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Equilibrium solubility of sodium 2-naphthalenesulfonate in binary (sodium chloride + water), (sodium sulfate + water), and (ethanol + water) solvent mixtures at temperatures from (278.15 to 323.15) K

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ABSTRACT

The equilibrium solubility of sodium 2-naphthalenesulfonate in binary (sodium chloride + water), (sodium sulfate + water), and (ethanol + water) solvent mixtures was measured at elevated temperatures from (278.15 to 323.15) K using a steady-state method. With increasing temperatures, the solubility increases in aqueous solvent mixtures. The results of these results were regressed by a modified Apelblat equation. The dissolution entropy and enthalpy determined using the method of the least-squares and the change of Gibbs free energy calculated with the values of $\Delta_{diff}S^o$ and $\Delta_{diff}H^o$ at $T = 278.15$ K.

1. Introduction

Sodium 2-naphthalenesulfonate (CAS Registry No. 532-02-5) is a critical intermediate which is used as a reactant in the production of 2-naphthol and the functionalized reduced graphene oxide stabilization of silver nanoparticles [1,2]. The compound is mainly produced from the sulphonation of naphthalene with concentrated sulfuric acid, followed by condensation of NaCl. The products formed from this method include sodium 1- and 2-naphthalenesulfonates in various proportions, which are obtained through sulphonation and condensation reactions, respectively. It is very important to purify sodium 2-naphthalenesulfonate via crystallization. Some studies used the method of ion exchange to separate sodium 2-naphthalenesulfonate from the β-salt mother liquor [3,4]. It is necessary to purify the sodium 2-naphthalenesulfonate product throughout the entire process. However, it is not easy to gain high-purity sodium 2-naphthalenesulfonate from the mixture. The profitable product of sodium 2-naphthalenesulfonate is produced via crystallization in NaCl, Na_2SO_4, or C_2H_5OH aqueous solutions. The solubility data of sodium 2-naphthalenesulfonate in binary (sodium chloride + water), (sodium sulfate + water), and (ethanol + water) solvent mixtures is very crucial for the crystallization process, however, to date, no literature has been reported on the solubility of sodium 2-naphthalenesulfonate [5–7]. Therefore, the present work focuses on a systematic determination of the solubility of sodium 2-naphthalenesulfonate in binary (sodium chloride + water), (sodium sulfate + water), and (ethanol + water) solvent mixtures, which was determined using a steady-state method from $T = (278.15$ to $323.15)$ K [8–12]. A modified Apelblat equation was used to correlate with the results of these measurements.

2. Experimental

2.1. Materials

Sodium 2-naphthalenesulfonate with a mass fraction purity of 0.995 was supplied by Aladdin Chemical Co. Ltd (China), which

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was used without further purification. The mass fraction purity of sodium 2-naphthalenesulfonate was analyzed using high-performance liquid chromatography and was determined to be no less than 0.995. Na_2SO_4 and NaCl had mass fraction purities of 0.998 and 0.996, respectively, and were supplied by Shenyang Chemical Reagent Co. The C_2H_5OH was purchased by Shanghai Chemical Reagent Co. had a mass fraction purity of 0.999. The water used to prepare the solutions was twice distilled water (conductivity < 5 $\mu S \cdot cm^{-1}$). The purities and suppliers of chemicals are listed in table 1.

2.2. Apparatus and procedure

To start, 50 mL of deionised water was placed into a 125 mL Erlenmeyer flask, which was then transferred into a constant-temperature water bath (Neslab, RTE-101) and re-circulated through a copper coil in the water bath (uncertainty of $T = \pm 0.01$ K). A condenser was used with the flask to prevent the solutions from evaporating. A Teflon-coated magnetic stirring bar was used to stir the water. Excess solute was placed into the flask, which equilibrated at a given temperature in the water bath for at least 3 days. Aliquots of the liquid phase were taken at 2 h intervals, and then analyzed using High Performance Liquid Chromatography (HPLC). The aliquots were taken to indicate when equilibration had been gained, which was evident when the composition of the solute became constant. It generally took about 11 h to achieve equilibrium. Stirring was performed on the mixtures to allow any solid phases to settle, and this was done ten minutes prior to sampling in order get the saturated liquid without a solid phase. Then, the liquid phase of approximately (1 to 2) cm^3 was taken out from the clear solution with preheated glass syringes at 2 h intervals and analyzed using HPLC. Equilibrium was achieved and verified by repetitive measurements after 3 or more days. Equilibrium was also approached from super saturation, which pre-equilibrated the solutions at a higher temperature. After equilibrium was reached, the liquid phase was taken out. The sample was measured with an electronic balance and quantitatively analyzed using HPLC afterwards.

