

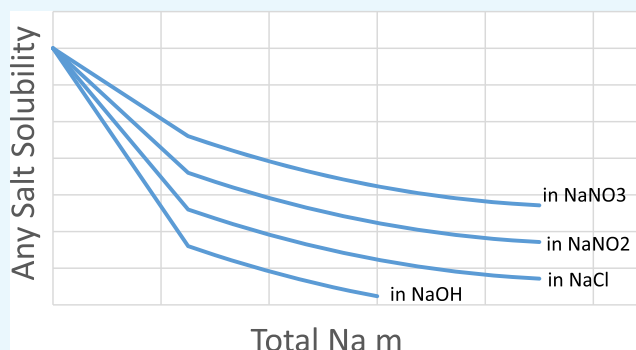


Salt Solubilities in Aqueous Solutions of NaNO_3 , NaNO_2 , NaCl , and NaOH : A Hofmeister-like Series for Understanding Alkaline Nuclear Waste

Jacob G. Reynolds*

Washington River Protection Solutions, LLC, Richland, Washington 99352, United States

ABSTRACT: Nonelectrolyte solubility in electrolyte solutions follow the Hofmeister series, but the applicability of the series to salt solubility has been less appreciated. This study, using solubility data for thirteen sodium-bearing salts, shows that salts are consistently salted out by electrolytes important to alkaline nuclear waste in the order $\text{NaOH} > \text{NaCl} > \text{NaNO}_2 > \text{NaNO}_3$ at 298.15 K, which is the same order as the Hofmeister series. Graphical presentation allowed for easy separation of the common ion effect (caused by the addition of Na^+) from the salting-out effect (caused by the presence of anions) because there is a large difference between the solubility of a given salt in different background electrolytes at a common Na^+ molality. The trend persists even in very high electrolyte concentrations where essentially all of the water molecules must be in the coordination sphere of an ion, which means that the effect of electrolytes on “bulk water” is not the cause of the trend. These specific interactions more likely result from the sharing of water molecules between ions, augmented by differences in ion-pairing of the electrolytes. The Hofmeister series has practical application to the management of alkaline high-level radioactive waste created at nuclear fuel reprocessing facilities, where a predictive understanding of salt solubility is essential for blending wastes of disparate compositions prior to treatment.



INTRODUCTION

Aqueous electrolyte solutions are one of the most common chemical systems in both nature and industry. Despite extensive investigation for more than 100 years, salt solubility in multicomponent aqueous electrolyte solutions are still not well described theoretically except in the most dilute solutions.¹ The cause of this difficulty is in part because of what are called “specific interactions”,² which are interactions between different constituents in the solution. All ions create an electric field in solution because they are charged. Specific interactions are all of those thermodynamic impacts of a specific ion that are above and beyond the impact of the electric field.

Specific interactions are captured experimentally in popular models of electrolyte solution thermodynamics through the activity coefficients of the ions.^{3–5} Unfortunately, the current models must be parameterized with the experimental data for concentrated solutions, which can require substantial experimentation to capture all of the specific interactions between all ions in systems with many components.¹ While it is certainly possible to determine a large number of interaction parameters experimentally, it is cost prohibitive in many cases. Voigt emphasized this point with seawater.^{6,7} Seawater has been studied for more than 100 years, yet there is still insufficient data to develop all of the important interaction parameters

over the whole range of salinities, temperatures, and pressures important to chemical oceanographers.

Alkaline nuclear waste in underground storage tanks at the Hanford and Savannah River Sites in the United States of America is another example of a many component aqueous system. The aqueous phase has high concentrations of nitrate, nitrite, aluminate, hydroxide, carbonate, phosphate, formate, acetate, chloride, fluoride, and oxalate anions counterbalanced with sodium and lesser amounts of potassium. Sodium, nitrate, nitrite, hydroxide, and aluminate are the most prevalent ions.⁸ Thus, the other ions in the waste possess a liquid phase with high concentrations of these electrolytes. There are hundreds of less prevalent species in the waste. The liquid phase is commonly saturated with four or more salts simultaneously, and the waste solution temperatures range from approximately 15–40 °C.⁹ There has been some work performed to quantify the specific interactions between ions in Hanford waste from the available data (for instance^{10–13}), but the data is simply unavailable for most ions over the concentration and temperature range relevant to Hanford waste processing.

Given the complexity of the Hanford waste, the question is asked: are there some trends that can be exploited to explain

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Hanford waste behavior? One of the most ubiquitously used trends in electrolyte chemistry is the Hofmeister series. In the 1880s, Hofmeister and students (translated by ref 14) determined that the solubility of proteins in aqueous solution depends on the identity of other dissolved ions, and that the order of that impact for the background ions was the same regardless of what protein was investigated. They went on to show that water activity and colloid stability in aqueous solution follow this same series.¹⁴

