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Solubility of NaF in NaF + NaX + H₂O (X = ClO₄ and NO₃) Ternary Systems and Density and Refractive Index of the Saturated Solutions at 298.15 K

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Data on the solubilities of NaF were determined in NaF + NaClO₄ + H₂O and NaF + NaNO₃ + H₂O ternary systems, and the density and refractive index of the saturated solutions were measured at 298.15 K. The solubility data and physical properties were determined for different molalities of the second electrolyte present in the ternary systems, within a range of 0 to 1.0 mol·kg⁻¹. Experimental data on the density and refractive index were fit to polynomials as a function of NaClO₄ or NaNO₃ concentration. Finally, a thermodynamic description was made of the solid−liquid equilibrium for the two ternary systems, based on the Reilly, Wood, and Robinson (R−W−R) model for calculation of the mean ionic activity coefficient of NaF in the ternary saturated solution. The Bromley model was used for the calculation of the activity and osmotic coefficients of the binary systems because these are required for making calculations with the R−W−R model.

Introduction

In a previous study,[1] we presented experimental data on the activity coefficients of NaF in the NaF + NaClO₄ + H₂O ternary system at 298.15 K. As a continuation of studies of the properties of this system, the present study reports data on the solubility of NaF and the values of density and the refractive index of its saturated solutions. We also present the same experimental information for the NaF + NaNO₃ + H₂O system.

Experimental data on solubility in these systems have not been found in the literature, despite the importance of this property for the design and simulation of crystallization operations. It is probable that these studies have not been carried out because the solubility of NaF gives values which are opposite to those shown by NaClO₄ and NaNO₃. These compounds are much more soluble than NaF. For example,[2] at 293.15 K, the molality of saturation of NaF is 0.967 mol·kg⁻¹, whereas for NaClO₄ and NaNO₃, it is 14.8 mol·kg⁻¹ and 10.2 mol·kg⁻¹, respectively.

In the present study, the experimental solubility data were correlated by following the procedures employed by Correa et al.[3] These authors used the Reilly−Wood−Robinson model[4] (R−W−R) to represent the solid−liquid equilibrium of various ternary systems. Following Correa et al., we used the Bromley[5] model for calculation of the activity coefficients for binary systems containing these electrolytes because these values are required for studying ternary systems using the R−W−R model. Finally, experimental data on density and the refractive index were correlated using polynomial equations with five and four empirical coefficients, respectively.

Experimental Section

Materials. Analytical-grade sodium fluoride, sodium perchlorate monohydrate, and sodium nitrate were supplied by

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Merck with minimum purities of 99 %, 99 %, and 99.5 %, respectively. All of the chemicals in this study were used without further purification. NaF and NaNO₃ were dried to constant weight for 48 h at 373.15 K prior to use. NaClO₄·H₂O was maintained in a desiccator, at ambient temperature, for 24 h prior to its use. The water employed in all the experiments was distilled and deionized (conductivity < 0.5 μS·cm⁻¹) before use.

Apparatus and Procedures. Known masses of water, NaClO₄ (or NaNO₃), and NaF, the latter being in excess to ensure saturation of the solutions, were measured on a Mettler-Toledo model AX204 analytical balance with a precision of 0.07 mg.

A rotary, thermostatically controlled water bath with a holder containing twelve 20 mL glass jars was used to obtain data on the phase equilibria. The system worked at 298.15 K, with an accuracy of 0.1 K. The samples were stirred for 72 h to reach equilibrium at the desired temperature. In all cases, the experiments were performed in duplicate. Following the agitation step, samples were allowed to decant for a further period of 4 h at constant temperature. The clear liquid of each equilibrium solution was collected by syringe and filtered using an Acrodisc 25 mm syringe filter, with a nominal pore size of 45 μm, for subsequent determinations of concentration, density, and refractive index. Syringes and other apparatuses used in the procedure were maintained at slightly elevated temperature to avoid any tendency of precipitation of salts from the solutions under study due to a decrease in temperature.

