Partition Coefficient of 4-Carboxybenzaldehyde between Crude Terephthalic Acid Crystals and the Corresponding Aqueous Acetic Acid Solution at (423.2 to 453.0) K

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By using a specially contrived experimental technique, the partition equilibrium of 4-carboxybenzaldehyde (4-CBA) between crude terephthalic acid crystals and the corresponding aqueous acetic acid solution was achieved. The equilibrium mole fractions of 4-CBA in both the liquid and solid phases were measured over a temperature range from (423.2 to 453.0) K, and the mass fractions of acetic acid in the solvent mixtures ranged from 0.800 to 0.995. The partition coefficients, defined as the ratio of the equilibrium mole fraction of 4-CBA in the solid phase to the equilibrium mole fraction of 4-CBA in the liquid phase, were experimentally determined. The experimental results show that: (1) within the temperature range of the measurements, the partition coefficient shows a decreasing trend as the temperature increases at a constant solvent composition, and (2) within the solvent composition range of the measurements, the partition coefficient increases with increasing water content in the solvents at a constant temperature. The experimental data are correlated by the nonrandom two liquids (NRTL) activity coefficient model, and the model parameters are determined in a nonlinear optimization. The fit of the correlated results is fairly good. The comparison of the predicted and experimental partition coefficients at temperatures of (423.2 to 453.0) K and the mass fraction of acetic acid in the solvent mixture at 0.950 shows that the NRTL activity coefficient model could be used as a suitable tool in predicting the partition coefficient of 4-CBA between crude terephthalic acid crystals and the corresponding aqueous acetic acid solution.

Introduction

Terephthalic acid (TPA) is a major commodity chemical manufactured by air oxidation of *para*-xylene (PX). TPA is a crystal which contains two carboxylic groups in the para position on a benzene ring. It reacts with ethylene glycol via a condensation reaction in the manufacture of polyethylene terephthalate (PET), which is widely used in the polyester industry.[1] Worldwide production of TPA has increased at an annual rate of more than 10 % for the last five years, and the demand for TPA exceeded 30 million tons last year.[2] Commercially, the majority of TPA is produced by air oxidation of PX in acetic acid (HAc), promoted by cobalt (Co), manganese (Mn), and bromine (Br) catalysts at (423.2 to 483.2) K.[1]

The impurities present in TPA crystals are generally intermediates, oxidation byproducts, and catalysts. The intermediate 4-carboxybenzaldehyde (4-CBA) is one of the most difficult contaminants to remove and unfortunately, probably one of the most deleterious.[1] The difference between 4-CBA and TPA is that 4-CBA contains an aldehyde group and a carboxylic group in the para position on a benzene ring. The aldehyde group is unable to undergo the condensation reaction with ethylene glycol and acts as a chain terminator in PET polymerization. This makes fibers break easily as well as causes a slower rate of polymerization. The removal of 4-CBA from TPA is, therefore, of great commercial importance.

The most direct and common method for the removal of 4-CBA from crude TPA is crystal aging, in which the basic steps occurring simultaneously are (1) removal of 4-CBA from within to the surface of the TPA crystals, (2) dissolution of 4-CBA from the surface of the TPA crystals to solution, and (3) oxidation of 4-CBA to TPA in solution.[3] In step 2, a solid–liquid partition equilibrium exists for 4-CBA at the interface on TPA crystals. To design and optimize the purification process, the partition coefficient of 4-CBA between crude TPA crystals and the corresponding aqueous acetic acid solution is necessary. Unfortunately, until now, no literature data of this are available. The purpose of this work is to experimentally determine the partition coefficients of 4-CBA over a temperature range from (423.2 to 453.0) K and a range in the mass fraction of acetic acid in the solvent mixture from 0.800 to 0.995. The experimental data are correlated by a nonrandom two liquid (NRTL) activity coefficient model.

