Solid−Liquid Equilibria of 1,4-Benzenedicarboxylic Acid in Binary Acetic Acid + Water Solvent Mixtures at Elevated Temperatures

Qinbo Wang,* Haibo Xu, and Xi Li

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

The solubilities of 1,4-benzenedicarboxylic acid in binary acetic acid (2) + water solvent mixtures were measured in a specially contrived vessel in the temperature range from (433.2 to 513.2) K and solvent composition range from (w_2 = 0.6 to 1.0) by the steady-state method. Results of these measurements were correlated by a modified Buchowski equation. For the five groups of data studied, the modified Buchowski equation was found to provide an accurate mathematical representation of the experimental data.

Introduction

As one of the most important aromatic compounds, polymerization-grade 1,4-benzenedicarboxylic acid is used extensively in organic synthesis, particularly in the polyester industry. To purify 1,4-benzenedicarboxylic acid using a simple method, measurements of the systemic and comprehensive solubility data of 1,4-benzenedicarboxylic acid in binary acetic acid + water solvent mixtures are needed. Unfortunately, very few data exist, especially for the industrial 1,4-benzenedicarboxylic acid purification process. The solubility of 1,4-benzenedicarboxylic acid in binary acetic acid (2) + water solvent mixtures from (w_2 = 0.746 to 1.0) was investigated by Chen and Ma[1] from (312.6 to 435.1) K, but it could not be extrapolated to the high temperature required by industrial 1,4-benzenedicarboxylic acid purification. Marquering[2] published the solubility data of 1,4-benzenedicarboxylic acid in binary acetic acid (2) + water solvent mixtures of w_2 = 0.9 from (293.2 to 523.2) K, but they could not be extrapolated to other solvent compositions and the data source was not given. In this work, we report the solubilities of 1,4-benzenedicarboxylic acid in binary acetic acid (2) + water solvent mixtures in the temperature range from (433.2 to 513.2) K and solvent composition range from (w_2 = 0.6 to 1.0). The data are correlated by a modified Buchowski equation.[3]

Experimental Section

Chemicals. 1,4-Benzenedicarboxylic acid was obtained from Shanghai Chemical Reagent Co. and had a purity of 0.995 mass fraction. Methanol and acetonitrile were obtained from USA Tedia Company, Inc. and had a purity of 0.999 mass fraction. All other materials used in the experiments were obtained from Hangzhou Chemical Reagent Co. and had a purity higher than 0.990 mass fraction.

Chromatographic Conditions. The concentration of 1,4-benzenedicarboxylic acid in the liquid phase was determined using a Shimadzu-6A high-performance liquid-phase chromatograph (HPLC). The Diamonsil C18 (150 mm × 4.6 mm) chromatographic column was used. Gradient elution was needed for complete separation of the analytes at room temperature. The mobile phase consisted of three eluents (i.e., water + acetonitrile + methanol), and the following three-component gradient evolution program was adopted: from 0 to 5 min, 95 mass % water and 5 mass % acetonitrile; from 5 to 8 min, the mixture composition changed linearly with time to become 55 mass % water, 10 mass % methanol, and 35 mass % acetonitrile; from 8 to 12 min, the mixture composition changed linearly with time to become 15 mass % water and 75 mass % acetonitrile, whereas methanol remained at 10 mass %; from 12 to 14 min, the mixture composition changed linearly with time to become pure acetonitrile; from 14 min on, 100 mass % acetonitrile. During the analysis process, isopropyl benzene was used as the internal standard. Each analysis took about 20 min. To verify the uncertainty of the measurement, 10 1,4-benzenedicarboxylic acid + isopropyl benzene + acetic acid solutions of known concentration were analyzed. Compared with the uncertainty of the known concentration, the uncertainty was less than 0.01 g of 1,4-benzenedicarboxylic acid per 100 g of solvent. To check the repeatability, the 10 solutions were measured at least 5 times, and the repeatability was evaluated with a mean relative deviation of less than 4%.

