Solubility of Butanedioic Acid in Different Solvents at Temperatures between 283 K and 333 K

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Using a laser monitoring observation technique, the solubilities of butanedioic acid in water, ethanol, 1-propanol, 2-propanol, acetone, and ethanoic acid were determined by the synthetic method at temperatures between 283 K and 333 K. A laser technique is used to determine the disappearance of solute particles. The experimental data can be well correlated by a semiempirical equation.

Introduction

Butanedioic acid is a white powered crystal produced as an intermediate of the tricarboxylic acid cycle and also as one of the fermentation products of energy metabolism.[1,2] The versatile properties of butanedioic acid make it an important ingredient in the manufacture of various specialty and commodity chemicals.[3] It is purified by crystallization in the final production step. To select the proper solvent and to design an optimized separation process, it is necessary to know its solubility in different solvents. To date, few solubilities of butanedioic acid in solvents have been reported in the literature.[8–10] In this work, the solubilities of butanedioic acid in water, ethanol, 1-propanol, 2-propanol, acetone, and ethanoic acid were experimentally determined using a laser monitoring technique.

Experimental Section

Materials. A white crystalline powder of butanedioic acid (CAS no. 110-15-6) (Powder X-ray Diffraction of the starting material confirmed that this was the butanedioic acid referred to the CCDC reference SUCACBO2) was obtained from Tianjin Kewei Chemical Reagent Co. Ltd. (China) with a melting point of $T = 461$ K measured with a NFTZSCH DSC-204 differential scanning calorimeter. The mass fraction purity is > 0.99. It was dried with molecular sieves before use. The ethanol, 1-propanol, 2-propanol, acetone, and ethanoic acid used for experiments were of analytical reagent grade. Their mass fraction purities are greater than 0.99.

Apparatus and Procedures. Solubility was measured by a synthetic method.[4–6,11] The apparatus for the solubility measurement and the procedure are the same as those described in the literature.[7] As shown in Figure 1, a laser beam was used to determine the dissolution of the solute in the solvent at a fixed temperature. The laser monitoring system consisted of a laser generator, a photoelectric transformer, and a light intensity display. The solubility apparatus consisted of a volume of a 100 cm[3] jacketed glass vessel maintained at a desired temperature by water circulated from a water bath with a digital thermoelectric controller (type CKW-2200, China). The jacket temperature could be maintained within ± 0.05 K of the required temperature. A mercury-in-glass thermometer with an uncertainty of ± 0.05 K was inserted into the inner chambers of the vessels for measurement of the solution temperature. Continuous stirring was achieved with a magnetic stirrer. A condenser was connected with the vessels to prevent the solvents from evaporating. Masses of solute and solvent were weighed using an analytical balance (type FA2004, China) with an accuracy of ± 0.1 mg.

First, predetermined known masses of butanedioic acid and solvent were transferred in the jacketed vessel. Then the contents

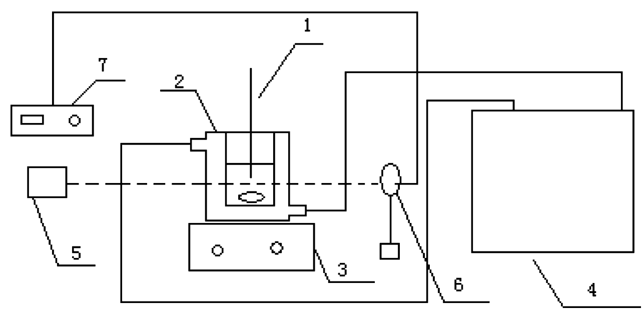

Figure 1. Apparatus for solubility measurements: 1, thermometer; 2, vessel; 3, magnetic stirrer; 4, thermostatic bath; 5, laser generator; 6, photoelectric transformer; 7, light intensity display.

