J. Chem. Eng. Data **2005,** *50,* 719−721

Solubilities of Terephthalic Acid in Dimethyl Sulfoxide + Water and in *N,N*-Dimethylformamide + Water from (301.4 to 373.7) K

Qinbo Wang,* Haibo Xu, and Xi Li

Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

By use of the static analytical method, the solubilities of terephthalic acid in binary dimethyl sulfoxide (2) + water and in binary *N,N*-dimethylformamide (2) + water solvent mixtures were determined in the temperature range from (301.4 to 373.7) K and solvent composition range from (w_2 = 0.8 to 1.0). The solubility data were correlated with an empirical equation.

Introduction

Terephthalic acid, also known as 1,4-benzenedicarboxylic acid, is an important starting material for the preparation of polyester, which is, in turn, used to make many materials of commerce having a variety of utilities. The major preparative method for obtaining terephthalic acid is the air oxidation of *p*-xylene in the solvent acetic acid, and one byproduct is water. The main disadvantage of the present oxidation technique is that the solvent is corrosive. A major research aspect in the *p*-xylene oxidation technique development is to select some solvents, which must be thermally and chemically stable and noncorrosive. To determine the proper solvent and design an optimized reactive crystallizer, it is necessary to know its solubility in different aqueous organic solvents. Dimethyl sulfoxide and *N,N*-dimethylformamide are two preferred solvents. However, from the point of view of the literature on terephthalic acid, except for aqueous acetic acid,[1] only solubilities of it in pure organic solvents were found.[2−6] No experimental solubility data of it in aqueous organic solvents has been reported. The scarcity of basic solubility data hinders the development of new oxidation techniques. In this work, the solubilities of terephthalic acid in binary dimethyl sulfoxide (2) + water and in binary *N,N*-dimethylformamide (2) + water solvent mixtures were determined in the temperature range from (301.4 to 373.7) K and the solvent composition range from (w_2 = 0.8 to 1.0). The experimental solubility data were correlated with an empirical equation for practical use.

Experimental Section

Chemicals. Terephthalic acid was obtained from Shanghai Chemical Reagent Co. and had a purity 0.995 in mass fraction. Dimethyl sulfoxide, *N,N*-dimethylformamide, and water were obtained from Hangzhou Chemical Reagent Co. and had a purity greater than 0.990 in mass fraction.

Apparatus and Procedure. Solubilities were measured by the static analytical method. Excess solute and solvent were placed in a jacketed glass bottle. The temperature was maintained to within ±0.1 K of the desired temperature with a thermoelectric controlling system. Continuous stirring was carried out for several hours with a magnetic bar. The attainment of solid−liquid equilibrium was verified by repetitive measurements during the next several hours until the results were reproducible to within 0.5%. The compositions of saturated solutions were determined by titration with standard sodium hydroxide solution using phenolphthalein as an indicator. To verify the uncertainty of the measurements, one other experiment was done in which the solubility of benzoic acid in water was determined. The experimental value differed from the literature value by less than 1%.[7] In this work, the estimated uncertainty in the solubility was less than 0.003 mole of terephthalic acid per liter of solvent. The measured mole concentration solubilities (S) of terephthalic acid in dimethyl sulfoxide (2) + water and in *N,N*-dimethylformamide (2) + water solvent mixtures in the temperature range from (301.4 to 373.7) K and solvent composition range from (w_2 = 0.8 to 1.0) are listed in Table 1 and Table 3.

Table 1. Solubilities of Terephthalic Acid (1) in Binary Dimethyl Sulfoxide (2) + Water Solvent Mixtures in the Temperature Range from (301.4 to 373.7) K

T/K	S/mol·L^{-1} [a]	S_c/mol·L^{-1} [b]	T/K	S/mol·L^{-1} [a]	S_c/mol·L^{-1} [b]
		w_2 = 1.0 [c]			
373.5	2.491	2.520	334.7	1.704	1.756
369.4	2.378	2.411	328.6	1.650	1.672
363.6	2.244	2.271	323.0	1.569	1.597
357.9	2.102	2.148	315.0	1.491	1.491
351.5	1.989	2.025	307.5	1.330	1.388
344.2	1.876	1.900	301.9	1.249	1.307
340.4	1.997	1.840			
		w_2 = 0.9 [c]			
373.6	1.570	1.564	330.4	0.713	0.743
366.1	1.362	1.335	326.3	0.683	0.712
359.4	1.174	1.167	319.4	0.642	0.671
351.1	1.088	1.000	314.1	0.616	0.645
345.1	0.914	0.905	307.8	0.581	0.620
341.6	0.857	0.858	301.6	0.558	0.598
336.6	0.790	0.800			
		w_2 = 0.8 [c]			
373.7	0.923	0.917	336.3	0.308	0.331
365.1	0.699	0.704	328.6	0.271	0.294
359.6	0.592	0.596	322.4	0.252	0.275
352.4	0.480	0.484	314.6	0.248	0.261
344.3	0.374	0.393	307.4	0.240	0.252
342.0	0.352	0.372	301.4	0.232	0.244

