Solubilities of 1,3-Benzenedicarboxylic Acid in Water + Acetic Acid Solutions

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The solubilities of 1,3-benzenedicarboxylic acid (isophthalic acid) in water, acetic acid, and acetic acid + water solutions with mass fractions of acetic acid on a solute-free basis of 0.2056, 0.4083, and 0.6082, respectively, were measured. The concentration of the solution was determined by a gravimetrical method. The measured solubility of isophthalic acid in water agrees with that reported in the literature. The logarithm of the solubility data shows good linearity against temperature.

Introduction

1,3-Benzenedicarboxylic acid, also called isophthalic acid, is a highly versatile chemical. It can be used as an intermediate for high-quality unsaturated polyesters and as an additive for poly(ethylene terephthalate) (PET) resin. Other applications include its use in the production of aramid fibers, polyester beverage bottles, and adhesives. Isophthalic acid offers excellent performance characteristics of hardness, flexibility, stain resistance, thermal stability, and low resin color.[1,2]

In industry, isophthalic acid is crystallized as a raw product from aqueous acetic acid solutions and is then purified by recrystallization from water. Thus, a knowledge of the solubility of isophthalic acid in water + acetic acid systems is very important for the separation and purification process.[1]

Solubility data of isophthalic acid in water[4] from (298 to 483) K determined by a titration method and in acetic acid[3] have been reported. However, there were only two published solubility data points of isophthalic acid in acetic acid from (298 to 373) K and their measurement procedure was unknown, and the data in acetic acid aqueous solution are not readily available. In this work, solubilities of isophthalic acid in water + acetic acid solutions of different composition (0, 0.2056, 0.4083, 0.6082, and 1, acetic acid mass fraction) were measured by a gravimetrical method.

Experimental Section

Materials. Analytical reagent isophthalic acid (Beijing Yanshan Petrochemical Co., 99.8+% by mass) was further purified by recrystallization from heated water. Demineralized water (density of 0.999 g/mL, refractive index of 1.3325, both at 298.15 K) and analytical-grade acetic acid (density of 1.045 g/mL, refractive index of 1.3700, both at 298.15 K) from Tianjin Chemical Reagent Co. were used.

Apparatus and Procedure. The experiments were carried out in a magnetically stirred, jacketed equilibrium cell with a working volume of 100 mL, as described by Wang.[5] The cell was sealed to prevent the evaporation of solvent. The temperature of the equilibrium cell was controlled by circulating water from a thermostat (type 501, Shanghai Laboratory Instrument Works Co. Ltd.) through a jacket of the cell, which is capable of maintaining the temperature within ±0.05 K. The temperature was measured using a glass thermometer with ±0.1 K uncertainty. An analytical balance (type TG328B, Shanghai Balance Instrument Works Co.) with uncertainty of ±0.1 mg was used during the mass measurements.

Solubility Measurement. The solubilities were measured by a gravimetric method.[6] For each measurement, an excess amount of isophthalic acid was added to a certain amount of solvent, which was prepared gravimetrically. Then the equilibrium cell was heated to some constant temperature with continuous stirring. After at least 1 h, the stirring was stopped and the solution was kept still for 30 min, and then the white solids could be observed to settle down in the lower portion of the equilibrium cell. A suitably warmed pipet withdrew the clear upper portion of the solution with the tip protected by a microscreen to another previously weighed measuring vial (m_0). The vial was quickly and tightly closed and weighed (m_1) to determine the mass of the sample ($m_1 - m_0$). Then the vial was uncovered and placed in an oven at about 393 K for evaporation. The vial was covered with a piece of filter cloth to prevent dust contamination. After the solvent in the vial had completely evaporated, the vial was dried for another 3 h and reweighed (m_2) to determine the mass of the constant residue solid ($m_2 - m_0$). Thus, the solid concentration of the sample solution in mole fraction could be determined from eq 1[6]

$$x = \frac{(m_2 - m_0)/M_1}{(m_2 - m_0)/M_1 + (m_1 - m_2)w_2/M_2 + (m_1 - m_2)(1 - w_2)/M_3} \tag{1}$$

where M_1, M_2, and M_3 stand for the molar masses of the solid, acetic acid, and water, which are 166.133 g/mol, 60.053 g/mol, and 18.015 g/mol, respectively, whereas w_2 is the mass fraction of acetic acid in the solvents.

Different dissolution times were tested to determine a suitable equilibrium time. It was found that 3 h was enough for isophthalic acid in all solvents to reach equilibrium. An average value is taken from three measurements at the same composition of solvent for each temper-

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Table 1. Experimental Solubilities of Isophthalic Acid (1) in Acetic Acid (2) + Water (3) in Mole Fraction

acetic acid (w_2)	T/K	10^4x_1 (measured)	$\frac{x_1^{\text{exptl}} - x_1^{\text{calcd}}}{x_1^{\text{exptl}}}$
0	301.45	0.1963	0.0428
(pure water)	314.15	0.2982	−0.0181
	325.15	0.4565	−0.008
	338.15	0.7243	−0.038
	349.65	1.128	−0.029
	356.65	1.496	−0.011
	359.63	1.702	−0.005
	366.58	2.320	0.051
0.2056	301.65	0.3761	−0.091
	308.85	0.5631	−0.002
	318.45	0.9181	0.060
	328.35	1.393	0.040
	338.05	2.118	0.031
	348.45	3.294	0.012
	358.35	5.006	−0.007
	368.35	7.448	−0.053
0.4083	298.65	1.031	−0.099
	308.15	1.708	0.033
	318.35	2.605	0.051
	328.35	3.771	0.025
	338.35	5.643	0.032
	348.35	8.231	0.014
	358.15	11.80	−0.014
	368.15	16.97	−0.047
0.6082	298.95	2.341	−0.083
	308.55	3.626	0.015
	318.45	5.193	0.022
	328.15	7.584	0.053
	337.95	10.63	0.042
	347.95	14.64	0.007
	358.15	20.69	−0.011
	368.15	28.35	−0.053
1	300.55	8.007	0.036
(pure acetic acid)	316.55	12.00	−0.007
	330.25	17.18	−0.032
	338.00	21.06	−0.046
	347.85	28.27	−0.027
	355.35	37.91	0.055
	364.03	47.42	0.037
	370.13	53.00	−0.022

