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Solubility of *o*-Phthalic Acid in Methanol + Water and Methanol + Butyl Acetate from (295.87 to 359.75) K

Bao-Zeng Ren,* Cui-Hong Hou, Hai-Gong Chong, Wei-Ran Li, and Huai-Jun Song

College of Chemical Engineering, Zhengzhou University, Zhengzhou, Henan 450002, People's Republic of China

The solubility of *o*-phthalic acid in methanol + water and methanol + butyl acetate was measured at temperatures ranging from (295.87 to 359.75) K using a laser-monitoring observation technique at atmospheric pressure. The experimental data were correlated with the Apelblat equation. The overall σ of 159 data points was 0.70 %. The apparent molar enthalpies of *o*-phthalic acid in the two systems have been determined and provide a heat transmission basis for the design of a crystallizer.

Introduction

o-Phthalic acid is an important organic chemical product and is a raw material used in the production of a range of chemicals. The acid can be dehydrated easily to produce *o*-phthalic anhydride. It is mainly used for making polyvinyl chloride plasticizer and polyester resin and in alkyoid resin preparation. It also has wide use in paint, dye, medicine, and agricultural applications.[1,2] At present, the solubility of *o*-phthalic acid has only been reported in water,[3] and there is no solubility data reported in other solvents or mixed solvents. In order to purify *o*-phthalic acid, accurate and systematic solubility data must be obtained. Therefore, the solubility of *o*-phthalic acid in methanol + water and methanol + butyl acetate systems is studied in this paper.

Experimental Section

Chemicals. Methanol and butyl acetate were purchased from the Tianjing Huadong Chemical Reagent Factory and were of AR grade with a purity of 99.5 % and 99.0 %, respectively. *o*-Phthalic acid, which was purchased from the Shanghai Chemical Reagent Research Institute, was of CP grade with a purity of 99.8 %. Deionized water was self-made. Butyl acetate was purified by fine distillation. The final purities of the chemicals used were as follows: *o*-phthalic acid (≥ 99.8 %), butyl acetate (≥ 99.5 %), and methanol (≥ 99.5 %).

Apparatus and Procedure. The solubility of *o*-phthalic in methanol + water and in methanol + butyl acetate was measured using a synthetic method with a computer monitor online.[4−12] The solubility apparatus[5] consisted of a jacketed glass vessel (120 cm^3) maintained at the desired temperature through circulating water that was provided by a constant temperature bath (type CS501, Shanghai Pudong Rongfeng Laboratory Instrument Works Co. Ltd). The water temperature was controlled by a workstation with a temperature accuracy of ± 0.1 K. A magnetic stirrer (type 85-2, Shanghai Sile Co.) achieved continuous stirring, and a condenser was fitted to reduce the solvent's evaporation. A thermometer with an uncertainty of ± 0.01 K was used to determine the temperature of the system. A laser beam was used to observe the system dissolving. The signal transmitted through the vessel was collected by a detector (type FGF-III) that measured the rate of temperature rise and estimated the equilibrium point of the given system, based on the signal change.

The solute and the solvent were prepared using an electronic balance (type AB204-N). The weighing range of the balance was to 210 g, with an uncertainty of ± 0.0001 g, and was produced by the Mettler-Toledo Group. The estimated uncertainty in the mole fraction was less than 0.001.

The solubility of *o*-phthalic acid in methanol + water and methanol + butyl acetate was measured as follows. Predetermined amounts of solute and solvents were placed into the jacketed vessel. The solution was heated slowly with continuous stirring. When the particles of the solute disappeared completely, the signal approached a maximum value. The workstation measured the signal difference at 10-min intervals; if less than 10, the workstation stopped heating and recorded the temperature. The temperature recorded is the dissolution temperature of the corresponding solution at a given composition when *o*-phthalic acid is dissolved completely.

