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Solubility of Sodium 4-Nitrobenzenesulfonate in Binary Sodium Chloride + Water, Sodium Sulfate + Water, and Ethanol + Water Solvent Mixtures at Elevated Temperatures

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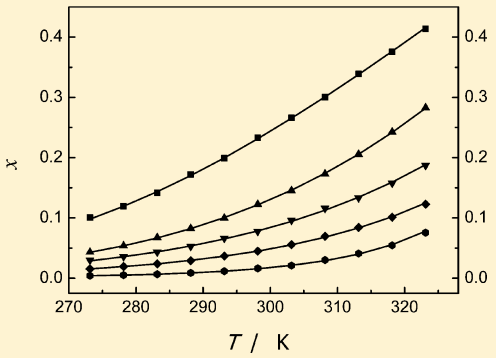
ABSTRACT: The solubilities of sodium 4-nitrobenzenesulfonate in binary sodium chloride + water, sodium sulfate + water, and ethanol + water solvent mixtures were measured with temperatures ranging from (273.15 to 323.15) K by a steady-state method. Results of these measurements were correlated by a modified Apelblat equation. Sodium chloride + water was found to be the best solvent mixture for purifying sodium 4-nitrobenzenesulfonate.



INTRODUCTION

As one of the most important aromatic compounds, high-purity sodium 4-nitrobenzenesulfonate is widely used in nucleophilic substitution reactions,[1] controlling the mode of polymorphic transition,[2] and the effect of ionic liquids on a class of charge-neutral nucleophiles is also studied.[3] It is in general produced by the sulfonation of nitrobenzene with concentrated sulfuric acid. The isomeric mixtures are formed in various proportions of sodium 3-nitrobenzenesulfonate and sodium 4-nitrobenzenesulfonate with this method. The entire usage requires purified sodium 4-nitrobenzenesulfonate product. It is very difficult to separate sodium 4-nitrobenzenesulfonate at a high purity from this reaction product mixture. High-purity sodium 4-nitrobenzenesulfonate can be separated from the mixture of isomeric sodium nitrobenzenesulfonate by recrystallization from sodium chloride, sodium sulfate, or ethanol aqueous solution. To purify sodium 4-nitrobenzenesulfonate using a simple method, measurements of the solubility data of sodium 4-nitrobenzenesulfonate in binary sodium chloride + water, sodium sulfate + water, and ethanol + water solvent mixtures are needed. Although the solubility of sodium 4-nitrobenzenesulfonate in sodium chloride, sodium sulfate, and ethanol aqueous solution is very important to the separation process, to the best of the authors' present knowledge, the solubility of sodium 4-nitrobenzenesulfonate has not been reported in literature.[4,5] In this work, we measure the solubility of sodium 4-nitrobenzenesulfonate in binary sodium chloride + water, sodium sulfate + water, and ethanol + water solvent mixtures using the steady-state method with the temperature range from (273.15 to 323.15) K.[6−8] The data are correlated by a modified Apelblat equation.

EXPERIMENTAL SECTION

Chemicals. Sodium 4-nitrobenzenesulfonate was purchased from YuanCheng Chemical Co. Ltd. (China) with a mass fraction of 0.995 and used without further purification. Sodium chloride and sodium sulfate, with a mass fraction of 0.996 and 0.998, respectively, were purchased from the factory chemical reagent in Shenyang. Ethanol was obtained from Shanghai Chemical Reagent Co. and had a mass purity of 0.999, which was used without further purification. The water used to prepare solutions was twice-distilled water (conductivity <5 $\mu S \cdot cm^{-1}$).

Apparatus and Procedure. A 125 mL Erlenmeyer flask is filled with 50 mL of deionized water and placed into a constant-temperature bath. The water temperature was controlled by a constant-temperature water bath (Neslab, model RTE-101) recirculated through a copper coil in the water bath with an uncertainty of 0.01 K. A condenser was connected to the flask to prevent the water from evaporating. The water was stirred using a Teflon-coated magnetic stirring bar. Excess solute was placed into flask and allowed to equilibrate in a constant temperature water bath at a given temperature for at least 3 days. Aliquots of the liquid phase were taken at 2 h intervals and analyzed using high-performance liquid chromatography (HPLC). When the composition of the liquid became constant, this was taken to indicate that equilibration had been attained. Generally, it took about 11 h to reach equilibrium. At 10 min prior to sampling, stirring was ceased to allow any solid phase to settle. Attainment of equilibrium was verified both by

