Solubilities of Benzoic Acid and Phthalic Acid in Acetic Acid + Water Solvent Mixtures

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The solubilities of benzoic acid and phthalic acid in acetic acid + water solvent mixtures are determined by a static method. The experimental temperature ranges from (298.3 to 367.9) K, and the mass fraction of acetic acid in the solvent mixtures ranges from 0.8 to 1.0. The experimental results show that, within the temperature range of the measurements, the solubility of benzoic acid and phthalic acid in all the mixtures shows an increasing trend as the temperature increases. The solubility of benzoic acid decreases with increasing mass fraction of water. For the solubility of phthalic acid in acetic acid + water within the solvent composition range of the measurements, below 325.2 K, the higher the mass fraction of water, the less the solubility. However, above 325.2 K the higher the mass fraction of water, the greater the solubility. A simple explanation was given for this "maximum-solubility effect". The experimental data was correlated by the Non-Random Two Liquids (NRTL) activity coefficient model, and the model parameters were regressed.

Introduction

Currently, polymerization-grade terephthalic acid is one of the main feedstocks for product polyester. After being oxidized by air in an oxidation reactor, *p*-xylene is conversed into terephthalic acid, which is called crude terephthalic acid. During the oxidation process, acetic acid is the solvent. Water and terephthalic acid are the main products. Sequentially, crude terephthalic acid must be purified from the mixture of acetic acid and water to produce polymerization-grade terephthalic acid.[1]

The impurities present in crude terephthalic acid are generally intermediates and oxidation byproducts, which are difficult to remove. There are two ways to improve the purity of terephthalic acid. One way is to control the reactive crystallization process in the oxidation reactor carefully to decrease the incorporation rate of impurities into terephthalic acid. The other way is to improve the subsequent purification process. Usually, crystallization and co-crystallization is used. Solubilities of terephthalic acid and the impurities in aqueous acetic acid become a crucial factor in designing the oxidation and separation equipment, as well as in controlling relevant operation conditions.[1]

The impurities present in crude terephthlic acid particles mainly include *p*-toluic acid, benzoic acid, phthalic acid, isophthalic acid, and 4-carboxybenzaldehyde.[1] There are some reports on the solubility of terephthalic acid,[2−4] *p*-toluic acid,[5] isophthalic acid,[6] and 4-carboxybenzaldehyde[5] in aqueous acetic acid. Some reports on the solubility of benzoic acid and phthalic acid in pure acetic acid or in pure water;[7−10] however, no reports on the solubility of benzoic acid and phthalic acid in aqueous acetic acid are available.

Furthermore, similar to terephthalic acid, benzoic acid, and phthalic acid can also be produced by the liquid-phase air oxidation of toluene and *o*-xylene in acetic acid. The solubilities of benzoic and phthalic acids in aqueous acetic acid are also essential for the control and design of the two oxidation process.[11] In this work, the solubilities of phthalic acid and benzoic acid in acetic acid + water solutions in the temperature range from (298.3 to 367.9) K are determined. The experimental solubility data are correlated by a suitable activity coefficient model. The Non-Radom Two Liquids (NRTL) activity coefficient model have relative higher fitting and prediction accuracy. Furthermore, only two-component parameters are needed in predicting the activity coefficient of multicomponent systems.[12] In the following data correlation, NRTL activity coefficient model is used.

Experimental Section

Materials. Solid samples of benzoic acid (mass fraction > 0.990) and phthalic acid (mass fraction > 0.985) were obtained from Shanghai Fine Chemical Reagent Company. Demineralized water and analytical-grade acetic acid (density of 1.045 g·cm^{-3}, refractive index of 1.3700, both at 298.15 K) were obtained from Hangzhou Chemical Reagent Co.

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 is continuously mechanically stirred, and the temperature was controlled within ± 0.1 K of the desired temperature with a thermoelectric controlling system. The uncertainty in the temperature measurements was estimated to be ± 0.1 K for all the experiments.