Results and Discussion

Results. The experimental solubility data of *o*-phthalic acid in methanol + water are presented in Table 1, where T is the absolute temperature, x (mole fraction) is the experimental solubility, and x_c is the calculated value. The experimental solubility data of *o*-phthalic acid in methanol + butyl acetate are presented in Table 2. The experimental data are correlated with the Apelblat equation:[11]

$$\ln x = A + B/T + C \ln T \qquad (1)$$

The parameters A, B, and C and the mean absolute error σ of each component are listed in Table 3. The standard deviation in eq 1, σ, is defined as

$$\sigma = \frac{\left[\sum_{i=1}^{N} |(x - x_c)/x|\right]}{N} \times 100 \qquad (2)$$

where N is the number of experimental points. The overall σ of the 159 experimental points for the methanol + water system and the methanol + butyl acetate system at various contents of

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* Corresponding author. E-mail: renbz@zzu.edu.cn. Tel/Fax: +86-371-63887318.

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Table 1. Solubility of *o*-Phthalic Acid in Methanol (w) + Water ($1 - w$)[a]

T/K	x	x_c	T/K	x	x_c	T/K	x	x_c	T/K	x	x_c
$w = 0.0000$											
295.87	0.0005788	0.0005921	308.97	0.001060	0.001035	325.43	0.002078	0.002066	342.10	0.003991	0.004105
298.65	0.0006513	0.0006671	311.96	0.001190	0.001175	328.20	0.002332	0.002318	344.37	0.004471	0.004503
301.17	0.0007433	0.0007429	315.53	0.001383	0.001365	332.07	0.002660	0.002720	347.35	0.005151	0.005082
303.79	0.0008477	0.0008307	319.27	0.001621	0.001598	335.95	0.003099	0.003192	350.23	0.005808	0.005709
306.55	0.0009426	0.0009342	322.78	0.001844	0.001850	339.21	0.003543	0.003648	352.45	0.006435	0.006244
$w = 0.1995$											
303.36	0.001923	0.001918	322.08	0.004915	0.004915	336.44	0.01010	0.01031	351.56	0.02267	0.02275
307.21	0.002327	0.002321	326.02	0.006090	0.006015	339.17	0.01208	0.01188	354.37	0.02639	0.02637
310.48	0.002738	0.002732	329.11	0.007101	0.007052	341.99	0.01397	0.01377	357.26	0.03042	0.03072
313.43	0.003151	0.003169	331.36	0.007806	0.007922	345.17	0.01655	0.01626			
317.56	0.003879	0.003905	334.21	0.009058	0.009182	348.74	0.01959	0.01961			
$w = 0.3998$											
300.77	0.005883	0.005983	315.41	0.01214	0.01222	329.67	0.02301	0.02295	347.66	0.04661	0.04686
302.96	0.006818	0.006689	318.75	0.01401	0.01425	333.14	0.02624	0.02651	351.70	0.05309	0.05441
306.10	0.007916	0.007827	321.87	0.01595	0.01638	335.65	0.02990	0.02937			
309.16	0.009162	0.009092	324.50	0.01800	0.01839	338.78	0.03429	0.03329			
312.13	0.01054	0.01048	326.28	0.02014	0.01986	342.91	0.03997	0.03912			
$w = 0.5998$											
301.38	0.01819	0.01815	311.64	0.02545	0.02550	323.16	0.03611	0.03638	337.98	0.05552	0.05539
304.35	0.02009	0.02008	315.27	0.02874	0.02861	327.59	0.04178	0.04142	343.23	0.06330	0.06370
308.00	0.02263	0.02266	319.43	0.03223	0.03252	332.70	0.04826	0.04790			
$w = 0.7997$											
302.01	0.03155	0.03109	310.7	0.03826	0.03888	318.42	0.04743	0.04673	330.64	0.06119	0.06098
304.94	0.03370	0.03359	313.07	0.04088	0.04119	322.66	0.05179	0.05143	336.04	0.06763	0.06797
308.16	0.03591	0.03649	315.77	0.04392	0.04394	326.37	0.05604	0.05575	340.53	0.07386	0.07409
$w = 1.000$											
302.67	0.05591	0.05593	311.55	0.06513	0.06514	319.71	0.07427	0.07428	327.35	0.08342	0.08340
305.75	0.05902	0.05903	314.35	0.06817	0.06820	322.29	0.07730	0.07730	329.83	0.08650	0.08648
308.63	0.06209	0.06202	317.03	0.07121	0.07120	324.85	0.08034	0.08036	332.25	0.08953	0.08954

