Solubility in the Na + F + NO_3 and Na + PO_4 + NO_3 Systems in Water and in Sodium Hydroxide Solutions

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Solubilities of the Na + F + NO_3 and Na + PO_4 + NO_3 systems in aqueous solution and in sodium hydroxide solutions have been measured at (25 and 50) °C. Natrophosphate, the double salt of sodium fluoride and sodium phosphate, has been identified in the tank waste at the Hanford site (Richland, Washington, USA). The brine in these tanks is often saturated in nitrate. Solubility experiments were undertaken to better understand the chemistry in the Na + F + PO_4 + NO_3 + OH system. As the initial part of this effort, measurements of solubility in the constituent binary systems, NaF + $NaNO_3$ and Na_3PO_4 + $NaNO_3$, with and without the presence of sodium hydroxide, were performed and are reported herein. The presence of nitrate in the solution resulted in a decrease in the solubility of either sodium fluoride or trisodium phosphate. The presence of hydroxide in the solution also resulted in decreased solubility for each component.

Introduction

One challenge to the remediation of the 53 million gallons of legacy nuclear waste at the Hanford site in Richland, Washington, USA, is effective dissolution and mobilization of saltcake waste contained in the underground storage tanks. The saltcake is a complex mixture of primarily sodium salts and is the source of very interesting chemistry. Sodium nitrate is the dominant salt found in the tanks, but the presence of other anions, including carbonate, sulfate, nitrite, fluoride, and phosphate, gives rise to a variety of crystalline species in the waste. These species vary from tank to tank, as different campaigns at the Hanford site resulted in waste streams of differing compositions. One species that has been problematic during retrieval of salt from the tanks is the sodium−fluoride−phosphate double salt, natrophosphate [$Na_7F(PO_4)_2 \cdot 19H_2O$]. As this congruent double salt forms, it results in a reduction in the water in the aqueous phase, as the 19 waters of hydration are taken out of solution. This gives rise to much higher concentrations of species remaining in the aqueous phase. In the absence of fluoride, the phosphate in the waste may precipitate as $Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$, also resulting in a reduction in the water in the aqueous phase. It is extremely important that the solubility of both natrophosphate and trisodium phosphate dodecahydrate be predicted with confidence at conditions present in nitrate-rich brine, so as to avoid problems with plugging as a result of precipitation of these phosphate species in pipelines. As the initial part of this effort to improve knowledge of the Na + F + PO_4 system in nitrate-rich brines, solubilities in the constituent binary systems, NaF + $NaNO_3$ and Na_3PO_4 + $NaNO_3$, were measured in both aqueous and sodium hydroxide solutions and are reported in this work.

Literature Review

Of interest in this work is the solubility of sodium nitrate in both aqueous solution and in sodium hydroxide solutions. The solubility of sodium nitrate in aqueous solution over a wide range of temperatures was compiled by Linke and Seidell.[1] More recently, Archer[2] presented a comprehensive review of the thermodynamics of the $NaNO_3$ + H_2O system. In his review, he used his extension of the Pitzer ion-interaction equation and fit parameters from a variety of thermodynamic measurements, including osmotic coefficients, freezing point depression, differential enthalpy of solution, and apparent molar heat capacities among others, and used the results of his parametrization to estimate the solubility of sodium nitrate in aqueous solution. He reported a calculated solubility of 10.839 m $NaNO_3$ [92.1 g of $NaNO_3$ (100 g of $H_2O)^{-1}$] at 25 °C and 13.453 m $NaNO_3$ [114.34 g of $NaNO_3$ (100 g of $H_2O)^{-1}$] at 50 °C.

