Solubility of Acesulfame Potassium in Ethanol + Water and Methanol + Water Systems from (275.84 to 322.90) K

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The solubilities of acesulfame potassium in pure solvents and mixed 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. All data were measured at atmospheric pressure and temperatures ranging from (275.84 to 322.90) K. The effect of solvent composition and temperature on the solubility was discussed. The experimental data were correlated with an empirical equation.

Introduction

Acesulfame potassium, a potassium salt of 3,4-dihydro-6-methyl-1,2,3-oxathiazine-4-one-2,2-dioxide, is a high-intensity calorie-free artificial sweetener. It is a white crystalline powder with a molecular formula of $C_4H_4NO_4KS$ and a molecular weight of 201.24. It is not metabolized by the body and is excreted unchanged. It was approved for use by the FDA in 1988 and has been evaluated 8 times for safety. Acesulfame potassium is about 200 times sweeter than sucrose or about half as sweet as aspartame or saccharin. Its taste is generally considered to be good. Under most processing and storage conditions used for foods and beverages, it seems to be virtually stable. No adverse reactions or unacceptable losses in sweetness have been observed. Acesulfame potassium is currently used in food, beverage, oral hygiene, and pharmaceutical products in about 90 countries. It can be used alone or in combination with other sweeteners (i.e., aspartame).[1,2]

In industrial manufacturing, acesulfame potassium is crystallized from aqueous solution in the purification step. Ethanol or methanol solvent may be used as washing liquor to wash filter cake. To design an optimized crystallization process and crystallizer, it is necessary to know its solubility in pure water, ethanol, methanol, and their mixed solvents. However, from a review of the literature on acesulfame potassium, it was found that only rough data in pure water and ethanol were available. No experimental solubility data of acesulfame potassium in pure methanol and ethanol + water or methanol + water solvents have been reported. The scarcity of basic solubility data hinders progress in the design of production flow processes or the expansion of production capacity. Therefore, in this work, the solubilities of acesulfame potassium in pure water, ethanol, methanol, and ethanol + water and methanol + water mixed solvents were measured using a synthetic method. As we know, methods of measuring the solubility of a solid in a liquid mixture can be classified as analytical and synthetic. Compared with the analytical method, the synthetic method is much faster and more readily produces solubility data. 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.[3–10] In this work, the last crystal disappearance method, a synthetic method, was used to determine the solubility data of acesulfame potassium in different solvents. The disappearance of the solid phase is achieved by changing the temperature. The effects of temperature and solvent composition on the solubility of acesulfame potassium were studied. The experimental solubility data were correlated with an empirical equation.

Experimental Section

Materials. Acesulfame potassium, a white crystal with a melting point of (229 ± 0.5) °C, was supplied by Jiangsu Haobo Co., Ltd. It was recrystallized twice from aqueous solution. It was dried in a vacuum oven for 12 h at 50 °C and stored in a desiccator. Its mass fraction purity, determined by HPLC, is higher than 0.995. The ethanol used is analytical reagent grade from Tianjin Chemical Reagent Co. of China. Its mass fraction purity was higher than 0.998, as determined by gas chromatography. Distilled–deionized HPLC-grade water was used.

Apparatus and Procedure. The solubility of acesulfame potassium was measured by the last crystal disappearance method. The laser monitoring observation technique was used to determine the disappearance of the last crystal in the solid + liquid mixture. The experimental apparatus consists of an equilibrium cell, a magnetic stirrer, a thermostat, and a laser monitoring system. 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 (60 mL). It was maintained at the desired temperature through circulating water through the outer jacket from the thermostat. A condenser was fitted to reduce the solvent's evaporation. A thermometer with an uncertainty of ± 0.01 K was used to determine the temperature of the system. The magnetic stirrer (type CJJ79-1) was used to stir the mixture of solute and solvent in the vessel. A laser beam generated by the laser generator was used to observe the dissolving process. The signal penetrating through the vessel was transferred to the recorder by the photoelectric transformer.

