Solid−Liquid Equilibria of Terephthalaldehydic Acid in Different Solvents

Dian-Qing Li,* David G. Evans, and Xue Duan

Key Laboratory of Science and Technology of Controllable Chemical Reactions, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China

Solubilities of terephthalaldehydic acid in water, acetic acid, chloroform, *N*, *N*-dimethylformamide, and *N*-methyl-2-pyrrolidone were determined by a static analytical method at temperatures ranging from 293.15 K to 371.15 K at atmospheric pressure. The Buchowski equation was used to correlate the solubility data with standard deviations in the range 0.006−3.438 g of terephthalaldehydic acid/100 g of solvent.

Introduction

As one of the most important aromatic compounds, terephthalic acid is widely used in organic synthesis, particularly in the polyester industry. During the manufacture of terephthalic acid by oxidation of *p*-xylene, many undesired compounds are formed, including terephthalaldehydic acid, which is a major component of the byproducts. To purify terephthalic acid using simple methods and to separate terephthalaldehydic acid from the reaction mixture, measurement of systemic and comprehensive solubility data of terephthalaldehydic acid in different solvents is needed. The solubilities of terephthalaldehydic acid in *N*-methyl-2-pyrrolidone measured by the synthetic method have been reported in a previous paper;[1] solubilities of terephthalaldehydic acid in water and in acetic acid with a mass fraction purity of 0.980, measured at temperatures above 397.2 K, have been reported,[2] but these solubility data are not accurate and have insufficient points for practical use. In this work we report solubilities of terephthalaldehydic acid in water, acetic acid, chloroform, *N*, *N*-dimethylformamide, and *N*-methyl-2-pyrrolidone in the temperature range from 293.15 K to 371.15 K at atmospheric pressure.

Experimental Section

Chemicals. Water used in the experiments was double-distilled. Acetic acid, chloroform, *N*,*N*-dimethylformamide, and *N*-methyl-2-pyrrolidone were obtained from Shanghai Chemical Reagent Co. and had mass fraction purities of 0.995, 0.990, 0.990, and 0.990, respectively. Terephthalaldehydic acid had a mass fraction purity of 0.998, which was obtained by purifying the commercial product that had a stated mass fraction purity of 0.980. First, terephthalaldehydic acid was dissolved in 10 wt % sodium hydroxide solution. Next, concentration and crystallization were conducted three times to remove the impurities. Then, acidification, washing, and recrystallization in water were carried out to obtain the purified terephthalaldehydic acid. The purity of this aromatic acid compound was analyzed with a high performance liquid chromatograph (LC-10A, Shimadzu). The melting point of terephthalaldehydic acid measured with a NETZSCH STA449C differential scanning calorimeter was 522.8 K and compares with the literature value 520.2 K.[3]

* To whom correspondence should be addressed. E-mail: Dellsson@371.net. Fax: 0086-10-64425385.

Table 1. Solubilities of Terephthalaldehydic Acid in Different Solvents

T	S	S_c	T	S	S_c
K	g·(100 g)$^{-1}$	g·(100 g)$^{-1}$	K	g·(100 g)$^{-1}$	g·(100 g)$^{-1}$
		Water			
293.15	0.035	0.025	338.15	0.229	0.251
298.15	0.041	0.034	343.15	0.287	0.312
303.15	0.053	0.044	348.15	0.351	0.387
308.15	0.065	0.058	353.15	0.437	0.476
313.15	0.078	0.076	358.15	0.543	0.583
318.15	0.098	0.098	363.15	0.687	0.709
323.15	0.121	0.125	368.15	0.865	0.860
328.15	0.147	0.159	371.15	1.005	0.963
333.15	0.183	0.200			
		Acetic Acid			
293.15	0.246	0.164	338.15	1.124	1.233
298.15	0.279	0.211	343.15	1.366	1.495
303.15	0.316	0.270	348.15	1.688	1.803
308.15	0.360	0.342	353.15	2.035	2.165
313.15	0.425	0.431	358.15	2.463	2.587
318.15	0.511	0.538	363.15	2.983	3.079
323.15	0.615	0.668	368.15	3.661	3.650
328.15	0.764	0.825	370.65	4.155	3.968
333.15	0.926	1.011			
		Chloroform			
293.15	0.104	0.096	318.15	0.212	0.219
298.15	0.118	0.114	323.15	0.247	0.255
303.15	0.135	0.136	328.15	0.293	0.295
308.15	0.156	0.160	332.15	0.339	0.331
313.15	0.183	0.188			
		N,*N*-Dimethylformamide			
298.15	54.473	50.146	338.15	69.132	69.194
303.15	55.729	52.148	343.15	71.239	72.172
308.15	57.500	54.243	348.15	73.796	75.320
313.15	59.159	56.437	353.15	76.092	78.653
318.15	60.736	58.739	358.15	78.544	82.189
323.15	62.682	61.157	363.15	80.879	85.946
328.15	64.904	63.698	368.15	83.699	89.947
333.15	66.911	66.384	370.35	85.172	91.790
		N-Methyl-2-pyrrolidone			
293.15	16.885	16.387	323.15	41.458	42.318
298.15	19.681	19.427	328.15	48.249	48.831
303.15	22.892	22.911	333.15	55.678	56.146
308.15	26.980	26.888	338.15	64.571	64.339
313.15	31.242	31.410	341.75	72.030	70.830
318.15	36.013	36.532			

