Solubility of Isophthalic Acid in Propyl Acetate and Partition Coefficient between Propyl Acetate and Water

Lei Feng,[†] Lijun Wang,*[,†] Ge Peng,[‡] Xia Guo,[†] and Xi Li[†]

Department of Chemical Engineering, Zhejiang University, Hangzhou, 310027 Zhejiang, P. R. China, and Department of Chemical Engineering, Ningbo University of Technology, Ningbo, 315010 Zhejiang, P. R. China

The solubility of isophthalic acid in propyl acetate and the partition coefficient between propyl acetate and water were measured in the temperature range from (303.2 to 363.2) K. The effect of composition on the partition coefficient was also investigated. The results showed that the changes of the initial concentration of isophthalic acid in the mixtures had a remarkable effect on the partition coefficient. The experimental solubility data were fitted by a logarithmic formula, and the experimental partition coefficient data were correlated with the NRTL activity coefficient model. The calculated results showed good agreement with the experimental data.

Introduction

Isophthalic acid is one of the main byproducts in the terephthalic acid process.[1] The byproducts are detrimental impurities in the terephthalic acid process and have to be removed from the system to recycle the catalyst in the aqueous solution. At present, three methods including evaporation, crystallization, and extraction have been adopted in industry to remove the byproducts. Compared with the other methods, extraction has more advantages, such as low energy consumption, high efficiency, and moderate operation conditions.

Propyl acetate has been used as the extractant in only a few industrial processes, and the solubility of the isophthalic acid in propyl acetate and the partition coefficient between propyl acetate and water are the crucial information in designing extraction equipment and controlling relevant operations. In the literature, there are some liquid−liquid equilibrium data on organic components in the water + acetate system published, such as acetic acid + water + (amyl acetate, 2-methyl ethyl acetate),[2] water + (ethyl acetate, butyl acetate) + acetic acid,[3] (isobutyl acetate, isobutyl alcohol) + acetic acid + water.[4] Moreover, Xiao has investigated the partition of acetic acid between water and propyl acetate.[5] However, the solubility of isophthalic acid in propyl acetate and the partition coefficients in aqueous organic mixtures are not available in the literature. In this work, the solubility of isophthalic acid in propyl acetate and the partition coefficients between propyl acetate and water were measured in the temperature range from (303.2 to 363.2) K, and the effect of initial amounts of isophthalic acid was determined. The experimental solubility data were fitted by a logarithmic formula, and the experimental partition coefficient data were correlated with the NRTL activity coefficient model. The experimental data and correlation could be used for industrial applications and operation optimization.

Experimental Section

Chemicals. Isophthalic acid (mass fraction > 0.98) was obtained from Tokyo Kasei Kogyo Co., Ltd. High-performance liquid-phase chromatography (HPLC) grade methanol and acetonitrile from Tedia Company, Inc. were used as the flow-phase in HPLC analysis. Deionized water was used throughout all the experiments. Propyl acetate (mass fraction > 0.99), isopropyl benzene (mass fraction > 0.99), and dimethyl sulfoxide (mass fraction > 0.98) were purchased from 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 which was continuously mechanically stirred. The temperature was controlled within ± 0.1 K of the desired temperature with a thermoelectric controlling system. The reliability of the experimental apparatus had been verified by our previous work.[6,7]

Solubility Measurement. The solubility of isophthalic acid in propyl acetate was measured by the static analytical method. An excess amount, about 1 g, of isophthalic acid was added into (50 ± 3) mL of solvent. Then the equilibrium bottle was heated to a desired temperature. Equilibrium time was determined by repetitive sampling and measurements at different moments in the same experiments until the results were reproducible within ± 3 %. It was found that 12 h was enough for isophthalic acid in propyl acetate to reach equilibrium. In the process of solubility measurement, the solution was kept isothermal for at least 24 h to ensure that the solution had been saturated. A preheated 5 mL syringe was used to withdraw about 3 mL of clear upper portion of the solution each time. As soon as possible, the sampled solution was injected into a test tube which had contained about 3 mL of dimethyl sulfoxide. Then, the syringe was washed at least five times by dimethyl sulfoxide, and the washing solutions were also collected together into the same test tube.

The sample obtained from the above operations was analyzed by HPLC and gas chromatography (GC). The internal standard method was used in the analysis. The isopropyl benzene acted

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* Corresponding author. E-mail: wang_lijun@zju.edu.cn.
[†] Zhejiang University.
[‡] Ningbo University of Technology.

