Solubility of Ethyl Maltol in Aqueous Ethanol Mixtures

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With a laser monitoring observation technique, the solubility of ethyl maltol in binary aqueous ethanol solvent mixtures in the temperature range of 293.15 K to 333.15 K was measured by a synthetic method. The solubility data were correlated with the combined nearly ideal binary solvent/Redlich−Kister (CNIBS/R−K) model. For the nine group data studied, the CNIBS/R−K model was found to provide an accurate mathematical representation of the experimental data.

Introduction

Ethyl maltol (CAS registry no. 4940-11-8) is 2-ethyl-3-hydroxy-4-pyrone. Figure 1 shows its molecular structure. It is a white or almost white crystalline powder and has a sweet odor that can be described as caramelized sugar and cooked fruit. An important flavor enhancer and stabilizer, it is widely used in the food, beverage, tobacco, and fragrance industries. Ethyl maltol is nontoxic, very pleasant to the human sense of smell, and 4 to 6 times more potent than maltol.[1]

Ethyl maltol is normally prepared by various synthesis methods.[2−5] In the final purification step of the production process, it is recrystallized from solution. Binary aqueous ethanol mixtures are the most often used solvents for the crystallization of ethyl maltol. In the synthesis and purification process of ethyl maltol, it is necessary to know the solubility data of ethyl maltol in the related solvents. However, a review of the literature on ethyl maltol indicated that only fragmentary solubility data were reported.[1] No systematic experimental solubility data of ethyl maltol in aqueous ethanol solvents were available. In this work, the solubilities of ethyl maltol in binary aqueous ethanol solvent mixtures were experimentally determined in the temperature range of 293.15 K to 333.15 K using a laser monitoring observation technique. The method employed in this work was classified as a synthetic method and was much faster and easier than the analytical method.[6]

Experimental Section

Materials. A white crystalline powder of ethyl maltol, with a melting temperature of 364.17 K was obtained from Beijing Tianlihai Chemical Industry. (The melting temperature of ethyl maltol was measured with a Netzsch STA 449C differential scanning calorimeter, and the experimental results conform to the literature values[1] of 362.15 K to 366.15 K.) Its purity was determined by UV spectrophotometry (UV-2401PC, Shimadzu) to be 0.997 in mass fraction. Ethanol was an analytical research grade reagent from Tianjin Chemical Reagent, and distilled deionized water of HPLC grade was used.

Apparatus and Procedure. The solubility was determined by the use of an apparatus similar to that described in the literature[7] and described only briefly here. A 100 mL jacked vessel was used to determine the solubility; the temperature was controlled to be constant (fluctuates within 0.05 K) through a thermostatted bath with an uncertainty of ± 0.05 K. The dissolution of the solute was examined by the laser beam penetrating the vessel. To prevent the evaporation of the solvent, a condenser vessel was introduced. The masses of the samples and solvents were determined by the use of an analytical balance (AUY220, Shimadzu) with an uncertainty of ± 0.0001 g.

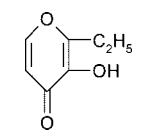

Figure 1. Chemical structure of ethyl maltol.

The solubility of ethyl maltol was determined by the laser method.[8−14] During experiments, the fluid in the glass vessel was monitored by a laser beam. Predetermined excess amounts of ethyl maltol and solvent of known mass were placed in the inner chamber of the jacked vessel. The contents of the vessel were stirred continuously at a required temperature, and the solvent was simultaneously added to the vessel. When the last portion of solute had just disappeared, the intensity of the laser beam penetrating the vessel reached the maximum, and the solvent mass consumed in the measurement was recorded. Together with the mass of the solute, the solubility was obtained. The same solubility experiment was conducted three times, and the mean values were used to calculate the mole fraction solubility, x_1, based on eq 1. The composition of solvent mixtures, x_2, is defined as eq 2.

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2 + m_3/M_3} \tag{1}$$

$$x_2 = \frac{m_2/M_2}{m_2/M_2 + m_3/M_3} \tag{2}$$

where m_1, m_2, and m_3 represent the mass of the solute, ethanol, and water, respectively, and M_1, M_2, and M_3 represent the molecular weight of the solute, ethanol, and water, respectively.