The ternary system comprised of sodium nitrate, sodium hydroxide, and water was examined by Plekhotkin and Bobrovskaya.[3] They reported density, viscosity, and refractive index as a function of composition as well as solubility for this system at (20 and 25) °C. Solubilities of 81.8 g (100 g of $H_2O)^{-1}$ and 88.0 g (100 g of $H_2O)^{-1}$ were reported for (20 and 25) °C, respectively, for sodium nitrate in aqueous solution. The solubility at 25 °C is lower than that calculated by Archer[2] by approximately 4 g of $NaNO_3$ (100 g of $H_2O)^{-1}$. The solubility of sodium nitrate was reduced in sodium hydroxide solution. Addition of sodium hydroxide in the amount of 8.7 g (100 g of $H_2O)^{-1}$ resulted in a solubility of 65.2 g of $NaNO_3$ (100 g of $H_2O)^{-1}$ at 20 °C, while addition of 9.1 g of NaOH (100 g of $H_2O)^{-1}$ resulted in a solubility of 70.1 g of $NaNO_3$ (100 g of $H_2O)^{-1}$ at 25 °C.

Kurnakov and Nikolaev[4] measured the solubility of sodium nitrate at both (25 and 65) °C in solutions of sodium hydroxide. They reported pure component solubilities of 91.5 g of $NaNO_3$ (100 g of $H_2O)^{-1}$ at 25 °C and 127.1 g of $NaNO_3$ (100 g of $H_2O)^{-1}$ at 65 °C. The addition of 6.1 g of sodium hydroxide per 100 g of H_2O resulted in a decrease in sodium nitrate

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Table 1. Solubilities in the Sodium Fluoride + Sodium Nitrate System at 25 °C

NaF	$NaNO_3$	NaOH	
g of NaF (100 g of H_2O)$^{-1}$	g of $NaNO_3$ (100 g of H_2O)$^{-1}$	g of NaOH (100 g of H_2O)$^{-1}$	solid-phase identification
In Aqueous Solution			
4.31	0.00	0.0	NaF
3.07	8.78	0.0	NaF
2.09	21.14	0.0	NaF
1.26	43.84	0.0	NaF
0.92	60.82	0.0	NaF
0.45	92.13	0.0	$NaNO_3$
0.45	91.30	0.0	$NaNO_3$
0.00	93.70	0.0	$NaNO_3$
In 1 m NaOH Solution			
2.53	0.00	4.0	NaF
1.72	10.49	4.0	NaF
0.95	33.02	4.0	NaF
0.65	52.63	4.0	NaF
0.43	74.70	4.0	NaF
0.43	76.06	4.0	NaF
0.40	75.75	4.0	NaF
0.50	81.11	4.0	NaF + $NaNO_3$
0	84.26	4.0	$NaNO_3$
In 3 m NaOH Solution			
1.15	0.00	12.0	NaF
0.80	11.84	12.0	NaF
0.67	33.32	12.0	NaF
0.46	48.74	12.0	NaF
0.42	62.17	12.0	NaF
0.48	64.89	12.0	NaF + $NaNO_3$
0.00	64.48	12.0	$NaNO_3$
In 5 m NaOH Solution			
0.51	0.00	20.0	NaF
0.50	10.68	20.0	NaF
0.29	31.97	20.0	NaF
0.225	46.17	20.0	NaF + $NaNO_3$
0.00	47.38	20.0	$NaNO_3$

Table 2. Solubilities in the Sodium Fluoride + Sodium Nitrate System at 50 °C

NaF	$NaNO_3$	NaOH	
g of NaF (100 g of H_2O)$^{-1}$	g of $NaNO_3$ (100 g of H_2O)$^{-1}$	g of NaOH (100 g of H_2O)$^{-1}$	solid-phase identification
In Aqueous Solution			
4.01	0.00	0.0	NaF
2.86	13.36	0.0	NaF
1.57	31.92	0.0	NaF
1.08	53.12	0.0	NaF
0.75	72.49	0.0	NaF
0.58	92.21	0.0	NaF
0.44	108.1	0.0	NaF
0.38	111.17	0.0	NaF + $NaNO_3$
0.00	112.06	0.0	$NaNO_3$
In 1 m NaOH Solution			
2.47	0.00	4.0	NaF
1.60	18.02	4.0	NaF
1.15	31.30	4.0	NaF
0.76	52.40	4.0	NaF
0.54	67.92	4.0	NaF
0.43	86.29	4.0	NaF
0.41	96.25	4.0	NaF + $NaNO_3$
0.00	97.27	4.0	$NaNO_3$
In 3 m NaOH Solution			
1.04	0.00	12.0	NaF
0.84	9.16	12.0	NaF
0.57	24.60	12.0	NaF
0.37	41.96	12.0	NaF
0.32	58.37	12.0	NaF
0.37	68.47	12.0	NaF + $NaNO_3$
0.00	69.34	12.0	$NaNO_3$
In 5 m NaOH Solution			
0.56	0.00	20.0	NaF
0.42	8.79	20.0	NaF
0.36	23.97	20.0	NaF
0.34	39.96	20.0	NaF
0.27	58.43	20.0	NaF
0.24	69.00	20.0	NaF + $NaNO_3$
0.00	74.43	20.0	$NaNO_3$

