Solubility of Erythritol in Different Solvents

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The solubilities of erythritol in different solvents were measured using a synthetic method. The laser monitoring observation technique was used to determine the disappearance of the solid phase in a solid + liquid mixture. The effect of solvent composition and temperature on the solubility was discussed. The solubility data was correlated with an empirical equation.

Introduction

Erythritol is 1,2,3,4-butanetetrol. It is a white crystalline powder that is odorless, with a clean sweet taste that is similar to sucrose. It is approximately 70% as sweet as sucrose and flows easily because of its nonhygroscopic character. Erythritol is a good-tasting bulk sweetener that is suitable for a variety of reduced-calorie and sugar-free foods. Since 1990, erythritol has been commercially produced and added to foods and beverages to provide sweetness as well as to enhance their taste and texture. Erythritol has a high digestive tolerance, is safe for people with diabetes, and does not promote tooth decay.[1] In industrial manufacturing, erythritol is crystallized from solution in the purification step. To determine the proper solvent and to design an optimized crystallizer, it is necessary to know its solubility in different solvents.[2] However, from a review of the literature on erythritol, it was found that only solubilities in water were available. No experimental solubility data of erythritol in aqueous + organic solvents has been reported. The scarcity of basic solubility data hinders progress in the design of production flow processes or the expansion of production capacity. In the production of erythritol, water is often used as a solvent and ethanol, methanol, and acetone may be used as washing solvents. Therefore, in this work the solubilities of erythritol in pure water, methanol, ethanol, and acetone and in methanol + water and ethanol + water mixed solvents were measured using a synthetic method. The effects of temperature and solvent composition on the solubility of erythritol were studied. The experimental solubility data was correlated with an empirical equation.

Methods of measuring the solubility of a solid in a liquid mixture can be classified as analytical and synthetic.[3,4] The advantage of the analytical method lies in the possibility of measuring a large number of samples simultaneously with a reliable method. The disadvantage is that it is tedious and time-consuming. The synthetic method involves weighing or measuring the individual components to obtain a system with a known composition; the state in which the solid phase just disappears is then determined for this system. The disappearance of the solid phase can be achieved either by a change in the temperature or by the addition of a known amount of solvent. With synthetic methods, solubility data can be obtained much faster and more readily.[5−7] In this work, the last crystal disappearance method, a synthetic method, was used to determine the solubility data of erythritol in different solvents.

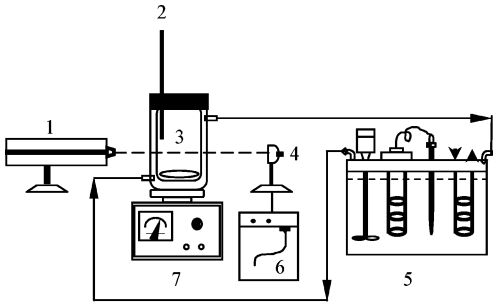

Figure 1. Schematic diagram of the apparatus: (1) laser generator; (2) thermometer; (3) equilibrium cell; (4) photoelectric transformer; (5) thermostat; (6) recorder; (7) magnetic stirrer.

Experimental Sections

Materials. A white crystalline powder of erythritol, with a melting point of (126 ± 0.5) °C, was prepared by recrystallization from aqueous solution. Its mass fraction purity, determined by HPLC, is higher than 99.8%. It was dried in vacuo at 50 °C for 24 h and stored in a desiccator. Methanol, ethanol, and acetone used for experiments were of analytical reagent grade. They were dehydrated with molecular sieves, and their mass fraction purity was higher than 99.8%, as determined by gas chromatography. Distilled deionized HPLC-grade water was used.

Apparatus and Procedure. The solubility of erythritol was measured by the last crystal disappearance method. The laser monitoring observation technique was used to determine the disappearance of the last crystal in solid + liquid mixture. A schematic diagram of the apparatus used is shown in Figure 1. Detailed information about the experimental apparatus has been reported in a previous study.[7] The laser monitoring system consists of a laser generator, a photoelectric transformer, and a recorder. The equilibrium cell is a cylindrical double-jacketed glass vessel. A constant desired temperature was maintained by circulating water through the outer jacket from a thermostat. The cell has a perforated rubber cover plate to prevent the

