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Solubility of Terephthalic Acid in Aqueous *N*-Methyl Pyrrolidone and *N*,*N*-Dimethyl Acetamide Solvents at (303.2 to 363.2) K

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Experimental solubilities are reported for terephthalic acid (TA) in binary mixtures of *N*-methyl pyrrolidone (1) + water (2) and *N*,*N*-dimethyl acetamide (1) + water (2) in the temperature range of (303.2 to 363.2) K. The mole fraction of water in the *N*-methyl pyrrolidone + water solvent mixtures x_2 ranges from 0 to 0.5791 and in the *N*,*N*-dimethyl acetamide + water solvent mixtures x_2 ranges from 0 to 0.5477. The experimental results show that the solubility of TA increases significantly with an increase in temperature and decreases significantly with an increase in x_2. The solubility data were correlated by a modified Buchowski equation.

Introduction

Purified terephthalic acid is an important intermediate in the production of polyesters for plastics and fiber applications, with an annual production capacity of more than 38 000 kilotons in the year 2006.[1] Commercial processes for the manufacture of terephthalic acid (TA) are based on the Co/Mn/Br catalyzed aerial oxidation of *p*-xylene in aqueous acetic acid solvent.[2,3] The TA residue is produced constantly and the quantity is about $4 \cdot 10^8$ kg every year, which will cause serious pollution unless effectively treated. Besides terephthalic acid, the TA residue also contains benzoic acid, *p*-toluic acid, 4-carboxybenzaldehyde, isophthalic acid, fluorenones- and anthraquinones-colored compounds, etc.[3–6] Considering the increased production of TA residue waste, it is necessary to reduce this waste from both economic and environmental concerns.

So far, solvent crystallization had been used to purify terephthalic acid by Lee et al.[7] It was shown that the good solvents for terephthalic acid included pyridine, dimethyl sulfoxides, *N*,*N*-dimethyl foramide, *N*,*N*-dimethyl acetamide, *N*-methyl pyrrolidone.[8,9] But some of these solvents suffer from being unstable in air or easily form solvates with terephthalic acid. Practicable solvents should be less reactive with terephthalic acid, thermally stable, nontoxic (environmentally safe), noncorrosive, and commercially available. Therefore, *N*-methyl pyrrolidone and *N*,*N*-dimethyl acetamide are possible preferred selective crystallization solvents for terephthalic acid purification, and the solubility of terephthalic acid decreases with the decrease in temperature remarkably.[7]

Usually, TA residue waste contains water[10,11] and the crystallization separation process of TA residue must be aqueous. Furthermore, results of our previous work had shown that solvent crystallization in aqueous *N*-methyl pyrrolidone and *N*,*N*-dimethyl acetamide solvent is a feasible method to recovery terephthalic aicd from TA residue. However, all the similar studies of solubility of terephthalic acid in *N*-methyl pyrrolidone and *N*,*N*-dimethyl acetamide concerned only the pure solvent,[7,8] and the solubility data of terephthalic acid in aqueous *N*-methyl pyrrolidone and *N*,*N*-dimethyl acetamide solvents is still unavailable. In this paper, an accurate and reliable procedure that had been used to measure the solubility of *N*-Hydroxyphthalimide satisfactorily[12] was used to measure the terephthalic acid solubility in aqueous *N*-methyl pyrrolidone and aqueous *N*,*N*-dimethyl acetamide solution from (303.2 to 363.2) K. The solubility data are correlated by a modified Buchowski equation.[13]

Experimental Methods

Chemicals. Terephthalic acid, which was the white crystals with the density of $1.510 \cdot 10^3$ kg·m^{-3} and had a mass fraction over 0.995, was obtained from Shanghai Chemical Reagent Co. Terephthalic acid is slightly soluble in ethanol and insoluble in water and ether. The molecular weight is 166.13 and the sublimation temperature is about 573 K. HPLC grade methanol and acetonitrile from U.S.A. Tedia Company were used as the flow-phase in liquid-chromatographic analysis. Deionized water was used throughout all the experiments. *N*-methyl pyrrolidone and *N*,*N*-dimethyl acetamide of analytical grade were supplied by Tianjin Chemical Reagent Co. and had a mass fraction purity greater than 0.995.

Apparatus and Procedure. Solubilities were measured by the static analytical method. Excessive solute and solvent were placed in a sealed glass bottle (100 mL). The temperature was controlled within ± 0.1 K of the desired temperature with a thermoelectric controlling system. Continuous stirring was carried out for 48 h with a magnetic bar. The bottle was sealed by a rubber stopper to prevent evaporation of solvent. Attainment of equilibrium was verified both by repetitive measurements after 48 h and by approaching equilibrium from supersaturation by pre-equilibrating the solutions at a higher temperature.