solubility to 77.5 g of $NaNO_3$ per 100 g of H_2O at 25 °C, while addition of 16.3 g of sodium hydroxide per 100 g of water further suppressed the solubility to 57.1 g of $NaNO_3$ (100 g of H_2O)$^{-1}$.

Literature data for the solubility of sodium fluoride were reviewed by Weber et al.[5,6] He noted the scatter associated with the sodium fluoride solubility data used by Linke and Seidell[1] to produce an average solubility envelope. Linke and Seidell reported a solubility of 4.14 g of NaF per 100 g of saturated solution at 25 °C, or 0.987 mol of NaF (kg of H_2O)$^{-1}$, taken from the smoothed solubility envelope. The solubility of sodium fluoride in aqueous solution at 25 °C was measured using the Solvent Evaporating method and reported as 0.973 ± 0.002 M by Aghaie and Samaie.[7] Morales et al.[8] recently reported a solubility of 0.982 moles of NaF per kilogram of saturated solution at 25 °C (4.30 g of NaF (100 g of H_2O)$^{-1}$). An uncertainty of ± 0.029 g of NaF per 100 g of saturated solution was estimated by the authors.

Solubility data for trisodium phosphate in aqueous solution were reviewed by Weber[5,6,9] and in multicomponent systems by Eysseltova.[10] Eysseltova notes the disagreement between reported solubilities and composition of the solid phase at different temperatures and concludes that "more work is needed to clarify the nature of the solid phases before the solubility data can be evaluated". Trisodium phosphate exists as a hydrate in the solid phase, with the degree of hydration a function of temperature. At 25 °C, the stable crystalline phase has been reported as $Na_3PO_4 \cdot 12H_2O$ by Apfel (in Linke and Seidell[1]), $Na_3PO_4 \cdot 1/7NaOH \cdot 12H_2O$ by Kobe and Leipper,[11] and $Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$ by Wendrow and Kobe.[12] The pure component solubility in aqueous solution for trisodium phosphate at 25 °C has been reported as 0.835 moles of Na_3PO_4 (kg of H_2O)$^{-1}$,[1] 0.70 moles of Na_3PO_4 (kg of H_2O)$^{-1}$,[11] and 0.887 moles of Na_3PO_4 (kg of H_2O)$^{-1}$.[12] The existence of hydrates for trisodium phosphate has also been examined by Bell,[13] who was able to produce only the hemihydrate ($1/2 \cdot H_2O$), the hexahydrate, and the octahydrate in the laboratory. The formation of a particular hydrate was dependent on the overall composition of the solution from which the hydrate was crystallized.

Wendrow and Kobe reported the transition to trisodium phosphate octahydrate ($Na_3PO_4 \cdot 8H_2O$) as occurring at approximately 55 °C and to trisodium phosphate hexahydrate ($Na_3PO_4 \cdot 6H_2O$) at approximately 65 °C[12] for solutions containing a constant sodium oxide/phosphorus pentoxide molar ratio of 3. However, they also reported solid phases along the 40 °C isotherm, as established in their laboratory, and identified four difference solid phases, for the range of P_2O_5 from (0.12 to 19.18) wt % (hemihydrate, hexahydrate, dodecahydrate, and octahydrate). $Na_3PO_4 \cdot 8H_2O$ was reported as the solid phase at 40 °C for solutions containing between (11.31 and 19.18) wt % P_2O_5.[14] More recently, Thermo-Raman spectroscopy was employed by Ghule et al.[15] to examine the $Na_2O + P_2O_5$ system, and they concluded that the $Na_3PO_4 \cdot 8H_2O$ was present at 41 °C. Bell[13] reported that the octahydrate crystal was similar to that of the sodium phosphate dodecahydrate in general appearance. However, the octahydrate crystal exhibited higher polarization colors and showed extinction angles of up to 22°,

