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SHORT ARTICLE

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Solubility of 1,6-Naphthalene Disulfonic Acid Disodium in Binary Sodium Chloride + Water, Sodium Sulfate + Water, and Ethanol + Water Solvent Mixtures at Elevated Temperatures

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ABSTRACT: The solubility of 1,6-naphthalene disulfonic acid disodium in binary sodium chloride + water, sodium sulfate + water, and ethanol + water solvent mixtures was measured in temperature range from (273.15 to 323.15) K by a steady-state method. Results of these measurements were correlated by a modified Apelblat equation. It was found that sodium chloride + water is the best solvent mixture for purifying 1,6-naphthalene disulfonic acid disodium.

INTRODUCTION

As one of the most important aromatic compounds, the high purity of 1,6-naphthalene disulfonic acid disodium is used extensively in the synthesis of dyes, agrochemicals, and brightening additives.[1] Generally, 1,6-naphthalene disulfonic acid disodium can easily be prepared by sulfonation of naphthalene with a sulfonating agent such as sulfuric acid or fuming sulfuric acid.[2−5] However, the disulfonation product ordinarily contains various isomers such as 1,5-naphthalene disulfonic acid disodium, 2,7-naphthalene disulfonic acid disodium, and 2,6-naphthalene disulfonic acid disodium,[4−9] and it is very difficult to separate 1,6-naphthalene disulfonic acid disodium at a high purity from this reaction product mixture. High-purity 1,6-naphthalene disulfonic acid disodium can be separated from the mixture of isomeric naphthalene disulfonic acids disodium by recrystallization from sodium chloride, sodium sulfate, or ethanol aqueous solution.[1,4,6] To purify 1,6-naphthalene disulfonic acid disodium using a simple method, measurements of the solubility data of 1,6-naphthalene disulfonic acid disodium in binary sodium chloride + water, sodium sulfate + water, and ethanol + water solvent mixtures are needed. Although the solubility of 1,6-naphthalene disulfonic acid disodium in sodium chloride, sodium sulfate, and ethanol aqueous solutions is very important to the separation process, to the best of the authors' present knowledge, the solubility of 1,6-naphthalene disulfonic acid disodium has not been reported in literature.[10] In this work, we measure the solubility of 1,6-naphthalene disulfonic acid disodium 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. The data are correlated by a modified Apelblat equation.

EXPERIMENTAL SECTION

Chemicals. 1,6-Naphthalene disulfonic acid disodium was obtained by Shanghai Kaisai Chemical Co. and had a mass fraction of 0.993. 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; it 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 was 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. Ten minutes prior to sampling, stirring was ceased to allow any solid phase to settle. The attainment of equilibrium was verified both by 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 1,6-naphthalene disulfonic acid disodium solutions were transferred into a tarred volumetric flask. The concentration of 1,6-naphthalene disulfonic acid disodium 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

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Table 1. Mole Fraction Solubility x of 1,6-Naphthalene Disulfonic Acid Disodium in $(1 - w)$ Water + w Sodium Chloride between (273.15 and 323.15) K[a]

T/K	w = 0		w = 0.05		w = 0.10		w = 0.15		w = 0.20	
	$10^2\,x_1$	10^2 RD	$10^2\,x_1$	10^2 RD	$10^2\,x_1$	10^2 RD	$10^2\,x_1$	10^2 RD	$10^4\,x_1$	10^2 RD
273.15	2.59	−2.70	0.87	3.44	0.38	−3.07	0.19	1.35	3.50	−1.47
278.15	3.08	−3.33	1.11	1.90	0.53	−0.63	0.24	−3.26	4.83	−3.11
283.15	3.69	−3.24	1.43	1.25	0.69	−2.47	0.33	1.52	6.65	−2.53
288.15	4.50	−1.66	1.83	0.81	0.93	−0.22	0.41	−1.69	9.03	−3.29
293.15	5.48	−0.29	2.34	0.39	1.23	0.19	0.55	0.28	12.71	−1.02
298.15	6.59	−0.22	3.01	1.25	1.58	−0.86	0.70	−0.25	17.34	−0.44
303.15	7.92	−0.49	3.82	0.88	2.04	−1.50	0.91	0.45	23.21	−1.33
308.15	9.65	0.54	4.84	0.70	2.66	−0.74	1.14	−0.84	30.75	−2.84
313.15	11.70	1.04	6.11	0.55	3.42	−0.78	1.47	0.38	41.29	−2.54
318.15	14.00	0.13	7.76	1.28	4.34	−1.57	1.84	−0.54	55.28	−2.15
323.15	16.66	−1.37	9.72	0.94	5.57	−0.86	2.33	−0.14	73.46	−2.11

