Solubilities of Terephthalic Acid, Phthalic Acid, and Isophthalic Acid in Tetrahydrofuran, Cyclohexanone, 1,2-Diethoxyethane, and Acetophenone

Yao-Kun Che, Yi-Xin Qu, and Shui Wang*

College of Chemical Engineering, Beijing University of Chemical Technology, Beijing, China 100029

Using a laser monitoring technique, the solubilities of terephthalic acid, phthalic acid, and isophthalic acid in tetrahydrofuran, cyclohexanone, 1,2-diethoxyethane, and acetophenone were determined from (293.15 to 343.85) K. The solubility data were correlated with a semiempirical equation.

Introduction

Terephthalic acid is an important intermediate for the preparation of polyester, which is used to make plastics and fibers. During the commercial processes for the manufacture, a lot of terephthalic acid residues which include terephthalic acid and isophthalic acid are produced constantly. It is of great value to recover terephthalic acid from the residues for both economic and environmental concerns.

Recrystallization is one of the effective methods for recovering useful components from terephthalic acid residues. So far, solubility data for terephthalic acid were reported in water, acetic acid, *N*,*N*-dimethyl formamide, *N*,*N*-dimethyl acetamide, dimethyl sulfoxide, *N*-methyl-2-ketopyrrolidine, ethanol, toluene, anisole, 3-pentanone, and 1,4-dioxane.[1−18] However, some of these solvents suffer from being unstable in air, or they easily form solvates with terephthalic acid.

In this work, the solubilities of terephthalic acid, isophthalic acid, and phthalic acid in tetrahydrofuran, cyclohexanone, 1,2-diethoxyethane, and acetophenone were determined. The experimental solubility data were correlated with an empirical equation.

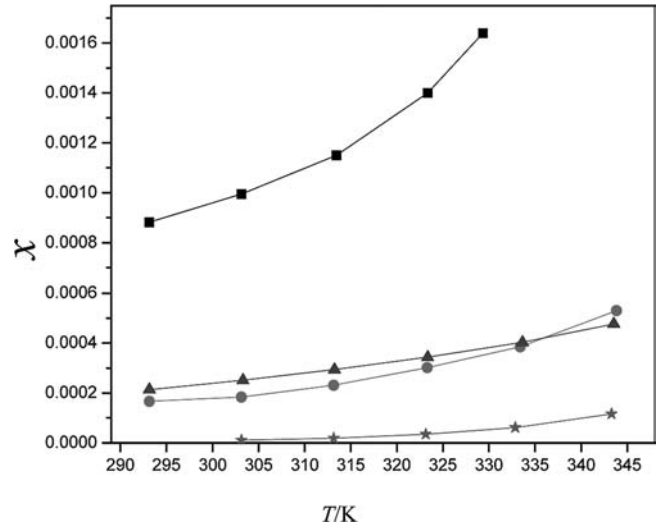

Figure 1. Mole fraction solubility x of terephthalic acid in tetrahydrofuran, cyclohexanone, 1,2-diethoxyethane, and acetophenone in the temperature range from (303.2 to 363.2) K: ■, tetrahydrofuran; ●, cyclohexanone; ▲, 1,2-diethoxyethane; □, acetophenone.

Experimental Section

Chemicals. Terephthalic acid, isophthalic acid, and phthalic acid were obtained from Sinopharm Chemical Reagent Co., Ltd. and had stated mass purities of 0.990, 0.990, and 0.998, respectively. Tetrahydrofuran was purchased from Tianjin Kermel Chemical Reagents Development Centre and has a mass purity of 0.990. Cyclohexanone, 1,2-diethoxyethane, and acetophenone were purchased from Tianjin Guangfu Fine Chemical Research Institute, and their mass fraction purities were all higher than 99.0 %.

Apparatus and Procedure. The solubilities were measured by the synthetic method.[1,2] The dissolution of the solute was carried out in a jacketed glass vessel which was maintained at the desired temperature by continuous forced water circulation from a thermostat (temperature uncertainty of ± 0.05 K). Continuous stirring was achieved with a magnetic stir bar. A calibrated mercury-in-glass thermometer (uncertainty of ± 0.05 K) was inserted into the inner chamber of the vessel for the temperature measurement. A laser beam penetrating the vessel was used to monitor the dissolution process. The laser monitoring system consisted of a laser generator, a photoelectric transformer, and a light-intensity display. To prevent the evaporation of the solvent, a condenser vessel was introduced. The masses of the samples and solvents were determined using an analytical balance (sartorius CP124S, Germany) with an uncertainty of ± 0.1 mg.

