Solubility of Na−F−SO_4 in Water and in Sodium Hydroxide Solutions

Rebecca K. Toghiani,[*,†,‡] **Valerie A. Phillips,**[†] **and Jeffrey S. Lindner**[†]

Diagnostic Instrumentation and Analysis Laboratory and Dave C. Swalm School of Chemical Engineering, Mississippi State University, Mississippi State, Mississippi 39762

Solubility was measured in the Na−F−SO_4 system at 25 °C and at 50 °C. Pure-component solubilities for NaF and Na_2SO_4 are in agreement with available literature data at 25 °C and at 50 °C. The influence of sodium hydroxide on the solubility of the sodium−fluoride−sulfate double salt (Na_3FSO_4) was also examined. The solubility of the double salt was decreased as the concentration of sodium hydroxide in solution increased.

Introduction

Over the next few decades, the United States is faced with the formidable task of cleanup and closure of nuclear waste storage sites, including the Hanford Site, located near Richland, WA, and the Savannah River Site, located near Aiken, SC. The wastes generated during process demonstration and weapons-grade plutonium production runs at the sites were deposited in underground storage tanks, with capacity up to 211 810 m^3 (10^6 gal). The acidic effluent streams were neutralized with caustic to produce an alkaline environment in the waste tanks. Many of the tanks have been in service longer than their design lifetimes, and thus, tank stabilization efforts have focused on draining brine and concentrating it by evaporation. The concentrated brines were then returned to the storage tanks, and as they cooled, salts precipitated. The salt waste comprises a major portion of the waste that must undergo remediation. Critical to the remediation effort is the retrieval of the waste from the tanks followed by pretreatment and transfer to facilities where vitrification or long-term stabilization will be performed. Thus, the chemistry of the dissolved salt cake is of interest. In particular, an understanding of how the solubilities of various species are suppressed in highly concentrated brine is required to properly predict how the material will behave as it is mobilized and transferred through pipelines and other staging areas within the tank farm. Remediation of this legacy nuclear waste requires an understanding of the solubility of various species at temperatures and concentrations relevant to the conditions present in the storage tanks. Unfortunately, experimental data for the solubilities of important inorganic systems are either lacking entirely or not available at relevant conditions.

In response to this need, the Office of Environmental Management of the Department of Energy supported experimental solubility measurements of select systems for which data are either lacking entirely or are not available at relevant conditions. In particular, this effort was directed at sodium salt systems that involve anions present in the waste. This paper represents the first in a series resulting from this experimental effort.

The Environmental Simulation Program (ESP), developed by OLI Systems, Inc., is used at the DOE sites for process operations modeling and planning. ESP is a thermodynamic equilibrium code based on Gibbs energy minimization. It is essential that model predictions are representative of the solution behavior that will be encountered during remediation. If the solubility of one species is underestimated, then the partitioning of other species may be predicted incorrectly. Incorporation of the measurements described in this work will extend the modeling range for the select system of interest and improve the reliability of model results at the Hanford site and others.

Literature Review

Much of the aqueous solubility information available for the pure components, sodium fluoride and sodium sulfate, was published in the 1920s and 1930s. The pure-component solubilities serve as anchors of the solubility envelope for the more complex ternary system. Measured pure-component solubilities were compared with available literature data in aqueous solution. Limited data are reported for either pure component in solutions of sodium hydroxide. Where possible, values measured in this work were compared with available literature data.

Solubility data for sodium fluoride were reviewed by Weber.[1,2] He concluded that the data exhibited significant scatter.[3,4] At 25 °C, the pure-component solubility reported by Linke and Seidell[4] is 0.986 mol·(kg H_2O)$^{-1}$ (4.14 g of NaF/100 g of H_2O). There are limited data available for the common-ion ternary sodium fluoride + sodium hydroxide + water. These data cover a temperature range of (0 to 94 °C) but a relatively small hydroxide concentration range (0 to 0.7 mol·(kg H_2O)$^{-1}$). At 20 °C, the range for hydroxide extends to 5.6 mol·(kg H_2O)$^{-1}$.

