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Solubilities of Benzene Carboxylic Acids in Isobutyl Acetate from (299.73 to 353.15) K

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ABSTRACT: Solubilities of benzoic acid, *p*-methylbenzoic acid, *o*-phthalic acid, *m*-phthalic acid, and terephthalic acid in isobutyl acetate were measured in the temperature range from (299.73 to 353.15) K. The solubility data showed notable distinction in terms of different orders of magnitude. The experimental data were correlated by the universal quasichemical activity coefficient (UNIQUAC) model and the Wilson model. Generally, the UNIQUAC model was slightly superior to the Wilson model.

INTRODUCTION

Purified terephthalic acid (PTA), with the formula $C_6H_4(COOH)_2$, produced mainly by the method of air oxidation of xylene, is a raw material for the polyester industry.[1,2] Because of the impurity of raw materials and the side reactions such as rearrangement and dismutation in the manufacturing process, a great deal of byproduct would be generated and discharged in the form of residue, which contains 0.5 % to 1 % of the PTA capacity. Benzene carboxylic acids such as benzoic acid (BA), *p*-methylbenzoic acid (*p*-MBA), *o*-phthalic acid (*o*-PTA), *m*-phthalic acid (*m*-PTA), and terephthalic acid (TA) are the main constituents of the residue.

Solvent extraction such as recrystallization is the main method to separate and utilize the residue in the recent years.[3,4] Accurate and comprehensive solid−liquid phase equilibrium (SLE) data are needed for designing separation equipment and predicting purification limits, as well as for controlling relevant operating conditions.[5,6] The solubilities of some benzoic carboxylic acids in solvents have been reported, such as *o*-PTA, *m*-PTA, TA in water,[7,8] BA, *p*-MBA, *o*-PTA, *m*-PTA, and TA in ethanol,[2] TA in a solvent mixture of acetic acid + water,[5] terephthalaldehydic, *p*-toluic, BA, *m*-PTA, and TA in *N*,*N*-dimethylformamide.[9]

In this paper, the solubilities of BA, *p*-MBA, *o*-PTA, *m*-PTA, and TA in isobutyl acetate (IBA) were measured as a function of temperature in the temperature range from (299.73 to 353.15) K. Furthermore, the universal quasichemical activity coefficient (UNIQUAC) model and the Wilson model were used to correlate the experimental data, and the parameters of the models were obtained.

EXPERIMENTAL SECTION

Materials. BA (CAS: 65-85-0, AR grade), *p*-MBA (CAS: 99-94-5, AR grade), *o*-PTA (CAS: 88-99-3, AR grade), *m*-PTA (CAS: 121-91-5, AR grade), TA (CAS: 100-21-0, AR grade), and IBA (CAS: 110-19-0, AR grade) were purchased from the Sinopharm Chemical Reagent Co. Ltd., which had a purity of 99.5 % and be used without any purification.

Dynamic Method. Solubilities of BA, *p*-MBA, and *o*-PTA were measured by a dynamic method which had been described in detail previously.[9−13] The main elements of the experimental apparatus are laser monitoring equipment, an equilibrium vessel, an electromagnetic stirrer, a thermostatic controller, and a water bath. A jacketed glass vessel (an intracavity volume of 40 cm^3) was maintained at the constant temperature by circulating water with a thermoelectric controller (type CS501, China). The jacket temperature could be maintained within ± 0.05 K at the required temperature. Continuous stirring was achieved with a magnetic stirrer, and a condenser was connected to the vessel to prevent the IBA from evaporating. The laser monitoring system consisted of a laser generator, a photoelectric transformer, and a light intensity display, which was run to observe the dissolving processes. A mercury thermometer was inserted into the inner chamber of the vessel for the measurement of the temperature of mixture. The thermometer has an accuracy of ± 0.05 K.

Predetermined amounts of a pure solute and IBA were placed into the jacketed vessel. The samples were measured by mass using an analytical balance (type AE200, America), with an accuracy of ± 0.0001 g. The mixtures in the vessel were heated very slowly (the initial heating rate was (1 to 2) $K\cdot h^{-1}$; the terminal heating rate was (0.5 to 1) $K\cdot h^{-1}$) with continuous stirring. At the instant that the last portion of the solid disappeared, the intensity of the transmitted laser light reached a maximum which was taken as the SLE temperature. The uncertainty of BA, *p*-MBA, and *o*-PTA is calculated to be within $\pm 1\cdot 10^{-3}$, $\pm 6\cdot 10^{-4}$, and $\pm 2\cdot 10^{-4}$ mole fraction, respectively.

