Solubility of 1,2,4-Benzenetricarboxylic Acid in Acetic Acid + Water Solvent Mixtures

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Using the static analytical method, the solubility of 1,2,4-benzenetricarboxylic acid in binary acetic acid + water solvent mixtures has been measured. The experimental temperatures range from (313.2 to 363.2) K, and the mole fractions of acetic acid in the solvent mixtures range from 0.416 to 1.000. The experimental solubilities were correlated by the Apelblat equation.

Introduction

The molecular structure of 1,2,4-benzenetricarboxylic acid under study is shown in Figure 1.

1,2,4-Benzenetricarboxylic acid is one of the most important fine chemicals. Along with its various ester derivatives, it is widely used as intermediates in the preparations of resins, plasticizers, insulating coatings, paints, etc. 1,2,4-Benzenetricarboxylic acid is usually produced by the liquid-phase catalytic oxidation of 1,2,4-trimethylbenzene with air. During the oxidation process, the solvent is acetic acid. 1,2,4-Benzenetricarboxylic acid and water are the main products. When the concentration of 1,2,4-benzenetricarboxylic acid in solution exceeds its solubility, it will crystallize.[1] Its solubility in aqueous acetic acid becomes a crucial factor in designing the reactive crystallization equipment as well as in controlling relevant operation conditions.

Although it is useful for the aforementioned reasons, very little data are available on the solubility of 1,2,4-benzenetricarboxylic acid in aqueous acetic acid solution. The solubility of 1,2,4-benzenetricarboxylic acid in aqueous acetic acid was measured by Tudorovskaya et al.,[2] but the paper is written in Russian and is difficult for common readers to understand. Furthermore, in the industrial 1,2,4-trimethylbenzene oxidation process, x_2, defined as the mole fraction of acetic acid in acetic acid + water solvent mixtures, ranges from about (0.40 to 1.00),[3] and only two groups of experimental data fell into the solvent range in the experiments of Tudorovskaya et al.[2] More experimental solubilities at x_2 = (0.40 to 1.00) are required for completeness. Apelblat measured the solubility of 1,2,4-benzenetricarboxylic acid in water and reviewed the literature-reported solubility for benzene polycarboxylic acids in water.[4]

In this work, the solubilities of 1,2,4-benzenetricarboxylic acid in acetic acid + water solvent mixtures were measured by an accurate and reliable procedure at the temperature range T = (313.2 to 363.2) K and x_2 = (0.416 to 1.000). The experimental data were correlated by the Apelblat equation,[4] and the model parameters were regressed. For completeness of discussion, the previously reported solubility of 1,2,4-benzenetricarboxylic acid in acetic acid + water solvent mixtures is also included in the analysis.

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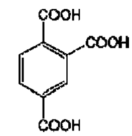

Figure 1. Molecular structure of 1,2,4-benzenetricarboxylic acid.

Experimental Section

Chemicals. A solid sample of 1,2,4-benzenetricarboxylic acid (mass fraction > 0.98) was supplied by Acros Organics (New Jersey, USA). High-performance liquid-phase chromatography (HPLC) grade methanol and acetonitrile from USA Tedia Company were used as the flow-phase in HPLC analysis. Deionized water was used throughout all the experiments. Glacial acetic acid, isopropyl benzene, and dimethyl sulfoxide of analytical grade were supplied by Hangzhou Chemical Reagent Co. All the chemicals were used as received without further purification.

Apparatus and Procedure. The experiments were carried out in a jacketed equilibrium glass bottle with a working volume of 100 mL. The bottle was sealed by a rubber stopper to prevent the evaporation of solvent and was put in a thermostatic water-circulator bath. The bath was continuously mechanically stirred, and the temperature was controlled within ± 0.2 K of the desired temperature with a thermoelectric controlling system. The uncertainty in the temperature measurements was estimated to be ± 0.2 K for all the experiments. The reliability of the experimental apparatus had been verified by the solubility measurements of benzoic acid and phthalic acid in aqueous acetic acid.[5]

