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Solubility of Sodium Naphthalene Disulfonate in Aqueous Solutions of Sulfuric Acid

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The solubilities of sodium 2,6-naphthalene disulfonate and sodium 2,7-naphthalene disulfonate in aqueous solutions of sulfuric acid were measured in the temperature range from (283.15 to 333.15) K by a steady-state method. The solubility of sodium 2,6-naphthalene disulfonate or sodium 2,7-naphthalene disulfonate increases with the increase in temperature from (283.15 to 333.15) K. With the increase in sulfuric acid concentrations, the solubilities of sodium 2,6-naphthalene disulfonate and sodium 2,7-naphthalene disulfonate decrease. At the same temperature and in the same composition of sulfuric acid + water solvent mixtures, the solubility of sodium 2,7-naphthalene disulfonate is larger than that of sodium 2,6-naphthalene disulfonate. Results of these measurements were correlated by a modified Apelblat equation.

Introduction

2,7-Naphthalene disulfonic acid is an important and valuable intermediate for use in the manufacturing of dyes, organic pigments, medicines, and agricultural chemicals.[1−9] Generally, 2,7-naphthalene disulfonic acid can easily be prepared by sulfonation of naphthalene with a sulfonating agent such as sulfuric acid, fuming sulfuric acid, or chlorosulfonic acid.[7,8] By controlling the various reaction parameters, it is possible to produce a disulfonated naphthalene which contains a high concentration of a particular isomer of the disulfonated naphthalene.

However, the disulfonation product normally contains various isomers such as 2,6-naphthalene disulfonic acid and 2,7-naphthalene disulfonic acid, and it is very difficult to separate a specific naphthalene disulfonic acid at a high purity from this reaction product mixture. Thus, only an extremely limited number of processes have been proposed for the separation and/or purification of naphthalene disulfonic acid. One process where sodium 2,6-naphthalene disulfonate is separated is by utilizing the solubility difference among salts of naphthalene disulfonic acids.[9] Since the solubility difference among isomers of naphthalene disulfonic acid sodium salts is not large at room temperature, the solubility difference at elevated temperatures could be utilized.

The optimization of process conditions is closely related to the solubility of sodium 2,6-naphthalene disulfonate and sodium 2,7-naphthalene disulfonate in aqueous solutions of sulfuric acid. Although the solubilities of sodium 2,6-naphthalene disulfonate and sodium 2,7-naphthalene disulfonate in aqueous solutions of sulfuric acid are very important for their separation process, to the authors' knowledge, the solubilities of sodium 2,6-naphthalene disulfonate and sodium 2,7-naphthalene disulfonate in aqueous solutions of sulfuric acid have not been reported in the literature.[10] In this work the solubilities of sodium 2,6-naphthalene disulfonate and sodium 2,7-naphthalene disulfonate in the systems of aqueous solutions of sulfuric acid are systematically determined by the steady-state method in the temperature range from (283.15 to 333.15) K and correlated using the empirical equation.

Experimental Section

Materials. Sodium 2,6-naphthalene disulfonate (CAS No.: 1655-45-4) and sodium 2,7-naphthalene disulfonate (CAS No.: 1655-35-2) were provided by Nantong Laijiali Chemical Co., Ltd., China. The mass fraction purity of sodium 2,6-naphthalene disulfonate is 99.7 %, and that of sodium 2,7-naphthalene disulfonate is 99.5 %. They were used without further purification. Sulfuric acid was obtained from Shanghai Chemical Reagent Co. and had a mass fraction purity of 98.1 %. The water used to prepare the solutions was twice distilled (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 in 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. When the composition of the liquid became constant, this was taken to indicate that equilibration had been attained. Generally, it took about 16 h to reach equilibrium. Ten minutes prior to sampling, stirring was ceased to allow any solid phase to settle. 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 and then quantitatively analyzed.

