J. Chem. Eng. Data **2008,** *53,* 2501–2504

Solubilities of 1,3,5-Benzenetricarboxylic Acid and 1,3-Benzenedicarboxylic Acid in Acetic Acid + Water Solvent Mixtures

Lei Feng,[†] Qinbo Wang,*[‡] and Xi Li[†]

Department of Chemical Engineering, Zhejiang University, Hangzhou, 310027 Zhejiang, P. R. China, and College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082 Hunan, P. R. China

---

Using the static analytical method, the solubilities of 1,3,5-benzenetricarboxylic acid and 1,3-benzenedicarboxylic acid in binary acetic acid (2) + water (3) solvent mixtures have been measured. The experimental temperature ranged from (303.2 to 363.2) K, and the mole fraction of acetic acid in the solvent mixtures ranged from (0.411 to 1.000) for 1,3,5-benzenetricarboxylic acid and $x_2 = (0.310 \text{ to } 1.000)$ for 1,3-benzenedicarboxylic acid. The experimental results showed that, within the temperature range of the measurements, the solubilities of 1,3,5-benzenetricarboxylic acid and 1,3-benzenedicarboxylic acid in all the mixtures showed an increasing trend as the temperature increased. The solubility of 1,3,5-benzenetricarboxylic acid increased with the increasing mole fraction of water. Below 323.2 K, as the mole fraction of water increased in the aqueous acetic acid solution, the solubility of 1,3-benzenedicarboxylic acid decreased within the range of measurements. However, above 323.2 K, the aqueous acetic acid solution, of which the mole fraction of acetic acid was 0.544, was the best solvent for 1,3-benzenedicarboxylic acid. A simple explanation was given for this “maximum-solubility effect”. The present results were compared with the data obtained from our previous work. The experimental solubilities had been correlated with the Buchowski equation, and the calculated results showed good agreement with the experimental solubilities.

Introduction

1,3,5-Benzenetricarboxylic acid and 1,3-benzenedicarboxylic acid are two important aromatic compounds. Polymerization-grade 1,3,5-benzenetricarboxylic acid is used extensively in organic synthesis,[1] and 1,3-benzenedicarboxylic acid can be applied in the synthesis of acid-modified copolyester, unsaturated polyester, and surface coating and is expected to be rapidly developing in the field of copolyester production in the following several years.[2]

The majority of 1,3,5-benzenetricarboxylic acid is produced by the liquid-phase catalytic oxidation of mesitylene with air in aqueous acetic acid solution.[3] The majority of 1,3-benzenedicarboxylic acid is produced by the liquid-phase catalytic oxidation of *meta*-xylene with air in aqueous acetic acid solution.[4] During the oxidation process, the solvent is binary acetic acid (2) + water (3) solvent mixtures, and the mole fraction of acetic acid in the solvent mixtures ranges from (0.411 to 1.000). When the 1,3,5-benzenetricarboxylic acid or 1,3-benzenedicarboxylic acid concentration in solution exceeds its solubility, it will crystallize. Therefore, their solubilities in aqueous acetic acid solution are the crucial factor in designing the reactive crystallization as well as in controlling relevant operation conditions. Unfortunately, no experimental solubility data of 1,3,5-benzenetricarboxylic acid in aqueous acetic acid solution was found, except for the solubilities of it in water.[5] The experimental solubility data of 1,3-benzenedicarboxylic acid have been reported by Long et al.[6] However, in that work, only one solvent composition ($x_2 = 1.000$) fell into the industrial solvent composition range ($x_2 = 0.411$ to 1.000), and more measured solubility data in the industrial solvent composition ranges are needed. In this work, we intended to measure the solubility of 1,3,5-benzenetricarboxylic acid in the acetic acid (2) + water (3) solvent mixtures in the temperature range from (313.2 to 363.2) K and the mole fraction of solvent acetic acid in the solvent mixture range from (0.411 to 1.000) and also the solubility of 1,3-benzenedicarboxylic acid in the acetic acid + water solvent mixtures at (313.2 to 363.2) K and $x_2 = (0.310$ to 1.000). The experimental solubility data were correlated with an empirical equation.