Experimental Section

Chemicals. Crude TPA crystals were obtained from a domestic manufacturer. The crystals were initially examined by a Malvern 2000S laser particle size analyzer and high-performance liquid chromatography (Shimadzu 6A HPLC). The average crystal size was estimated to be (28.0 ± 1.3) μm, and the content of impurity of 4-CBA in TPA crystals was estimated to be (4400 ± 35) ppm. Methanol and acetonitrile were obtained from the USA Tedia Company, Inc. and had a mass fraction purity of 0.999. Demineralized water, glacial acetic acid, and analytical-grade isopropyl benzene were obtained from the Hangzhou Chemical Reagent Co. The physicochemical properties of the pure components TPA and 4-CBA are shown in Table 1.[5]

Analytical Method. The partition coefficient of 4-CBA between crude TPA crystals and the corresponding aqueous

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Table 1. Molar Fusion Enthalpy and Fusion Temperature of TPA and 4-CBA

compound	$\Delta_{\mathrm{fus}}H_i$ / $\mathrm{kJ \cdot mol^{-1} \cdot K^{-1}}$	$T_{\mathrm{fus},i}$ / K
TPA	41.5	697.9
4-CBA	28.9	575.2

acetic acid solution in quaternary TPA (1) + 4-CBA (2) + HAc (3) + H_2O (4) mixtures is defined as the ratio of equilibrium mole fraction of 4-CBA in the solid phase to the equilibrium mole fraction of 4-CBA in the liquid phase; i.e.

$$\varphi_{\mathrm{SL}} = \frac{x_2^{\mathrm{S}}}{x_2^{\mathrm{L}}} \tag{1}$$

To determine the partition coefficient, the mole fractions of 4-CBA in both the liquid and solid phases must be determined.

In this work, the 4-CBA concentration in the solid phase was determined by Agilent-1000 high-performance liquid-phase chromatography (HPLC). A Hypersil SAX ion chromatographic column was used. The mobile phase consisted of water and acetonitrile. During the analytical process, the mass fraction of water was maintained at 90 %, and the mass fraction of acetonitrile was maintained at 10 %. Each analysis took about 9 min.

The 4-CBA concentration in the solution was determined by HPLC and gas chromatography (GC). The internal standard method was used in the analysis. The mass ratio of 4-CBA 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 three-component gradient evolution program is shown in Figure 1. Each analysis took about 20 min.

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

To verify the uncertainty of the concentration measurement of 4-CBA in the liquid phase, 10 4-CBA + isopropyl benzene + acetic acid solutions of known concentration were analyzed. Compared with the known concentration, the uncertainty was less than 20 ppm. To check the repeatability, the 10 solutions were measured at least five times, and the repeatability evaluated with mean relative deviation was less than 2 %. To verify the uncertainty of the concentration measurement of 4-CBA in the solid phase, 10 TPA + 4-CBA of known concentration were analyzed. Compared with the known concentration, the uncertainty was less than 35 ppm. To check the repeatability, the 10 mixtures were measured at least five times, and the repeatability evaluated with mean relative deviation was less than 3 %.

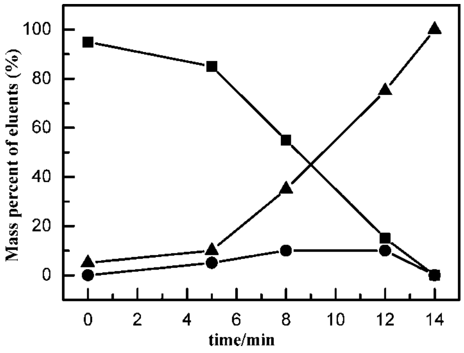

Figure 1. Three-component gradient evolution of HPLC during determination of the concentration of 4-CBA in the solution: ■, water; ▲, acetonitrile; ●, methanol.