The Hofmeister series has been used extensively in the fields of colloid science and biophysics over the last 130 years to explain many different phenomena in aqueous electrolyte solutions.^{15,16} There was also much early work on the solubility of nonelectrolytes, showing that their solubilities in aqueous solutions follow the Hofmeister series.^{17,18} These early studies showed that the solubility of gases and organic nonelectrolytes depended on the concentration and identity of background electrolytes; but at a given molality of electrolytes, the relative solubility of each nonelectrolyte in each electrolyte solution followed the trend $\text{NaNO}_3 > \text{NaCl} > \text{NaOH}$.¹⁸ Those studies did not include NaNO_2 , but a recent study determined that the solubility of nonelectrolyte chlorouridine 1 followed the solubility trend $\text{NaNO}_3 > \text{NaNO}_2 > \text{NaCl} > \text{NaOH}$.¹⁹

The Hofmeister series has been studied more thoroughly for nonelectrolyte solubilities than salts, even though Brønsted noted nearly a hundred years ago that the salting-out effect is much larger for salts than most nonelectrolytes.²⁰ Extending the Hofmeister series to salt solubilities may provide qualitative trends that can be used to evaluate solubilities in systems where empirical data is unavailable. This study shows that the solubilities of key salts in the Hanford radioactive waste follow the Hofmeister series, at least for the electrolytes NaNO_3 , NaNO_2 , NaCl , and NaOH . This trend can be used to constrain the magnitude of specific interactions between other ions in the waste and these four ions.

METHODS

As noted earlier, this work seeks to answer the question “do the relative solubility of salts in aqueous solutions containing NaNO_3 , NaNO_2 , NaCl , and NaOH follow a trend similar to the Hofmeister series?” The Hofmeister series for nonelectrolytes in aqueous solutions of these background electrolytes follows the trend $\text{NaNO}_3 > \text{NaNO}_2 > \text{NaCl} > \text{NaOH}$, so this study hypothesizes that the relative solubility of salts in these electrolytes would follow this same trend. The salts that are evaluated are NaF , Na_2MoO_4 , NaBr , NaBrO_3 , $\text{Na}_2\text{C}_2\text{O}_4$, NaHCO_3 , Na_2WO_4 , NaIO_3 , Na_3PO_4 , and Na_2SO_4 . This study will also evaluate the solubilities of NaNO_3 , NaNO_2 , and NaCl themselves. Highly hydrated salts, such as $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ or $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, were not included in this study because their solubilities are highly dependent on the water activity (to the 10th power), so the impact of the background electrolytes on water activity confounds the relative impacts of specific interactions.

Graphical analysis is the primary tool used here to determine the relative solubility of the target salt as a function of sodium concentration because the trends are so readily apparent graphically. Data from the literature were used to generate these graphs, most commonly from the compilation by Silcock²¹ because it has a large amount of data reported in consistent concentration units. When data important to the Hanford waste were unavailable in Silcock,²¹ a literature review was conducted in an attempt to locate the data. Solubilities

were evaluated at 25 °C because this temperature had the most solubility data for the target electrolytes.

RESULTS

In the electrolyte chemistry literature, it is rare to hear of a salt described as being “salted out” by another electrolyte. Terms like “salting-out” are more commonly applied to the solubility of nonelectrolytes. The effect of electrolytes on the solubility of salts is described by the common ion effect in which the background electrolyte contains an ion in common with the salt that suppresses the salt solubility. The common ion effect is readily seen in Figure 1, which shows the solubility of NaF in

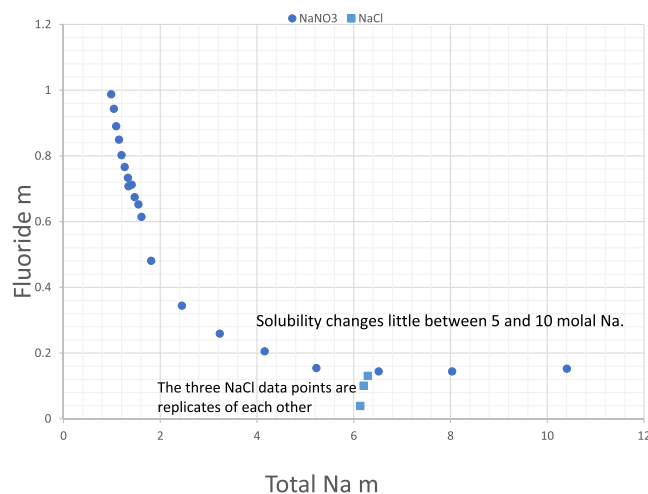
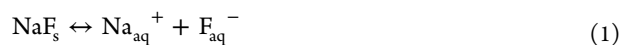


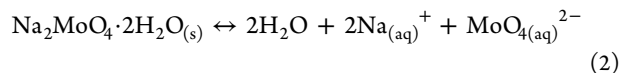
Figure 1. Solubility of NaF in electrolyte solutions (data from refs^{22–26}).

aqueous solutions of NaNO_3 . Sodium fluoride salt is frequently present in the Hanford waste.²⁷ The solubility of NaF in pure water is about 0.987 m at 25 °C.²⁴ Therefore, the lowest sodium and highest fluoride concentration in Figure 1 is 0.987 m because NaF salt breaks up into one sodium ion and one fluoride ion during dissolution via the following reaction



