756 *J. Chem. Eng. Data* **2004,** *49,* 756−759

Solid−Liquid Equilibria of Several Systems Containing Acetic Acid

Mingming Chen* and Peisheng Ma

Key Laboratory for Green Chemical Technology of State Education Ministry, School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, People's Republic of China

Solubilities of three binary systems and five ternary systems involving terephthalic acid, *p*-toluic acid, and 4-carboxyl-benzaldehyde dissolved in pure acetic acid and aqueous acetic acid have been measured using a laser technique from 300 K to 440 K. The experimental data were compared with predicted results using the modified universal quasichemical functional group activity coefficient (UNIFAC) method. The results show that the modified UNIFAC model alone is not reliable for systems with strong interactions between molecules.

Introduction

Currently, polymerization-grade terephthalic acid is one of the main feedstocks for product polyester, which plays an important role in our modern life. After oxidized by air in an oxidization reactor, *p*-xylene is conversed into terephthalic acid. During all the oxidization process, acetic acid is the solvent. Water and terephthalic acid are the main products. Sequentially, terephthalic acid must be purified from the mixture of acetic acid and water. Usually, crystallization is used to obtain products with a high purity.[1] Solubilities of terephthalic acid in aqueous acetic acid become a crucial factor in designing separation equipment, as well as in controlling relevant operating conditions.

In addition, industrial products always contain impurities such as trace quantity of 4-carboxyl-benzaldehyde and *p*-toluic acid in the terephthalic acid. Both of the impurities have an ability to intervene in the polymerization of terephthalic acid, resulting in a significant reduction of polymerization velocity, as well as a degree of polymerization. Moreover, when the concentration of 4-carboxyl-benzaldehyde accumulates up to 25 ppm in the mixture, it will seriously reduce the color grading of the polyester. Thereupon, the solubility of 4-carboxyl-benzaldehyde and *p*-toluic acid should be required in developing a crystallization technology for pure terephthalic acid manufacture.

Generally, solid−liquid equilibrium (SLE) can be described by an equation that involves the properties of pure solute, such as enthalpy of fusion, melting point, and so on[2]

$$\ln(\gamma_i x_i) = -\frac{\Delta_{\mathrm{fus}}H_i}{R}\left[\frac{1}{T} - \frac{1}{T_{\mathrm{fus},i}}\right] - \frac{\Delta_{\mathrm{trs}}H_i}{R}\left[\frac{1}{T} - \frac{1}{T_{\mathrm{trs},i}}\right] \quad (1)$$

In eq 1, $\Delta_{\mathrm{fus}}H_i$ is the molar enthalpy of fusion of solute i, $T_{\mathrm{fus},i}$ the fusion temperature, $\Delta_{\mathrm{trs}}H_i$ the molar enthalpy of solid−solid phase transition, $T_{\mathrm{trs},i}$ the transition temperature, T the absolute temperature, R the universal gas constant, x_i the real mole fraction, and γ_i the activity coefficient.

If a solid−solid phase transition does not occur, the last term can be neglected and thereby the equation becomes[3]

$$\ln(\gamma_i x_i) = -\frac{\Delta_{\mathrm{fus}}H_i}{R}\left[\frac{1}{T} - \frac{1}{T_{\mathrm{fus},i}}\right] \quad (2)$$

Because the activity coefficient depends on the mole fraction and temperature, eq 2 must be solved iteratively. For the definition of the activity coefficient, the group contribution modified universal quasichemical functional group activity coefficient (UNIFAC) method was used.[4]

To calculate the solubility, fusing temperature $T_{\mathrm{fus},i}$ and molar enthalpy of fusion of solute i $\Delta_{\mathrm{fus}}H_i$ are required. Among all the parameters for calculating SLE systems, only $T_{\mathrm{fus},i}$ of all the three kinds of solutes and $\Delta_{\mathrm{fus}}H_i$ of 4-carboxyl-benzaldehyde can be obtained from ref 5 directly while $\Delta_{\mathrm{fus}}H_i$ of both terephthalic acid and *p*-toluic acid are absent and must be estimated. Here, we choose the following empirical eq 3 to do the estimation

$$\Delta_{\mathrm{fus}}H_i = 4.184KT_{\mathrm{fus},i} \quad (3)$$

where K is an empirical parameter related to the properties of the solute. For organic compounds, K ranges from 10 to 16, so that the optimum algorithm was used to determine the optimum value of K for terephthalic acid and *p*-toluic acid. Table 1 gives the pure solutes' properties.[5]

This paper presents the experimental SLE data for three binary systems and five ternary systems related to terephthalic acid manufacture. The binary SLE data can be used to extend the supporting data at high temperatures required for the purification of terephthalic acid.