The content of fluoride in the ternary systems was obtained by an ion-selective electrode method (4500-F⁻ method[6]) using a Fischer Scientific accumet model 25 pH/ion meter and a VWR Scientific fluoride electrode (catalog number 34105-106).

Samples for chemical analysis of approximately 4.0 g were diluted in a volume of 250 mL with deionized water having a conductivity of 0.5 μS·cm⁻¹. Respective dilutions were then made such that a calibration line could be obtained. The calibration line was obtained using aqueous solutions of F⁻ from 0.5 to 2

Table 1. Solubility of NaF (S), Density (ρ), and Refractive Index (n_D) in NaF + NaX + H$_2$O (X = ClO$_4$ or NO$_3$) Ternary Systems at 298.15 K

m_2	S	ρ	n_D	m_2	S	ρ	n_D
mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3}		mol·kg^{-1}	mol·kg^{-1}	g·cm^{-3}	
NaF(1) + NaClO$_4$(2) + H$_2$O(3)				NaF(1) + NaNO$_3$(2) + H$_2$O(3)			
0.0000	0.982	1.03790	1.3374	0.0000	0.982	1.03790	1.3374
0.1145	0.904	1.04457	1.3380	0.1000	0.943	1.04148	1.3375
0.2285	0.826	1.05154	1.3386	0.2001	0.890	1.04503	1.3381
0.3420	0.775	1.05875	1.3392	0.2999	0.849	1.04852	1.3388
0.4550	0.717	1.06568	1.3398	0.3999	0.802	1.05249	1.3394
0.5677	0.646	1.07452	1.3405	0.5000	0.766	1.05615	1.3401
0.6798	0.580	1.08227	1.3412	0.6000	0.733	1.05987	1.3408
0.7916	0.534	1.09080	1.3419	0.6999	0.712	1.06371	1.3414
0.9028	0.493	1.10045	1.3427	0.7997	0.674	1.06766	1.3421
1.0136	0.441	1.10974	1.3436	0.8999	0.652	1.07152	1.3427
				0.9999	0.614	1.07540	1.3434

Table 2. Values for Coefficients in Equations 1 and 2

system	β_1^I	β_2^I	β_3^I	β_4^I	β_5^I
	density				
NaF(1) + NaClO$_4$(2) + H$_2$O(3)	1.03786	0.06002	−0.00701	0.03052	−0.01282
NaF(1) + NaNO$_3$(2) + H$_2$O(3)	1.03789	0.03623	−0.00519	0.01480	−0.00844

system	β_1^{II}	β_2^{II}	β_3^{II}	β_4^{II}
	refractive index			
NaF(1) + NaClO$_4$(2) + H$_2$O(3)	1.3374	0.00527	−0.00042	0.00123
NaF(1) + NaNO$_3$(2) + H$_2$O(3)	1.3374	0.00330	0.00530	−0.00261

ppm. The solubility values of the ternary systems represent the means of two independent replicates. On the basis of the preceding, the uncertainty was ± 0.029 g of NaF/100 g of solution (± 0.007 mol·kg^{-1}) for the NaF + NaClO$_4$ + H$_2$O system and ± 0.013 g of NaF/100 g of solution (± 0.003 mol·kg^{-1}) for the NaF + NaNO$_3$ + H$_2$O system.

The NaF concentration in the binary system (NaF + H$_2$O) was determined by evaporation of known masses of filtered saturated solutions at 393.15 K. Taking into account that the experiments were carried out in duplicate, the uncertainty was ± 0.01 g of NaF/100 g of solution.

Density measurements were carried out in triplicate using a Mettler-Toledo model DE50 oscillation densimeter, with a resolution of ± 1 × 10^{-5} g·cm^{-3}. The temperature was thermostatically controlled to 298.15 ± 0.1 K by means of a self-contained Peltier system provided with the densimeter. Density values represent the average of two independent experiments, with the measured values being reproducible to within ± 8 × 10^{-5} g·cm^{-3}.