Excessive solvent and solute of known mass (determined by a preliminary experiment) were placed in the inner chamber of the vessel. In the early stages of the experiment, the intensity of the laser beam increased gradually with the dissolving of the sample particles in the solution. When the solute dissolved completely, the solution was clear, and the laser intensity reached maximum. Then, a little additional solute of known mass was introduced into the vessel. This procedure was repeated until the penetrated laser intensity could not return to a maximum or, in other words, the last addition no longer dissolved completely in the solvent. The interval of addition depended on the speed of dissolving at that temperature, and it should last more than 60 min. The total amount of the solute consumed was recorded. The same solubility experiment was conducted three times and each

* Corresponding author. E-mail: wangshui2000@sohu.com.

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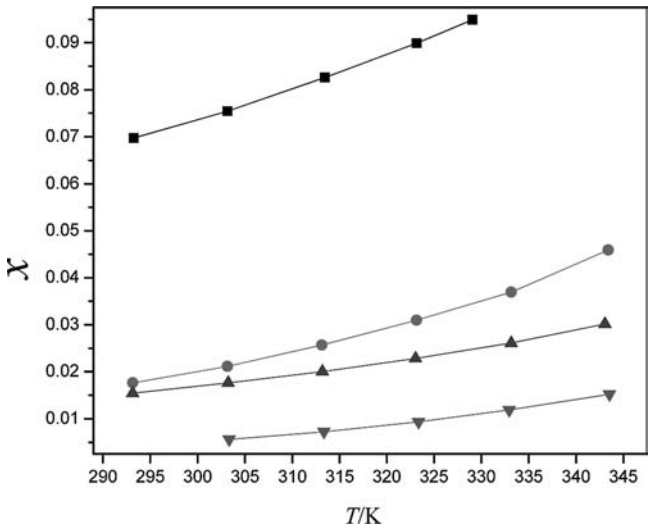

Figure 2. Mole fraction solubility x of phthalic acid in tetrahydrofuran, 1,2-diethoxyethane, cyclohexanone, and acetophenone in the temperature range from (303.2 to 363.2) K: ■, tetrahydrofuran; ●, cyclohexanone; ▲, 1,2-diethoxyethane; ▼, acetophenone.

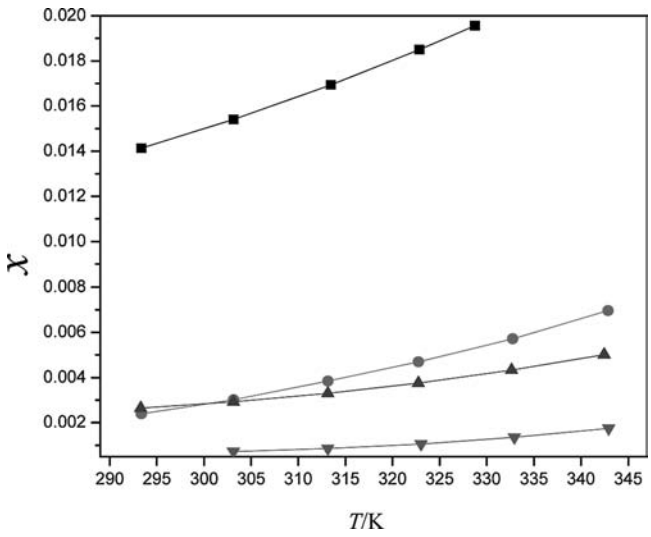

Figure 3. Mole fraction solubility x of isophthalic acid in tetrahydrofuran, 1,2-diethoxyethane, cyclohexanone. and acetophenone in the temperature range from (303.2 to 363.2) K: ■, tetrahydrofuran; ●, cyclohexanone; ▲, 1,2-diethoxyethane; ▼, acetophenone.

time had good agreement. The mean values were used to calculate the mole fraction solubility x based on

$$x = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \quad (1)$$

where m_1 and m_2 represent the mass of the solute and solvent and M_1 and M_2 are the molecular weight of the solute and solvent, respectively. The estimated uncertainty of the solubility values based on error analysis and repeated observations was within 0.5 %.

Results and Discussion

The experimental results of solubility in mole fraction x are given in Figures 1 to 3 and listed in Tables 1 to 3. The conclusion can be drawn from Figures 1 to 3 that for all systems solubility is a function of temperature, and solubility increases with temperature.