When Na^+ is added to a saturated solution of NaF , the fluoride concentration is suppressed by the common ion effect; that is, the concentration of fluoride decreases with increasing sodium added as NaNO_3 (Figure 1). What the common ion effect cannot explain is the nearly complete independence of fluoride concentration on sodium concentration between about 5 and 10 m Na^+ (Figure 1). This effect is caused by specific interactions that are captured in models such as that of Pitzer.¹³ Figure 1 also shows the solubility of NaF in NaCl media, and all three data points are replicates of each other (two by ref 25 and one by ref 26), although with significant scatter in the result. Despite the scatter, all three replicates in NaCl media exhibit lower solubility than in NaNO_3 media at the same sodium molality. This indicates that there is likely some difference in the solubility of NaF in nitrate media compared with chloride media, indicating some specific interaction from nitrate and chloride. This was recognized by Brønsted²⁰ nearly 100 years ago, but we have found no discussion in the literature of the consistent relative ability of different background electrolytes to “salt-out” a large variety of salts.

A broader comparison of the solubility of the salts in different electrolytes is required to make a trend of specific ion effects self-evident. Therefore, sodium molybdate is investigated because much more data is available than for NaF at 25 °C. Sodium molybdate salt $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ is relatively soluble in pure water at ambient temperatures, dissolving via the following reaction



Once the sodium molybdate concentration in solution is large enough to reach saturation, any sodium added from another electrolyte should drive the equilibrium to the left in eq 2, suppressing the molybdate concentration. This is illustrated in Figure 2, where the solubility of sodium

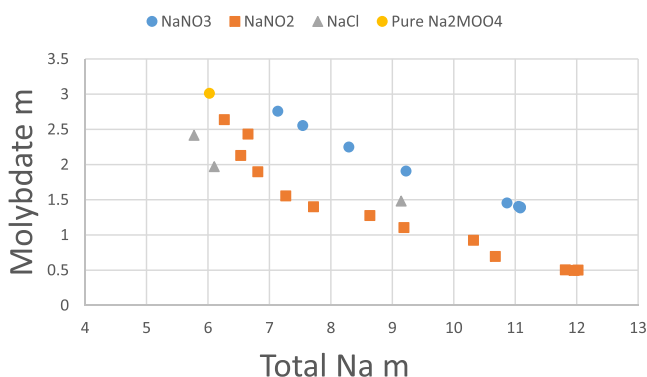


Figure 2. Solubility of sodium molybdate in aqueous solutions of NaNO_3 , NaNO_2 , and NaCl at 298.15 K (data from refs^{21,28,29}).

molybdate is increasingly suppressed as NaNO_3 , NaNO_2 , or NaCl are added (data from refs^{21,28,29}). Figure 2 demonstrates that it greatly matters which anion is added with the sodium, with the solubility of sodium molybdate being much higher in NaNO_3 solutions than NaCl solutions of the same total sodium molality, illustrating the “specific interactions” between ions in this system.^{2,20} Adding 0.9 mol of NaCl per kg of water to a solution of Na_2MoO_4 at saturation can precipitate more sodium as $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ salt than sodium added as NaCl (Figure 2). Figure 2 also shows that the solubility of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in NaNO_2 solutions is between that of NaNO_3 and NaCl , with the exception of one stray data point. This relative impact of these electrolytes ($\text{NaNO}_3 > \text{NaNO}_2 > \text{NaCl}$) on $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ solubility is the same as the relative impact of these same electrolytes on the solubility of neutral organic molecules as predicted by the Hofmeister series.¹⁹

$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ is a hydrated salt, having two water molecules in its crystal structure.³⁰ Therefore, the solubility would depend on the water activity (to the second power) in addition to the sodium molality per eq 2. Thus, we need to ensure that the impact of different electrolytes on the solubility of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ observed in Figure 2 is not solely caused by the effects of the background electrolyte on water activity.

The impact of water activity on the solubility of the salt can be observed in the equilibrium expression for hydrated salts, here using $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ as an example.

$$K = (\text{Na})^2 (\text{MoO}_4^{2-}) (\text{H}_2\text{O})^2 \quad (3a)$$

Here, K is the equilibrium constant, and the parentheses denote activities of the species inside. This can be solved for

the molybdenum activity (a function of the concentration) to put it on the same basis as Figure 2.

$$(\text{MoO}_4^{2-}) = \frac{K}{(\text{Na})^2 (\text{H}_2\text{O})^2} \quad (3b)$$

The activity of water appears in the denominator of eq 3a, so an increase in water activity should result in a decrease in the molybdate concentration. Therefore, any background electrolyte that changes the water activity must change the solubility of the salt. The background electrolyte with the highest water activity at a given sodium molality should decrease the solubility of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ the most, if the water activity were the only way that the anion was affecting the solubility. Figure 3 shows the water activity as a function of sodium