Equilibrium Method. Despite the advantages such as being simple and rapid, the dynamic method is not applicable to the system of low dissolving speed and low solubility, where it is difficult to confirm whether equilibrium reached. Thus, the equilibrium method is introduced to measure the solubility data of *m*-PTA and TA solved in IBA.

The sealed flask that contained an excess of solute powder in the presence of a fixed volume of IBA were equilibrated with continuous stirring for 2 h at each temperature, which was totally immersed in the thermostatic controller (type SYC-1015D, China) to keep at a constant temperature.[14] A condenser and a mercury thermometer were connected to the flask to prevent

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Table 1. Solubility of BA in IBA

T/K	x_{exp}	T/K	x_{exp}
299.73	0.140	336.03	0.338
302.46	0.149	337.33	0.349
307.34	0.178	337.67	0.351
313.61	0.208	338.76	0.358
322.93	0.254	339.37	0.362
328.98	0.293	339.86	0.369
332.24	0.311	341.48	0.379
334.34	0.325	342.69	0.390
335.58	0.337	343.67	0.399

Table 2. Solubility of *p*-MBA in IBA

T/K	x_{exp}	T/K	x_{exp}
300.19	0.0328	332.48	0.0735
303.04	0.0338	333.91	0.0774
306.43	0.0356	335.96	0.0813
310.28	0.0421	337.49	0.0848
312.70	0.0434	339.46	0.0885
315.36	0.0475	341.07	0.0918
319.97	0.0525	342.68	0.0954
323.16	0.0573	344.69	0.0994
324.84	0.0612	345.82	0.1031
325.76	0.0653	347.26	0.1067
329.67	0.0692	348.41	0.1100

Table 3. Solubility of *o*-PTA in IBA

T/K	x_{exp}	T/K	x_{exp}
300.68	0.0011	326.85	0.0032
302.37	0.0012	331.86	0.0037
304.42	0.0012	335.27	0.0050
309.58	0.0016	340.04	0.0062
312.72	0.0022	342.69	0.0077
317.36	0.0026	348.70	0.0092

Table 4. Solubility of *m*-PTA in IBA

T/K	$x_{\mathrm{exp}}\cdot 10^4$	T/K	$x_{\mathrm{exp}}\cdot 10^4$
308.15	3.52	333.15	9.17
313.15	3.88	338.15	13.00
318.15	4.38	343.15	16.63
323.15	5.07	348.15	20.09
328.15	6.91	353.15	22.09

solvent volatilization and measure the temperature of the mixture. After the solubility equilibrium was reached, the excess solid was allowed to settle for 2 h, and the composition of the liquid phase was determined via UV spectroscopy (Cary5000, America) with quartz cells at the corresponding wavelength of the maximum of absorbance. The selected determining wavelength of *m*-PTA and TA was 280 nm and 252 nm, respectively. The samples were diluted volumetrically with the solvent to obtain absorbance in the linear calibration range for each system.

Table 5. Solubility of TA in IBA

T/K	$x_{\mathrm{exp}}\cdot 10^5$	T/K	$x_{\mathrm{exp}}\cdot 10^5$
305.15	2.38	328.15	5.78
308.15	2.57	333.15	7.07
313.15	3.22	338.15	8.25
318.15	3.41	343.15	8.91
323.15	3.86	348.15	10.43

The uncertainty of *m*-PTA and TA is calculated to be within $\pm 5\cdot 10^{-5}$ and $\pm 2\cdot 10^{-6}$ mole fraction, respectively.

■ SOLUBILITY DATA AND CORRELATION

Solubility Data. The experimental solubilities of the five solutes are presented in Tables 1 to 5, where T (K) is the absolute temperature and x_{exp} (mole fraction) stands for the experimental solubility.

Correlation. A relation for the calculation of SLE can be derived starting from the isofugacity criterion.[15] The fugacity of component i in the liquid phase must be equal to the fugacity of component i in the solid phase:[16]

$$f_i^{\mathrm{S}} = f_i^{\mathrm{L}} \tag{1}$$

With some useful simplifications (the contributions of the heat capacities are neglected), it leads to the following formula which was described elsewhere:[17]

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

If a solid–solid phase transition does not occur, the last term can be neglected, and thereby eq 2 simplifies to:[18]

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

where i stands for the solute, L stands for the liquid phase, x_i^{L} is the mole fraction, γ_i^{L} is the activity coefficient, $\Delta_{\mathrm{fus}}H_i$ is the molar enthalpy, $T_{\mathrm{fus},i}$ is the fusion temperature, $\Delta_{\mathrm{trs}}H_i$ is the molar enthalpy of solid–solid phase transition, $T_{\mathrm{trs},i}$ is the transition temperature, T is the absolute temperature, and R is the universal gas constant.

