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

Qinbo Wang,* Haibo Xu, and Xi Li

Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, PR China

Using the steady-state method, solubilities of 4-carboxybenzaldehyde and 1,4-benzenedicarboxylic acid in the solvent *N*-methyl-2-pyrrolidone in the temperature range from (343.2 to 468.2) K at a pressure of 1.6 MPa were determined. The experimental results were correlated by an empirical equation.

Introduction

Purified 1,4-benzenedicarboxylic acid is a starting material for the formation of polyester resin, which is, in turn, used to make many materials of commerce having a variety of utilities. 4-Carboxybenzaldehyde is one of the most difficult to remove contaminants present in 1,4-benzenedicarboxylic acid and, unfortunately, is one of the most deleterious.[1] Selective crystallization is a new and effective method to purify crude 1,4-benzenedicarboxylic acid.[2] For the conventional solvent, it is known from the literature that some solvents are toxic and corrosive, some have less dissolution ability, and others can exist only in the liquid phase over a narrow temperature range.[3−6] Therefore, they are not very suitable for the purification process. *N*-Methyl-2-pyrrolidone is nonaqueous, thermally stable, and nontoxic (environmentally safe) and is a preferred selective crystallization solvent. Li determined the solubilities of 1,4-benzenedicarboxylic acid and 4-carboxybenzaldehyde in *N*-methyl-2-pyrrolidone from (296.3 to 341.3) K but did not cover the temperature range required by industrial 1,4-benzenedicarboxylic acid purification.[6,7] In this work, we report the solubilities of 1,4-benzenedicarboxylic acid in the solvent *N*-methyl-2-pyrrolidone in the temperature range from (343.2 to 468.2) K and 4-carboxybenzaldehyde in the solvent *N*-methyl-2-pyrrolidone in the temperature range from (353.2 to 421.2) K at a pressure of 1.6 MPa.

Experimental Section

Chemicals. 1,4-Benzenedicarboxylic acid was obtained from Shanghai Chemical Reagent Co. and had a purity of 0.995 mass fraction. *N*-Methyl-2-pyrrolidone had a refractive index n^{20}_D of 1.4686 ($n^{20}_D = 1.4684$ in the literature[8]). 4-Carboxybenzaldehyde used for experiments had a mass fraction of 0.998, which was obtained by purifying the industrial product that had a stated mass fraction 0.980. First, 4-carboxybenzaldehyde was dissolved in a 1 M 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 4-carboxybenzaldehyde. The purities of 1,4-benzenedicarboxylic acid and 4-carboxybenzaldehyde were determined with a high-performance liquid chromatograph (Shimadzu 6A HPLC).

* Corresponding author. E-mail: wang_qinbo@zju.edu.en.

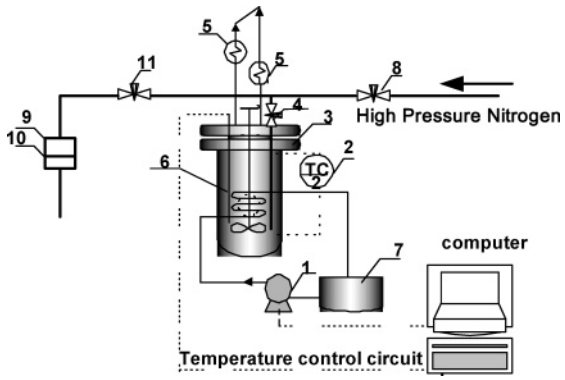

Figure 1. Experimental apparatus for solubility determination: 1, peristaltic pump; 2, heating control circuit; 3, equilibrium vessel; 4, sampling valve; 5, condenser; 6, thermal resistance thermometer; 7, cooling oil tank; 8, high-pressure nitrogen valve; 9, sample cell; 10, filter; 11, pressure relief valve.

Apparatus and Procedure. Solubilities were measured by the steady-state method. The solid−liquid equilibrium of the solute in the solvent was achieved in a titanium vessel. Two condensers were connected to the vessel to prevent the solvents from evaporating. The pressure was controlled by a back-pressure valve to be 1.6 MPa. A Pt100 thermal resistance thermometer was inserted into the vessel for the measurement of temperature. Two thermometers were used during the measurement. One had a measurement range from (323.2 to 423.2) K, and the other had a measurement range from (423.2 to 553.2) K. All of the thermometers had an uncertainty of ±0.1 K.

