Solubility of 4,4′-Bis[[4-morpholino-6-(*p*-sulfonatoanilino)-1,3,5-triazin-2-yl]amino]stilbene-2,2′-disulphonate in Sodium Chloride + Water from (273.15 to 313.95) K

Mian Yang, Wei-Lan Xue,* Zuo-Xiang Zeng, and Yi Jin

Institute of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China

The solubilities of 4,4′-bis[[4-morpholino-6-(*p*-sulfonatoanilino)-1,3,5-triazin-2-yl]amino]stilbene-2,2′-disulphonate (FBA 210) in sodium chloride + water were measured by a synthetic method in the temperature range from (273.15 to 313.95) K. The solubility data are correlated with the modified Apelblat equation, and the parameters are estimated by the nonlinear least-squares regression method. Computation shows that the equation can predict the observed solubility behavior with an average deviation of about 2.1 %. The parameters *A*, *B*, and *C* are expressed as a function of the mass fraction (*w*) of sodium chloride in sodium chloride + water. The solubilities of FBA 210 in sodium chloride + water can be calculated by interpolation with acceptable precision for an industrial application.

Introduction

4,4′-Bis[[4-morpholino-6-(*p*-sulfonatoanilino)-1,3,5-triazin-2-yl]amino]stilbene-2,2′-disulphonate (FBA 210) (CAS RN [28950-61-0]) is a triazine fluorescent brightening agent. It is a light yellow powder with a molecular formula of $C_{40}H_{36}N_{12}O_{14}S_4\cdot 4Na$ and a molecular weight of 1129.08. Its chemical structure is shown in Figure 1.

FBA 210 is used as a functional pigment in the process of bleaching of fiber, paper, and pulp in order to make them appear brighter and more colorful. In general, the process of bleaching occurs in aqueous solution.[1] On the other hand, the synthesis process of FBA 210 also takes place in aqueous solution, and the product is crystallized by salting-out which is the critical step to reach the purity specification of the final product.[2,3] Therefore, it is necessary to know the solubilities of FBA 210 in aqueous solutions. The solubilities of FBA 210 have not been reported previously.

In this work, the solubilities of FBA 210 in sodium chloride + water were measured from (273.15 to 313.95) K. The experimental data are correlated with the modified Apelblat equation.

Experimental Section

Materials. FBA 210 was prepared in the laboratory by three condensation reaction steps[4,5] which are shown in Figure 2. The chemical structures of the intermediates (I, II) are shown in Figure 3. In every reaction step, sodium hydroxide solution needs to be added to neutralize the hydrochloric acid produced. When the last step is finished, FBA 210 is formed in aqueous solution. The final product was obtained by recrystallization from sodium chloride solution with a mass fraction of 5 % three times to reach the high purity. Its mass fraction purity, determined by HPLC, was higher than 98.5 %. The analytical process of HPLC was as follows: FBA 210 was dissolved in water, and the liquid sample was passed through an Alltima C_{18} column (150 mm × 4.6 mm × 5 μm) using methanol + water (45:55, volume/volume) as the mobile phase at a flow rate of 1.0 $mL\cdot min^{-1}$ and a temperature of 40 °C. The UV detector worked at 350 nm.

Cyanuryl chloride (CAS RN [108-77-0]) was supplied by Hebei Chengxin Co. Ltd. with a purity of 99.3 %. 4,4′-Diaminostilbene-2,2′-disulfonic acid (CAS RN [81-11-8]) was supplied by Zibo Baoze Chemical Co. Ltd. (total amino value on total paste basis was higher than 47 %, and total amino value of dry product on total sample basis was higher than 95 %). Morpholine (CAS RN [110-91-80]) was supplied by Jinan Hengjia Chemical Co. Ltd. with a purity of 99.8 %. Sulfanilic acid (CAS RN [121-57-3]), sodium hydroxide, and sodium chloride with chemical reagent grade were supplied by Shanghai Chemistry Reagent Co. Distilled water was used. The binary mixed solvents were prepared with sodium chloride and distilled water by mass fraction of (0.0 to 15.0) %.

Experimental Methods. The solubilities of solid + liquid mixture are measured by two kinds of methods, namely, the analytical method[6,7] and the synthetic method.[8–10] Compared with the analytical method, the synthetic method is much faster. In this work, the synthetic method was used to measure the solubilities of FBA 210 in sodium chloride + water, and the last crystal disappearance was achieved by changing the temperature. A laser monitoring observation technique was used to monitor the disappearance of the last crystal in the solid + liquid mixture of known composition.[11,12] The laser monitoring observation was more accurate than the traditional visual observation. By varying the composition of the aqueous solution, the effect of composition on the phase transition conditions was studied.