Analysis. Aliquots of saturated sodium 2,6- or 2,7-naphthalene disulfonate solutions were transferred through a coarse filter into a tarred volumetric flask. The concentration of sodium 2,6- or 2,7-naphthalene disulfonate in aqueous solutions of sulfuric acid was

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Table 1. Mole Fraction Solubility x of Sodium Naphthalene Disulfonate in $(1 - w)$ Water + w Sulfuric Acid at Different Temperatures[a]

T	$w = 0$	$w = 0.10$	$w = 0.30$	$w = 0.50$
K	$10^2\ x$			
	Sodium 2,6-Naphthalene Disulfonate			
283.15	0.3228	0.2787	0.1764	0.0855
288.15	0.3426	0.2877	0.1811	0.0887
293.15	0.3664	0.3008	0.1889	0.0914
298.15	0.4016	0.3248	0.2000	0.0956
303.15	0.4370	0.3458	0.2141	0.1008
308.15	0.4777	0.3822	0.2315	0.1075
313.15	0.5232	0.4118	0.2522	0.1159
318.15	0.5628	0.4458	0.2762	0.1266
323.15	0.6111	0.4844	0.3035	0.1378
328.15	0.6572	0.5314	0.3343	0.1526
333.15	0.7196	0.5835	0.3686	0.1686
	Sodium 2,7-Naphthalene Disulfonate			
283.15	1.2792	0.8875	0.4329	0.1481
288.15	1.4029	0.9354	0.4879	0.1601
293.15	1.5876	1.0480	0.5781	0.1903
298.15	1.8933	1.2357	0.6640	0.2281
303.15	2.2355	1.4741	0.8127	0.2923
308.15	2.6824	1.7702	0.9996	0.3617
313.15	3.2300	2.1540	1.2847	0.4528
318.15	3.8308	2.6120	1.5713	0.5760
323.15	4.7293	3.2037	1.9274	0.7309
328.15	5.8351	3.8624	2.3860	0.8943
333.15	7.5023	4.8468	3.1239	1.0893

[a] w is the mass fraction.

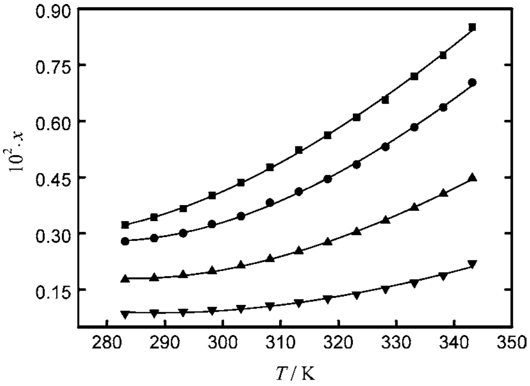

Figure 1. Solubility x of sodium 2,6-naphthalene disulfonate in aqueous solutions of sulfuric acid at different temperatures: ■, $w = 0$ H_2SO_4; ●, $w = 0.10$ H_2SO_4; ▲, $w = 0.30$ H_2SO_4; ▼, $w = 0.50$ H_2SO_4; —, calculated values.

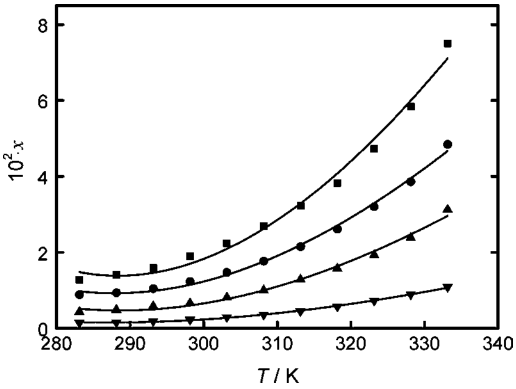

Figure 2. Solubility x of sodium 2,7-naphthalene disulfonate in aqueous solutions of sulfuric acid at different temperatures: ■, $w = 0$ H_2SO_4; ●, $w = 0.10$ H_2SO_4; ▲, $w = 0.30$ H_2SO_4; ▼, $w = 0.50$ H_2SO_4; —, calculated values.