Experimental Section

Chemicals. 1,3,5-Benzenetricarboxylic acid (mass fraction > 0.98) was obtained from Alfa Aesar. 1,3-Benzenedicarboxylic acid (mass fraction > 0.99) was obtained from Tokyo Kasei Kogyo Co., Ltd. High-performance liquid-phase chromatography (HPLC) grade methanol and acetonitrile from Tedia Company, Inc. were used as the flow phase in HPLC analysis. Deionized water was used throughout all the experiments. Glacial acetic acid, isopropyl benzene, and dimethyl sulfoxide were obtained from Hangzhou Chemical Reagent Co. All the chemicals were used as received without further purification.

Apparatus and Procedure. The experiments were carried out in a jacketed equilibrium glass bottle with a working volume of 100 mL. The bottle was sealed by a rubber stopper to prevent the evaporation of solvent and was put in a thermostatic water-circulator bath. The bath was continuously mechanically stirred, and the temperature was controlled within ± 0.1 K of the desired temperature with a thermoelectric controlling system. The uncertainty in the temperature measurements was estimated to be ± 0.1 K for all the experiments. The reliability of the experimental apparatus had been verified by the solubility measurements of benzoic acid, phthalic acid, and 1,2,4-benzenetricarboxylic acid in aqueous acetic acid solution.[7,8]

---

* Corresponding author. E-mail: wang_qinbo@hnu.cn.
[†] Zhejiang University.
[‡] Hunan University.

10.1021/je800353s CCC: $40.75

The solubility was measured by the static analytical method. For each experiment, an excess amount, about 5 g, of 1,3,5-benzenetricarboxylic acid or 1,3-benzenedicarboxylic acid was added to (50 ± 3) mL of solvent. Then, the equilibrium bottle was heated to a constant temperature. Different dissolution times were tested to determine a suitable equilibrium time. The attainment of solid−liquid equilibrium was verified by repetitive sampling and measurements in the same experiments during the following several hours until the results were reproducible within ± 3 %. It was found that 12 h was enough for 1,3,5-benzenetricarboxylic acid and 1,3-benzenedicarboxylic acid in aqueous acetic acid solution to reach equilibrium. At each temperature, the solution was kept isothermal for at least 24 h to ensure that the solution had been saturated. A 5 mL syringe was used to withdraw about 3 mL of the clear upper portion of the solution each time. As soon as possible, the sampled solution was deposited into a test tube which had contained about 3 mL of dimethyl sulfoxide. Then, the syringe was washed at least twice by dimethyl sulfoxide, and the washing solutions were also collected together in the same test tube.

Analytical Method. The 1,3,5-benzenetricarboxylic acid or 1,3-benzenedicarboxylic acid concentration in the solution was determined by HPLC and gas chromatography (GC). The internal standard method was used in the analysis. The isopropyl benzene was used as the internal standard substance. The mass ratio of 1,3,5-benzenetricarboxylic acid or 1,3-benzenedicarboxylic acid to the internal standard substance in the solution was determined by an Agilent 1100 Series HPLC. A Diamonsil C18 (250 mm × 4.6 mm) chromatographic column was used. Gradient elution was used for complete separation of the analytes at room temperature. The mass ratio of solvent acetic acid to the internal standard substance in the solution was determined by a Kexiao GC-1690 with a hydrogen flame ionization detector. The SE-54 (30 m) capillary chromatographic column was used. A detailed analytical program and method for HPLC and GC have been given in detail in our recent articles.[7,8]

Results and Discussion

Solubility of 1,3,5-Benzenetricarboxylic Acid. The measured solubilities of 1,3,5-benzenetricarboxylic acid in acetic acid + water solutions were summarized in Table 1 where *S* was the solubility of 1,3,5-benzenetricarboxylic acid. As shown in Figure 1, it could be seen that within the temperature range of the measurements the solubility of 1,3,5-benzenetricarboxylic acid in all of the investigated acetic acid + water solvent compositions showed an increasing trend as the measured temperature increased. The solubility of 1,3,5-benzenetricarboxylic acid in pure acetic acid was the lowest, and it increased with increasing water concentration in the mixed acetic acid + water solvent at constant temperature.

