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Solubility of 3-Chlorophthalic Anhydride and 4-Chlorophthalic Anhydride in Organic Solvents and Solubility of 3-Chlorophthalic Acid and 4-Chlorophthalic Acid in Water from (283.15 to 333.15) K

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The solubility of 3-chlorophthalic anhydride and 4-chlorophthalic anhydride in ethyl acetate, acetone, and 1,4-dioxane and the solubility of 3-chlorophthalic acid and 4-chlorophthalic acid in water were measured using Schreinemaker's wet residue method at temperatures ranging from (283.15 to 333.15) K at atmospheric pressure. Results of these measurements were correlated with the modified Apelblat equation.

Introduction

3-Chlorophthalic anhydride and 4-chlorophthalic anhydride are white or almost white crystalline powder and are useful chemicals for an intermediate for the synthesis of polyurethane, dyes, medicines, and agrochemicals.[1−5] They are in general produced by chlorination of phthalic anhydride, either in the liquid or vapor phase.[6−12] These methods suffer from the lack of selectivity of chlorine (be it one, two, or more) and a complicated separation procedure to obtain a pure product. A second strategy toward monochlorophthalic anhydrides involves nitration of phthalic anhydride or its phthalimide derivative, followed by chlorodenitration of the resultant nitrophthalic acid or nitrophthalimide.[13,14] The isomeric mixtures are formed in various proportions of 3- and 4-chlorophthalic anhydride with these methods. However only a few studies have been made to purify 3- or 4-chlorophthalic anhydride and to separate them from the isomeric mixtures by distillation.[15] During the separation process of monochlorophthalic anhydride from its isomeric mixtures by crystallization, the optimization of process conditions and the rational choice of solvents are closely related to the solubility of 3-chlorophthalic anhydride or 4-chlorophthalic anhydride in solvents. It is very important to measure the solubility of 3-chlorophthalic anhydride and 4-chlorophthalic anhydride in different solvents. Although the solubilities of 3- and 4-chlorophthalic anhydride in solvents are very important for their separation process, a few solubility data are reported in previous work.[16] In this paper, the solubility of 3-chlorophthalic anhydride and 4-chlorophthalic anhydride in ethyl acetate, acetone, and 1,4-dioxane and the solubility of 3-chlorophthalic acid and 4-chlorophthalic acid in water are measured experimentally using Schreinemaker's wet residue method[17] at temperatures ranging from (283.15 to 333.15) K at atmospheric pressure.

Experimental Section

Materials. 3-Chlorophthalic anhydride (CAS Registry No. 117-21-5) and 4-chlorophthalic anhydride (CAS Registry No. 118-45-6) are provided from ZiBo XinPeng Chemical Promoter Factory, with a mass fraction of 98.3 % and 98.2 %. The crude 3-chlorophthalic anhydride was recrystallized from a mixture of benzene and naphtha and formed nearly colorless needles with a purity of 99. 5%. The crude 4-chlorophthalic anhydride was recrystallized from *tert*-amyl alcohol, giving a product which had a purity of 99.6 %. The water used to prepare solutions is twice distilled water (conductivity < 5 μS·cm^{-1}).

Apparatus and Procedure. A 125 mL Erlenmeyer flask was used to determine the solubility. The flask was placed into a constant-temperature bath. The water temperature is controlled by a constant-temperature water bath (Neslab, model RTE-101) recirculated through a copper coil in the water bath. The actual temperature in the water bath was monitored by a resistance thermometer (type, TES1300; accuracy, ± 0.01 K). A condenser is connected to the flask to prevent the solvent from evaporating. The water is stirred using a Teflon-coated magnetic stirring bar. Excess solute is placed in the flask and allowed to equilibrate in a constant-temperature water bath at a given temperature for at least 3 days. One hour prior to sampling, stirring is ceased to allow any solid phase to settle. Attainment of equilibrium is verified both by repetitive measurements after a minimum of 3 additional days and by approaching equilibrium from supersaturation by preequilibrating the solutions at a higher temperature. After equilibrium was achieved, the solid and liquid phases were separated by filtration at studied temperature, and then both were analyzed. The same solubility experiment was conducted three times, and the mean values were used to calculate the mole fraction solubility (x) based on

$$x = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \tag{1}$$

where m_1 and m_2 represent the mass of the solute and solvent, respectively, and M_1 and M_2 are the molecular weight of the solute and solvent.