The solubility apparatus consisted of a jacketed glass (250 cm^3) vessel maintained at a desired temperature by circulating water through the outer jacket from a thermostat (temperature uncertainty of ± 0.05 K). The masses of FBA 210 and solvent were determined using a Mettler H542 balance with an uncertainty of ± 0.00001 g. The estimated uncertainty in the mole fraction is less than 0.06 %.

The solubilities of FBA 210 in sodium + water were measured as follows. Predetermined amounts of FBA 210 and

* Corresponding author. E-mail: wlxue@ecust.edu.cn.

10.1021/je8002145 CCC: $40.75
Published on Web 08/13/2008

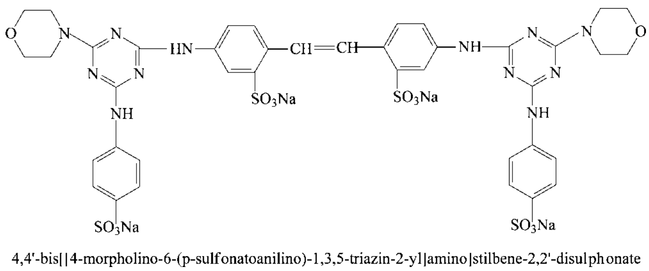

Figure 1. Chemical structure of FBA 210.

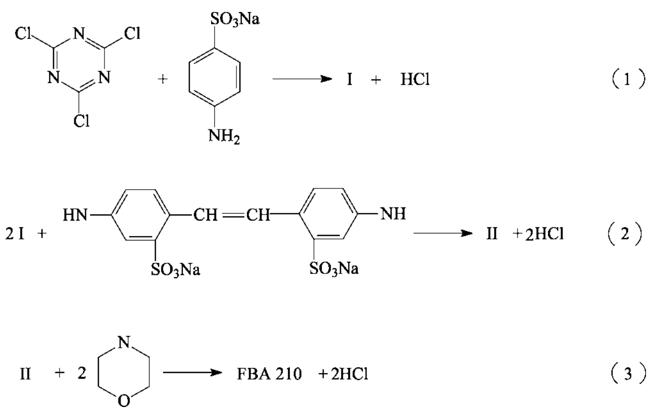

Figure 2. Three condensation reaction steps to synthesize FBA 210.

solvent were placed in the jacketed vessel, and the initial mass of the solvent was known precisely (about 100 g ± 0.001 g). In the early stages of the experiment, the solute was excessive. So, some undissolved particles of FBA 210 existed. The vessel was heated very slowly at a rate less than 2 $K \cdot h^{-1}$ with continuous stirring in a thermostat. Along with the dissolution of FBA 210, the intensity of the laser beam increased gradually. When the last portion dissolved completely, the solution was clear and transparent, and the intensity of the laser beam penetrating the vessel attained the maximum. The temperature was recorded as the saturation temperature of the FBA 210 solution at a given composition. The same solubility experiment was repeated three times to check the reproducibility until the penetrated laser intensity could not return to maximum. The temperature difference based on the reproducibility was within ± 0.10 K.

The saturated mole fraction solubility of the solute (x_1) in sodium chloride + water can be obtained as follows

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2 + m_3/M_3} \tag{1}$$

where m_1, m_2, and m_3 represent the masses of solute, sodium chloride, and water, respectively. M_1, M_2, and M_3 represent the molecular weights of solute, sodium chloride, and water, respectively. With regard to pure water, m_2 was 0.

Results and Discussion

The solubilities of FBA 210 in sodium chloride + water were measured in the temperature range from (273.15 to 313.95) K, and the data are shown in Table 1. The mass fraction (w) of sodium chloride in sodium chloride + water is (0.0, 3.6, 5.6, 6.2, 7.4, 8.6, 9.8, 10.8, 12.3, and 15.0) %, respectively. The temperature dependence of FBA 210 solubility at given solvent composition is correlation to data with the modified Apelblat equation[13–16]

$$\ln x = A + B/(T/\mathrm{K}) + C \ln(T/\mathrm{K}) \tag{2}$$

where x is the mole fraction solubility of FBA 210; T is the absolute temperature; and A, B, and C are the model parameters in eq 2. The values of the parameters A, B, and C estimated by the nonlinear least-squares regression method are presented in Table 2. The comparison between experimental data and calculated values using eq 2 is shown in Table 1. The average deviation of 100 data points for the FBA 210 + water system at various compositions of sodium chloride in the mixed solvent is 2.1 %. The results show that the calculated solubilities of FBA 210 set a satisfactory coherence with the experimental values.

