ parameters can be evaluated with a least-squares regression analysis.

In the present study, we extend our solubility measurements to binary solvent mixtures containing propyl acetate and an alcohol cosolvent. Experimental solubilities are reported for anthracene dissolved in six binary mixtures containing propyl acetate with 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-butanol, and 3-methyl-1-butanol at 298.15 K. Results

of these measurements are used to calculate the $S_{IJ,i}$ curve-fit coefficients. To date, the solubility behavior of anthracene in binary propyl acetate + alcohol solvent mixtures has not been studied.

Experimental Methods

Anthracene (Aldrich, 99+ %) was recrystallized several times from 2-propanone to yield a purified sample having a melting point temperature of $T/K = 489$. Propyl acetate (Aldrich, 99 %, anhydrous), 1-propanol (Aldrich, 99+ %, anhydrous), 2-propanol (Aldrich, 99+ %, anhydrous), 1-butanol (Aldrich, 99+ %, anhydrous), 2-butanol (Aldrich, 99+ %, anydrous), 2-methyl-1-propanol (Aldrich, 99+ %, anhydrous), and 3-methyl-1-butanol (Aldrich, 99 %, anhydrous) 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 so that composition could be calculated to 0.0001 mole 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 to facilitate dissolution of the solid. Attainment of equilibrium was verified by repetitive measurements after a minimum of three additional days and by approaching equilibrium from supersaturation 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. 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 $\epsilon/(\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}) = 7450$ to $\epsilon/(\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}) = 7150$ for anthracene compositions ranging from $C/(\text{mol} \cdot \text{L}^{-1}) = 6.75 \cdot 10^{-5}$ to $C/(\text{mol} \cdot \text{L}^{-1}) = 2.25 \cdot 10^{-4}$. Identical molar absorptivities were obtained for select anthracene standard solutions that contained volume fractions up to 5 % of the

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Table 1. Experimental Mole Fraction Solubilities, x_A^{sat}, of Anthracene in Binary Propyl Acetate (B) + Alcohol (C) Solvent Mixtures at 298.15 K

x_B^o	x_A^{sat}	x_B^o	x_A^{sat}
Propyl Acetate (B) + 1-Propanol (C)			
0.0000	0.000591	0.5377	0.00309
0.0872	0.000917	0.7587	0.00438
0.1634	0.001211	0.8699	0.00504
0.3403	0.00205	1.0000	0.00588
0.4416	0.00252		
Propyl Acetate (B) + 2-Propanol (C)			
0.0000	0.000411	0.5016	0.00280
0.0714	0.000672	0.7254	0.00410
0.1352	0.000931	0.8374	0.00479
0.3510	0.001973		
0.4018	0.00225		
Propyl Acetate (B) + 1-Butanol (C)			
0.0000	0.000801	0.5377	0.00352
0.0872	0.001189	0.7587	0.00478
0.1634	0.001548	0.8699	0.00538
0.3403	0.00241		
0.4416	0.00297		
Propyl Acetate (B) + 2-Butanol (C)			
0.0000	0.000585	0.5447	0.00335
0.0842	0.000946	0.7581	0.00464
0.1636	0.001311	0.8652	0.00523
0.3427	0.00221		
0.4310	0.00269		
Propyl Acetate (B) + 2-Methyl-1-propanol (C)			
0.0000	0.000470	0.5508	0.00309
0.0853	0.000791	0.7562	0.00441
0.1755	0.001185	0.8650	0.00513
0.3477	0.001987		
0.4462	0.00248		
Propyl Acetate (B) + 3-Methyl-1-butanol (C)			
0.0000	0.000727	0.5842	0.00354
0.0890	0.001085	0.7905	0.00478
0.1932	0.001552	0.8877	0.00532
0.3811	0.00242		
0.4848	0.00294		

Table 2. Mathematical Representation of Anthracene Solubilities in Several Binary Propyl Acetate (B) + Alcohol (C) Solvent Mixtures Based on eq (3)

solvent (B) + solvent (C)	S_i^a	$100 \cdot dev.^b$
propyl acetate + 1-propanol	1.707	0.9
	−0.948	
	0.604	
propyl acetate + 2-propanol	2.274	1.0
	−1.566	
	1.132	
propyl acetate + 1-butanol	1.656	0.5
	−0.706	
	0.729	
propyl acetate + 2-butanol	1.994	0.9
	−1.118	
	1.026	
propyl acetate + 2-methyl-1-propanol	2.048	0.7
	−1.218	
	1.187	
propyl acetate + 3-methyl-1-butanol	1.544	0.6
	−0.745	
	0.705	

^{a} Curve-fit coefficients are ordered as S_0, S_1, and S_2. ^{b} Deviation = $\sum |[(x_A^{sat})^{calcd} - (x_A^{sat})^{exptl}]/(x_A^{sat})^{exptl}|/N$.

$$\ln x_A^{sat} = x_B^o \ln(x_A^{sat})_B + x_C^o \ln(x_A^{sat})_C + x_B^o x_C^o \sum_{i=0}^{r} S_{BC,i}(x_A^{sat} - x_C^o)^i \quad (3)$$

The ability of eq 3 to represent mathematically the experimental solubility of anthracene in the six binary propyl acetate + alcohol solvent mixtures is summarized in Table 2 in the form of the "curve-fit" parameters and the average absolute percent deviations in back-calculated solubilities. The parameters S were computed from a polynomial least-squares analysis of

$$[\ln x_A^{sat} - x_B^o \ln(x_A^{sat})_B - x_C^o \ln(x_A^{sat})_C]/(x_B^o x_C^o) = S_0 + S_1(x_B^o - x_C^o) + S_2(x_B^o - x_C^o)^2 \quad (4)$$

using the commercial software TableCurve (Janel Scientific, Corte Madera, California). Careful examination of Table 2 reveals that eq 3 does provide an accurate mathematical representation for how the solubility of anthracene varies with solvent composition. The overall average absolute deviation between back-calculated and experimental values is ± 0.8 %, which is less than the uncertainty associated with the measured mole fraction solubilities. The calculated curve-fit coefficients, when combined with our previously reported values for anthracene dissolved in binary alcohol + alcohol[6,7] solvent mixtures, allow one to estimate the solubility of anthracene in ternary propyl acetate + alcohol + alcohol solvent mixtures containing the alcohol cosolvents of 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, and 3-methyl-1-butanol.

neat propyl acetate 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 six binary propyl acetate + alcohol mixtures studied are listed in Table 1. Numerical values represent the average of between four and eight independent determinations, with the measured mole fraction solubilities being reproducible to within ± 1.5 %. Calculated standard deviations ranged from $\sigma_{n-1} = 0.000004$ to $\sigma_{n-1} = 0.000038$ mole fraction. The larger standard deviations were observed for the solutions having the larger mole fraction solubilities. Here, an extra dilution was required to get the measured absorbance to fall on the working curve established by the standard solutions.

Results and Discussion

For a binary solvent mixture, eq 2 takes the mathematical form of

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