

large two-liquid-phase regions) may be useful model systems in examining additives that might suppress phase separation in Th(NO<sub>3</sub>)<sub>4</sub>-TAP-alkane systems.

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**Supplementary Material Available:** Experimental phase boundary and tie-line composition data for the TPP and TiBP systems (3 pages). Ordering information is given on any current masthead page.

## Solubility of Pyrene in Binary Solvent Mixtures Containing Cyclohexane

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**Solubilities are reported for pyrene at 26.0 °C in binary mixtures of cyclohexane with *n*-hexane, *n*-heptane, *n*-octane, isooctane, and cyclooctane. The results of these measurements are compared to the predictions of equations developed previously for solubility in systems of nonspecific interactions. The nearly ideal binary solvent (NIBS) model predicts these solubilities with a maximum deviation of 4.6%, using as input data the solubility of pyrene in each pure solvent. The NIBS model correctly predicts a small maxima for the mole fraction solubility of pyrene in cyclohexane + *n*-heptane mixtures.**

#### Introduction

The use of binary solvents for influencing solubility and multiphase partitioning has many potential applications in the chemical industry. Maximum realization of these applications depends on the development of equations that enable a priori prediction of solution behavior in mixed solvents from a minimum number of experimental observations. The nearly ideal binary solvent (NIBS) approach developed previously (1-5) provides a relatively simple method for estimating the excess partial molar properties of a solute, ( $\Delta\bar{Z}_3^{\text{ex}}$ )\* at infinite dilution in a binary solvent (components 1 and 2)

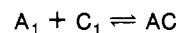
$$(\Delta\bar{Z}_3^{\text{ex}})^* = f_1^0(\Delta\bar{Z}_3^{\text{ex}})_1^* + f_2^0(\Delta\bar{Z}_3^{\text{ex}})_2^* - \Gamma_3(X_1^0\Gamma_1 + X_2^0\Gamma_2)^{-1}\Delta\bar{Z}_{12}^{\text{ex}} \quad (1)$$

$$f_1^0 = 1 - f_2^0 = X_1^0\Gamma_1 / (X_1^0\Gamma_1 + X_2^0\Gamma_2)$$

in terms of a weighted mole fraction average of the properties of the solute in the two pure solvents ( $(\Delta\bar{Z}_3^{\text{ex}})_1^*$  and  $(\Delta\bar{Z}_3^{\text{ex}})_2^*$

and a contribution due to the unmixing of the solvent pair by the presence of the solute. Equation 1 leads to accurate predictions of enthalpies of solution (1), gas-liquid partition coefficients (3), and solubilities (2, 4-11) in systems of nonspecific interactions when the weighting factors ( $\Gamma_i$ ) are approximated with molar volumes.

The success of the NIBS in predicting solubility in noncomplexing solvent mixtures suggested the possibility that this solution model may provide a foundation for approximations of the physical interactions even in a system known to contain chemical interactions. To pursue this idea further, Acree et al. (12) extended the basic NIBS model to systems containing association between the solute (component A) and a complexing cosolvent (component c)



$$K_{AC} = \phi_{AC} / \phi_A\phi_C,$$

Postulating the formation of a 1:1 anthracene-benzene complex, the authors demonstrated that the solubility of anthracene in benzene + *n*-heptane and benzene + isooctane could be described to within a maximum deviation of 4% using a single equilibrium constant. More importantly, it was noted that the determination of solute-solvent equilibrium constants from solubility measurements does depend on the manner in which nonspecific interactions are incorporated into the model.

Continued development of solution models for predicting the properties of a solute in binary solvent systems requires that a large data base be available for assessing the applications and limitations of derived predictive expressions. Currently, only a limited data base exists for crystalline nonelectrolyte solubility in binary solvent systems. For these reasons, we report the solubility of pyrene in mixtures containing cyclohexane with