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Table 1. Mole Fraction Solubility (x_1) of Ethyl Maltol in Binary Ethanol (2) + Water (3) Solvent Mixtures in the Temperature Range of 293.15 K to 333.15 K

x_2	x_1	$10^3(x_1 - x_1^{calc})$	x_2	x_1	$10^3(x_1 - x_1^{calc})$	x_2	x_1	$10^3(x_1 - x_1^{calc})$
				$T = 293.15$ K				
0.0000	0.0021	0.0000	0.4771	0.0246	−0.0001	0.8814	0.0776	−0.0009
0.1435	0.0115	0.0004	0.6100	0.0462	0.0018	0.9504	0.0715	0.0009
0.2811	0.0246	−0.0009	0.7787	0.0624	−0.0012	1.0000	0.0599	−0.0001
				$T = 298.15$ K				
0.0000	0.0023	0.0000	0.4771	0.0648	−0.0005	0.8814	0.0930	−0.0015
0.1435	0.0152	0.0001	0.6100	0.0799	0.0010	0.9504	0.0902	0.0014
0.2811	0.0373	−0.0002	0.7787	0.0928	0.0000	1.0000	0.0798	−0.0015
				$T = 303.15$ K				
0.0000	0.0027	0.0000	0.4771	0.0847	−0.0022	0.8814	0.1126	−0.0031
0.1435	0.0216	0.0002	0.6100	0.1023	0.0030	0.9504	0.1097	0.0012
0.2811	0.0540	−0.0002	0.7787	0.1142	0.0006	1.0000	0.0974	0.0002
				$T = 308.15$ K				
0.0000	0.0033	0.0000	0.4771	0.1185	−0.0008	0.8814	0.1620	0.0008
0.1435	0.0319	0.0001	0.6100	0.1341	0.0011	0.9504	0.1486	−0.0018
0.2811	0.0804	−0.0002	0.7787	0.1551	−0.0003	1.0000	0.1329	0.0009
				$T = 313.15$ K				
0.0000	0.0040	0.0000	0.4771	0.1672	−0.0034	0.8814	0.1871	−0.0074
0.1435	0.0466	0.0006	0.6100	0.1761	0.0005	0.9504	0.1811	−0.0049
0.2811	0.1221	−0.0003	0.7787	0.1987	0.0096	1.0000	0.1739	0.0048
				$T = 318.15$ K				
0.0000	0.0051	0.0000	0.4771	0.2200	−0.0084	0.8814	0.2445	−0.0054
0.1435	0.0733	0.0013	0.6100	0.2271	0.0069	0.9504	0.2340	−0.0083
0.2811	0.1878	−0.0005	0.7787	0.2426	0.0061	1.0000	0.2272	0.0067
				$T = 323.15$ K				
0.0000	0.0067	−0.0001	0.4771	0.2856	−0.0082	0.8814	0.3126	−0.0091
0.1435	0.1182	0.0055	0.6100	0.2808	0.0113	0.9504	0.3020	−0.0112
0.2811	0.2699	−0.0105	0.7787	0.3024	0.0067	1.0000	0.2907	0.0100
				$T = 328.15$ K				
0.0000	0.0089	−0.0001	0.4771	0.3592	−0.0164	0.8814	0.3968	−0.0184
0.1435	0.1573	0.0053	0.6100	0.3577	0.0142	0.9504	0.3857	−0.0145
0.2811	0.3636	−0.0064	0.7787	0.3976	0.0163	1.0000	0.3669	0.0140
				$T = 333.15$ K				
0.0000	0.0126	−0.0002	0.4771	0.4495	−0.0204	0.8814	0.4724	−0.0238
0.1435	0.1976	0.0094	0.6100	0.4490	0.0210	0.9504	0.4649	−0.0200
0.2811	0.4370	−0.0144	0.7787	0.4799	0.0200	1.0000	0.4594	0.0198

One other experiment was done in our previous work[8] to verify the uncertainty of the measurement, and it is estimated that the uncertainty in the solubility values is less than 1 %.

Results and Discussion

The solubilities of ethyl maltol in aqueous ethanol mixtures in the temperature range of 293.15 K to 333.15 K are presented in Table 1.