Excess solute and solvent (800 mL) were deposited in the titanium vessel. The contents of the vessel were heated very slowly at rates of less than 0.5 K min^{-1} to the experimental temperature. The temperature was maintained within ±0.5 K of the desired temperature with a controlling system as shown in Figure 1. When the temperature was higher than the desired point, the computer program would start the peristaltic pump, and cooling oil would flow through the spiral coil in the vessel to cool the contents of the vessel. When the temperature was lower than the desired point, the computer program would start the heater controlling circuit, and the vessel wall would be electrically heated. Continuous stirring was achieved for several hours with a turbine impeller. The attainment of equilibrium was verified by repetitive measurements

10.1021/je049706p CCC: $30.25
Published on Web 12/21/2004

Table 1. Solubilities of Different Solutes in *N*-Methyl-2-pyrrolidone

T/K	S/g(100 g)$^{-1}$	S_c/g(100 g)$^{-1}$	T/K	S/g(100 g)$^{-1}$	S_c/g(100 g)$^{-1}$
4-Carboxybenzaldehyde					
353.2	65.2	63.6	389.2	116.6	116.6
357.2	69.2	67.9	393.2	125.5	124.8
361.2	74.1	72.6	397.2	132.4	133.6
365.2	78.0	77.6	401.2	142.9	143.0
369.2	84.0	83.0	405.2	152.5	152.9
373.2	89.6	88.8	409.2	162.3	163.5
377.2	95.2	95.1	413.2	174.0	174.8
381.2	103.1	101.7	417.2	187.0	186.8
385.2	110.0	108.9	421.2	199.7	199.5
1,4-Benzenedicarboxylic Acid					
343.2	10.9	12.7	408.2	33.7	32.6
348.2	12.4	13.4	413.2	35.3	35.7
353.2	13.3	14.2	418.2	39.5	39.3
358.2	15.0	15.1	423.2	42.7	43.2
363.2	15.9	16.0	428.2	46.8	47.5
368.2	17.1	17.1	433.2	49.4	52.2
373.2	17.8	18.3	438.2	55.6	57.4
378.2	19.5	19.6	443.2	61.4	63.1
383.2	21.4	21.2	448.2	66.0	69.2
388.2	23.1	22.9	453.2	73.1	75.9
393.2	26.0	24.9	458.2	82.6	83.1
398.2	27.2	27.2	463.2	92.2	90.9
403.2	30.2	29.7	468.2	103.6	99.3

Table 2. Parameters for Correlation Equations of Different Solutes

solute	a	b	10^2c	10^5d	σ
4-carboxybenzaldehyde	−2127	19.82	−6.252	6.785	0.93
1,4-benzenedicarboxylic acid	−1278	11.13	−3.241	3.187	0.84

during the next several hours until the results were reproducible to within 0.5%. To determine the composition of the solution, we transferred the saturated solution from the equilibrium vessel to a titanium pipe between the pressure relief valve and high-pressure nitrogen valve. The titanium pipe was electrically heated around the wall, and the wall temperature was controlled to be equal to the experimental temperature. The solution was then pressed toward a porous stainless steel filter with an internal aperture size of 1 μm. The filtered solution was then cooled, and the composition of the solution was determined by a mass analytical method in which the amount of solute in the weighed solution was determined by mass after drying in vacuo at 323.2 K for more than 6 h; an electrical balance with an accuracy of 0.0001 g was used. About 10 mL of the saturated solution was sampled each time. 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%.[3] In this work, the estimated uncertainty in the solubility was less than 0.1 g of solute/100 g of solvent.

Results and Discussion

The experimental results of solubilities in g solute/100 g solvent in the systems 1,4-benzenedicarboxylic acid + *N*-methyl-2-pyrrolidone and 4-carboxybenzaldehyde + *N*-methyl-2-pyrrolidone are presented in Table 1. For the two systems, solubility is a function of temperature, and the solubility increases with increasing temperature.