Table I. Comparison between Experimental and Predicted Values for Pyrene Solubilities in Several Binary Solvents at 26 °C

solvent (1) + solvent (2)	$X_1^0$	$X_3^{\text{sat } b}$	% dev of calcd values <sup>a</sup>			$\Delta\bar{G}_{12}^{\text{ex}}$ ref
			(2)	(3)	(4)	
C <sub>6</sub> H <sub>12</sub> + <i>n</i> -C <sub>6</sub> H <sub>14</sub>	0.0000	0.00852				18
	0.2195	0.00942	-2.4	-2.4	-2.3	
	0.4365	0.01016	-3.3	-3.0	-2.9	
	0.5513	0.01049	-3.4	-3.0	-2.8	
	0.6503	0.01066	-2.7	-2.2	-2.0	
	0.8300	0.01099	-2.5	-1.9	-1.7	
	1.0000	0.01089				
C <sub>6</sub> H <sub>12</sub> + <i>n</i> -C <sub>7</sub> H <sub>16</sub>	0.0000	0.01101				19
	0.2572	0.01145	-1.9	-1.4	-1.1	
	0.4685	0.01152	-2.1	-1.1	-0.8	
	0.5682	0.01156	-2.6	-1.5	-1.1	
	0.6592	0.01151	-2.5	-1.4	-1.0	
	0.8382	0.01134	-2.3	-1.4	-1.2	
	1.0000	0.01089				
C <sub>6</sub> H <sub>12</sub> + <i>n</i> -C <sub>8</sub> H <sub>18</sub>	0.0000	0.01379				20
	0.2840	0.01350	-2.2	-0.1	0.2	
	0.5005	0.01314	-4.4	-1.4	-0.9	
	0.6063	0.01281	-4.6	-1.5	-0.9	
	0.6938	0.01246	-4.3	-1.3	-0.7	
	0.8577	0.01171	-2.8	-0.9	-0.5	
	1.0000	0.01089				
C <sub>6</sub> H <sub>12</sub> + <i>i</i> -C <sub>8</sub> H <sub>18</sub>	0.0000	0.00721				21
	0.2874	0.00803	2.6	-0.5	-0.2	
	0.4993	0.00887	1.9	-2.2	-1.7	
	0.6003	0.00926	1.7	-2.2	-1.6	
	0.7007	0.00958	2.3	-1.2	-0.6	
	0.8533	0.01027	1.0	-1.2	-0.7	
	1.0000	0.01089				
C <sub>6</sub> H <sub>12</sub> + <i>c</i> -C <sub>8</sub> H <sub>16</sub>	0.0000	0.01956				22
	0.2387	0.01780	-3.8	-1.2	-1.1	
	0.4680	0.01572	-4.5	-0.8	-0.6	
	0.5624	0.01489	-4.6	-0.9	-0.7	
	0.6655	0.01400	-4.6	-1.1	-0.9	
	0.8363	0.01250	-3.7	-1.4	-1.2	
	1.0000	0.01089				

<sup>a</sup> Deviation = 100 ln ( $X_3^{\text{sat}}/X_3^{\text{calcd}}$ ). <sup>b</sup> Standard deviations for representative solvent mixtures are 0.00007 for cyclohexane, 0.00007 for cyclooctane, 0.00004 for *n*-hexane, 0.00007 for *n*-heptane, and 0.00007 for *n*-octane.

*n*-hexane, *n*-heptane, *n*-octane, isooctane, and cyclooctane. Results of these measurements are compared to the predictions of the NIBS model.

## Materials and Methods

Pyrene (Aldrich 99%) was recrystallized three times from absolute ethanol, giving a melting point of 151.1 ± 0.5 °C (literature values are 151.3 (13) and 149–150 °C (14)). Cyclohexane (Aldrich HPLC grade), *n*-hexane (Aldrich 99%), *n*-heptane (Aldrich Gold Label), *n*-octane (Aldrich Gold Label), cyclooctane (Aldrich Gold Label), and isooctane (Fisher 99%) were stored over molecular sieves (Type 4A) to remove trace amounts of water. Binary solvent mixtures were prepared by weight so that solvent compositions could be calculated to 0.0001 mole fraction.

Excess pyrene and solvent were placed in amber glass bottles and allowed to equilibrate in a constant temperature bath at 26.0 ± 0.1 °C for several days. Random duplicate samples were allowed to equilibrate for a longer period of time, but no significant difference in the saturation solubility was observed. Aliquots of saturated pyrene solutions were transferred through a coarse filter into a tared volumetric flask to determine the amount of sample, and diluted quantitatively with methanol. Concentrations were determined spectrophotometrically at 372 nm on a Bausch and Lomb Spectronic 2000. Experimental solubilities of pyrene in several binary solvent mixtures are given in Table I. Experimental results at each composition represent the average of 4–8 determinations with a maximum deviation of about 1%.