The refractive index of each solution was determined using a Mettler-Toledo model RE40 refractometer with a resolution of ± 1 × 10^{-4}. The measurements were repeated at least three times with no appreciable variation. As in the case of the densimeter, the refractometer temperature was controlled to 298.15 ± 0.1 K by a self-contained Peltier system. Refractive index values represent the average of two independent experiments, with the measured values being reproducible to within ± 1 × 10^{-4}.

Results and Discussion

Solubility. Table 1 shows the solubility values of NaF (S) expressed as molality for both ternary systems evaluated in this study. It is observed that in both systems the solubility of NaF decreases with the molality of the second electrolyte (m_2) present in the system. In the NaF + NaClO$_4$ + H$_2$O system, the solubility decreases from 0.982 mol·kg^{-1} in a solution without NaClO$_4$ to 0.441 mol·kg^{-1} when the NaClO$_4$ reaches a molality of approximately 1.0 mol·kg^{-1}. However, in the NaF + NaNO$_3$ + H$_2$O system, the interval of decrease in the solubility is less,

going from 0.982 mol·kg^{-1} (solution without NaNO$_3$) to 0.614 mol·kg^{-1} when the NaNO$_3$ has a molality of approximately 1.0 mol·kg^{-1}.

The decrease in the solubility of NaF can be explained by the common ion effect. The contribution of sodium ions to the system by NaClO$_4$ or NaNO$_3$ tends to set back the dissociation equilibrium of the salt; that is, it is displaced more toward the formation of NaF than to its dissociation into F$^-$ and Na$^+$ ions, and therefore the solubility of the salt decreases. On the basis of the experimental results, this effect is greater when NaClO$_4$ is present.

The solubility of NaF in water in this study (0.982 mol·kg^{-1}) is near the values given in the literature. Linke and Seidell[7] reported that at 25 °C the value was 3.98 g of NaF/100 g of solution, representing a molality of 0.987 mol·kg^{-1}. Recently, Aghaie and Samaie[8] reported a value of 0.973 mol·L^{-1}. Converting our experimental datum to molarity, using the corresponding density value from Table 1, we obtained 0.979 mol·L^{-1}.

Physical Properties. Table 1 also presents experimental density values (ρ) and the refractive index (n_D) of the saturated solutions of the systems studied. For density, with a constant value for m_2, it can be noted that the density values of the NaF + NaClO$_4$ + H$_2$O system are always greater than those of the NaF + NaNO$_3$ + H$_2$O system. This indicates that the total mass of the dissolved salt in the first system is larger. For example, when NaClO$_4$ has an m_2 value of 0.9 mol·kg^{-1} (equal to 110.2 g of NaClO$_4$/1000 g of H$_2$O), the solubility of NaF is 0.493 mol·kg^{-1} (equal to 20.7 g of NaF/1000 g of H$_2$O), which leads to a value of 130.9 g of salt/1000 g of H$_2$O. When the molality of NaNO$_3$ is 0.9 mol·kg (76.5 g of NaNO$_3$/1000 g of H$_2$O), the solubility of NaF is 0.65 mol·kg^{-1} (27.3 g of NaF/1000 g of H$_2$O), which leads to a value of only 103.8 g of salt/1000 g of H$_2$O.

Table 1 shows that the values for the refractive index of both systems are not markedly different. For m_2 less than 0.45 mol·kg^{-1}, the system containing NaClO$_4$ shows greater n_D values; however, beginning from this value of m_2, both systems tend to have similar values for n_D.
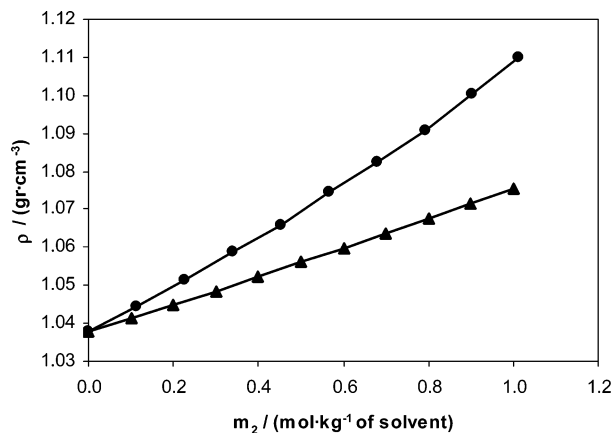
Figure 1. Density as a function of the molality of $NaClO_4$ or $NaNO_3$ at 298.15 K. Experimental points: ▲, $NaF + NaNO_3 + H_2O$ system; ●, $NaF + NaClO_4 + H_2O$ system; —, calculated from eq 1.