Analysis. Aliquots of saturated 3- or 4-chlorophthalic anhydride solutions are transferred through a coarse filter into a tarred volumetric flask and hydrolyzed with excessive water at (353 to 373) K for 15 min. 3-Chlorophthalic anhydride and 4-chlorophthalic anhydride are converted to 3- and 4-chlorophthalic acid in water. The solubility values in water in this paper are exactly the solubility of 3- and 4-chlorophthalic acid, respectively. The concentration of 3- or 4-chlorophthalic acid is determined using a Shimadzu-6A high-performance liquid-phase chromatograph (HPLC). The chromatographic column used is an unimicro Kromasil C18, 5 μm (250 mm × 4.6 mm)

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Table 1. Mole Fraction Solubility of 3- and 4-Chlorophthalic Anhydride in Organic Solvents

	3-chlorophthalic anhydride		4-chlorophthalic anhydride	
T/K	x_1	100 RD	x_2	100 RD
		Ethyl Acetate		
283.15	0.1067	−0.04	0.1777	2.08
288.15	0.1123	−0.69	0.1843	−2.38
293.15	0.1213	−0.55	0.2056	−0.68
298.15	0.1328	−0.81	0.2275	−0.84
303.15	0.1544	3.33	0.2607	1.57
308.15	0.1688	−0.04	0.2929	1.12
313.15	0.1909	−1.46	0.3261	−1.05
318.15	0.2246	−0.14	0.3773	−0.12
323.15	0.265	0.248	0.4366	0.12
		Acetone		
283.15	0.1669	−0.56	0.2012	2.46
288.15	0.1824	0.06	0.2223	−0.17
293.15	0.2022	1.75	0.2456	−1.63
298.15	0.2184	0.49	0.287	0.24
303.15	0.2344	−1.76	0.3155	−1.86
308.15	0.2612	−0.51	0.369	0.52
313.15	0.2915	0.57	0.4274	1.71
318.15	0.3198	−0.29	0.4735	0.91
323.15	0.3569	0.29	0.5219	−0.82
		1,4-Dioxane		
283.15	0.185	−3.03	0.0825	−1.30
288.15	0.2256	0.06	0.0992	−0.41
293.15	0.2681	2.56	0.1237	3.74
298.15	0.296	−0.35	0.142	−0.40
303.15	0.3281	−1.13	0.1664	−2.76
308.15	0.3672	0.74	0.2052	−0.13
313.15	0.3959	0.43	0.2502	1.16
318.15	0.4202	0.02	0.2978	−0.05
323.15	0.4393	−0.48	0.359	−0.14

Table 2. Mole Fraction Solubility of 3- and 4-Chlorophthalic Acid in Water

	3-chlorophthalic acid		4-chlorophthalic acid	
T/K	$x_1 \cdot 10^3$	100 RD	x_2	100 RD
283.15	2.0136	−1.64	0.08021	1.76
288.15	2.2087	−3.58	0.09132	−1.12
293.15	2.4834	−2.78	0.1093	1.42
298.15	2.8053	−1.32	0.1250	−0.48
303.15	3.1473	−0.39	0.1451	−0.74
308.15	3.4609	−1.31	0.1686	−0.57
313.15	3.8346	−1.30	0.1996	1.59
318.15	4.3010	0.11	0.2262	−0.37
323.15	4.7276	−0.35	0.2615	−0.19
328.15	5.1734	−1.11	0.2987	−1.01
333.15	5.6000	−2.84	0.3494	0.71

maintained at 308.1 K. The HPLC system consisted of a Shimadzu SPD-6A UV single wavelength spectrophotometric detector set to 254 nm. The mobile phase consisted of 60 (mL)/40 (mL)/3.3 (mL)/2.65 (g) methanol/water/H_3PO_4/Na_2SO_4. The uncertainty of the measurement is less than 0.001 g of 3- or 4-chlorophthalic anhydride per 100 g of water. Each analysis is repeated three times, and the average value of the three measurements is considered as the final value of the analysis (precision: ± 0.1 %).