[a] S: Experimental solubilities. [b] S_c: Calculated solubilities. [c] w_2: Mass fraction of dimethyl sulfoxide in dimethyl sulfoxide (2) + water solvent mixtures.

* To whom correspondence may be addressed. E-mail: wang_qinbo@zju.edu.cn. Fax: 86-571-87951227.

10.1021/je049577c CCC: $30.25
Published on Web 02/19/2005

Table 2. Curve-Fitting Parameters of Terephthalic Acid in Binary Dimethyl Sulfoxide (2) + Water Solvent Mixtures in the Temperature Range from (301.4 to 373.7) K and Solvent Composition Range from (w_2 = 0.8 to 1.0)

	a/mol·L^{-1}	b/mol·L^{-1}	c/10^{-3} mol·L^{-1}	d/10^{-6} mol·L^{-1}	σ/mol·L^{-1}
w_2 = 1.0	−59.10	0.5414	−1.648	1.714	0.0567
w_2 = 0.9	−55.88	0.5525	−1.813	1.996	0.0343
w_2 = 0.8	−62.20	0.6051	−1.958	2.116	0.0156

Table 3. Solubilities of Terephthalic Acid (1) in Binary *N,N*-Dimethylformamide (2) + Water Solvent Mixtures in the Temperature Range from (301.4 to 373.7) K

T/K	S/mol·L^{-1a}	S_c/mol·L^{-1b}	T/K	S/mol·L^{-1a}	S_c/mol·L^{-1b}
		w_2 = 1.0^c			
373.5	0.621	0.618	334.7	0.474	0.480
369.4	0.611	0.602	328.6	0.452	0.460
363.6	0.575	0.579	323.0	0.440	0.444
357.9	0.552	0.558	315.0	0.418	0.420
351.5	0.539	0.536	307.5	0.392	0.400
344.2	0.520	0.511	301.9	0.381	0.385
340.4	0.490	0.498			
		w_2 = 0.9^c			
373.6	0.369	0.364	330.4	0.255	0.253
366.1	0.348	0.342	326.3	0.249	0.244
359.4	0.321	0.323	319.4	0.225	0.230
351.1	0.299	0.301	314.1	0.212	0.220
345.1	0.285	0.286	307.8	0.218	0.209
341.6	0.274	0.278	301.6	0.204	0.198
336.6	0.262	0.267			
		w_2 = 0.8^c			
373.7	0.174	0.165	336.3	0.115	0.112
365.1	0.158	0.151	328.6	0.107	0.103
359.6	0.146	0.142	322.4	0.101	0.097
352.4	0.136	0.132	314.6	0.091	0.089
344.3	0.127	0.121	307.4	0.081	0.083
342.0	0.124	0.119	301.4	0.072	0.078

^{a} S: Experimental solubilities. ^{b} S_c: Calculated solubilities. ^{c} w_2: Mass fraction of *N,N*-dimethylformamide in *N,N*-dimethylformamide (2) + water solvent mixtures.

Table 4. Curve-Fitting Parameters of Terephthalic Acid in Binary *N,N*-Dimethylformamide (2) + Water Solvent Mixtures in the Temperature Range from (301.4 to 373.7) K and Solvent Composition Range from (w_2 = 0.8 to 1.0)

	a/mol·L^{-1}	b/10^{-3} mol·L^{-1}	c/10^{-5} mol·L^{-1}	d/10^{-8} mol·L^{-1}	σ/mol·L^{-1}
w_2 = 1.0	−0.2047	2.860	−0.826	1.740	0.0063
w_2 = 0.9	−0.3878	4.519	−1.622	2.546	0.0052
w_2 = 0.8	−0.4701	4.942	−1.740	2.334	0.0051