[a] w is mass fraction. x_c is the calculated value from eq 1, and x is the experimental value. Both are mole fractions.

Table 2. Solubility of *o*-Phthalic Acid in Methanol (w) + Butyl Acetate ($1 - w$)[a]

T/K	x	x_c	T/K	x	x_c	T/K	x	x_c	T/K	x	x_c
$w = 0.0000$											
304.89	0.002573	0.002592	325.33	0.004080	0.004103	341.55	0.006117	0.006025	359.75	0.009362	0.009406
310.12	0.002958	0.002906	330.25	0.004587	0.004603	345.83	0.006724	0.006683			
315.87	0.003294	0.003304	334.75	0.005060	0.005120	352.01	0.007751	0.007771			
320.35	0.003640	0.003658	338.99	0.005583	0.005666	356.07	0.008515	0.008588			
$w = 0.1997$											
303.10	0.01863	0.01871	313.56	0.02182	0.02182	324.07	0.02478	0.02487	334.30	0.02792	0.0277
305.82	0.01953	0.01953	316.52	0.02276	0.02269	327.66	0.02586	0.02588			
309.65	0.02082	0.02067	320.44	0.02377	0.02383	332.67	0.02704	0.02724			
$w = 0.3992$											
304.57	0.03555	0.03570	314.04	0.04053	0.04046	324.25	0.04592	0.04598	334.26	0.05187	0.05177
307.20	0.03711	0.03699	317.66	0.04230	0.04237	327.82	0.04783	0.04800			
310.62	0.03879	0.03871	320.77	0.04409	0.04405	330.86	0.04981	0.04976			
$w = 0.6001$											
300.46	0.04255	0.04263	309.74	0.04906	0.04908	318.86	0.05573	0.05573	327.74	0.06248	0.06244
303.37	0.04471	0.04462	312.88	0.05125	0.05134	321.70	0.05792	0.05785	330.77	0.06480	0.06477
306.50	0.04687	0.04679	315.77	0.05344	0.05345	324.82	0.06020	0.06021	333.94	0.06717	0.06723
$w = 0.8000$											
303.62	0.05167	0.05187	312.13	0.05910	0.05891	320.96	0.06696	0.06711	328.99	0.07576	0.07546
306.24	0.05412	0.05395	315.22	0.06168	0.06167	324.22	0.06975	0.07040	332.06	0.07901	0.07889
309.46	0.05662	0.05661	317.91	0.06429	0.06417	326.24	0.07268	0.07250	335.20	0.08247	0.08254
$w = 1.000$											
302.67	0.05591	0.05593	311.55	0.06513	0.06514	319.71	0.07427	0.07428	327.35	0.08342	0.08340
305.75	0.05902	0.05903	314.35	0.06817	0.06820	322.29	0.07730	0.07730	329.83	0.08650	0.08648
308.63	0.06209	0.06202	317.03	0.07121	0.07120	324.85	0.08034	0.08036	332.25	0.08953	0.08954

[a] w is mass fraction.

o-phthalic acid in the mixed solvent is 0.70 %. It can be seen that the experimental data satisfy eq 1 very well.

Figure 1 and Figure 2 show that *o*-phthalic acid is reasonably soluble in solutions of ethanol + water and methanol + butyl acetate at different mixture proportions, especially in the ethanol + water system, which shows that water, ethanol, and its mixtures are good solvents for extracting and separating *o*-phthalic acid from other solid materials that contain *o*-phthalic acid.