Experimental Procedure

Terephthalic acid and *p*-toluic acid were from Aldrich Co. 4-Carboxyl-benzaldehyde was from Fluka Co. Their purities were provided by the two companies and are listed in Table 1. After being dried, they were stored in a desiccator. Water was distilled twice, and acetic acid was

Table 1. Purities and Pure Properties of the Applied Chemicals

compound	purity/mass %	$\Delta_{\mathrm{fus}}H/\mathrm{J\cdot mol^{-1}}$	$T_{\mathrm{fus}}/\mathrm{K}$
terephthalic acid	99.95	39.4×10^3 [a]	698.15
p-toluic aid	>99.0	20.6×10^3 [a]	451.75
4-carboxyl-benzaldehyde	>98.5	21.3×10^3	452.15

[a] Estimated by eq 3.

---

* To whom correspondence may be addressed. E-mail: chmm@vip.sina.com. Fax: 86-22-27403389.

10.1021/je034114c CCC: $27.50

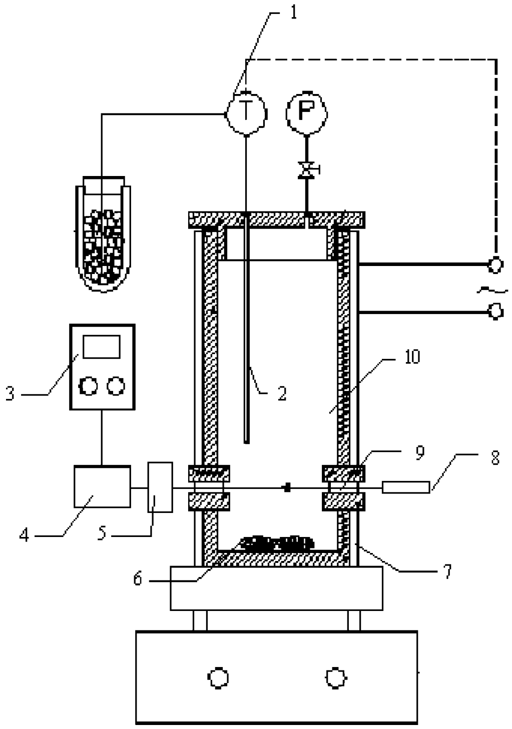

Figure 1. Schematic diagram of the experimental apparatus for determination of SLE using the advanced synthetic method. 1, temperature controller; 2, thermometer; 3, photovoltage displayer; 4, photoelectric transformer; 5, transmitted light receiver; 6, magnetic stir spin; 7, thermostat jacket; 8, semiconductor laser device; 9, quartz window; 10, SLE cell.

purified to 99.9 mass % (gas chromatography). All the chemicals were weighted by an electrical balance with a precision of 0.0001 g.

All systems were measured by a synthetic method using a laser technique. By comparison with the conventional synthetic methods[6,7] where the dissolving process is observed visually, the characteristic of this method is that optics and chemistry principles were combined, so that it will be much more helpful in getting SLE data, especially for low solubilities. During the experiments, the dissolving processes were indirectly observed by a laser. The main apparatus is shown in Figure 1, which includes a titanium SLE cell, a laser-detecting system, a temperature-controlling and measurement system, and a magnetic stirring system. The magnetic stirrer is to ensure the mass transfer from the solid phase to the liquid phase is easy and timely. The equilibrium cell is approximately 100 cm^3 and is made of titanium to avoid corrosion caused by acetic acid, especially at high temperatures. There are two quartz windows symmetrically placed near the bottom and in the wall of the cell allowing for the laser beam. Light is emitted out of a semiconductor laser device of 5 mW. When the laser beam goes through the mixture, it will be scattered and the transmitted intensity will reduce because of the presence of solids. The more solid that exists, the less the laser light is transmitted. We will obtain two transmitted intensity values at the same temperature, being at a static state without stirring and a dynamic state with stirring. When the two transmitted intensities become equal, it corresponds to a dissolution temperature. In the experiment, transmitted laser light intensities are expressed by output photovoltages.