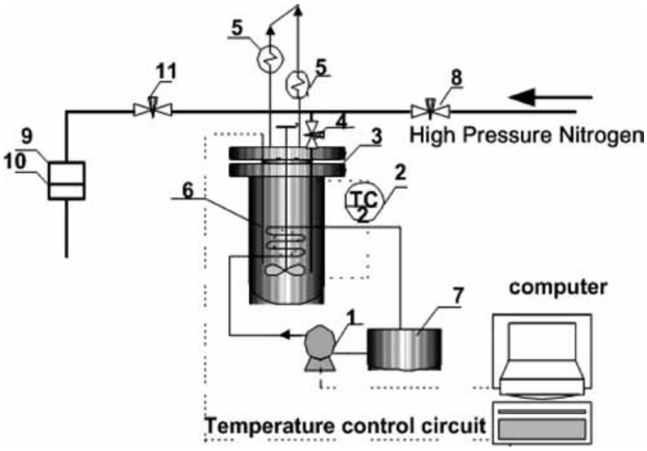

Figure 2. Experimental apparatus for partition coefficient determination. 1, peristaltic pump; 2, vessel wall heating control circuit; 3, equilibrium vessel; 4, sampling valve; 5, condenser; 6, thermal resistance thermometer; 7, cooling oil tank; 8, nitrogen sweeping valve; 9, solid-phase collector; 10, sintered metallic filter; 11, atmospheric valve.

Apparatus and Procedure. The partition coefficients of 4-CBA between crude TPA crystals and the corresponding aqueous acetic acid were measured by a static analytical method, and the experimental apparatus is shown in Figure 2. The partition equilibrium was achieved in a titanium vessel. Two condensers were connected with the vessel to prevent the solvent from evaporating. The pressure was controlled by a back-pressure valve to be about 2.3 MPa. A Pt100 thermal resistance thermometer was inserted into the vessel to measure temperature, and the thermometer had an uncertainty of ± 0.1 K. In each experiment, about 350 g of crude TPA crystals and 1400 g of solvent were deposited into the titanium vessel. The contents of the vessel were heated very slowly at rates of less than 0.5 $\mathrm{K \cdot min^{-1}}$ to the experimental temperature. The temperature was controlled to within ± 0.5 K of the desired temperature by a PID controlling system. Continuous stirring was achieved with a turbine impeller during the experiments. Attainment of the partition equilibrium was verified by repetitive measurements during the following several hours until the results were reproducible to within 2 %. To simultaneously determine the concentration of the impurity 4-CBA in the liquid and solid phases, the slurry must be transferred from the equilibrium reactor into a titanium pipe between the atmospheric valve and nitrogen sweeping valve. The titanium pipe was electric heated around the wall, and the wall temperature was approximately equal to the experimental temperature. The slurry was then pressed toward a porous sintered metallic filter with an internal aperture size of 1 μm. The filtered solution was then collected and cooled, and the concentration of 4-CBA in the liquid phase was determined by the HPLC-GC method. Details about the sampling apparatus and procedure have been described elsewhere.[3] The filtered crystals in the solid-phase sample collector were taken out, and the crystals were washed at least two times by TPA saturated alcohol to replace the residual liquid. The concentration of 4-CBA in the solid was determined by the HPLC method. About 10 mL of saturated solution and 3.5 g of

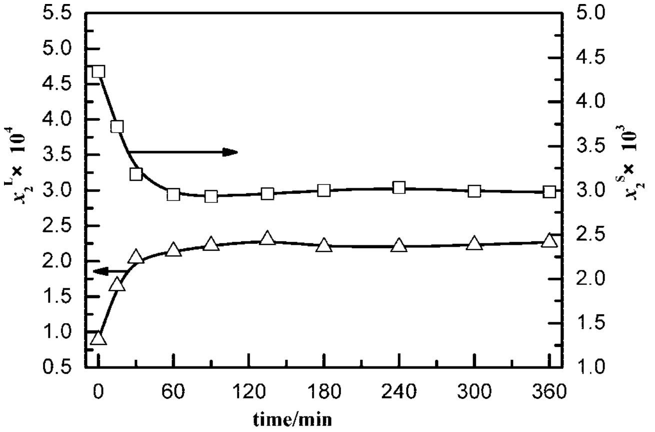

Figure 3. Mole fraction of 4-CBA in solid and liquid phases at different sampling times at 423.2 K.

solid were sampled each time. The experimental runs' reproducibility was verified by repeating each of them at least twice.[1] An averaged value was taken from at least four measurements at the same composition of solvent for each temperature. The estimated associated uncertainty of the partition coefficient based on error analysis and repeated observation was within ± 5 %.