Table 1. Solubilities of 1,3,5-Benzenetricarboxylic Acid (1) in Binary Acetic Acid (2) + Water (3) Solvent Mixtures in the Temperature Range from (313.2 to 363.2) K[a]

T/K	*S*/g (solute) per kg of solvent	S_c/g (solute) per kg of solvent	RD/%
$x_2 = 1.000$			
313.2	4.203 ± 0.126	4.173	−0.721
323.2	4.695 ± 0.131	4.875	3.834
333.2	5.929 ± 0.178	6.033	1.764
343.2	7.012 ± 0.210	7.335	4.600
353.2	8.731 ± 0.262	8.812	0.933
363.2	11.138 ± 0.334	10.538	−5.388
$x_2 = 0.728$			
313.2	6.530 ± 0.196	6.367	−2.501
323.2	8.238 ± 0.247	8.233	−0.058
333.2	10.389 ± 0.312	10.492	0.989
343.2	12.383 ± 0.371	13.144	6.149
353.2	16.805 ± 0.504	16.279	−3.127
363.2	20.345 ± 0.610	19.943	−1.976
$x_2 = 0.546$			
313.2	9.345 ± 0.280	9.107	−2.551
323.2	12.042 ± 0.361	12.098	0.461
333.2	15.573 ± 0.467	15.867	1.887
343.2	19.645 ± 0.589	20.522	4.462
353.2	27.057 ± 0.812	26.119	−3.466
363.2	33.177 ± 0.995	32.768	−1.234
$x_2 = 0.411$			
313.2	13.319 ± 0.400	12.783	−4.027
323.2	16.519 ± 0.496	16.916	2.401
333.2	22.196 ± 0.666	22.015	−0.816
343.2	26.862 ± 0.806	28.206	5.002
353.2	34.768 ± 1.043	35.616	2.438
363.2	47.318 ± 1.420	44.435	−6.093

[a] The *S* stands for the experimental solubility. The S_c stands for the calculated solubility from eq 1. x_2 stands for the mole fraction of acetic acid in the acetic acid (2) + water (3) solvent mixtures.

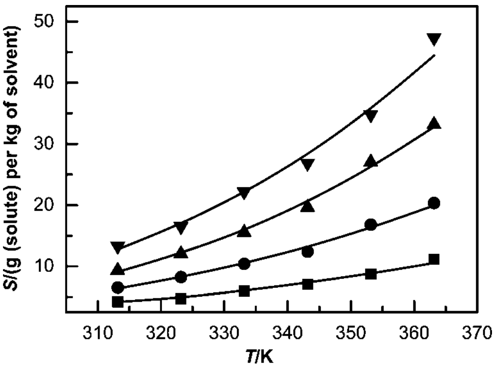

Figure 1. Experimentally determined solubilities of 1,3,5-benzenetricarboxylic acid in acetic acid (2) + water (3). Scatter: ▼, this work, $x_2 = 0.411$; ▲, this work, $x_2 = 0.546$; ●, this work, $x_2 = 0.728$; ■, this work, $x_2 = 1.000$. Line: solubility curve calculated from eq 1.

