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Measurement and Correlation of the Solubilities of *m*-Phthalic Acid in Monobasic Alcohols

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The solubilities of *m*-phthalic acid in seven monobasic alcohols, methanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, and 1-hexanol, were experimentally determined by a gravimetric method in the temperature range of (278 to 358) K. The measured solubilities of *m*-phthalic acid in methanol agreed well with literature data. The experimental results showed that methanol had the best solubility, whereas 1-hexanol presented the lowest solubility, and the solubility decreased with an increase in the carbon atom number in the alcohol structure. For the isomer alcohols, 1-propanol had less solubility than 2-propanol, whereas 1-butanol showed better solubility than 2-butanol. The measured solubility data were correlated with the λh equation (Buchowski−Ksiazczak equation). The parameters in the equation were regressed from the measured data, and the calculated root-mean-square deviation (rmsd) was $3.33 \cdot 10^{-4}$ for the total 123 data points.

Introduction

m-Phthalic acid (1,3-benzenedicarboxylic acid, isophthalic acid, CAS registry no. 121-91-5) is an important chemical with a wide range of industrial applications. It is mainly used as an intermediate for high-quality unsaturated polyesters and as an additive for poly(ethylene terephthalate) (PET) resin. Also, it is used in the production of aramid fibers, polyester beverage bottles, and adhesives with the excellent performance characteristics of hardness, flexibility, stain resistance, thermal stability, and low resin color.[1]

In industry, the raw *m*-phthalic acid is obtained by oxidizing *m*-xylene with air as oxidant and acetic acid as solvent. Then, it is purified by a two-step crystallization process: first crystallized from aqueous acetic acid solutions, then recrytallized from water. For each crystallization process, knowledge of the solubility of *m*-phthalic acid is of great importance because it greatly affects some characteristics of the products such as yield, purity, and the final crystal size distribution.[2] In our previous work, we measured the solubility of *m*-phthalic acid in water, acetic acid,[3] acetone, ethanol, and acetic ether.[4] The experimental results showed that ethanol had better solubility than the traditional solvent, acetic acid, which is of rather high corrodibility.

In this work, we continued our investigation of the solubility of *m*-phthalic acid in different alcohols. The solubility of *m*-phthalic acid in seven monobasic alcohols, methanol (CAS RN 67-56-1), 1-propanol (CAS RN 71-23-8), 2-propanol (CAS RN 67-63-0), 1-butanol (CAS RN 71-36-3), 2-butanol (CAS RN 78-92-2), 1-pentanol (CAS RN 71-41-0), and 1-hexanol (CAS RN 111-27-3), were experimentally determined by a gravimetric method. The experimental solubility data were correlated by the λh equation (Buchowski−Ksiazczak equation).

Experimental Section

Materials. The *m*-phthalic acid was obtained from the Beijing Yanshan Petrochemical Co. with stated purity of > 99.8 % by mass. Methanol, 1-propanol, 2-propanol, and 1-butanol were purchased from the Beijing Chemical Reagent Co., and 2-butanol, 1-pentanol, and 1-hexanol were obtained from the China National Pharmaceutical Foreign Trade Co. (Beijing Branch). All of the alcohols were analytical grade with least stated purity of > 99 % and used as received. Density and refractive indices of the alcohols were measured at 293.15 K and are listed in Table 1. In the table, the corresponding literature data are also presented for comparison, and good agreement is observed.

Table 1. Comparison of Measured Densities and Refractive Indices of the Pure Components with Literature Values at 293.15 K

	$\rho/(\mathrm{g \cdot cm^{-3}})$		n_D	
	this work	lit.[a]	this work	lit.[a]
methanol	0.7917	0.7914	1.3291	1.3288
1-propanol	0.8038	0.8035	1.3853	1.3850
2-propanol	0.7849	0.7855	1.3780	1.3776
1-butanol	0.8103	0.8098	1.3997	1.3993
2-butanol	0.8026	0.8080	1.3955	1.3954
1-pentanol	0.8129	0.8144	1.4092	1.4101
1-hexanol	0.8138	0.8136	1.4175	1.4178

[a] Data from ref 5.