The measured mole fraction solubilities of terephthalic acid in *N*-methyl pyrrolidone (1) + water (2) and *N*,*N*-dimethyl acetamide (1) + water (2) solvent mixtures in the temperature range from (303.2 to 363.2) K and solvent composition range from ($x_2 = 0$ to 0.6) are listed in Tables 1 and 2. At each temperature, a part of the saturated terephthalic acid solutions, namely, the clear upper portion of the solution, was transferred through a 5 mL syringe into a 25 mL volumetric flask. The syringe wall was washed by methanol at least four times to remove the crystallized solute to the volumetric flask, which

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Table 1. Solubilities of Terephthalic Acid (3) in Binary *N*-Methyl Pyrrolidone (1) + water (2) Solvent Mixtures in the Temperature Range from (303.2 to 363.2) K

T	$x_2 = 0$		$x_2 = 0.2160$		$x_2 = 0.3804$		$x_2 = 0.5791$	
K	10^3x_3	10^3x_3 (cal)	10^3x_3	10^3x_3 (cal)	10^3x_3	10^3x_3 (cal)	10^3x_3	10^3x_3 (cal)
303.2	13.34	13.77	5.764	5.813	3.770	4.018	2.877	2.965
313.2	15.52	16.15	8.077	7.087	5.223	5.494	4.024	3.954
323.2	18.85	17.76	10.52	10.29	7.397	7.365	6.036	5.178
333.2	21.65	21.59	13.73	13.33	10.39	9.694	6.634	6.670
343.2	25.59	24.63	16.77	16.99	12.55	12.55	7.879	8.462
353.2	28.69	27.88	20.81	21.34	16.52	16.00	10.15	10.59
363.2	32.76	31.33	25.95	26.45	20.61	20.11	13.23	13.08

Table 2. Solubilities of Terephthalic Acid (3) in Binary *N*,*N*-Dimethyl Acetamide (1) + water (2) Solvent Mixtures in the Temperature Range from (303.2 to 363.2) K

T	$x_2 = 0$		$x_2 = 0.2032$		$x_2 = 0.3498$		$x_2 = 0.5477$	
K	10^3x_3	10^3x_3 (cal)	10^3x_3	10^3x_3 (cal)	10^3x_3	10^3x_3 (cal)	10^3x_3	10^3x_3 (cal)
303.2	15.97	17.25	9.282	9.895	6.965	6.076	2.658	2.611
313.2	21.09	21.39	13.15	13.04	8.022	8.252	3.799	3.662
323.2	26.90	26.14	17.44	16.87	11.62	10.99	5.015	5.026
333.2	33.11	31.54	20.94	21.47	13.80	14.37	6.449	6.717
343.2	38.50	37.60	27.38	26.97	17.78	18.49	8.830	8.948
353.2	45.16	44.33	33.78	33.27	22.20	23.42	11.41	11.64
363.2	52.37	51.74	40.20	40.59	28.94	29.25	14.70	14.91

was diluted quantitatively with methanol to 25 mL. The amount of terephthalic aicd in the volumetric flask was determined by high-performance liquid chromatography (HPLC) analysis using the external reference method and was carried out using an Agilent 1100.[10,11] The Diamonsil C18 (150 mm × 4.6 mm) chromatographic column and UV detector (254 nm) were used at room temperature. The mobile phase consisted of three eluents (i.e., water + acetonitrile + methanol), and the following three-component gradient elution program was adopted: from 0 min to 2 min, the mass fraction of water changed linearly with time from 100 % to 40 %, the mass fraction of methanol changed linearly with time from 0 to 10 %, the mass fraction of acetonitrile changed linearly with time from 0 % to 50 %; from 2 min to 3.5 min, the mixture composition changed linearly with time to become 0 % water, 10 % methanol, and 90 % acetonitrile; from 3.5 min to 4 min, the mixture composition changed linearly with time to become 0 % water, 0 % methanol, and 100 % acetonitrile.

Results and Discussion

The Buchowski equation,[12] eq 1, is used to correlate solid−liquid equilibrium data. Although only two parameters (h and λ) are involved, this equation is thermodynamically correct and gives an excellent description of experimental data without considering the activity coefficients of the components

$$\ln\left(1+\frac{\lambda(1-x_3)}{x_3}\right) = \lambda h\left(\frac{1}{T}-\frac{1}{T_m}\right) \qquad (1)$$

In eq 1, T is the absolute temperature of solid−liquid equilibrium; x_3 is the mole fraction of a solute terephthalic acid in the saturated solution, T_m is melting point of TA (T_m = 745.93 K),[13] and h and λ are two parameters. As the Buchowski equation is effective only for constant solvent composition, the values of h and λ change with different solvent composition. We assumed that the parameters h and λ were quadratic polynomial functions of x_2 as described in eq 2

$$\begin{aligned} \lambda &= a_1x_2^2 + b_1x_2 + c_1 \\ h &= a_2x_2^2 + b_2x_2 + c_2 \end{aligned} \qquad (2)$$

Equations 1 and 2 were used to correlate the experimental solubility of terephthalic acid (x_3) at different solvent compositions and in the temperature range from (303.2 to 363.2) K. For comparison with the experimental values of this work, the calculated solubility x_3 (cal) from eqs 1 and 2 at different x_2 and temperatures conditions is listed in Table 1 and 2 together with x_3. The comparison between the calculated results x_3 (cal) and the experimental x_3 is also shown in Figures 1 and 2.