There are considerable solubility data available for sodium sulfate. Much of the data was measured in the 1930s and 1940s. Okorafor[5] examined the solubility of sodium sulfate in methanol−water solutions in conjunction with salting-out studies and presented more recent solubility data for the pure component in water. He reported solubilities of 18.95 g of Na_2SO_4/100 g of H_2O at 20 °C and 46.31 g of Na_2SO_4/100 g of H_2O at 50 °C. (Values are given in g of solute/100 g of saturated solution in Okorafor's[5]

---

[*] Corresponding author. E-mail: rebecca@che.msstate.edu.
[†] Diagnostic Instrumentation and Analysis Laboratory.
[‡] Dave C. Swalm School of Chemical Engineering.

10.1021/je050087+ CCC: $30.25

original publication.) These values are in agreement with more recent measurements reported of the solubility of the pure component by Brenner et al.[6] The aqueous solubilities of sodium sulfate compiled in Linke and Seidell[4] are 28 g of Na_2SO_4/100 g of H_2O (1.97 mol·kg^{-1}) at 25 °C and 46.4 g of Na_2SO_4/100 g of H_2O (3.27 mol·kg^{-1}) at 50 °C. At 25 °C, the stable crystalline phase in aqueous solution is the sodium sulfate decahydrate salt, whereas above 32.4 °C the stable crystalline phase in aqueous solution is anhydrous sodium sulfate.[4] The temperature at which the phase transition from sodium sulfate decahydrate to anhydrous sodium sulfate occurs is suppressed in the presence of sodium hydroxide. At 25 °C, the phase transition occurs at a hydroxide loading of just over 3 mol·kg^{-1} (3.07 mol·kg^{-1}), whereas at 0 °C a hydroxide loading of 7.58 mol·kg^{-1} induces the transition to the anhydrous sodium sulfate salt. At 50 °C, the stable crystalline phase in equilibrium with aqueous solution and in solutions containing elevated hydroxide loadings is the anhydrous sodium sulfate salt. Sodium sulfate solubility in hydroxide solutions was reported by Windmaisser and Stockl[7] for temperatures ranging from 0 to 30 °C and at 50 °C by both Itkina[8] and Prihodko.[9]

The common-ion ternary system—sodium fluoride, sodium sulfate, and water—was examined by Foote and Schairer.[10] The sodium fluoride sulfate salt is a congruent double salt and has the chemical formula $NaF{\cdot}Na_2SO_4$, which is sometimes given as Na_3FSO_4. Foote and Schairer[10] reported solubility data at 25 °C and 35 °C. These data serve as the basis for the solubility representation used within the PUBLIC database of the Environmental Simulation Program. An extensive literature search revealed no solubility data for this system in the presence of sodium hydroxide.

Experimental Section

Materials. Sodium fluoride (NaF >99.9 %) was purchased from Advanced Research Chemicals, Inc. (Catoosa, OK). Anhydrous Na_2SO_4 (>99.9 %) and sodium hydroxide (>98.7 %) were purchased from Sigma Aldrich, Inc. The sodium sulfate was heated overnight at 110 °C prior to use. All other chemicals were used as received. Type I water with a resistivity of less than 17.8 mΩ·cm^{-1} from a Barnstead Nanopure Infinity water purification system was used for all preparations. Standards for ion chromatography were obtained from Inorganic Ventures Inc. and were traceable to the National Institute of Standards and Technology.

