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Solubility of 2,7-Dihydroxynaphthalene in Binary Sodium Chloride + Water, Sodium Sulfate + Water, and Ethanol + Water Solvent Mixtures at Elevated Temperatures

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ABSTRACT: The solubility of 2,7-dihydroxynaphthalene in binary sodium chloride + water, sodium sulfate + water, and ethanol + water solvent mixtures was measured in the temperature range from (283.15 to 328.25) K by a steady-state method. The results of these measurements were correlated by a modified Apelblat equation.

INTRODUCTION

As one of the most important aromatic compounds, 2,7-dihydroxynaphthalene (CAS Registry No. 582-17-2), also named naphthalene-2,7-diol or 2,7-naphthalenediol, mainly was used as resins,[1−3] pharmaceutical intermediates,[4,5] liquid crystals,[6,7] and dyes.[8,9] In the solid state, the structure of 2,7-dihydroxynaphthalene is stabilized by both van der Waals interactions and O−H···O intermolecular forces.[10] It is crystallized in orthorhombic space group *Pna*21, with $a = 7.826(6)$, $b = 17.448(9)$, and $c = 5.740(4)$.[11] Generally, 2,7-dihydroxynaphthalene can be prepared by the alkali fusion of sodium 2,7-naphthalenedisulfonic acid at above 550 K.[12−15] The reaction mixture of alkali fusion is added gradually into hydrochloric acid solution. A given amount of sodium sulfate and sodium chloride is added to the filtrate. Sodium chloride and ethanol are all used during the purification process of 2,7-dihydroxynaphthalene. As a result, the solubility of 2,7-dihydroxynaphthalene in solutions is very important in the preparation of 2,7-dihydroxynaphthalene. However, to the best of the authors' present knowledge, the solubility data are not reported in literature. In this work, the solubility of 2,7-dihydroxynaphthalene in binary sodium chloride + water, sodium sulfate + water, and ethanol + water solvent mixtures was measured using the steady-state method with the temperature range from (283.15 to 328.25) K. The data are correlated by a modified Apelblat equation.

EXPERIMENTAL SECTION

Chemicals. 2,7-Dihydroxynaphthalene was obtained by Nantong Laijiali Chemical Co., Ltd., and had a mass fraction of 0.997. Sodium chloride and sodium sulfate, with a mass fraction of 0.996 and 0.998, respectively, were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Ethanol was obtained from Shanghai Chemical Reagent Co. and had a mass purity of 0.999. The raw materials were 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 solvent 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. When composition of the liquid phase became constant, this was taken to indicate that equilibration had been attained. Attainment of equilibrium was verified both by repetitive measurements after a minimum of 3 additional days and by approaching equilibrium from supersaturation by pre-equilibrating the solutions at a higher temperature. Generally, it took about 13 h to reach equilibrium. About 30 min prior to sampling, stirring was ceased to allow any solid phase to settle. After equilibrium was achieved, the liquid phase was taken out and then analyzed quantitatively.

Analysis. Aliquots of saturated 2,7-dihydroxynaphthalene solutions were transferred into a tarred volumetric flask. The concentration of 2,7-dihydroxynaphthalene in aqueous solutions was 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 308.2 K. The HPLC system consisted of a Shimadzu SPD-6A UV single wavelength spectrophotometric detector set to 254 nm.[16] The mobile phase consisted of 450 mL + 550 mL + 1.6 g of methanol + water + tetra-*N*-butylammonium bromide. The concentration ranges from (0 to 1) $mg \cdot mL^{-1}$ of analysts were used for the construction of calibration curves. Each analysis is 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 2,7-dihydroxynaphthalene, m_2 represents the mass of sodium chloride, sodium sulfate, or

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ethanol, and m_3 represents the mass of water; M_1, M_2, and M_3 are the molecular weight of the solute 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 2,7-dihydroxynaphthalene 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 3. It can be learned from these figures that the solubility of 2,7-dihydroxynaphthalene increases with the increase in temperature range from (283.15 to 328.25) K. With the increase in sodium chloride or sodium sulfate concentrations, the solubility of 2,7-dihydroxynaphthalene decreases. Because the polarity of the drug is closer to the first, the solubility of 2,7-dihydroxynaphthalene in water is higher than that in sodium chloride or sodium sulfate aqueous solutions.