The values for the density and refractive index at saturation were correlated as a function of the molality of the second electrolyte (m_2) present in the system ($NaClO_4$ or $NaNO_3$), following eqs 1 and 2

$$\rho \ (\text{g/cm}^3) = \beta_1^I + \beta_2^I m_2 + \beta_3^I m_2^2 + \beta_4^I m_2^3 + \beta_5^I m_2^4 \quad (1)$$

$$n_D = \beta_1^{II} + \beta_2^{II} m_2 + \beta_3^{II} m_2^2 + \beta_4^{II} m_2^3 \quad (2)$$

where β_i^j are empirical coefficients. The optimized values of these coefficients are given in Table 2. The average absolute deviation (AAD) between the experimental density values and those calculated using eq 1 is 1.7×10^{-4} g·cm⁻³ for the first ternary system ($NaF + NaClO_4 + H_2O$) and 4.7×10^{-5} g·cm⁻³ for the second ternary system ($NaF + NaClO_4 + H_2O$). For the refractive index, both systems have an AAD value of 1×10^{-4}. These results confirm the good fit of the experimental data to the physical properties studied. Figure 1 presents a comparison between the experimental density values and those calculated using eq 1.

Thermodynamic Representation of the Solid−Liquid Equilibrium. The solid−liquid equilibrium of the two ternary systems at 298.15 K was analyzed following the procedure described by Correa et al.[3] These authors successfully applied the Reilly−Wood−Robinson[4] and the Bromley[5] models to correlate the solubility data of four ternary systems having a common ion. All the systems were analyzed at 298.15 K, and the electrolytes were of the 1:1 type.

In the thermodynamic analysis of the present study, the R−W−R model permits estimation of the activity coefficient of NaF in the ternary system, whereas the Bromley model is used for calculating the activity coefficient of the $NaF + H_2O$ system and the osmotic coefficients of the $NaF + H_2O$, $NaClO_4 + H_2O$, and $NaNO_3 + H_2O$ binary systems.

For systems of two 1:1 electrolytes, with a common ion, saturated with respect to component 1, and without forming hydrates, the solubility product (Kps) is given by

$$\text{Kps} = (m_1^* \gamma_1^*)^2 = m_1(m_1 + m_2)\gamma_1^2 \quad (3)$$

where m_1^* and γ_1^* are the molality and mean ionic activity coefficient of component 1 in the binary saturated system and m_1, m_2, and γ_1 are the molalities of components 1 and 2 and the mean ionic activity coefficient of component 1 in the ternary system.

Table 3. Ion-Interaction Parameters of the R−W−R Model at 298.15 K

system	E	F	AAD
	kg·mol⁻¹	kg²·mol⁻²	mol·kg⁻¹
$NaF(1) + NaClO_4(2) + H_2O(3)$	0.29687	−0.01732	0.005
$NaF(1) + NaNO_3(2) + H_2O(3)$	0.17293	−0.12953	0.004

Following eq 3, the value of Kps can be obtained starting from the information from a saturated binary solution, which in this case has a value of 0.318. For this estimation, we assume that the experimental value of m_1^* is 0.982 mol·kg⁻¹ (obtained from Table 1), and for this concentration, γ_1^* has a value of 0.574, determined from the Bromley[5] model using $B_{NaF} = 0.0041$ kg·mol⁻¹.

For a fixed temperature, the solubility of NaF in the ternary system (m_1) can be calculated from eq 3, given the Kps and the mean ionic activity coefficient of NaF in the ternary system (γ_1). In this way, the description of the solubility of NaF can be provided as a function of the molality of the second electrolyte present in the ternary system (m_2).