Prediction of Apparent Molar Enthalpy. Based on the principle of solid/liquid equilibium, when a solid is dissolved in a solvent and achieves dissolution equilibium, the solute

Table 3. Parameters of Equation 1 for the Methanol + Water System and the Methanol + Butyl Acetate System at Various Contents of *o*-Phthalic Acid in the Mixed Solvent

	methanol + water system				methanol + butyl acetate system			
w	A	B	C	σ	A	B	C	σ
0.0000	−141.77	2746.6	21.977	1.67	−146.09	4646.2	21.836	0.816
0.1995	−265.04	7828.8	40.766	0.836	86.726	−5340.1	−12.791	0.391
0.3992	28.175	−5449.4	−2.6595	1.52	−6.1655	−943.45	1.0370	0.219
0.6001	11.080	−3330.9	−0.70726	0.480	29.997	−2705.3	−4.2326	0.106
0.8000	49.774	−4475.5	−6.7291	0.802	−47.260	823.08	7.2764	0.273
1.000	15.381	−2208.7	−1.9198	0.027	15.381	−2208.7	−1.9198	0.027

fugacity in the solid phase is equal to that of the liquid phase from which the generalization of the solubility equation[13] may be derived:

$$\ln \lambda x = \frac{\Delta H_{\mathrm{tp}}}{R}\left(\frac{1}{T_{\mathrm{tp}}} - \frac{1}{T}\right) - \frac{\Delta C_p}{R}\left(\ln \frac{T_{\mathrm{tp}}}{T} - \frac{T_{\mathrm{tp}}}{T} + 1\right) - \frac{\Delta V}{RT}(p - p_{\mathrm{tp}}) \tag{3}$$

where x and λ are the mole fraction and the activity coefficient of solute in solution, respectively; ΔH_{tp} is the solid melting heat at the triple point T_{tp}; ΔC_p and ΔV are the heat capacity change and specific volume change of solute between the liquid state and the solid state, respectively; and p is the vapor pressure.

In general, changes of pressure and specific volume are small and can be neglected, so the triple-point temperature approaches the dissolution temperature T_{m} at atmospheric pressure. Equation 3 simplifies to

$$\ln \lambda x = \frac{\Delta H_{\mathrm{m}}}{R}\left(\frac{1}{T_{\mathrm{m}}} - \frac{1}{T}\right) \tag{4}$$

and, as with eq 3, x and λ are the mole fraction and the activity coefficient of solute in the solution, respectively; R is the gas constant; ΔH_{m} is similar to ΔH_{tp}, which is the apparent molar enthalpy under the dissolution temperature T_{m}.

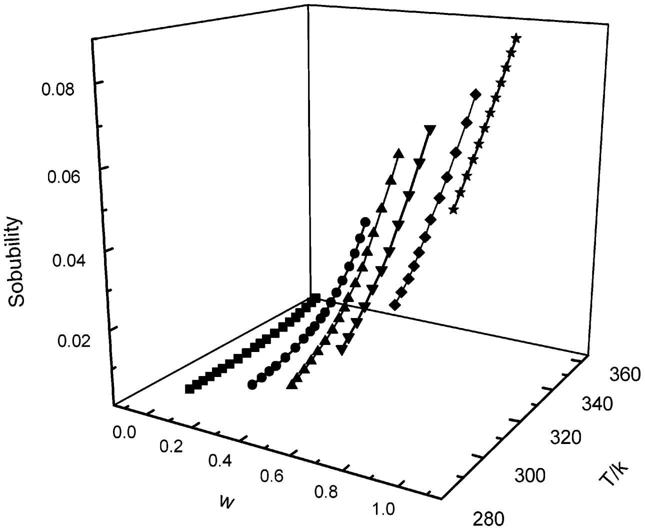

Figure 1. 3-D diagram of solubility of *o*-phthalic acid in methanol + water.

