

# Solubility of Pyrene in Ternary Propanol + Butanol + Cyclohexane Solvent Mixtures at 299.15 K

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Experimental solubilities are reported for pyrene dissolved in ternary 1-propanol + 1-butanol + cyclohexane, 2-propanol + 1-butanol + cyclohexane, 1-propanol + 2-butanol + cyclohexane, and 2-propanol + 2-butanol + cyclohexane solvent mixtures at 26 °C and atmospheric pressure. 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 1.2%, 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, dibenzothiophene, and xanthene) have been published in the recent chemical literature. For a listing of references, see refs 1–3. 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.

In the present study pyrene solubilities have been measured in four ternary propanol + butanol + cyclohexane systems at  $(26.0 \pm 0.1)^\circ\text{C}$ . 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. Subsequent studies will interpret the measured pyrene solubilities using both mobile order theory and the Kretschmer–Wiebe association model. Powell *et al.*<sup>4</sup> and McHale *et al.*<sup>5</sup> showed that these latter two solution models provided reasonably accurate descriptions for the solubility behavior of pyrene and anthracene in binary alkane + alcohol and alcohol + alcohol solvent mixtures. Neither model has been used to describe solubility in ternary solvent systems.

## Experimental Methods

Pyrene (Aldrich, 98%) was recrystallized three times from anhydrous methanol. 1-Propanol (Aldrich, 99+%, anhydrous), 2-propanol (Aldrich, 99+%, anhydrous), 1-butanol (Aldrich, HPLC, 99.8+%), 2-butanol (Aldrich, 99+%, anhydrous), and cyclohexane (Aldrich, HPLC, 99.9+%) 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.<sup>6</sup> Experimental pyrene solubilities in the four propanol + butanol + 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

Acree and co-workers<sup>7–9</sup> suggested the combined NIBS/Redlich–Kister equation for the mathematical representation of isothermal solubility data in binary solvent systems

$$\ln x_A^{\text{sat}} = x_B^{\circ} \ln(x_A^{\text{sat}})_B + x_C^{\circ} \ln(x_A^{\text{sat}})_C + x_B^{\circ} x_C^{\circ} \sum_{i=0}^N S_i (x_B^{\circ} - x_C^{\circ})^i \quad (1)$$

where  $x_B^{\circ}$  and  $x_C^{\circ}$  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. Equation 1 has been shown to provide very accurate mathematical representations of anthracene, pyrene, and carbazole solubilities in a large number of both complexing and noncomplexing solvent mixtures.<sup>1–3</sup>

For a ternary solvent system, the mathematical representation takes the form

$$\begin{aligned} \ln x_A^{\text{sat}} = & x_B^{\circ} \ln(x_A^{\text{sat}})_B + x_C^{\circ} \ln(x_A^{\text{sat}})_C + x_D^{\circ} \ln(x_A^{\text{sat}})_D + \\ & x_B^{\circ} x_C^{\circ} \sum_{i=0}^r S_{i,BC} (x_B^{\circ} - x_C^{\circ})^i + x_B^{\circ} x_D^{\circ} \sum_{j=0}^s S_{j,BD} (x_B^{\circ} - x_D^{\circ})^j + \\ & x_C^{\circ} x_D^{\circ} \sum_{k=0}^t S_{k,CD} (x_C^{\circ} - x_D^{\circ})^k \quad (2) \end{aligned}$$

Recent studies have shown that eq 2 provides reasonably accurate predictions for anthracene solubilities in ternary

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**Table 1. Experimental Mole Fraction Solubilities of Pyrene ( $x_A^{\text{sat}}$ ) in Ternary Propanol (B) + Butanol (C) + Cyclohexane (D) Solvent Mixtures at 299.15 K**