Determination of 1,4-Benzenedicarboxylic Acid Concentration. Assuming that in a solution the mass of 1,4-benzenedicarboxylic acid is m_1, the mass of isopropyl benzene is m_2, and the corresponding peak area of the chromatography response is A_1 and A_2, one gets eq 1

$$\frac{m_1}{m_2} = \frac{KA_1}{A_2} \tag{1}$$

where K stands for the instrument constant that must be experimentally determined. Known masses of 1,4-benzenedicarboxylic acid were dissolved in dimethyl sulfoxide. Subsequently, a known mass of isopropyl benzene was added to the dimethyl sulfoxide + 1,4-benzenedicarboxylic acid solution. The solution was then analyzed by HPLC, and a series of m_1/m_2 and corresponding A_1/A_2 were obtained. The instrument constant was obtained by linear regression through eq 1 to give 0.0517 with an uncertainty of ±0.0006. When determining the concentration of 1,4-benzenedicarboxylic acid in binary acetic acid + water solvent mixtures, we added a known mass of isopropyl benzene to the 1,4-benzenedicarboxylic acid + acetic acid + water solution and measured the corresponding peak area. Then according to eq 1, the concentration of 1,4-benzenedicarboxylic acid was determined.

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

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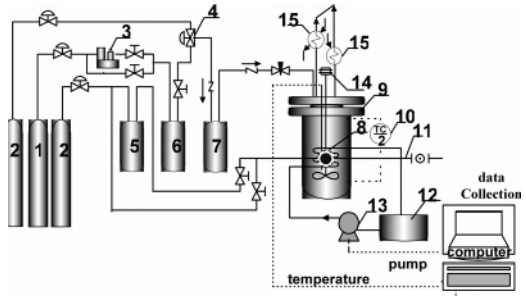

Figure 1. Experimental apparatus for solubility determination of 1,4-benzenedicarboxylic acid in binary acetic acid + water solvent mixtures in the temperature range from (423.2 to 513.2) K: 1, air cylinder; 2, nitrogen cylinder; 3, mass flowmeter; 4, air inlet valve; 5, solvent pot; 6, air buffer drum; 7, gas buffer drum; 8, sampler; 9, dissolution tank; 10, heating control circuit; 11, sample cell; 12, cool tank; 13, peristalic pump; 14, agitator; 15, condenser.

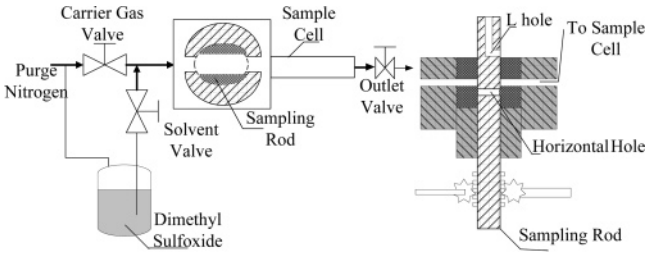

Figure 2. Sketch of the sampler.