Solubility Measurements. The solubility of *m*-phthalic acid in different alcohols was measured using a gravimetric method.[3,4] The experiments were carried out in a magnetically stirred, jacketed equilibrium cell with a working volume of 100 mL. The cell was sealed to prevent the evaporation of solvent. The temperature of the equilibrium cell was controlled by circulating water from a thermostat (type DTY-8A, Beijing DeTianYou) through the jacket of the cell, which is capable of maintaining the temperature within ± 0.05 K. The temperature was measured using a glass thermometer with ± 0.1 K uncertainty. An analytical balance (type Adventurer AR2140, OHAUS) with uncertainty of ± 0.1 mg was used during the mass measurements. For each measurement, an excess amount of solute was added to a certain amount of solvent gravimetrically. Then, the equilibrium cell was heated to some constant temperature with continuous stirring. After enough time of mixing, the stirrer was stopped, and the solution was kept still for at least 1 h at the same temperature. During the standing process, the undissolved white solids could be observed to settle down in the lower

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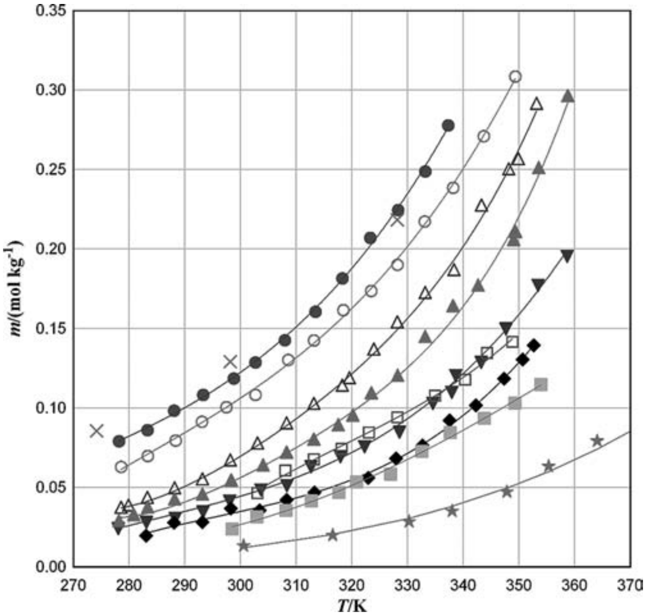

Figure 1. Solubility (molarity) of *m*-phthalic acid in different alcohols: ●, methanol; ×, methanol, data from ref 2; ○, ethanol, data from ref 4; ▲, 1-propanol; △, 2-propanol; ▼, 1-butanol; ◆, 2-butanol; □, 1-pentanol; ■, 1-hexanol; ★, acetic acid, data from ref 3. The lines represent modeling using the λh equation.

portion of the equilibrium cell. A suitably warmed pipet withdrew the clear upper portion of the solution with the tip protected by a microscreen to another previously weighed measuring vial (m_0). The vial was quickly tightly closed and weighed (m_1) to determine the mass of the sample ($m_1 - m_0$). Then, the vial was uncovered and placed in an oven at about 323 K for evaporation. The vial was covered with a piece of filter cloth to prevent dust contamination. After the solvent in the vial was visually completely evaporated, the vial was dried for another 2 h and weighed again (m_2) to determine the mass of the constant residue solid ($m_2 - m_0$). Therefore, the solute concentration (solubility) of the sample saturated solution could be determined accordingly. If it was expressed in molar faction, then the solubility x_1 can be calculated to be

$$x_1 = \frac{(m_2 - m_0)/M_1}{(m_2 - m_0)/M_1 + (m_1 - m_2)/M_2} \tag{1}$$

where M_1 and M_2 stand for the molar weight ($\text{g}\cdot\text{mol}^{-1}$) of *m*-phthalic acid and the solvent, respectively. If the concentration was expressed in molality ($\text{mol}\cdot\text{kg}^{-1}$), which was defined as the amount of solutes in 1000 g solvent, then the solubility, m_1, can be calculated to be

$$m_1 = 1000\frac{(m_2 - m_0)/M_1}{(m_1 - m_2)} \tag{2}$$

Different dissolution times were tested to determine a suitable equilibrium time. It was found that 2 h was enough for *m*-phthalic acid in methanol, 1-propanol, and 2-propanol to reach equilibrium, whereas for other solvents, 5 h or longer was needed, especially at temperatures lower than ambient temperature. An average value was taken from at least three agreeing independent measurements for each temperature. The estimated uncertainty of the solubility values based on error analysis and repeated observations was within 2 %.