Solubility Measurements. The solubilities were measured by the static analytical method. For each experiment, an excess amount of benzoic acid or phthalic acid was added to 80 ± 5 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

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Table 1. Solubilities of Benzoic Acid (1) in Binary Acetic Acid (2) + Water (3) Solvent Mixtures at the Temperature Range from (298.3 to 358.6) K

T/K	S/g·(100 g)$^{-1}$)	S_c/(g·(100 g)$^{-1}$)	RD/%	T/K	S/(g·(100 g)$^{-1}$)	S_c/(g·(100 g)$^{-1}$)	RD/%
$w_2 = 1.00$							
298.3	25.06 ± 0.94	24.58	−1.92	338.0	53.15 ± 2.04	52.11	−1.96
308.4	30.68 ± 0.57	30.96	0.91	348.3	59.88 ± 1.36	59.19	−1.15
318.3	38.05 ± 0.22	37.94	−0.29	358.6	69.76 ± 2.65	68.41	−1.94
328.2	44.68 ± 1.07	45.21	1.19				
$w_2 = 0.95$							
298.3	25.09 ± 0.98	24.59	−1.99	338.0	49.06 ± 1.86	48.11	−1.94
308.4	30.35 ± 0.08	30.31	−0.13	348.3	53.64 ± 1.58	54.42	1.45
318.3	36.22 ± 0.18	36.31	0.25	358.6	62.16 ± 0.08	62.12	−0.06
328.2	41.54 ± 1.69	42.37	2.00				
$w_2 = 0.85$							
298.3	23.15 ± 0.02	23.16	0.04	338.0	40.75 ± 1.01	40.24	−1.25
308.4	27.88 ± 0.69	27.53	−1.28	348.3	45.03 ± 0.18	44.94	−0.20
318.3	31.73 ± 0.44	31.95	0.69	358.6	50.48 ± 2.04	51.48	1.98
328.2	36.16 ± 0.10	36.21	0.14				
$w_2 = 0.80$							
298.3	22.02 ± 0.02	22.01	−0.05	338.0	36.55 ± 0.04	36.53	−0.05
308.4	25.29 ± 1.02	25.79	1.98	348.3	40.43 ± 0.16	40.51	0.20
318.3	29.94 ± 0.98	29.44	−1.67	358.6	45.17 ± 1.52	45.92	1.66
328.2	33.54 ± 1.14	32.96	−1.73				

Table 2. Solubilities of Phthalic Acid (1) in Binary Acetic Acid(2) + Water (3) Solvent Mixtures at the Temperature Range from (298.3 to 367.9) K

T/K	S/(g·(100 g)$^{-1}$)	S_c/(g·(100 g)$^{-1}$)	RD/%	T/K	S/(g·(100 g)$^{-1}$)	S_c/(g·(100 g)$^{-1}$)	RD/%
$w_2 = 1.0$							
298.3	2.96 ± 0.10	2.91	−1.69	338.0	12.04 ± 0.45	11.81	−1.91
308.4	4.22 ± 0.16	4.30	1.90	348.3	16.33 ± 0.51	16.07	−1.59
318.3	6.29 ± 0.24	6.17	−1.91	358.6	21.53 ± 0.44	21.75	1.02
328.2	8.78 ± 0.33	8.61	−1.94	367.9	27.52 ± 1.10	28.06	1.96
$w_2 = 0.95$							
298.3	2.85 ± 0.08	2.81	−1.40	338.0	13.62 ± 0.41	13.82	1.47
308.4	4.36 ± 0.16	4.44	1.83	348.3	19.72 ± 0.69	19.37	−1.77
318.3	6.82 ± 0.22	6.71	−1.61	358.6	26.24 ± 1.04	26.75	1.94
328.2	9.57 ± 0.37	9.75	1.88	367.9	33.46 ± 1.28	34.09	1.88
$w_2 = 0.90$							
298.3	2.63 ± 0.10	2.58	−1.90	338.0	15.13 ± 0.18	15.04	−0.59
308.4	4.23 ± 0.16	4.33	1.89	348.3	22.32 ± 0.84	21.89	−1.93
318.3	6.94 ± 0.20	6.84	−1.44	358.6	30.03 ± 0.52	29.77	−0.87
328.2	10.59 ± 0.39	10.39	−1.89	367.9	37.87 ± 1.49	38.60	1.93
$w_2 = 0.85$							
298.3	2.26 ± 0.08	2.30	1.77	338.0	16.06 ± 0.63	15.74	−1.99
308.4	3.98 ± 0.14	4.05	1.76	348.3	23.14 ± 0.12	23.08	−0.26
318.3	6.61 ± 0.12	6.67	0.91	358.6	32.15 ± 0.42	32.36	0.65
328.2	10.70 ± 0.41	10.49	−1.96	367.9	41.58 ± 1.63	42.38	1.92
$w_2 = 0.80$							
298.3	1.99 ± 0.04	2.01	1.01	338.0	16.39 ± 0.57	16.10	−1.77
308.4	3.74 ± 0.08	3.70	−1.07	348.3	23.73 ± 0.42	23.94	0.88
318.3	6.49 ± 0.25	6.36	−2.00	358.6	35.04 ± 0.95	34.56	−1.37
328.2	10.60 ± 0.41	10.39	−1.98	367.9	44.78 ± 1.55	45.54	1.70