The masses of solute and the solvent were weighed using an electronic analytic balance (type AB204-N) with an uncertainty of ± 0.0001 g. The maximum weighing mass of the balance

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Table 1. Solubility of Acesulfame Potassium in Pure Solvents

water			methanol			ethanol		
T/K	10^2X^{exptl}	10^2X^{calcd}	T/K	10^3X^{exptl}	10^3X^{calcd}	T/K	10^4X^{exptl}	10^4X^{calcd}
277.98	1.5120	1.5895	277.70	1.5585	1.5712	277.10	1.2259	1.0389
281.23	1.6726	1.7319	281.79	1.7293	1.7063	282.39	1.5369	1.2777
284.73	1.8612	1.8978	286.10	1.8883	1.8623	287.47	1.7592	1.5573
288.35	2.0718	2.0841	290.39	2.0489	2.0328	292.30	2.0000	1.8782
294.90	2.4935	2.4624	294.20	2.2217	2.1981	297.55	2.2600	2.3002
298.02	2.7061	2.6631	298.51	2.3752	2.4022	302.65	2.5865	2.7980
301.03	2.9203	2.8703	302.21	2.5555	2.5932	307.90	2.9968	3.4196
304.01	3.1422	3.0893	307.80	2.8831	2.9121	312.93	3.9632	4.1399
307.07	3.3773	3.3295	311.39	3.1287	3.1380	317.87	4.9616	4.9895
310.24	3.6288	3.5955	315.47	3.4064	3.4166	322.90	6.3400	6.0275
313.53	3.8969	3.8914	319.30	3.7142	3.7010			
317.30	4.1910	4.2567	322.80	4.0093	3.9819			
322.30	4.7443	4.7878						

Table 2. Solubility of Acesulfame Potassium in Ethanol (1) + Water (2) Mixed Solvents[a]

$w_1 = 0.19897$			$w_1 = 0.39755$			$w_1 = 0.50016$		
T/K	10^2X^{exptl}	10^2X^{calcd}	T/K	10^2X^{exptl}	10^2X^{calcd}	T/K	10^2X^{exptl}	10^2X^{calcd}
278.11	0.94829	0.94768	277.70	0.76145	0.80069	275.84	0.64122	0.73655
282.97	1.1857	1.1900	280.29	0.92190	0.90195	281.04	0.83043	0.87707
286.79	1.4024	1.4067	285.70	1.1525	1.1407	286.03	1.0191	1.0349
290.14	1.6243	1.6160	289.87	1.3596	1.3505	290.05	1.1816	1.1808
293.87	1.8710	1.8701	293.75	1.5660	1.5660	293.77	1.3542	1.3326
297.73	2.1548	2.1559	297.05	1.7755	1.7646	297.75	1.5450	1.5148
301.76	2.4824	2.4780	300.72	1.9958	2.0015	301.75	1.7681	1.7210
306.16	2.8536	2.8553	304.06	2.2274	2.2315	306.09	2.0274	1.9738
310.58	3.2609	3.2586	307.47	2.4849	2.4796	310.91	2.3290	2.2947
314.97	3.6800	3.6798	311.42	2.7779	2.7827	315.70	2.6653	2.6609
318.63	4.0388	4.0438	315.31	3.0949	3.0962	320.95	3.0528	3.1237
321.64	4.3549	4.3501	321.77	3.6591	3.6449			