The values of the root-mean-square deviations (rmsd) and the correlation coefficients R^2 are listed in Table 2. The rmsd (σ) of the mole fraction is defined as

$$\sigma = \left\{\left[\sum_{i=1}^{N}(x_i - x_{i\mathrm{calcd}})^2\right]\Big/N\right\}^{1/2} \tag{3}$$

where N is the number of experimental points; $x_{i\mathrm{calcd}}$ represents the solubility value calculated from eq 2; and x_i represents the experimental solubility value. From Table 2, it is obvious that the modified Apelblat equation can be used to correlate the solubility data of FBA 210 in sodium chloride + water.

The solubility curves of FBA 210 in the sodium chloride + water with mass fractions of (0.0, 3.6, and 5.4) %, (6.2, 7.4, and 8.6) %, and (9.8, 10.8, 12.3, and 15.0) % are shown in

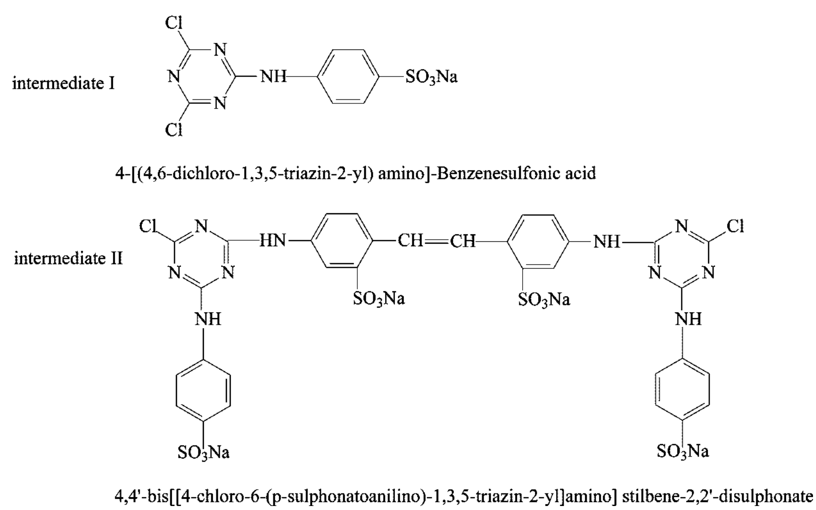

Figure 3. Chemical structures of intermediates I, II.

Table 1. Experimentally Determined Solubility Data of FBA 210 (1) in Sodium Chloride (*w*) + Water (1 − *w*) with *w* = Mass Fraction

