Solubility in the Na + SO_4 + NO_3 and Na + SO_4 + NO_2 Systems in Water and in Sodium Hydroxide Solutions

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Solubility isotherms are reported for the binary systems, $NaNO_3$ + Na_2SO_4 and $NaNO_2$ + Na_2SO_4, in aqueous solution and in 1 m NaOH and 3 m NaOH solutions. Measurements were conducted at both (25 and 50) °C for the $NaNO_2$ + Na_2SO_4 system and at (25, 35, and 50) °C for the $NaNO_3$ + Na_2SO_4 system. The presence of either sodium nitrate or sodium nitrite in solution results in a reduction of the solubility of sodium sulfate. At 25 °C, a transition of the stable crystalline phase from sodium sulfate decahydrate to anhydrous sodium sulfate occurs as the amount of either sodium nitrate or sodium nitrite in aqueous solution increases. The presence of sodium hydroxide in solution also results in decreased solubility over the entire isotherm, with an increase in sodium hydroxide concentration giving rise to lower solubilities. In the $NaNO_3$ + Na_2SO_4 system, the incongruent double salt, darapskite, $NaNO_3 \cdot Na_2SO_4 \cdot H_2O$, was identified as the stable crystalline phase over a portion of the solubility isotherm at all temperatures examined. TGA experiments were performed to determine the correct number of waters of hydration for darapskite.

Introduction

The chemistry of sodium salts in high ionic strength solution is pertinent to the retrieval of saltcake from the waste tanks at the Hanford U.S. Department of Energy site in Richland, Washington, USA. Originating from the variety of processes that were employed during process demonstration and production runs at the site, the saltcake is one fraction of the 53 million gallons of legacy waste from the production of nuclear armaments; the other major fractions are liquid supernate and sludge. The presence of multiple anions, including nitrate, nitrite, sulfate, phosphate, fluoride, chloride, and carbonate in the waste, along with sodium originating from sodium hydroxide used to neutralize waste as it was placed in the tanks, gives rise to the formation of complex salts, such as the sodium−nitrate−sulfate double salt, more commonly known as darapskite, $NaNO_3 \cdot Na_2SO_4 \cdot H_2O$. Knowledge of the solubility isotherms for the binary systems sodium nitrate + sodium sulfate and sodium nitrite + sodium sulfate in the presence of sodium hydroxide will aid in the planning of saltcake retrieval operations at the Hanford site.

Literature Review

Of interest in this work are the solubilities of sodium nitrate, of sodium nitrite and of sodium sulfate in an aqueous solution, and in sodium hydroxide solutions. Pelkhotkin and Bobrovskaya[1] examined the ternary systems sodium nitrite + sodium hydroxide + water and sodium nitrate + sodium hydroxide + water. In addition to reporting solubility for these systems at (20 and 25) °C, the physical properties, density, viscosity, and refractive index, were reported as a function of composition. The solubility of sodium nitrite was given as 87.6 g $(100\ g\ H_2O)^{-1}$ at 20 °C and 90.8 g $(100\ g\ H_2O)^{-1}$ at 25 °C. For sodium nitrate in aqueous solution, solubilities of 81.8 g $(100\ g\ H_2O)^{-1}$ and 88.0 g $(100\ g\ H_2O)^{-1}$ were reported for (20 and 25) °C, respectively. In sodium hydroxide solution, the solubility of either sodium salt is reduced. For example, the addition of sodium hydroxide in the amount of 8.7 g $(100\ g\ H_2O)^{-1}$ resulted in a solubility of 65.2 g $NaNO_3$ $(100\ g\ H_2O)^{-1}$ at 20 °C, while an addition of 9.1 g NaOH $(100\ g\ H_2O)^{-1}$ resulted in a solubility of 70.1 g $NaNO_3$ $(100\ g\ H_2O)^{-1}$ at 25 °C. For sodium nitrite at 20 °C, the reported solubility was 68.7 g $NaNO_2$ $(100\ g\ H_2O)^{-1}$ in the presence of 7.4 g NaOH $(100\ g\ H_2O)^{-1}$. At 25 °C, a solubility of 72.1 g $NaNO_2$ $(100\ g\ H_2O)^{-1}$ in the presence of 8.1 g NaOH $(100\ g\ H_2O)^{-1}$ was reported by Pelkhotkin and Bobrovskaya. Kurnakow and Nikolajew[2] also examined the solubility of sodium nitrate in sodium hydroxide solutions at 25 °C and at 65 °C. Selvaraj[3] also examined the solubility of sodium nitrate in hydroxide solutions at 25 °C and at 50 °C. A discussion of the available literature data on sodium sulfate solubility as a function of temperature and as a function of sodium hydroxide in solution was presented in ref 4.