For sparingly soluble solute, the sensitivity limit is a key attribute to establish a reliable experiment method for SLE. Our experimental method was verified using the comparison of the solubilities measured with the traditional visual method and our laser method. Terephthalic acid in water was chosen to be a frame of reference because of its low solubilities,[8] only 1.1×10^{-6} (mole fraction) at 309.57 K measured by visual method. While measured again using the laser-aid apparatus, the corresponding temperature at the same solubility is 309.45 K. The judgment of the dissolving temperature is shown in Figure 2. The intersection point of the two trendlines is just the dissolving point matching a certain solubility. During the repeat, the adjustable resistances on the output services were manually adjusted to get an adequate sensitivity. As shown in Figure 2, a temperature increase of 0.1 K may cause an increase of about 0.25 mV of the photovoltage when the dissolving point is near.

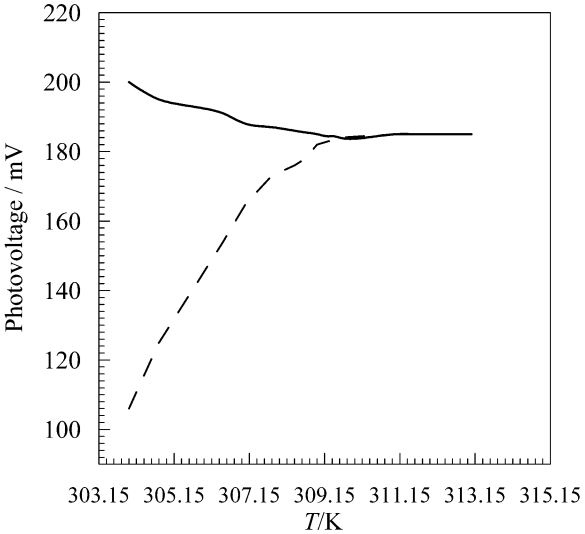

Figure 2. Dissolving temperature determination (terephthalic acid + water, $T = 309.57$ K $x_1 = 1.1 \times 10^{-6}$ (mole fraction)). Solid line, static state; dashed line, dynamic state.

Table 2. Experimental Solubilities for the System *p*-Toluic Acid (1) + Water

T/K	x_1	T/K	x_1	T/K	x_1
290.25	2.445×10^{-5}	317.25	7.884×10^{-5}	339.85	1.673×10^{-4}
299.55	3.869×10^{-5}	320.05	8.685×10^{-5}	344.95	1.937×10^{-4}
301.35	4.168×10^{-5}	327.75	1.134×10^{-4}	348.35	2.076×10^{-4}
311.25	5.930×10^{-5}	335.35	1.466×10^{-4}		

Table 3. Experimental Solubilities for the System *p*-Toluic Acid (1) + Acetic Acid

T/K	x_1	T/K	x_1	T/K	x_1
291.95	3.421×10^{-2}	311.95	4.829×10^{-2}	340.45	9.625×10^{-2}
292.45	3.440×10^{-2}	318.25	5.505×10^{-2}	344.45	1.093×10^{-1}
297.35	3.724×10^{-2}	324.95	6.397×10^{-2}	348.85	1.270×10^{-1}
301.65	4.006×10^{-2}	328.25	6.868×10^{-2}	349.75	1.303×10^{-1}
307.75	4.488×10^{-2}	335.05	8.225×10^{-2}		

By use of the apparatus, measurements between 288 K and 440 K can be performed. The thermocouples were calibrated in the Tianjin Metering Institute, and the deviation of the temperature was determined to be ±0.05 K. Second, the rate of temperature increases is controlled to be less than 0.1 K every 10 min, especially near the SLE point. The uncertainty of the given composition is calculated to be within ±0.0001 mole fraction.

Results

The experimental SLE data for the eight systems investigated are given in Tables 2−9.