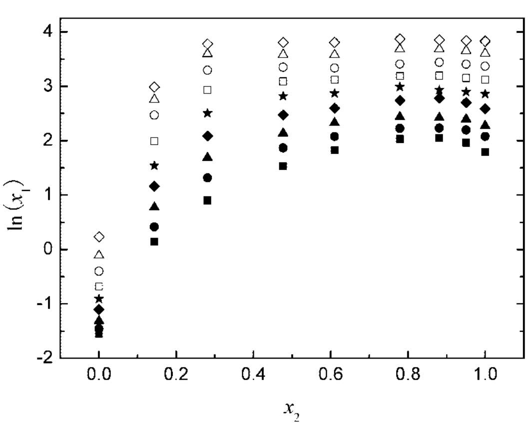

Figure 2. Solubilities of ethyl maltol in binary ethanol (2) + water (3) solvent mixtures: ■, 293.15 K; ●, 298.15 K; ▲, 303.15 K; ◆, 308.15 K; ★, 313.15 K; □, 318.15 K; ○, 323.15 K; △, 328.15 K; ◇, 333.15 K.

Table 2. Parameters of Equation 4 for Ethyl Maltol in Binary Ethanol (2) + Water (3) Solvent Mixtures in the Temperature Range of 293.15 K to 333.15 K

T/K	B_0	B_1	B_2	B_3	B_4	10^3(RMSD)
293.15	−6.1424	15.4627	−32.6746	36.3883	−15.8464	0.9416
298.15	−6.0626	17.5415	−36.5826	37.3772	−14.7977	0.8532
303.15	−5.9176	19.9132	−44.4478	46.3925	−18.2715	1.7799
308.15	−5.7084	22.2793	−53.4035	58.2048	−23.3973	0.9200
313.15	−5.5099	23.9834	−57.2243	60.0299	−23.0558	5.0946
318.15	−5.2777	26.7546	−67.8664	73.2421	−28.3644	6.1278
323.15	−4.9910	29.1098	−78.3448	87.4680	−34.5122	9.2640
328.15	−4.7066	29.4572	−80.5206	90.9747	−36.2461	13.9167
333.15	−4.3555	27.7929	−74.4864	82.6379	−32.4110	19.0585

The solubility data in binary ethanol + water solvent mixtures are described by the combined nearly ideal binary solvent/Redlich−Kister (CNIBS/R−K) model. Acree and coworkers[15−17] suggested the CNIBS/R−K model

$$\ln x_1 = x_2 \ln(x_1)_2 + x_3 \ln(x_1)_3 + x_2 x_3 \sum_{i=0}^{N} S_i (x_2 - x_3)^i \quad (3)$$

as a possible mathematical representation for describing how the experimental isothermal solubility of a crystalline solute dissolved in a binary solvent mixture varies with binary solvent composition. S_i is the model constant, and N can be equal to 0, 1, 2, or 3. Depending on the value of N, four equations can be obtained from eq 3. x_2 and x_3 refer to the initial mole fraction composition of the binary solvent, which was calculated as if the solute was not present, and $(x_1)_i$ is the saturated mole fraction solubility of the solute in pure solvent i. When $N = 2$, eq 3 can be written as eq 4

$$\ln x_1 = B_0 + B_1 x_2 + B_2 x_2^2 + B_3 x_2^3 + B_4 x_2^4 \qquad (4)$$

where N is the number of experimental points, $x_{1,i}^{\text{calc}}$ is the solubility calculated from eq 4; and $x_{1,i}$ is the experimental value of solubility.

The experimental solubility data correlate with eq 4, and the difference between experimental and calculated results ($x_1 - x_1^{\text{calc}}$) is also listed in Table 1. For the comparison of each of the experimental points, the values of the solubilities of ethyl maltol in binary ethanol + water solvent mixtures in the temperature range of 293.15 K to 333.15 K are presented in Figure 2. The values of the five parameters B_0, B_1, B_2, B_3, and B_4 are listed in Table 2 together with the root-mean-square deviations (RMSDs). The RMSD is defined as

$$\text{RMSD} = \left[\frac{\sum_{i=1}^{N}\left(x_{1,i} - x_{1,i}^{\text{calc}}\right)^2}{N-1}\right]^{\frac{1}{2}} \qquad (5)$$

From Tables 1 and 2 and Figure 2, the following conclusions can be drawn: (1) The solubility of ethyl maltol in binary ethanol + water solvent mixtures is a function of temperature, and solubility increase with an increase of temperature. (2) With increase of ethanol in the solvent mixture, the solubility experiences a sharp increase at first, after the slow increase, then a slow decline. In other words, there is a maximum peak in the isothermal solubility curve with an increase of the composition of solvent mixtures x_2. (3) These experimental data can be regressed by eq 4 for each solvent mixture. The experimental solubility and correlation equation in this work can be used as essential data and models in the purification process of ethyl maltol.

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