Solubility of 1,3-Benzenedicarboxylic Acid. The solubility data of 1,3-benzenedicarboxylic acid in acetic acid + water solutions were summarized in Table 2 where *S* was the solubility of 1,3-benzenedicarboxylic acid. From Table 2, it could be seen that within the temperature range of the measurements the solubility of 1,3-benzenedicarboxylic acid in all of the investigated acetic acid + water solvent compositions showed an increasing trend as the measured temperature increased. The measured solubility data of 1,3-benzenedicarboxylic acid in pure acetic acid were compared with the literature data[6] in Figure 2. From Figure 2, it could be seen that most of the solubility data of 1,3-benzenedicarboxylic acid in pure acetic acid reported in this work were in agreement with the literature data.[6]

By comparison of all the solubilities of 1,3-benzenedicarboxylic acid in aqueous acetic acid solution with those in pure acetic acid, an interesting result came up as shown in Figure 3. Below 323.2 K, acetic acid with mole fraction of 100 % had the best dissolving capacity for 1,3-benzenedicarboxylic acid within the solvent composition range of the measurements. It indicated that, as the mole fraction of water increased in the aqueous acetic acid solution, the solubility of 1,3-benzenedicarboxylic acid decreased within the range of measurements.

However, above 323.2 K, the aqueous acetic acid solution, of which the mole fraction of acetic acid was 0.544, was the best solvent for 1,3-benzenedicarboxylic acid. As shown in Figure 3, when the temperature was above 323.2 K, the slope coefficient of the solubility curve changed with the mole fraction of acetic acid: as the mole fraction of acetic acid was less than 0.544, the slope coefficient of the solubility curve was positive;

Table 2. Solubilities of 1,3-Benzenedicarboxylic Acid (1) in Binary Acetic Acid (2) + Water (3) Solvent Mixtures in the Temperature Range from (313.2 to 363.2) K

T/K	S/g (solute) per kg of solvent	S_c/g (solute) per kg of solvent	RD/%
	$x_2 = 1.000$		
313.2	3.272 ± 0.098	3.076	−5.977
323.2	3.978 ± 0.119	4.104	3.160
333.2	5.126 ± 0.154	5.409	5.526
343.2	7.073 ± 0.212	6.995	−1.096
353.2	8.728 ± 0.262	8.945	2.481
363.2	11.738 ± 0.352	11.259	−4.077
	$x_2 = 0.727$		
313.2	3.086 ± 0.093	2.998	−2.859
323.2	4.159 ± 0.125	4.213	1.301
333.2	5.561 ± 0.167	5.757	3.530
343.2	7.669 ± 0.230	7.784	1.502
353.2	10.553 ± 0.317	10.329	−2.120
363.2	13.499 ± 0.405	13.464	−0.256
	$x_2 = 0.544$		
313.2	3.069 ± 0.092	2.969	−3.252
323.2	4.211 ± 0.126	4.273	1.468
333.2	5.757 ± 0.173	5.985	3.959
343.2	8.089 ± 0.243	8.228	1.718
353.2	11.216 ± 0.336	11.087	−1.152
363.2	14.965 ± 0.449	14.769	−1.308
	$x_2 = 0.412$		
313.2	3.016 ± 0.090	2.917	−3.269
323.2	4.169 ± 0.125	4.186	0.401
333.2	5.679 ± 0.170	5.890	3.717
343.2	7.873 ± 0.236	8.108	2.990
353.2	10.893 ± 0.327	10.944	0.467
363.2	15.021 ± 0.451	14.540	−3.202
	$x_2 = 0.310$		
313.2	2.824 ± 0.085	2.864	1.424
323.2	4.224 ± 0.127	4.082	−3.371
333.2	5.772 ± 0.173	5.682	−1.557
343.2	7.361 ± 0.221	7.776	5.639
353.2	10.635 ± 0.319	10.463	−1.614
363.2	14.001 ± 0.420	13.852	−1.065

as the mole fraction of acetic acid was higher than 0.544, the slope coefficient of the solubility curve was negative. The plot of experimental solubility versus solvent composition (solute-free basis) exhibited a maximum. This was called "maximum-solubility effect" predicted by the Scatchard−Hildebrand theory.[13] The theory suggested that when a solid solute was dissolved in a mixture of two carefully selected solvents a plot of solubility versus (solute-free) solvent composition should go through a maximum. Wang et al. verified the theory by experimentally measuring the solubility of phthalic acid in the mixture of acetic acid and water,[7] and Chen and Ma also verified the theory by experimentally measuring the solubility of terephthalic acid in the mixture of acetic acid and water.[14]