By comparison of all the solubilities of terephthalic acid in aqueous acetic acid with those in pure acetic acid,[8] an

Table 4. Experimental Solubilities for the System 4-Carboxyl-benzaldehyde (1) + Acetic Acid

T/K	x_1	T/K	x_1	T/K	x_1
288.95	1.318×10^{-3}	298.65	1.849×10^{-3}	315.45	3.266×10^{-3}
292.85	1.437×10^{-3}	303.85	2.332×10^{-3}	322.55	4.103×10^{-3}
293.55	1.729×10^{-3}	308.75	2.678×10^{-3}	329.95	5.063×10^{-3}

Table 5. Experimental Solubilities for the System *p*-Toluic Acid (1) + Aqueous Acetic Acid (84.2 mass %)

T/K	x_1	T/K	x_1	T/K	x_1
290.55	9.119×10^{-3}	319.75	2.397×10^{-2}	338.95	4.899×10^{-2}
302.65	1.367×10^{-2}	323.35	2.958×10^{-2}	349.05	6.921×10^{-2}
312.95	1.914×10^{-2}	329.45	3.712×10^{-2}	350.85	7.723×10^{-2}

Table 6. Experimental Solubilities for the System 4-Carboxyl-benzaldehyde (1) + Aqueous Acetic Acid (84.2 mass %)

T/K	x_1	T/K	x_1	T/K	x_1
288.25	9.656×10^{-4}	309.65	2.062×10^{-3}	330.35	3.838×10^{-3}
293.25	1.269×10^{-3}	316.95	2.454×10^{-3}	336.45	4.727×10^{-3}
301.95	1.574×10^{-3}	323.35	3.040×10^{-3}	344.35	6.257×10^{-3}

Table 7. Experimental Solubilities for the System Terephthalic Acid (1) + Aqueous Acetic Acid (91.36 mass %)

T/K	x_1	T/K	x_1	T/K	x_1
310.60	2.333×10^{-6}	350.20	9.419×10^{-5}	403.95	9.120×10^{-4}
313.95	3.228×10^{-6}	356.95	1.327×10^{-4}	409.25	1.122×10^{-3}
319.45	5.035×10^{-6}	370.75	2.570×10^{-4}	417.15	1.862×10^{-3}
330.10	1.690×10^{-5}	381.65	3.890×10^{-4}	422.65	2.399×10^{-3}
337.10	3.296×10^{-5}	384.35	4.074×10^{-4}	431.25	4.454×10^{-3}
342.95	5.572×10^{-5}	391.85	5.623×10^{-4}	439.35	6.846×10^{-3}

Table 8. Experimental Solubilities for the System Terephthalic Acid (1) + Aqueous Acetic Acid (84.2 mass %)

T/K	x_1	T/K	x_1	T/K	x_1
312.63	2.426×10^{-6}	344.30	4.457×10^{-5}	404.35	7.691×10^{-4}
318.89	4.027×10^{-6}	355.35	8.690×10^{-5}	414.15	1.151×10^{-3}
330.95	1.300×10^{-5}	371.15	2.333×10^{-4}	419.85	1.560×10^{-3}
334.35	1.690×10^{-5}	383.65	4.365×10^{-4}	426.55	2.307×10^{-3}
335.55	2.333×10^{-5}	396.75	5.916×10^{-4}	437.95	4.563×10^{-3}

Table 9. Experimental Solubilities for the System Terephthalic Acid (1) + Aqueous Acetic Acid (74.6 mass %)

T/K	x_1	T/K	x_1	T/K	x_1
312.90	2.138×10^{-6}	347.75	3.793×10^{-5}	389.90	3.715×10^{-4}
321.65	4.550×10^{-6}	349.15	3.945×10^{-5}	404.65	7.379×10^{-4}
328.95	8.337×10^{-6}	354.55	6.683×10^{-5}	412.20	1.081×10^{-3}
334.75	1.300×10^{-5}	360.30	9.419×10^{-5}	417.65	1.300×10^{-3}
341.15	2.483×10^{-5}	368.60	1.592×10^{-4}	427.15	1.910×10^{-3}
345.35	3.228×10^{-5}	379.30	2.483×10^{-4}	435.05	2.748×10^{-3}

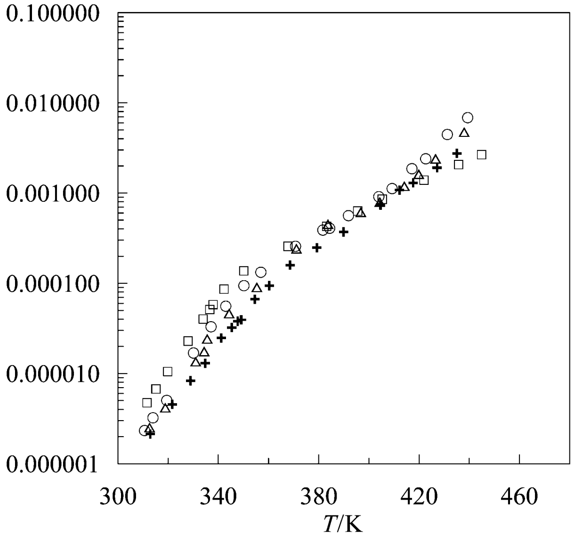

Figure 3. Comparison of the solubilities (molar fraction) of terephthalic acid in aqueous acetic acid: □, 100 mass %; ○, 91.36 mass %; △, 84.2 mass %; +, 74.6 mass %.