Solubility Measurements. The solubility was measured by the static analytical method. For each experiment, an excess amount of 1,2,4-benzenetricarboxylic acid was added to (50 ± 3) mL of solvent. Then the equilibrium bottle was heated to a constant temperature. Different dissolution times were tested to determine a suitable equilibrium time. Attainment of solid–liquid equilibrium was verified by repetitive measurements during the following several hours until the results were reproducible within ± 3 %. It was found that 12 h was enough for 1,2,4-benzenetricarboxylic acid in aqueous acetic acid solution to reach equilibrium. At each temperature, the solution was kept isothermal for at least 24 h to ensure that the solution had been saturated. A 5 mL syringe was used to withdraw about 3 mL clear upper portion of the solution each time. The sampled

10.1021/je700452m CCC: $40.75
Published on Web 10/26/2007

solution was deposited into a test tube. The syringe was washed at least twice by dimethyl sulfoxide, and the washing solutions were also collected together in the test tube. Some of the solubility experiments were conducted two or three times to check the repeatability in this work, and the repeatability evaluated by mean relative deviation was less than 3 %.

Analytical Method. The concentration of 1,2,4-benzenetricarboxylic acid in the solution was determined by HPLC and gas chromatography (GC). The internal standard method was used in the analysis. The mass ratio of 1,2,4-benzenetricarboxylic acid to the internal standard substance in the solution was determined using a Shimadzu-6A HPLC. A Diamonsil C18 (250 mm × 4.6 mm) chromatographic column was used. Gradient elution was used for complete separation of the analytes at room temperature. The mobile phase consisted of three eluents (i.e., water + acetonitrile + methanol), and the following mass fraction of a three-component gradient elution program was adopted: from (0 to 3) min, 55 % water, 10 % methanol, and 35 % acetonitrile; from (3 to 9) min, the mixture mass fraction changed linearly with time to be 15 % water, 10 % methanol, and 75 % acetonitrile; from (9 to 12) min, the mixture mass fraction changed linearly with time to become 100 % acetonitrile. From 12 min on, pure acetonitrile was used. Each analysis took about 16 min.

The mass ratio of solvent acetic acid to the internal standard substance in the solution was determined by GC using a Kexiao GC-1690 with a hydrogen flame ionization detector. The SE-54 (30 m) capillary chromatographic column was used. Isopropyl benzene was used as the internal standard substance to correlate the data obtained from HPLC and GC analysis.

Assuming that in a solution the mass of 1,2,4-benzenetricarboxylic acid is m_1; the mass of isopropyl benzene is m_3; and the corresponding peak area of the chromatography response is $A_{\mathrm{HPLC},1}$ and $A_{\mathrm{HPLC},3}$ for HPLC analysis, one gets eq 1

$$\frac{m_1}{m_3} = K_{\mathrm{HPLC}}\frac{A_{\mathrm{HPLC},1}}{A_{\mathrm{HPLC},3}} \qquad (1)$$

Similarly, assuming that in the same solution the mass of solvent acetic acid is m_2 and the corresponding peak area for solvent acetic acid and the internal substance isopropyl benzene is $A_{\mathrm{GC},2}$ and $A_{\mathrm{GC},3}$ for GC analysis, one gets eq 2

$$\frac{m_2}{m_3} = K_{\mathrm{GC}}\frac{A_{\mathrm{GC},2}}{A_{\mathrm{GC},3}} \qquad (2)$$

where K_{HPLC} and K_{GC} stand for the instrument constant which must be experimentally determined. Thus, one can obtain the solubility of 1,2,4-benzenetricarboxylic acid in the acetic acid + water system by eqs 1 and 2 as

$$x_1 = \frac{\dfrac{m_1/m_3}{m_2/m_3}M_2x_2}{\dfrac{m_1/m_3}{m_2/m_3}M_2x_2 + M_1} \qquad (3)$$

where x_1 is the solubility of 1,2,4-benzenetricarboxylic acid, defined as the mole fraction of 1,2,4-benzenetricarboxylic acid in saturated 1,2,4-benzenetricarboxylic acid (1) + acetic acid (2) + water (3) solutions. x_2 is the mole fraction of acetic acid in the solvent mixtures, and M_1 and M_2 are the mole masses of 1,2,4-benzenetricarboxylic acid and acetic acid.

To verify the reliability and reproducibility of the analysis method, 20 1,2,4-benzenetricarboxylic acid + acetic acid + water solutions of known concentration were analyzed. Compared with the uncertainty of the known concentration, the uncertainty was less than 3 %. To check the repeatability, the 20 solutions were measured at least five times, and the repeatability was evaluated with a mean relative deviation of less than 4 %.