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Table 1. Solubility of Isophthalic Acid in Propyl Acetate at the Temperature Range from (303.2 to 363.2) K

T/K	$x\cdot 10^3$	$x_c\cdot 10^3$	RD/%
303.2	0.791	0.788	−0.4
313.2	0.934	0.927	−0.7
323.2	1.082	1.090	0.7
333.2	1.321	1.282	2.9
343.2	1.379	1.508	9.4
353.2	1.797	1.774	−1.3
363.2	2.145	2.087	−2.7

as the internal standard substance. A detailed analytical program and method for HPLC and GC have been given in our recent articles.[6,7]

Partition Coefficients Measurement. The partition coefficients of isophthalic acid between propyl acetate and water were measured by adding different amounts of isophthalic acid (less solubility at a temperature) in the jacketed equilibrium glass bottles of deionized water + propyl acetate mixtures of fixed mass ratio, and then agitation was started. The initial amount of deionized water added into each bottle was 25 g, and the initial amount of propyl acetate added into each bottle was also 25 g. After at least 6 h, the agitation was stopped, and the solution was kept still for 24 h. Then the clear upper and lower portion of the solution was withdrawn, respectively, with two preheated syringes. As soon as possible, the sampled solution was injected into a test tube which had contained dimethyl sulfoxide. Then, the syringe was washed at least five times by dimethyl sulfoxide, and the washing solutions were also collected together in the same test tube.

The concentration of isophthalic acid in the mixtures was determined by HPLC. Distinct from solubility analysis, an external standard method was used in the partition measurement because of much smaller concentration of the solute in the mixtures. A series of the standard solutions of isophthalic acid were prepared with a concentration near that of the test sample to determine the response factors of isophthalic acid. A Hypersil SAX ion chromatographic column was used, and gradient elution was adopted. The mobile phase consisted of water and acetonitrile, and the following mass fraction of a two-component gradient elution program was adopted: from (0 to 4) min, 85 % water and 15 % acetonitrile; from (4 to 5) min, the mixture mass fraction changed linearly with time to be 70 % water and 30 % acetonitrile; from 5 min on, the mass fraction of water was maintained at 70 %, and the mass fraction of acetonitrile was maintained at 30 %. Each analysis took about 9.5 min. The concentration of isophthalic acid was then determined by comparison of the chromatograms of both sample solution and standard solution. The concentration of water in the mixtures was measured by the Karl Fischer method. The concentration of propyl acetate was determined by gas chromatography (GC). The internal standard method was used in the analysis, and methanol was used as the internal standard substance. The mass ratio of solvent propyl acetate to the internal standard substance in the solution was determined by a Kexiao GC-1690 with a hydrogen flame ionization detector. The SE-54 (30 m) capillary chromatographic column was used. The estimated uncertainty of the partition coefficient values based on error analysis and repeated sampling and measurements was within ± 3 %.

Results and Discussion

Solubility of Isophthalic Acid. The measured solubility of isophthalic acid in propyl acetate, namely x, was listed in Table 1. The data were expressed in units of mole fraction. As shown in Figure 1, it was found that within the temperature range of the measurements the solubility of isophthalic acid in propyl acetate increased with the temperature. The solubility of isophthalic acid in water showed the same trend as that in propyl acetate but varied steeper. Under a constant temperature condition, the solubility of isophthalic acid in propyl acetate was much greater than that in water.

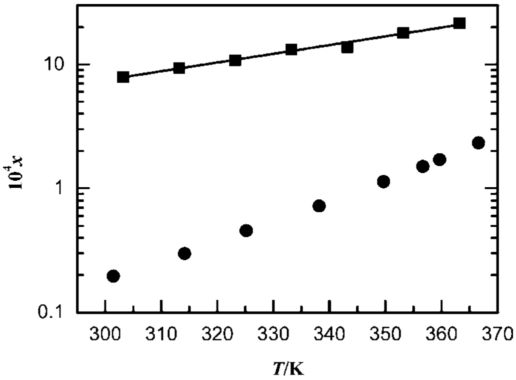

Figure 1. Solubility of isophthalic acid in propyl acetate and in water. ■, the solubility of isophthalic acid in propyl acetate, this work; ●, the solubility of isophthalic acid in water, ref 8. Line: solubility curve calculated from eq 2.