Results and Discussion

The mole fraction solubilities of 3-chlorophthalic anhydride and 4-chlorophthalic anhydride in ethyl acetate, acetone, and 1,4-dioxane at different temperatures (283.15 to 323.15) K are summarized in Table 1. The mole fraction solubilities of 3-chlorophthalic acid and 4-chlorophthalic acid in water between (283.15 and 333.15) K are presented in Table 2. The variation of solubility with temperature is also shown in Figures 1, 2, and 3. It is observed that solubility of 3-chlorophthalic anhydride and 4-chlorophthalic anhydride in ethyl acetate, acetone, and 1,4-dioxane increases with an increase in temperature. The solubility of 3-chlorophthalic anhydride is higher in 1,4-dioxane than that in ethyl acetate and acetone. However, the solubility of 4-chlorophthalic anhydride is lower in 1,4-dioxane than that in ethyl acetate and acetone.

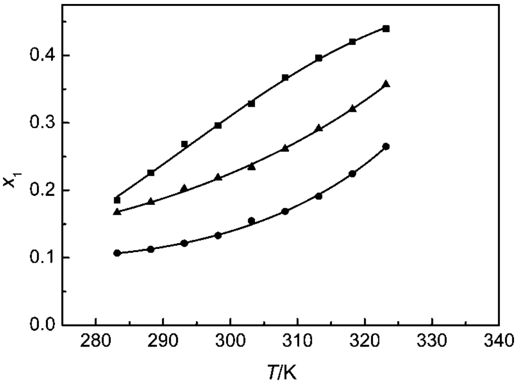

Figure 1. Mole fraction solubility of 3-chlorophthalic anhydrides (x_1) in organic solvents: ■, 1,4-dioxane; ▲, acetone; ●, ethyl acetate; —, the calculated solubility from eq 2.

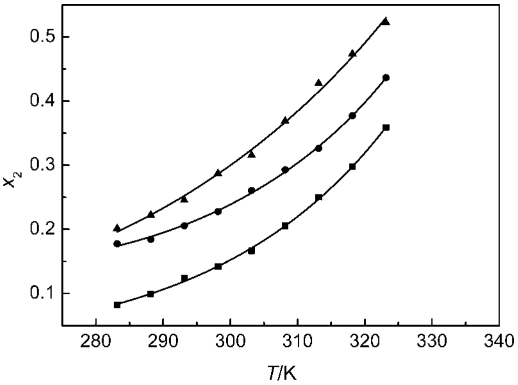

Figure 2. Mole fraction solubility of 4-chlorophthalic anhydrides (x_2) in organic solvents: ▲, acetone; ●, ethyl acetate; ■,1,4-dioxane; —, the calculated solubility from eq 2.

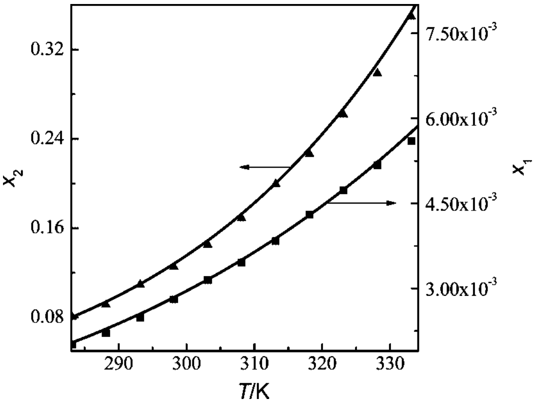

Figure 3. Mole fraction solubility of 3-chlorophthalic acid (x_1) and 4-chlorophthalic acid (x_2) in water: ▲, 4-chlorophthalic acid; ■, 3-chlorophthalic acid; —,the calculated solubility from eq 2.

Figure 3 is the solubity of of 3-chlorophthalic acid and 4-chlorophthalic acid in water. It shows that solubility of 4-chlorophthalic acid in water increases greatly with an increase in temperature; on the contrary, the solubility of 3-chlorophthalic acid in water increases slightly with an increase in temperature. It can also be seen from Figure 3 that the solubility of 4-chlorophthalic acid in water is higher than that of 3-chlorophthalic acid.