Results and Discussion

Determination of Partition Equilibrium Time. Partition equilibrium is necessary for determination of the partition coefficient of 4-CBA between crude TPA crystals and the corresponding aqueous acetic acid solution. To determine the isothermal time needed to achieve the partition equilibrium, we carried out a partition equilibrium experiment at $T = 423.2$ K and $w_3 = 0.995$. The experimentally determined time evolutions of 4-CBA mole fractions in both the liquid and solid phases are scattered in Figure 3. It shows that the mole fraction of 4-CBA in the solid phase decreases, eventually reaching a plateau. Because the mass of 4-CBA in the system is constant, accordingly the mole fraction of 4-CBA in the liquid phase increases, also eventually reaching a plateau. Figure 3 clearly indicates that when the slurry had been kept isothermal for about 70 min the partition equilibrium for 4-CBA between crude TPA crystals and the corresponding aqueous acetic acid solution had been achieved.

As Wang et al. suggested,[3] the transfer of 4-CBA in TPA crystals is due to molecular diffusion in the crystals. If the concentration of 4-CBA at the interface on any TPA crystal is greater than the equilibrium concentration, 4-CBA will be transferred from the crystals to the solution, the rate of which is controlled by the molecular diffusion in the TPA crystals. Conversely, if the concentration of 4-CBA at the interface on any TPA crystal is smaller than the equilibrium concentration, 4-CBA will be transferred from solution to the TPA crystals, the rate of which is controlled by the incorporation rate of 4-CBA. When the incorporation rate equals the molecular diffusion rate, the partition equilibrium of 4-CBA between solid and liquid phases is achieved. The rate of molecular diffusion or incorporation will increase with increasing temperature, leading to a time reduction to achieve partition equilibrium with an increase of temperature. The experimental results scattered in Figure 3 clearly show that 70 min of isothermal preservation is enough time to achieve the partition equilibrium at 423.2 K. It can be concluded that 70 min of isothermal preservation is also enough to achieve the partition equilibrium for experiments performed at temperatures higher than 423.2 K. The experimental results obtained in this work are the averaged value of at least four measurements after 90 min of isothermal preservation. In this sense, we can conclude that the experimentally measured 4-CBA mole fractions in the solid and liquid phases are in partition equilibrium.

Table 2. Partition Equilibrium of 4-CBA between Crude Terephthalic Acid Crystals and the Corresponding Aqueous Acetic Acid Solution at (423.2 to 453.0) K

T/K	$x_2^L \cdot 10^4$	$x_2^S \cdot 10^3$	$\varphi_{SL,exptl}$	$\varphi_{SL,calcd}$	RD/%
		$w_3 = 0.995$			
423.2	2.172	2.988	13.756	13.706	0.36
428.2	2.341	2.844	12.149	12.225	−0.63
433.2	2.504	2.705	10.802	10.932	−1.20
438.2	2.661	2.570	9.6578	9.7999	−1.47
443.2	2.812	2.439	8.6761	8.8060	−1.50
448.2	2.956	2.313	7.8251	7.9309	−1.35
453.0	3.089	2.196	7.1094	7.1873	−1.10
		$w_3 = 0.950$			
423.2	1.973	2.872	14.557	14.307	1.72
428.2	2.125	2.752	12.947	12.724	1.72
433.2	2.274	2.625	11.545	11.344	1.74
438.2	2.419	2.492	10.303	10.137	1.61
443.2	2.560	2.353	9.1902	9.0795	1.20
448.2	2.698	2.208	8.1818	8.1493	0.40
453.0	2.827	2.063	7.2951	7.3600	−0.89
		$w_3 = 0.906$			
423.2	1.708	2.586	15.147	14.968	1.18
428.2	1.941	2.596	13.373	13.272	0.76
433.2	2.139	2.557	11.957	11.795	1.35
438.2	2.301	2.471	10.740	10.506	2.18
443.2	2.426	2.337	9.6302	9.3777	2.62
448.2	2.516	2.154	8.5623	8.3872	2.05
453.0	2.569	1.934	7.5311	7.5482	−0.23
		$w_3 = 0.800$			
423.2	1.681	2.959	17.607	17.140	2.65
428.2	1.843	2.851	15.466	15.086	2.46
433.2	2.057	2.721	13.224	13.305	−0.61
438.2	2.156	2.569	11.916	11.757	1.33
443.2	2.266	2.396	10.574	10.408	1.57
448.2	2.388	2.202	9.2196	9.2286	−0.10
453.0	2.516	1.995	7.9273	8.2345	−3.88