Partition Coefficient of Isophthalic Acid. The experimental compositions of the equilibrium phases of the ternary system isophthalic acid + propyl acetate + water are listed in Table 2 where x is the mole fraction of the equilibrium phase of the ternary system and the superscripts l and u stand for lower and upper phases, respectively. D represents the partition coefficient of isophthalic acid between propyl acetate and water and was determined from eq 1[9,10]

$$D = \frac{x_1^{\mathrm{u}}}{x_1^{\mathrm{l}}} \tag{1}$$

The partition coefficients of isophthalic acid between propyl acetate and water at temperatures ranging from (303.2 to 363.2) K were also listed in Table 2 and plotted in Figure 2. As shown in Figure 2, it was found that within the temperature range of the measurements the partition coefficient of isophthalic acid in the mixtures decreased with the temperature, which could be explained by the different temperature-dependent relationship of isophthalic acid activity coefficient in propyl acetate and in water. Otherwise, the partition coefficient of isophthalic acid between propyl acetate and water increased with the initial isophthalic acid amount in the mixture at constant temperature. This phenomenon might be the result of the nonideality of the ternary system isophthalic acid + propyl acetate + water.

Correlation of Experimental Data. The measured data of the solubility of isophthalic acid in propyl acetate were correlated with a logarithmic function of temperature T

$$\lg x = 0.00705(T/\mathrm{K}) - 5.24107 \tag{2}$$

where T/K was the absolute temperature of solid−liquid equilibrium. The relative deviation (RD) between the calculated and experimental values and the average absolute deviation (ARD) were defined by

$$\mathrm{ARD} = \frac{1}{n}\sum_{i=1}^{n}\mathrm{abs}(\mathrm{RD}_i), \qquad \mathrm{RD}_i = \frac{x_{ci} - x_i}{x_i}\cdot 100 \tag{3}$$

where x_c was the solubility calculated by eq 2 and n was the number of experimental points. The calculated solubility and

Table 2. Partition Coefficient of Isophthalic Acid (1) between Propyl Acetate (2) and Water (3) in the Temperature Range from (303.2 to 363.2) K[a]

T/K	$x_1^{u}\cdot 10^4$	$x_2^{u}\cdot 10$	$x_1^{l}\cdot 10^6$	$x_2^{l}\cdot 10^3$	D	D_c	RD/%
			$m_0 = 0.0139$ g				
303.2	2.754	8.946	7.054	1.529	39.042	40.068	2.6
313.2	2.687	8.745	7.894	1.796	34.037	34.425	1.1
323.2	2.621	8.578	9.068	2.293	28.908	28.688	−0.8
333.2	2.585	8.428	11.522	2.581	22.435	23.136	3.1
343.2	2.525	8.300	13.236	3.025	19.075	18.006	−5.6
353.2	2.381	8.193	16.217	3.645	14.684	13.470	−8.3
363.2	2.251	8.060	21.721	3.899	10.365	9.526	−8.1
			$m_0 = 0.0109$ g				
303.2	2.137	8.947	6.484	1.529	32.958	32.486	−1.4
313.2	2.076	8.746	6.998	1.796	29.671	27.915	−5.9
323.2	2.020	8.579	8.260	2.293	24.460	23.293	−4.8
333.2	2.011	8.429	9.896	2.581	20.326	18.842	−7.3
343.2	1.923	8.300	12.792	3.025	15.031	14.749	−1.9
353.2	1.839	8.193	15.236	3.645	12.072	11.149	−7.6
363.2	1.792	8.060	20.147	3.899	8.893	8.034	−9.7
			$m_0 = 0.0083$ g				
303.2	1.580	8.948	5.690	1.529	27.759	27.011	−2.7
313.2	1.575	8.746	6.324	1.796	24.905	23.248	−6.6
323.2	1.561	8.579	7.375	2.293	21.172	19.460	−8.1
333.2	1.474	8.429	8.712	2.581	16.923	15.824	−6.5
343.2	1.377	8.301	10.229	3.025	13.457	12.491	−7.2
353.2	1.326	8.194	12.525	3.645	10.588	9.566	−9.6
363.2	1.304	8.061	16.787	3.899	7.766	7.033	−9.4
			$m_0 = 0.0053$ g				
303.2	0.983	8.948	4.226	1.529	23.263	22.183	−4.6
313.2	1.006	8.747	5.007	1.796	20.086	19.163	−4.6
323.2	1.008	8.580	5.867	2.293	17.176	16.130	−6.1
333.2	1.001	8.430	7.028	2.581	14.248	13.228	−7.2
343.2	0.947	8.301	8.141	3.025	11.636	10.568	−9.2
353.2	0.907	8.194	10.101	3.645	8.980	8.228	−8.4
363.2	0.848	8.061	13.176	3.899	6.435	6.190	−3.8
			$m_0 = 0.0031$ g				
303.2	0.531	8.948	2.966	1.529	17.904	19.275	7.7
313.2	0.569	8.747	3.511	1.796	16.214	16.712	3.1
323.2	0.568	8.580	4.087	2.293	13.903	14.145	1.7
333.2	0.543	8.430	4.696	2.581	11.561	11.688	1.1
343.2	0.513	8.302	5.722	3.025	8.968	9.433	5.2
353.2	0.517	8.194	7.316	3.645	7.069	7.441	5.3
363.2	0.472	8.061	7.931	3.899	5.946	5.692	−4.3

[a] m_0 is the initial amount of isophthalic acid (less solubility at a temperature) dissolved in the propyl acetate (2) + water (3) mixtures.

