Solubility of 4-Methylbenzoic Acid between 288 K and 370 K

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Using a laser monitoring observation technique, the solubilities of 4-methylbenzoic acid in *N*-methyl-2-pyrrolidone, *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, trichloromethane, acetic acid, and water were measured by a synthetic method at temperatures ranging from 288 K to 370 K at atmospheric pressure. A solubility equation was proposed and verified by experimental results. Differential scanning calorimetry experiments were also performed and discussed.

Introduction

4-Methylbenzoic acid is widely used to produce medicines, pesticides, and organic pigments. During the manufacture of terephthalic acid, oxidation residues are created, with 4-methylbenzoic acid being a major component. To purify 4-methylbenzoic acid and separate it from the oxidation residue, solubilities of 4-methylbenzoic acid in solvents are needed. Only a few solubilities of 4-methylbenzoic acid in water below 343 K have been reported in the literature.[1,2] In this work we report solubilities in the systems 4-methylbenzoic acid + *N*-methyl-2-pyrrolidone, 4-methylbenzoic acid + *N*,*N*-dimethylformamide, 4-methylbenzoic acid + *N*,*N*-dimethylacetamide, 4-methylbenzoic acid + trichloromethane, 4-methylbenzoic acid + acetic acid, and 4-methylbenzoic acid + water in the temperature range from 288 K to 370 K at atmospheric pressure.

Experimental Section

Solubilities were determined by a laser monitoring observation of the dissolution temperature for a mixture of known composition.[3,4] The laser monitoring system consisted of a laser generator, a photoelectric transformer, and a light intensity display. The solubility apparatus consisted of a jacketed glass vessel maintained at the required temperature by water circulated from a water bath (type 501 thermoelectric controller, China). The jacket temperature could be maintained within ±0.02 K. Continuous stirring was achieved with a magnetic stir bar. A condenser was connected with the vessel to prevent the solvent from evaporating. A mercury-in-glass thermometer was inserted into the inner chamber of the vessel for the measurement of the temperature, which had an uncertainty of ±0.05 K. The error of temperature measurement was 0.05 K.

Mixtures were prepared by mass using a balance (type TG332A, China). The balance had a range of measurement up to 20 g, with an uncertainty of ±0.000 01 g. Masses above 20 g were measured using a balance (type TG328A, China), with an uncertainty of ±0.0001 g.

4-Methylbenzoic acid used during the solubility measurement had a purity of 0.997 (mass fraction), and it was obtained by purifying the commercial product, which had a mass fraction 0.985. First, primary 4-methylbenzoic acid was extracted by trichloromethane to get a purer 4-methylbenzoic acid without terephthalic acid and its isomers. Then, recrystallizations were carried out in acetic acid and water, respectively. Water used in experiments was double-distilled water. *N*-Methyl-2-pyrrolidone, *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, trichloromethane, and acetic acid were all analytical reagents.

Known masses of 4-methylbenzoic acid and a solvent were placed into the jacketed vessel. The contents of the vessel were heated very slowly at rates less than 2 K·h^{-1} with continuous stirring. When the last portion of 4-methylbenzoic acid just dissolved, the intensity of the laser beam penetrating the vessel reached a maximum, and the temperature was recorded as the liquidus temperature. The error for the experimental solubility in mole fraction was estimated as $<1 \times 10^{-5}$ for 4-methylbenzoic acid + water and $<1 \times 10^{-4}$ for 4-methylbenzoic acid + organic solvent.

A NETZSCH STA449C differential scanning calorimetry instrument was used to measure the enthalpy of fusion of 4-methylbenzoic acid. The amount of the sample was about 5 mg, and the rate of temperature increase was 10 K·min^{-1}. To prevent 4-methylbenzoic acid from sublimating during the measurement, the sample pot was sealed. The enthalpy of fusion of 4-methylbenzoic acid was 23.81 kJ·mol^{-1} (literature value,[5] 22.73 kJ·mol^{-1}) , with an uncertainty ±0.15 kJ·mol^{-1}.

Results and Discussion

Measured solubilities of 4-methylbenzoic acid in water and five organic solvents are presented in Table 1. The results for the system 4-methylbenzoic acid + water are shown in Figure 1 together with the measurements of Sugunan et al.[1] and Apelblat et al.[2] In Table 1 and Figure 1 T is the absolute temperature and x is the experimental solubility in mole fraction. It is clear from Figure 1 that our experimental results show good agreement with the literature data. Compared with the literature data, the deviation of the solubility is <3%.