However, with the increase in ethanol concentrations, the solubility of 2,7-dihydroxynaphthalene increases. Obviously ethanol can increase the solubility of 2,7-dihydroxynaphthalene. The reason is explained as follows. Ethanol that solubilizes a 2,7-dihydroxynaphthalene molecule via specific interactions such as complexation interact with the ethanol molecule in a noncovalent manner that lowers the chemical potential of the molecules in solution. These noncovalent bulk and specific solubility-enhancing

Table 1. Mole Fraction Solubility x of 2,7-Dihydroxynaphthalene in $(1 - w)$ Water + w Sodium Chloride between (283.15 and 328.15) K[a]

T	$w = 0.05$		$w = 0.10$		$w = 0.15$		$w = 0.20$	
K	$10^4 x$	10^2 RD	$10^4 x$	10^2 RD	$10^4 x$	10^2 RD	$10^4 x$	10^2 RD
283.15	1.50	−4.39	1.11	3.11	0.72	−3.96	0.42	4.22
288.15	2.13	−1.12	1.31	−4.97	0.91	−0.62	0.46	−3.03
293.15	2.91	0.54	1.75	0.03	1.16	2.85	0.54	−5.83
298.15	3.78	−0.66	2.24	1.11	1.41	0.56	0.65	−7.26
303.15	4.84	−1.25	2.87	2.74	1.71	−2.52	0.80	−6.95
308.15	5.96	−3.86	3.58	2.18	2.13	−3.55	1.08	0.27
313.25	7.43	−3.33	4.36	−0.34	2.66	−4.92	1.40	2.12
318.15	9.06	−3.30	5.34	−1.91	3.48	−1.79	1.86	5.10
323.25	11.02	−1.85	6.65	−1.39	4.58	0.96	2.28	−0.85
328.25	13.20	−0.42	8.51	2.21	5.75	−1.24	2.81	−7.74

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

Table 3. Mole Fraction Solubility x of 2,7-Dihydroxynaphthalene in $(1 - w)$ Water + w Ethanol between (283.15 and 328.15) K

T	$w = 0.05$		$w = 0.10$		$w = 0.15$		$w = 0.20$	
K	$10^4 x$	10^2 RD	$10^4 x$	10^2 RD	$10^4 x$	10^2 RD	$10^4 x$	10^2 RD
283.15	4.58	1.27	6.08	1.18	7.76	−0.74	9.44	1.36
288.15	5.70	2.50	7.42	1.76	8.99	−3.64	11.04	1.19
293.15	7.04	3.22	9.19	3.96	11.06	−0.41	13.20	3.08
298.15	8.76	4.90	11.10	3.90	13.10	−1.02	15.40	2.48
303.15	10.60	4.15	13.30	3.25	15.60	−1.07	18.10	2.51
308.15	12.6	1.89	15.70	1.32	18.30	−2.61	20.90	0.73
313.25	15.10	0.64	18.70	0.43	21.80	−2.55	24.80	1.58
318.15	18.30	0.72	22.50	0.73	26.40	−0.77	29.30	1.96
323.25	22.60	2.88	27.60	3.10	31.30	−1.09	34.60	2.25
328.25	27.70	4.49	33.10	3.42	36.70	−2.49	40.80	2.37

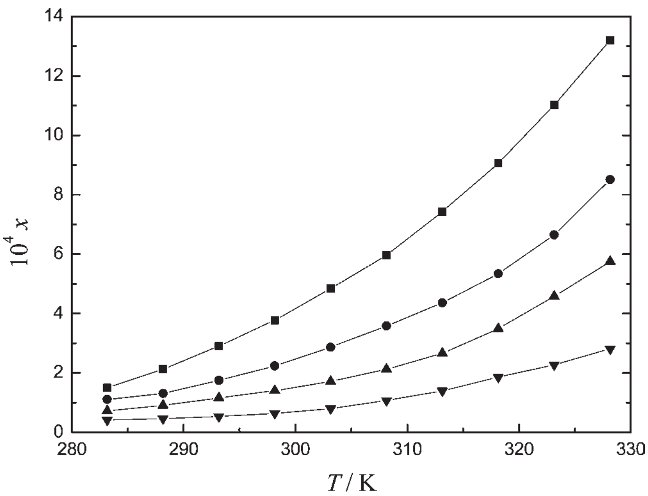

Figure 1. Solubility x of 2,7-dihydroxynaphthalene in aqueous solutions of sodium chloride at different temperatures: ■, 5 % NaCl; ●, 10 % NaCl; ▲, 15 % NaCl; ▼, 20 % NaCl; —, calculated values.