Experimental Results. The experiments of the partition equilibrium of 4-CBA between crude TPA crystals and the corresponding aqueous acetic acid solution were performed at $w_3 = 0.995$, 0.950, 0.906, and 0.800. At each solvent composition, the partition equilibrium was measured at $T = (423.2$, 428.2, 433.2, 438.2, 443.2, 448.2, and $453.0)$ K. The experimental results are summarized in Table 2.

The experimental results show that (1) within the temperature range of the measurements, the partition coefficient shows a decreasing trend as the temperature increases at a constant solvent composition and (2) within the solvent composition range of the measurements, the partition coefficient increases with increasing water content in the solvents at a constant temperature. The two conclusions indicate that higher temperature and lower content of water are preferred in the purification of crude TPA by crystal aging.

Correlation

Model. Generally, solid–liquid equilibrium can be approximated by the following equation which involves the properties of pure solute, such as enthalpy of fusion, melting point, etc.[4]

$$\ln\left(\frac{f_i^{\mathrm{L}}}{f_i^{\mathrm{S}}}\right) = \ln\left(\frac{x_i^{\mathrm{S}}\gamma_i^{\mathrm{S}}}{x_i^{\mathrm{L}}\gamma_i^{\mathrm{L}}}\right) = \frac{\Delta_{\mathrm{fus}}H_i}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{fus},i}}\right) + \frac{\Delta_{\mathrm{trs}}H_i}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{trs},i}}\right) \tag{2}$$

If a solid–liquid phase transition does not occur, the last term can be neglected. The activity coefficient of the solid phase usually can be assumed equal to one; therefore, the equation becomes

$$\ln\frac{x_i^{\mathrm{S}}}{x_i^{\mathrm{L}}\gamma_i^{\mathrm{L}}} = \frac{\Delta_{\mathrm{fus}}H_i}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{fus},i}}\right) \tag{3}$$

In eqs 2 and 3, $\Delta_{\mathrm{fus}}H_i$ is the molar enthalpy of fusion for solute i; $T_{\mathrm{fus},i}$ is the fusion temperature; $\Delta_{\mathrm{trs}}H_i$ is the molar enthalpy of the solid–solid phase transition; $T_{\mathrm{trs},i}$ is the transition temperature; T is the absolute temperature; R is the universal gas constant; γ_i^{L} is the activity coefficient of solute i in solution; γ_i^{S} is the activity coefficient of solute i in the solid phase; x_i^{L} is the mole fraction of solute i in solution; and x_i^{S} is the mole fraction of solute i in the solid phase. The fusion temperature $T_{\mathrm{fus},i}$ and molar enthalpy of fusion $\Delta_{\mathrm{fus}}H_i$ for TPA and 4-CBA are listed in Table 1.