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

Table 2. Mole Fraction Solubility x of 1,6-Naphthalene Disulfonic Acid Disodium in $(1 - w)$ Water + w Sodium Sulfate between (273.15 and 323.15) K

T/K	w = 0.04		w = 0.08		w = 0.12		w = 0.16	
	$10^2\,x_1$	10^2 RD	$10^2\,x_1$	10^2 RD	$10^2\,x_1$	10^2 RD	$10^2\,x_1$	10^2 RD
273.15	0.90	4.53	0.71	2.33	0.62	6.65	0.51	3.66
278.15	1.00	−3.39	0.83	0.31	0.65	−4.15	0.55	−1.05
283.15	1.20	−2.79	0.95	−2.93	0.75	−4.70	0.61	−2.60
288.15	1.44	−2.13	1.13	−2.53	0.88	−5.07	0.70	−2.92
293.15	1.72	−1.78	1.36	−0.98	1.08	−0.32	0.80	−2.65
298.15	2.15	3.74	1.63	0.53	1.33	4.18	0.96	0.04
303.15	2.47	0.92	1.97	2.59	1.54	2.18	1.16	3.79
308.15	2.98	3.50	2.30	1.77	1.82	2.47	1.35	3.17
313.15	3.38	0.17	2.67	0.21	2.13	1.36	1.57	2.00
318.15	3.85	−2.55	3.18	1.45	2.51	0.76	1.81	−0.48
323.15	4.58	−0.59	3.58	−2.92	2.84	−4.14	2.09	−3.28

HPLC system consisted of a Shimadzu SPD-6A UV single wavelength spectrophotometric detector was set to 254 nm. The eluent consisted of three components that were methanol, water, and tetra-*N*-butyl ammonium bromide. The concentration ranges from (0 to 1.5) $mg \cdot mL^{-1}$ of analytes were used for 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. The mole fraction solubility (x) was calculated based on

$$x = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2 + m_3/M_3} \quad (1)$$

where m_1 represents the mass of 1,6-naphthalene disulfonic acid disodium, m_2 represents the mass of sodium chloride, sodium sulfate, or ethanol, and m_3 represents the mass of water; M_1, M_2, and M_3 are the molecular weight of the solutes and solvent, respectively.

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 solubility of 1,6-naphthalene disulfonic acid disodium in aqueous solutions of sodium chloride, sodium sulfate, and ethanol is presented in Tables 1, 2, and 3, respectively. The corresponding solubility curves are shown in Figures 1, 2, and 3. It can be learned from these figures that the solubility of 1,6-naphthalene disulfonic acid disodium increases with the increase in temperature range from (273.15 to 323.15) K. However, with the increase in sodium chloride, sodium sulfate, or ethanol concentrations, the solubility of 1,6-naphthalene disulfonic acid disodium decreases. Because the polarity of the drug is closer to the first, the solubility of 1,6-naphthalene disulfonic acid disodium 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 1, 6-naphthalene disulfonic acid disodium in sodium chloride + water mixture is lower than that in sodium sulfate + water or ethanol + water solvent mixtures at the same conditions. The sodium chloride + water mixture is the best solvent mixture for purifying 1,6-naphthalene disulfonic acid disodium.

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Table 3. Mole Fraction Solubility x of 1,6-Naphthalene Disulfonic Acid Disodium in $(1 - w)$ Water + w Ethanol between (273.15 and 318.15) K

