Solubilities of 4-Formylbenzoic Acid in Ethanoic Acid, Water, and Ethanoic Acid/Water Mixtures with Different Compositions from (303.2 to 473.2) K†

Weizhen Sun, Wanbing Qu, and Ling Zhao*

State-Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

The solid−liquid equilibrium data of 4-formylbenzoic acid in four solvents was measured by the steady-state method at temperatures ranging from (303.2 to 473.2) K, including ethanoic acid, water, and aqueous ethanoic acid with 0.8 and 0.9 mass fractions of ethanoic acid, respectively. The solubility model modified from the Apelblat equation was used to correlate the experimental data. The average relative deviations of these correlations are 0.06 and 0.04 for solubilities in ethanoic acid and water at temperatures above 403.2 K, respectively, and no more than 0.03 for those in aqueous ethanoic acid.

Introduction

As one of the main feed stocks to produce polyester, polymerization grade terephthalic acid (TPA) has become an important and fast-growing chemical. Presently, the vast majority of the commercial production of TPA is implemented by the liquid-phase oxidation of 1,4-dimethylbenzene (*p*-xylene, PX) in aqueous ethanoic acid at temperatures ranging from (430 to 470) K. Although the yield of TPA in PX oxidation is more than 0.96, there are still small amounts of impurities remaining in TPA, which would cause negative effects on polyester production. Particularly, 4-formylbenzoic acid is regarded as the major impurity, because compared with other impurities it is hard to eliminate, due to its similarity to TPA in molecular structure. The concentration of 4-formylbenzoic acid in solid TPA is expected to be as low as possible by PX oxidation and subsequent crystallization steps in aqueous ethanoic acid. So, the solubility data of 4-formylbenzoic acid in aqueous ethanoic acid are fundamental to the design and optimization of the PX oxidation reactor and subsequent crystallizers.

The solubility of 4-formylbenzoic acid in ethanoic acid and/or water was investigated at the temperatures from (293.15 to 370.65) K by Li et al.[1] and from (288.95 to 329.95) K by Chen and Ma.[2] Unfortunately, these solubility data are far from industrial conditions. In this work, we report the solubilities of 4-formylbenzoic acid in four solvents at temperatures ranging from (303.2 to 473.2) K, including ethanoic acid, water, and aqueous ethanoic acid with different compositions. Besides, these solubility data are correlated by the solubility model modified from the Apelblat equation.[3,4]

Experimental Procedure

Ethanoic acid (CAS No. 64-19-7) with a mass fraction purity of 0.995 was purchased from Shanghai Chemical Reagent Company. 4-Formylbenzoic acid (CAS No. 619-66-9) had a mass fraction purity of 0.98, which was purchased from Alfa Aesar Company. Water used in the experiment was distilled twice. All of the chemicals are accurately weighed by the electrical balance with a precision of 0.0001 g.

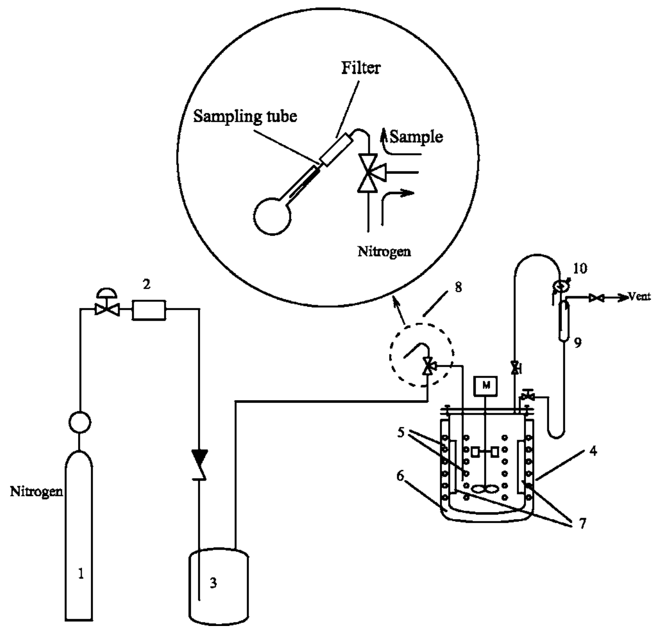

Figure 1. Schematic diagram of experimental setup: 1, cylinder; 2, flow controller; 3, ethanoic acid tank; 4, solubility measurement vessel; 5, cooling coil; 6, oil-bath; 7, baffle; 8, sampler; 9, reflux splitter; 10, condenser.

Solubilities of 4-formylbenzoic acid in four solvents were measured by the steady-state method, a frequently used method for solubility determination.[1,5] The experimental setup is shown in Figure 1. Before each experimental run was performed, solvent and excess solute were weighed and then put into the jacketed vessel made of titanium to resist the corrosion of ethanoic acid. The temperature was monitored by a thermocouple with an uncertainty of ± 0.1 K and controlled by a computer. Continuous stirring was carried out until the desired temperature was reached. The pre-experiments showed that when the temperature reached to 473.2 K at the rise rate of less than 0.5 K·min^{-1} the concentration of 4-formylbenzoic acid in liquid-phase solution would become constant within 90 min, which indicated that the solid−liquid equilibrium was attained.[6] Then, after another 90 min, the solution would become homogeneous, and all of the suspended particles deposit on the

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* To whom correspondence should be addressed. E-mail: zhaoling@ecust.edu.cn. Fax: +86-21-64253528.