## Results and Discussion

The general NIBS expressions for predicting solubilities in systems of nonspecific interactions depend on two different models of solution ideality:

$$RT \ln (a_3^{\text{solid}}/X_3^{\text{sat}}) = (1 - x_3^{\text{sat}})^2 [x_1^0 (\Delta\bar{G}_3^{\text{ex}})_1^* + X_2^0 (\Delta\bar{G}_3^{\text{ex}})_2^* - \Delta\bar{G}_{12}^{\text{ex}}] \quad (2)$$

$$RT \ln (a_3^{\text{solid}}/X_3^{\text{sat}}) = (1 - \phi_3^{\text{sat}})^2 [\phi_1^0 (\Delta\bar{G}_3^{\text{ex}})_1^* + \phi_2^0 (\Delta\bar{G}_3^{\text{ex}})_2^* - \bar{V}_3 (X_1^0 \bar{V}_1 + X_2^0 \bar{V}_2)^{-1} \Delta\bar{G}_{12}^{\text{ex}}] \quad (3)$$

$$RT \left[ \ln (a_3^{\text{solid}}/\phi_3^{\text{sat}}) - (1 - \phi_3^{\text{sat}}) \times \left( 1 - \frac{\bar{V}_3}{(X_1^0 \bar{V}_1 + X_2^0 \bar{V}_2)} \right) \right] = (1 - \phi_3^{\text{sat}})^2 [\phi_1^0 (\Delta\bar{G}_3^{\text{m}})_1^* + \phi_2^0 (\Delta\bar{G}_3^{\text{m}})_2^* - \bar{V}_3 (X_1^0 \bar{V}_1 + X_2^0 \bar{V}_2)^{-1} \Delta\bar{G}_{12}^{\text{m}}] \quad (4)$$

Equations 2 and 3 based on Raoult's law and eq 4 based on the Flory–Huggins model. In the above expressions  $a_3^{\text{solid}}$  is the activity of the solid solute relative to the pure hypothetical subcooled liquid,  $X_i$  is mole fraction,  $\phi_i$  is volume fraction, and  $\bar{V}_i$  is the molar volume of pure component  $i$ . Binary solvent properties  $\Delta\bar{G}_{12}^{\text{ex}}$  and  $\Delta\bar{G}_{12}^{\text{m}}$  refer to excess Gibbs free energies relative to Raoult's law and the Flory–Huggins model, respectively. The superscript (0) denotes the initial binary solvent composition calculated as if the solute were not present. With the three equations, solubility data measured in each of the pure solvents can be used to calculate the excess partial molar Gibbs free energy of the solute ( $(\Delta\bar{G}_3^{\text{ex}})_i^*$  and  $(\Delta\bar{G}_3^{\text{m}})_i^*$ ). These quantities are then combined with the excess free energy

**Table II. Solvent Properties Used in the NIBS Predictions**

solvent	$\bar{V}_i^a$ , cm <sup>3</sup> /mol	solvent	$\bar{V}_i^a$ , cm <sup>3</sup> /mol
cyclohexane	108.76	<i>n</i> -octane	163.46
<i>n</i> -hexane	131.51	isooctane	166.09
<i>n</i> -heptane	147.48	cyclooctane	134.88

<sup>a</sup>Numerical values correspond to the molar volumes at 25 °C.

of the binary solvent to predict solubility in mixed solvents.

Comparisons between experimental and predicted pyrene solubilities are shown in the last three columns of Table I for the five binary solvent systems studied. Properties used in the calculations include  $\bar{V}_3 = 166.5$  cm<sup>3</sup>/mol, based on the partial molar volume of pyrene in carbon tetrachloride (15), and the activity of the solute,  $a_3^{\text{solid}} = 0.1312$ , calculated from

$$\ln a_3^{\text{solid}} = \frac{-\Delta\bar{H}_3^{\text{fus}}(T_{\text{mp}} - T)}{RTT_{\text{mp}}} \quad (5)$$

the enthalpy of fusion data,  $\Delta\bar{H}_3^{\text{fus}} = 4.09$  kcal/mol (13), at the normal melting point temperature  $T_{\text{mp}} = 424.4$  K. Solvent properties used in the NIBS predictions are listed in Table II.