$w_1 = 0.59933$			$w_1 = 0.70031$			$w_1 = 0.79947$		
T/K	10^3X^{exptl}	10^3X^{calcd}	T/K	10^3X^{exptl}	10^3X^{calcd}	T/K	10^3X^{exptl}	10^3X^{calcd}
278.20	6.1391	6.2443	278.95	4.4003	4.3721	281.73	1.9686	2.2276
283.50	7.5936	7.5710	285.06	5.3059	5.3534	288.50	2.8449	2.8235
287.39	8.7623	8.6782	288.70	6.0091	6.0307	294.15	3.4415	3.4346
291.45	9.9918	9.9645	292.13	6.7515	6.7404	298.60	4.0458	4.0029
295.43	11.340	11.365	295.88	7.6551	7.6039	302.75	4.6720	4.6128
299.36	12.921	12.892	299.90	8.6631	8.6420	306.41	5.2486	5.2232
303.67	14.754	14.743	303.69	9.7226	9.7387	309.55	5.9089	5.8075
307.57	16.575	16.586	307.53	10.930	10.979	313.11	6.6131	6.5452
311.87	18.774	18.817	311.35	12.352	12.357	315.85	7.1894	7.1727
316.72	21.562	21.598	315.45	14.032	14.011	318.33	7.7886	7.7897
321.87	24.918	24.877	321.68	16.886	16.918	321.27	8.4450	8.5865

[a] w_1 is the mass fraction of ethanol in the mixed solvents in the table.

Table 3. Solubility of Acesulfame Potassium in Methanol (1) + Water (2) Mixed Solvents[a]

$w_1 = 0.20144$			$w_1 = 0.39899$			$w_1 = 0.60080$			$w_1 = 0.79817$		
T/K	10^3X^{exptl}	10^3X^{calcd}	T/K	10^3X^{exptl}	10^3X^{calcd}	T/K	10^3X^{exptl}	10^3X^{calcd}	T/K	10^3X^{exptl}	10^3X^{calcd}
277.55	9.1088	10.372	278.70	7.9299	8.5410	277.85	5.4923	5.9062	278.63	3.0102	3.1302
282.10	11.173	12.023	283.67	9.5289	10.090	281.50	6.5721	6.6516	283.06	3.6636	3.6044
286.30	13.161	13.769	286.85	10.971	11.215	286.65	7.7806	7.8603	287.77	4.2471	4.1780
289.55	15.138	15.285	291.25	12.888	12.965	290.15	8.8983	8.8001	291.93	4.7723	4.7508
292.95	17.218	17.042	295.69	15.177	14.987	294.05	10.092	9.9753	295.55	5.3228	5.3051
296.46	19.383	19.059	300.17	17.677	17.323	297.65	11.350	11.193	299.25	5.9259	5.9305
299.15	21.512	20.758	304.39	20.337	19.830	300.57	12.395	12.285	301.99	6.4764	6.4352
302.59	23.745	23.143	308.00	22.713	22.239	304.45	13.874	13.896	306.05	7.1803	7.2536
305.97	26.333	25.740	311.60	25.259	24.910	307.97	15.606	15.531	309.50	7.9785	8.0205
309.81	29.684	29.030	315.05	27.839	27.748	311.63	17.598	17.427	313.09	8.8693	8.8945
314.43	33.904	33.520	318.19	30.458	30.590	315.80	19.855	19.858	316.50	9.8527	9.8023
318.50	37.984	38.019	321.45	33.180	33.826	319.83	22.281	22.514	320.40	10.957	10.941
322.40	41.688	42.867				321.72	23.873	23.873	322.30	11.529	11.537

[a] w_1 is the mass fraction of methanol in the mixed solvents in the table.

was 210 g. The estimated uncertainty in the mole fraction was less than 0.001.

The solubilities of acesulfame potassium in pure water, ethanol, methanol, and ethanol + water and methanol + water mixed solvents were measured as follows. Predetermined amounts of solute and solvents were placed into the jacketed vessel. At the beginning of the experiment, the solute was excessive. So some undissolved particles of acesulfame potassium existed. The mixture was heated slowly at rates of less than 2 $K \cdot h^{-1}$ with continuous stirring. In the early stage of the experiment, the laser beam was blocked by the undissolved particles of acesulfame potassium 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