Methods. All samples were prepared gravimetrically using an AND model GR-120 analytical balance accurate to ±0.1 mg. The amounts of sodium fluoride and sodium sulfate were varied so as to provide full coverage of the solubility envelope. Available literature data at 25 °C were used to estimate the required amounts of sodium fluoride, sodium sulfate, and water. Pure-component solubilities were also measured, and at least 10 samples were prepared along the solubility envelope. Samples were prepared to ensure that sufficient amounts of sodium fluoride, sodium sulfate, or both were present such that a solid phase would be present at the end of the equilibration period. All samples were prepared in polypropylene screw-cap vials at elevated temperature to dissolve the solid sodium fluoride and sodium sulfate. The samples were then cooled and held at temperature (either 25 °C or 50 °C) for the required equilibration period. For the solubility studies at elevated hydroxide levels, ESP was used to provide estimates of the required amounts of sodium fluoride and sodium sulfate at saturation. In general, samples containing approximately (105 to 110) % of the saturation value with respect to fluoride and sulfate were made. In some cases, the samples based on the ESP predictions did not yield a solid phase in equilibrium with a liquid phase at the end of the equilibration period; consequently, a second series of samples were prepared with slightly greater amounts of sodium fluoride and sodium sulfate. After equilibration, these samples did yield a solid phase in equilibrium with a liquid phase.

Table 1. Temporal Study of Equilibration at 25 °C

equilibration time weeks	fluoride molality mol·(kg of H_2O)$^{-1}$	sulfate molality mol·(kg of H_2O)$^{-1}$
1	0.196	1.126
2	0.097	0.425
3	0.084	0.439
4	0.084	0.438

A temporal study of liquid-phase concentrations of fluoride and sulfate anions allowed the establishment of an adequate equilibration period. Approximately 10 samples were prepared with fluoride and sulfate loadings representative of the solubility envelope in aqueous, in 1 mol·(kg of H_2O)$^{-1}$ NaOH, and in 3 mol·(kg of H_2O)$^{-1}$ NaOH solutions. An aliquot of the liquid phase was periodically removed from each sample and analyzed for fluoride and sulfate levels. Sampling continued until the liquid-phase molality of each analyte no longer changed. Liquid-phase molalities for sulfate and fluoride in a 3 mol·(kg of H_2O)$^{-1}$ NaOH solution are shown in Table 1 as a function of equilibration time. The most significant change is observed for either anion during the second week. A period of 3 weeks was established as the duration needed to attain equilibrium.

Once prepared, samples were maintained at temperature using a constant-temperature water bath, in which the samples were immersed. Samples were periodically shaken to ensure adequate mixing. Upon equilibration, each sample was vacuum filtered into a receiving flask containing a known mass of water. This initial dilution served to prevent any formation of solids in the receiving flask. The masses of both solid crystals and liquid filtrate were recorded and provided an indication of the mass balance for the particular sample. A small aliquot of the liquid filtrate was diluted a second time to obtain samples for analysis by ion chromotagraphy. A Dionex model 500 series ion chromatograph was employed in this work. The mobile phase was KOH, detection was by conductivity, and samples were injected in duplicate. Aqueous phase dilutions were based on the expected concentrations of the equilibrated solutions accounting for the initial dilution during filtration and a second dilution necessary to coincide with the specific anion IC response. Uncertainties were estimated for the mass of solute (either NaF or Na_2SO_4) per 100 g of H_2O in solution from the experimental measurements. The average uncertainty for sodium fluoride was determined to be ±0.004 g of NaF, with a maximum uncertainty of 0.02 g of NaF (one data point). For sodium sulfate, the average uncertainty was an order of magnitude greater, at ±0.03 g of Na_2SO_4, reflecting the larger dilutions performed to obtain sulfate concentrations that fell within the calibration range for the IC.

Solids were collected, dried, and weighed. Images of the crystals were obtained using an Olympus BXP/BX50 polarized-light microscope equipped with a color camera. Crystal identification was based on the previously published work

Table 2. Solubility/g·(100 g of H_2O)$^{-1}$ at 25 °C

aqueous solution

NaF	Na_2SO_4	NaOH	solid phase	NaF	Na_2SO_4	NaOH	solid phase
0.000	28.00	0.0	$Na_2SO_4 \cdot 10H_2O$	2.380	11.08	0.0	Na_3FSO_4
0.446	28.00	0.0	Na_3FSO_4	2.860	9.37	0.0	Na_3FSO_4
0.901	21.41	0.0	Na_3FSO_4	3.769	5.25	0.0	NaF
1.311	17.28	0.0	Na_3FSO_4	4.090	0.00	0.0	NaF
1.845	13.63	0.0	Na_3FSO_4				