2.3. Analysis

The analysis method was the same in previous works [13]. The mass fraction of sodium 2-naphthalenesulfonate in aqueous solutions was analyzed by a Shimadzu-6A HPLC. The HPLC Columns were unimicro Kromasil C18, 5 μm (250 · 4.6) mm and kept at a temperature of 308.2 K. The wavelength was 199 nm, and was determined using a Shimadzu SPD-6A UV single spectrophotometric detector. The average value of the three data points was considered as the ultimate value of the analysis [14,15]. The following equation was used to calculate the mole fraction solubility (x):

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

where m_1 represents the mass of sodium 2-naphthalenesulfonate, m_2 represents the mass of NaCl, Na_2SO_4 or C_2H_5OH, and m_3 represents the mass of H_2O. M_1, M_2, and M_3 represent the molar mass of the solute and different solvents, respectively. The solute with the subscript 1 represents sodium 2-naphthalenesulfonate, the solvent with the subscript 2 represents NaCl, Na_2SO_4 or C_2H_5OH, and the solvent with the subscript 3 represents water. The uncertainty of the experimental solubility values is less than 1 %, which may be due to uncertainties in the measurements of temperature and the weighing process.

3. Results and discussion

The solubility results for sodium 2-naphthalenesulfonate in binary (sodium chloride + water), (sodium sulfate + water), and (ethanol + water) solvent mixtures are presented in tables 2–4, respectively. Figures 1–3 show the corresponding solubility curves, respectively. The solubility of sodium 2-naphthalenesulfonate in (sodium chloride + water), (sodium sulfate + water), or (ethanol + water) solvent mixtures is lower than that in pure water.

From the figures 1–3, it is clear that the solubility of sodium 2-naphthalenesulfonate in the (ethanol + water) solvent mixture or sodium chloride mixture is lower than that in (sodium

TABLE 1
Provenance and mass fraction purity of chemical studied.

Compound	Mass fraction purity	Sources	Purification method	Analytical method
Sodium 2-naphthalenesulfonate	⩾0.995	Aladdin Chemical Co. Ltd (China)	None	HPLC
Na_2SO_4	0.998	Shenyang Chemical Reagent Co.	None	
NaCl	0.996	Shenyang Chemical Reagent Co.	None	
C_2H_5OH	0.999	Shanghai Chemical Reagent Co.	None	

TABLE 2
Mole fraction solubility x of sodium 2-naphthalenesulfonate in {(1 − w) water + w sodium sulfate} between T = (278.15 and 323.15) K under pressure of 0.1 MPa.[a]

T/K	w = 0		w = 0.05		w = 0.10		w = 0.15		w = 0.20	
	x_i	10^3 RD	x_i	10^3 RD	x_i	10^3 RD	x_i	10^3 RD	x_i	10^3 RD
278.15	0.00215	−1.21	0.00153	−0.28	0.00110	4.06	0.00080	4.68	0.00054	3.08
283.15	0.00228	−3.13	0.00167	−1.63	0.00121	−0.09	0.00086	−1.19	0.00058	−0.81
288.15	0.00262	1.19	0.00190	0.30	0.00137	−1.59	0.00096	−3.79	0.00066	−0.96
293.15	0.00299	3.02	0.00213	−0.08	0.00153	−4.66	0.00113	−1.80	0.00075	−1.56
298.15	0.00336	1.76	0.00247	2.13	0.00186	0.84	0.00135	1.42	0.00087	−0.47
303.15	0.00379	−0.64	0.00279	1.05	0.00213	0.17	0.00154	−0.29	0.00101	−0.50
308.15	0.00452	1.12	0.00315	−0.75	0.00247	0.67	0.00181	0.69	0.00120	0.89
313.15	0.00519	−2.22	0.00365	−0.56	0.00289	1.99	0.00211	0.59	0.00140	−0.27
318.15	0.00632	−0.85	0.00422	−1.16	0.00323	−1.30	0.00245	−0.15	0.00169	1.30
323.15	0.00781	0.84	0.00503	0.78	0.00378	−0.03	0.00287	−0.22	0.00198	−0.72

[a] RD = $(x_i - x_i^{calc})/x_i$; w, mass fraction of sodium sulfate in water. Standard uncertainties u are $u_r(w) = 0.02$, $u(T) = 0.05$ K, $u_r(x) = 0.02$, $u(P) = 2$ kPa.