Zhuravlev and Kolesnikova[5] examined the solubility in aqueous solutions for the sodium nitrite + sodium sulfate system at (0, 25, and 50) °C . The solubility envelopes at 0 °C and at 50 °C each exhibited two distinct legs. At either (0 or 50) °C, one leg corresponds to sodium nitrite ($NaNO_2$) as the equilibrium solid phase. At 0 °C, the other leg corresponds to an equilibrium solid phase of sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$), while at 50 °C, this other leg corresponds to an equilibrium solid phase of anhydrous sodium sulfate (Na_2SO_4). At 25 °C, the solubility envelope exhibits three distinct legs, one corresponding to sodium sulfate decahydrate as the equilibrium solid phase at low nitrite loadings, one corresponding to anhydrous sodium sulfate as the equilibrium solid phase at moderate nitrite loadings, and one corresponding to sodium nitrite as the equilibrium solid phase at high nitrite

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loadings. The appearance of the third leg (corresponding to anhydrous sodium sulfate) at 25 °C is expected as the increased ionic strength of the solution suppresses the temperature at which the sodium sulfate decahydrate/anhydrous sodium sulfate phase transition occurs. In aqueous solution, this transition occurs at approximately 32.4 °C.[6] No literature data were identified for the solubility of the sodium nitrite + sodium sulfate system in sodium hydroxide solutions.

The ternary system, sodium nitrate + sodium sulfate + water, was examined by Chretien,[7,8] by Foote,[9] and by Makin.[10] Chretien examined the solubility in this ternary system over the temperature range of (0 to 100) °C[7] and as a component of a quaternary system over a slightly wider temperature range, (−21 to 121) °C.[8] In this system, an incongruent double salt forms in a portion of the solubility envelope at certain temperatures. The molar ratio of sodium nitrate to sodium sulfate in the incongruent double salt is 1:1; however, the number of waters of hydration attributed to the double salt in the literature has been reported as one ($NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$)[7–9] and as two ($NaNO_3 \cdot Na_2SO_4 \cdot 2H_2O$).[10] Herting identified this double salt in a core sample from tank TX-113 at the Hanford site.[11] This particular tank contains significant amounts of nitrate and sulfate in the saltcake fraction. Poletaev and Krasnenkova[12] reviewed the $NaNO_3 + Na_2SO_4 + H_2O$ system as part of an effort to examine nitrate and sulfate salts of sodium, rubidium, and cesium at (25 and 75) °C. They reported that the 25 °C isotherm consisted of four distinct regions, corresponding to $Na_2SO_4 \cdot 10H_2O$, Na_2SO_4, $NaNO_3 \cdot Na_2SO_4 \cdot 2H_2O$, and $NaNO_3$, and that the 75 °C isotherm contained only two regions, corresponding to anhydrous Na_2SO_4 and to $NaNO_3$. No literature data were identified for the solubility of the sodium nitrate + sodium sulfate system in sodium hydroxide solutions.

Experimental Section

Materials. Sodium nitrite (> 99.6 %) and sodium nitrate (> 99.1 %) used in the solubility experiments were ACS reagent grade and purchased from Fischer Scientific. Anhydrous sodium sulfate (> 99.9 %) was purchased from Sigma Aldrich. Sodium hydroxide (> 98.7 %) was purchased from Fischer Scientific. Prior to use, sodium nitrite and sodium nitrate were pretreated by heating overnight in a muffle oven to remove any moisture. The pretreated chemicals were then stored in a desiccator until use. Sodium sulfate was heated at 110 °C overnight prior to use. Type I water with a resistivity less than 17.8 $m\Omega \cdot cm^{-1}$ from a Barnstead Nanopure Infinity Water Purification System was used for all preparations. Standards for ion chromatography were purchased from Inorganic Ventures/UV Laboratories.

Methods. All samples were prepared gravimetrically using an AND model GR-120 analytical balance accurate to ± 0.1 mg. Available literature data were used to guide the preparation of solutions when water was the solvent. Sufficient quantities of stock 1 m NaOH and 3 m NaOH solutions were mixed to allow all samples in 1 m NaOH or 3 m NaOH solutions to be prepared. The prepared samples were sealed, then placed in either a Precision Thelco Laboratory Oven (model 130D) or a Precision Low Temperature Incubator (model 815), both having sensitivities of 0.1 °C. Sealing of the samples during equilibration prevented exposure to atmospheric carbon dioxide and also prevented evaporation of water from the sample. The temperature was maintained at the desired equilibration temperature for the duration of equilibration. Previous experiments had demonstrated that approximately two weeks at the temperature was sufficient to ensure that liquid phase concentrations were no longer changing.[4]

After equilibration at that temperature for a period of two weeks, each sample was filtered using a Buckner funnel and maintained at that temperature using a water bath, which circulated water at the equilibration temperature through the funnel housing. Each sample was filtered into a vessel containing a premeasured mass of water to ensure that reprecipitation of solids did not occur in the filtrate. This step resulted in filtrate dilution, effectively lowering the hydroxide concentration in the sample by at least 50 %. The recovered diluted filtrate was stored in a sealed vial. Solids were collected on filter paper and then dried before weighing. Polarized light microscopy (PLM) was used to identify the crystalline phases present in the dried solids. The filtrate from each sample was analyzed using ion chromatography (IC), with dilutions required to obtain concentrations in the calibration range. These dilutions varied, depending on the sample. For sulfate, the calibration range was (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. For nitrite, the calibration range was (0 to 100) ppm, with a detection limit of 0.02 ppm. Uncertainties in reported solubilities were evaluated for each data point using the standard deviation of repeated measurements or the detection limit (whichever was greater), along with the dilution factors employed in preparing the sample for IC analysis. The uncertainties were averaged for each component. The uncertainties in reported solubilities are 0.80 g $NaNO_2$ (100 g $H_2O)^{-1}$, 0.93 g $NaNO_3$ (100 g $H_2O)^{-1}$, and 0.41 g Na_2SO_4 (100 g $H_2O)^{-1}$.