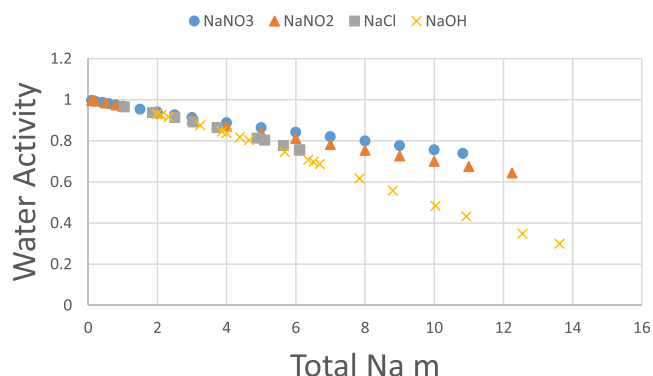


Figure 3. Water activity as a function of sodium molarity in aqueous solutions of NaNO_3 , NaNO_2 , NaCl , and NaOH (data from refs^{31–34}).

molality for background electrolytes in this study, demonstrating that the water activity is always $\text{NaNO}_3 > \text{NaNO}_2 > \text{NaCl}$ over the entire sodium molality range. This is the same order as the impact of the electrolytes on the solubility, but it is the exact opposite of the effect expected if their impact on the water activity were the only cause of the different solubilities in different electrolytes. Thus, the impact of the electrolytes on $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ solubility is due to specific interactions rather than their impact on the water activity. Indeed, the impact of the specific interactions overcomes their impact on the water activity.

The relative impact of NaNO_3 , NaNO_2 , and NaCl on the solubility of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ as well as the impact of NaNO_3 versus NaCl on NaF solubility is consistent with the Hofmeister series for these three background electrolytes. These results show the salting-out effect of the background electrolytes and show they are different from the common ion effect. These, however, are just two salts, with very limited data, and there are no data at 25 °C for either of them in aqueous NaOH solutions. Thus, the next section will look at a broader set of salts.

OTHER SALTS

The solubility of NaCl is available in NaNO_3 , NaNO_2 , and NaOH solutions, whereas NaBr solubility is only available in NaNO_3 and NaOH solutions. Figures 4 and 5 plots these solubilities. Individually, NaCl and NaBr are consistently more soluble in NaNO_3 solutions than NaOH solutions at the same sodium molality (Figures 4 and 5). The solubility of NaCl at constant sodium molality follows the trend $\text{NaNO}_3 > \text{NaNO}_2 > \text{NaOH}$ (Figure 4).

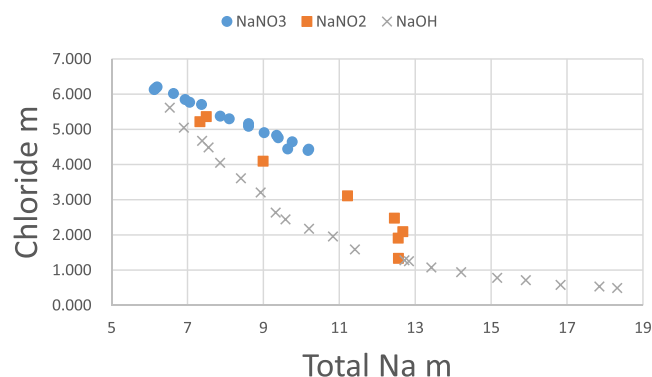


Figure 4. NaCl solubility in aqueous solutions of NaNO_3 , NaNO_2 , or NaOH (data from refs ^{35–38}).

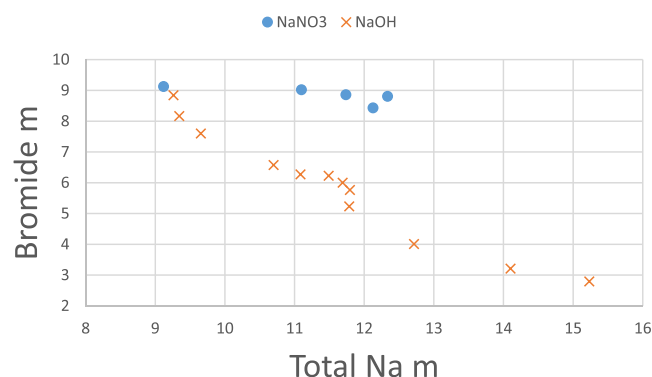


Figure 5. Solubility of NaBr in aqueous solutions of NaNO_3 and NaOH (data from ref 21).

Figures 6 and 7 show that the oxyhalides NaBrO_3 and NaIO_3 are always more soluble in NaNO_3 solution than in

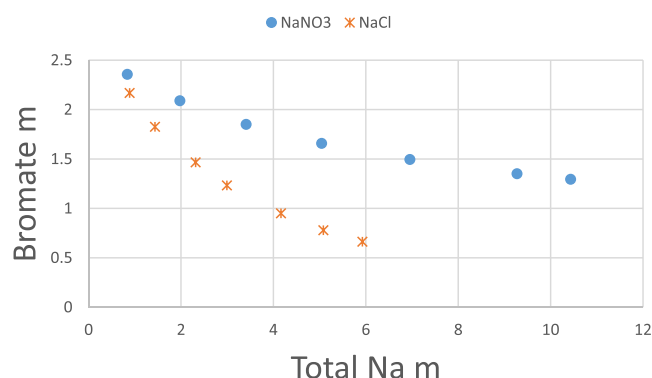


Figure 6. Solubility of NaBrO_3 in aqueous solutions of NaNO_3 and NaCl (data from ref 21).