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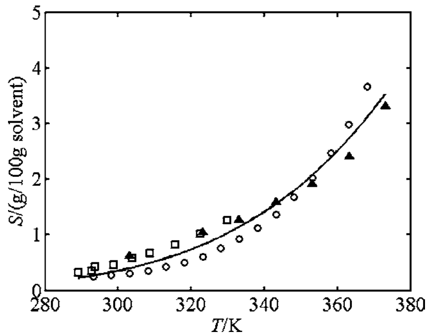

Figure 2. Solubility of 4-formylbenzoic acid in ethanoic acid at lower temperatures: ▲, this work; □, Chen and Ma;[2] ○, Li et al.;[1] —, calculated from eq 6.

bottom, which was verified by sediment experiments carried out in a visual glass container at ambient temperature.

Before taking a sample, N_2 was introduced to purge the tube that connects the solution. Then the valve was switched to the sampling position, and about 10 mL solution was guided to a volumetric flask via a sampling tube connected to the filter. To avoid the loss of solvents by vaporization during sampling, the flask was quickly cooled to ambient temperature by cooling water. After the sampling, the volumetric flask and the sampling tube were weighed together to determine the weight of the sample. Then the sampling tube was washed by dimethyl sulfoxide (DMSO) to collect any residue in the sampling tube into the flask. The detailed descriptions concerning the experimental setup and sampling can be seen in literature.[7,8] A high-performance liquid chromatograph (HPLC) with an ion-exchange column was used to determine the solubility of 4-formylbenzoic acid.[9] Each experimental point was repeated at least twice to check the repeatability of solubility data. In this work, the estimated uncertainty of experimental solubility is 0.03 g of 4-formylbenzoic acid per 100 g of solvent.

Results and Discussion

The experimental solubilities of 4-formylbenzoic acid in ethanoic acid at lower temperatures is shown in Figure 2, as well as the data reported by other researchers.[1,2] It can be seen that the solubilities presented in this work have small discrepancy with those measured by Li et al.[1] but have a good agreement with Chen and Ma's results.[2] The solubilities of 4-formylbenzoic acid in different solvents are presented in Tables 1 to 4.

At constant pressure, eq 1 was recommended by Apelblat and Manzurola[3] and Wang et al.[4] to be used to correlate the solubility of solid solute in liquid solution.

$$\frac{\partial \ln(m/\mathrm{mol\cdot kg^{-1}})}{\partial \ln(1/(T/\mathrm{K}))} = \frac{-\Delta_{\mathrm{sol}}H_{\mathrm{m}}/\mathrm{J\cdot mol^{-1}}}{R\cdot\left(1 + \dfrac{\partial \ln \gamma}{\partial \ln(m/\mathrm{mol\cdot kg^{-1}})}\right)\cdot(T/\mathrm{K})} \quad (1)$$

where m and γ are the molality of solute and its activity coefficient at saturation point, respectively, $\Delta_{\mathrm{sol}}H_{\mathrm{m}}$ stands for the molar enthalpy of solution, and R is the gas constant. Since activity coefficients γ in the investigated systems are unknown, it is possible to determine only the apparent enthalpies of solution by neglecting the activity coefficient term in eq 1. So, eq 1 can be simplified to the following equation:

Table 1. Solubilities of 4-Formylbenzoic Acid in Ethanoic Acid

T/K	S/g·(100 g)$^{-1}$	S_c/g·(100 g)$^{-1}$	100·RD	T/K	S/g·(100 g)$^{-1}$	S_c/g·(100 g)$^{-1}$	100·RD
303.2	0.625	0.529	15.4	403.2	4.118	4.176	1.4
323.2	1.049	0.885	15.6	423.2	5.270	5.616	6.6
333.2	1.276	1.119	12.3	433.2	5.980	6.446	7.8
343.2	1.591	1.396	12.3	443.2	6.487	7.353	13.3
353.2	1.927	1.720	10.7	453.2	7.964	8.339	4.7
363.2	2.405	2.094	12.9	463.2	9.344	9.405	0.7
373.2	3.322	2.524	24.0	473.2	11.653	10.555	9.4

Table 2. Solubilities of 4-Formylbenzoic Acid in Aqueous Ethanoic Acid with the Mass Fraction of Ethanoic Acid w = 0.9

T/K	S/g·(100 g)$^{-1}$	S_c/g·(100 g)$^{-1}$	100·RD	T/K	S/g·(100 g)$^{-1}$	S_c/g·(100 g)$^{-1}$	100·RD
423.2	4.801	4.735	1.4	453.2	5.525	5.547	0.4
433.2	4.983	5.004	0.4	463.2	5.799	5.821	0.4
443.2	5.222	5.275	1.0	473.2	6.149	6.096	0.9