Table 2. Solubility Data of *m*-Phthalic Acid in Methanol, 1-Propanol, 2-Propanol and 1-Butanol

T/K	10^3x	$100((x^{\text{calcd}} - x^{\text{exptl}})/x^{\text{exptl}})$	T/K	10^3x	$100((x^{\text{calcd}} - x^{\text{exptl}})/x^{\text{exptl}})$
Methanol					
278.15	2.530	–4.58	313.45	5.118	3.99
283.25	2.755	–0.70	318.25	5.784	1.24
288.05	3.142	–2.40	323.25	6.589	–2.09
293.25	3.455	0.05	328.25	7.144	–0.75
298.75	3.787	3.18	333.15	7.913	–1.92
302.65	4.110	3.46	337.25	8.823	–5.29
307.95	4.555	4.40			
1-Propanol					
278.15	1.685	–0.93	320.17	5.636	7.33
280.84	1.901	–3.57	323.50	6.461	2.25
283.34	2.198	–9.12	328.20	7.128	4.66
288.17	2.493	–5.88	333.15	8.576	–1.47
293.15	2.677	2.91	338.15	9.711	–1.67
298.35	3.205	1.08	342.65	10.47	1.48
304.05	3.769	2.04	349.05	12.15	1.42
308.25	4.248	2.31	349.37	12.45	–0.29
313.15	4.731	5.55	353.55	14.80	–7.87
317.55	5.281	6.74	358.75	17.44	–12.38
2-Propanol					
278.55	2.185	–3.51	319.56	7.035	3.25
279.87	2.260	–2.39	323.95	8.105	0.49
283.25	2.550	–3.02	328.15	9.110	–0.53
288.15	2.910	–0.16	333.15	10.20	0.55
293.15	3.253	4.67	338.35	11.05	5.18
298.15	3.961	0.21	343.25	13.43	–2.95
303.05	4.594	–0.05	348.15	14.77	–1.32
308.25	5.346	–0.25	349.87	15.13	0.05
313.15	6.074	0.64	353.15	17.15	–5.10
318.25	6.754	3.89			
1-Butanol					
278.06	1.872	–9.54	322.25	5.661	3.44
283.11	2.157	–7.84	328.54	6.333	7.53
288.27	2.339	–0.40	334.57	7.655	2.30
293.3	2.649	2.11	337.96	8.166	3.53
298.06	3.149	–1.53	338.64	8.924	–3.81
303.66	3.664	–1.10	343.2	9.537	–0.48
308.36	3.860	6.54	347.67	11.06	–5.54
312.66	4.736	–2.83	353.44	13.04	–9.53
317.94	5.200	1.23	358.67	14.37	–8.64

Table 3. Solubility Data of *m*-Phthalic Acid in 2-Butanol, 1-Pentanol and 1-Hexanol

T/K	10^3x	$100((x^{\text{calcd}} - x^{\text{exptl}})/x^{\text{exptl}})$	T/K	10^3x	$100((x^{\text{calcd}} - x^{\text{exptl}})/x^{\text{exptl}})$
2-Butanol					
283.05	1.455	–0.05	322.95	4.134	12.90
288.05	1.721	–0.55	327.95	5.035	5.25
293.15	2.085	–3.54	332.65	5.634	5.64
298.25	2.349	0.00	337.55	6.785	–1.29
303.45	2.625	4.34	342.25	7.479	–0.03
308.25	3.113	0.92	347.35	8.695	–3.38
313.25	3.457	4.38	350.65	9.585	–5.64
318.15	3.910	5.29	352.65	10.23	–7.60
1-Pentanol					
303.05	4.081	8.40	328.15	8.232	–1.29
308.05	5.323	–5.50	334.95	9.400	0.46
313.15	5.935	–3.76	340.35	10.28	3.07
318.15	6.513	–1.04	344.25	11.73	–1.97
323.05	7.402	–2.30	348.85	12.32	2.50
1-Hexanol					
298.48	2.435	9.00	326.96	5.930	3.50
302.97	3.204	–4.51	332.56	7.372	–3.41
308.15	3.617	–0.82	337.65	8.570	–5.30
312.7	4.235	–2.99	343.76	9.458	–0.06
317.67	4.766	–0.45	349.25	10.42	3.51
320.84	5.439	–4.61	353.94	11.59	4.03

Results and Discussion

The measured solubility data of *m*-phthalic acid in different alcohol solvents at different temperatures are listed in Tables 2 and 3. The data in the tables were reported as molar fraction (calculated by eq 1) for the purpose of thermodynamics correlation. However, to make a meaningful comparison of the solubilities, it is better express the solubility data on the same basis. As such, in Figure 1, the solubility data are shown as molality (calculated by eq 2), which express the solubility data of different solvents on a fixed amount of 1000 g. It can be seen from Figure 1 that in all alcohol solvents, *m*-phthalic acid showed positive solubilities against temperature and similar dependencies on temperature. The results of Long et al.[4] showed that ethanol had much greater solubility than the traditional solvent acetic acid and might be an alternative solvent. In Figure 1, all of the alcohol solvents investigated in this work revealed better solubility than acetic acid, and methanol showed the highest solubility, whereas 1-hexanol presented the lowest solubility. Meanwhile, the solubilities decreased with an increase in the number of carbon atoms in the monobasic alcohol structure, except for 1-pentanol, which had comparative solubility to 1-butanol but higher solubility than 2-butanol. For the alcohols with isomers, different dependencies were observed. 1-propanol had less solubility than 2-propanol, whereas 1-butanol showed better solubility than 2-butanol. For the solubilities in methanol, our results showed very good agreement with literature data.