1 *m* NaOH solution

NaF	Na_2SO_4	NaOH	solid phase	NaF	Na_2SO_4	NaOH	solid phase
0.000	24.93	4.0	$Na_2SO_4 \cdot 10H_2O$	1.597	8.62	4.0	Na_3FSO_4
0.278	24.11	4.0	$Na_2SO_4 \cdot 10H_2O$	2.315	5.93	4.0	NaF
0.421	20.49	4.0	Na_3FSO_4	2.233	2.73	4.0	NaF
0.654	15.06	4.0	Na_3FSO_4	2.225	0.00	4.0	NaF
0.994	12.29	4.0	Na_3FSO_4				

3 *m* NaOH solution

NaF	Na_2SO_4	NaOH	solid phase	NaF	Na_2SO_4	NaOH	solid phase
0.000	25.03	12.0	Na_2SO_4	0.738	4.42	12.0	Na_3FSO_4
0.085	25.10	12.0	Na_2SO_4	1.094	2.53	12.0	NaF
0.132	20.52	12.0	Na_2SO_4	1.206	1.33	12.0	NaF
0.133	14.81	12.0	Na_3FSO_4	1.348	0.00	12.0	NaF
0.260	9.61	12.0	Na_3FSO_4				

Table 3. Solubility/g·(100 g H_2O)$^{-1}$ at 50 °C

aqueous solution

NaF	Na_2SO_4	NaOH	solid phase	NaF	Na_2SO_4	NaOH	solid phase
0.000	46.34	0.0	Na_2SO_4	2.869	10.65	0.000	Na_3FSO_4
0.109	36.74	0.0	Na_2SO_4	3.183	8.49	0.000	Na_3FSO_4
0.236	33.34	0.0	Na_3FSO_4	3.492	3.99	0.000	NaF
0.559	23.66	0.0	Na_3FSO_4	4.353	0.00	0.000	NaF
1.450	13.11	0.0	Na_3FSO_4				

1 *m* NaOH solution

NaF	Na_2SO_4	NaOH	solid phase	NaF	Na_2SO_4	NaOH	solid phase
0.000	34.66	4.0	Na_2SO_4	0.838	10.43	4.0	Na_3FSO_4
0.081	32.49	4.0	Na_2SO_4	1.694	6.05	4.0	Na_3FSO_4
0.200	28.71	4.0	Na_3FSO_4	2.071	4.04	4.0	NaF
0.466	15.16	4.0	Na_3FSO_4	2.286	0.00	4.0	NaF

3 *m* NaOH solution

NaF	Na_2SO_4	NaOH	solid phase	NaF	Na_2SO_4	NaOH	solid phase
0.000	20.43	12.0	Na_2SO_4	0.459	4.77	12.0	Na_3FSO_4
0.054	20.45	12.0	Na_2SO_4	0.974	2.54	12.0	NaF
0.187	15.70	12.0	Na_3FSO_4	1.035	0.00	12.0	NaF
0.197	9.18	12.0	Na_3FSO_4				

as well as the compilation by Winchell and Winchell[11] and more recent work performed by Herting et al.[12]

Results and Discussion

Solubilities measured in this work are given in Table 2 (25 °C) and Table 3 (50 °C). The pure-component solubility for sodium fluoride at 25 °C reported in the literature[4] is 4.14 g of NaF/100 g of H_2O, whereas the experimentally measured value in this work was 4.09 g of NaF/100 g of H_2O. At 50 °C, the sodium fluoride solubility reported in the literature is 4.54 g of NaF/100 g of H_2O, and the experimentally measured value in this work was 4.35 g of NaF/100 g of H_2O. For sodium sulfate, the experimentally measured solubilities of 28.00 g of Na_2SO_4/100 g of H_2O at 25 °C and 46.34 g of Na_2SO_4/100 g of H_2O at 50 °C are in agreement with the literature values (28.0 g of Na_2SO_4/100 g of H_2O at 25 °C and 46.4 g of Na_2SO_4/100 g of H_2O at 50 °C).