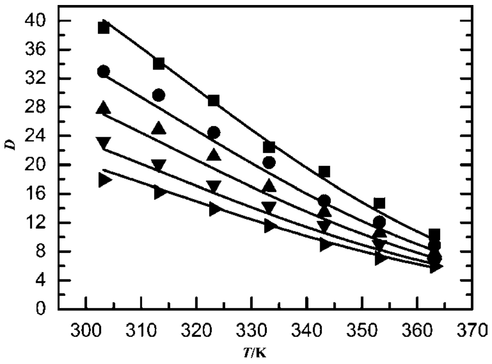

Figure 2. Partition coefficient of isophthalic acid between propyl acetate and water. ■, this work, $m_0 = 0.0139$ g; ●, this work, $m_0 = 0.0109$ g; ▲, this work, $m_0 = 0.0083$ g; ▼, this work, $m_0 = 0.0053$ g; solid triangle pointing right, this work, $m_0 = 0.0031$ g. m_0 is the initial amount of isophthalic acid (less solubility at a temperature) dissolved in the propyl acetate (2) + water (3) mixtures. Line: calculated curves by the NRTL model.

the relative deviation (RD) were also given in Table 1 and Figure 1. The average absolute deviation was 0.026. From Figure 1, it could be shown that the calculated solubility showed good agreement with the experimental values.

Table 3. Binary Parameters of the NRTL Model for the Ternary System Isophthalic Acid (1) + Propyl Acetate (2) +Water (3)

i	1	1	2
j	2	3	3
a_{ij}	−11898.919	−10.334	−1.661
a_{ji}	16.780	17.470	2.915
b_{ij}/K	4330793.480	3741.601	1018.855
b_{ji}/K	−338.773	19.015	690.406

Regarding the partition of isophthalic acid between propyl acetate and water, the NRTL model was adopted to correlate the experimental data. In multicomponent liquid−liquid equilibria, the equation of equilibrium, for every component i, was

$$(\gamma_i x_i)' = (\gamma_i x_i)'' \tag{4}$$

where ′ and ″ referred to the two equilibrated liquid phases.[11] Liquid−liquid equilibria were quite sensitive to small changes in the effect of composition on activity coefficient. The NRTL model was suitable to apply in that field. The NRTL activity coefficient model used in the work was expressed as follows[12]

$$\ln \gamma_i = \frac{\sum_{j=1}^{m} x_j \tau_{ji} G_{ji}}{\sum_{l=1}^{m} x_l G_{li}} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{l=1}^{m} x_l G_{lj}} \left(\tau_{ij} - \frac{\sum_{r=1}^{m} x_r \tau_{rj} G_{rj}}{\sum_{l=1}^{m} x_l G_{lj}} \right)$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}),\ \alpha_{ij} = \alpha_{ji} \tag{5}$$

The effective interaction parameter τ_{ij} was defined by

$$\tau_{ij} = \exp\left(a_{ij} + \frac{b_{ij}}{T}\right) \tag{6}$$

where a_{ij} and b_{ij} were the binary parameters of the NRTL equation and T/K was the temperature. These parameters were determined by minimizing deviation between the experimental data and model calculated values. The term α_{ij} in the NRTL model was fixed at 0.3, recommended by Prausnitz[12] according to the molecular polarity. The regressed results of the NRTL binary parameters were listed in Table 3. The relative deviation (RD) between the calculated and experimental partition coefficient data was defined by

$$\mathrm{RD}_i = \frac{D_{ci} - D_i}{D_i} \cdot 100 \tag{7}$$

where D_c was the partition coefficient of isophthalic acid between propyl acetate and water calculated by eqs 1 and 4. The calculated partition coefficient and the relative deviation (RD) were also given in Table 2 and Figure 2. From Figure 2, it was found that the calculated partition coefficients showed good agreement with the experimental values. These results showed that the NRTL model could be used to correlate the experimental data. The experimental data and the correlation equations in this work could be utilized as essential data and models in the separation and purification process of isophthalic acid.

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