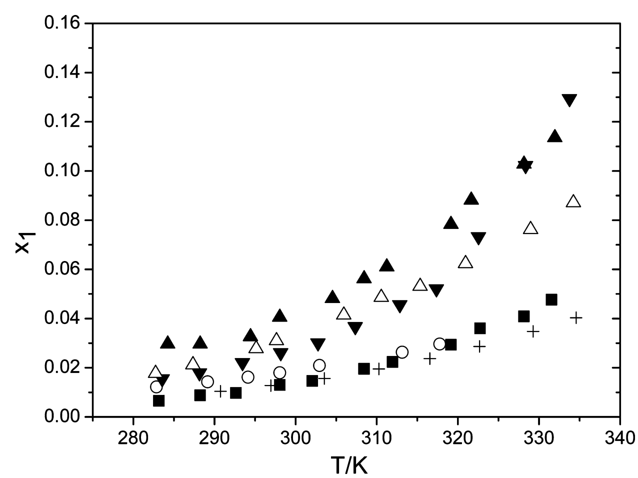

Figure 2. Mole fraction solubility of butanedioic acid in □, water; ○, acetone; ▲, ethanol; ▼, 1-propanol; Δ, 2-propanol; and +, ethanoic acid.

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Table 1. Mole Fraction x_1 Solubility of Butanedioic Acid in Different Solvents As a Function of Temperature T along with Differences from the Calculated Mole Fraction x_{calcd} of Equation 2 with Parameters of Table 2

T/K	$10^3 x_1$	$10^4(x_1 - x_{calcd})$	T/K	$10^3 x_1$	$10^4(x_1 - x_{calcd})$
water					
283.15	6.54	−0.40	311.95	22.35	−2.69
288.25	8.79	4.84	319.15	29.42	−5.28
292.65	9.83	−2.73	322.75	36.02	16.88
298.05	13.05	2.85	328.15	40.90	−10.52
302.05	14.68	−4.34	331.55	47.71	2.41
308.45	19.61	−0.51			
acetone					
282.85	12.26	1.24	302.95	20.95	3.98
289.15	14.30	−0.74	313.15	26.30	−1.77
294.15	16.20	−1.96	317.75	29.65	0.54
298.05	18.01	−1.29			
ethanol					
284.25	29.62	35.97	311.25	61.03	−3.53
288.25	29.67	0.35	319.15	78.25	0.05
294.45	32.64	−35.38	321.65	88.16	37.33
298.05	40.48	−0.97	328.15	102.78	0.73
304.55	48.19	−16.27	331.95	113.53	−15.15
308.45	56.16	−1.13			
1-propanol					
283.55	15.53	−11.28	312.85	45.65	1.40
288.15	17.94	−6.82	317.35	52.14	−39.11
293.45	22.09	4.14	322.55	73.32	9.50
298.15	26.16	8.71	328.35	102.20	42.78
302.75	30.11	2.11	333.75	129.44	−23.14
307.35	36.71	8.14			
2-propanol					
282.75	17.70	0.34	310.55	48.58	15.52
287.35	21.18	−0.84	315.35	53.10	−9.01
295.15	27.78	−6.91	320.95	62.33	−4.99
297.65	31.03	−0.58	328.95	76.21	−4.52
305.95	41.44	5.67	334.25	87.01	4.56
ethanoic acid					
290.75	10.39	0.79	316.55	23.74	−0.33
296.95	12.78	0.66	322.65	28.70	1.13
303.55	15.60	−1.91	329.25	34.78	0.58
310.25	19.53	−0.23	334.55	40.37	−0.71

of the vessel were stirred until the temperature fluctuation varied by less than 0.05 K, and a suitable dose of solute was added so that it did not exceed the solubility too much. Then the solvent was added by an injector. The interval of addition was 1 h. Then known amounts of either solute or solvent were added. When the last portion of solids disappeared, the light penetrating the vessel reached its maximum and the total amounts of solute and solvent were recorded. The saturated mole fraction solubility of solute could be obtained as follows

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \tag{1}$$

where m and M represent mass and mole weight and subscripts 1 and 2 represent solute and solvent, respectively. All the experiments were repeated three times at each temperature, and estimated uncertainties of the experimental values were about 0.5 %.

Results and Discussion

The results of butanedioic acid solubility in different solvents are listed in Table 1. Figure 2 gives the plot of the solubility of butanedioic acid in these solvents at a temperature range of about 283 K to 333 K. In Figure 3, the solubilities of butanedioic acid in water in this work and in the literature by titration[9] and a solid-disappearance method[10] and by an unstated method[8] are compared. The data are consistent with the literature data. The figure 4 shows that the max deviation of the solubilities of butanedioic acid in water in this work and in the literature[8,9] from values calculated is less than 10 %.

