Solubilities of Terephthalaldehydic, *p*-Toluic, Benzoic, Terephthalic, and Isophthalic Acids in *N*-Methyl-2-pyrrolidone from 295.65 K to 371.35 K

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Using a laser monitoring observation technique, the solubilities of terephthalaldehydic acid, *p*-toluic acid, benzoic acid, terephthalic acid, and isophthalic acid in *N*-methyl-2-pyrrolidone were determined by the synthetic method from (295.65 to 371.35) K. The experimental results were correlated by an empirical equation.

Introduction

With the development of the polyester industry, large amounts of oxidation residue have been created during the manufacturing process of purified terephthalic acid (PTA). Terephthalaldehydic acid, *p*-toluic acid, benzoic acid, terephthalic acid, and isophthalic acid are the major components in the residue. For the sake of environmental protection and sufficient utilization of natural resources, it is necessary to pay attention to the separation and recovery of oxidation residues. To recover the useful components from the residue, systemic and comprehensive solubility data are required. Unfortunately, only the solubilities of a few components in water, acetic acid, xylene, methanol, and ethanol have been reported in the literature.[1–5] From the literature it is known that some solvents are toxic, volatile, and corrosive, some have less dissolution ability, and others can only exist in liquid phase state over a narrow temperature range. Therefore, they are not very suitable for the recovery process. On the preparatory research for recovering residues we find that *N*-methyl-2-pyrrolidone has a good ability to dissolve the major components of the oxidation residue, including terephthalic acid. Furthermore, it is colorless and basically nontoxic, and can exist in liquid phase state over a larger temperature range. Up to now, solubilities of the residue components in *N*-methyl-2-pyrrolidone were scarce. In this work we report solubilities in the systems *N*-methyl-2-pyrrolidone + terephthalaldehydic acid, + *p*-toluic acid, + benzoic acid, + terephthalic acid, and + isophthalic acid in the temperature range from (295.65 to 371.35) K at atmospheric pressure.

Experimental Section

Chemicals. Benzoic acid, terephthalic acid, isophthalic acid, and *N*-methyl-2-pyrrolidone were of AR grade, were obtained from Shanghai Chemical Reagent Co., and had the purities 0.995, 0.995, 0.995, and 0.990 in mass fraction, respectively. *N*-Methyl-2-pyrrolidone had the refractive index n^{20}_D 1.4686 (n^{20}_D 1.4684, in the literature).[6] *p*-Toluic acid had a mass fraction 0.997, which was obtained through purifying the industrial product that had a stated mass fraction 0.985. First, *p*-toluic acid was extracted by trichlo-

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Table 1. Melting Point of the Solute Used for Measurement

solute	T_m/K	
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terephthalaldehydic acid	522.8	520.2,[a] 529.2[b]
p-toluic acid	555.1	555.2[a]
benzoic acid	395.5	395.6[a]
isophthalic acid	621.2	621.2[a]

[a] Reference 7. [b] Reference 6.

romethane at room temperature so that terephthalic acid, isophthalic acid, and phthalic acid were removed to get a purer *p*-toluic acid, and then recrystallizations were carried out in acetic acid and water, respectively. Terephthalaldehydic acid used for experiments had a mass fraction 0.998, which was also obtained by purifying the industrial product that had a stated mass fraction 0.980. First, terephthalaldehydic acid was dissolved into sodium hydroxide solution. Next, concentration and crystallization were conducted to remove the impurities. Then, acidification, washing, and recrystallization in water were carried out to get a much purer terephthalaldehydic acid. The purities of *p*-toluic acid and terephthalaldehydic acid were determined with a high performance liquid chromatograph (LC-10A, Shimadzu). Melting points of the solutes are reported in Table 1 and compared with the literature data.[6,7]

Apparatus and Procedure. Solubilities were measured by a synthetic method.[8–10] A laser beam was used to determine the dissolution temperature of a solid–liquid mixture of known composition. The laser monitoring system consisted of a laser generator, a photoelectric transformer, and a light intensity display. The solubility apparatus consisted of a jacketed glass vessel maintained at a desired temperature by water circulated from a water bath with a thermoelectric controller (type 501, China). The jacket temperature could be maintained within ±0.02 K of the required temperature. Two sizes of jacketed glass vessels were used, with internal volumes of approximately 120 cm³ and 20 cm³. Continuous stirring was achieved with a magnetic stir bar. A condenser was connected with the vessels to prevent the solvents from evaporating. A mercury-in-glass thermometer was inserted into the inner chambers of the vessels for the measurement of the temperature. Two

Table 2. Solubilities of Different Solutes in N-Methyl-2-pyrrolidone

T/K	x	x_c	T/K	x	x_c
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Terephthalaldehydic Acid (x)

T/K	x	x_c	T/K	x	x_c
296.25	0.1091	0.1091	326.05	0.2312	0.2304
300.15	0.1219	0.1216	329.15	0.2469	0.2468
306.35	0.1425	0.1435	331.95	0.2621	0.2623
308.85	0.1539	0.1530	335.05	0.2804	0.2803
312.65	0.1679	0.1682	337.45	0.2944	0.2948
317.85	0.1914	0.1907	338.65	0.3021	0.3022
321.65	0.2086	0.2084	340.95	0.3175	0.3169
322.45	0.2118	0.2123	341.75	0.3223	0.3221

p-Toluic Acid (x)