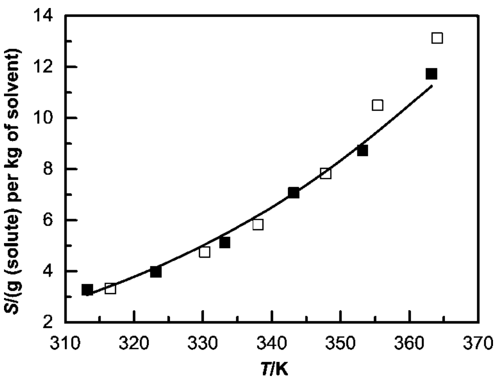

Figure 2. Determined solubilities and literature data of 1,3-benzenedicarboxylic acid in pure acetic acid (2). Scatter: ■, this work, x_2 = 1.000; □, ref 6, x_2 = 1.000. Line: solubility curve calculated from eq 1.

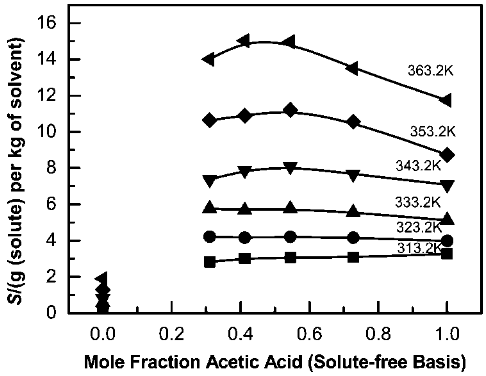

Figure 3. Experimentally determined solubilities of 1,3-benzenedicarboxylic acid in acetic acid (2) + water (3). The scatters with x_2 = 0.000 are the literature data obtained from ref 5. Line: smoothed experimental data (symbols).

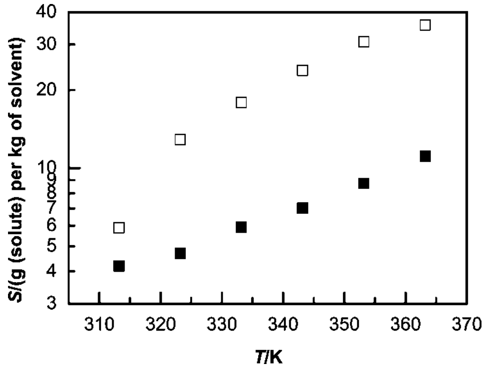

Figure 4. Solubilities of 1,3,5-benzenetricarboxylic acid and 1,2,4-benzenetricarboxylic acid in acetic acid (2) + water (3). Scatter: ■, the solubilities of 1,3,5-benzenetricarboxylic acid, this work, x_2 = 1.000; □, the solubilities of 1,2,4-benzenetricarboxylic acid, ref 8, x_2 = 1.000.

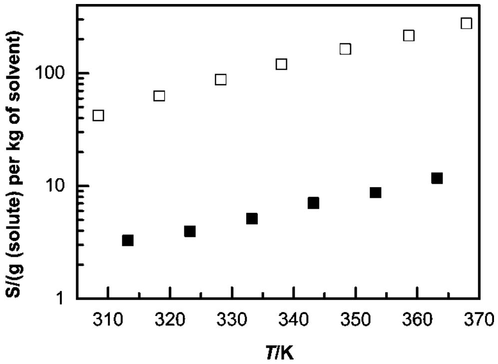

Figure 5. Solubilities of 1,3-benzenedicarboxylic acid and 1,2-benzenedicarboxylic acid in acetic acid (2) + water (3). Scatter: ■, the solubilities of 1,3-benzenedicarboxylic acid, this work, x_2 = 1.000; □, the solubilities of 1,2-benzenedicarboxylic acid, ref 7, x_2 = 1.000.