NaCl solution at the same sodium molality. Solubility data in NaNO_2 and NaOH solutions are unavailable for these oxyhalides.

The salts with divalent anions Na_2WO_4 and Na_2SO_4 (Figures 8 and 9) show trends similar to the previous salts investigated. Hence, Na_2WO_4 is always more soluble in NaNO_3 than in NaNO_2 , and anhydrous Na_2SO_4 solubility follows the trend $\text{NaNO}_3 > \text{NaNO}_2 > \text{NaOH}$ over the entire sodium molality range (Figures 8 and 9). Note that NaCl is not included in Figure 9 because NaCl is not soluble enough to reduce the water activity enough to precipitate anhydrous Na_2SO_4 at 25 °C, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ precipitates instead.²¹

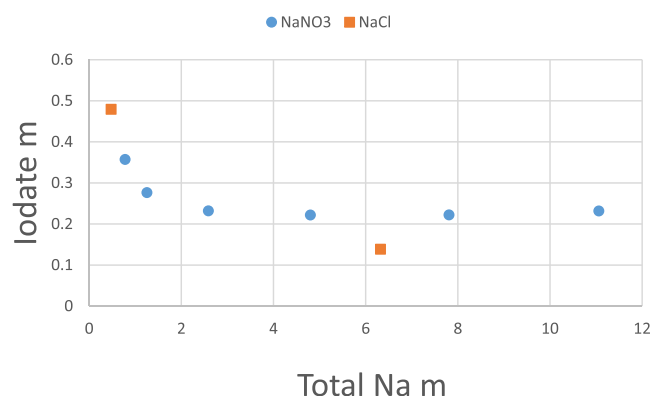


Figure 7. Solubility of NaIO_3 in aqueous solutions of NaNO_3 and NaCl (data from ref 21).

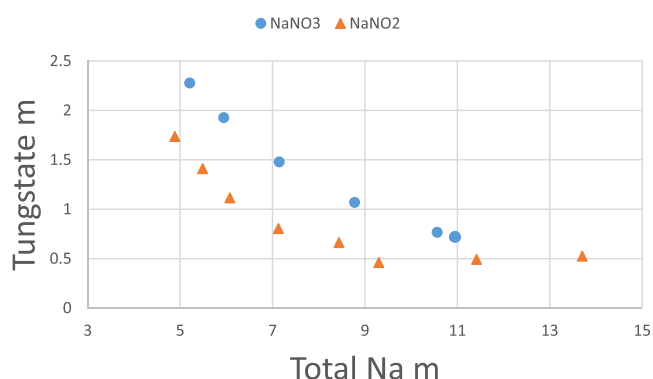


Figure 8. Solubility of Na_2WO_4 in aqueous solutions of NaNO_3 and NaNO_2 (data from refs 39 and 40).

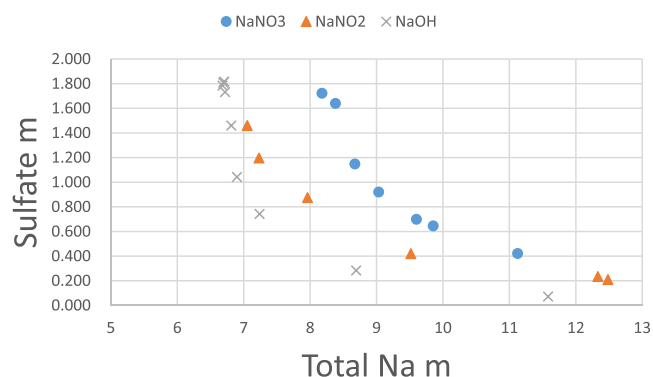


Figure 9. Solubility of Na_2SO_4 in aqueous solutions of NaNO_3 , NaNO_2 , and NaOH (data from refs ^{41–43}).

The solubility of $\text{Na}_3\text{PO}_4 \cdot 0.25\text{NaOH} \cdot 12\text{H}_2\text{O}$ follows the trend $\text{NaNO}_3 > \text{NaNO}_2 > \text{NaCl} > \text{NaOH}$ like other salts (with the exception of a couple of stray data points) but has an interesting feature (Figure 10). As noted earlier, highly hydrated salts such as $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ or $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ were not considered in this study because the impact of the background electrolyte on solubility through the water activity obscured the specific interactions. $\text{Na}_3\text{PO}_4 \cdot 0.25\text{NaOH} \cdot 12\text{H}_2\text{O}$ has 12 waters of hydration, so its solubility should be proportional to the water activity to the 12th power. The impact of the background electrolytes on the water activity should thus have an enormous impact on the solubility of $\text{Na}_3\text{PO}_4 \cdot 0.25\text{NaOH} \cdot 12\text{H}_2\text{O}$ by influence on the water activity. Nonetheless, the impact of the specific interactions between