The R−W−R model was used to calculate γ_1, the expression of which for ternary systems with a common ion and 1:1 electrolytes is given by[3]

$$\ln \gamma_1 = \ln \gamma_1^0 + Y_2(\varphi_2^0 - \varphi_1^0) + Y_2 m[E + 0.5(1 + Y_1)Fm] \quad (4)$$

where γ_1 and γ_1^0 are the mean ionic activity coefficients of NaF in the ternary solution at its molality m_1 and in the binary solution at a total molality m, respectively, where $m = m_1 + m_2$. The symbols φ_1^0 and φ_2^0 represent the osmotic coefficients of the binary solutions of NaF and the second electrolyte ($NaClO_4$ or $NaNO_3$), respectively, evaluated at a total molality m. Y_1 and Y_2 are the molar fractions (free of water) of the NaF and the second electrolyte in the ternary solution ($NaClO_4$ or $NaNO_3$). E and F are parameters of the mixture, which are related to the interactions of the different ions but are equal in charge. In this case, this is represented by the interactions $F-ClO_4$ (for the $NaF + NaClO_4 + H_2O$ system) and $F-NO_3$ (for the $NaF + NaNO_3 + H_2O$ system).

The values of γ_1^0, φ_1^0, and φ_2^0 are determined using the Bromley model. The advantage of this model is that it requires the use of only one parameter, symbolized by B. For 1:1 electrolytes at a temperature of 25 °C, these expressions are given by[5]

$$\ln \gamma_1^0 = 2.303 \left[\frac{-0.511m^{1/2}}{1 + m^{1/2}} + \frac{(0.06 + 0.6B_1)m}{(1 + 1.5m)^2} + B_1 m \right] \quad (5)$$

$$1 - \varphi_i^0 = 2.303 \times$$
$$\left[\frac{0.511P(m^{1/2})}{m} - (0.06 + 0.6B_i)0.5mR(1.5m) - 0.5B_i m \right] \quad (6)$$

where $i = 1, 2$ (1 = NaF, 2 = $NaClO_4$ or $NaNO_3$)

$$P(m^{1/2}) = (1 + m^{1/2}) - \frac{1}{(1 + m^{1/2})} - 2 \ln(1 + m^{1/2}) \quad (7)$$

$$R(1.5m) = \frac{2}{1.5m} \left[\frac{1 + 3m}{(1 + 1.5m)^2} - \frac{\ln(1 + 1.5m)}{1.5m} \right] \quad (8)$$

With eq 3 and the knowledge of parameters E and F (eq 4), we can predict the solubility values; nevertheless, these are unknown and will be determined using experimental information produced in this study. Thus, the correlation of the experimental
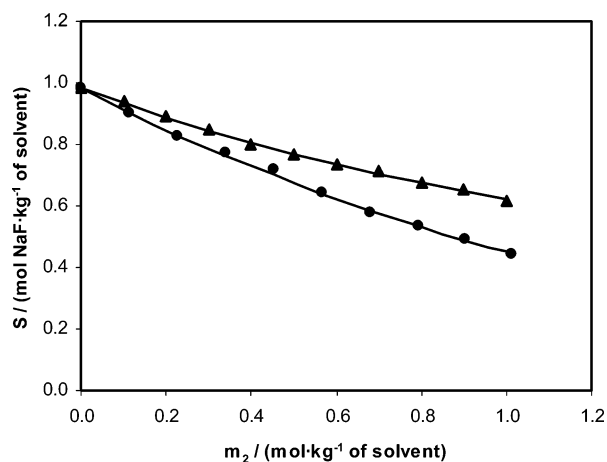
Figure 2. Solubility of NaF as a function of the molality of $NaClO_4$ or $NaNO_3$ at 298.15 K. Experimental points: ▲, $NaF + NaNO_3 + H_2O$ system; ●, $NaF + NaClO_4 + H_2O$ system; −, calculated from eqs 3 and 4.

solubility data is carried out using the following iterative procedure: for a given experimental value of m_2 ($NaClO_4$ or $NaNO_3$), one finds the value of m_1 and the values of parameters E and F which permit the simultaneous solutions of eqs 3 and 4. In the iterative process for electrolytes $NaClO_4$ and $NaNO_3$, the values for the B parameter used were[5] 0.0330 kg·mol^{-1} and -0.0128 kg·mol^{-1}, respectively. The value of this parameter for NaF has been presented in the preceding paragraph as 0.0041 kg·mol^{-1}.