Effect of Carboxylic Group Position on the Solubility. Taking the solubilities of concerned aromatic acids in pure acetic acid as an example, as shown in Figure 4 and Figure 5, the solubilities could be arranged in the following series at the same temperature: 1,3,5-benzenetricarboxylic acid < 1,2,4-benzenetricarboxylic acid and 1,3-benzenedicarboxylic acid < 1,2-benzenedicarboxylic acid. At least qualitatively, these series could be related to the position of the carboxylic groups in the benzene ring and their possibility to form hydrogen-bonded dimeric units between carboxylic groups of the same acid.[5] The carboxylic groups of 1,3-benzenedicarboxylic acid and 1,3,5-

Table 3. Curve Fitting Parameters of 1,3,5-Benzenetricarboxylic Acid in Binary Acetic Acid (2) + Water Solvent Mixtures in the Temperature Range from (313.2 to 363.2) K and Solvent Composition Range from (x_2 = 0.411 to 1.000)

	λ	h/K	ARD/%
$x_2 = 1.000$	0.0170	131653.7	2.873
$x_2 = 0.728$	0.0403	64329.1	2.467
$x_2 = 0.546$	0.0833	35042.9	2.343
$x_2 = 0.411$	0.0877	32304.3	3.463

Table 4. Curve Fitting Parameters of 1,3-Benzenedicarboxylic Acid in Binary Acetic Acid (2) + Water Solvent Mixtures in the Temperature Range from (313.2 to 363.2) K and Solvent Composition Range from (x_2 = 0.310 to 1.000)

	λ	h/K	ARD/%
$x_2 = 1.000$	0.0434	67978.0	3.719
$x_2 = 0.727$	0.0715	47797.9	1.928
$x_2 = 0.544$	0.0856	42592.1	2.143
$x_2 = 0.412$	0.0734	49771.5	2.341
$x_2 = 0.310$	0.0571	62838.0	2.445

benzenetricarboxylic acid were far apart and probably unable to form the internal dimers. However, 1,2-benzenedicarboxylic acid and 1,2,4-benzenetricarboxylic acid had the adjacent carboxylic groups in the ring to form mostly the internal dimers. So, the solubility of 1,2-benzenedicarboxylic acid was higher than that of 1,3-benzenedicarboxylic acid, and the solubility of 1,2,4-benzenetricarboxylic acid was higher than that of 1,3,5-benzenetricarboxylic acid.

Correlation of Experimental Data. Buchowski and co-workers developed an equation for the systems in which solutes exhibit self-association.[9] This equation is also applicable to most solid−liquid equilibrium systems and gives excellent correlation without considering the activity coefficients of the components, especially to the solid−liquid equilibrium for aromatic acid in aqueous acetic acid solution.[10,11] The Buchowski equation is given by eq 1

$$\ln\left(1+\frac{\lambda(1-x_1)}{x_1}\right)=\lambda h\left(\frac{1}{T}-\frac{1}{T_m}\right) \tag{1}$$

where T is the absolute temperature of solid−liquid equilibrium and T_m is the melting temperature of the solute. In this work, T_m was chosen to be 653.2 K for 1,3,5-benzenetricarboxylic acid and 620.2 K for 1,3-benzenedicarboxylic acid.[12] λ and h are two model parameters. Although only two parameters (λ and h) are involved, this equation is thermodynamically correct and gives an excellent description of experimental data without considering activity coefficients of the components. x_1 is the real mole fraction of solute in solution, which can be calculated from the solubility S.