To determine the proper number of waters of hydration in the sodium nitrate sulfate double salt (darapskite), thermogravimetric analysis (TGA) was performed. A Perkin-Elmer/Pyris Diamond TGA/DTA 6300 (thermogravimetric analysis/differential thermal analysis) was employed for this purpose. The preparation method for darapskite detailed by Herting et al.[13] was followed. Crystals formed during the equilibration period were confirmed as darapskite using polarized light microscopy. Two samples of the dried crystal (13.641 mg, 15.559 mg) were subjected to TGA, where the temperature was ramped and weight loss recorded as a function of time. During the heating, the water(s) of hydration are driven off, and the difference in the initial and final masses was used to determine the amount of water loss. The % mass lost was 4.997 % and 4.36 % of the initial mass for the two samples, respectively. This % mass loss is slightly less than the % mass lost that would correspond to 1 mol of hydration water per mole of sodium sulfate and of sodium nitrate. Thus, the molecular formula for darapskite is $NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$.

Results and Discussion

The Environmental Simulation Program (ESP: OLI Systems, Inc.) was employed for aqueous electrolyte modeling in this work. For representation of the $NaNO_3 + Na_2SO_4$ and $NaNO_2 + Na_2SO_4$ systems in the presence of sodium hydroxide, representation of the systems $NaNO_3$ + NaOH, $NaNO_2$ + NaOH, and Na_2SO_4 + NaOH must reproduce the available literature data. Initial computations using the PUBLIC database within ESP V7.0 indicated that the pure component solubilities in water for each of the sodium salts ($NaNO_3$, Na_2SO_4, and $NaNO_2$) were well predicted; however, in the presence of sodium hydroxide, deviations between the available literature data and the model predictions were evident. To eliminate these deviations, and in the case of Na_2SO_4, also to allow the depression of the transition temperature for the phase transition between the anhydrous and decahydrate forms to be predicted, like-ion interactions were included in ESP and stored in a private

Table 1. Anion−Anion Interactions Considered for $NaNO_3$ + NaOH, $NaNO_2$ + NaOH, and Na_2SO_4 + NaOH Systems and Fitted Parameters, Obtained through Regression of Available Literature Data

parameter	NO_2^-/OH^-	NO_3^-/OH^-	$NaSO_4^-/OH^-$	SO_4^{2-}/OH^-
B_1	0.05092964	−0.1220882	−0.196167	0.06757067
B_2	1.65892e−04	9.89048e−04	0.008436918	−0.002195756
B_3	0.0	0.0	−4.02861e−05	0.0
C_1	−0.01699002	0.005315534	0.007299739	−0.00126333
C_2	1.11407e−04	−4.47554e−05	−0.001050792	6.42999e−05
C_3	0.0	0.0	5.02556e−06	0.0
D_1	7.09137e−04	4.25096e−05	2.99648e−04	1.23111e−04
D_2	−7.80266e−06	−1.53349e−06	3.07256e−05	4.66022e−06
D_3	0.0	0.0	−1.50819e−07	0.0

database (V7DBLSLT). The ion activity coefficient within ESP is represented using the Bromley−Zemaitis[14,15] formalism

$$\log(\gamma_{i,j}) = \frac{-A|Z_iZ_j|\sqrt{I}}{1+\sqrt{I}} + \frac{(0.06 + 0.6B)|Z_iZ_j|I}{\left(1 + \frac{1.5}{|Z_iZ_j|I}\right)^2} + BI + CI^2 + DI^3 \quad (1)$$

where A is the Debye–Huckel constant; I is the ionic strength; Z_i and Z_j are the charge of the ions i and j, respectively; and B, C, and D are interaction constants, expressed as quadratic functions of temperature (only B is shown)

$$B = B_1 + B_2T + B_3T^2 \quad (2)$$

In the PUBLIC database of ESP, only cation–anion, cation−neutral, anion−neutral, and/or neutral–neutral interactions have been included to represent known behaviors. Specifically, to improve predictions in the systems examined in this work, anion−anion interactions were defined, and regression of available literature data was performed to determine the set of parameters (B_i, C_i, D_i) that best represents the data. The anion−anion interactions employed, along with the parameter set, are shown in Table 1. For both the $NaNO_2$ + NaOH + H_2O and $NaNO_3$ + NaOH + H_2O systems, inclusion of a single anion−anion interaction resulted in improved predictions of the influence of sodium hydroxide in solution on the solubility of the individual salt. Figure 1 provides a comparison of the literature data at 25 °C for the $NaNO_2$ + NaOH + H_2O system with the ESP V7.0 PUBLIC prediction and with the ESP V7.0, V7DBLSLT prediction. Representation is improved through inclusion of the like-ion interaction between nitrite and hydroxide. Figure 2 provides a similar comparison for the $NaNO_3$ + NaOH + H_2O system at both (25 and 65) °C. While representation of the solubility envelope at 25 °C with the ESP V7.0 PUBLIC database agrees with available literature data, the solubility is overestimated somewhat at 65 °C, particularly at increased hydroxide loadings. The inclusion of the like-ion interaction between nitrate and hydroxide improved solubility representation at both temperatures.