Procedure. Solubilities were measured by the static analytical method.[4−6] Excess solute and solvent were placed in a jacketed glass bottle. The temperature was maintained within ±0.05 K of the desired temperature with a thermoelectric controlling system (type 501, Shanghai Scientific Instruments). Continuous stirring was carried out for several days with a magnetic bar. Attainment of equilib-

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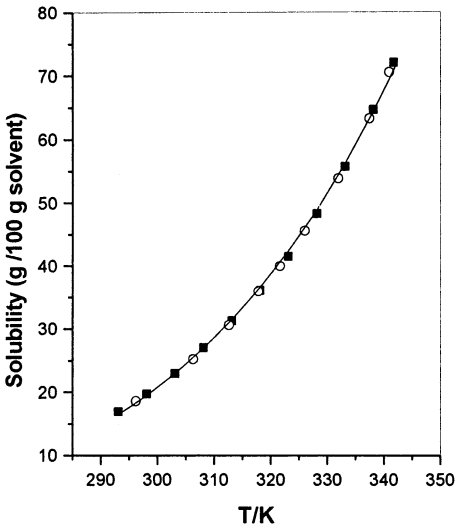

Figure 1. Solubility of terephthalaldehydic acid in *N*-methyl-2-pyrrolidone: ○, previous work;[1] ■, this work; —, the values calculated by eq 1.

Table 2. Parameters for Correlation Equations of Different Solvents

solvent	λ	h/K	σ_x/g·(100 g)$^{-1}$
water	0.05911	85611.42	0.022
acetic acid	0.49649	8912.83	0.093
chloroform	0.07003	43160.69	0.006
N,*N*-dimethylformamide	2.879×10^{-8}	2842.26	3.438
N-methyl-2-pyrrolidone	8.68477	337.94	0.557

rium was verified by repetitive measurements during the following several days until the results were reproducible within 0.5%. With the exception of the system terephthalaldehydic acid + acetic acid, compositions of saturated solutions were determined by titration with standard sodium hydroxide solution using phenolphthalein as indicator. As for the system terephthalaldehydic acid + acetic acid, the compositions of saturated solutions were determined by a mass analytical method, in which the amount of terephthalaldehydic acid in the weighed solution was determined by mass after drying in vacuo at 50 °C for more than 6 h. To test the uncertainty of the measurements, one other experiment was done in which the solubility of phthalic acid in water was determined. The experimental value differed from the literature value by less than 1%.[7] The solubilities of terephthalaldehydic acid in the five solvents are listed in Table 1. Values represent the average of three or four independent determinations. In this work the estimated uncertainty of solubility was less than 0.001 g of terephthalaldehydic acid/100 g of solvent.

Results and Discussion

Measured solubilities of terephthalaldehydic acid in *N*-methyl-2-pyrrolidone are shown in Figure 1 together with our previous measurements using the synthetic method.[1] It is clear from Figure 1 that solubility data measured using the two methods are in close agreement. Because *N*,*N*-dimethylformamide and *N*-methyl-2-pyrrolidone are polar solvents, terephthalaldehydic acid has larger solubilities in these two solvents than in the other three.

Buchowski and co-workers[8] developed an equation to deal with systems in which solutes exhibit self-association effects. In fact, this equation is also applicable to most solid−liquid equilibrium systems giving excellent correlation results without considering the activity coefficients of components. The Buchowski equation is given by eq 1,

$$\ln[1 + 100\lambda M_{\text{solute}}/(SM_{\text{solvent}})]_{\text{sat}} = \lambda h(T^{-1} - T_{\text{m}}{}^{-1}) \quad (1)$$

where λ and h are two parameters, T is the absolute temperature, T_{m} is the melting point of the solute, S stands for the solubility in grams of solute/100 grams of solvent, and M_{solute} and M_{solvent} are the molecular weight of solute and solvent, respectively. The parameter h is related to the enthalpy of solution per mole of solute with units of K, and λ is identified as the approximate mean size of multimer molecules of the solute.

The solubility data were correlated with eq 1, and the calculated solubilities S_{c} are listed in Table 1 for comparison with the experimental values. The values of the two parameters λ and h together with the root-mean-square deviations (RMSDs) are listed in Table 2. The RMSD is defined as

$$\sigma_x = \left[\frac{1}{n}\sum_{i=1}^{n}(S_{ci} - S_i)^2\right]^{1/2} \quad (2)$$

where S_{ci} is the solubility calculated by eq 1 and n is the number of experimental points. From Tables 1 and 2 the calculated solubilities show good agreement with the experimental values. The experimental solubilities and correlation equation in this work can used to improve the design of the terephthalic acid purification process and the separation of terephthalaldehydic acid.

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