Short Articles

Solubility of Sebacic Acid in Binary Water + Ethanol Solvent Mixtures

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Solubilities of sebacic acid in binary ethanol + water solvent mixtures were measured by the dynamic method using a laser monitoring observation technique at a temperature range from (288 to 352) K. The mole fraction of ethanol in the solvent mixtures ranges from 0 to 1. The melting temperature and enthalpy of fusion of sebacic acid were determined by differential scanning calorimetry. The experimental results show that the slope of the solubility−temperature curve increases significantly with an increase in the mole fraction of ethanol in the solvent. The Wilson equation is applied to describe measured systems. The model parameters of the Wilson equation were expressed as a function of temperature.

Introduction

Sebacic acid $C_{10}H_{18}O_4$ (CASRN 111-20-6) is a white powdered crystal, which is extremely valuable in the production of nylon, alkyd resins, plasticizers, lubricants, and cosmetics, etc.[1–4] Presently, sebacic acid is manufactured from the caustic fusion of castor oil in China. China is the second largest castor oil producer after India.[5] However, this process depends on natural product castor oil and thus has problems in the purity of the sebacic acid. To purify sebacic acid, solubilities of sebacic acid in various solvents are needed, but limited information is available in the literature on the solubility of sebacic acid. Bonhomme[6] reported solubility data for sebacic acid in ethanol + water binary mixtures at 298 K, and the mass fraction contents of ethanol in the binary mixtures were 0 %, 20 %, 40 %, 60 %, 80 %, 90 %, and 100 %. During the experiment, trace HCl (10^{-3}N) was added to the ethanol + water binary mixtures to prevent ionization of sebacic acid. Tudorovskaya[7] determined solubility data of sebacic acid in water at temperatures ranging from (346.1 to 386.3) K by the visual polythermal method in a sealed glass ampuls. In this paper, the solubilities of sebacic acid in ethanol + water binary mixtures have been measured by a dynamic method at a temperature range from (288 to 352) K. The experiment data were correlated with the Wilson equation.

Experimental Section

Materials. The purity of sebacic acid purchased from Hengshui Dongfeng Chemical Co. Ltd., Hebei, China, was 99.4 %. This obtained solid was recrystallized several times from hot water and stored over silica gel after drying in a dryer at 360 K to remove water. The purity of sebacic acid used in the solubility measurements was higher than 99.8 % as analyzed by GC. Ethanol had a purity of 99.9 %. It was purchased from Guangfu Chemical Reagents Co., Tianjin, China, and was used without further purification.

Apparatus and Procedure. The solubility was determined by the dynamic method.[8–10] A jacketed glass vessel (several vessels with a volume of (100 to 250) mL were chosen according to solubility) was used to determine the solubility. Water was forced to continuous circulation from a refrigerated/heating circulator (Julabo FP45-HE, Germany, temperature stability ± 0.01 K) to the jacket of the vessel to maintain the temperature. The temperature was measured by a platinum resistance thermometer Pt-100, which was calibrated with an uncertainty of 0.01 K. The masses of the solid and solvents were determined using an analytical balance (Gibertini, Crystal 200, Italy, uncertainty of 0.1 mg) and placed in the inner chamber of the vessel. To prevent the evaporation of the solvent, a condenser was connected on the top of the vessel, and the open end of the condenser was sealed by a rubber plug.

A predetermined sample was heated slowly with continuous stirring. At the same time, the laser monitoring system was run to detect the intensity of the laser beam penetrating the vessel. As the solid dissolved with the temperature increase, the intensity of the laser beam increased gradually. The temperature at which the solid disappeared and the intensity of the laser beam reached a maximum was taken as the solid–liquid equilibrium temperature of the sample. The sample would be heated at less than $0.2\ \text{K}\cdot\text{h}^{-1}$ at near the solid–liquid equilibrium temperature. The measurement procedure was repeated two times, and the uncertainty of measured T was ± 1 K. Mixtures were prepared by weighing the pure components with an uncertainty of ± 1 mg.

Melting temperature, molar enthalpy of fusion, and solid–solid phase transitions of sebacic acid have been measured with the differential scanning calorimetry Perkin-Elmer Pyris Diamond at $5\ \text{K}\cdot\text{min}^{-1}$. Measurements were performed in triplicate.

Result and Discussion

The experimental solubility data of sebacic acid (1) in ethanol (2) + water (3) solvent mixtures are listed in Table 1, where T^{exptl} is the measured absolute temperature; x_1 is mole fraction solubility; and x_2 is mole fraction of ethanol in the solution. Figure 1 is a plot of the experiment results as x_1 versus temperature at different ethanol mole fractions of solute-free.