For the TPA (1) + 4-CBA (2) + HAc (3) + H_2O (4) system, according to eq 1 for the partition coefficient, eq 3 can be rewritten into

$$\varphi_{\mathrm{SL}} = \frac{x_2^{\mathrm{S}}}{x_2^{\mathrm{L}}} = \gamma_2^{\mathrm{L}}\exp\left(\frac{\Delta_{\mathrm{fus}}H_2}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{fus},2}}\right)\right) \tag{4}$$

Because the activity coefficient γ_2^{L} depends on the composition of the solution and temperature, eq 4 must be solved iteratively. The nonrandom two liquid (NRTL) activity coefficient model has relatively higher fitting and prediction accuracy.[1,5,9,14] Furthermore, only two-component parameters are needed in predicting the activity coefficient of multicomponent systems. In the following data correlation, the NRTL activity coefficient model is used. For the definition of the activity coefficient, the NRTL activity coefficient model was used as[6]

$$\ln\gamma_2^{\mathrm{L}} = \frac{\sum_{j=1}^{4} x_j\tau_{j2}G_{j2}}{\sum_{k=1}^{4} x_k G_{k2}} + \sum_{j=1}^{4}\frac{x_j G_{2j}}{\sum_{k=1}^{4} x_k G_{kj}}\left[\tau_{2j} - \frac{\sum_{k=1}^{4} x_k\tau_{kj}G_{kj}}{\sum_{k=1}^{4} x_k G_{kj}}\right] \tag{5}$$

where τ_{ij} and G_{ij} are NRTL model parameters, which can be calculated by

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

Model Parameters Determination. Using the model in eqs 2 to 6, the partition equilibrium coefficients of 4-CBA between crude TPA crystals and the corresponding aqueous acetic acid solution were correlated, and the model parameters were optimized. In the optimization process, as Renon and Prausnitz proposed, α in eq 6 was chosen as 0.3.[7]

The mixture of acetic acid + water associates and exhibits behavior not usually observed in nonpolar fluids.[8] Considering the undissociated acid, self-associated acid, and water in the acetic acid + water system, by using the chemical equilibrium theory, Wang fit literature reported data for the acetic acid + water system and obtained the interaction parameters in the NRTL model for the acetic acid + water system, which are listed in Table 3. These parameters can be used at (293.0 to 502.9) K.[9]

Table 3. NRTL Model Parameters for TPA (1) + 4-CBA (2) + HAc (3) + H_2O (4)

i	j	a_{ij}	a_{ij}	b_{ij}/K	b_{ji}/K	α
1	3	2.2371	−3.6379	$-1.7159 \cdot 10^3$	$3.5941 \cdot 10^3$	0.3
1	4	2.0032	−7.6607	$-1.5470 \cdot 10^3$	$5.9289 \cdot 10^3$	
1	2	−1.6126	7.6750	$-9.0373 \cdot 10^2$	$-8.4323 \cdot 10^2$	
2	3	21.078	0.0613	$-5.8089 \cdot 10^3$	$-1.7377 \cdot 10^2$	
2	4	−4.7306	6.0967	$1.6692 \cdot 10^3$	$-9.2987 \cdot 10^2$	
3	4	−1.9763	3.3293	$6.0989 \cdot 10^2$	$-7.2389 \cdot 10^2$	

The solid–liquid equilibrium of TPA (1) in acetic acid (3) + water (4) solvent mixtures over a temperature range from (423.2 to 493.2) K has been studied by us.[1,10,11] In this work, the interaction parameters in the NRTL model for the TPA (1) + acetic acid (3) + water (4) system are regressed from these experimental data. The parameters are determined by a nonlinear optimization, minimizing the relative difference between correlated and experimental solubility of TPA (1) in acetic acid (3) + water (4) solvent mixtures. The objective function, F_1, is the sum of squares of all residuals.

$$F_1 = \sum_{i=1}^{N_{\mathrm{S}}}\left(\frac{S_{\mathrm{calcd},i} - S_{\mathrm{exptl},i}}{S_{\mathrm{exptl},i}}\right)^2 \tag{7}$$

where S is the solubility of TPA in acetic acid (3) + water (4) solvent mixtures and defined by the mass of TPA in 100 g of solvent. N_{S} is the number of experimentally measured solubility data. The Nelder−Mead Simplex method has been used in the optimizations.[12] The method is implemented in the Matlab Optimization Toolbox (The Mathworks). The simulation program is written in Matlab to use its optimization routine. The optimized model parameters are listed in Table 3. The correlated and experimental solubilities are shown in Figure 4 for comparison. Generally, the correlated results agree well with the experimental values.