The $\lambda-h$ equation of Buchowski[6] was defined as

$$\ln[1 + \lambda(1 - x_2)/x_2] = \lambda h(T^{-1} - T_m^{-1}) \qquad (1)$$

where λ and h are constants, T is the absolute temperature, T_m is the melting temperature of solute 2, and x_2 represents the solubility of the solute 2 in solvent 1 in mole fraction. The experimental solubilities were correlated with eq 1, and the calculated solubilities x'_c are listed in Table 1 in comparison with the experimental values. With the excep-

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Table 1. Solubilities of 4-Methylbenzoic Acid in Different Solvents

T/K	10^3x	10^3x_c	$10^3x'_c$	T/K	10^3x	10^3x_c	$10^3x'_c$
			Water				
288.35	0.036	0.030	0.026	328.45	0.142	0.160	0.156
290.95	0.039	0.034	0.030	331.75	0.160	0.181	0.178
291.05	0.039	0.034	0.030	337.55	0.201	0.222	0.223
296.25	0.046	0.043	0.039	342.25	0.243	0.261	0.266
298.35	0.049	0.047	0.043	346.85	0.291	0.304	0.315
302.55	0.056	0.057	0.052	352.25	0.360	0.363	0.384
307.85	0.067	0.071	0.066	356.45	0.431	0.414	0.446
310.95	0.075	0.081	0.076	360.85	0.517	0.474	0.521
315.25	0.086	0.097	0.091	366.25	0.639	0.558	0.630
319.15	0.100	0.113	0.107	368.65	0.688	0.599	0.685
322.95	0.115	0.130	0.126	370.95	0.757	0.640	0.742
328.25	0.139	0.159	0.155				
			N-Methyl-2-pyrrolidone				
295.65	67.9	66.9	57.2	343.35	247.4	255.5	266.6
298.65	74.5	73.7	64.4	346.65	266.3	276.5	288.8
303.35	86.6	85.5	77.1	351.45	296.6	309.4	322.5
308.55	101.3	100.1	93.3	355.75	327.9	341.2	353.9
313.75	117.5	116.7	112.0	360.65	370.5	380.5	391.0
319.55	138.8	137.7	135.7	364.05	410.0	409.6	417.5
323.45	154.2	153.3	153.4	366.55	445.3	432.1	437.0
328.75	174.7	176.7	179.9	369.25	485.1	457.4	458.6
334.85	203.8	206.9	213.8	370.05	500.5	465.1	464.8
340.25	230.1	236.9	246.6				
			N,*N*-Dimethylformamide				
295.65	118.5	118.1	113.3	324.55	267.5	270.6	274.4
298.75	130.9	130.1	126.5	326.85	285.8	287.3	290.6
303.05	149.1	148.2	146.4	328.95	301.1	303.1	305.7
307.55	168.9	169.3	169.4	331.65	324.1	324.5	325.5
311.05	186.9	187.2	188.7	333.05	336.9	336.0	335.9
315.55	210.5	212.4	215.4	335.05	356.5	353.0	351.1
320.45	240.8	242.8	246.7	335.55	363.6	357.4	354.9
			N,*N*-Dimethylacetamide				
296.65	176.7	174.5	168.7	319.75	300.0	304.1	307.5
301.35	198.5	196.7	193.5	323.05	322.7	327.1	330.3
306.45	223.0	223.1	222.5	327.25	355.1	358.1	360.0
309.75	241.1	241.6	242.4	328.85	371.9	370.4	371.5
312.85	257.2	259.8	261.9	331.25	393.2	389.5	388.9
315.95	276.1	279.1	282.0	332.85	412.4	402.6	400.6
			Trichloromethane				
291.55	16.8	16.7	16.8	310.95	34.5	34.4	34.4
294.85	18.9	19.0	19.1	314.95	39.4	39.5	39.5
296.25	20.1	20.1	20.1	318.55	44.5	44.6	44.6
298.25	21.7	21.7	21.7	321.05	48.5	48.4	48.4
300.25	23.5	23.4	23.4	323.75	53.1	52.8	52.8
303.65	26.5	26.5	26.5	326.35	57.7	57.4	57.4
305.35	28.2	28.2	28.2	329.05	62.2	62.5	62.4
308.15	31.2	31.2	31.2	331.95	68.0	68.3	68.2
			Acetic Acid				
296.25	30.3	32.5	32.3	333.95	89.2	92.0	91.4
300.35	36.9	36.8	36.6	337.95	98.6	101.4	100.8
302.95	41.4	39.8	39.6	342.45	109.8	112.8	112.4
305.35	46.3	42.8	42.4	347.65	124.8	127.1	127.0
310.35	50.8	49.4	49.0	354.75	147.6	148.7	149.3
313.95	55.2	54.6	54.2	357.95	157.8	159.3	160.4
318.65	61.9	62.1	61.6	360.65	169.1	168.7	170.2
323.05	69.3	69.8	69.2	364.45	184.9	182.6	184.9
324.45	71.4	72.4	71.8	367.35	199.3	193.7	196.8
330.05	82.0	83.5	82.9	370.35	212.9	205.7	209.7

tion of 4-methylbenzoic acid + *N*-methyl-2-pyrrolidone, the systems show satisfactory agreement between the experimental solubilities and the calculated values.