interesting result comes up. In Figure 3, it is notable that there is a total change in dissolve tendency. Before 410 K, acetic acid of 100 mass % has the best dissolving capacity for terephthalic acid among the solvents with four different concentrations. Actually water can only dissolve a little terephthalic acid at a normal temperature,[8] which means that the more water contained in solvents, the less solubility obtained. Therefore, acetic acid of 100 mass % has the largest capacity for terephthalic acid among the four different solvents at a temperature below 410 K. In fact, due to association, especially dimerization of acetic acid, fairly low solubilities have been measured in all four of the solvents.

However, changes have taken place when the temperature rises to approximately 410 K and above. Acetic acid of 91.36 mass % turns out to be the best solvent for terephthalic acid, 84.2 mass % is second, 74.6 mass % is third, and 100 mass % is fourth. In other words, within this temperature range, there is a slope presenting the change of solubility influenced by solvent concentrations at a certain temperature. This is called "maximum-solubility effect" predicted by the Scatchard−Hildebrand theory.[9] The theory suggests that, when a solid solute is dissolved in a mixture of two carefully selected solvents, a plot of solubility vs (solute-free) solvent composition should go through a maximum. Gordon and Scott[10] also verified its authenticity by experimentally measuring the solubility of phenanthrene in the mixture of cyclohexane and methylene iodide.

Terephthalic acid, *p*-toluic acid, and 4-carboxyl-benzaldehyde have different solubilities in the same solvent 84.2 mass % acetic acid, presented in Tables 5, 6, and 8, respectively. *p*-Toluic acid has a solubility of 10−100 times as much as 4-carboxyl-benzaldehyde and terephthalic acid, while 4-carboxyl-benzaldehyde is almost the same with terephthalic acid. So, through crystallization, 4-carboxyl-benzaldehyde cannot be easily separated from terephthalic acid. However, the solubility data indicates to us that if 4-carboxyl-benzaldehyde is first hydrogenated to *p*-toluic acid, it will be easier to get rid of the *p*-toluic acid in the terephthalic acid by crystallizations. These data thus serve as a basis for purification of terephthalic acid.

In our experiments, 4-carboxyl-benzaldehyde was found having no solubility in pure water. So this paper does not contain the data on a binary system of 4-carboxyl-benzaldehyde + water.

To ensure whether the modified UNIFAC method could be used as a suitable tool in predicting SLE systems containing associating solvent acetic acid, calculations has been carried out on *p*-toluic acid + 84.2 mass % aqueous acetic acid. *p*-Toluic acid was defined as a new group. The corresponding interaction parameters in the modified UNIFAC method were regressed (shown in Table 10) based on the data shown in Tables 2 and 3. The prediction (Figure 4) of the ternary system *p*-toluic acid + 84.2 mass % aqueous acetic acid was poor. Actually, it mainly results from the strong interactions by hydrogen bonds between two acetic acid molecules. Although, in the modified UNIFAC model, ψ_{mn} represents the interaction forces, the hydrogen bond inside is too strong to be fully evaluated. Cases are the same for the other ternary systems containing terephthalic acid and 4-carboxyl-benzaldehyde.

Table 10. Modified UNIFAC Interaction Parameters

groups		interaction parameters[a]					
m	n	a_{mn}/K	b_{mn}	c_{mn}/K^{-1}	a_{nm}/K	b_{nm}	c_{nm}/K^{-1}
p-toluic acid	CH_3	−848.61	1.9058	0.0102300	−140.79	2.3693	−0.0060554
p-toluic acid	COOH	−1025.80	1.1084	0.0071924	92.70	0.6910	−0.0057835
p-toluic acid	H_2O	101.65	1.2296	0.0116880	130.33	0.9308	−0.0018893

[a] $\psi_{mn} = \exp(-(a_{mn} + b_{mn}T + c_{mn}T^2)/T)$.