Apparatus and Procedure. Solubilities were measured by the steady-state method. Solid−liquid equilibria of 1,4-benzenedicarboxylic acid in binary acetic acid + water solvent mixtures were achieved in a titanium vessel as illustrated in Figure 1. Continuous stirring was achieved with a turbine impeller. Two condensers were connected with the vessel to prevent solvents from evaporating. A Pt100 thermal resistance thermometer was inserted into the vessel for the measurement of the temperature. The thermometer had a measurement range from (423.2 to 523.2) K and had an uncertainty of ±0.1 K. In each experiment, excess 1,4-benzenedicarboxylic acid and 300 mL of a known concentration of aqueous acetic acid were deposited into the vessel. The contents of the vessel were continuously stirred and heated very slowly at rates of less than 1.0 K·min^{-1}. The suspension temperature was continuously recorded and was controlled within ±1.0 K. In the pre-experiments, it was found that when the temperature increased to 473.2 K at less than 1.0 K·min^{-1} the concentration of 1,4-benzenedicarboxylic acid would become constant after 1 h, which indicated that the solution had been saturated. However, sedimentation experiment indicated that the solution would be homogeneous after 90 min at 293.2K. When the temperature reached the experimental point, stirring was stopped, and the whole system was kept isothermal for at least 2 h to ensure that the solution had been saturated and the suspended particles had been deposited on the bottom. Then a gear drag-bar sampler as illustrated in Figure 2 was used to sample the saturated solution at high temperature. On the bottom of the sampling rod there were an "L" hole entryway and a horizontal hole entryway. The diameter of each hole was 1.5 mm. One could pull the sampling rod out of the vessel to a fixed position so that the "L" hole could be connected with the sample cell. At this moment, the solution in the vessel would flow into the sample cell at the system pressure until the sample cell was filled with liquid-phase sample. It should be emphasized that at this moment the outlet valve, the carrier-gas valve, and the solvent valve should be closed. Then one could push the sampling rod into the vessel so that the sample was enclosed in the sampling cell. To avoid the loss of solvents by evaporation, the sample was cooled to room temperature quickly by the water cooling jacket surrounding the sample cell, in which most of the solute would crystallize. Then the outlet valve and the carrier gas valve were opened, and the solution in the sample cell was swept out by the high-pressure carrier gas into a sampling bottle. To collect the crystallized solute into the sample bottle, the solvent valve was open, and the sample cell was flushed by the solvent dimethyl sulfoxide at least three times. In each measurement, 2 mL of the saturated solution was sampled, with an uncertainty of 0.05 mL. Dimethyl sulfoxide (2 mL) was added to the sample to dissolve all of the 1,4-benzenedicarboxylic acid. Isopropyl benzene (1 mL) was also added to the sample, and the solution was diluted to 25 mL with methanol. The sample was then analyzed using the method introduced in the Chromatographic Conditions section, and eq 1 was used to determine the concentration of 1,4-benzenedicarboxylic acid. Some of the solubility experiments were conducted two or three times to check the repeatability. To verify the uncertainty of the measurements, we did one other experiment in which the solubility of benzoic acid in water was determined. The experimental value differed from the literature value by less than 1%. In this work, the uncertainty of the experimental solubility in mass was less than 0.1 g of 1,4-benzenedicarboxylic acid per 100 g of solvent.

Table 1. Solubilities of 1,4-Benzenedicarboxylic Acid (1) in Binary Acetic Acid (2) + Water Solvent Mixtures in the Temperature Range from (433.2 to 513.2) K[a]

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)$^{-1}$
		$w_2 = 1.0$			
433.2	0.61	0.59	483.2	1.98	2.00
443.2	0.82	0.77	493.2	2.48	2.49
453.2	1.02	0.99	503.2	3.09	3.07
463.2	1.27	1.27	513.2	3.86	3.76
473.2	1.59	1.60			
		$w_2 = 0.8$			
433.2	0.95	0.88	483.2	3.66	3.71
443.2	1.30	1.20	493.2	4.75	4.79
453.2	1.68	1.62	503.2	6.16	6.14
463.2	2.18	2.16	513.2	7.98	7.79
473.2	2.82	2.85			
		$w_2 = 0.7$			
433.2	1.03	1.00	483.2	4.98	4.82
443.2	1.53	1.40	493.2	6.58	6.37
453.2	2.06	1.95	503.2	8.69	8.32
463.2	2.85	2.67	513.2	11.49	10.78
473.2	3.76	3.61			
		$w_2 = 0.6$			
433.2	1.52	1.44	483.2	6.76	7.49
443.2	2.05	2.06	493.2	9.11	10.03
453.2	2.77	2.90	503.2	12.27	13.27
463.2	3.73	4.03	513.2	16.53	17.39
473.2	5.02	5.53			

[a] S: experimental solubilities of 1,4-benzenedicarboxylic acid (1) in acetic acid (2) + water solvent mixtures. S_c: calculated solubilities of 1,4-benzenedicarboxylic acid (1) in acetic acid (2) + water solvent mixtures by eq 2. w_2: mass fraction of acetic acid in acetic acid (2) + water solvent mixtures.