The values of the six parameters a_1, b_1, c_1, a_2, b_2, and c_2 in eq 2, which were regressed using a nonlinear optimization method, are listed in Table 3 and 4 together with the average relative standard deviation between the experimental and calculated values. The average relative standard deviation σ is defined as

$$\sigma = \left[\frac{i}{n}\sum_{i=1}^{n}\left(\frac{x_3 - x_{3(\text{cal})}}{x_3}\right)^2\right]^{1/2} \qquad (3)$$

where x_3 is the experimental solubility of terephthalic acid, n is the number of experimental points, and x_3 (cal) is the solubility calculated from eqs 1 and 2. The calculated solubility values of terephthalic acid are also given in Tables 1 and 2. It can be seen that the obtained agreement is in general satisfactory. The

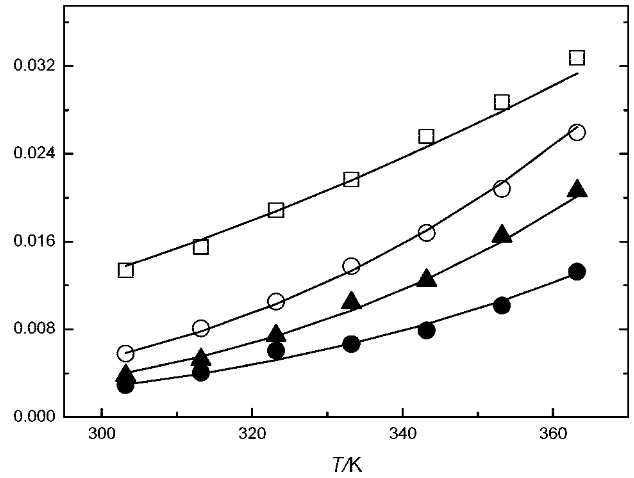

Figure 1. Mole fraction solubility x of terephthalic acid in *N*-methyl pyrrolidone (1) + water (2) solvent mixtures in the temperature range from (303.2 to 363.2) K; □, x_2 = 0; ○, x_2 = 0.2160; ▲, x_2 = 0.3804; ●, x_2 = 0.5791; -, calculated from eqs 1 and 2.

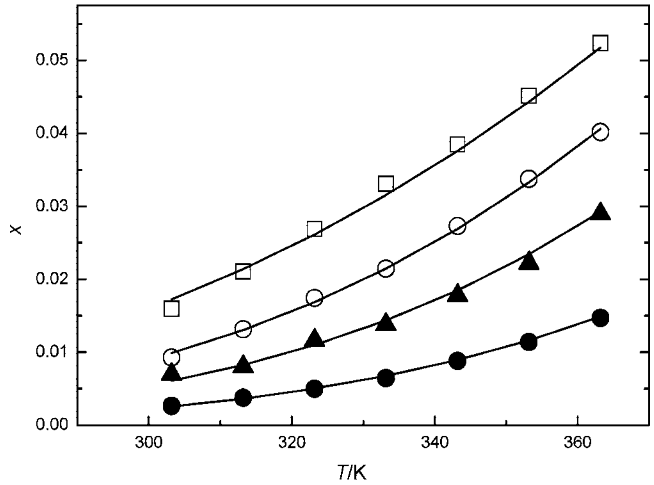

Figure 2. Mole fraction solubility x of terephthalic acid in *N*,*N*-dimethyl acetamide (1) + water (2) solvent mixtures in the temperature range from (303.2 to 363.2) K; □, $x_2 = 0$; ○, $x_2 = 0.2032$; ▲, $x_2 = 0.3498$; ●, $x_2 = 0.5477$; -, calculated from eqs 1 and 2.

Table 3. Quadratic Polynomial Parameters in Equation *2* and σ in *N*-Methyl Pyrrolidone (1) + Water (2) Solvent Mixtures

x_2	a_i	b_i	c_i
$i = 1$	−4.636	2.906	0.1049
$i = 2$	99506	−62739	14698
σ	0.0526		

Table 4. Quadratic Polynomial Parameters in Equation *2* and σ in *N*,*N*-Dimethyl Acetamide (1) + Water (2) Solvent Mixtures

x_2	a_i	b_i	c_i
$i = 1$	−3.164	2.002	0.3798
$i = 2$	23953	−11967	5480
σ	0.0481		

average relative standard deviation of the simulated value and the experimental data is less than 6 %.

From Figures 1 and 2 and Tables 1 and 2, the experimental values of the solubilities of terephthalic acid in the range of $x_3 = 10^{-2}$ to 10^{-3} show good agreement with the calculated solubilities correlated by a modified Buchowski equation. The solubilities of terephthalic acid increase significantly with increasing temperature and decrease with increasing x_2. The experimental solubility and correlation equation in this work can provide essential data for the study of terephthalic acid recovery from TA residue by crystallization in aqueous *N*-methyl pyrrolidone and *N*,*N*-dimethyl acetamide solvents.

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