Table 3. Solubilities of 4-Formylbenzoic Acid in Aqueous Ethanoic Acid with the Mass Fraction of Ethanoic Acid w = 0.8

T/K	S/g·(100 g)$^{-1}$	S_c/g·(100 g)$^{-1}$	100·RD	T/K	S/g·(100 g)$^{-1}$	S_c/g·(100 g)$^{-1}$	100·RD
423.2	4.566	4.380	4.1	453.2	4.827	5.045	4.5
433.2	4.622	4.602	0.4	463.2	5.096	5.267	3.4
443.2	4.710	4.823	2.4	473.2	5.786	5.488	5.2

Table 4. Solubilities of 4-Formylbenzoic Acid in Water

T/K	S/g·(100 g)$^{-1}$	S_c/g·(100 g)$^{-1}$	100·RD	T/K	S/g·(100 g)$^{-1}$	S_c/g·(100 g)$^{-1}$	100·RD
303.2	0.058	0.112	93.1	423.2	1.378	1.281	7.0
323.2	0.146	0.190	30.1	433.2	1.533	1.477	3.7
333.2	0.220	0.242	10.0	443.2	1.688	1.692	0.2
343.2	0.263	0.304	15.6	453.2	1.834	1.926	5.0
353.2	0.301	0.377	25.2	463.2	2.153	2.181	1.3
403.2	1.011	0.943	6.7	473.2	2.471	2.457	0.6

$$\frac{\partial \ln(m/\text{mol}\cdot\text{kg}^{-1})}{\partial \ln(1/(T/\text{K}))} = \frac{-\Delta_{\text{sol}}H_{\text{m}}/\text{J}\cdot\text{mol}^{-1}}{R\cdot(T/\text{K})} \quad (2)$$

Define the solubility S with the unit of $\text{g}\cdot(100\ \text{g})^{-1}$ solvent. So m can be expressed as the function of S:

$$m/\text{mol}\cdot\text{kg}^{-1} = \frac{0.1\cdot S/(\text{g}/100\ \text{g})}{M_{\text{solute}}/(\text{g}\cdot\text{mol}^{-1})} \quad (3)$$

where M_{solute} stands for the molecular weight of solute 4-formylbenzoic acid. Substitute m in eq 2 by eq 3, so,

$$\frac{\partial \ln(S/(\text{g}/100\ \text{g}))}{\partial \ln(1/(T/\text{K}))} = \frac{-\Delta_{\text{sol}}H_{\text{m}}/\text{J}\cdot\text{mol}^{-1}}{R\cdot(T/\text{K})} \quad (4)$$

For simplification, it is assumed that the relation between $\Delta_{\text{sol}}H_{\text{m}}$ and the temperature T is linear over the investigated temperature range. So, introducing $S^0 = 1\ \text{g}\cdot(100\ \text{g})^{-1}$, the integration of eq 4 will be:

$$\ln\left(\frac{S}{S^0}\right) = A + \frac{B}{T/\text{K}} + C\ln(T/\text{K}) \quad (5)$$

Using the optimum procedure provided by MATLAB, together with the experimental solubility data in this work, the parameters A, B, and C were estimated. The results showed that parameter C is very small compared with A and B. It indicates that $\Delta_{\text{sol}}H_{\text{m}}$ is not sensitive to the temperature variation over the investigated temperature range. So, the parameter C can be assumed to be 0. Accordingly, the solubility equation changes to

$$\ln\left(\frac{S}{S^0}\right) = A + \frac{B}{T/\text{K}} \quad (6)$$

Using eq 6, recorrelate the solubility data. The values of parameters A and B are listed in Table 5. Compared with the experimental data, the calculated values are presented in Tables 1 to 4, as well as the relative deviations (RDs). The definition of RD is given by

$$\text{RD} = \frac{|S - S_{\text{c}}|}{S} \quad (7)$$

Table 5. Estimated Parameters in Equation 6 for Different Solvents

solvent	A	B
ethanoic acid	7.6967	$-2.5270\cdot10^3$
aqueous ethanoic acid ($w^a = 0.9$)	3.9453	$-1.0116\cdot10^3$
aqueous ethanoic acid ($w = 0.8$)	3.6108	$-0.9030\cdot10^3$
water	6.4144	$-2.6099\cdot10^3$

[a] w: the mass fraction of ethanoic acid.

where S_{c} is the calculated value from eq 6. For the PX oxidation reactor and subsequent crystallizers, the operating temperatures generally exceed 430 K. Tables 1 to 4 show that the RDs are comparatively small for the data measured within this temperature range. For example, with respect to solubilities in ethanoic acid and water above 403.2 K, the average RDs are 0.06 and 0.04, respectively. Especially for two groups of solubilities in aqueous ethanoic acid shown in Tables 2 and 3, the average RDs are only 0.007 and 0.03, respectively. So, the measured solubility data and the correlation equation in this work can be applied to the design and optimization for the production and purification process of TPA.

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