For the Na_2SO_4 + NaOH + H_2O system, representation using a single like-ion interaction between sulfate and hydroxide ions failed to adequately capture the complex behavior exhibited by the available literature solubility data. In this system, the stable crystalline phase in aqueous solution is the sodium sulfate decahydrate, for temperatures up to 32.4 °C; however, anhydrous sodium sulfate is the stable crystalline phase in aqueous solution at temperatures above 32.4 °C. As evidenced in the literature data (Figure 3), the temperature at which this transition occurs is strongly influenced by the presence of sodium hydroxide in solution. The transition temperature is depressed significantly as the sodium hydroxide concentration is increased. The ESP V7.0 V7DBLSLT predictions shown in Figure 3 were obtained using two like-ion interactions, the SO_4^{-2}/OH^- and the $NaSO_4^-/OH^-$ interactions. Inclusion of both like-ion interactions provides for the complex behavior of this system to be adequately predicted.

Solubilities in the $NaNO_2$ + Na_2SO_4 system in aqueous solution and in (1 and 3) m NaOH solutions are reported in Tables 2 and 3, for temperatures of (25 and 50) °C, respectively. Also included in Tables 2 and 3 is the identification of the solid phase present at equilibrium with the liquid solution for each data point. The experimental pure component solubilities at 25

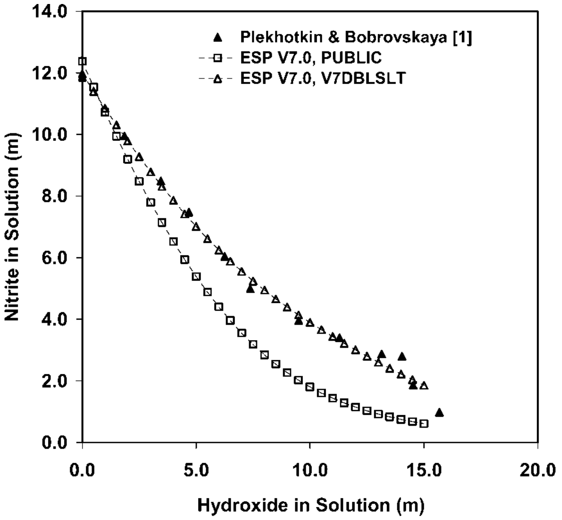

Figure 1. Effect of sodium hydroxide in solution on the solubility of pure sodium nitrite at 25 °C.

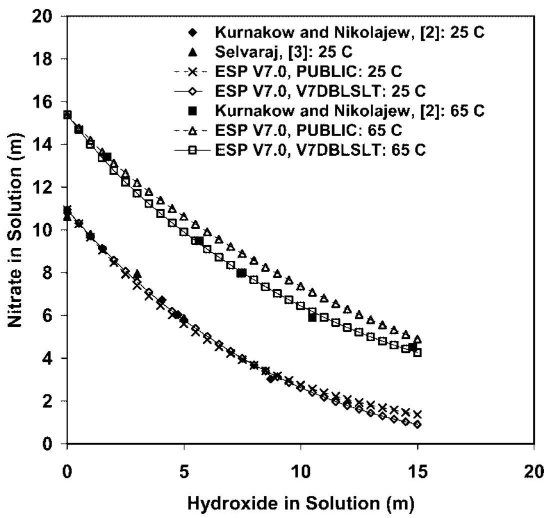

Figure 2. Effect of sodium hydroxide in solution on the solubility of pure sodium nitrate.

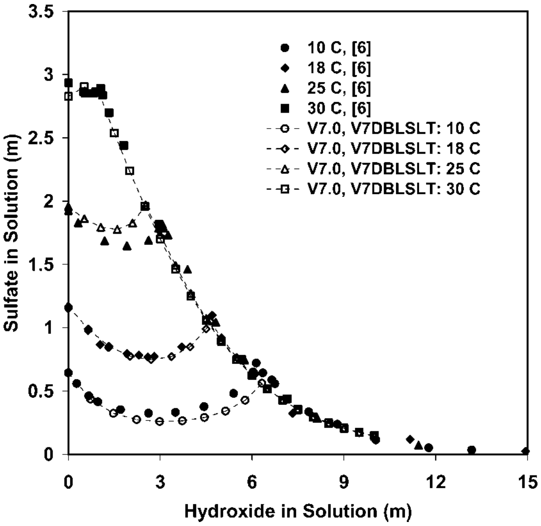

Figure 3. Effect of sodium hydroxide in solution on the solubility of pure sodium sulfate.

Table 2. Solubility in the Sodium Nitrite + Sodium Sulfate System in Water, 1 m NaOH, and 3 m NaOH Solutions at 25 °C/(g solute (100 g H_2O)$^{-1}$)

