Solubility of Fumaric Acid in Propan-2-ol, Ethanol, Acetone, Propan-1-ol, and Water

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The solubility of fumaric acid in propan-2-ol, ethanol, acetone, and propan-1-ol was measured by a synthetic method at temperatures ranging from (279 to 352) K at atmospheric pressure. The laser monitoring observation technique was used to determine the disappearance of the solid phase in a solid + liquid mixture. The results of these measurements were correlated by a modified Apelblat equation.

Introduction

Fumaric acid [CAS No.110-17-8] (*trans*-butenedioic acid) is a dicarboxylic acid and is one of the most important acidulent agents in the food industry.[1] In addition, fumaric acid has important practical applications in the polymer industry and in medicine, in particular as antifungicides and as a counterion for salt formation.[2]

It is well-known that crystallization processes are the critical steps that determine the quality of the final product, and crystallization in organic solvents is often employed in the manufacture of pharmaceuticals and chemical products. The solubility data of solid compounds in different solvents play a crucial role in the development and operation of crystallization processes. In industrial manufacture, fumaric acid is crystallized from solution in the purification step. The published works relating to fumaric acid are mainly concerned with synthesis, degradation, and application study. Descamps studied the solubility of fumaric acid in some common organic solvents and in mixtures of the latter with ether or benzene at 293 K.[3] To the best of our knowledge, there are no systematic solubility studies available on fumaric acid in organic solvents. To choose proper solvents and to design an optimized crystallizer, it is necessary to know its solubility in different solvent systems.

In this paper, the solubility of fumaric acid in propan-2-ol, ethanol, acetone, and propan-1-ol from (279 to 352) K was measured. The experimental data were correlated by the modified Apelblat equation.[4]

Experimental Section

A white powdered crystal of fumaric acid was used, and its mass fraction purity was higher than 99.0 %. Powder X-ray diffraction confirmed that the fumaric acid was the α polymorph.[5] The solvents used (purchased from Tianjin Kewei Co. of China) were of analytical reagent grade, and their mass fraction purity is more than 99.5 %.

The solubility of fumaric acid in different solvents was measured by a synthetic method which is described in the literature.[6−8] During the measurement, predetermined excess amounts of solute and solvent of known masses were transferred to the equilibrium vessel. The uncertainty in temperature was ± 0.05 K. The contents of the vessel were stirred continuously at the required temperature for 30 min. Then, additional solvent of known mass was introduced into the cell. When the last portion of solute just disappeared, the intensity of the laser beam penetrating the vessel reached the maximum, and the solvent mass added in the measurement would be recorded. Together with the mass of solute, the solubility would be obtained, and the saturated mole fraction solubility of fumaric acid was calculated.

Table 1. Mole Fraction Solubility of Fumaric Acid in Different Solvents

T/K	$x_1 \cdot 10^3$	$100(x_1 - x_1^{calcd})/x_1$	T/K	$x_1 \cdot 10^3$	$100(x_1 - x_1^{calcd})/x_1$
Propan-1-ol			Propan-2-ol		
279.00	8.470	−9.24	279.00	10.92	−11.1
285.00	10.25	−3.56	285.00	13.78	−3.90
291.00	12.17	0.07	291.00	16.85	0.30
297.00	14.25	2.09	297.00	20.23	3.05
303.00	16.48	3.05	303.00	23.59	3.42
309.00	18.91	3.15	309.00	27.25	3.38
315.00	21.52	2.56	315.00	30.97	2.17
321.00	24.33	1.37	321.00	34.92	0.56
327.00	27.36	−0.34	327.00	39.10	−1.33
333.00	30.62	−2.46	333.00	43.48	−3.58
339.00	35.46	−1.08	342.00	53.79	−0.81
345.00	39.84	−2.70	351.00	65.62	1.27
351.80	48.59	2.28			
Ethanol			Acetone		
279.00	12.56	0.73	279.00	3.437	−1.53
285.00	14.03	−0.95	285.00	4.191	0.03
291.00	15.68	−2.47	291.00	4.985	0.49
297.00	17.83	−2.16	297.00	5.831	0.53
303.00	20.50	−0.75	303.00	6.730	0.30
309.00	23.28	−0.40	309.00	7.677	0.09
315.00	26.66	0.88	315.00	8.671	−0.21
321.00	30.49	2.04	321.00	9.722	−0.28
327.00	34.41	2.03	327.00	10.83	−0.16
333.00	38.31	0.75	333.00	12.00	0.26
343.00	45.11	−2.77			
Water			Water		
279.00	0.136	−17.57	315.00	2.650	−0.01
285.00	0.435	−15.13	321.00	3.283	0.71
291.00	0.813	−11.35	327.00	4.148	3.56
297.00	1.252	−10.24	333.00	5.412	9.83
303.00	1.711	−1.08	339.00	6.235	4.73
309.00	2.213	3.29	353.00	8.835	−4.59