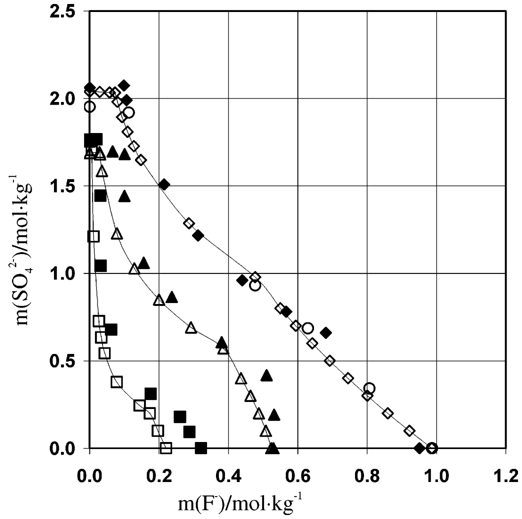

Figure 1. Influence of sodium hydroxide on solubility in the Na−F−SO_4 system at 25 °C: ○, ref 10; ◆, this work, in aqueous solution; -◇-, ESP prediction, in aqueous solution; ▲, this work, in 1 *m* NaOH; -△-, ESP prediction in 1 *m* NaOH; -■-, this work, in 3 m NaOH; -□-, ESP prediction in 3 *m* NaOH.

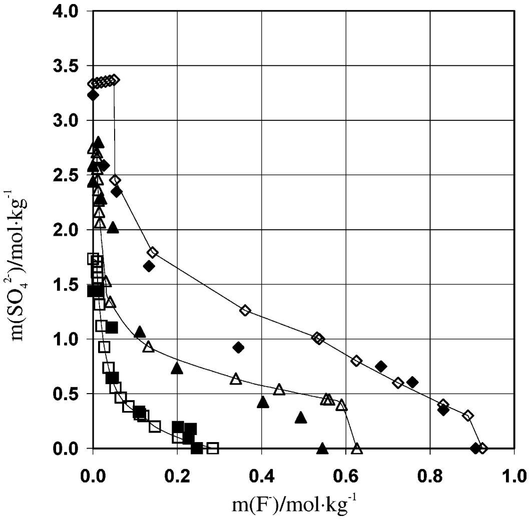

Figure 2. Influence of sodium hydroxide on solubility in the Na−F−SO_4 system at 50 °C: ◆, this work, in aqueous solution; -◇-, ESP prediction, in aqueous solution; ▲, this work, in 1 *m* NaOH; -△-, ESP prediction in 1 *m* NaOH; -■-, this work, in 3 *m* NaOH; -□-, ESP prediction in 3 *m* NaOH.

The solubility measurements in aqueous solution at 25 °C are in good agreement with the literature data of Foote and Schairer.[10] Figure 1 provides a comparison of the literature data and the experimental measurements in this work. Molalities of each species are plotted (moles of solute/kg of H_2O). Also included are predictions of the solubility in this system obtained using ESP with a specialized database, DBLSLTDB. This specialized database was developed in-house using available literature data and the experimental measurements reported in this work to improve the representation of the Na−F−SO_4−OH system. The strong influence of sodium hydroxide on the solubility in this system is evident in Figure 1. As the concentration of sodium hydroxide is increased from 0 *m* (water) to 1 *m* NaOH to 3 *m* NaOH, the solubility envelope is shifted to lower equilibrium concentrations of the anions. The region over which sulfate and fluoride can be present in solution yet not precipitate as the sodium fluoride sulfate double salt is much reduced in the presence of sodium hydroxide. This finding is of importance at the Hanford site because the waste in the tanks typically contains sodium hydroxide at these or higher concentrations.