$NaNO_2$	Na_2SO_4	NaOH	solid phase
	In Aqueous Solution		
0.000	28.291	0.000	$Na_2SO_4 \cdot 10H_2O$
9.741	26.910	0.000	$Na_2SO_4 \cdot 10H_2O$
26.317	20.110	0.000	$Na_2SO_4 \cdot 10H_2O$
30.583	16.959	0.000	Na_2SO_4
40.366	10.580	0.000	Na_2SO_4
53.549	5.904	0.000	Na_2SO_4
75.485	3.595	0.000	Na_2SO_4
80.879	2.839	0.000	$Na_2SO_4 + NaNO_2$
81.424	2.490	0.000	$Na_2SO_4 + NaNO_2$
81.686	1.103	0.000	$NaNO_2$
87.685	0.000	0.000	$NaNO_2$
	In 1 m NaOH Solution		
0.000	24.93	4.000	$Na_2SO_4 \cdot 10H_2O$
4.995	24.595	4.000	$Na_2SO_4 \cdot 10H_2O$
8.775	22.095	4.000	Na_2SO_4
21.000	19.062	4.000	Na_2SO_4
28.678	13.402	4.000	Na_2SO_4
32.580	13.060	4.000	Na_2SO_4
38.361	7.931	4.000	Na_2SO_4
54.305	3.702	4.000	Na_2SO_4
61.422	3.080	4.000	Na_2SO_4
70.985	2.370	4.000	Na_2SO_4
76.624	2.394	4.000	Na_2SO_4
75.891	1.524	4.000	$Na_2SO_4 + NaNO_2$
77.418	1.273	4.000	$Na_2SO_4 + NaNO_2$
79.103	0.000	4.000	$NaNO_2$
	In 3 m NaOH Solution		
0.000	24.765	12.000	Na_2SO_4
7.119	17.816	12.000	Na_2SO_4
16.503	11.069	12.000	Na_2SO_4
23.419	8.619	12.000	Na_2SO_4
29.716	7.277	12.000	Na_2SO_4
50.857	3.082	12.000	Na_2SO_4
59.417	2.064	12.000	Na_2SO_4
61.746	1.737	12.000	$Na_2SO_4 + NaNO_2$
66.100	0.000	12.000	$NaNO_2$

Table 3. Solubility in the Sodium Nitrite + Sodium Sulfate System in Water, 1 m NaOH, and 3 m NaOH Solutions at 50 °C/(g solute (100 g H_2O)$^{-1}$)

$NaNO_2$	Na_2SO_4	NaOH	solid phase
	In Aqueous Solution		
0.000	46.340	0.000	Na_2SO_4
7.727	45.242	0.000	Na_2SO_4
13.677	37.362	0.000	Na_2SO_4
22.790	31.147	0.000	Na_2SO_4
29.170	22.901	0.000	Na_2SO_4
36.243	20.993	0.000	Na_2SO_4
45.075	11.208	0.000	Na_2SO_4
67.157	6.990	0.000	Na_2SO_4
88.008	4.084	0.000	Na_2SO_4
92.526	2.514	0.000	Na_2SO_4
103.396	0.000	0.000	$NaNO_2$
	In 1 m NaOH Solution		
0.000	34.660	4.000	Na_2SO_4
8.006	28.545	4.000	Na_2SO_4
18.395	25.328	4.000	Na_2SO_4
28.842	16.319	4.000	Na_2SO_4
34.945	12.704	4.000	Na_2SO_4
48.080	10.018	4.000	Na_2SO_4
62.617	6.155	4.000	Na_2SO_4
67.233	5.789	4.000	Na_2SO_4
86.733	3.205	4.000	Na_2SO_4
91.598	1.516	4.000	$Na_2SO_4 + NaNO_2$
90.848	1.480	4.000	$Na_2SO_4 + NaNO_2$
93.617	0.000	4.000	$NaNO_2$
	In 3 m NaOH Solution		
0.000	20.430	12.000	Na_2SO_4
5.671	17.798	12.000	Na_2SO_4
14.730	12.311	12.000	Na_2SO_4
24.401	8.097	12.000	Na_2SO_4
42.857	4.281	12.000	Na_2SO_4
60.460	2.669	12.000	Na_2SO_4
66.530	2.153	12.000	Na_2SO_4
66.496	1.479	12.000	$Na_2SO_4 + NaNO_2$
67.235	1.121	12.000	$NaNO_2$
68.940	0.000	12.000	$NaNO_2$

°C for sodium sulfate are 28.291 g Na_2SO_4 (100 g H_2O)$^{-1}$, 24.93 g Na_2SO_4 (100 g H_2O)$^{-1}$, and 24.765 g Na_2SO_4 (100 g H_2O)$^{-1}$ for aqueous, 1 m NaOH and 3 m NaOH solutions, respectively. At 50 °C, experimental solubilities for sodium sulfate are (46.340, 34.660, and 20.430) g Na_2SO_4 (100 g H_2O)$^{-1}$ in aqueous, 1 m NaOH and 3 m NaOH solutions. These values compare well with the literature data. For the aqueous and 1 m NaOH solutions, $Na_2SO_4 \cdot 10H_2O$ was identified as the solid phase at 25 °C, while in 3 m NaOH solution, anhydrous Na_2SO_4 was the solid phase in equilibrium with the liquid solution. At 50 °C, the solid phase in equilibrium with the liquid for aqueous, 1 m NaOH, and 3 m NaOH solutions is anhydrous Na_2SO_4. The pure component solubilities in the compilation by Linke and Seidell[6] are 28 g Na_2SO_4 (100 g H_2O)$^{-1}$ at 25 °C and 46.4 g Na_2SO_4 (100 g H_2O)$^{-1}$ at 50 °C, and the experimental measurements in aqueous solution in this work agree well with these data. Pure component solubilities for sodium nitrite measured in the present work were also in agreement with available literature data. At 25 °C, the experimental solubilities were (87.685, 79.103, and 66.100) g $NaNO_2$ (100 g H_2O)$^{-1}$, in aqueous, 1 m NaOH and 3 m NaOH solutions, respectively, compared to literature data of 87.6 g $NaNO_2$ (100 g H_2O)$^{-1}$ in aqueous solution at 25 °C and 72.1 g $NaNO_2$ (100 g H_2O)$^{-1}$ when 8.1 g NaOH per 100 g H_2O is in solution (approximately 2 m NaOH).