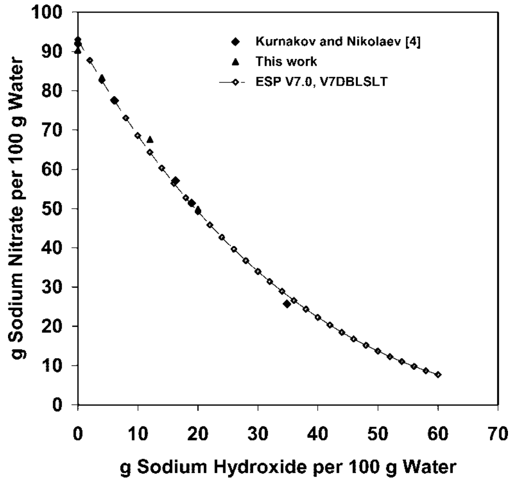

Figure 1. Solubility of sodium nitrate in sodium hydroxide solutions at 25 °C.

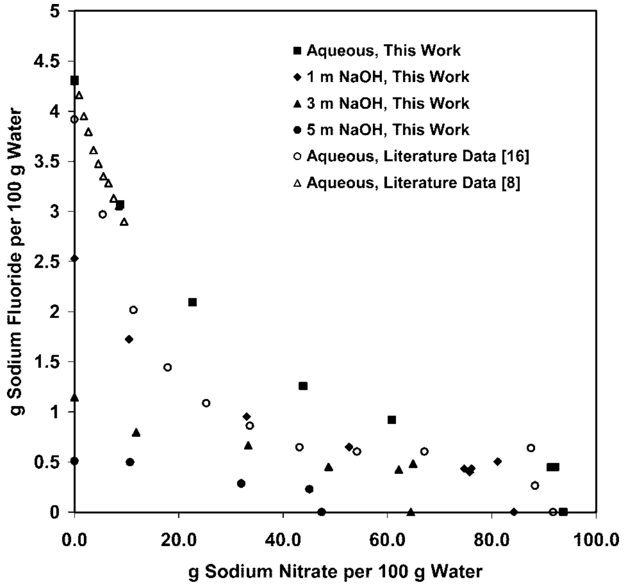

Figure 2. Solubility in the $NaF + NaNO_3 + NaOH + H_2O$ system at 25 °C.

depending on crystal orientation, while the dodecahydrate exhibits only parallel extinction.[13]

Solubility in the sodium nitrate + sodium fluoride system in aqueous solution at 25 °C was experimentally determined by Zhikharev et al.[16] They reported a pure component solubility of 3.77 mass % (liquid phase) for sodium fluoride and a pure component solubility of 47.85 mass % (liquid phase) for sodium nitrate. This pure component solubility at 3.92 g of NaF (100 g of H_2O)$^{-1}$ is between (5 and 8) % lower than the values reported by Linke and Seidell,[1] Aghaie and Samaie,[7] and Morales et al.[8] The influence of sodium nitrate on the solubility of sodium fluoride is marked; with the addition of approximately 11.33 g of $NaNO_3$ to 100 g of H_2O, the solubility of sodium fluoride is reduced from 3.92 g of NaF (100 g of H_2O)$^{-1}$ to 2.02 g of NaF (100 g of H_2O)$^{-1}$. Petrov et al.[17] examined this same system at its bubble point at atmospheric pressure. For both studies, the authors reported only the presence of the simple sodium salts, either sodium nitrate or sodium fluoride, as the equilibrium solid phase. Morales et al.[8] examined the influence of sodium nitrate in solution on the solubility of sodium fluoride at 25 °C, over a limited range of sodium nitrate concentrations (up to a concentration of ~ 1.1 moles $NaNO_3$ per kg of H_2O). The presence of sodium nitrate in solution suppressed the solubility of sodium fluoride, with the addition of 9.55 g of $NaNO_3$ (100 g of H_2O)$^{-1}$ resulting in a sodium fluoride solubility of 2.9 g of NaF (100 g of H_2O)$^{-1}$.