The solubility data were correlated with the empirical equation

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

where S represents the solubility of the two solutes in *N*-methyl-2-pyrrolidone, T is the absolute temperature, and

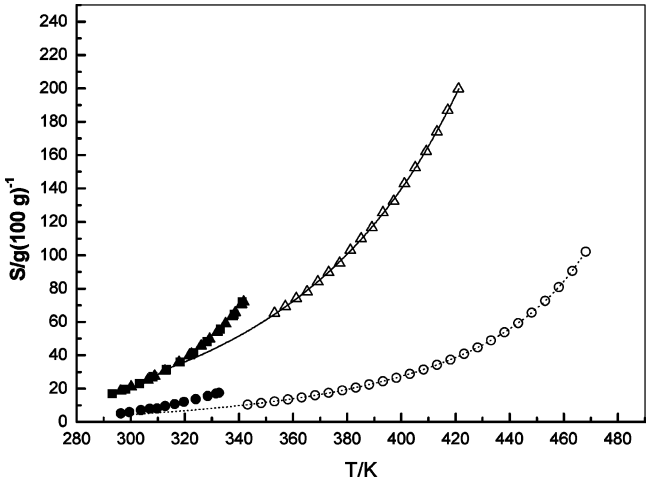

Figure 2. Solubilities of 4-carboxybenzaldehyde and 1,4-benzenedicarboxylic acid in *N*-methyl-2-pyrrolidone: △, 4-carboxybenzaldehyde, this work; ▲, 4-carboxybenzaldehyde, Li et al.;[6] ■, 4-carboxybenzaldehyde, Li et al.;[7] ○, 1,4-benzenedicarboxylic acid, this work; ●, 1,4-benzenedicarboxylic acid, Li et al.;[7] −, 4-carboxybenzaldehyde, calculated by eq 1; ···, 1,4-benzenedicarboxylic acid, calculated by eq 1.

a, b, c, and d are empirical constants. The values of these constants together with the root-mean-square deviations (rmsd's) are listed in Table 2. The rmsd is defined as

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

where S_{ci} is the solubility calculated by eq 1, S_i is the solubility from the ith experiment, and n is the number of experimental points. The calculated solubilities are also listed in Table 1. From Tables 1 and 2, the calculated solubilities show good agreement with the experimental values.

The solubilities determined in this work and by Li et al.[6,7] along with the calculated values from eq 1 are given in Figure 2 for comparison. As can be seen, if the experimental points from this work are extrapolated to lower temperatures, then 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 a solute and *N*-methyl-2-pyrrolidone were weighed and deposited into a jacketed vessel with an internal volume of approximately 20 cm^3. The solvent *N*-methyl-2-pyrrolidone was easy to volatilize. Although a condenser was connected with 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 the solvent was achieved in the vessel. In the gas phase, large amounts of solvent existed. The higher the temperature, the more solvent that existed in the condenser and the gas phase, but Li et al. neglected this solvent loss. Therefore, 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. The experimental solubility and correlation equation in this work can be used as essential data and models in the process of 1,4-benzenedicarboxylic acid purification at elevated temperatures.

Literature Cited

(1) Raghavendrachar, P.; Ramachadran, S. Liquid-phase Catalytic Oxidation of p-Xylene. *Ind. Eng. Chem. Res.* **1992**, *31*, 453−462.
(2) Lee, F. M.; Lamshing, W. Method and Apparatus for Preparing Purified Terephthalic Acid. U.S. Patent 5,840,968.
(3) Stephen, H.; Stephen, T. *Solubilities of Inorganic and Organic Compounds*; Pergamon Press: Oxford, England, 1963.
(4) Chen, M. M.; Ma, P. S. Solid−Liquid Equilibria of Several Systems Containing Acetic Acid. *J. Chem. Eng. Data* **2004**, *49*, 756−759.
(5) Marquering, M. W. Crystal Aging of Terephthalic Acid in 90 Mass % Acetic Acid Solution. M.S. Thesis, Polytechnic University, New York, 1989.
(6) Li, D. Q.; Evans, D. G.; Duan, X. Solid−Liquid Equilibria of Terephthalaldehydic Acid in Different Solvents. *J. Chem. Eng. Data* **2002**, *47*, 1220−1221.
(7) Li, D. Q.; Liu, D. Z.; Wang, F. A. Solubilities of Terephthalaldehydic, *p*-Toluic, Benzoic, Terephthalic, and Isophthalic Acid in *N*-Methyl-2-pyrrolidone from 295.15 K to 373.15 K. *J. Chem. Eng. Data* **2001**, *46*, 172−173.
(8) *Handbook of Chemistry and Physics*, 73rd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1992.

Received for review August 15, 2004. Accepted November 4, 2004.

JE049706P