Table 1. Experimental Solubilities of 1,2,4-Benzenetricarboxylic Acid (1) in Acetic Acid (2) + Water (3) Solvent Mixtures at the Temperature Range from (313.2 to 363.2) K

T/K	10^2x_1
$x_2 = 1.000$	
313.2	0.168 ± 0.005
323.2	0.311 ± 0.009
333.2	0.480 ± 0.014
343.2	0.676 ± 0.020
353.2	0.870 ± 0.026
363.2	1.060 ± 0.032
$x_2 = 0.730$	
313.2	0.541 ± 0.016
323.2	0.689 ± 0.021
333.2	0.870 ± 0.026
343.2	1.087 ± 0.033
353.2	1.295 ± 0.039
363.2	1.472 ± 0.045
$x_2 = 0.527$	
313.2	0.795 ± 0.024
323.2	0.981 ± 0.030
333.2	1.157 ± 0.035
343.2	1.354 ± 0.041
353.2	1.533 ± 0.047
363.2	1.846 ± 0.056
$x_2 = 0.416$	
313.2	0.879 ± 0.027
323.2	1.055 ± 0.032
333.2	1.252 ± 0.038
343.2	1.431 ± 0.044
353.2	1.666 ± 0.051
363.2	2.012 ± 0.062

Results and Discussion

Experimental Results. The measured solubilities of 1,2,4-benzenetricarboxylic acid in acetic acid + water solutions as a function of temperature are summarized in Table 1, where the associated uncertainties were estimated as twice the standard deviation of the mean of the at least two measurements performed. The measured solubility data of 1,2,4-benzenetricarboxylic acid in acetic acid + water solutions are compared with reported solubilities determined by Tudorovskaya et al.[2] in Figure 2. From Figure 2, it can be seen that the solubility data reported in this work are in agreement with the data from the literature, and the biggest relative deviation calculated between the solubility of the literature and the measured solubility of this work is less than 10 %. From Table 1, it can be seen that within the temperature range of the measurements the solubilities of 1,2,4-benzenetricarboxylic acid in all the mixtures increase as the temperature increases. The solubility of 1,2,4-benzenetricarboxylic acid in pure acetic acid is the lowest, and it increases with an increasing mass fraction of water in the mixed acetic acid + water at constant temperature.

Correlation. The temperature dependence solubility of nonhydrated nonelectrolytes in aqueous solutions is expressed by the Williamson equation.[6]

$$\frac{\partial \ln(m/m_0)}{\partial(1/T)}f = -\frac{\Delta_{\mathrm{sol}}H_{\mathrm{m}}}{R}, f = \left(1 + \frac{\partial \ln \gamma}{\partial(m/m_0)}\right)_T \qquad (4)$$

where $\Delta_{\mathrm{sol}}H_{\mathrm{m}}$ is the mole enthalpy of solution; R is the gas constant; γ is the activity coefficient of solute; and $m_0 = 1$

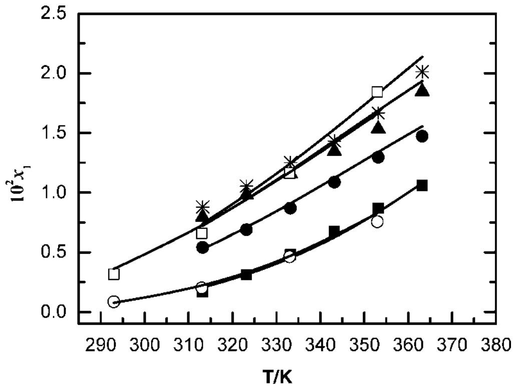

Figure 2. Solubility, x_1, defined as the mole fraction of 1,2,4-benzenetricarboxylic acid in saturated 1,2,4-benzenetricarboxylic acid (1) + acetic acid (2) + water (3) solution. Scatter: *, this work, $x_2 = 0.416$; ▲, this work, $x_2 = 0.527$; •, this work, $x_2 = 0.730$; ■, this work, $x_2 = 1.000$; □, ref 2, $x_2 = 0.546$; ○, ref 2, $x_2 = 1.000$. Line: model correlated solubility.