Table 4. Parameters of Equation 2 for Acesulfame Potassium in Different Solvents[a]

	water	methanol	ethanol	methanol (1) + water (2) mixed solvents			
				$w_1 = 0.20144$	$w_1 = 0.39899$	$w_1 = 0.60080$	$w_1 = 0.79817$
$10A$	−5.2946	−9.3347	−12.799	−9.6397	−8.1764	−10.013	−5.7833
10^3B	0.30600	2.3258	2.4153	1.7181	1.0127	1.8447	0.072535
C	8.4768	13.955	19.577	15.222	13.031	15.703	9.2020
10^4 rmsd	4.5375	0.22915	0.22639	6.8456	4.0443	1.6011	0.52496

	ethanol (1) + water (2) mixed solvents					
	$w_1 = 0.19897$	$w_1 = 0.39755$	$w_1 = 0.50016$	$w_1 = 0.59933$	$w_1 = 0.70031$	$w_1 = 0.79947$
$10A$	20.986	17.857	−7.7294	1.7197	−7.5080	−9.9837
10^3B	−12.194	−10.752	0.83336	−3.3733	0.72271	1.6034
C	−30.326	−25.714	12.342	−1.8030	11.908	15.607
10^4 rmsd	0.39280	1.4441	4.6917	0.48592	0.32158	0.99446

[a] w_1 is the mass fraction of solvent (1) in the mixed solvents in the table.

acesulfame potassium dissolved. When the last particles of the solute disappeared completely, the intensity of the laser beam penetrating the vessel reached a maximum. The temperature was recorded as the saturation temperature of the acesulfame potassium solution at a given composition. The mass fraction solubility was calculated.

The saturated mole fraction solubility of the solute (x_A) in binary ethanol (methanol) + water solvent mixtures can be obtained as follows

$$x_A = \frac{m_A/M_A}{m_A/M_A + m_B/M_B + m_C/M_C} \tag{1}$$

where m_A, m_B, and m_C are the masses of solute, ethanol (methanol), and water, respectively. M_A, M_B, and M_C are the molecular weights of solute, ethanol (methanol), and water, respectively. The same solubility experiment was performed three times.

Results and Discussion

The experimental mole fraction solubility data of acesulfame potassium in pure water, ethanol, and methanol are presented in Table 1. The solubilities of acesulfame potassium in ethanol + water and methanol + water mixed solvents are presented in Table 2 and Table 3, respectively. The temperature dependence of acesulfame potassium solubility in different solvents was correlated by the modified Apelblat equation[11]

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

where x is the mole fraction solubility of acesulfame potassium; T (K) is the absolute temperature, and A, B, and C are the model parameters. The calculated solubility values of acesulfame potassium are also given in Tables 1 to 3. The values of parameters A, B, and C and root-mean-square deviations (rmsd) are listed in Table 4. The rmsd is defined as

$$\mathrm{rmsd} = \left\{\frac{1}{N}\sum_{i=1}^{N}(X_i^{\mathrm{calcd}} - X_i^{\mathrm{exptl}})^2\right\}^{1/2} \tag{3}$$

where N is the number of experimental points; X_i^{calcd} represents the solubility calculated from eq 2; and X_i^{exptl}represents the experimental solubility values.

From data listed in Tables 1 to 3, it can be seen that the solubility of acesulfame potassium in various solvents increases with increasing temperature. The solubility of acesulfame potassium in pure water is higher than in other pure solvents and mixed solvents. The solubility of acesulfame potassium in pure ethanol is the minimum. In the ethanol + water and methanol + water mixed solvents, the existence of ethanol or methanol has an apparent influence on the solubility of acesulfame potassium. The solubility of acesulfame potassium in ethanol + water and methanol + water mixed solvents decreases with increasing ethanol and methanol content at constant temperature. According to the principle of "like dissolves like", acesulfame potassium which is a kind of strong polar solute dissolves well in strong polar solvent. The polar order of solvent is water > methanol > ethanol, so the solubility of acesulfame potassium decreases as one moves from water to methanol and ethanol. From Table 1 to 3, it was found that the calculated solubility of acesulfame potassium showed good agreement with the experimental values. This shows that eq 2 is appropriate to describe the temperature dependence of the solubility of acesulfame potassium.

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