Again, the presence of sodium hydroxide in solution results in a significant decrease in the solubility of pure sodium sulfate and a slight decrease in the solubility of pure sodium nitrite. Solubility envelopes are shown in Figures 4 and 5 for the $NaNO_2$ + Na_2SO_4 system at 25 °C and at 50 °C, respectively. At 25 °C in either aqueous solution or in 1 m NaOH solution, the solubility envelope consists of three distinct legs: at low concentrations of sodium nitrite in solution, the first leg corresponds to solutions in equilibrium with sodium sulfate decahydrate as the stable crystalline phase; at moderate to fairly high concentrations of sodium nitrite in solution, the liquid solution is in equilibrium with anhydrous sodium sulfate as the

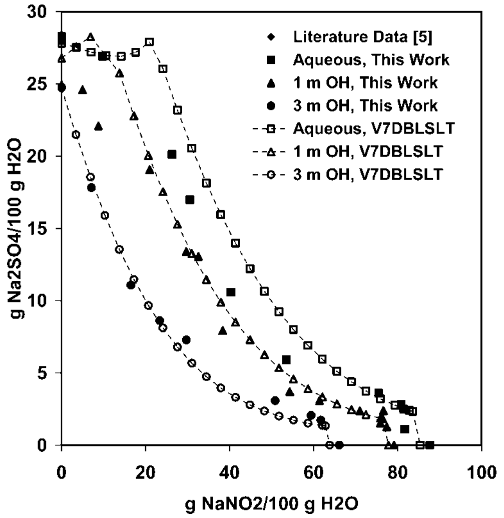

Figure 4. Solubility in the $NaNO_2 + Na_2SO_4 + NaOH + H_2O$ system at 25 °C.

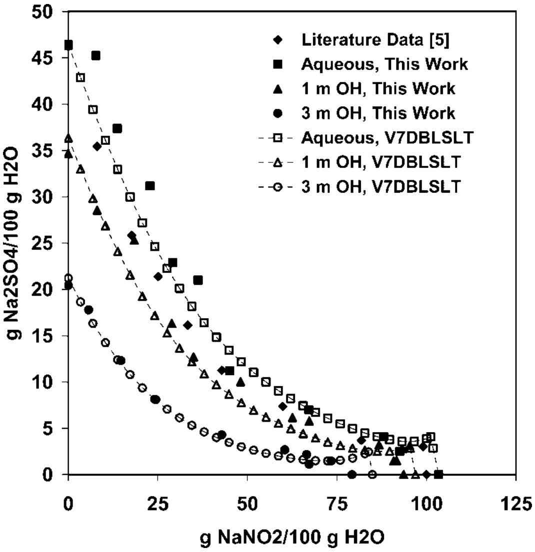

Figure 5. Solubility in the $NaNO_2 + Na_2SO_4 + NaOH + H_2O$ system at 50 °C.

stable crystalline phase; and at very high concentrations of sodium nitrite and low concentrations of sodium sulfate, the stable crystalline phase is sodium nitrite. In 3 m NaOH at 25 °C and in all solutions (aqueous, 1 m NaOH, 3 m NaOH) at 50 °C, the solubility envelope consists only of two distinct legs, one corresponding to anhydrous sodium sulfate as the solid phase precipitate and one corresponding to sodium nitrite as the solid phase precipitate. The presence of sodium nitrite in solution has the effect of significantly lowering the sodium sulfate solubility, whether in aqueous solution or in caustic solutions. Also depicted in Figures 4 and 5 are solubility envelope predictions obtained using ESP V7.0 with the V7DBLSLT database. The representation obtained with ESP was improved through incorporation of a like-ion interaction between the nitrite ion and the sulfate ion (NO_2^-/SO_4^{2-} interaction), and these are the ESP predictions shown in these figures.

Table 4. Solubility in the Sodium Nitrate + Sodium Sulfate System in Water, 1 m NaOH, and 3 m NaOH Solutions at 25 °C/(g solute (100 g H_2O)$^{-1}$)