T/K	10^4x_1	$(x_1 - x_{1calcd})/x_1$	T/K	10^4x_1	$(x_1 - x_{1calcd})/x_1$
		w = 0.0 %			
273.15	2.902	−0.037	298.75	13.702	−0.014
278.45	3.993	−0.046	303.15	17.905	0.004
283.35	5.453	−0.032	307.55	21.903	−0.042
288.75	7.574	−0.026	310.75	26.406	−0.032
293.25	9.903	−0.022	313.95	31.905	−0.017
		w = 3.6 %			
273.15	1.793	0.037	298.15	7.283	−0.012
278.45	2.312	−0.015	303.95	10.504	0.018
283.75	3.123	−0.023	308.15	12.902	−0.019
288.35	4.224	0.012	311.45	16.201	0.018
293.65	5.681	0.001	313.35	17.605	−0.008
		w = 5.4 %			
273.15	1.223	−0.027	298.25	5.843	−0.016
278.65	1.814	0.027	303.45	7.984	−0.026
283.35	2.381	0.010	308.15	11.405	0.040
288.95	3.362	0.002	311.75	13.805	0.010
293.75	4.413	−0.019	313.15	14.602	−0.020
		w = 6.2 %			
273.55	0.893	0.040	298.35	3.843	0.002
278.45	1.144	−0.007	303.35	5.132	−0.012
283.95	1.682	0.047	308.85	7.161	−0.012
288.55	2.113	−0.002	310.75	8.114	−0.003
293.45	2.884	0.012	313.85	9.914	0.009
		w = 7.4 %			
273.85	0.753	−0.045	298.25	3.054	−0.006
278.35	0.984	−0.036	303.55	4.193	0.014
283.25	1.392	0.046	308.45	5.445	−0.001
288.75	1.773	−0.018	310.75	6.163	−0.005
293.95	2.424	0.004	313.85	7.381	0.001
		w = 8.6 %			
273.75	0.412	−0.010	298.95	1.778	0.024
278.55	0.542	−0.005	303.15	2.143	−0.030
283.45	0.723	−0.001	308.85	3.047	0.003
288.75	0.971	0.001	311.15	3.383	−0.024
293.15	1.289	0.032	313.45	4.012	0.018
		w = 9.8 %			
274.15	0.247	0.013	298.75	1.038	0.040
278.45	0.314	−0.019	303.15	1.254	−0.021
283.75	0.413	−0.044	308.95	1.732	−0.017
288.15	0.526	−0.037	310.85	1.987	0.019
293.35	0.748	0.029	313.45	2.243	−0.005
		w = 10.8 %			
273.65	0.132	−0.016	298.95	0.586	0.033
278.55	0.173	−0.039	303.55	0.726	−0.024
283.35	0.235	−0.040	308.15	0.967	0.021
288.25	0.316	0.029	311.95	1.184	0.009
293.45	0.412	−0.020	313.75	1.274	−0.015
		w = 12.3 %			
273.55	0.086	−0.041	298.15	0.452	0.036
278.15	0.119	−0.027	303.15	0.576	−0.019
283.65	0.182	0.034	308.55	0.779	−0.030
288.45	0.244	0.019	311.35	0.934	−0.007
293.45	0.331	0.011	313.65	1.090	0.018
		w = 15.0 %			
273.95	0.068	0.014	298.15	0.219	−0.036
279.15	0.091	0.022	303.45	0.287	0.010
284.25	0.120	0.024	307.35	0.338	0.017
289.45	0.152	0.001	310.45	0.381	0.018
293.95	0.182	−0.032	313.95	0.419	−0.017

Figures 4 to 6, respectively. From the Figures 4 to 6, it can be seen that the solubility values of FBA 210 increase with the increase in temperature at given solvent composition and decrease sharply with the increase of sodium chloride compositions at fixed temperature. For example, at the temperature of 313.95 K, when the composition changes from (0.0 to 15.0) %, the mole fraction order of magnitude changes from 10^{-3} to 10^{-5} accordingly. The observed behavior is as expected. On the basis of the solubility values, the crystallization process of FBA 210 can be designed at fixed temperature and given sodium chloride composition to reach the separation quickly.

Table 2. Parameters of Equation 2 for the FBA 210 + Sodium Chloride + Water System at Various Compositions of Sodium Chloride (*w*) in Sodium Chloride + Water

100 w	A	B	C	R^2	$10^5\sigma$
0	−105.370	61.501	17.297	0.9994	4.49
3.6	−210.291	4653.924	32.903	0.9993	1.42
5.4	−226.526	5071.599	35.468	0.9983	2.03
6.2	−233.687	5461.146	36.417	0.9997	0.55
7.4	−227.715	5532.911	35.289	0.9997	0.34
8.6	−194.698	3983.175	30.300	0.9987	0.44
9.8	−168.785	2871.343	26.311	0.9987	0.24
10.8	−137.550	1439.151	21.572	0.9989	0.14
12.3	−45.968	−2958.151	8.047	0.9987	0.12
15.0	135.849	−9833.334	−19.931	0.9982	0.05

The parameters of the modified Apelblat equation (A, B, and C) are expressed as a function of the mass fraction (w) of sodium chloride by polynomials. The empirical formulas of A, B, and C as a function of w are as follows, respectively

$$A = -99.678 - 47.835w + 4.2164w^2 \tag{4}$$

$$B = -118.57 + 2016.9w - 177.97w^2 \tag{5}$$

$$C = 16.433 + 7.1728w - 0.6364w^2 \tag{6}$$

Equations 4 to 6 can be used to estimate A, B, and C for sodium chloride + water at any mass fraction of sodium chloride

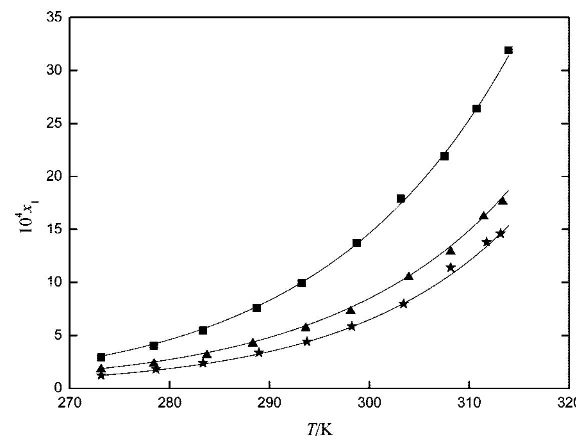

Figure 4. Solubility (x_1) of FBA 210 in sodium chloride + water with w = mass fraction: ■, w = 0.0 %; ▲, w = 3.6 %; ★, w = 5.4 %; −, calculated values.