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Table 1. Mass Fraction Solubility x of Sodium 4-Nitrobenzenesulfonate in $(1 - w)$ Water + w Sodium Chloride between (273.15 and 323.15) K[a]

	w = 0		w = 0.04		w = 0.08		w = 0.15		w = 0.20	
T/K	x_i	10^2 RD	x_i	10^2 RD	x_i	10^2 RD	x_i	10^2 RD	x_i	10^2 RD
273.15	0.1006	2.69	0.0433	1.15	0.0298	2.86	0.0154	−1.30	0.0041	1.05
278.15	0.1194	0.00	0.0538	−0.02	0.0357	0.00	0.0193	0.00	0.0052	−0.39
283.15	0.1417	−1.27	0.0672	0.46	0.0435	−0.69	0.0239	0.04	0.0066	−1.31
288.15	0.1722	1.10	0.0825	0.10	0.0526	−1.71	0.0290	−2.21	0.0087	−1.34
293.15	0.1990	−0.35	0.0998	−0.85	0.0663	1.93	0.0368	0.79	0.0117	−0.09
298.15	0.2332	0.77	0.1226	0.73	0.0777	−1.03	0.0449	−0.25	0.0162	3.09
303.15	0.2662	0.38	0.1453	−0.54	0.0958	1.52	0.0557	0.63	0.0210	−0.95
308.15	0.3003	−0.20	0.1731	−0.54	0.1158	2.61	0.0695	2.12	0.0301	3.65
313.15	0.3389	0.24	0.2054	−0.19	0.1332	−0.89	0.0842	0.96	0.0411	2.58
318.15	0.3755	−0.24	0.2426	0.37	0.1575	−1.19	0.1012	−0.89	0.0545	−2.15
323.15	0.4137	−0.44	0.2829	0.32	0.1870	−0.69	0.1227	−1.69	0.0756	−3.04

[a]RD = $(x_i - x_i^{calc})/x_i$; w, mass fraction.

Table 2. Mass Fraction Solubility x of Sodium 4-Nitrobenzenesulfonate in $(1 - w)$ Water + w Sodium Sulfate between (273.15 and 323.15) K

	w = 0.04		w = 0.08		w = 0.15		w = 0.20	
T/K	x_i	10^2 RD	x_i	10^2 RD	x_i	10^2 RD	x_i	10^2 RD
273.15	0.0430	−0.63	0.0244	1.80	0.0127	−0.79	0.0049	2.97
278.15	0.0515	0.06	0.0312	0.03	0.0170	0.00	0.0069	−0.14
283.15	0.0599	−3.17	0.0399	−0.25	0.0222	−0.90	0.0101	2.51
288.15	0.0731	−2.12	0.0517	1.93	0.0286	−2.10	0.0134	−2.99
293.15	0.0917	1.15	0.0637	0.19	0.0385	1.74	0.0191	1.05
298.15	0.1152	3.96	0.0785	−0.38	0.0493	1.64	0.0252	−1.75
303.15	0.1400	2.99	0.0948	−2.08	0.0612	−0.78	0.0341	−0.03
308.15	0.1700	1.48	0.1174	−0.33	0.0788	1.10	0.0445	−0.43
313.15	0.2051	−1.18	0.1403	−1.24	0.0988	1.21	0.0585	1.40
318.15	0.2545	−1.37	0.1717	1.13	0.1189	−2.15	0.0745	1.07
323.15	0.3151	−2.17	0.2036	1.07	0.1498	−0.37	0.0919	−1.09

Table 3. Mass Fraction Solubility x of Sodium 4-Nitrobenzenesulfonate in $(1 - w)$ Water + w Ethanol between (273.15 and 318.15) K

	w = 0.08		w = 0.17		w = 0.35		w = 0.54		w = 0.70	
T/K	x_i	10^2 RD	x_i	10^2 RD	x_i	10^2 RD	x_i	10^2 RD	x_i	10^2 RD
273.15	0.0619	−1.45	0.0514	1.69	0.0478	2.09	0.0411	−0.97	0.0394	−0.51
278.15	0.0799	0.05	0.0655	0.03	0.0591	0.02	0.0523	0.00	0.0485	−0.06
283.15	0.1012	1.28	0.0841	1.07	0.0724	−1.70	0.0654	0.61	0.0581	−1.10
288.15	0.1236	0.65	0.1055	1.71	0.0915	1.11	0.0802	0.49	0.0704	−0.14
293.15	0.1477	−0.62	0.1261	−0.71	0.1097	−0.29	0.0975	0.93	0.0849	1.36
298.15	0.1760	−0.61	0.1513	−1.11	0.1335	1.01	0.1132	−2.13	0.0985	−0.19
303.15	0.2054	−1.37	0.1789	−1.33	0.1562	−0.45	0.1369	0.14	0.1149	−0.32
308.15	0.2383	−1.36	0.2083	−1.65	0.1874	1.51	0.1591	−0.50	0.1354	1.18
313.15	0.2764	−0.08	0.2408	−1.26	0.2152	0.09	0.1821	−1.79	0.1552	0.77
318.15	0.3152	0.65	0.2803	1.17	0.2474	−0.32	0.2133	0.37	0.1745	−0.92

repetitive measurements after a minimum of 3 additional days and by approaching equilibrium from supersaturation by preequilibrating the solutions at a higher temperature. After equilibrium was achieved, the liquid phase was taken out, weighed with electronic balance, and then analyzed quantitatively.