$x_B^0$	$x_C^0$	$x_A^{\text{sat}}$	$x_B^0$	$x_C^0$	$x_A^{\text{sat}}$
1-Propanol (B) + 1-Butanol (C) + Cyclohexane (D)					
0.3996	0.3217	0.008 26	0.1954	0.1593	0.01177
0.1828	0.6929	0.007 18	0.7515	0.1345	0.00587
0.3156	0.2545	0.009 60	0.5642	0.2383	0.00701
0.3003	0.4963	0.007 62	0.1414	0.2154	0.01159
0.7506	0.0984	0.006 17	0.1262	0.7009	0.00756
0.7400	0.1808	0.005 33	0.2726	0.1028	0.01118
0.2374	0.6769	0.006 65	0.1407	0.4232	0.01015
0.1367	0.5129	0.009 21	0.4867	0.1066	0.00925
0.4579	0.4597	0.006 22	0.5812	0.1014	0.00817
0.5612	0.3576	0.005 95			
2-Propanol (B) + 1-Butanol (C) + Cyclohexane (D)					
0.4549	0.2995	0.006 84	0.1786	0.1734	0.01082
0.1788	0.7010	0.006 69	0.7434	0.1399	0.00473
0.3076	0.2679	0.008 87	0.5627	0.2380	0.00603
0.2958	0.4970	0.006 96	0.1376	0.2218	0.01101
0.7460	0.0979	0.004 95	0.1316	0.7029	0.00715
0.7437	0.1814	0.004 29	0.2681	0.1042	0.01056
0.2443	0.6615	0.006 17	0.1360	0.4241	0.00965
0.1300	0.5116	0.008 98	0.4748	0.1071	0.00835
0.4572	0.4615	0.005 30	0.5665	0.1045	0.00727
0.5517	0.3664	0.004 99			
1-Propanol (B) + 2-Butanol (C) + Cyclohexane (D)					
0.4037	0.3266	0.007 33	0.2072	0.1706	0.01080
0.1889	0.6895	0.005 65	0.7413	0.1413	0.00560
0.3144	0.2626	0.009 00	0.5650	0.2337	0.00648
0.3088	0.4762	0.006 67	0.1479	0.2207	0.01087
0.7493	0.0941	0.006 08	0.1338	0.6917	0.00634
0.7448	0.1788	0.005 17	0.2636	0.1214	0.01064
0.2384	0.6688	0.005 29	0.1357	0.4208	0.00933
0.1330	0.5069	0.008 49	0.4769	0.1107	0.00897
0.4606	0.4567	0.005 21	0.5716	0.1049	0.00797
0.5526	0.3608	0.005 17			
2-Propanol (B) + 2-Butanol (C) + Cyclohexane (D)					
0.3935	0.3290	0.006 82	0.1975	0.1683	0.01058
0.1841	0.6901	0.005 56	0.7449	0.1408	0.00443
0.3142	0.2591	0.008 73	0.5560	0.2438	0.00570
0.3008	0.4867	0.006 32	0.1389	0.2273	0.01071
0.7502	0.0973	0.004 88	0.1324	0.7012	0.00603
0.7393	0.1797	0.004 20	0.2614	0.1141	0.01048
0.2415	0.6756	0.004 98	0.1380	0.4184	0.00913
0.1350	0.5138	0.008 21	0.4650	0.1198	0.00823
0.4476	0.4691	0.004 60	0.5674	0.1067	0.00698
0.5398	0.3687	0.004 58			

**Table 2. Summarized Comparison between Observed Pyrene Solubilities in Ternary Propanol + Butanol + Cyclohexane Solvent Mixtures and Predicted Values Based upon the Combined NIBS/Redlich–Kister Equation (Eq 2)**

ternary solvent mixture	% dev <sup>a</sup>
1-propanol (B) + 1-butanol (C) + cyclohexane (D)	1.43
2-propanol (B) + 1-butanol (C) + cyclohexane (D)	1.06
1-propanol (B) + 2-butanol (C) + cyclohexane (D)	0.96
2-propanol (B) + 2-butanol (C) + cyclohexane (D)	1.44

<sup>a</sup> Deviation (%) =  $(100/N) \sum [(x_A^{\text{sat}})^{\text{calc}} - (x_A^{\text{sat}})^{\text{exp}}] / (x_A^{\text{sat}})^{\text{exp}}$ , 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.

two alkane + alcohol<sup>10,11</sup> and alkane + two alcohol<sup>12–14</sup> solvent mixtures. Such systems exhibit fairly large deviations from solution ideality arising 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.