To solve eq 3, the activity coefficient of solute i in liquid phase, γ_i^{L}, has to be calculated. There are many thermodynamic models that can be used for the calculation. In this study, two semi-empirical models, the UNIQUAC model and the Wilson model, were used to describe the SLE of the present investigated systems and estimate the model parameters from experimental data.

The UNIQUAC and Wilson models' parameters were obtained by fitting the experimental solubility data using an iterative computer program, based on the Nelder–Mead simplex search method. The objective function, F, which was used to adjust the model parameters, is of the form:

$$F = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{x_{\mathrm{exp},i} - x_{\mathrm{cal},i}}{x_{\mathrm{exp},i}}\right|\cdot 100 \tag{4}$$

where N, $x_{\mathrm{exp},i}$ (mole fraction), and $x_{\mathrm{cal},i}$ (mole fraction) are the number of experimental data points, the experimental solubility, and the solubility calculated from the model, respectively.

Table 6. Melting Temperature and Enthalpy of Fusion of the Solute

	$T_{\mathrm{fus},i}$	$\Delta_{\mathrm{fus}}H_i$	V_m
solute	K	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{cm^3 \cdot mol^{-1}}$
BA	395.50[9]	17489.4[9]	93.0091[19]
p-MBA	555.10[9]	22587.8[9]	90.7680[19]
o-PTA	483.15[7]	52299.4[7]	113.4583[19]
m-PTA	621.15[9]	48194.3[9]	113.4583[19]
TA	698.15[7]	53566.6[7]	113.4583[19]

Table 7. UNIQUAC Structural Parameters of the Solute

solute	*r*	*q*
BA	4.32	3.34
p-MBA	5.06	3.91
o-PTA	5.46	4.29
m-PTA	5.46	4.29
TA	5.46	4.29
IBA	4.83	4.19

Table 8. Model Parameters of the UNIQUAC Model

	$(u_{ij} - u_{jj})$	$(u_{ji} - u_{ii})$	RD
system	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1}}$	%
BA + IBA	−1136.6	1651.2	1.06
p-MBA + IBA	436.5	−1021.0	5.74
o-PTA + IBA	−2831.3	4570.1	6.39
m-PTA + IBA	−1874.8	1875.5	10.90
TA + IBA	−3543.6	5584.4	6.38

Table 9. Model Parameters of the Wilson Model

	$(g_{ij} - g_{jj})$	$(g_{ji} - g_{ii})$	RD
system	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1}}$	%
BA + IBA	885.0	620.9	0.85
p-MBA + IBA	−2298.8	734.0	4.76
o-PTA + IBA	−4080.0	110737.4	19.75
m-PTA + IBA	−5620.4	110109.3	11.56
TA + IBA	−9204.2	104503.3	27.52

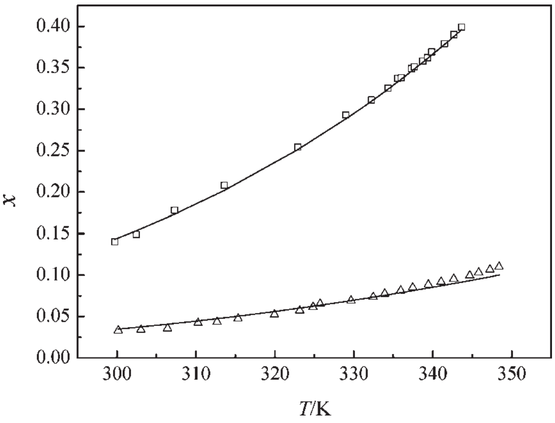

Figure 1. Solubility of BA and *p*-MBA in IBA: □, BA; △, *p*-MBA; —, solubility curve calculated from the UNIQUAC model.

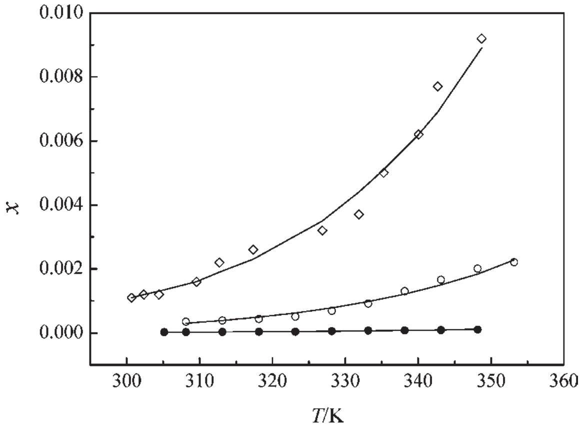

Figure 2. Solubility of *o*-PTA, *m*-PTA, and TA in IBA: ◇, *o*-PTA; ○, *m*-PTA; ●, TA; —, solubility curve calculated from the UNIQUAC model.