Similar behavior was identified in the system at 50 °C. In Figure 2, experimental data measured in this work are plotted along with the predictions of the Environmental Simulation Program. The identification of the sodium−fluoride−sulfate double salt in equilibrated solutions at 50 °C allows the extension of the temperature range over which this species forms within ESP. (The previous upper limit based on the data of Foote and Schairer was 35 °C.)

Conclusions

Solubilities in the Na−F−SO_4−OH system at 25 °C and 50 °C in the presence of sodium hydroxide have been experimentally determined. Pure-component and double-salt solubilities in aqueous solution are in agreement with previously published values. Solubility data for this system in the presence of 1 *m* and 3 *m* caustic have not been reported previously. An increase in hydroxide loading was found to result in decreased solubility at both 25 °C and 50 °C.

Acknowledgment

We acknowledge Mr. Dan Reynolds and Mr. Blaine Barton of CH2MHill Hanford Group for their interest in this work.

Literature Cited

(1) Weber, C. F. A Solubility Model for Aqueous Solutions Containing Sodium, Fluoride, and Phosphate. Ph.D. Dissertation, The University of Tennessee, Knoxville, TN, 1998.

(2) Weber, C. F.; Beahm, E. C.; Lee, D. D.; Watson, J. S. A Solubility Model for Aqueous Solutions Containing Sodium, Fluoride, and Phosphate Ions. *Ind. Eng. Chem. Res.* **2000**, *39*, 518−526.

(3) Guiot, J. C. The system H_2O, Na^+, F^-, PO_4^{-3}. *Rev. Chim. Miner.* **1967**, *4*, 85−128.

(4) Linke, W. F.; Seidell, A. *Solubilities, Inorganic and Metal Organic Compounds; A Compilation of Solubility Data from the Periodical Literature*, 4th ed.; Van Nostrand: Princeton, NJ, 1958.

(5) Okorafor, O. C. Solubility and Density Isotherms for the Sodium Sulfate−Water−Methanol System. *J. Chem. Eng. Data* **1999**, *44*, 488−490.

(6) Brenner, D. K.; Anderson, E. W.; Lynn, S.; Prausnitz, J. M. Liquid−Liquid Equilibria for Saturated Aqueous Solutions of Sodium Sulfate + 1-Propanol, 2-Propanol, or 2-Methylpropan-2-ol. *J. Chem. Eng. Data* **1992**, *37*, 419−422.

(7) Windmaisser, F.; Stockl, F. Basic Alkali Sulfates and Selenates. *Monatsh. Chem.* **1952**, *83*, 151−153.

(8) Itkina, L. S. The solubility isotherm of the system Na_2SO_4-Na_2CO_3-NaCl-NaOH-H_2O at 50°. *Zh. Prikl. Khim.* **1949**, *22*, 278−289.

(9) Prikhodko, G. V. Solubility of sodium carbonate and sodium sulfate in the presence of sodium hydroxide at various temperatures. *Zh. Prikl. Khim.* **1932**, *5*, 31−33.

(10) Foote, H. W.; Schairer, J. F. The System Na_2SO_4−NaF−NaCl−H_2O. I. The Ternary Systems with Water and Two Salts. *J. Am. Chem. Soc.* **1930**, *52*, 4202−4209.

(11) Winchell, A. N.; Winchell, H. *The Microscopical Characters of Artificial Inorganic Solid Substances or Artificial Minerals*; John Wiley and Sons: New York, 1931.

(12) Herting, D. L.; Cooke, G. A.; Warrant, R. W. Identification of Solid Phases in Saltcake from Hanford Site Waste Tanks. HNF-11575, Rev. 0, Fluor Hanford: Richland, WA, 2002.

Received for review March 7, 2005. Accepted May 10, 2005. The authors acknowledge support from the United States Department of Energy under Cooperative Agreement No. DE-FC26-98FT40395.

JE050087+