The predictive ability of eq 2 is summarized in Table 2 for pyrene dissolved in the four propanol + butanol +

**Table 3. Combined NIBS/Redlich–Kister Parameters Calculated from Pyrene Solubilities in the Sub-binary Solvent Systems**

solvent (B) + solvent (C)	$S_i^a$
2-propanol (B) + cyclohexane (C)	1.726
	0.165
	0.372
2-butanol (B) + cyclohexane (C)	1.426
	−0.064
	0.447
1-propanol (B) + cyclohexane (C)	1.396
	−0.268
	0.226
1-butanol (B) + cyclohexane (C)	0.976
	−0.462
	0.472
1-propanol (B) + 1-butanol (C)	0.127
	−0.065
2-propanol (B) + 1-butanol (C)	0.215
1-propanol (B) + 2-butanol (B)	none <sup>b</sup>
2-propanol (B) + 2-butanol (C)	0.270

<sup>a</sup> Combined NIBS/Redlich–Kister curve-fit parameters are ordered as  $S_0$ ,  $S_1$ , and  $S_2$ . <sup>b</sup> Experimental solubility data accurately described without the use of the  $S_i$  curve-fit parameters.

cyclohexane systems. Published papers<sup>15–17</sup> have reported the calculated  $S_i$  parameters for pyrene dissolved in seven of the eight sub-binary solvent systems. Solubility data for the remaining binary solvent system are available in the chemical literature; however, the authors did not use the combined NIBS/Redlich–Kister equation at the time the data were originally published. We have determined the numerical values of the  $S_i$  parameters for the binary 1-butanol + cyclohexane solvent system by curve fitting the experimental pyrene mole fraction solubility data of Borders *et al.*<sup>18</sup> in accordance with eq 1. Numerical values of the  $S_i$  parameters have been tabulated in Table 3 for convenience. Experimental mole fraction solubilities in 1-propanol ( $x_A^{\text{sat}} = 0.004\ 26$ ), 2-propanol ( $x_A^{\text{sat}} = 0.002\ 90$ ), 1-butanol ( $x_A^{\text{sat}} = 0.006\ 22$ ), 2-butanol ( $x_A^{\text{sat}} = 0.004\ 39$ ), and cyclohexane ( $x_A^{\text{sat}} = 0.011\ 00$ ) were also taken from the chemical literature.<sup>19–22</sup> Examination of the numerical entries in Table 2 reveals that eq 2 predicts the solubility of pyrene to within an overall average absolute deviation of 1.2%, which is comparable to the experimental uncertainty of  $\pm 1.5\%$ . For the four systems studied, eq 2 was found to provide very accurate predictions of the observed solubility behavior.

## Literature Cited

- (1) Acree, W. E., Jr. *Polycyclic Aromatic Hydrocarbons in Pure and Binary Solvents*; Volume 54 in IUPAC Solubility Data Series; Oxford University Press: Oxford, U.K., 1994.
- (2) Acree, W. E., Jr. *Polycyclic Aromatic Hydrocarbons: Binary Nonaqueous Systems: Part 1 (Solutes A–E)*; Volume 58 in IUPAC Solubility Data Series; Oxford University Press: Oxford, U.K., 1995.
- (3) Acree, W. E., Jr. *Polycyclic Aromatic Hydrocarbons: Binary Nonaqueous Systems: Part 2 (Solutes F–Z)*; Volume 59 in IUPAC Solubility Data Series; Oxford University Press: Oxford, U.K., 1995.
- (4) Powell, J. R.; McHale, M. E. R.; Kauppila, A.-S. M.; Acree, W. E., Jr.; Flanders, P. H.; Varanasi, V. G.; Campbell, S. W. Prediction of Anthracene Solubility in Alcohol + Alkane Solvent Mixtures Using Binary Alcohol + Alkane VLE Data. Comparison of Kretschmer-Wiebe and Mobile Order Models. *Fluid Phase Equilib.* **1994**, *134*, 185–200.
- (5) McHale, M. E. R.; Zvaigzne, A. I.; Powell, J. R.; Kauppila, A.-S. M.; Acree, W. E., Jr.; Campbell, S. W. Thermochemical Investigations of Hydrogen-Bonded Solutions. Part 9. Comparison of Mobile Order Theory and the Kretschmer-Wiebe Association Model for Predicting Pyrene Solubilities in Binary Alcohol + Alcohol Solvent Mixtures. *Phys. Chem. Liq.* **1996**, *32*, 67–87.