Table 3. Molar Fusion Enthalpy and Fusion Temperature of Benzoic Acid and Phthalic Anhydride

compound	$\Delta_{fus}H_i$/(kJ·mol^{-1}·K^{-1})	$T_{fus,i}$/K
benzoic acid	17.317	395.6
phthalic acid	55.497[a]	481.2

[a] Estimated by eq 8.

during the following several hours until the results were reproducible with ± 3 %. It was found that 9 h was enough for benzoic acid and phthalic acid in aqueous acetic acid 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 10 mL syringe previously weighed (m_1) was used to withdraw the clear upper portion of the solution and then weighed again (m_2) to determine the mass of the sample ($m_2 - m_1$). The sampled solution was deposited to a weighed vial (m_3), and the syringe wall was washed by acetic acid for at least four times to remove the crystallized solute to the vial. Then the vial was placed in vacuo at 50 °C for more than 3 h for drying. 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 reweighed (m_4) to determine the mass of the constant residue solid ($m_4 - m_3$). An analytical balance with uncertainty of ± 0.1 mg was used during the mass measurements. In this work, the solubility was defined as the mass of solute in 100 g of solvent when the solution was saturated. Thus, the solubility of solute in aqueous acetic acid could be determined from eq 1:

$$S = \frac{m_4 - m_3}{(m_2 - m_1) - (m_4 - m_3)} \times 100 \qquad (1)$$

An averaged value is taken from at least four measurements at the same composition of solvent for each temperature. The

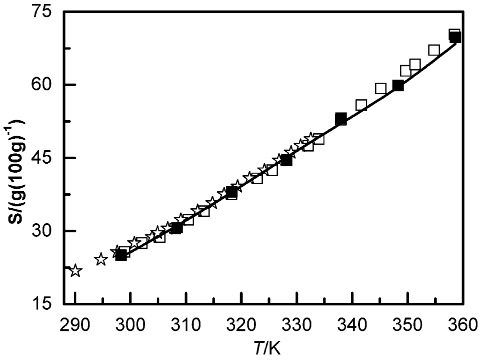

Figure 1. Determined solubilities and literature data of benzoic acid in pure acetic acid (2): ■, experimental data ($w_2 = 1.0$); □, literature data ($w_2 = 1.0$) from Liu;[8] ☆, literature data ($w_2 = 1.0$) from Ma;[7] —, solubility curve calculated from NRTL model eqs 2 to 8.

estimated associated uncertainty of the measured solubility values based on error analysis and repeated observations was within 4 %.

Results and Discussion

Solubility of Benzoic Acid. The solubility data of benzoic acid in acetic acid + water solutions are summarized in Table 1, while the associated uncertainties were estimated as twice the standard deviation of the mean of the at least four measurements performed. The measured solubility data of benzoic acid in acetic acid are compared with the literature data in Figure 1. From Figure 1, it can be seen that the solubility data of benzoic acid in acetic acid reported in this work are in agreement with the data from the literature and that the biggest relative deviation calculated between the solubility of the literature and the measured solubility of this work is less than 2 %. From Table 1, it can be seen that within the temperature range of the measurements, the solubility of benzoic acid in all of the mixtures shows an increasing trend as the temperature increases. The solubility of benzoic acid in pure acetic acid shows the highest, and it decreases with an increasing concentration of water in the mixed acetic acid + water at constant temperature.

Solubility of Phthalic Acid. The solubility data of phthalic acid in acetic acid + water are summarized in Table 2, where the associated uncertainties were estimated as twice the standard deviation of the mean of at least four measurements. By comparison of all the solubilities of phthalic acid in aqueous acetic acid with those in pure acetic acid, an interesting result comes up as shown in Figure 2. Below 325.2 K, acetic acid with mass fraction of 100 % has the best dissolving capacity for phthalic acid within the solvent composition range of the measurements. It indicates that the higher the mass fraction of water, the less the solubility.