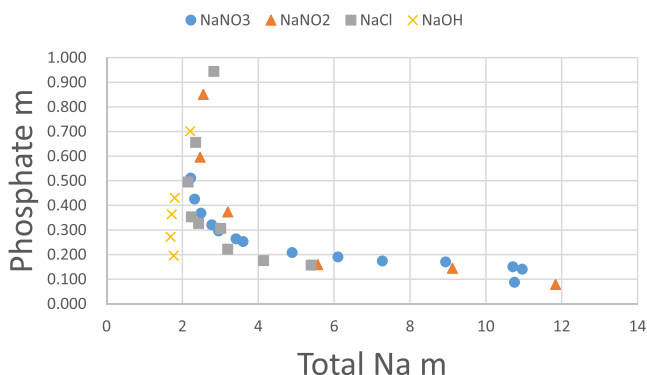


Figure 10. Solubility of $\text{Na}_3\text{PO}_4 \cdot 0.25\text{NaOH} \cdot 12\text{H}_2\text{O}$ in aqueous solutions of NaNO_3 , NaNO_2 , NaCl , and NaOH (data from refs ^{44–47}).

phosphate and the background electrolytes is apparently even greater because the relative impact of NaNO_3 , NaNO_2 , NaCl , and NaOH on $\text{Na}_3\text{PO}_4 \cdot 0.25\text{NaOH} \cdot 12\text{H}_2\text{O}$ solubility is the exact opposite of their impacts via the water activity (Figure 3).

The solubility of NaHCO_3 is higher in NaNO_2 than in NaCl solutions (Figure 11). Sodium bicarbonate is not stable in

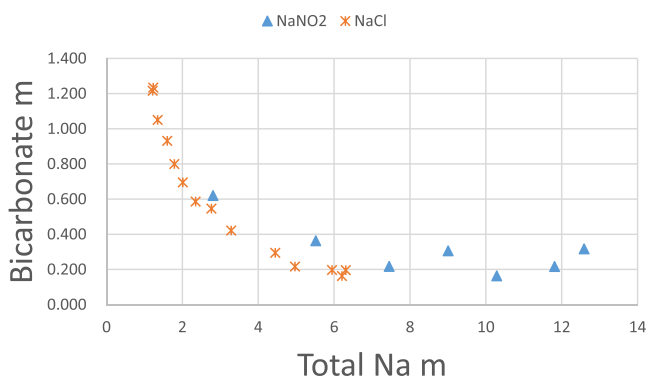


Figure 11. Solubility of NaHCO_3 in aqueous solutions of NaNO_2 and NaCl (data from ref ²¹).

NaOH solutions, so the impact of NaOH on NaHCO_3 solubility cannot be evaluated. Sodium oxalate also follows the solubility trend $\text{NaNO}_3 > \text{NaCl} > \text{NaOH}$ at a given sodium molality (Figure 12).

The data on the solubility of NaNO_3 and NaNO_2 in the other background electrolytes is consistent with the trend $\text{NaNO}_3 > \text{NaNO}_2 > \text{NaCl} > \text{NaOH}$ (Figures 13 and 14),

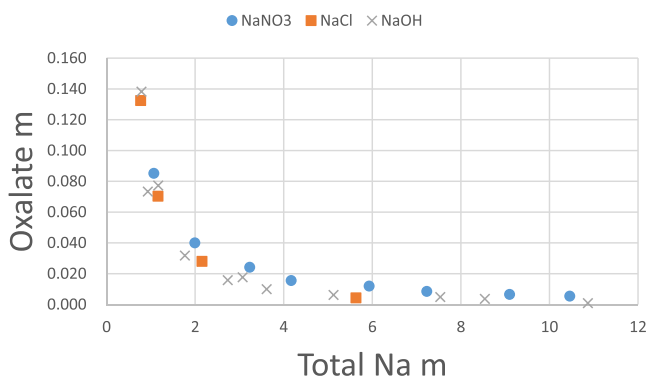


Figure 12. Solubility of $\text{Na}_2\text{C}_2\text{O}_4$ in aqueous solutions of NaNO_3 , NaCl , and NaOH (data from refs ⁴⁸ and ⁴⁹).

which in turn is consistent with the Hofmeister series for the impact of these background electrolytes on nonelectrolyte organic molecules.

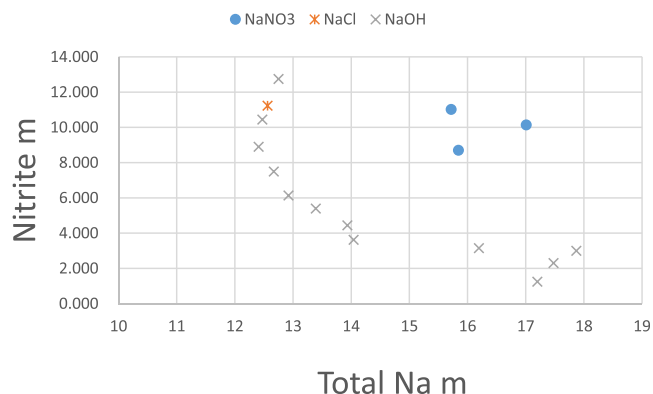


Figure 13. Solubility of NaNO_2 in aqueous solutions of NaNO_3 , NaCl , and NaOH (data from refs ^{36,50,51}).