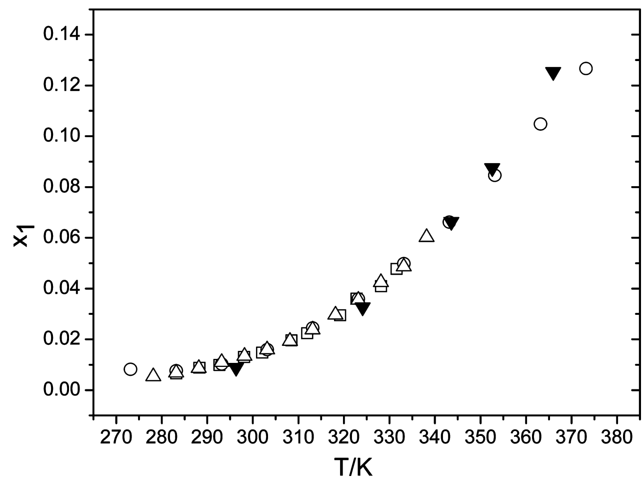

Figure 3. Mole fraction solubility of x_1 of β-butanedioic acid in water: □, experimental data; ○, data in ref 8; Δ, data in ref 9; and ▼, data in ref 10.

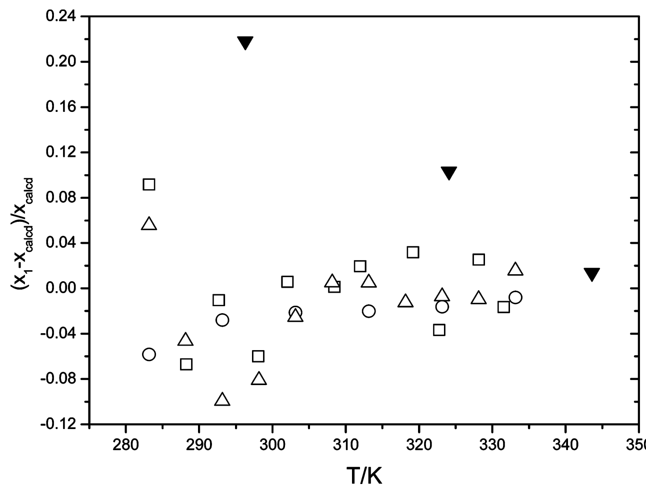

Figure 4. Mole fraction solubility deviations of β-butanedioic acid in water from calculated values: □, experimental data; ○, data in ref 8; Δ, data in ref 9; and ▼, data in ref 10.

The solubility can be correlated by a semiempirical equation[8]

$$\ln x_1 = A + \frac{B}{T/\mathrm{K}} + C \ln(T/\mathrm{K}) \tag{2}$$

where T is temperature and A, B, and C are all empirical constants listed in Table 2. Root-mean-square deviation, rmsd, are defined as follows

Table 2. Parameters of Equation 2 for β-Butanedioic Acid in Different Solvents

solvents	A	B	C	$10^5 \times$ rmsd
water	−25.76	2273.22	5.09	67.068
acetone	−46.68	−146.88	7.17	19.58
ethanol	−83.86	1189.24	13.46	201.12
1-propanol	−592.37	23585.03	89.44	198.3
2-propanol	115.67	−7907.16	−16.25	68.5
ethanoic acid	−38.67	−977.02	6.604	9.338

$$\mathrm{rmsd} = \left[\frac{1}{N}\sum_{i=1}^{N}(x_1^{\mathrm{exp}\ i} - x_1^{\mathrm{calcd}\ i})^2\right]^{1/2} \quad (3)$$

Conclusions

The solubility of butanedioic acid in water, acetone, ethanol, 1-propanol, 2-propanol, and ethanoic acid was determined using a laser monitoring technique. The results show that solubility in six solvents increases as temperature rises, but the increment with temperature varies according to different solvents. The solubilities of butanedioic acid in water in this work are consistent with the literature data.[8–10] The calculated solubility data are proved to be in fine agreement with experimental values, inferring that the correlated equation in our work could provide essential data for manufacturing and purifying processes in industry.

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