However, at approximately 325.2 K or above, acetic acid of 80 % mass fraction is the best solvent for phthalic acid. It indicates that above 325.2 K the more water contained in the solvents, the greater the solubility obtained. In other words, within this temperature range, there is a slope presenting the change of solubility influenced by solvent concentrations at a certain temperature. This is called “maximum-solubility effect” predicted by the Scatchard−Hildebrand theory. The theory suggests that, when a solid solute is dissolved in a mixture of two carefully selected solvents, a plot of solubility versus (solute-free) solvent composition should go through a maximum. Chen and Ma also verified its authenticity by experimentally measuring the solubility of terephthalic acid in the mixture of acetic acid and water.[2]

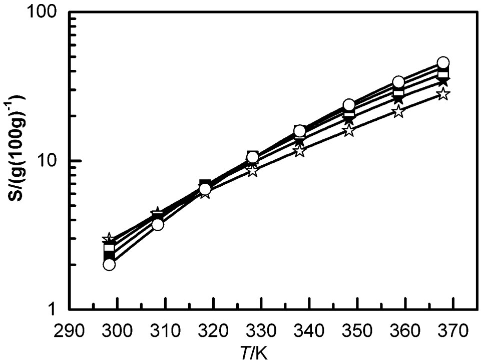

Figure 2. Experimentally determined solubilities of phthalic acid (1) in acetic acid (2) + water (3): ○, $w_2 = 0.80$; ■, $w_2 = 0.85$; □, $w_2 = 0.90$; ★, $w_2 = 0.95$; ☆, $w_2 = 1.0$; —, solubility curve calculated from NRTL model eqs 2 to 8.

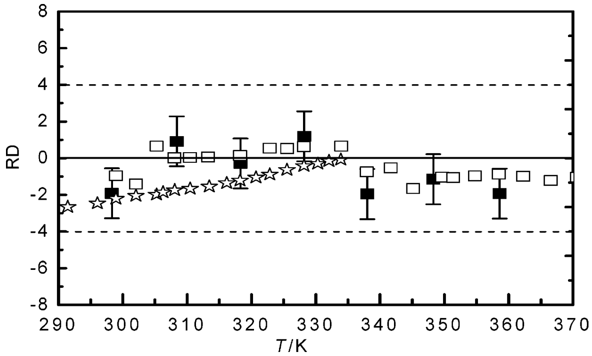

Figure 3. Relative deviations of the experimental solubilities of benzoic acid in pure acetic acid (2) with the correlation results by eqs 2 to 8 as a function of temperature *T*. ■, this work ($w_2 = 1.0$), with error bars representing the expanded uncertainty, estimated with the error analysis and repeated observations; □, ref 8; ☆, ref 7; and - - -, uncertainty of the measurements.

Correlation of Experimental Data. Generally, solid−liquid equilibrium can be approximated by an equation that involves the properties of pure solute, such as enthalpy of fusion, melting point, etc.:[7]

$$\ln(\gamma_1 x_1) = -\frac{\Delta_{\text{fus}}H}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{fus}}}\right) - \frac{\Delta_{\text{trs}}H}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{trs}}}\right) \tag{2}$$

If a solid−solid phase transition does not occur, the last term can be neglected; therefore, the equation becomes

$$\ln(\gamma_1 x_1) = -\frac{\Delta_{\text{fus}}H}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{fus}}}\right) \tag{3}$$

In eqs 2 and 3, $\Delta_{\text{fus}}H$ is the molar enthalpy of fusion of solute, T_{fus} is the fusion temperature, $\Delta_{\text{trs}}H$ is the molar enthalpy of solid−solid phase transition, T_{trs} is the transition temperature, T is the absolute temperature, R is the universal gas constant, γ_1 is the activity coefficient of solute, and x_1 is the real mole fraction of solute in solution, which can be calculated from the solubility S by

$$x_1 = \frac{S/M_1}{100\, w/M_2 + 100(1 - w)/M_3 + S/M_1} \tag{4}$$

In eq 4, S is the solubility defined by eq 1; w is the mass fraction of acetic acid in binary acetic acid + water solvent mixtures; M_1, M_2, and M_3 are the molar weight of solute, acetic acid, and

Table 4. NRTL Model Parameters in Equation 6 for Benzoic Acid + Acetic Acid + Water and Phthalic Acid + Acetic Acid +Water

i	j	a_{ij}	a_{ji}	b_{ij}	b_{ji}	$\eta_{ij} = \eta_{ji}$
benzoic acid	acetic acid	−5.2526	37.955	2.7098×10^3	-1.5272×10^4	0.3
benzoic acid	water	−26.933	49.342	1.1486×10^4	-1.7649×10^4	
acetic acid	water	−1.9763	3.3293	6.0989×10^2	-7.2389×10^2	
phthalic acid	acetic acid	−1.0710	3.4546	-3.9196×10^2	-3.5745×10^2	
phthalic acid	water	−2.1704	−2.7038	4.8820×10^2	1.2828×10^3	
ARD/%		1.35				

water. Because the activity coefficient depends on the mole fraction and temperature, eq 3 must be solved iteratively. For the definition of the activity coefficient, the NRTL activity coefficient model was used as

$$\ln \gamma_1 = \frac{\sum_{j=1}^{3} \tau_{j1} G_{j1} x_j}{\sum_{k=1}^{3} G_{k1} x_k} + \sum_{j=1}^{3} \frac{x_j G_{1j}}{\sum_{k=1}^{3} G_{kj} x_k} \left[\tau_{1j} - \frac{\sum_{k=1}^{3} x_k \tau_{kj} G_{kj}}{\sum_{k=1}^{3} G_{kj} x_k} \right] \quad (5)$$