Table 2. Mole Fraction Solubility x of 2,7-Dihydroxynaphthalene in $(1 - w)$ Water + w Sodium Sulfate between (283.15 and 328.15) K

T	$w = 0$		$w = 0.05$		$w = 0.10$		$w = 0.15$		$w = 0.20$	
K	$10^4 x$	10^2 RD	$10^4 x$	10^2 RD	$10^4 x$	10^2 RD	$10^4 x$	10^2 RD	$10^4 x$	10^2 RD
283.15	2.91	3.80	1.88	2.56	1.16	3.79	0.67	2.23	0.34	1.42
288.15	3.47	1.58	2.31	−0.16	1.44	0.16	0.82	−1.75	0.45	−0.85
293.15	4.07	−1.83	2.76	−4.76	1.74	−5.49	1.04	−1.17	0.60	0.32
298.15	5.01	0.13	3.51	−1.92	2.21	−5.14	1.29	−2.68	0.78	3.12
303.15	6.11	1.63	4.35	−0.78	2.94	0.76	1.64	−1.39	0.96	2.26
308.15	7.41	3.01	5.38	1.04	3.71	1.99	2.11	1.35	1.13	0.12
313.25	8.91	3.99	6.59	2.72	4.73	4.90	2.69	3.40	1.31	−1.50
318.15	10.49	3.34	7.81	1.95	5.73	3.56	3.26	0.75	1.52	−0.75
323.25	12.1	1.10	9.09	0.15	6.7	−0.66	4.02	0.05	1.72	−0.40
328.25	14.12	0.35	10.41	−2.56	7.91	−3.41	4.87	−2.19	1.96	2.63

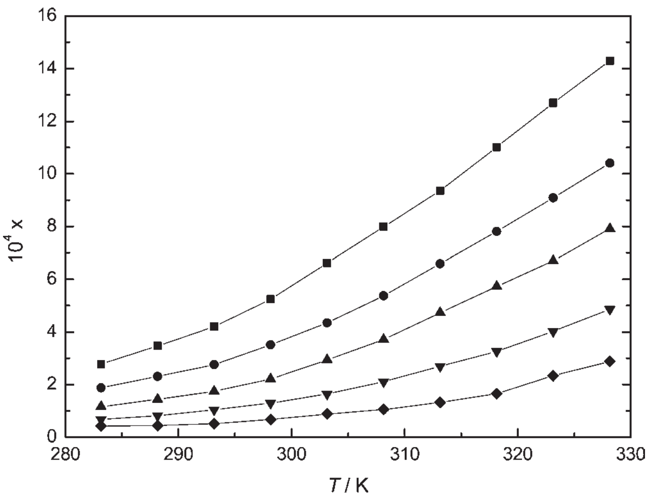

Figure 2. Solubility x of 2,7-dihydroxynaphthalene in aqueous solutions of sodium sulfate at different temperatures: ■, water; ●, 5 % Na_2SO_4; ▲, 10 % Na_2SO_4; ▼, 15 % Na_2SO_4; ♦, 20 % Na_2SO_4; —, calculated values.

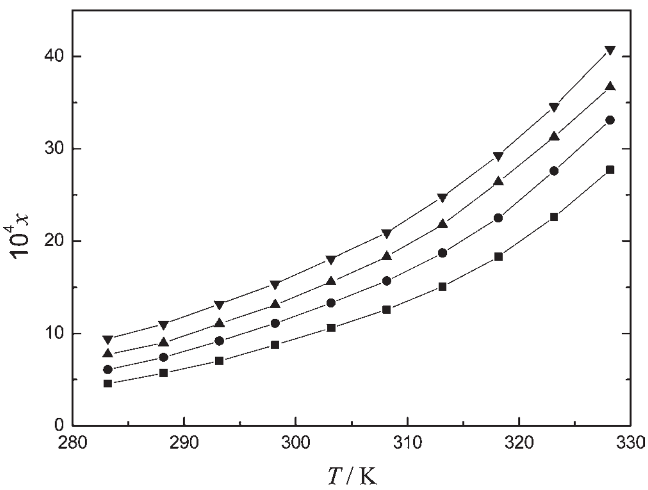

Figure 3. Solubility x of 2,7-dihydroxynaphthalene in aqueous solutions of ethanol at different temperature: ■, 5 % C_2H_5OH; ●, 10 % C_2H_5OH; ▲, 15 % C_2H_5OH; ▼, 20 % C_2H_5OH; —, calculated values.

interactions are the basis of the phenomenon that "like dissolves like" and include van der Waals forces, hydrogen bonding, dipole—dipole, and ion—dipole interactions. The solubility of 2,7-dihydroxynaphthalene typically increases with an increase in the fraction of ethanol.