- (6) McHale, M. E. R.; Coym, K. S.; Fletcher, K. A.; Acree, W. E., Jr. Solubility of Pyrene in Binary Alcohol + 2-Methyl-2-butanol Solvent Mixtures at 299.2 K. *J. Chem. Eng. Data* **1997**, *42*, 511–513.
- (7) Acree, W. E., Jr. Mathematical Representation of Thermodynamic Properties. Part 2. Derivation of the Combined Nearly Ideal Binary Solvent (NIBS)/Redlich–Kister Mathematical Representation from a Two-Body and Three-Body Interactional Mixing Model. *Thermochim. Acta* **1992**, *198*, 71–79.
- (8) Acree, W. E., Jr.; Zvaigzne, A. I. Thermodynamic Properties of Nonelectrolyte Solutions. Part 4. Estimation and Mathematical Representation of Solute Activity Coefficients and Solubilities in Binary Solvents Using the NIBS and Modified Wilson Equations. *Thermochim. Acta* **1991**, *178*, 151–167.
- (9) Acree, W. E., Jr.; McCargar, J. W.; Zvaigzne, A. I.; Teng, I.-L. Mathematical Representation of Thermodynamic Properties. Carbazole Solubilities in Binary Alkane + Dibutyl Ether and Alkane + Tetrahydropyran Solvent Mixtures. *Phys. Chem. Liq.* **1991**, *23*, 27–35.
- (10) Deng, T.; Acree, W. E., Jr. Solubility of Anthracene in Ternary Propanol + 2,2,4-Trimethylpentane + Cyclohexane and Butanol + 2,2,4-Trimethylpentane + Cyclohexane Solvent Mixtures. *J. Chem. Eng. Data* **1998**, *43*, 1059–1061.
- (11) Deng, T.; Hernández, C. E.; Roy, L. E.; Acree, W. E., Jr. Solubility of Anthracene in Ternary (Propanol + Heptane + Cyclohexane) and (Butanol + Heptane + Cyclohexane) Solvent Mixtures. *J. Chem. Thermodyn.* **1999**, *31*, 205–210.
- (12) Deng, T.; Acree, W. E., Jr. Solubility of Anthracene in Ternary Propanol + Butanol + Cyclohexane Solvent Mixtures. *J. Chem. Eng. Data* **1998**, *43*, 1062–1064.
- (13) Deng, T.; Childress, S. D.; De Fina, K. M.; Sharp, T. L.; Acree, W. E., Jr. Solubility of Anthracene in Ternary Propanol + Butanol + 2,2,4-Trimethylpentane Solvent Mixtures. *J. Chem. Eng. Data* **1998**, *43*, 1065–1067.
- (14) Deng, T.; Childress, S. D.; De Fina, K. M.; Acree, W. E., Jr. Solubility of Anthracene in Ternary Propanol + Butanol + Heptane Solvent Mixtures. *Chem. Eng. Commun.* **1999**, *172*, 217–224.
- (15) Zvaigzne, A. I.; Acree, W. E., Jr. Solubility of Pyrene in Binary Alkane + 1-Propanol and Alkane + 2-Propanol Solvent Mixtures. *J. Chem. Eng. Data* **1993**, *38*, 393–395.
- (16) Hernández, C. E.; Coym, K. S.; Roy, L. E.; Powell, J. R.; Acree, W. E., Jr. Solubility of Pyrene in Binary (Alkane + 2-Butanol) Solvent Mixtures. *J. Chem. Thermodyn.* **1998**, *30*, 37–42.
- (17) Zvaigzne, A. I.; Miller, B. J.; Acree, W. E., Jr. Solubility of Pyrene in Binary Alcohol + 1-Propanol and Alcohol + 2-Propanol Solvent Mixtures. *J. Chem. Thermodyn.* **1995**, *40*, 1267–1269.
- (18) Borders, T. L.; McHale, M. E. R.; Powell, J. R.; Coym, K. S.; Hernández, C. E.; Roy, L. E.; Acree, W. E., Jr.; Williams, C. D.; Campbell, S. W. Thermodynamics of Mobile Order Theory: Comparison of Experimental and Predicted Anthracene and Pyrene Solubilities in Binary Alkane + Alcohol Solvent Mixtures. *Fluid Phase Equilib.* **1998**, *146*, 207–221.

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