Table 2. Curve-Fitting Parameters of Equation 1 for Sodium 2,6-Naphthalene Disulfonate and Sodium 2,7-Naphthalene Disulfonate in $(1 - w)$ Water + w Sulfuric Acid

solute	solvent	A	B	C	σ_x[a]
sodium 2,6-naphthalene disulfonate	$w = 0$	−79.73	2082.30	11.80	$4.93 \cdot 10^{-5}$
	$w = 0.10$	−176.58	6590.47	26.11	$4.39 \cdot 10^{-5}$
	$w = 0.30$	−230.26	9028.58	34.01	$2.02 \cdot 10^{-5}$
	$w = 0.50$	−305.88	12549.22	45.08	$4.15 \cdot 10^{-5}$
sodium 2,7-naphthalene disulfonate	$w = 0$	436.12	16879.37	65.91	$1.97 \cdot 10^{-3}$
	$w = 0.10$	−456.90	17840.53	68.92	$8.60 \cdot 10^{-4}$
	$w = 0.30$	−440.58	16683.84	66.63	$7.86 \cdot 10^{-4}$
	$w = 0.50$	−385.99	13974.24	58.46	$1.38 \cdot 10^{-4}$

[a] σ_x is the rmsd.

determined using a Shimadzu-6A high-performance liquid phase chromatograph (HPLC). The chromatographic column used is a unimicro Kromasil C18, 5 μm (250 mm × 4.6 mm), maintained at 308.1 K. The HPLC system consisted of a Shimadzu SPD-6A UV single wavelength spectrophotometric detector set to 254 nm. The mobile phase consisted of 450 mL + 550 mL + 1.6 g of methanol + water + tetra-*N*-butyl ammonium bromide. The concentration range from (0 to 1.5) $mg \cdot mL^{-1}$ of analytes was used for the construction of calibration curves. The uncertainty of the measurement is less than 0.1 %. Each analysis is repeated three times, and the average value of the three measurements is considered the final value of the analysis.

Results and Discussion

The measured solubilities of sodium 2,6-naphthalene disulfonate and sodium 2,7-naphthalene disulfonate in aqueous solutions of sulfuric acid are presented in Table 1. The corresponding solubility curves are shown in Figures 1 and 2, respectively. It can be seen from Figures 1 and 2 that the solubility of sodium 2,6-naphthalene disulfonate or sodium 2,7-naphthalene disulfonate increases with the increase in the temperature range from (283.15 to 333.15) K. However, at the same temperature and in the same composition of sulfuric acid + water solvent mixtures, the solubility of sodium 2,7-naphthalene disulfonate is larger than that of sodium 2,6-naphthalene disulfonate. The substituents are in 2- and 7-positions of the naphthalene ring (sodium 2,7-naphthalene disulfonate), and their behavior reflects the steric effect and conjugate effect in the molecule, which makes the electron in sodium 2,7-naphthalene disulfonate more disperse than in sodium 2,6-naphthalene disulfonate. As a result, the solubility of sodium 2,7-naphthalene disulfonate in solvent is larger than that of sodium 2,6-naphthalene disulfonate. Figures 1 and 2 also show that, with the increase in sulfuric acid concentrations, the solubilities of sodium 2,6-naphthalene disulfonate and sodium 2,7-naphthalene disulfonate decrease in the temperature range from (283.15 to 333.15) K.

The experimental values are correlated by a modified Apelblat equation,[11] which is a semiempirical equation

$$\ln(x) = A + \frac{B}{(T/\mathrm{K})} + C \ln(T/\mathrm{K}) \qquad (1)$$

where A, B, and C are parameters, T is the absolute temperature, and x stands for the solubility of the solute sodium 2,6-naphthalene disulfonate or sodium 2,7-naphthalene disulfonate in aqueous solutions of sulfuric acid in mole fraction.

The regressed values of A, B, and C together with the root-mean-square deviations (rmsd's) are given in Table 2. The rmsd is defined as

$$\sigma_x = \left[\frac{1}{N}\sum_{i=1}^{N}(x_{ci} - x_i)^2\right]^{1/2} \qquad (2)$$

where N is the number of experimental points. Table 2 shows that the values of parameters B and C increase with the increase

Table 3. Curve-Fitting Parameters of Equation 3 for Sodium 2,6-Naphthalene Disulfonate and Sodium 2,7-Naphthalene Disulfonate in (1 − *w*) Water + *w* Sulfuric Acid

solute		a_i	b_i	c_i	σ_x[a]
sodium	A ($i = 1$)	−92.31	−654.07	472.74	15.69
2,6-naphthalene	B ($i = 2$)	2676.48	30173.78	−21747.88	740.87
disulfonate	C ($i = 3$)	13.66	96.77	−70.64	2.32
sodium	A ($i = 1$)	−438.47	−202.12	617.66	2.92
2,7-naphthalene	B ($i = 2$)	17033.28	8041.53	−28550.12	191.90
disulfonate	C ($i = 3$)	66.22	30.30	−92.12	0.39