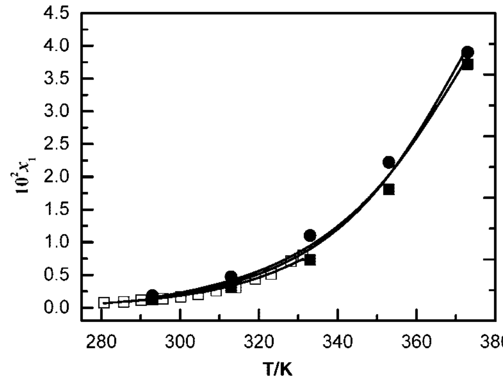

Figure 3. Comparison of literature reported and correlation equation calculated solubility of 1,2,4-benzenetricarboxylic acid in saturated 1,2,4-benzenetricarboxylic acid (1) + acetic acid (2) + water (3) solution. Scatter: •, ref 2, $x_2 = 0.032$; ■, ref 2, $x_2 = 0.000$; □, ref 4, $x_2 = 0.000$. Line: model correlated solubility of this work.

Table 2. Parameters in the Apelblat Equation for the Solubility of 1,2,4-Benzenetricarboxylic Acid in Acetic Acid + Water Solvent Mixtures

	A_i	B_i	C_i
0	–74.56	–384.96	13.00
1	743.46	–28944.00	–112.66
2	–524.96	18961.00	80.10

$mol \cdot kg^{-1}$. In eq 4, it is assumed that the dissociation of 1,2,4-benzenetricarboxylic acid at the saturation point is small, and they can be treated as nonelectrolytes.[4] As the change of activity coefficients with m near the saturation point is unknown, the factor f can be replaced by unity and the enthalpy of solution becomes the apparent mole enthalpy of solution.[4] If it is assumed that the enthalpy of solution depends linearly on the temperature, the integral form of eq 4 is

$$\ln(m/m_0) = A + \frac{B}{T} + C \ln T \qquad (5)$$

which is the famous Apelblat equation and has been used to correlate the solubilities of benzene polycarboxylic acid in aqueous acetic acid successfully.[4,7] In this work, to correlate the solubility of 1,2,4-benzenetricarboxylic acid (1) in acetic acid (2) + water (3) solvent mixtures, we use the semi-empirical Apelblat equation (eq 5) in the following form

$$\ln x_1 = A + \frac{B}{T} + C \ln T \qquad (6)$$

To correlate the solubility of 1,2,4-benzenetricarboxylic acid in aqueous acetic acid solutions, the following empirical correlations were adopted

$$\begin{aligned} A &= A_0 + A_1 x_2 + A_2 x_2^2 \\ B &= B_0 + B_1 x_2 + B_2 x_2^2 \\ C &= C_0 + C_1 x_2 + C_2 x_2^2 \end{aligned} \qquad (7)$$

where A_i, B_i, and C_i are model parameters.

To illustrate the agreement between the experimental and model correlated solubilities, they are plotted in Figure 2. It can be seen that the correlated values agree with the experimental results. The results show that the Apelblat equation can be used to correlate the solubility of 1,2,4-benzenetricarboxylic acid in acetic acid + water solution. The optimized model parameters of 1,2,4-benzenetricarboxylic acid in acetic acid + water solvent mixtures are listed in Table 2.

Model Verification. To verify whether the Apelblat equation and above empirical admixture rule could be used as a suitable method to calculate the solubility of 1,2,4-benzenetricarboxylic acid in the acetic acid + water system, the solubility of 1,2,4-benzenetricarboxylic acid in acetic acid (2) + water (3) at $x_2 =$ 0 and 0.032 was calculated. The calculated results are shown in Figure 3. For comparison, the reported solubility of 1,2,4-benzenetricarboxylic acid in water measured by Tudorovskaya et al.[2] and Apelblat et al.[4] is also shown in Figure 2. It shows that the calculated results agree well with the literature data. The experimental solubility and correlation equation in this work can be used for the synthetic process of 1,2,4-benzenetricarboxylic acid.

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Received for review August 09, 2007. Accepted October 02, 2007. This project was granted financial support from the China Postdoctoral Science Foundation (20060101044).

JE700452M