In terms of thermodynamics, the solubility of a solute in a solvent was calculated using the relationship[7]

$$\ln(\gamma_2 x_2) = (\Delta_{fus}H/R)(T_m^{-1} - T^{-1}) \qquad (2)$$

where $\Delta_{fus}H$ is the enthalpy of fusion of solute 2, x_2 is the solubility of solute 2 in solvent 1 in mole fraction, R is the gas constant, T_m is the melting temperature of solute 2, and γ_2 represents the activity coefficient of solute 2. Prausnitz pointed out that activity coefficients of components in real solution show a weak dependence on temperatures when the temperatures were far from the critical region,[8] giving

$$\ln \gamma_2 = c + d/T \qquad (3)$$

We combine eq 2 with eq 3 to give the result below

$$\ln x_2 = \Delta_{fus}H/(RT_m) - c - (\Delta_{fus}H/R + d)/T \qquad (4)$$

For the systems studied we make the following substitu-

Table 2. Parameters of Correlation Equation for Various Solvents

system	*a*	*b*	10^2RMSD
4-methylbenzoic acid + *N*-methyl-2-pyrrolidone	6.9384	−2850.8	1.23
4-methylbenzoic acid + *N*,*N*-dimethylformamide	7.1775	−2753.7	0.23
4-methylbenzoic acid + *N*,*N*-dimethylacetamide	5.9401	−2280.0	0.39
4-methylbenzoic acid + trichloromethane	7.4706	−3370.5	0.02
4-methylbenzoic acid + acetic acid	5.7987	−2733.2	0.27

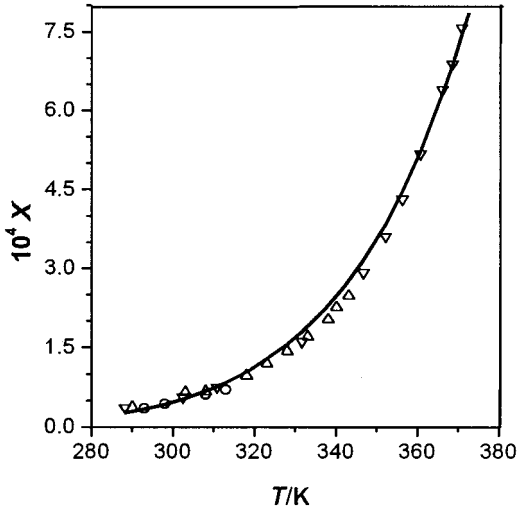

Figure 1. Solubility of 4-methylbenzoic acid in water: ∇, this work; ○, Sugunan et al.;[1] △, Apelblat et al.;[2] —, the values calculated by the $\lambda-h$ equation[6]

tions for eq 4

$$a = \Delta_{fus}H/(RT_m) - c \quad (5)$$

$$b = -\Delta_{fus}H/R - d \quad (6)$$

Thus, a simple solubility equation is obtained

$$\ln x_2 = a + b/T \quad (7)$$

Equation 7 was used to correlate the experimental solubilities in Table 1, and the calculated solubilities x_c are also listed in Table 1 in comparison with the experimental values. The parameters *a* and *b* in eq 7 for the five systems are presented in Table 2 together with the root-mean-square deviations (RMSDs). The RMSD is defined as

$$\mathrm{RMSD} = [\sum_{i=1}^{N}(x_{ci} - x_i)^2/N]^{1/2} \quad (8)$$

where *N* is the number of experimental points and x_{ci} and x_i refer to the solubility values calculated from eq 7 and to the experimental solubility. With the exception of 4-methylbenzoic acid + water, the systems show satisfactory agreement between the experimental solubilities and the calculated values.

Equation 1 and eq 7 are two-parameter solubility equations. If we assume that the molar enthalpies of solution depend linearly on temperature, the three-parameter solubility equation of Apelblat et al. in the form $\ln x = a + b/T + c \ln T$ is obtained from the Clausius−Clapeyron equation.[2] Using this three-parameter equation to correlate the experimental solubilties, the correlation accuracy is a little better. The RMSDs caused by this three-parameter equation for the systems 4-methylbenzoic acid + *N*-methyl-2-pyrrolidone, 4-methylbenzoic acid + trichloromethane, and 4-methylbenzoic acid + acetic acid, for example, are 8.2×10^{-3}, 0.2×10^{-3}, and 1.9×10^{-3}, respectively.

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