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An equation for the calculation of solid–liquid phase equilibrium can be derived from the isofugacity criterion. The equation which includes the first-order solid–solid phase transition is

$$-\ln x_1\gamma_1 = \frac{\Delta H_{\mathrm{m1}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{m1}}}\right) + \frac{\Delta H_{\mathrm{tr1}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{tr1}}}\right) - \frac{\Delta Cp_{\mathrm{m1}}}{R}\left(\ln\frac{T}{T_{\mathrm{m1}}} + \frac{T_{\mathrm{m1}}}{T} - 1\right) \quad (1)$$

where T, x_1, η_1, T_{m1}, ΔH_{m1}, ΔH_{tr1}, and ΔCp_{m1} stand for equilibrium temperature, mole fraction of solute, activity coefficient, melting temperature, enthalpy of fusion at melting temperature, enthalpy of solid–solid phase transition, temperature of phase transition, and difference in solute heat capacity between the solid and liquid at the melting temperature, respectively.

The melting temperature and fusion enthalpy of sebacic acid were observed to be $T_{\mathrm{ml}} = (405.62 \pm 0.02)$ K and $\Delta H_{\mathrm{m1}} = (45.3 \pm 0.7)$ kJ·mol^{-1}. The number after the symbol "±" is the uncertainty of the measurement for the melting temperature or fusion enthalpy of sebacic acid, which is calculated from three times measurement results. These data are similar with the result reported by James.[11] However, no solid–solid phase transition has been observed in present study, which is different from a previous report.[11] In addition, the contributions of the heat capacities are neglected. Therefore, the following simplified equation can be obtained[12]

$$-\ln x_1\gamma_1 = \frac{\Delta H_{\mathrm{m1}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{m1}}}\right) \quad (2)$$

Table 1. Experimental Mole Fraction Solubilities of Sebacic Acid (1) in Binary Ethanol (2) + Water (3) Solvent Mixtures

10^2x_2	10^3x_1	T^{exptl}/K	Δ/K	10^2x_2	10^3x_1	T^{exptl}/K	Δ/K
0.000	0.03622	321.95	0.28	26.07	72.41	346.55	−1.31
0.000	0.06372	327.45	0.05	25.57	90.06	351.35	−1.10
0.000	0.08783	329.44	−2.53	60.56	7.184	288.85	−0.65
0.000	0.09386	331.61	−0.44	60.37	10.21	293.85	−1.10
0.000	0.1212	334.01	−1.58	60.27	11.95	296.35	−1.16
0.000	0.1524	336.96	−1.65	60.08	15.05	300.45	−1.05
0.000	0.1716	339.68	−0.20	59.85	18.69	304.05	−1.13
0.000	0.2095	341.72	−1.20	59.49	24.62	309.35	−0.99
0.000	0.2372	343.83	−0.81	59.20	29.38	313.45	−0.58
0.000	0.2606	347.40	1.80	59.01	32.56	315.35	−0.68
0.000	0.3169	350.20	1.57	58.34	43.46	321.65	−0.50
8.354	0.04101	302.05	−0.20	57.69	54.12	325.95	−0.89
8.353	0.1365	310.55	0.06	56.76	69.38	331.55	−0.98
8.353	0.2406	315.65	−0.49	56.56	72.65	333.35	−0.41
8.352	0.3314	319.85	0.28	55.70	86.74	337.55	−0.39
8.351	0.4481	323.55	0.50	55.23	94.46	339.25	−0.67
8.350	0.587 0	325.65	−0.48	54.57	105.3	342.45	−0.14
8.348	0.7989	328.35	−1.20	53.13	129.0	347.75	0.24
8.346	1.057	331.95	−0.80	52.44	140.2	350.35	0.81
8.343	1.401	334.85	−0.88	51.71	152.2	352.75	1.24
8.338	1.964	337.95	−1.03	51.33	158.4	353.45	0.98
8.332	2.689	341.55	−0.47	98.77	12.28	289.75	0.82
8.323	3.756	344.65	−0.21	98.49	15.08	293.22	0.37
8.307	5.738	348.25	0.08	98.22	17.84	296.45	0.20
8.286	8.267	350.15	−0.43	98.08	19.23	298.15	0.24
8.246	12.98	352.75	−1.07	97.70	23.01	301.61	0.07
28.07	1.076	288.65	−1.24	97.32	26.76	304.52	−0.10
28.07	1.205	290.15	−1.28	97.10	29.01	307.33	0.41
28.05	1.672	293.45	−1.75	96.69	33.12	309.95	0.25
28.04	2.202	296.45	−1.83	96.17	38.30	313.21	0.23
28.02	2.895	299.95	−1.47	95.63	43.73	315.97	0.04
28.00	3.654	302.95	−1.07	94.81	51.94	320.31	0.12
27.95	5.200	307.75	−0.27	94.22	57.79	322.90	0.07
27.91	6.624	310.95	0.20	93.59	64.13	325.42	−0.02
27.89	7.484	312.75	0.52	92.82	71.82	328.18	−0.16
27.83	9.649	316.25	0.97	91.94	80.60	331.73	0.13
27.80	10.70	317.75	1.15	91.02	89.76	334.38	−0.07
27.60	17.83	324.75	1.35	90.14	98.56	336.53	−0.37
27.38	25.66	329.75	0.91	89.08	109.2	339.11	−0.60
26.96	40.69	336.85	0.11	88.24	117.6	341.19	−0.64
26.52	56.15	342.05	−0.74				