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Table 1. Solubility of Erythritol in Pure Solvents

water			methanol			ethanol			acetone		
T/K	S^{exptl}	S^{calcd}	T/K	$10S^{exptl}$	$10S^{calcd}$	T/K	10^2S^{exptl}	10^2S^{calcd}	T/K	10^3S^{exptl}	10^3S^{calcd}
288.85	0.2987	0.2879	287.35	0.1639	0.1554	287.55	0.3464	0.3845	286.35	0.3098	0.3096
298.85	0.3579	0.3663	291.15	0.1687	0.1663	289.75	0.3719	0.3790	292.05	0.3890	0.4268
303.35	0.3966	0.4012	294.65	0.1825	0.1867	293.75	0.4213	0.4128	296.55	0.5487	0.5657
308.05	0.4319	0.4374	297.95	0.2218	0.2150	299.45	0.5547	0.5588	301.45	0.8385	0.7636
312.15	0.4646	0.4687	302.25	0.2806	0.2651	303.45	0.8320	0.7300	305.05	0.9286	0.9399
316.65	0.5073	0.5030	307.65	0.3594	0.3491	307.15	0.9519	0.9388	310.75	1.3010	1.2726
323.35	0.5587	0.5535	310.25	0.3876	0.3979	312.65	1.3456	1.3387	314.75	1.5262	1.5450
328.35	0.5960	0.5908	313.50	0.4615	0.4666	317.95	1.8095	1.8253	318.15	1.6889	1.8026
332.85	0.6281	0.6242	318.00	0.5760	0.5758	322.75	2.3567	2.3519	321.45	2.0689	2.0746
338.15	0.6649	0.6632	320.00	0.6254	0.6296	325.35	2.5738	2.6712	324.45	2.3393	2.3410
346.20	0.7230	0.7219	322.75	0.7231	0.7089	335.95	4.1785	4.2206	328.35	2.7474	2.7146
350.55	0.7520	0.7532	327.35	0.8621	0.8551	339.15	4.8504	4.7665			
354.25	0.7769	0.7798									

Table 2. Solubility of Erythritol in Ethanol (1) + Water (2) Mixed Solvents

$w_1 = 24.62\%$			$w_1 = 49.76\%$			$w_1 = 74.91\%$		
T/K	S^{exptl}	S^{calcd}	T/K	S^{exptl}	S^{calcd}	T/K	$10S^{exptl}$	$10S^{calcd}$
288.35	0.1856	0.1897	287.35	0.1010	0.1001	286.15	0.3667	0.3774
293.95	0.2379	0.2376	290.25	0.1216	0.1172	291.05	0.4659	0.4579
297.65	0.2679	0.2692	293.55	0.1360	0.1376	294.95	0.5481	0.5476
303.45	0.3168	0.3186	297.85	0.1654	0.1656	299.25	0.6819	0.6726
309.75	0.3705	0.3721	303.95	0.2083	0.2084	305.85	0.9194	0.9180
317.05	0.4351	0.4338	310.35	0.2562	0.2568	312.75	1.2358	1.2438
321.25	0.4675	0.4692	317.55	0.3205	0.3159	319.95	1.6493	1.6593
325.15	0.5016	0.5019	326.35	0.3969	0.3945	324.35	1.9516	1.9511
332.95	0.5659	0.5672	333.15	0.4592	0.4601	329.15	2.3092	2.3024

Table 3. Solubility of Erythritol in Methanol (1) + Water (2) Mixed Solvents

$w_1 = 25.11\%$			$w_1 = 49.76\%$			$w_1 = 75.54\%$		
T/K	S^{exptl}	S^{calcd}	T/K	S^{exptl}	S^{calcd}	T/K	$10S^{exptl}$	$10S^{calcd}$
287.55	0.1852	0.1891	308.57	0.1156	0.1174	288.75	0.4874	0.4987
293.05	0.2335	0.2320	314.45	0.1549	0.1534	294.75	0.6570	0.6269
296.29	0.2562	0.2578	318.85	0.1825	0.1833	297.65	0.7691	0.7155
299.15	0.2803	0.2810	322.35	0.2083	0.2088	301.4	0.8312	0.8558
304.85	0.3279	0.3281	327.15	0.2461	0.2465	304.25	1.0327	0.9819
309.95	0.3720	0.3715	332	0.2883	0.2875	308.95	1.2829	1.2264
315.25	0.4184	0.4176	334.95	0.3147	0.3140	311.25	1.3478	1.3627
319.95	0.4622	0.4596	337.15	0.3370	0.3344	314.45	1.5960	1.5706
325.95	0.5136	0.5144	342.15	0.3841	0.3833	318.35	1.8973	1.8525
329.55	0.5466	0.5480	347.15	0.4352	0.4354	322.15	2.2185	2.1574
						328.05	2.6586	2.6899