The interaction parameters in the NRTL model for the 4-CBA (2) + acetic acid (3) + water (4) system can be obtained from solubilities of 4-CBA in acetic acid (3) + water (4) solvent mixtures. Chen et al. measured the solubilities of 4-CBA at temperatures of (288.3 to 344.4) K and solvent composition w_3 = 1.00 and 0.842.[13] We have also measured the solubilities of 4-CBA in pure water at temperatures of (303.2 to 363.2) K.[1] The solubilities of 4-CBA at higher temperature were not available from the literature until now. The solubilities determined by Chen et al. and us are scattered in Figure 5. Although

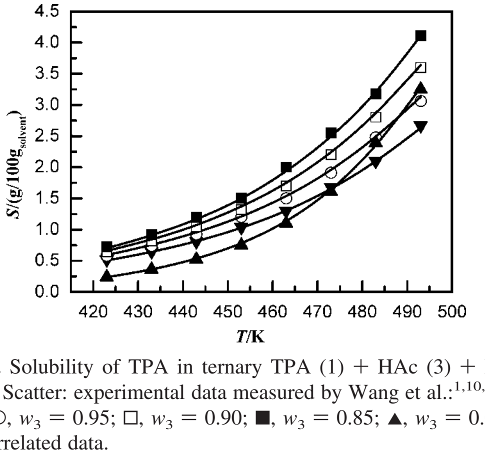

Figure 4. Solubility of TPA in ternary TPA (1) + HAc (3) + H_2O (4) mixtures. Scatter: experimental data measured by Wang et al.:[1,10,11] ▼, w_3 = 1.00; ○, w_3 = 0.95; □, w_3 = 0.90; ■, w_3 = 0.85; ▲, w_3 = 0.00; line, model correlated data.

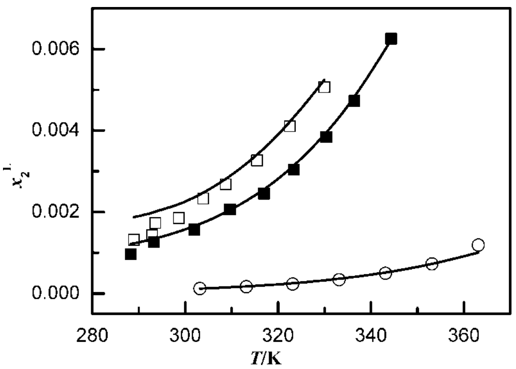

Figure 5. Equilibrium mole fraction of 4-CBA in ternary 4-CBA (2) + HAc (3) + H_2O (4) mixtures. Scatter: □, literature data (w_3 = 1.00) from Chen et al.;[13] ■, literature data (w_3 = 0.842) from Chen et al.;[13] ○, experimental data (w_3 = 0.00) measured by Wang et al.;[1] line, model correlated data.

from these data the interaction parameters in the NRTL model for 4-CBA (2) + acetic acid (3) + water (4) system could be obtained, this was not done because the experimental temperature did not cover the temperature range of industrial operations. Alternatively, we coupled the results in Figure 5 with the partition equilibrium data listed in Table 2 to regress the NRTL model parameters since the data reported in Table 2 are measured at temperatures of (423.2 to 453.0) K, which partly covered the range of industrial operations. The parameters are also determined by a nonlinear optimization, minimizing the relative difference between correlated and experimental mole fractions of 4-CBA (2) in acetic acid (3) + water (4) solvent mixtures, and the partition coefficient of 4-CBA between crude TPA crystals and the corresponding aqueous acetic acid solution. The objective function, F_2, is the sum of squares of all residuals.