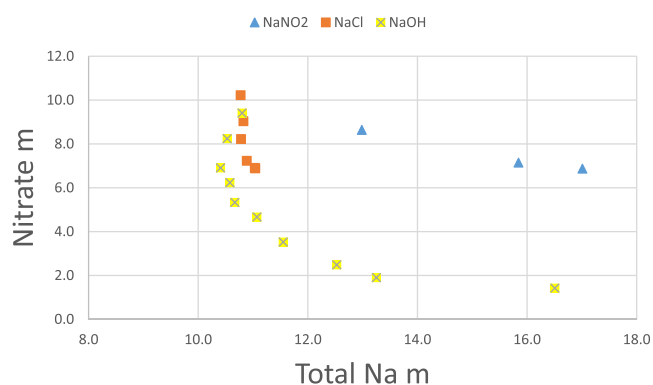


Figure 14. Solubility of NaNO_3 in aqueous solutions of NaNO_2 , NaCl , and NaOH (data from refs ^{37,50,51}).

Here, the solubilities of 13 salts followed the Hofmeister series $\text{NaNO}_3 > \text{NaNO}_2 > \text{NaCl} > \text{NaOH}$ over the entire composition region, with the exception of only a few stray data points. While only one salt could be investigated in all four background electrolytes ($\text{Na}_3\text{PO}_4 \cdot 0.25\text{NaOH} \cdot 12\text{H}_2\text{O}$), all salts followed this trend with the data available. Thus, it can be concluded that the solubility of sodium salts in these background electrolytes can usually be expected to follow the Hofmeister series for at least these four background electrolytes.

DISCUSSION

The Hofmeister series has long been associated with the ion size and charge, where “salting-out” of a nonelectrolyte by smaller ions is greater than that by larger ions of the same charge (Grover and Ryall, 2005).⁵² The impact of the electrolytes on the solubility of salts here is also in the same order of their ionic radius, where hydroxide with the shortest radius salts out more than nitrate with the longest radius.⁵³

Thermodynamically, when background electrolytes influence the solubility of another salt, they must either change the activity coefficients of the dissolved species or change the concentration of free sodium ion by forming ion pairs. The ion pairing would decrease the free Na^+ concentration because adding the background electrolyte would form an ion pair

instead of completely dissociating into ions. Recent solubility models for sodium oxalate and sodium sulfate have combined ion pairing of the background electrolyte with impacts on activity coefficients.^{10–12} However, salt-electrolyte systems can be modeled just as well by adding terms to the interaction factors between the ions rather than including ion pairing in the model.⁵⁴ Indeed, one of the main reasons that the present study used graphical analysis rather than models to show the trends is that there are so many interrelated empirically determined parameters in most electrolyte thermodynamic models. This makes it difficult to associate the parameters with underlying physical processes.¹

There is a correlation between the polarizability of the ions and their position in the Hofmeister series in dilute solutions.⁵⁵ Early researchers explained the Hofmeister series by assuming the background electrolytes have an electrostatic effect of the ions on the bulk water.⁵² There has been much debate in the literature concerning the impact of dissolved ions on the water molecules beyond the ion's coordination sphere, with the current evidence indicating that there is minimal long-range effect of monovalent ions on the structure of water.^{56–58} Nonetheless, such electrostatic effects on “bulk” water would never have been operative in the highly concentrated systems studied here. Here, the Hofmeister effect was clearly evident even when the electrolyte concentration was over 6 *m*, where little “bulk” water remains because all of the water molecules are in the ions' inner coordination spheres.⁵⁷ Indeed, the specific interactions tended to be highest at the highest electrolyte concentrations.

The quantity of “bulk water” can be estimated from the number of water molecules in the ion coordination spheres as determined by diffraction methods. Diffraction data indicates that sodium, nitrate, nitrite, and chloride all have approximately six coordinating water molecules, whereas hydroxide has five.^{59–66} These coordinating water molecules form hydrogen bonds with the ions.^{63–68} With 55.5 mol of water per kilogram and six water molecules per ion, a solution with more than 9.25 mol of ions per kilogram water (or 4.63 mol of fully dissociated monovalent electrolyte) does not have enough water to provide each ion with six water molecules without sharing. This means that in a solution with greater than 4.63 *m* of 1:1 electrolyte (or 5.05 *m* for NaOH), the ions are either not fully dissociated, or the ions must be sharing at least some water molecules with each other. It seems logical that the hydrogen bond between water and an ion will have at least some effect on the ability of the same water molecule to simultaneously form a hydrogen bond with another ion. Therefore, the effect of ions on the solubility of other ions in concentrated solutions is likely related to how they impact water's ability to form hydrogen bonds with neighboring ions. Indeed, the order of the Hofmeister series for anions is the same as their relative ability to accept hydrogen bonds.⁶⁹ This is consistent with the recent work that has correlated the Hofmeister series with the impact of the ions on hydrogen bonds in the hydration shell.^{70–72}

There are many potential practical applications of this trend. One potential use is to estimate coefficients for more complicated thermodynamic models. There was only one salt evaluated here that had solubility data available in all four electrolytes, and solubility data are most commonly used to parameterize the liquid phase interaction factors in most thermodynamic models.⁴ Consequently, it is not possible to determine interaction factors between all ions in this study.