Analysis. Aliquots of saturated sodium 4-nitrobenzenesulfonate solutions were transferred into a tarred volumetric flask. The concentration of sodium 4-nitrobenzenesulfonate in aqueous solutions was determined using a Shimadzu-6A high-performance liquid phase chromatograph (HPLC). The chromatographic column used was a unimicro Kromasil C18, 5 μm (250 mm × 4.6 mm) maintained at 308.2 K. The HPLC system consisted of a Shimadzu SPD-6A UV single wavelength spectrophotometric detector set to 270 nm. The mobile phase consists of three eluents which are water, Na_2SO_4, and H_3PO_4. The concentration range from (0 to 1.5) mg·mL^{-1} of analytes was used for the construction of calibration curves. Each analysis was repeated three times, and the average value of the three measurements was considered as the final value of the analysis.[9,10] The mass fraction solubility (x) was calculated based on

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$$x = \frac{m_1}{m_1 + m_2 + m_3} \quad (1)$$

where m_1 represents the mass of sodium 4-nitrobenzenesulfonate, m_2 represents the mass of sodium chloride, sodium sulfate, or ethanol, and m_3 represents the mass of water.

The uncertainty of the experimental solubility values is about 2.0 %. The uncertainty in the solubility can be due to uncertainties in the temperature measurements and weighing procedure.

RESULTS AND DISCUSSION

The measured solubilities of sodium 4-nitrobenzenesulfonate in aqueous solutions of sodium chloride, sodium sulfate, and ethanol are presented in Tables 1, 2, and 3, respectively. The corresponding solubility curves are shown in Figures 1, 2, and

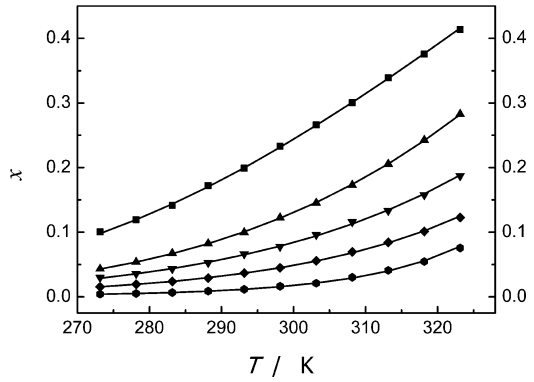

Figure 1. Solubility x of sodium 4-nitrobenzenesulfonate in aqueous solutions of sodium chloride at different temperatures: ■, w = 0 NaCl; ▲, w = 0.04 NaCl; ▼, w = 0.08 NaCl; ◆, w = 0.15 NaCl; ●, w = 0.20 NaCl; —, calculated values.

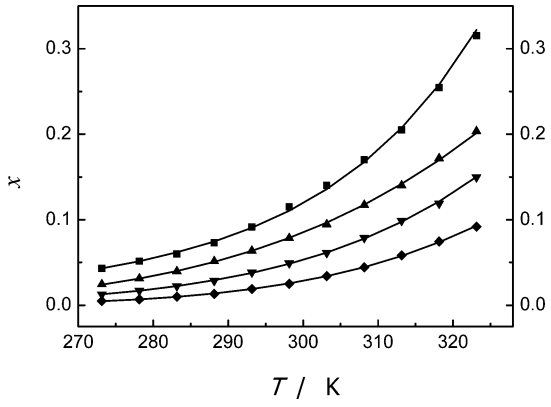

Figure 2. Solubility x of sodium 4-nitrobenzenesulfonate in aqueous solutions of sodium sulfate at different temperatures: ■, w = 0.04 Na_2SO_4; ▲, w = 0.08 Na_2SO_4; ▼, w = 0.15 Na_2SO_4; ◆, w = 0.20 Na_2SO_4; —, calculated values.

3. Because the polarity of drug is closer to the first, the solubility of sodium 4-nitrobenzenesulfonate in water is higher than that in sodium chloride, sodium sulfate, or ethanol aqueous solutions.