ature. The estimated uncertainty of the solubility values based on error analysis and repeated observations was within 2%.

Results and Discussion

The solubility data of isophthalic acid, x (mole fraction), in acetic acid + water solutions are summarized in Table 1 and plotted as ln x versus temperature in Figure 1. In both the Table and Figure, the composition of the solvent is given as the mass fraction of acetic acid in the solution on a solute-free basis. The measured solubility data of isophthalic acid in water are compared with the literature data, and the deviations of the solubility are less than 4%.

The solubilities (mole fraction) of isophthalic acid were correlated as a function of temperature (T/K) by adopting a logarithmic equation:

$$\ln x = A + B(T/K) \tag{2}$$

Parameters A and B for each solvent are listed in Table 2. The relative deviation of calculated solubilities of isophthalic acid using eq 1 are given in Table 1. The root-mean-square deviations (rmsd's) δ, defined by eq 3, are also presented in Table 2.

$$\delta = \sqrt{\sum_{i=1}^{n} \frac{(x_i^{\text{exptl}} - x_i^{\text{calcd}})^2}{n - 1}} \tag{3}$$

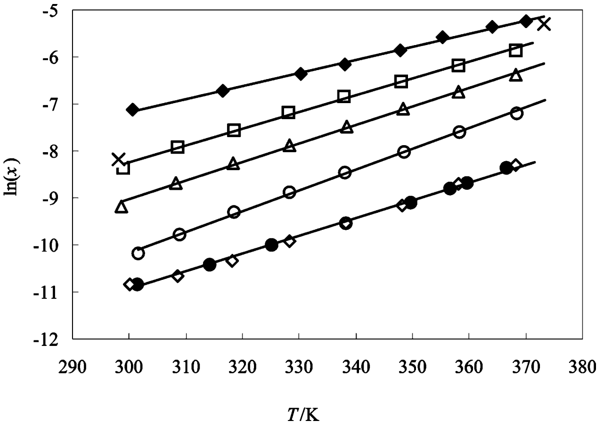

Figure 1. Determined mole fraction solubilities of isophthalic acid in acetic acid (2) + water (3): ◆, $w_2 = 1$; □, $w_2 = 0.2056$; △, $w_2 = 0.4083$; ○, $w_2 = 1$; ●, $w_2 = 0$; ◇, literature data ($w_2 = 0$) from Han;[2] ×, literature data ($w_2 = 1$) from ref 3; −, solubility curve calculated from eq 2.

Table 2. Parameters of Equation 2 and Root-Mean-Square Deviations of the Measured Solubility Calculated from Equation 3

solvent (acetic acid wt %)	A	B	$10^4\delta$ (rmsd)
0	−22.273	0.0378	0.05
20.56	−23.448	0.0442	0.16
40.83	−20.913	0.0396	0.33
60.82	−18.932	0.0356	0.63
100	−15.586	0.0280	1.24

where the superscript exptl stands for the experimental data and calcd stands for the calculated values and n is the number of experimental points. The results show that eq 2 can be used to correlate the measured solubility data.

From Figure 1, it can be seen that the two solubility data points of isophthalic acid in acetic acid reported from the literature are only a little different from the data reported in this work. However, no details of their measurement procedure are available and our values are repeatable, whereas the solubility data of isophthalic acid in water are consistent with the literature values. Within the temperature range of the measurements, the solubilities of isophthalic acid in all of the investigated solvents showed an increasing trend as the measured temperature increased. The solubility of isophthalic acid in pure acetic acid shows the highest value, and it decreases with the increasing concentration of water in the mixed acetic acid−water solvent at constant temperature.

Literature Cited

(1) Huntingdon Research Centre. Amoco Isophthalic Acid 220: Bacterial Mutation Assay HRC Report 1991, No. AOM 2/91617.

(2) Wang, H.-T. The Production and Application of Isophthalic Acid. *Petrochem. Ind. Trends* **1998**, *6(6)*, 56−60.

(3) Su, J.-M. *Polyester Technology*; Chemical Industry Press: Beijing, 1982.

(4) Han, N.-Y.; Wang, L.-S.; Fu, R.-N. Aqueous Solubility of m-phthalic Acid, o-phthalic acid and p-phthalic from 298 to 483 K. *Sep. Purif. Technol.* **1999**, *16*, 175−180.

(5) Wang, L.-S.; Wang, X.-L. Solubilities of Dichlorophenylphosphine Sulfide and Bis(4-carboxyphyl)phenylphosphine Oxide in Water. *J. Chem. Eng. Data* **2000**, *45*, 743−745.

(6) Zhu, M. Solubility and Density of the Disodium Salt Hemiheptahydrate of Ceftriaxone in Water + Ethanol Mixtures. *J. Chem. Eng. Data* **2001**, *46*, 175−176.

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