$NaNO_3$	Na_2SO_4	NaOH	solid phase
	In Aqueous Solution		
0.000	28.000	0.000	$Na_2SO_4 \cdot 10H_2O$
8.272	28.828	0.000	$Na_2SO_4 \cdot 10H_2O$
25.187	28.844	0.000	$Na_2SO_4 \cdot 10H_2O$
34.914	28.705	0.000	Na_2SO_4
48.287	27.353	0.000	Na_2SO_4
56.566	20.644	0.000	Na_2SO_4
59.768	13.440	0.000	Na_2SO_4
76.435	9.919	0.000	$NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
84.746	6.241	0.000	$NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
80.103	6.426	0.000	$NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
78.178	7.560	0.000	$NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
88.816	6.307	0.000	$NaNO_3 + NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
92.973	3.516	0.000	$NaNO_3$
91.987	0.000	0.000	$NaNO_3$
	In 1 m NaOH Solution		
0.00	24.930	4.000	$Na_2SO_4 \cdot 10H_2O$
9.037	29.342	4.000	$Na_2SO_4 \cdot 10H_2O$
17.336	26.847	4.000	Na_2SO_4
23.395	17.664	4.000	Na_2SO_4
35.608	13.912	4.000	$NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
42.651	10.999	4.000	$NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
67.457	5.701	4.000	$NaNO_3 + NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
84.260	0.000	4.000	$NaNO_3$
	In 3 m NaOH Solution		
0.000	25.030	12.000	Na_2SO_4
0.787	23.316	12.000	Na_2SO_4
2.085	23.757	12.000	Na_2SO_4
3.829	22.663	12.000	Na_2SO_4
20.720	17.765	12.000	Na_2SO_4
27.209	15.933	12.000	$NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
35.223	11.779	12.000	$NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
47.550	7.286	12.000	$NaNO_3 + NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
52.903	6.439	12.000	$NaNO_3 + NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
63.720	4.416	12.000	$NaNO_3$
64.337	3.860	12.000	$NaNO_3$
62.153	3.045	12.000	$NaNO_3$
66.176	1.692	12.000	$NaNO_3$
67.191	0.000	12.000	$NaNO_3$

Table 5. Solubility in the Sodium Nitrate + Sodium Sulfate System in Water at 35 °C/(g solute (100 g H_2O)$^{-1}$)

$NaNO_3$	Na_2SO_4	solid phase
0.000	57.649	Na_2SO_4
20.553	43.256	Na_2SO_4
42.197	25.633	Na_2SO_4
65.233	15.770	$NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
61.329	14.047	$NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
79.749	12.592	$NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
87.002	9.891	$NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
94.302	5.993	$NaNO_3 + NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
97.098	5.143	$NaNO_3 + NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
107.880	0.000	$NaNO_3$

Solubilities in the $NaNO_3 + Na_2SO_4$ system in aqueous solution and in (1 and 3) m NaOH solutions are reported in Tables 4, 5, and 6, for temperatures of (25, 35, and 50) °C, respectively. The identification of the solid phase/phase(s) present at equilibrium with the liquid solution is also given for each data point. The presence of sodium hydroxide has a significant impact on the solubility in this system at (25 and 50) °C. Solubility envelopes are shown in Figures 6 and 7 for these temperatures. Experimental data are shown along with available literature data and predictions using ESP V7.0 with V7DBLSLT. The representation obtained with ESP was improved through incorporation of a like-ion interaction between the nitrate ion and the sulfate ion (NO_3^-/SO_4^{2-} interaction). At 25 °C, the solubility envelope consists of four distinct legs. At low concentrations of sodium nitrate, the equilibrium solid phase is sodium sulfate decahydrate. The phase transition to anhydrous sodium sulfate occurs at 25 °C, and Na_2SO_4 is the equilibrium solid phase, once the sodium nitrate concentration exceeds approximately 30 g $NaNO_3$ (100 g H_2O)$^{-1}$. The third leg of the solubility envelope corresponds to the double salt,

Table 6. Solubility in the Sodium Nitrate + Sodium Sulfate System in Water, 1 m NaOH, and 3 m NaOH Solutions at 50 °C/(g solute (100 g H_2O)$^{-1}$)

$NaNO_3$	Na_2SO_4	NaOH	solid phase
		In Aqueous Solution	
0.000	46.340	0.000	Na_2SO_4
0.000	45.407	0.000	Na_2SO_4
4.815	39.773	0.000	Na_2SO_4
8.693	35.639	0.000	Na_2SO_4
26.835	27.151	0.000	Na_2SO_4
38.465	18.481	0.000	Na_2SO_4
51.346	13.231	0.000	Na_2SO_4
63.432	12.167	0.000	Na_2SO_4
83.963	9.729	0.000	$NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
80.170	9.759	0.000	$NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
102.945	8.268	0.000	$NaNO_3 + NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
103.234	7.036	0.000	$NaNO_3 + NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
107.712	5.713	0.000	$NaNO_3$
116.535	4.503	0.000	$NaNO_3$
113.879	2.976	0.000	$NaNO_3$
115.451	0.000	0.000	$NaNO_3$
		In 1 m NaOH Solution	
0.000	34.660	4.000	Na_2SO_4
10.299	33.533	4.000	Na_2SO_4
25.115	21.705	4.000	Na_2SO_4
38.892	17.499	4.000	Na_2SO_4
49.271	13.431	4.000	Na_2SO_4
62.385	10.807	4.000	Na_2SO_4
67.567	8.636	4.000	Na_2SO_4
83.524	8.462	4.000	$NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
86.761	5.917	4.000	$NaNO_3 + NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$
108.513	0.000	4.000	$NaNO_3$
109.186	0.000	4.000	$NaNO_3$
		In 3 m NaOH Solution	
0.000	20.430	12.000	Na_2SO_4
0.000	20.385	12.000	Na_2SO_4
2.012	21.705	12.000	Na_2SO_4
4.296	18.296	12.000	Na_2SO_4
7.977	17.871	12.000	Na_2SO_4
8.779	16.469	12.000	Na_2SO_4
18.282	11.833	12.000	Na_2SO_4
42.555	7.845	12.000	Na_2SO_4
60.265	4.830	12.000	Na_2SO_4
77.359	2.891	12.000	Na_2SO_4
81.604	2.418	12.000	$NaNO_3$
91.566	2.381	12.000	$NaNO_3$
90.523	0.000	12.000	$NaNO_3$

$NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$, as the equilibrium solid phase and occurs at sodium nitrate levels over a fairly narrow range of between approximately (75 to 85) g $NaNO_3$ (100 g H_2O)$^{-1}$. Finally, at high levels of sodium nitrate in solution, the equilibrium solid phase is $NaNO_3$. The combined effects of both sodium hydroxide and sodium nitrate are to lower the salt solubility. In 1 m NaOH solutions, the solubility envelope at 25 °C consists of the same four distinct legs, while in 3 m NaOH solutions, only three distinct legs are present. At this concentration of sodium hydroxide in solution, the transition to anhydrous sodium sulfate as the equilibrium solid phase at 25 °C occurs for solutions containing only sodium sulfate. At 50 °C, the solubility envelopes in water and in 1 m NaOH solutions exhibit three distinct legs, one corresponding to anhydrous sodium sulfate as the equilibrium solid phase, the middle leg corresponding to the sodium nitrate/sodium sulfate double salt as the equilibrium solid phase, and the third leg corresponding to pure sodium nitrate as the equilibrium solid phase. In 3 m NaOH solution, only two branches were present in the solubility envelope, one corresponding to anhydrous sodium sulfate and one corresponding to sodium nitrate as the equilibrium solid phase, respectively. Formation of the double salt was not observed in solutions containing the higher sodium hydroxide concentration at 50 °C. This behavior is explained by considering the presence of sodium hydroxide in solution lowering the temperature at which a phase transition can occur. The solubility envelope reported for this system in aqueous solution at 75 °C by Poletaev and Krasnenkova[12] consisted only of two distinct branches, with no formation of the double salt. The presence of 3 m sodium hydroxide in solution is sufficient to eliminate the branch corresponding to the double salt at 50 °C in the present work.

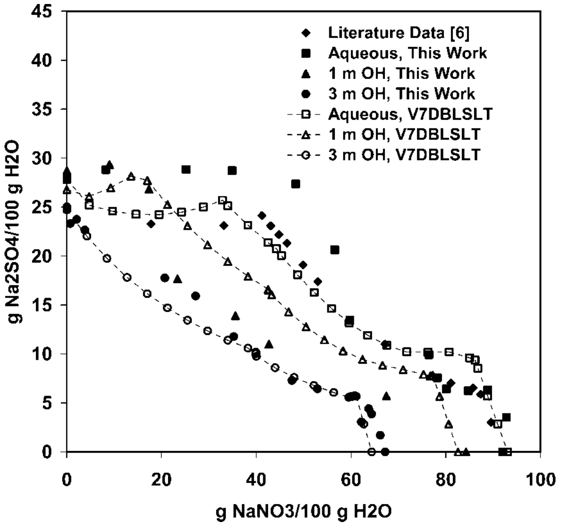

Figure 6. Solubility in the $NaNO_3 + Na_2SO_4 + NaOH + H_2O$ system at 25 °C.

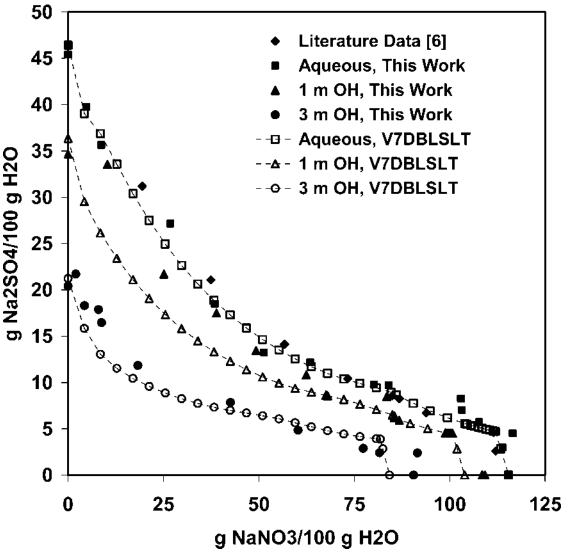

Figure 7. Solubility in the $NaNO_3 + Na_2SO_4 + NaOH + H_2O$ system at 50 °C.

Conclusions

Solubilties in the $NaNO_2 + Na_2SO_4 + NaOH + H_2O$ and $NaNO_3 + Na_2SO_4 + NaOH + H_2O$ systems have been measured at two temperatures, (25 and 50) °C, and in aqueous solution, as well as in 1 m NaOH and 3 m NaOH solutions. Data obtained in this work have been combined with available literature data to obtain like-ion interaction parameters for these systems, which result in improved predictive capabilities for these systems within the ESP V7.0 program. In the $NaNO_3$ + Na_2SO_4 system, the sodium nitrate + sodium sulfate double salt was observed under differing conditions. While observed at 25 °C in aqueous, 1 m NaOH, and 3 m NaOH solutions, this double salt was only observed in aqueous and in 1 m NaOH solutions at 50 °C. TGA confirmed that the sodium nitrate + sodium sulfate double salt contained no more than one water of hydration, and its corresponding molecular formula is $NaNO_3 \cdot Na_2SO_4 \cdot 1H_2O$.

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