[a] σ_x is the rmsd.

in sulfuric acid concentration for sodium 2,6-naphthalene disulfonate, while the values of parameter *A* decrease. However, for sodium 2,7-naphthalene disulfonate, the values of parameters *B* and *C* increase first and then decrease with the increase in sulfuric acid concentration, and the values of parameter *A* decrease first and then increase. The rmsd's are very small for each system. From Figures 1 and 2, we can see that the calculated solubility shows good agreement with the experimental values.

Equation 1 was effective only for constant solvent composition. To use eq 1 to correlate the solubility of sodium 2,6-naphthalene disulfonate and sodium 2,7-naphthalene disulfonate at different solvent compositions, parameters *A*, *B*, and *C* were assumed to be a function of sulfuric acid mass fraction w

$$\begin{aligned} A &= a_1 + b_1 w + c_1 w^2 \\ B &= a_2 + b_2 w + c_2 w^2 \\ C &= a_3 + b_3 w + c_3 w^2 \end{aligned} \tag{3}$$

where a_1, b_1, c_1, a_2, b_2, c_2, a_3, b_3, and c_3 are coefficients. The calculated solubilities of x at solvent compositions of $w = 0$, 0.10, 0.30, and 0.50 and in the temperature range from (283.15 to 333.15) K are plotted in Figures 1 and 2. The values of coefficients a_1, b_1, c_1, a_2, b_2, c_2, a_3, b_3, and c_3 are listed in Table 3 together with the rmsd's. The values of parameters *A*, *B*, and *C* can be calculated with eq 3 according to these values of coefficients. It can be seen from Tables 2 and 3 that the calculated values of parameters *A*, *B*, and *C* show good agreement with the regressed values.

The experimental solubility and correlation equation in this work can be used as essential data and models in the process of sodium 2,6-naphthalene disulfonate and sodium 2,7-naphthalene disulfonate purification and manufacturing.

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Literature Cited

(1) David, H. E. F.; Hasle, A. W. About the disulfuration of naphthalene. *Helv. Chim. Acta* **1923**, *6*, 1133–1146.
(2) Ambler, J. A.; Lynch, D. F. J.; Haller, H. L. Naphthalenesulfonic acids. VI-Sulfonation of naphthalene in the vapor phase. *Ind. Eng. Chem.* **1924**, *16*, 1264–1266.
(3) Masato, T.; Akihiro, Y.; Yoshihiro, N.; Naoichi, S. Production of 2,7-naphthalenedisulfonic acid. Japan Patent 63,225,352, Sept 20, 1988.
(4) Akihiro, Y.; Masato, T.; Yoshihiro, N.; Naoichi, S. Production of 2,6-naphthalenedisulfonic acid. Japan Patent 63,280,055, Nov 17, 1988.
(5) Masato, T.; Setsu, T.; Akihiro, Y.; Naoichi, S. Separation of 2,6-naphthalenedisulfonic acid. Japan Patent 63,225,351, Sept 20, 1988.
(6) Masato, T.; Akihiro, Y.; Yoshihiro, N. Separation of 2,7-naphthalenedisulfonic acid. Japan Patent 63,225,350, Sept 20, 1988.
(7) Akihiro, Y.; Hiroyuki, S.; Makoto, T.; Takeo, S. Production of 2,6-naphthalenedisulfonic acid and 2,7-naphthalenedisulfonic acid. Japan Patent 63,060,962, Mar 17, 1988.
(8) Hiroki, F.; Takeshi, N.; Nobuyori, S. Preparation of naphthalene-2,7-disulfonic acid. Japan Patent 56,077,254, Jul 25, 1981.
(9) Hironory, F.; Thuyoshi, N.; Nobuyori, S. Process for separation of naphthalenedisulfonic acids. U.S. Patent 4,324,742, Apr 13, 1982.
(10) Stephen, H.; Stephen, T. *Solubility of Inorganic and Organic Compounds*; Pergamon: Oxford, U.K., 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.

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