Zhikharev et al.[18] examined the aqueous solubility in sodium nitrate + sodium phosphate at 25 °C and at the atmospheric boiling point. They identified either sodium nitrate ($NaNO_3$) or sodium orthophosphate dodecahydrate ($Na_3PO_4 \cdot 12H_2O$) as the stable crystalline phases at 25 °C. Phosphate concentration in the liquid phase was determined using a colormetric method.[18] Again, the influence of sodium nitrate on the solubility of sodium phosphate was notable, with the addition of 8.9 g of $NaNO_3$ to 100 g of H_2O resulting in a decrease in solubility of sodium phosphate from 14.13 g of Na_3PO_4 per 100 g of H_2O to 6.97 g of Na_3PO_4 per 100 g of H_2O.

No literature data were identified for either of the binary systems, sodium nitrate + sodium fluoride or sodium nitrate + sodium phosphate, in sodium hydroxide solutions.

Experimental Section

Materials. All chemicals used were ACS grade or better with assays of ≥ 99 % purity. Sodium hydroxide was purchased from Fisher Scientific. Trisodium phosphate dodecahydrate ($Na_3PO_4 \cdot 12H_2O$) was purchased from Sigma Chemical Co. and sodium nitrate ($NaNO_3$) from Aldrich Chemical Co. Sodium fluoride (NaF, ≥ 99.9 % purity) was purchased from Advance Research Chemicals, Inc. (Catoosa, OK). Standards required for ion chromatography were obtained from Inorganic Ventures, Inc., and were traceable to NIST.

Methods. All solutions were prepared gravimetrically using an AND model GR-120 analytical balance accurate to ± 0.1 mg. Type I water with a resistivity less than 17.8 MΩ-cm from a Barnstead Nanopure Infinity water purification system was used for all preparations. For the $NaF + NaNO_3$ binary system, samples were prepared in water, 1 m NaOH, 3 m NaOH, and 5 m NaOH solutions. For the $Na_3PO_4 + NaNO_3$ binary system, samples were prepared in water, 1 m NaOH, and 3 m NaOH solutions. Sufficient quantities of the sodium hydroxide solutions were prepared as stock solutions. Approximately 20 g of the solvent (either water or the stock NaOH solution) was measured into a polypropylene sample vessel. An appropriate amount of each solute was weighed and added to the sample vessel in sequence. Upon the addition of a solute, the mixture was shaken vigorously, to ensure complete dissolution of the solids. In some cases, when the solute did not dissolve completely, the mixture was sealed in the sample vessel and left at elevated temperature for a few minutes. In extreme cases, a few hours at elevated temperature were needed to ensure complete dissolution of the solutes. All samples were sealed and allowed to equilibrate at a temperature (either (25 or 50) °C) for a period of two weeks. Previous solubility studies had examined the temporal behavior of ion concentrations in the solution, and two weeks was established as a sufficient length of time for equilibration.[19] Shaking of each mixture was performed daily.

Following the equilibration period, each sample was filtered using a vacuum. The filtration process was carried out at the equilibration temperature using a ceramic filter, with a jacketed circulation path through which water was passed from a constant temperature circulation bath. A premeasured mass of water was added to the collection flask prior to the start of filtration. This initial dilution of the filtrate prevented the formation of solids in the filtrate arising from a decrease in temperature during filtration. The diluted filtrate was weighed. Crystal images were