$$F_2=\sum_{j=1}^{n_{4\text{-CBA}}}\left(\frac{x^{\mathrm{L}}_{2,\mathrm{calcd},j}-x^{\mathrm{L}}_{2,\mathrm{exptl},j}}{x^{\mathrm{L}}_{2,\mathrm{exptl},j}}\cdot 100\right)^2+\sum_{i=1}^{i_{\max}}(\mathrm{RD}_i)^2 \qquad (8)$$

where $n_{4\text{-CBA}}$ is the number of experimentally determined solubility data used in the optimization, and $i_{\max}$ is the number of experimentally determined partition coefficient data in the optimization. RD is the relative difference between the correlated and experimental partition coefficient, defined by

$$\mathrm{RD}_i=\frac{\varphi_{\mathrm{SL,calcd},i}-\varphi_{\mathrm{SL,exptl},i}}{\varphi_{\mathrm{SL,exptl},i}}\cdot 100 \qquad (9)$$

The Nelder–Mead Simplex method has also been used in the optimizations. The optimized model parameters are listed in Table 3. The correlated and experimental solubilities of 4-CBA are shown in Figure 5 for comparison. Generally, the correlated results agree well with the experimental values.

The calculated partition coefficients and RD are also given in Table 2. The correlated and experimental partition coefficients are shown in Figure 6 for comparison. These results show that the NRTL activity coefficient model can be used to correlate the partition coefficient of 4-CBA between crude TPA crystals and the corresponding aqueous acetic acid solution.

Model Verification. To ensure whether the NRTL activity coefficient model could be used as a suitable tool in predicting the partition coefficient of 4-CBA between crude TPA crystals and the corresponding aqueous acetic acid solution, predictions for the partition coefficient have been carried out at temperatures of (423.2 to 453.0) K and w_3 = 0.950. The predicted and experimental partition coefficients are shown in Figure 7 for comparison. It shows that the prediction of partition coefficients at temperatures of (423.2 to 453.0) K and w_3 = 0.950 is fairly good. The experimental partition coefficients and correlation equation in this work can be used as essential data and as a model for the synthetic and purification process of crude TPA crystals.

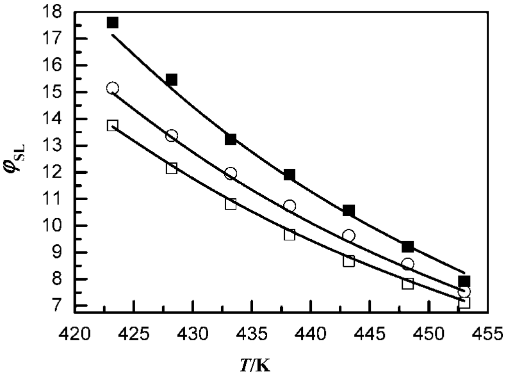

Figure 6. Partition coefficient of 4-CBA between crude terephthalic acid crystals and the corresponding aqueous acetic acid solution. Scatter: experimental partition coefficient: ■, w_3 = 0.800; ○, w_3 = 0.905; □, w_3 = 0.995; line, model correlated partition coefficient.

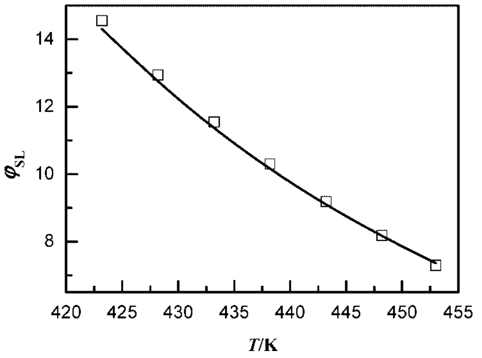

Figure 7. Partition coefficient of 4-CBA between crude terephthalic acid crystals and the corresponding aqueous acetic acid solution at w_3 = 0.950. Scatter, experimental partition coefficient; line, model correlated partition coefficient.

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