Figures 1 to 3 further illustrate that the solubility of sodium 4-nitrobenzenesulfonate in sodium chloride + water is lower than that in ethanol + water solvent mixtures or sodium sulfate + water mixture at the same conditions. Sodium chloride + water mixture is shown to be the best solvent mixture for purifying sodium 4-nitrobenzenesulfonate.

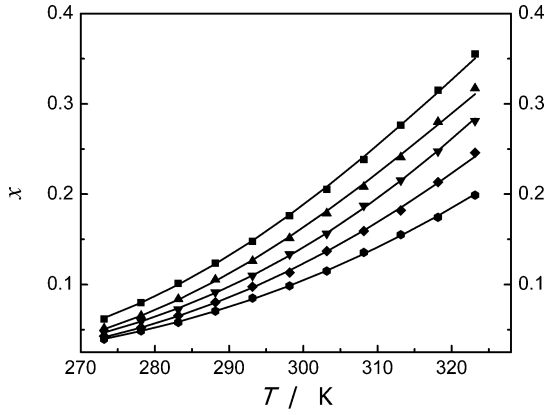

Figure 3. Solubility x of sodium 4-nitrobenzenesulfonate in aqueous solutions of ethanol at different temperatures: ■, w = 0.08 C_2H_5OH;▲, w = 0.17 C_2H_5OH; ▼, w = 0.35 C_2H_5OH; ◆, w = 0.54 C_2H_5OH; ●, w = 0.70 C_2H_5OH; —, calculated values.

The relationship between temperature and solubility of sodium 4-nitrobenzenesulfonate is correlated by a modified Apelblat equation,[11−15] which is a semiempirical equation

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

where A, B, and C are parameters, T is the absolute temperature, and x stands for the solubility of the sodium 4-nitrobenzenesulfonate in aqueous solutions of sodium chloride, sodium sulfate, or ethanol in mass fraction. A, B, and C are parameters. The C value represents the effect of temperature on the fusion enthalpy, as a deviation of heat capacity (ΔC_p). The values of constants A and B reflect the variation in the solute activity coefficient and provide an indication of the effect of solution nonidealities on the solubility of the solute. The values of parameters A, B, and C were evaluated by multidimensional unconstrained nonlinear minimization using MATLAB software. The relative deviations (RDs) between experimental and calculated results are also presented in Tables 1, 2, and 3, respectively. The regressed values of A, B, and C together with the root-mean-square deviations (rmsd's) are given in Table 4. The rmsd is defined as follows:

$$\mathrm{rmsd} = \left[\frac{1}{N-1} \sum_{i=1}^{N} (x_i^{\mathrm{calc}} - x_i)^2 \right]^{1/2} \quad (3)$$

where N is the number of experimental points. x_i^{calc} is the solubility calculated from eq 2, and x_i is the experimental value of the solubility. Figure 1 shows that the calculated solubility shows good agreement with the experimental values.

From Tables 1 to 3, we could elicit the following conclusions: (1) The solubility of sodium 4-nitrobenzenesulfonate in aqueous sodium chloride, sodium sulfate, or ethanol solutions increases with increasing temperature. (2) The effect of sodium chloride, sodium sulfate, or ethanol on the solubility of sodium 4-nitrobenzenesulfonate is due to the salting-out effect. (3) The experimental data can be regressed by eq 2 for each group. The solubility data and correlation equation obtained in this work are useful for the separation and purification of sodium 4-nitrobenzenesulfonate in industry.

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Table 4. Parameters of Equation 2 for Sodium 4-Nitrobenzenesulfonate in Aqueous Solutions of Different Mass Fractions

solvent		A	$B \cdot 10^3$	C	10^{-4} rmsd
sodium chloride	w = 0	152.58	−9.00	−21.74	15.42
	w = 0.04	52.94	−5.27	−6.56	7.20
	w = 0.08	−23.87	−1.87	4.84	14.77
	w = 0.15	−117.05	1.92	18.87	9.22
	w = 0.20	−465.52	16.02	71.54	9.65
sodium sulfate	w = 0.04	−272.61	8.97	42.18	33.97
	w = 0.08	78.66	−6.80	−10.25	13.05
	w = 0.15	5.95	−4.10	0.84	10.70
	w = 0.20	151.34	−11.34	−20.53	5.139
ethanol	w = 0.08	208.84	−11.92	−29.94	22.41
	w = 0.17	242.98	−13.59	−34.98	29.41
	w = 0.35	123.18	−8.26	−17.11	14.83
	w = 0.54	141.32	−9.01	−19.88	19.32
	w = 0.70	73.49	−5.79	−9.89	10.06

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