The relationship between temperature and solubility of 2,7-dihydroxynaphthalene is correlated by a modified Apelblat equation, which is a semiempirical equation

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

where T is the absolute temperature, and x stands for the solubility of 2,7-dihydroxynaphthalene in aqueous solutions of sodium chloride, sodium sulfate, or ethanol in mole 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

Table 4. Parameters of Equation 1 for 2,7-Dihydroxynaphthalene in Aqueous Solutions of Different Mass Fractions

solvent		A	B	C	rmsd·10^4
sodium chloride	w = 0.05	288.11	−17155.42	−41.85	0.17
	w = 0.10	−70.17	−783.51	11.30	0.09
	w = 0.15	−331.56	11034.57	50.14	0.06
	w = 0.20	−526.27	19885.58	78.98	0.08
sodium sulfate	w = 0	180.80	−11473.99	−26.30	0.40
	w = 0.05	64.96	−6390.86	−9.03	0.13
	w = 0.10	12.26	−4422.40	−1.02	0.15
	w = 0.15	−109.88	1033.05	17.11	0.05
	w = 0.20	−570.79	21915.78	85.59	0.37
ethanol	w = 0.05	−94.97	890.09	14.90	0.53
	w = 0.10	−100.89	1335.90	15.72	0.54
	w = 0.15	−130.33	2856.15	20.03	0.43
	w = 0.20	−145.33	3747.80	22.16	0.54

Table 5. Curve-Fitting Parameters of Equation 3 for 2,7-Dihydroxynaphthalene in Aqueous Solutions of Different Mass Fractions

solute		a_i	b_i	c_i	rmsd
sodium chloride	A (i = 1)	720.62	−9498.31	16357.00	3.90
	B (i = 2)	−36891.09	433904.66	−752090.00	204.84
	C (i = 3)	−106.08	1410.41	−2431.00	0.56
sodium sulfate	A (i = 1)	142.56	984.42	−21702.29	64.07
	B (i = 2)	−9696.06	−52085.61	1002460.00	2949.05
	C (i = 3)	−20.64	−143.25	3215.43	9.51
ethanol	A (i = 1)	−84.10	−134.04	−908.00	4.90
	B (i = 2)	241.44	9040.76	44584.00	219.86
	C (i = 3)	13.32	19.43	131.00	0.73

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 difference between experimental and calculated results is 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:

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

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. Table 4 shows that the values of parameters B and C increase with the increase in sodium chloride, sodium sulfate, and ethanol concentrations for 2,7-dihydroxynaphthalene, while the values of parameter A decrease. From Figures 1 to 3, 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 2 to correlate the solubility of 2,7-dihydroxynaphthalene at different solvent compositions, parameters A, B, and C were assumed to be a function of sodium chloride, sodium sulfate, or ethanol in mass fraction w,

$$\begin{cases} A = a_1 + b_1 w + c_1 w^2 \\ B = a_2 + b_2 w + c_2 w^2 \\ C = a_3 + b_3 w + c_3 w^2 \end{cases} \quad (4)$$

where a_1, b_1, c_1, a_2, b_2, c_2, a_3, b_3, and c_3 are coefficients. The calculated solubility of x at solvent compositions of w = 0, 0.05, 0.10, 0.15, and 0.20 and in the temperature range from (283.15 to 328.15) K is plotted in Figures 1 to 3. 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 5 together with the root-mean-square deviations. 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 Table 4 that the calculated values of parameters A, B, and C show good agreement with the regressed values.

From Tables 1 to 3, we could elicit the following conclusions: (1) The solubility of 2,7-dihydroxynaphthalene in aqueous sodium chloride, sodium sulfate, or ethanol solutions increases with temperature, but the increase with temperature varies according to different mass concentrations of solute solution. (2) The experimental data can be regressed by eq 1 for each group. The experimental solubility and correlation equation in this work can be useful in the manufacturing and separating processes of 2,7-dihydroxynaphthalene in industry.