Table 4. Parameters of Equation 1 for Erythritol in Different Solvents

					ethanol (1) + water (2) mixed solvents			methanol (1) + water (2) mixed solvents		
	water	methanol	ethanol	acetone	$w_1 = 24.62\%$	$w_1 = 49.76\%$	$w_1 = 74.91\%$	$w_1 = 25.11\%$	$w_1 = 49.76\%$	$w_1 = 75.54\%$
A	−2.4699	3.3093	1.4859	0.07897	−2.4900	2.2230	5.7612	−0.3094	4.5160	8.2250
10^3B	11.200	−23.060	−10.244	−0.5642	10.010	−20.540	−41.282	−4.2100	−34.250	−58.140
10^6C	−5.7210	40.360	17.701	1.0110	−2.4860	45.770	74.368	20.670	64.800	103.30
10^3rmsd	5.0510	0.8915	0.5066	0.04974	1.8490	2.4020	0.7293	1.7610	1.2380	4.0320

solvent from evaporating, through which a mercury thermometer with an uncertainty of ±0.05 K was inserted into the inner chamber of the vessel. The mixtures of solute and solvent in the vessel were stirred with a magnetic stirrer. The masses of the solvent and solute were weighed using an analytical balance with an accuracy of ±0.0001 g.

In experiments, erythritol solid and solvent of known masses were transferred into the equilibrium vessel. The solid + liquid mixture was maintained at a fixed temperature for about 1 h. Then the solid + liquid mixtures were heated slowly at rates of less than 2 K·h^{-1} with continuous stirring. This procedure was repeated until the last crystal disappeared completely. This process lasts more than 5 h. In an early stage of the experiment, the laser beam was blocked by the undissolved particles of erythritol in the solution, so the intensity of the laser beam penetrating the vessel was low. The intensity increased gradually along with the increase in the amount of erythritol dissolved. When the last portion of erythritol disappeared, the intensity of the laser beam penetrating the vessel reached a maximum. The temperature was recorded as the saturation temperature of erythritol, and the mass fraction solubility was calculated. The same solubility experiment was conducted two times. To verify the reliability of this experiment, we compared the experimental solubility of erythritol in pure water at 25 °C with literature data.[8,9] The experimental and literature mass fraction solubilities are 35.8% and about 37%, respectively. The difference is less than 3%. The estimated uncertainty in the solubility measurement is about 4%.

Results and Discussion

The solubility data of erythritol in pure water, methanol, ethanol, and acetone are presented in Table 1. The solubility of erythritol in ethanol + water mixed solvents is presented in Table 2. The solubility of erythritol in metha-

nol + water mixed solvents is presented in Table 3. The temperature dependence of erythritol solubility in different solvents was correlated with the equation[4]

$$S = A + B(T/\mathrm{K}) + C(T/\mathrm{K})^2 \quad (1)$$

where S is the mass fraction solubility of erythritol, T is the absolute temperature, and A, B, and C are the parameters. Calculated solubility values of erythritol are also given in Tables 1 to 3. The values of parameters A, B, and C and the root-mean-square deviations (rmsd's) are listed in Table 4. The rmsd is defined as

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

where N is the number of experimental points, S_i^{calcd} represents the solubilities calculated from eq 1, and S_i^{exptl} represents the experimental values of solubility.

From data listed in Tables 1 to 3, it can be seen that the solubility of erythritol in various solvents increases with increasing temperature. The solubility of erythritol in pure water is higher than in other pure solvents and mixed solvents. The solubility of erythritol in pure acetone is the minimum. In the ethanol + water and methanol + water mixed solvents, the existence of ethanol and methanol has an apparent influence on the solubilities of erythritol. The solubility of erythritol in ethanol + water and methanol + water mixed solvents decreases with increasing ethanol or methanol content at constant temperature. From Table 4, it was found that the calculated solubilities of erythritol in different solvents show good agreement with the experimental values. This shows that eq 1 is appropriate to describe the temperature dependence of the solubility of erythritol.

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