In eq 5, τ_{ij} and G_{ij} are NRTL model parameters that need to be experimentally determined by

$$G_{ij} = \exp(-\eta_{ij}\tau_{ij}), \quad \tau_{ij} = a_{ij} + b_{ij}/T, \quad \eta_{ij} = \eta_{ji}, \quad \tau_{ij} \neq \tau_{ji}, \quad \tau_{ii} = 0 \quad (6)$$

To calculate the solubility, fusing temperature (T_{fus}) and molar enthalpy of fusion of solute ($\Delta_{\text{fus}}H$) are required. For benzoic acid, T_{fus} and $\Delta_{\text{fus}}H$ can be obtained from the literature.[7] For phthalic acid, only T_{fus} can be obtained from the literature,[13] while $\Delta_{\text{fus}}H$ is unavailable and must be estimated. The enthalpy of fusion $\Delta_{\text{fus}}H$ is defined as the difference of the enthalpies of a unit mole of a solid and liquid at its melting temperature and one atmosphere pressure of a pure component. There are no generally applicable estimation techniques that are very accurate. However, if the melting temperature is known, the atomic group contribution method of Chickos et al. yields approximate results:[14,15]

$$\Delta_{\text{fus}}H = T_{\text{fus}}\Delta_{\text{fus}}S \quad (7)$$

where $\Delta_{\text{fus}}S$ is the entropy of fusion at the melting temperature and is only related to the properties of the solute.[14,15] On the basis of eq 7, we choose the following empirical equation to do the estimation:[7]

$$\Delta_{\text{fus}}H = KT_{\text{fus}} \quad (8)$$

where K is an empirical parameter related to the properties of the solute. The optimum algorithm was used to determine the optimum value of K for phthalic acid. Table 3 gives the pure solutes' properties.

Using model eqs 2 to 8, the solubilities of benzoic acid and phthalic acid in acetic acid + water solvent mixtures were correlated, and the model parameters were optimized. In the optimization process, as Renon and Prausnitz proposed, η_{ij} was chosen as 0.3.[12] Table 4 shows the optimized NRTL model parameters in eq 6. The optimum algorithm applied in the parameter estimation program was the Nelder−Mead Simplex approach.[16] A simplex is a geometrical figure formed by $r + 1$ points in an r-dimensional space. In two-dimensional space, a simplex is a triangle, and in three-dimensional space, it is a pyramid. The algorithm is based on evaluating the objective function at the vertexes of a simplex, finding the worst vertex of the simplex, forming its symmetrical image through the center of the opposite face, and generating a new simplex based on the new vertex. This shrinks the volume of the simplex if the newly found point is better than the older point. This step is repeated until the volume of the simplex is smaller than some user-defined preset value. Any commercially available software may be used for this purpose. Function *fminsearch* in the optimization toolbox of Matlab (Mathwork, MA) uses the Nelder−Mead Simplex approach and can be employed for the minimization of the objective function, which is the averaged relative deviation (ARD) between the experimental and calculated solubility defined by

$$\text{ARD} = \frac{1}{n} \sum_{i=1}^{n} \text{abs}(\text{RD}_i), \quad \text{RD}_i = \frac{S_{\text{c}i} - S_i}{S_i} \times 100 \quad (9)$$

where S_{c} is the solubility calculated by eqs 2 to 8, and n is the number of experimental points. The calculated solubility and the relative deviation (RD) between the experimental and correlated values of benzoic acid and phthalic acid are also given in Table 1, Table 2, Figure 1, and Figure 2. The RDs of the experimental solubilities of benzoic acid in pure acetic acid with the correlation results by eqs 2 to 8 as a function of temperature T are shown in Figure 3, which shows that relative deviations in this work are in agreement with the data from the literatures. These results show that the NRTL activity coefficient model equations can be used to correlate the solubility of benzoic acid and phthalic acid in acetic acid + water solution. The experimental solubility and correlation equation in this work can be used as essential data and models for the synthetic and purification process of terephthalic acid, benzoic acid, and phthalic acid.

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