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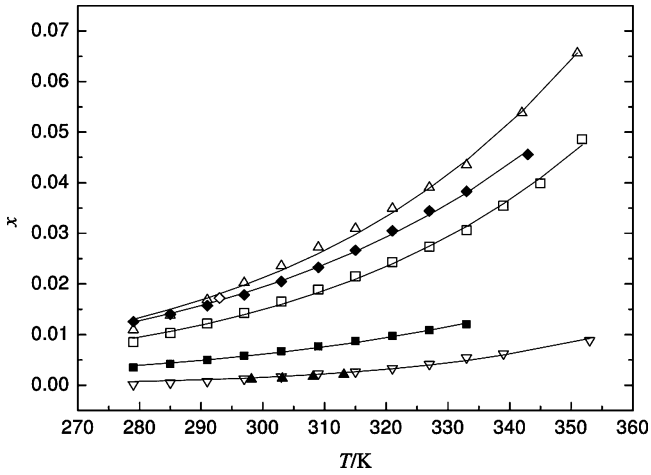

Figure 1. Mole fraction solubility of fumaric acid in different solvents from (279 to 352) K. Δ, propan-2-ol; ◆, ethanol; □, propan-1-ol; ■, acetone; ∇, water; ▲, water in the literature;[1] ◇, ethanol in the literature.[3]

Table 2. Curve-Fitting Parameters of Fumaric Acid in Different Solvents

solvent	*A*	*B*	*C*	10^2 rmsd
propan-1-ol	−82.553	1765.6	12.704	3.396
propan-2-ol	−14.644	−1427.4	2.7256	4.005
ethanol	−52.635	557.16	8.2111	1.658
acetone	91.278	−6166.9	−13.288	0.565
water	−96.630	630.24	15.413	1.217

All the experiments were conducted three times, and the mean values were used to calculate the mole fraction solubility. The relative uncertainty of the experimental solubility values is within 0.05.

Results and Discussion

The measured solubility of fumaric acid from (279 to 352) K is listed in Table 1 and graphically plotted in Figure 1. To verify the uncertainty of the measurement, the solubility of fumaric acid in water in this work was measured and compared with the literature data.[1] Compared with the literature data, the relative deviation of the solubility was lower than 0.05. x_1 is the experimental solubility, and x_1^{calcd} is the calculated solubility in Table 1. The solubility data of fumaric acid are described by the modified Apelblat equation.

$$\ln x = A + B/T\,(\text{K}) + C \ln T\,(\text{K}) \qquad (1)$$

where x is the mole fraction solubility of fumaric acid; T is the absolute temperature; and A, B, and C are the model parameters. The values of parameters A, B, and C and the root deviation (rmsd) are listed in Table 2. The rmsd is defined as

$$\text{rmsd} = \left\{\frac{1}{N}\sum_{i=1}^{N}(x_i^{\text{calcd}} - x_i)^2\right\}^{1/2} \qquad (2)$$

where N is the number of experimental points.

Conclusions

From Tables 1 and 2 and Figure 1, we can draw the following conclusions: (1) The solubility of fumaric acid in 2-propanol, ethanol, acetone, and *n*-propanol is a function of temperature, and it increases with an increase in temperature. (2) The solubility of fumaric acid in four solvents basically ranks as propan-2-ol > ethanol > propan-1-ol > acetone. (3) The calculated solubility of fumaric acid is in good agreement with the experimental values, and the experimental solubility and correlation equation in this work can be used as essential data and models in the crystallization for fumaric acid.

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