T/K	w = 0.08		w = 0.17		w = 0.35		w = 0.54		w = 0.76	
	$10^2\,x_1$	10^2 RD	$10^2\,x_1$	10^2 RD	$10^2\,x_1$	10^2 RD	$10^2\,x_1$	10^2 RD	$10^2\,x_1$	10^2 RD
273.15	0.65	0.00	0.59	0.53	0.54	0.57	0.49	0.61	0.42	0.29
278.15	0.72	−0.08	0.65	−0.32	0.60	0.02	0.53	−0.83	0.46	0.11
283.15	0.80	0.02	0.73	−0.35	0.65	−1.03	0.60	0.30	0.51	−0.23
288.15	0.90	0.44	0.81	−0.46	0.73	−0.59	0.66	−0.31	0.56	−0.15
293.15	1.00	−0.10	0.90	−0.15	0.82	0.60	0.73	−0.21	0.62	−0.72
298.15	1.11	−0.46	1.01	0.53	0.91	0.19	0.82	0.05	0.70	−0.31
303.15	1.25	−0.16	1.12	0.33	1.02	0.52	0.91	0.15	0.78	−0.02
308.15	1.40	−0.08	1.26	0.32	1.13	0.14	1.02	0.35	0.89	1.55
313.15	1.59	1.02	1.40	−0.17	1.26	−0.07	1.14	0.62	0.99	0.73
318.15	1.76	−0.56	1.56	−0.29	1.40	−0.33	1.26	−0.73	1.09	−1.29

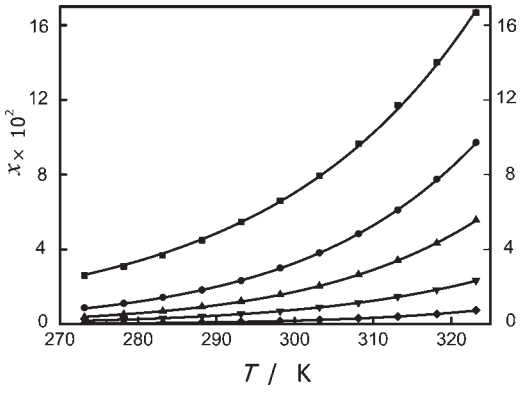

Figure 1. Solubility x of 1,6-naphthalene disulfonic acid disodium in aqueous solutions of sodium chloride at different temperatures: ■, $w = 0$ NaCl; ●, $w = 0.05$ NaCl; ▲, $w = 0.10$ NaCl; ▼, $w = 0.15$ NaCl; ♦, $w = 0.20$ NaCl; —, calculated values.

The relationship between temperature and solubility of 1,6-naphthalene disulfonic acid disodium is correlated by a modified Apelblat equation,[11] which is a semiempirical equation

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

where A, B, and C are parameters, T is the absolute temperature, and x stands for the solubility of the 1,6-naphthalene disulfonic acid disodium in aqueous solutions of sodium chloride, sodium sulfate, or ethanol in mole fraction. 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) are given in Table 4. The rmsd is defined as follows:

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

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.

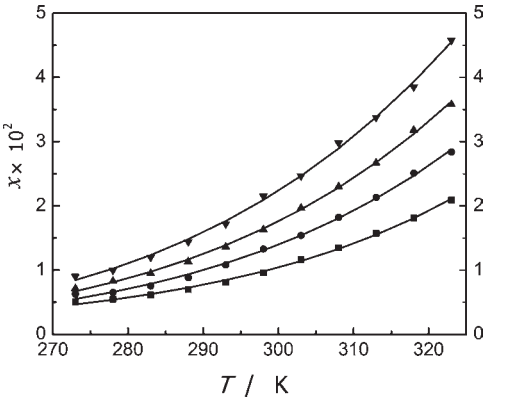

Figure 2. Solubility x of 1,6-naphthalene disulfonic acid disodium in aqueous solutions of sodium sulfate at different temperatures: ▼, $w = 0.04$ Na_2SO_4; ▲, $w = 0.08$ Na_2SO_4; ●, $w = 0.12$ Na_2SO_4; ■, $w = 0.16$ Na_2SO_4; —, calculated values.

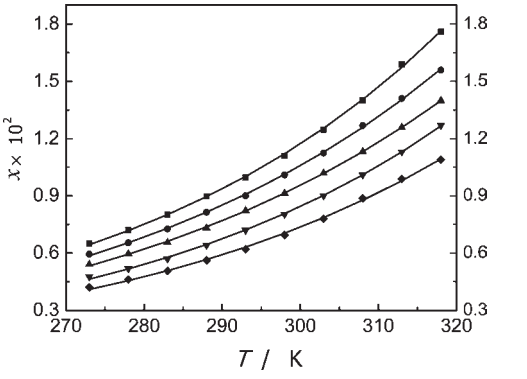

Figure 3. Solubility x of 1,6-naphthalene disulfonic acid disodium in aqueous solutions of ethanol at different temperatures: ■, $w = 0.08$ C_2H_5OH; ●, $w = 0.17$ C_2H_5OH; ▲, $w = 0.35$ C_2H_5OH; ▼, $w = 0.54$ C_2H_5OH; ♦, $w = 0.76$ C_2H_5OH; —, calculated values.