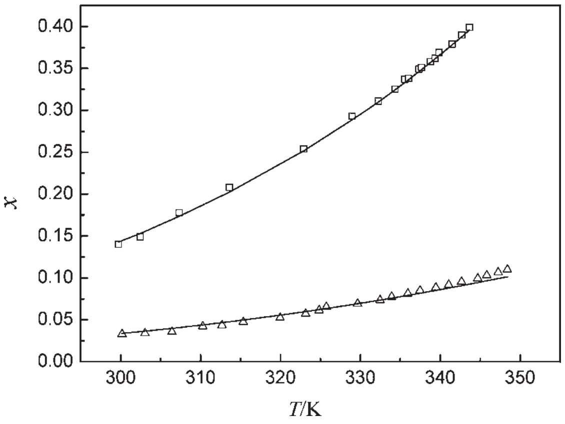

Figure 3. Solubility of BA and *p*-MBA in IBA: □, BA; △, *p*-MBA; —, solubility curve calculated by Wilson model.

To calculate the solubility, the melting temperature, the enthalpy of fusion, and the molar volumn of the five solutes are required, which are listed in Table 6. The values for the UNIQUAC structural parameters (*r* and *q*) are listed in Table 7, which were calculated with group contribution method. The optimized parameters of the two models, along with the average relative deviation (RD) are presented in Tables 8 and 9, respectively. The solubility curves are shown in Figures 1 to 4.

As shown in the results in Tables 8 and 9, the Wilson model provides slightly better results than that given by the UNIQUAC model for the solubility of BA and *p*-MBA. However, for *o*-PTA, *m*-PTA, and TA, the UNIQUAC model is better than the Wilson model, especially for *o*-PTA and TA. The solubility of *o*-PTA, *m*-PTA, and TA in IBA is very low, which means the molecular polarity of solute and solvent vary considerably. That is the possible reason why the UNIQUAC model fits experimental results better for *o*-PTA, *m*-PTA, and TA.

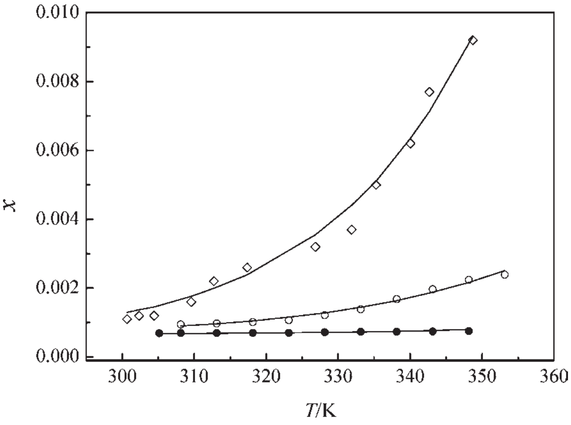

Figure 4. Solubility of *o*-PTA, *m*-PTA, and TA in IBA: ◇, *o*-PTA; ○, *m*-PTA; ●, TA; —, solubility curve calculated by Wilson model.

■ DISCUSSION AND CONCLUSION

Solubilities of BA, *p*-MBA, *o*-PTA, *m*-PTA, and TA in IBA as a function of temperature have been measured at a temperature range from (299.73 to 353.15) K in this study. It is clear from the data that the solubilities increase with temperature but vary in systems. The solubilities cover several orders of magnitude. Solubilities of BA, *p*-MBA, and *o*-PTA in IBA were measured with dynamic method, which orders of magnitude were 10^{-1}, 10^{-2}, and 10^{-3}, respectively. Solubilities of *m*-PTA and TA in IBA were measured with the equilibrium method, which orders of magnitude were 10^{-4} and 10^{-5}, respectively.

The experimental data were correlated with the UNIQUAC model and the Wilson model. For those five kinds of solute, the correlation error of the UNIQUAC model were 1.06 %, 5.74 %, 6.39 %, 10.90 %, and 6.38 %, respectively, while those of the Wilson model were 0.85 %, 4.76 %, 19.75 %, 11.56 %, and 27.52 %. It can be observed that the Wilson model is slightly better than the UNIQUAC model for BA and *p*-MBA. In the case of *o*-PTA, *m*-PTA, and TA, the UNIQUAC model is better than the Wilson model.

The solubility data showed a notable solubility distinction in terms of different orders of magnitude. It can be concluded that IBA could be taken as a suitable solvent for recrystallization to treat the PTA residue.

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