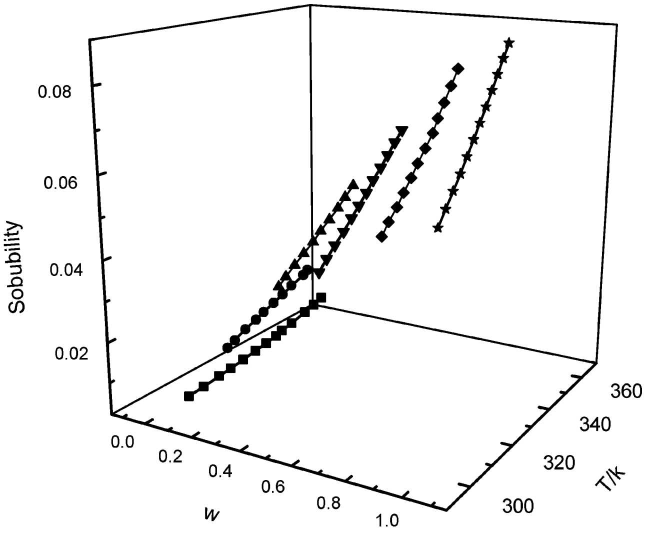

Figure 2. 3-D diagram of solubility of *o*-phthalic acid in methanol + butyl acetate.

Prausnitz[14] pointed out that among the limited temperature range far from the critical temperature, in the real solution the activity quotient of a component hardly depends on the temperature T. Therefore, eq 4 may be approximated as follows:

$$\ln x = D + \frac{E}{T} \tag{5}$$

in which

$$D = \frac{\Delta H_{\mathrm{m}}}{RT_{\mathrm{m}}} - \ln \lambda, \qquad E = -\frac{\Delta H_{\mathrm{m}}}{RT}$$

Equation 5 was used by Wang and co-workers[15,16] in studying the solubility of quinolone medicines and acrylamide where the coherence of experimental values and the predicted values were found to be good.

The coefficients in eq 5 were evaluated by the method of unweighted multivariate least-squares on the solubility data presented in Table 1 and Table 2. The apparent molar enthalpies of *o*-phthalic acid could be worked out by adopting eq 5. The apparent molar enthalpies of *o*-phthalic acid in the methanol + water system (w = 0.0000, 0.1995, 0.3998, 0.5998, 0.7997, and 1.000) are (36.15, 46.47, 38.14, 25.80, 19.29, and 13.24) kJ·mol^{-1}, respectively. Similarly, the apparent molar enthalpies of *o*-phthalic acid in the methanol + butyl acetate system (w = 0.0000, 0.1997, 0.3992, 0.6001, 0.8000, and 1.000) are (23.10, 9.99, 10.65, 11.22, 12.68, and 13.24) kJ·mol^{-1} , respectively.

From the experimental results, it can be seen that apparent molar enthalpy of *o*-phthalic acid in a pure solvent such as water or butyl acetate is large, but when a second solvent is added, the apparent molar enthalpy changes. As to the methanol + water system, when it is pure water (w = 0.0000), the apparent molar enthalpy is 36.15 kJ·mol^{-1}; but when methanol is added in, the apparent molar enthalpy increases and then decreases with the increment of the amount of methanol until a value of 13.24 kJ·mol^{-1} (w = 1.000, pure methanol) is obtained. As to the methanol + butyl acetate system, when it is pure butyl acetate (w = 0.0000), the apparent molar enthalpy is 23.10 kJ·mol^{-1}; when methanol is added, the apparent molar enthalpy decreases and then increases with the increment of the amount of methanol until a value of 13.24 kJ·mol^{-1} (w = 1.000, pure methanol) is obtained.

Conclusions

The solubility of *o*-phthalic acid in the methanol + water and methanol + butyl acetate systems has been studied. The

Apelblat equation $\ln x = A + B/T + C \ln T$ has been used to correlate the experimental data. The apparent molar enthalpy of *o*-phthalic acid in the two systems has been determined, which provides a heat transmission basis for the design of a crystallizer.

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