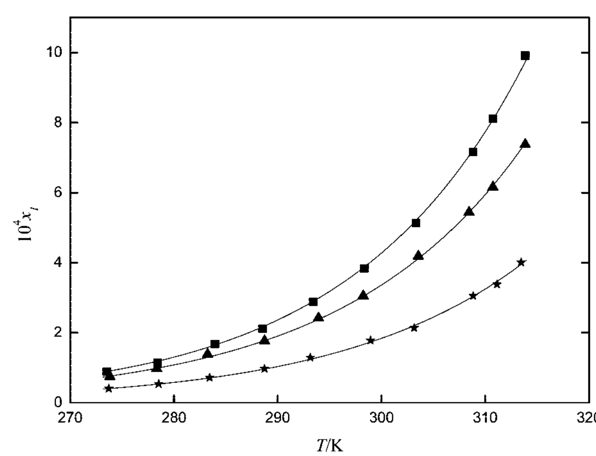

Figure 5. Solubility (x_1) of FBA 210 in sodium chloride + water with w = mass fraction: ■, w = 6.2 %; ▲, w = 7.4 %; ★, w = 8.6 %; −, calculated values.

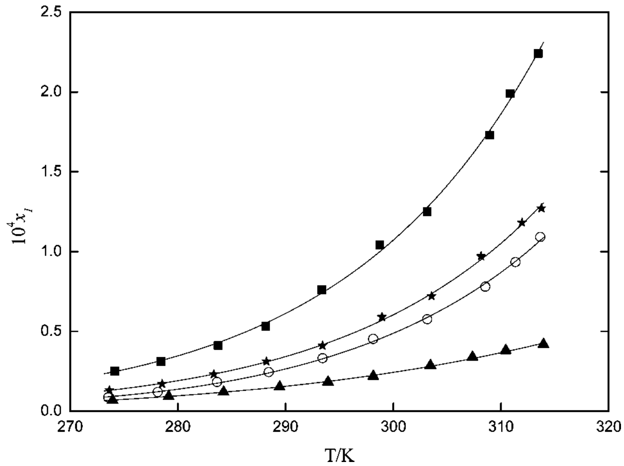

Figure 6. Solubility (x_1) of FBA 210 in sodium chloride + water with w = mass fraction: ■, w = 9.8 %; ★, w = 10.8 %; ○, w = 12.3 %; ▲, w = 15.0 %; −, calculated values.

Table 3. Interpolating Prediction of Solubility of FBA 210 in Sodium Chloride (w) + Water ($1 - w$) by the Empirical Model with w = Mass Fraction

100 w	T/K	10^4x_1	10^4x_{1calcd}	$(x_1 - x_{1calcd})/x_1$
1.2	275.45	3.349	3.209	0.042
2.4	279.35	3.207	3.070	0.043
3.8	283.65	2.836	2.810	0.009
4.6	283.65	2.262	2.285	−0.010
5.5	293.15	3.245	3.171	0.023
6.9	298.55	2.874	2.949	−0.026
7.5	298.55	2.544	2.470	0.033
9.3	301.75	1.628	1.695	−0.041
11.3	304.45	1.019	0.992	0.027
13.7	310.35	0.515	0.528	−0.025

from 0.0 % to 15.0 %. By substituting eqs 4, 5, and 6 for A, B, and C, respectively, the solubility of FBA 210 in sodium chloride + water can be predicted at any temperature from (273.15 to 313.95) K. Some solubility data which were calculated by interpolation are listed and compared with experimental results in Table 3. From Table 3, it can be known that the accuracy of the interpolation calculation for the modified Apelblat equation model can meet the demand of the crystallization of FBA 210 to some degree.