For practical use in industry, the temperature dependence of 1,3,5-benzenetricarboxylic acid and 1,3-benzenedicarboxylic acid solubilities at fixed solvent composition in the experimental temperature range was correlated with the Buchowski equation. As the Buchowski equation is effective only for constant solvent composition, the values of λ and h change with different solvent compositions. The obtained Buchowski equation model parameters, along with the averaged relative deviations (ARD), at different solvent compositions were listed in Table 3 and Table 4. The ARD is defined as

$$\mathrm{ARD}=\frac{1}{n}\sum_{i=1}^{n}\mathrm{abs}(\mathrm{RD}_i),\qquad \mathrm{RD}_i=\frac{S_{ci}-S_i}{S_i}\cdot 100 \tag{2}$$

where S_c is the solubility calculated by eq 1 and n is the number of experimental points. The calculated solubility and the relative deviation (RD) between the experimental and correlated values of 1,3,5-benzenetricarboxylic acid and 1,3-benzenedicarboxylic acid were also given in Table 1, Table 2, Figure 1, and Figure 2. From Figure 1 and Figure 2, we could see that the calculated solubilities showed good agreement with the experimental values. The experimental solubility and the correlation equation in this work could be used as essential data and models in the synthetic and purification process of 1,3,5-benzenetricarboxylic acid and 1,3-benzenedicarboxylic acid.

Literature Cited

(1) Reeve, A. C. Method for Producing Purified Trimesic Acid. United States Patent 5,107,020, 1992-04-21.

(2) Zhang, G. G.; Zhu, C. Y.; Li, J. L.; Ma, Y. G. Production Technology and Application of Isophthalic Acid. *China Synth. Fiber Ind.* **2005**, *04*, 43–45.

(3) Liang, T. S.; Zhang, C. R.; Su, D. M.; Zhang, H.; Wang, F. Preparation of Trimesic Acid by Liquid Phase Oxidation of Mesitylene. *Chem. Adhes.* **2003**, *04*, 207–208.

(4) Li, Z. G. Production Evolution and Market Prospect of Isophthalic Acid of Worldwide. *Pet. Petrochem. Today* **2007**, *44*, 34–36.

(5) Apelblat, A.; Manzurola, E.; Balal, N. A. J. The Solubilities of Benzene Polycarboxylic Acid in Water. *J. Chem. Thermodyn.* **2006**, *38*, 565–571.

(6) Long, B. W.; Wang, L. S.; Wu, J. S. Solubility of 1,3-Benzenedicarboxylic Acid in Water + Acetic Acid Solutions. *J. Chem. Eng. Data* **2005**, *50*, 136–137.

(7) Wang, Q. B.; Hou, L. X.; Cheng, Y. W.; Li, X. Solubilities of Benzoic Acid and Phthalic Acid in Acetic Acid + Water Solvent Mixtures. *J. Chem. Eng. Data* **2007**, *52*, 936–940.

(8) Li, L.; Feng, L.; Wang, Q. B.; Li, X. Solubility of 1,2,4-Benzenetricarboxylic Acid in Acetic Acid + Water Solvent Mixtures. *J. Chem. Eng. Data* **2008**, *53*, 298–300.

(9) Buchowski, H.; Ksiazczak, A.; Pietrzyk, S. Solvent Activity along a Saturation Line and Solubility of Hydrogen-Bonding Solids. *J. Phys. Chem.* **1980**, *84*, 975–979.

(10) Wang, Q. B.; Xu, H. B.; Li, X. Solid-liquid Equilibrium of 1,4-Benzenedicarboxylic Acid in Binary Acetic Acid + Water Solvent Mixtures at Elevated Temperatures. *J. Chem. Eng. Data* **2005**, *50*, 258–260.

(11) Wang, Q. B. Reactive Crystallization in the Oxidation of para-Xylene. Ph.D. Dissertation, Zhejiang Univeristy, Hangzhou, China, 2006.

(12) *Handbook of Chemistry and Physics*, 73rd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1992.

(13) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed.; Prentice Hall PTR: NJ, 1999.

(14) Chen, M. M.; Ma, P. S. Solid−Liquid Equilibria of Several Systems Containing Acetic Acid. *J. Chem. Eng. Data* **2004**, *49*, 756–759.

Received for review April 14, 2008. Accepted August 24, 2008.

JE800353S