In general, eq 3 and 4 are comparable, with overall average (RMS) deviations of 1.6% and 1.2%, respectively, and are slightly superior to eq 2 which has an overall average (RMS) deviation of 3.1%. All three equations correctly predict a slight maximum mole fraction solubility in binary solutions of cyclohexane with *n*-heptane. Such synergistic effects are usually explained by solubility parameter theory

$$RT(\ln a_3^{\text{solid}}/X_3^{\text{sat}}) = (1 - \phi_3^{\text{sat}})^2 \bar{V}_3(\delta_3 - \delta_{\text{solvent}})^2 \quad (6)$$

$$\delta_{\text{solvent}} = \phi_1^0 \delta_1 + \phi_2^0 \delta_2$$

in terms of the solubility parameter of the solute being bracketed,  $\delta_1 < \delta_3 < \delta_2$ , by the solubility parameters of the two pure solvents (16, 17). However, the estimated solubility parameter of pyrene ( $\delta_3 = 10.6$ ) is far greater than either of the solubility parameters of cyclohexane ( $\delta_1 = 8.2$ ) or *n*-heptane ( $\delta_2 = 7.4$ ). Similar failures of eq 6 have been noted for benzoic acid in cyclohexane + *n*-heptane and cyclohexane + *n*-hexane mixtures (4) and for anthracene in cyclohexane + *n*-heptane mixtures (8). The fact that the NIBS model correctly predicts maximum solubilities in these four systems suggests its greater applicability.

### Glossary

- $a_3^{\text{solid}}$  activity of the solid solute, defined as the ratio of the fugacity of the solid to the fugacity of the pure subcooled liquid
- $(\Delta\bar{G}_3^{\text{ex}})^*$  partial molar Gibbs free energy of the solute (Raoult's law), extrapolated back to infinite dilution

- $(\Delta\bar{G}_3^{\text{fn}})^*$  partial molar Gibbs free energy of the solute (Flory-Huggins model), extrapolated back to infinite dilution
- $\Delta\bar{G}_{12}^{\text{ex}}$  excess Gibbs free energy of the binary solvent mixture based on Raoult's law
- $\Delta\bar{G}_{12}^{\text{fn}}$  excess Gibbs free energy of the binary solvent mixture based on Flory-Huggins model, calculated from  $\Delta\bar{G}_{12}^{\text{ex}}$  values as  $\Delta\bar{G}_{12}^{\text{fn}} = \Delta\bar{G}_{12}^{\text{ex}} + RT[\ln(X_1^0 \bar{V}_1 + X_2^0 \bar{V}_2) - X_1^0 \ln \bar{V}_1 - X_2^0 \ln \bar{V}_2]$
- $\Delta\bar{H}_3^{\text{fus}}$  enthalpy of fusion of solute
- $\bar{V}_i$  molar volume of component *i*
- $X_1^0, X_2^0$  mole fraction compositions of solvent mixture, calculated as if the solute were not present
- $X_3^{\text{sat}}$  mole fraction solubility of solute
- $\phi_1^0, \phi_2^0$  ideal volume fraction compositions of the solvent mixture, calculated as if the solute were not present
- $\phi_3^{\text{sat}}$  ideal volume fraction solubility of solute
- $\delta_i$  solubility parameter of component *i*, (cal/cm<sup>3</sup>)<sup>1/2</sup>
- $\Gamma_i$  weighting factor of component *i*
- RMS =  $(100/N^{1/2})\{\sum^N [\ln(X_{\text{calcd}}^{\text{sat}}/X_{\text{expt}}^{\text{sat}})]^2\}^{1/2}$ , %
- dev

**Registry No.** C<sub>6</sub>H<sub>12</sub>, 110-82-7; *n*-C<sub>6</sub>H<sub>14</sub>, 110-54-3; *n*-C<sub>7</sub>H<sub>16</sub>, 142-82-5; *n*-C<sub>8</sub>H<sub>18</sub>, 111-65-9; *i*-C<sub>8</sub>H<sub>18</sub>, 540-84-1; *c*-C<sub>8</sub>H<sub>18</sub>, 292-64-8; pyrene, 129-00-0.

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