In this work, the solubility data were modeled by the λh equation, which was originally proposed by Buchowski et al.[6] and distinguished as an accurate nonactivity coefficient model with a rather simple expression. The original λh equation is given to be

$$\ln\left[1 + \lambda\frac{x_1}{1 - x_1}\right] = \lambda h\left(\frac{1}{T} - \frac{1}{T_m}\right) \tag{3}$$

where T and T_m are the equilibrium temperature and the melting point of the solute, respectively. λ and h are two adjustable parameters obtained from the solubility data. Transforming eq 3 for an explicit form of x_1 yields

$$x_1 = \frac{\lambda}{e^{\lambda h(T^{-1} - T_m^{-1})} - 1 + \lambda} \tag{4}$$

Then, the model parameters λ and h could be estimated by minimization of the following objective function using the Levenberg−Marquardt method

$$\mathrm{Min}\, f(\lambda, h) = \sum^{Np}\left(\frac{x_1^{\text{calcd}} - x_1^{\text{exptl}}}{x_1^{\text{exptl}}}\right)^2 \tag{5}$$

where Np refers to the number of data points for each alcohol solvent, and the superscripts exptl and calcd stand for the experimental and the calculated data, respectively.

The optimized parameters λ and h for *m*-phthalic acid in different alcohols are summarized in Table 4 together with the calculated root-mean-square deviations (rmsd). The rmsd is given to be

$$\mathrm{rmsd} = \left[\frac{1}{Np}\sum_{i=1}^{Np}(x_{1,i}^{\text{exptl}} - x_{1,i}^{\text{calcd}})^2\right]^{1/2} \tag{6}$$

Table 4. Regressed Parameters and the rmsd for *m*-Phthalic Acid in Different Alcohols

solvent	T/K range	Np	λ	$10^{-4}h$	10^4rmsd
methanol	278 to 338	13	0.1016	1.865	1.74
ethanol	278 to 350[a]	15[a]	0.1696[a]	1.223[a]	1.96[a]
1-propanol	278 to 358	20	0.3630	0.7471	5.79
2-propanol	278 to 353	19	0.4151	0.6431	2.96
1-butanol	278 to 358	18	0.2366	1.049	4.50
2-butanol	283 to 353	16	0.2356	1.124	3.15
1-pentanol	303 to 348	10	0.2362	1.000	2.34
1-hexanol	278 to 353	12	0.3793	0.7523	2.60
total		123			3.33

[a] Results from ref 4.

From the table, good agreements were observed with the overall average rmsd of $3.33 \cdot 10^{-4}$ for the total 123 data points. In the λh equation, the parameters λ could be approximately regarded to be the mean association number of all of the "real" polymers in the solution if the nonideality of the solution could be interpreted as the association of the solute, and h is related to the enthalpy of solution per mole of solute, as discussed by Buchowski et al.[6] and Li et al.[7] Therefore, from the λ values in Table 4, it is indicated that there is no obvious high association during the dissolution of *m*-phthalic acid in the alcohol solvents. The enthalpy of mixing (H^E) can easily be estimated by the following expression with regressed h values and the solubility and enthalpy of fusion (ΔH_m) to be[4,6,7]

$$H^E = (hR - \Delta H_m)x_1 \tag{7}$$

Conclusions

We experimentally determined the solubilities of *m*-phthalic acid in seven monobasic alcohols, methanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, and 1-hexanol, by using a gravimetric method in the temperature range of (278 to 358) K. All of the alcohol solvents revealed better solubility than acetic acid, which was the traditional solvent for *m*-phthalic acid production. Among the different alcohol solvents, methanol showed the best solubility, and the solubilities decreased with an increase in the carbon atoms in the monobasic alcohol structure. The λh equation was used to correlate the measured solubility data, and good agreement was observed by the regressed model parameters. The experimental solubility and correlation results could be very helpful in the purification process of *m*-phthalic acid.

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