Table 3. Solubilities in the Sodium Phosphate + Sodium Nitrate System at 25 °C

Na_3PO_4	$NaNO_3$	NaOH	
g of Na_3PO_4 (100 g of $H_2O)^{-1}$	g of $NaNO_3$ (100 g of $H_2O)^{-1}$	g of NaOH (100 g of $H_2O)^{-1}$	solid-phase identification
In Aqueous Solution			
10.64	0.00	0.0	$Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$
6.46	8.10	0.0	$Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$
3.34	24.72	0.0	$Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$
2.45	41.20	0.0	$Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$
1.85	58.01	0.0	$Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$
0.00	90.35	0.0	$NaNO_3$
In 1 m NaOH Solution			
3.14	0.00	4.0	$Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$
2.23	8.71	4.0	$Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$
1.70	24.07	4.0	$Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$
1.50	40.20	4.0	$Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$
1.38	56.39	4.0	$Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$
0.00	80.13	4.0	$NaNO_3$
In 3 m NaOH Solution			
0.73	0.00	12.0	$Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$
0.70	9.32	12.0	$Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$
0.66	24.09	12.0	$Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$
0.66	39.97	12.0	$Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$
0.64	52.17	12.0	$Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$
0.00	60.32	12.0	$NaNO_3$

Table 4. Solubilities in the Sodium Phosphate + Sodium Nitrate System at 50 °C

Na_3PO_4	$NaNO_3$	NaOH	
g of Na_3PO_4 (100 g of $H_2O)^{-1}$	g of $NaNO_3$ (100 g of $H_2O)^{-1}$	g of NaOH (100 g of $H_2O)^{-1}$	solid-phase identification
In Aqueous Solution			
39.01	0.00	0.0	$Na_3PO_4 \cdot 8H_2O$
22.69	7.96	0.0	$Na_3PO_4 \cdot 8H_2O$
15.68	23.98	0.0	$Na_3PO_4 \cdot 8H_2O$
9.10	41.39	0.0	$Na_3PO_4 \cdot 8H_2O$
10.55	47.74	0.0	$Na_3PO_4 \cdot 8H_2O$
0.00	112.06	0.0	$NaNO_3$
In 1 m NaOH Solution			
23.23	0.00	4.0	$Na_3PO_4 \cdot 8H_2O$
12.71	7.89	4.0	$Na_3PO_4 \cdot 8H_2O$
9.22	21.89	4.0	$Na_3PO_4 \cdot 8H_2O$
6.83	37.85	4.0	$Na_3PO_4 \cdot 8H_2O$
5.53	44.04	4.0	$Na_3PO_4 \cdot 8H_2O$
0.00	97.27	4.0	$NaNO_3$
In 3 m NaOH Solution			
9.78	0.00	12.0	$Na_3PO_4 \cdot 8H_2O$
4.25	7.95	12.0	$Na_3PO_4 \cdot 8H_2O$
5.23	23.82	12.0	$Na_3PO_4 \cdot 8H_2O$
6.16	42.08	12.0	$Na_3PO_4 \cdot 8H_2O$
5.97	56.98	12.0	$Na_3PO_4 \cdot 8H_2O$
0.00	69.34	12.0	$NaNO_3$

obtained using an Olympus BXP/BX50 polarized light microscope (PLM) equipped with a color camera. Crystal identification was accomplished through comparison with the compilation of Winchell and Winchell[20] and the more recent work of Herting et al.[21] The distinction between the dodecahydrate and octahydrate of trisodium phosphate was based on the aspect ratio of the obtained crystals, with the octahydrate having a smaller length/diameter ratio, and on the observed extinction angle.

Analysis of ion concentrations was performed using a Dionex 500 series Ion Chromatograph. Prior to analysis, a small aliquot of diluted filtrate was weighed and diluted a second time to ensure that the ion concentration for the particular anion of interest was within the calibration range for the IC. For fluoride, dilution was required to achieve a concentration in the range of (0 to 20) ppm, with a detection limit of 0.02 ppm. For phosphate, dilution was required to achieve a concentration in the range of (0 to 150) ppm, with a detection limit of 0.06 ppm. For nitrate, the calibration range was (0 to 100) ppm, with a detection limit of 0.05 ppm. All dilutions were performed using mass, rather than volume. All analyses were performed in duplicate. Using the standard deviation of the IC measurements or the detection limit for the particular anion, whichever was greatest, uncertainties in the reported solubilities were determined for each data point and then averaged to obtain an average uncertainty. Uncertainties in reported solubilities are ± 0.02 g of Na_3PO_4 (100 g of $H_2O)^{-1}$, ± 0.01 g of NaF (100 g of $H_2O)^{-1}$, and ± 0.40 g of $NaNO_3$ (100 g of $H_2O)^{-1}$.