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REFERENCES

(1) Mori, K.; Kimoto, S.; Inoue, T.; Akiyama, T.; Kida, S. *Manufacture of High-molecular-weight Novolak Resins having 2,7-Dihydroxynaphthalene Skeletons*. Japan Patent 2,010,248,407, November 4, 2010.

(2) Yasushi, S. *Naphthalenone Skeleton-containing Epoxy Resins, their Manufacture, their Compositions, their Cured Products with Good Solvent Solubility, and Printed Circuit Boards using Them*. Japan Patent 2,011,016,891, January 27, 2011.

(3) Yan, H. Q.; Chen, S.; Qi, G. R. Synthesis, Cure Kinetics and Thermal Properties of the 2,7-Dihydroxynaphthalene dicyanate. *Polymer* **2003**, *44*, 7861–7867.

(4) Thisayukta, J.; Nakayama, Y.; Kawauchi, S.; Takezoe, H.; Watanabe, J. Distinct Formation of a Chiral Smectic Phase in Achiral Banana-Shaped Molecules with a Central Core Based on a 2,7-Dihydroxynaphthalene Unit. *J. Am. Chem. Soc.* **2000**, *122*, 7441–7448.

(5) Bloom, C. R.; Heymann, R; Kaarsholm, N. C.; Dunn, M. F. Binding of 2,6- and 2,7-Dihydroxynaphthalene to Wild-type and E-B13Q Insulins: Dynamic, Equilibrium, and Molecular Modeling Investigations. *Biochemistry* **1997**, *36*, 12746–12758.

(6) Novikova, N. S.; Gorecka, E.; Kondratyeva, R. V.; Kilimenchuk, E. D. New Bent-Shaped Liquid Crystalline Derivatives of 2,7-Dihydroxynaphthalene containing Lateral Bromine atoms. *Liq. Cryst.* **2008**, *35*, 743–750.

(7) Jin, J.l.; Chang, J. H.; Jo, B. W. Dependence of Properties of Liquid-Crystalline Aromatic Copolyesters on Monomer Sequence. Copolyesters Derived from Terephthalic Acid, 2,7-Naphthalenediol and *p*-Hydroxybenzoic Acid. *Polym. Bull.* **1988**, *20*, 525–530.

(8) Baharvand, A. R.; Zaidi, Z. H.; Machwe, M. K. Fluorescence Characteristics of 1,3-, 1,4-, 2,3- and 2,7-Dihydroxynaphthalene Radical Cations. *Curr. Sci.* **1991**, *60*, 171–173.

(9) Eskelinen, A.; Molitor, C.; Kanerva, L. Allergic Contact Dermatitis from 2,7-Dihydroxynaphthalene in Hair Dye. *Contact Dermatitis* **1997**, *36*, 312–313.

(10) Ewa, R. S.; Marciniak, B.; Pavlyuk, V. Naphthalene-2,7-diol. *Acta Crystallogr., Sect. E* **2005**, *E61*, o114–o115.

(11) Ahmed, N. A. Space Group of Naphthalene-2,7-diol. *Egypt. J. Phys.* **1978**, *9*, 67–68.

(12) Wei, D. S.; Deng, B. C. Improvement on the Alkaline Fusion Process of 2,7-Dihydroxynaphthalene. *Anhui Chem. Ind.* **2004**, *30*, 32–33.

(13) Kozlov, V. V.; Zhuk, D. S. The Synthesis and New Applications of Dihydroxynaphthalenes. *Khim. Referat. Zhur.* **1941**, *4*, 123–125.

(14) Vorozhtsov, N. N. J.; Shein, S. M. Replacement of the Sulfo Group by Hydroxyl in the Aromatic Series. II. In Sodium 2,6- and 2,7-Naphthalenedisulfonates. *Ukr. Khem. Zh.* **1958**, *24*, 213–216.

(15) Shein, S. M. The Interaction between the Sodium Salts of Naphthalenesulfonic Acids and Solutions of Hydroxides. *Khim. Promysh.* **1961**, *37*, 109–112.

(16) Daglish, C. Ultraviolet Absorption Spectra of Some Hydroxynaphthalenes. *J. Am. Chem. Soc.* **1950**, *72*, 4859–4864.