From Tables 1 to 3, we could elicit the following conclusions: (1) The solubility of 1,6-naphthalene disulfonic acid disodium in aqueous sodium chloride, sodium sulfate, or ethanol solutions increases with increasing temperature. (2) The effect of sodium

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Table 4. Parameters of eq 2 for 1,6-Naphthalene Disulfonic Acid Disodium in Aqueous Solutions of Different Mass Fraction

solvent		A	B	C	rmsd·10^4
sodium chloride	w = 0	−167.74	4541.25	26.29	9.67
	w = 0.05	−101.12	662.99	16.74	1.51
	w = 0.10	−76.08	−787.38	13.09	1.22
	w = 0.15	−64.47	−1163.53	11.13	5.87
	w = 0.20	−124.40	676.39	20.32	1.60
sodium sulfate	w = 0.04	−248.45	8576.93	37.74	264.12
	w = 0.08	−180.19	5353.40	27.71	379.61
	w = 0.12	−101.43	1807.41	16.02	196.44
	w = 0.16	−51.82	−398.16	8.65	274.38
ethanol	w = 0.08	−126.98	3748.44	19.29	42.71
	w = 0.17	−108.63	2983.31	16.50	36.94
	w = 0.35	−97.70	2516.24	14.84	50.32
	w = 0.54	−111.02	3108.21	16.81	48.62
	w = 0.76	−152.35	4896.69	22.99	73.47

chloride, sodium sulfate or ethanol on the solubility of 1, 6-naphthalene disulfonic acid disodium is due to the salting-out effect. (3) The experimental data can be regressed by eq 2 for each groups. The solubility data and correlation equation obtained in this work are useful for the separation and purification of 1,6-naphthalene disulfonic acid disodium in industry.

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REFERENCES

(1) Li, X.; Sun, L. F.; Cao, P. Preparation of 1,6-Dihydroxynaphthalene. *Liaoning Tussah Silk* **2007**, *35*, 9−10 (in Chinese).

(2) Takehiko, S. *Selective Production of 1,6-Naphthalenedisolfonic Acid*. Japan Patent 55,040,648, March 22, 1980.

(3) David, H. E. F.; Hasle, A. W. About the Disulfuration of Naphthalene. *Helv. Chim. Acta* **1923**, *6*, 1133–1146.

(4) Ambler, J. A.; Scanlan, J. T. Naphthalenesulfonic Acids. VII-Hydrolysis of Naphthalene 1,6-Disulfonic Acid. *Ind. Eng. Chem.* **1927**, *19*, 417–421.

(5) Hironory, F.; Thuyoshi, N.; Nobuyori, S. *Process for Separation of Naphthalenedisulfonic Acids*. U.S. Patent 4,324,742, April 13, 1982.

(6) Wang, Y. C.; Song, D. M.; Zhang, Y. H. A Study on the Synthesis of Naphthalene Sulfonic Acids. *Dyest. Ind.* **2008**, *38*, 37−39 (in Chinese).

(7) Masato, T.; Setsu, T.; Akihiro, Y.; Naoichi, S. *Separation of 2, 6-Naphthalenedisulfonic Acid*. Japan Patent 63,225,351, September 20, 1988.

(8) Masato, T.; Akihiro, Y.; Yoshihiro, N. *Separation of 2,7-Naphthalenedisulfonic Acid*. Japan Patent 63,225,350, September 20, 1988.

(9) Akihiro, Y.; Hiroyuki, S.; Makoto, T.; Takeo S. *Production of 2,6-Naphthalenedisulfonic Acid and 2,7-Naphthalenedisulfonic Acid*. Japan Patent 63,060,962, March 17, 1988.

(10) Stephen, H.; Stephen, T. *Solubility of Inorganic and Organic Compounds*; Pergamon: Oxford, 1979.

(11) Zhao, H. K.; Li, R. R.; Ji, H. Z.; Zhang, D. S.; Tang, C.; Yang, L. Q. Equilibrium Solubility of 3- and 4-Nitrophthalic Acids in Water. *J. Chem. Eng. Data* **2007**, *52*, 2072–2073.