Results and Discussion

Solubility data measured for the sodium fluoride−sodium nitrate system in water, 1 m, 3 m, and 5 m NaOH solutions at 25 °C and at 50 °C are presented in Tables 1 and 2, respectively. The pure component solubility for sodium fluoride at 25 °C in aqueous solution was 4.31 g of NaF (100 g of $H_2O)^{-1}$, which is in excellent agreement with the most recently reported aqueous solubility measurements of Morales et al.[8] The presence of either sodium nitrate in solution or sodium hydroxide in solution, or both, results in a significant decrease in the solubility of sodium fluoride. For example, at 25 °C, the addition of 8.78 g of $NaNO_3$ per 100 g of H_2O results in a lowering of the solubility of sodium fluoride from (4.31 to 3.07) g of NaF per 100 g of H_2O. This mirrors the reduction observed by Morales et al.[8] at the upper end of the sodium nitrate concentration range they examined. Addition of greater amounts of sodium nitrate results in the solubility of sodium fluoride decreasing. Addition of 60.82 g of $NaNO_3$ per 100 g of H_2O results in a reduction of the sodium fluoride in solution to 0.92 g of per 100 g of H_2O. This represents a ∼ 75 % decrease in the solubility of sodium fluoride.

The addition of sodium hydroxide to the solution also impacts the solubility of either sodium fluoride or sodium nitrate in solution. In 1 m NaOH solution, representing an addition of 4.0 g of NaOH per 100 g of H_2O, the solubility of sodium fluoride decreased from 4.31 g per 100 g of H_2O to 2.43 g per 100 g of H_2O, while the solubility of sodium nitrate decreased from 90.35 g per 100 g of H_2O to 80.13 g per 100 g of H_2O. For sodium nitrate, the pure component solubilities in sodium

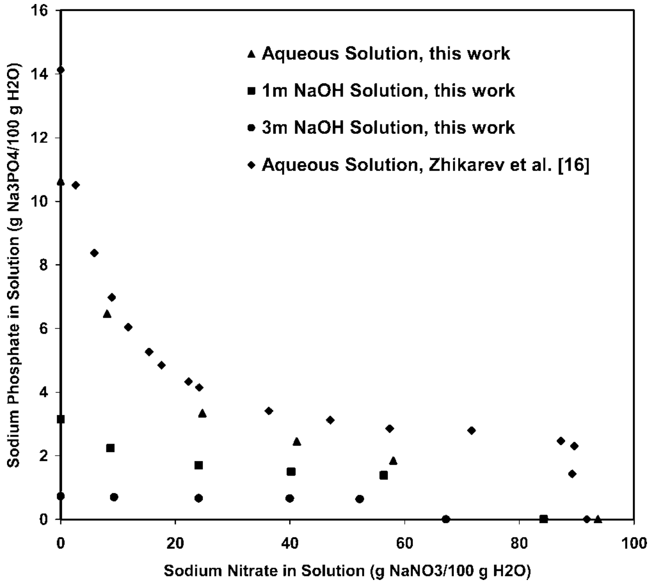

Figure 3. Solubility in the Na_3PO_4 + $NaNO_3$ + NaOH + H_2O system at 25 °C.

hydroxide solutions obtained in the present work at 25 °C are compared with available literature data from ref 4 in Figure 1. Also shown in Figure 1 is a prediction obtained using the Environmental Simulation Program (ESP V7.0, OLI Systems, Inc.) with a private databank (V7DBLSLT; developed at ICET) where the influence of sodium hydroxide on the solubility of sodium nitrate has been included through use of like-ion interactions. The measurements obtained in this work are in excellent agreement with the available literature data.