T/K	x	x_c	T/K	x	x_c
295.65	0.0679	0.0632	343.35	0.2474	0.2436
298.65	0.0745	0.0746	346.65	0.2663	0.2645
303.35	0.0866	0.0909	351.45	0.2966	0.2991
308.55	0.1013	0.1074	355.75	0.3279	0.3348
313.75	0.1175	0.1233	360.65	0.3705	0.3817
319.55	0.1388	0.1413	364.05	0.4100	0.4184
323.45	0.1542	0.1541	366.55	0.4453	0.4477
328.75	0.1747	0.1733	369.25	0.4851	0.4818
334.85	0.2038	0.1989	370.05	0.5005	0.4924
340.25	0.2301	0.2259			

Benzoic Acid (x)

T/K	x	x_c	T/K	x	x_c
296.35	0.5162	0.5173	338.85	0.6082	0.6085
301.15	0.5235	0.5247	343.25	0.6228	0.6234
305.05	0.5302	0.5310	347.75	0.6395	0.6403
307.95	0.5353	0.5358	351.15	0.6535	0.6541
311.05	0.5409	0.5413	355.05	0.6691	0.6713
314.25	0.5470	0.5472	359.85	0.6933	0.6945
318.35	0.5535	0.5553	364.55	0.7181	0.7195
321.95	0.5607	0.5630	369.05	0.7447	0.7458
327.35	0.5744	0.5758	371.35	0.7592	0.7601
333.55	0.5913	0.5924			

Terephthalic Acid (x)

T/K	x	x_c	T/K	x	x_c
296.35	0.0301	0.0295	316.25	0.0605	0.0597
299.55	0.0341	0.0335	319.65	0.0668	0.0661
303.75	0.0401	0.0393	324.05	0.0757	0.0749
307.05	0.0451	0.0442	328.45	0.0849	0.0843
309.75	0.0489	0.0485	331.55	0.0922	0.0913
312.75	0.0539	0.0535	332.65	0.0945	0.0939

Isophthalic Acid (x)

T/K	x	x_c	T/K	x	x_c
296.35	0.0893	0.0879	323.55	0.1518	0.1507
298.85	0.0943	0.0929	326.55	0.1608	0.1593
303.55	0.1037	0.1026	331.25	0.1756	0.1740
307.05	0.1115	0.1101	336.25	0.1925	0.1911
310.25	0.1183	0.1172	340.75	0.2095	0.2081
313.65	0.1268	0.1251	343.55	0.2213	0.2194
316.95	0.1346	0.1331	345.25	0.2278	0.2266
320.45	0.1437	0.1422	346.55	0.2340	0.2323

Table 3. Parameters for Correlation Equations of Different Solutes

solute	a	b	$10^4 c$	$10^7 d$	$10^3 \sigma_x$
terephthalaldehydic acid	−2.4515	0.027 76	−1.104 30	1.549 36	0.5
p-toluic acid	−32.6862	0.308 78	−9.781 25	10.430 70	5.2
benzoic acid	−6.0581	0.064 80	−2.178 13	2.497 84	1.2
terephthalic acid	0.8315	−0.006 02	0.091 45	0.068 73	0.7
isophthalic acid	−6.9703	0.068 77	−2.297 31	2.633 46	1.4

Results and Discussion

The experimental results of solubilities in mole fraction in the systems terephthalaldehydic acid + N-methyl-2-pyrrolidone, p-toluic acid + N-methyl-2-pyrrolidone, benzoic acid + N-methyl-2-pyrrolidone, terephthalic acid + N-methyl-2-pyrrolidone, and isophthalic acid + N-methyl-2-pyrrolidone are presented in Table 2. For all systems solubility is a function of temperature, and solubility increases with increase of temperature.

The solubility data were correlated with the equation

$$x = a + bT + cT^2 + dT^3 \qquad (1)$$

where x represents the solubility of five solutes in N-methyl-2-pyrrolidone, T is the absolute temperature, and a, b, c, and d are empirical constants. The values of these constants together with the root-mean-square deviations (RMSDs) are listed in Table 3. The RMSD is defined as

$$\sigma_x = \left[\frac{1}{n} \sum_{i=1}^{n} (x_{ci} - x_i)^2 \right]^{1/2} \qquad (2)$$

where x_c is the solubility calculated by eq 1 and n is the number of experimental points. The calculated solubilities are also listed in Table 2. From Tables 2 and 3 the calculated solubilities show good agreement with the experimental values. The experimental solubility and correlation equation in this work can be used as essential data and models to serve the process design of recovery of PTA oxidation residues.

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thermometers were used during the measurement. One had a measurement range from (271.15 to 325.15) K, and the other was from (321.15 to 375.15) K. All of the thermometers had an accuracy of ±0.05 K.

Solid−liquid mixtures were prepared by mass using an analytical balance (type TG332A, China). The balance had a range of measurement up to 20 g, with an accuracy of ±0.000 01 g.

Predetermined amounts of a solute and N-methyl-2-pyrrolidone were weighed and deposited into the jacketed vessel. The contents of the vessel were heated very slowly at rates less than 2 K·h^{-1} with continuous stirring. When the last portion of solute just disappeared, the intensity of the laser beam penetrating the vessel reached the maximum, and the temperature was recorded as the liquidus temperature. Some of the solubility experiments were conducted two or three times to check the reproducibility. To verify the uncertainty of the measurement, two other experiments were done in which the solubilities of benzoic acid in water and sodium chloride in water were determined. Compared with the literature data, the deviation of the solubility was <1%.[1] In this work the estimated error of solubility in mole fraction was less than 0.0005.