Table 1. Terephthalic Acid Solubility

solvent	T/K	10^4x	$100[(x - x_c)/x]$	$10^4\sigma_x$
tetrahydrofuran	293.15	8.816	−1.23	0.11
	303.15	9.952	0.90	
	313.45	11.54	−0.35	
	323.35	13.98	−1.50	
	329.35	16.40	0.00	
cyclohexanone	293.15	1.671	4.61	0.05
	303.15	1.834	−4.20	
	313.15	2.311	−1.90	
	323.30	3.019	1.06	
	333.40	3.855	−0.26	
	343.85	5.302	2.96	
1,2-diethoxyethane	293.15	2.137	0.66	0.02
	303.30	2.513	0.40	
	313.25	2.936	−0.07	
	323.35	3.439	−0.35	
	333.65	4.034	−0.67	
	343.55	4.770	0.63	
acetophenone	303.15	0.107	10.28	0.01
	313.15	0.187	1.07	
	323.15	0.347	0.00	
	332.85	0.617	−1.46	
	343.30	1.158	0.35	

Table 2. Phthalic Acid Solubility

solvent	T/K	10^4x	$100[(x - x_c)/x]$	$10^4\sigma_x$
tetrahydrofuran	293.25	697.3	−0.47	2.75
	303.15	754.3	−0.27	
	313.45	826.3	0.13	
	323.15	899.1	−0.24	
	329.05	949.3	−0.43	
cyclohexanone	293.15	176.3	−0.17	1.10
	303.15	211.7	−0.33	
	313.15	256.8	0.47	
	323.15	309.6	0.58	
	333.15	369.7	−0.24	
	343.40	459.1	2.40	
1,2-diethoxyethane	293.15	154.4	0.45	0.90
	303.25	176.7	0.51	
	313.20	200.3	−0.25	
	323.05	228.3	−0.39	
	333.15	261.3	−0.50	
	343.05	301.7	0.53	
acetophenone	303.35	56.01	−0.41	0.32
	313.35	72.36	−0.23	
	323.35	93.33	0.14	
	332.95	118.6	0.42	
	343.55	152.5	−0.26	

The solubility data were correlated with the modified Apelblat equation, which is a semiempirical equation

$$\ln x = a + \frac{b}{T/\mathrm{K}} + c \ln(T/\mathrm{K}) \quad (2)$$

where T is the absolute temperature and a, b, and c are dimensionless constants. The values of these constants are listed in Table 4.

The difference between experimental data and solubilities calculated from eq 2 together with the root-mean-square deviations are also given in Tables 1 to 3. The root-mean-square relation deviation σ_x is defined as

$$\sigma_x = \left[\sum_{i=1}^{n} \frac{(x_{ci} - x_i)^2}{n}\right]^{1/2} \quad (3)$$

where x_{ci} is the solubility calculated from eq 2; x_i is the experimental value of solubility; and n is the number of experimental points. Tables 1 to 3 give the information that the calculated solubilities show good agreement with the experi-

Table 3. Isophthalic Acid Solubility

solvent	*T*/K	10^4x	$100[(x - x_c)/x]$	$10^4\sigma_x$
tetrahydrofuran	293.35	141.4	−0.28	0.37
	303.15	154.1	0.19	
	313.45	169.3	0.30	
	322.85	184.9	0.05	
	328.75	195.6	−0.20	
cyclohexanone	293.35	23.92	−2.63	0.49
	303.15	30.17	−1.06	
	313.15	38.47	1.61	
	322.75	46.93	1.17	
	332.75	57.10	0.05	
	342.85	69.69	−0.53	
1,2-diethoxyethane	293.30	26.51	0.23	0.07
	303.15	29.29	−0.14	
	313.15	32.97	−0.24	
	322.75	37.59	0.19	
	332.65	43.31	0.18	
	342.45	50.17	−0.06	
acetophenone	303.15	7.249	0.95	0.07
	313.15	8.585	−0.64	
	323.05	10.54	−1.23	
	332.95	13.50	0.00	
	342.95	17.48	−0.11	

Table 4. Parameters and Coefficients of Determination of Correlation Equations

solute/ solvent		tetrahydrofuran	cyclohexanone	1,2-diethoxyethane	acetophenone
terephthalic acid	*a*	−397.52	−256.51	−61.352	−90.392
	b	16627	9662.9	1131.2	−1694.1
	c	58.757	37.813	8.6320	14.774
phthalic acid	*a*	−78.560	−78.708	−59.994	−78.865
	b	2796.4	1933.1	1482.7	1321.7
	c	11.682	11.984	8.9357	12.131
isophthalic acid	*a*	−79.312	−58.711	−139.95	−272.87
	b	2713.1	679.31	5175.9	10667
	c	11.583	8.8686	20.483	40.328

mental values, thus the solubility at other temperatures may be reliably obtained by interpolation. The experimental solubility and correlation equation in this work can be used as essential data and models to serve the process design for recovery of useful components from TA residues.

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