Results and Discussion

For practical use in industry, the temperature dependence of terephthalic acid solubility at fixed solvent composition in the temperature range from (301.4 to 373.7) K was correlated with the empirical equation

$$S/\mathrm{mol{\cdot}L^{-1}} = a/\mathrm{mol{\cdot}L^{-1}} + b/\mathrm{mol{\cdot}L^{-1}}(T/\mathrm{K}) + c/\mathrm{mol{\cdot}L^{-1}}(T/\mathrm{K})^2 + d/\mathrm{mol{\cdot}L^{-1}}(T/\mathrm{K})^3 \quad (1)$$

where S is the solubility of terephthalic acid, T is the absolute temperature, and a, b, c, and d are parameters. The calculated solubility values of terephthalic acid are also given in Table 1. The values of parameters a, b, c, and d and the root-mean-square deviations (RMSD) are listed in Table 2 and Table 4. The RMSD is defined as

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

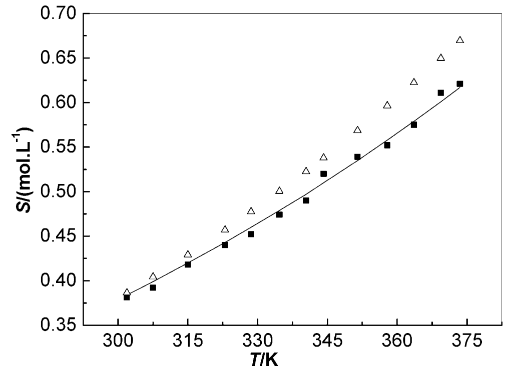

Figure 1. Mole concentration solubility S of terephthalic acid in *N,N*-dimethylformamide + water in the temperature range from (301.4 to 373.7) K: ■, this work; △, data of Li et al.; −, calculated from eq 1.

where S_c is the solubility calculated by eq 1 and n is the number of experimental points.

The solubilities of terephthalic acid in *N,N*-dimethylformamide determined in this work and by Li et al.[6] along with the values calculated with eq 1 are given in Figure 1 for comparison. As can be seen, the solubilities determined in this work are lower than that obtained by Li et al., and with the increase in temperature, the discrepancies increase. In the work of Li et al., predetermined amounts of solute and solvent were weighed and deposited into a jacketed vessel with internal volumes of approximately 20 cm^3. The solvent was easy to volatilize. Although a condenser was connected to the vessel to prevent solvent from evaporating, in the condenser there should be some solvent. Furthermore, the vessel was not full of liquid solvent, and gas−liquid equilibrium of solvent was achieved in the vessel. In the gas phase, large amounts of solvent existed. The higher the temperature was, the more solvent existed in the condenser and the gas phase. However, Li et al. neglected these solvent losses, so the solubility obtained by Li et al. was larger than the true solubility, and the higher the temperature, the larger the discrepancy. In this work, the solubility was determined by the steady-state method; the evaporation of solvent in the vessel had no effect on the solubility determination.

From data listed in Tables 1 to 4, the calculated solubilities show good agreement with the experimental values, and the existence of water has an apparent influence on the solubility of terephthalic acid in the temperature range from (301.4 to 373.7) K. The solubility of terephthalic acid in binary dimethyl sulfoxide + water and in binary *N,N*-dimethylformamide + water solvent mixtures decreases with increasing water content at constant temperature. The experimental solubility and the correlation equation in this work can be used as essential data and models in the new process development of *p*-xylene oxidation.

Literature Cited

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

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

(3) Ma, P. S.; Xia, Q. Determination and Correlation for solubility of Aromatic Acids in Solvents. *Chinese J. Chem. Eng.* **2001**, *9*, 39−44.

(4) Wang, Q. B.; Xu, H. B.; Li, X. Solubilities of 4-Carboxybenzaldehyde and 1,4-Benzenedicarboxylic Acid in *N*-Methyl-2-pyrrolidone in the Temperature Range from (343.2 to 468.2) K. *J. Chem. Eng. Data* **2005**, *50*, 243−245.

(5) Li, D. Q.; Liu, D. Z.; Wang, F. A. Solubilities of Terephthalaldehydic, *p*-Toluic, Benzoic, Terephthalic, and Isophthalic Acids in *N*-Methyl-2-pyrrolidone from 295.65 K to 371.35 K. *J. Chem. Eng. Data* **2001**, *46*, 172−173.

(6) Li, D. Q.; Liu, J. C.; Liu, D. Z.; Wang, F. A. Solubilities of Terephthaladehydic, p-Toluic, Benzoic, Terephthalic and Isophthalic Acids in *N,N*-dimethylformamide from 294.75 K to 370.45 K. *Fluid Phase Equilib.* **2002**, *200*, 69−74.

(7) Stephen, H.; Stephen, T. *Solubilities of Inorganic and Organic Compounds*; Pergamon Press: Oxford, U.K., 1963.

Received for review December 1, 2004. Accepted January 17, 2005.

JE049577C