Table 3. Parameters of Equation 2 for Solubility of 3- and 4-Chlorophthalic Anhydride in Organic Solvents and 3- and 4-Chlorophthalic Acid in Water

solvent	*A*	*B*	*C*	10^3 rmsd	*A*	*B*	*C*	10^3 rmsd
		3-Chlorophthalic Anhydride				4-Chlorophthalic Anhydride		
ethyl acetate	−450.47	18436	67.86	2.15	−305.90	11926	46.41	3.13
acetone	−147.32	5107.19	22.58	2.18	−77.11	1487.49	12.44	6.97
1,4-dioxane	334.20	−16737.20	−49.02	3.68	−181.26	5243.13	28.39	2.57
		3-Chlorophthalic Acid				4-Chlorophthalic Acid		
water	−42.03	−3.84	6.35	0.04	−64.18	464.96	10.63	1.85

When the chloro is in the para-position of the phenyl ring (4-chlorophthalic anhydride), the chloro behaves to some extent of steric effect and conjugate effect in the molecule, which makes the electron in 4-chlorophthalic anhydride more disperse than in 4-chlorophthalic anhydride. As a result, the solubility of 3-chlorophthalic anhydride is higher in 1,4-dioxane than in the other solvents, and the solubility of 4-chloropatalic anhydride is higher in ethyl acetate and acetone than in 1,4-dioxane.

As shown in Figures 1, 2, and 3, the mole fraction solutility (x) of 3-chlorophthalic anhydride and 4-chlorophthalic anhydride or its corresponding acid was correlated as a function of temperature. The temperature dependence of solubility in solvents is described by the modified Apelblat equation,[18,19] which is a semiempirical equation

$$\ln x = A + \frac{B}{T/\mathrm{K}} + C \ln(T/\mathrm{K}) \tag{2}$$

where x is the mole fraction solubility of solute; T is the absolute temperature; and A, B, and C are the empirical parameters in eq 2. The values of these parameters are given in Table 3. The solubility values of 3/4-chlorophthalic anhydride and 3/4-chlorophthalic acid can be calculated according to these empirical parameters. The experimental solubility in the studied solvents was compared with calculated solubility (x_i^{calc}). The relative deviations (RD) between the experimental and calculated values of solubilities are also calculated by eq 3 and are given in Tables 1 and 2.

$$\mathrm{RD} = \frac{x - x^{\mathrm{calc}}}{x} \tag{3}$$

Further, the root-mean-square deviations (rmsd), calculated by eq 4, are listed in Table 3.

$$\mathrm{rmsd} = \left[\frac{\sum_{j=1}^{N} (x_{1,j} - x_{1,j}^{\mathrm{calc}})^2}{N-1}\right]^{1/2} \tag{4}$$

where N is the number of experimental points; $x_{1,j}^{\mathrm{calc}}$ represents the solubility calculated from eq 2; and $x_{1,j}$ represents the experimental solubility values.

Conclusions

The solubility of 3-chlorophthalic anhydride and 4-chlorophthalic anhydride in ethyl acetate, acetone, and 1,4-dioxane and the solubility of 3-chlorophthalic acid and 4-chlorophthalic acid in water were determined using Schreinemaker's wet residue method at temperatures ranging from (283.15 to 333.15) K. The solubility of 3-chlorophthalic anhydrides and 4-chlorophthalic anhydrides increases with an increase in temperature in the studied organic solvents. The solubility of 3-chlorophthalic anhydride is higher in 1,4-dioxane than that in ethyl acetate and acetone, while the solubility of 4-chlorophthalic anhydride is lower in 1,4-dioxane. The solubility of 4-chlorophthalic acid in water increases greatly with an increase in temperature; however, the solubility of 3-chlorophthalic acid in water increases slightly. Besides, the solubility of 4-chlorophthalic acid in water is higher than that of 3-chlorophthalic acid. The calculated solubility shows good agreement with the experimental values. These experimental data were able to be regressed by eq 2 for each solvent. The experimental solubility and correlation equation in this work can be used as essential data and models in the purification process of 3-chlorophthalic anhydride and 4-chlorophthalic anhydride.

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