The values of parameters E and F obtained from the iteration for the ternary systems are shown in Table 3. In this table are also included the AADs between the experimental solubility values and those estimated by the iteration process. Figure 2 shows in graphic form the good agreement existing between the experimental and the calculated values for different concentrations of the second electrolyte present in the system (m_2).

Supposing that the values of the parameters B, E, and F remain constant with temperature, it would be possible to predict the solubility values at other temperatures, following the procedures given in this study. To carry out such a prediction for a given temperature, we must know the solubility of the $NaF + H_2O$ system to then estimate the Kps. If we do not have this information, the Kps can be estimated using the van't Hoff equation. This type of prediction is useful in the design and operation of crystallizers; nevertheless, it is only possible to carry out for temperatures near 298.15 K because the parameters of the models are temperature dependent.

Conclusions

Data are presented on the solubility of NaF, at 298.15 K, for the $NaF + NaClO_4 + H_2O$ and $NaF + NaNO_3 + H_2O$ systems. The results showed that the increase in the concentration of the $NaClO_4$ or $NaNO_3$ produced a decrease in the solubility of NaF.

It is concluded that this behavior was a consequence of the common ion effect. It was shown that the Reilly−Wood−Robinson and Bromley thermodynamic models were good alternatives for representing the solid−liquid equilibria of both ternary systems.

We also presented data on the density (ρ) and refractive index (n_D) of the saturated solutions at 298.15 K. The results showed that both properties increased with increases in the concentrations of $NaClO_4$ or $NaNO_3$ in the system, and the values could be represented using a polynomial as a function of the concentration of $NaClO_4$ or $NaNO_3$. In general, the values of n_D in both ternary systems are similar; nevertheless, the values of ρ in the $NaF + NaClO_4 + H_2O$ system are greater than those of the $NaF + NaNO_3 + H_2O$ system. This indicated that the total mass of dissolved salts was greater in the first system.

Literature Cited

(1) Hernández-Luis, F.; Benjumea, D.; Vázquez, M.; Galleguillos, H. Activity Measurements in the $NaF + NaClO_4 + H_2O$ Ternary System at 298.15 K. *Fluid Phase Equilib.* **2005**, *235*, 72−82.

(2) Dean, J. D. *Lange's Handbook of Chemistry*, 40th ed.; McGraw-Hill: New York, 1992.

(3) Correa, H.; Vega, R.; Flores, F. Equilibrio Sólido-Líquido en Soluciones Acuosas de Electrolitos Fuertes. I. Uso de Modelos de Reilly-Wood-Robinson y de Bromley. *Contrib. Cient. Tecnol.* **1980**, *44*, 5−13.

(4) Reilly, P. J.; Wood, R. H.; Robinson, R. A. The Prediction of Osmotic and Activity Coefficients in Mixed-Electrolyte Solutions. *J. Phys. Chem.* **1971**, *75*, 1305−1315.

(5) Bromley, L. A. Thermodynamics Properties of Strong Electrolytes in Aqueous Solutions. *AIChE J.* **1973**, *19*, 313−320.

(6) *Standard Methods for the Examination of Water and Wastewater*, 19th ed.; Prepared and Published Jointly by American Public Health Association, American Water Works Association, and Water Environment Federation: Washington, DC, 1995.

(7) Linke, W. F.; Seidell, A. *Solubilities of Inorganic and Metal Organic Compounds*; American Chemical Society: Washington ,DC, 1965.

(8) Aghaie, M.; Samaie, E. Non-ideality and Ion-paring in Saturated Aqueous Solution of Sodium Fluoride at 25 °C. *J. Mol. Liq.* **2006**, *126*, 72−74.