Conclusions

The solubilities of FBA 210 in sodium chloride + water are measured by the synthetic method. From Tables 1 to 3 and Figures 4 to 6, we can draw the following conclusions: (1) From the data of the experimental solubility, the solubility of FBA 210 increases with the increase in temperature at given composition and decreases with the increase of sodium chloride composition at fixed temperature. (2) When the mass fraction (w) of sodium chloride in sodium chloride + water is close to 15.0 %, the solubilities of FBA 210 are very low. So the purification and crystallization process can be done under this condition. (3) The parameters (A, B, and C) for sodium chloride solution are expressed as a function of mass fraction (w) by polynomials, and the solubility of FBA 210 in the solution at any mass fraction from 0.0 % to 15.0 % can be predicted by interpolation. (4) The calculated solubilities of FBA 210 set a good coherence with the experimental values, and the experimental solubility and correlation equation in this work can be used as fundamental data and model in the crystallization of FBA 210.

Literature Cited

(1) Brayan, B.; Mobile, A. Stable Purified Aqueous Solutions of Fluorescent Whitening Agent. US 4468341, 1984.
(2) Prejmereanu, I.; Culie, C. V.; Bondrlc, C. Procede D'Obtenir UN Decolorant Optique En Solution. RO 75467, 1981.
(3) Schmid, H. R. Aqueous optical brightener compositions. US 4717502, 1988.
(4) Peter, R.; Giulietti, M. Fluorescent Whitening Agents. US 6210449 B1, 2001.
(5) Bajguzova, L. V.; Shatilova, N. N.; Shuvalova, A. A.; Mikheeva, N. N. 4,4′-bis[[4-Morpholino-6-(p-Sulphonatoanilino)-Symm-Triazin-2-yl]Amino]Stilbene-2,2′-Disulfoacid Tetrasodium Salt as Optically Bleach Agent. SU 1646260A1, 1989.
(6) Tsavas, P.; Polydorou, S.; Faflia, I.; Voutsas, E. C.; Tassios, D. Solubility of Glucose in Mixtures Containing 2-Methyl-2-butanol, Dimethyl Sulfoxide, Acids, Esters, and Water. *J. Chem. Eng. Data* **2002**, *47*, 807–810.
(7) Chen, X. H.; Zeng, Z. X.; Xue, W. L. Solubility of 2,6-Diaminopyridine in Toluene, o-Xylene, Ethylbenzene, Methanol, Ethanol, 2-Propanol, and Sodium Hydroxide Solutions. *J. Chem. Eng. Data* **2007**, *52*, 1911–1915.
(8) Nyvlt, J. *Solid-Liquid Phase Equilibria*; Czechoslovak Academia of Sciences: Praha, Czechoslovakia, 1977.
(9) Roberts, K. L.; Rousseau, R. W.; Teja, A. S. Solubility of Long-Chain n-Alkanes in Heptane between 280 and 350 K. *J. Chem. Eng. Data* **1994**, *39*, 793–795.
(10) Jakob, A.; Joh, R.; Rose, C.; Gmehling, J. Solid-Liquid Equilibria in Binary Mixtures of Organic Compounds. *Fluid Phase Equilib.* **1995**, *113*, 117–126.
(11) Domanska, U.; Kozlowska, M. K. Solubility of Imidazoles in Ethers. *J. Chem. Eng. Data* **2003**, *48*, 557–563.
(12) Ren, B. Z.; Chong, H. G.; Li, W. R.; Wang, F. A. Solubility of Potassium p-Chlorophenoxyacetate in Ethanol + Water from (295.61 to 358.16) K. *J. Chem. Eng. Data* **2005**, *50*, 907–909.
(13) Apelblat, A.; Manzurola, E. Solubilities of o-Acetylsalicylic, 4-Aminosalicylic, 3,5-Dinitrosalicylic, and ρ-Toluic acid, and Magnesium-DL-Aspartate in Water from T = (278 to 348) K. *J. Chem. Thermodyn.* **1999**, *31*, 85–91.
(14) Wang, L. C.; Wang, F. A. Solubility of Niacin in 3-Picoline + Water from (287.65 to 359.15) K. *J. Chem. Eng. Data* **2004**, *49*, 155–156.
(15) Walas, S. M. *Phase Equilibria in Chemical Engineering*; Butterworth: Boston, 1985.
(16) Wang, Z.; Wang, J. K.; Zhang, M.; Dang, L. Solubility of Erythromycin A Dihydrate in Different Pure Solvents and Acetone + Water Binary Mixtures between 293 and 323 K. *J. Chem. Eng. Data* **2006**, *51*, 1062–1065.

Received for review March 27, 2008. Accepted May 30, 2008.

JE8002145