Similar behavior is observed for the solubility of sodium fluoride when both sodium hydroxide and sodium nitrate are present in solution. Shown in Figure 2 is a comparison of the solubility envelopes for the sodium fluoride + sodium nitrate system in the presence of sodium hydroxide solutions of increasing concentration. The available literature data for the NaF + $NaNO_3$ system in aqueous solution from refs 8 and 16 are included. An examination of Figure 2 indicates that the measurements taken in this work are in excellent agreement with the data reported by Morales[8] for the limited concentration range they examined. The data from ref 16 are not in good agreement with either the data reported by Morales et al.[8] or measurements obtained in the present work. The pure component solubility at 25 °C for sodium fluoride reported in ref 16 is some (5 to 8) % lower than more recent measurements.[8,19] The measurements obtained in this work are in excellent agreement with these more recent measurements. The suppression of the sodium fluoride solubility with increasing caustic in solution is dramatic, with a reduction of almost 90 % realized in the 5 m NaOH solution compared to aqueous solution. At 50 °C, similar behaviors are observed for the solubility envelopes. Of note is that, under all experimental conditions examined, the stable crystalline phases are sodium fluoride and/or sodium nitrate.

Solubility data measured for the sodium phosphate−sodium nitrate system in water, 1 m NaOH, and 3 m NaOH solutions at (25 and 50) °C are presented in Tables 3 and 4, respectively. The solubility of sodium phosphate is also dramatically affected by the presence of sodium nitrate, or sodium hydroxide, or both in solution. The pure component solubility for sodium phosphate measured in aqueous solution at 25 °C was 10.64 g of Na_3PO_4 per 100 g of H_2O. This is slightly lower than the lowest reported value of 0.70 moles of Na_3PO_4 (kg of $H_2O)^{-1}$ reported by Kobe and Leipper[11] (11.47 g of Na_3PO_4 per 100 g of H_2O). The stable crystalline phase at 25 °C was identified through PLM as $Na_3PO_4 \cdot 0.25NaOH \cdot 12H_2O$. Shown in Figure 3 is a comparison of the solubility envelopes for the sodium phosphate + sodium nitrate system at 25 °C in the presence of sodium hydroxide solutions of increasing concentration.

The addition of sodium hydroxide at a level of 12.0 g of NaOH (100 g of $H_2O)^{-1}$ results in an experimental solubility of 0.73 g of Na_3PO_4 (100 g of $H_2O)^{-1}$, a decrease of more than 90 % compared to the solubility in aqueous solution. At 50 °C, the experimental solubility in aqueous solution was 39.01 g of Na_3PO_4 (100 g of $H_2O)^{-1}$. This value is bracketed by the literature data available at this temperature of Mulder (in Linke and Seidell[1]), 42.9 g of Na_3PO_4 (100 g of $H_2O)^{-1}$, and of Apfel (in Linke and Seidell[1]), 29.3 g of Na_3PO_4 (100 g of $H_2O)^{-1}$. At this temperature, the stable crystalline phase, identified through PLM, was the octahydrate of trisodium phosphate, $Na_3PO_4 \cdot 8H_2O$. At 50 °C, the presence of sodium hydroxide in solution at levels of (4.0 and 12.0) g of NaOH (100 g of $H_2O)^{-1}$ also resulted in a significant decrease in the solubility of sodium phosphate in solution.

Conclusion

Solubilities for the sodium fluoride−sodium nitrate and for the sodium phosphate−sodium nitrate systems in aqueous solution and in sodium hydroxide solutions have been measured and reported. The presence of either sodium nitrate or sodium hydroxide in solution results in a decrease in the solubility of sodium fluoride and in the solubility of sodium phosphate, with a greater decrease occurring as the concentration of either sodium nitrate or of sodium hydroxide increases. The measurements have important implications on process operations at the Hanford site, where reduced solubility of sodium phosphate arising from the presence of sodium nitrate and sodium hydroxide in solution could lead to unwanted precipitation of trisodium phosphate or other phosphate-based salts during waste transfers. Use of these measurements to improve predictive capabilities of the Environmental Simulation Program for retrieved waste streams will provide for greater confidence in the phase equilibria estimations involving these systems during process operations planning at the Hanford site.

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