Results and Discussion

Buchowski and co-workers developed an equation for systems in which solutes exhibit self-association.[3] This equation is also applicable to most solid−liquid equilibrium systems and gives excellent correlation without considering

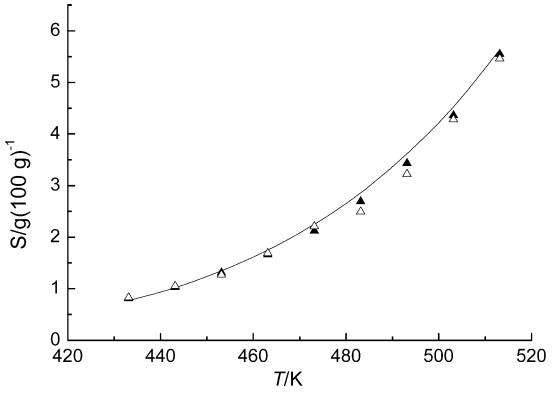

Figure 3. Solubilities of 1,4-benzenedicarboxylic acid in binary acetic acid (2) + water solvent mixtures at $w_2 = 0.9$: ▲, this work; △, Marquering[2]; −, calculated from eq 2.

the activity coefficients of the components. The Buchowski equation is given by eq 2

$$\ln\left(1 + \frac{100\lambda M_{\text{solute}}}{SM_{\text{solvent}}}\right) = \lambda h(T^{-1} - T_{\text{m}}^{-1}) \tag{2}$$

where λ and h are two parameters, T is the absolute temperature, T_{m} is the melting temperature of the solute, S stands for the solubility in g of solute per 100 g of solvent, and M_{solute} and M_{solvent} are the molecular mass of solute and solvent, respectively. Equation 2 was effective only for constant solvent composition. To use eq 2 to correlate the solubility of 1,4-benzenedicarboxylic acid at different solvent compositions, parameters λ and h were assumed to be a function of w_2:

$$\lambda = a_1 + b_1 \exp(c_1 w_2) \tag{3}$$

$$h = a_2 + b_2 \exp(c_2 w_2) \tag{4}$$

The experimental solubility values S correlated with eq 2 and the calculated solubility S_{c} at solvent compositions of $w_2 = 1.0$, 0.8, 0.7, and 0.6 and in the temperature range from (433.2 to 513.2) K are listed in Table 1. For comparison with the experimental values of this work and the literature,[2] the calculated values of the solubility of 1,4-benzenedicarboxylic acid in binary acetic acid (2) + water solvent mixtures at $w_2 = 0.9$ and in the temperature range from (433.2 to 513.2) K were given in Figure 3. Compared with the literature data, the deviation of the solubility was less than 3%.

Table 2. Curve-Fitting Parameters of 1,4-Benzenedicarboxylic Acid in Binary Acetic Acid (2) + Water Solvent Mixtures in the Temperature Range from (433.2 to 513.2) K and Solvent Composition Range from (w_2 = 0.6 to 1.0)

	a_i	b_i	c_i
$i = 1$	0.0589	61.308	−0.0566
$i = 2$	−1883.05	656.9	0.0343
variance		0.051	

The values of the six parameters a_1, b_1, c_1, a_2, b_2, and c_2 are listed in Table 2 together with the variance between the experimental and calculated values. The variance is defined as

$$\text{variance} = \left[\frac{1}{n}\sum_{i=1}^{n}\left(\frac{S_{\text{c},i} - S_i}{S_i}\right)^2\right]^{1/2} \tag{5}$$

where n is the number of experimental points.

From Figure 3 and Tables 1 and 2, the calculated solubilities show good agreement with the experimental values, and with the increase in temperature and w_3, the solubility of 1,4-benzenedicarboxylic acid in binary acetic acid (2) + water (3) solvent mixtures in the temperature range from (433.2 to 513.2) K increases. 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 and manufacture.

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