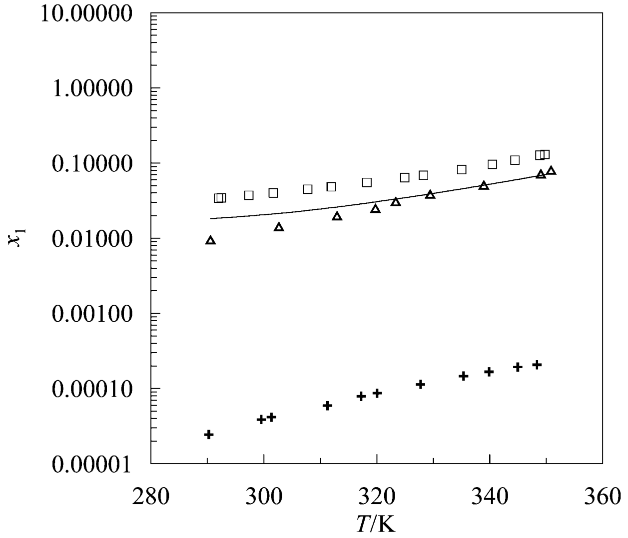

Figure 4. Solubilities (molar fraction) of p-toluic acid in: □, 100 mass % acetic acid; △, 84.2 mass % aqueous acetic acid; +, H_2O; solid line, modified UNIFAC.

All the abovementioned shows that the modified UNIFAC model alone is not reliable for such complex systems.

Summary

A brand new experimental method for SLE determination was brought forward, in which optics and chemistry principles were combined. It is helpful in getting SLE data, especially for minor solubilities at a high pressure. By use of this method, SLE data for three binary systems and five ternary systems containing associating solvents and organic solutes from 300 K to 440 K were measured. The results show that although water has a lower capacity for terephthalic acid, the addition of water will enhance the solubility of solute when the temperature rises up to 410 K. Because of association, prediction using the modified UNIFAC model for ternary systems presents poor consistency with the experimental data.

Literature Cited

(1) Wynn, N. P. Separate Organics by Melt Crystallization. *Chem. Eng. Prog.* **1992**, *88*, 52−60.
(2) Lonmann, J.; Ropke, T.; Gmehling, J. Solid−Liquid Equilibria of Several Binary Systems with Organic Compounds. *J. Chem. Eng. Data* **1998**, *43*, 856−860.
(3) Gmehling, J.; Anderson, T. F.; Prausnitz, J. M. Solid−Liquid Equilibria Using UNIFAC. *Ind. Eng. Chem. Fundam.* **1978**, *17*, 269−273.
(4) Gmehling, J.; Li, Jiding; Schiller Martin. A Modified UNFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties. *Ind. Eng. Chem. Process Res.* **1993**, *32*, 178−193.
(5) Edition Committee of Encyclopedia of Chemical Engineering. *Encyclopedia of Chemical Engineering*; Chemical Industry Press: Beijing, 1990.
(6) Jakob, A.; Joh, R.; Rose, C.; Gmehling, J. Solid−Liquid Equilibria in Binary Mixtures of Organic Compounds. *Fluid Phase Equilib.* **1995**, *113*, 117−126.
(7) Fiege, C.; Joh, R.; Petri, M.; Gmehling, J. Solid−Liquid Equilibria for Different Heptanones with Benzene, Cyclohexanone, and Ethanol. *J. Chem. Eng. Data* **1996**, *41*, 1431−1433.
(8) Mingming, Chen; Peisheng, Ma; Lin, Wang; Feng, Chen. Solid−Liquid Equilibria of Terephthalic Acid in Acetic Acid and Water. *Fluid Phase Equilib.*, submitted.
(9) Prausnitz, J. M.; Lichenthaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed.; Prentice Hall PTR: Upper Saddle River, NJ, 1999; pp 313−326.
(10) Gordon, L. J.; Scott, R. L. Enhanced Solubility in Solvent Mixtures. I. The System Phenanthrene−Cyclohexane−Methylene Iodide. *J. Am. Chem. Soc.* **1952**, *74*, 4138−4140.

Received for review June 10, 2003. Accepted March 22, 2004. The authors would like to thank Sinopec joint-stock company for the financial support (No. 200049).

JE034114C