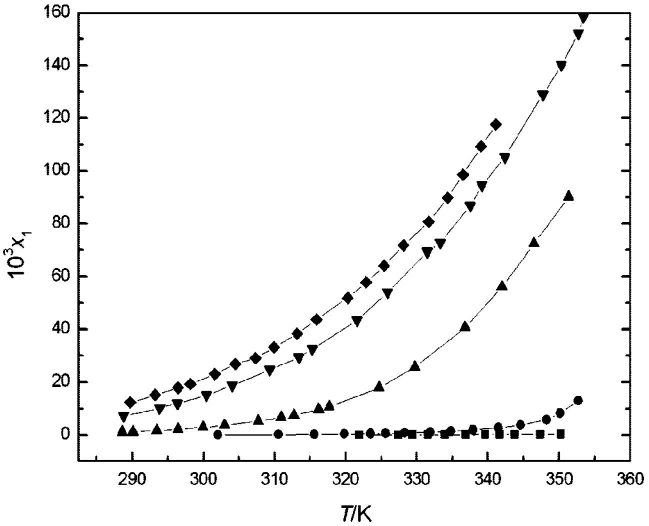

Figure 1. Mole fraction solubilities x_1 of sebacic acid in binary ethanol + water solvent mixtures. Mole fraction of ethanol of solute-free is: ■, 0 %; ●, 8.355 %; ▲, 28.11 %; ▼, 60.99 %; ♦, 100 %.

Table 2. Model Parameters of the Wilson Equation for Sebacic Acid (1) Solubilities in Binary Ethanol (2) + Water (3) Solvent Mixtures (Defined by Equation 4)

	$\Delta_{1,2}$	$\Delta_{2,1}$	$\Delta_{1,3}$	$\Delta_{3,1}$	$\Delta_{2,3}$	$\Delta_{3,2}$
$a_{i,j}$	−0.041688	−6.8047	0.021375	−2.5584	0.13470	−10.015
$b_{i,j}$/K	15.123	3606.0	−6.5783	1201.0	−0.68996	3660.3

In this study, the Wilson equation is used to calculate the activity coefficient[13]

$$\ln\gamma_i = 1 - \ln\left(\sum_j^n(\Lambda_{i,j}x_j)\right) - \sum_k^n\left(\frac{\Lambda_{k,i}x_k}{\sum_j^n(\Lambda_{k,j}x_j)}\right) \quad (3)$$

where n is the number of components in the mixture. $\Delta_{i,j}$ is a the model parameter which is expressed by

$$\Lambda_{i,j} = a_{i,j} + b_{i,j}/T \quad (4)$$

The model parameters were determined using the Nelder−Mead simplex method. The objective function in the Nelder−Mead simplex method was the root-mean-square deviation σ between the experimental equilibrium temperature and the calculated equilibrium temperature which is defined by

$$\sigma = \left[\sum_{i=1}^N(T^{\mathrm{exptl}} - T)^2/(N-1)\right]^{0.5} \quad (5)$$

where N is number of experimental data points; T^{exptl} is the experimental equilibrium temperature which is listed in Table 1; and T is the calculated equilibrium temperature which is calculated from eq 2 to eq 4.

The model parameters of the Wilson equation are listed in Table 2. The temperature deviations between experimental temperature and calculated temperature ($\Delta = T^{\mathrm{exptl}} - T$) are listed in Table 1.

Figure 1 shows that the slope of the solubility−temperature curve increases significantly with an increase in the ethanol mole fraction of solute-free. The solubility of sebacic acid in ethanol is much higher than the solubility of sebacic acid in water and increases with the temperature more quickly. When the ethanol content in the solvent mixtures increases, sebacic acid solubility increases and also the slope of the solubility−temperature curve increases. The existence of ethanol has an apparent influence on the solubility of sebacic acid in the measured temperature range. From the data listed in Table 1, the calculated temperatures show good agreement with the experimental values, and the σ of all experimental data is 0.88 K. The Wilson equation model parameters listed in Table 2 can be used to predict the solubility of sebacic acid in ethanol aqueous solutions.

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