Nonetheless, the data that are available can constrain the solubility in background electrolytes, where no other data are available. For instance, data on the solubility of Na₂C₂O₄ in aqueous solutions of NaNO₂ are unavailable, but the Hofmeister series here indicates that the solubility of Na₂C₂O₄ in aqueous NaNO₂ solutions is going to lie somewhere between its solubility in NaCl and NaNO₃ solutions. Fitting the NaNO₂ interaction factors to Na₂C₂O₄ solubility in NaCl or NaNO₃ will not be as accurate as fitting to the actual data in NaNO₂ solutions, but it would be more accurate than assuming no interaction at all.

While NaNO₃, NaNO₂, NaCl, and NaOH are all major electrolytes in the Hanford waste, another major dissolved electrolyte in the Hanford waste is sodium aluminate [NaAl(OH)₄].⁷³ Sodium aluminate was not included as a background electrolyte in this study because it is only stable in the presence of NaOH, which confounds the interpretation of the data, and because very few data exist on the solubility of salts in sodium aluminate solutions. Sodium aluminate is likely higher on the Hofmeister series (i.e. less precipitating) than NaOH because the location in the Hofmeister series is correlated with the impact of the electrolyte on water activity (Figure 2)¹⁴ and the water activity of NaOH/NaAl(OH)₄ mixtures is higher than NaOH at the same sodium molality.⁷⁴

Given the data presented here, showing that salt solubility follows the Hofmeister series for model systems, can the same trend be applied to complex Hanford waste? Assuming that (1) the most important specific interactions in the Hanford waste are from the major electrolytes NaNO₃, NaNO₂, NaCl, NaAl(OH)₄, and NaOH and (2) the location of NaAl(OH)₄ on the Hofmeister series is somewhere between NaOH and NaNO₃, the solubility of salts in the Hanford waste should always lie somewhere between their solubilities in simple NaOH and NaNO₃ aqueous solutions. Historic Hanford Site waste characterization data can be used to test this assumption. Sodium oxalate had a relatively narrow solubility spread between background electrolytes, whereas NaNO₃ had a very wide spread (Figures 12 and 14). Consequently, these two electrolytes are evaluated in real nuclear waste as the two more extreme cases.

The real waste data used in this evaluation was taken from the Hanford Site tank farms characterization database called Tank Waste Inventory Network System (TWINS). Data for wastes that are known to have solid sodium oxalate were used. These data are compared to data in just NaNO₃ and NaOH aqueous solutions in Figure 15. The plot shows that the majority of the actual waste data falls between the solubility in aqueous NaNO₃ and in NaOH solutions, though two data points are slightly outside. Nonetheless, even these two data points are just barely outside, so for practical purposes, the solubility of sodium oxalate in alkaline tank waste can be assumed to be between its solubility in NaNO₃ and NaOH solutions.

Unlike sodium oxalate, there is a large difference in sodium nitrate solubility in different background electrolytes. Sodium nitrate is 3–4 times more soluble in NaNO₂ solutions than NaOH solutions at the same sodium molality (Figure 14). Liquid phase concentrations of sodium and nitrate were collected from the TWINS database for samples that are known to have solid phase NaNO₃ in them (and thus are likely at saturation with NaNO₃). These data are plotted in Figure 16, showing that the real waste data are in-between the solubilities of NaNO₃ in pure aqueous solutions of NaNO₂ and

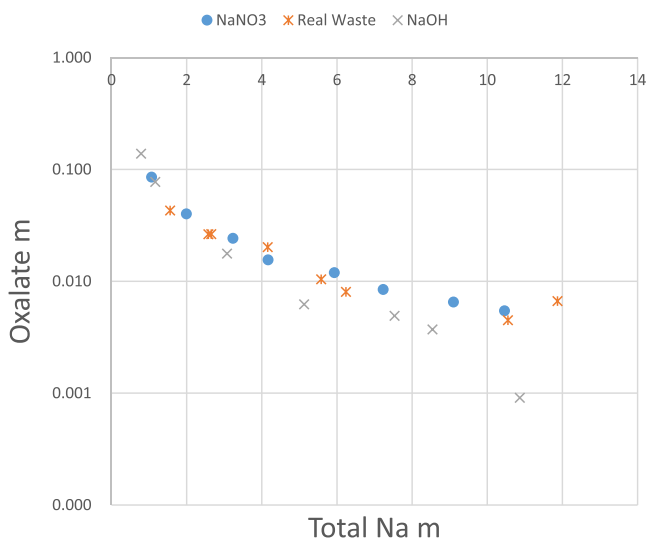


Figure 15. Comparison of $\text{Na}_2\text{C}_2\text{O}_4$ solubility in the Hanford waste to simple NaNO_3 and NaOH solutions (data from TWINS database as well as refs 48 and 49).

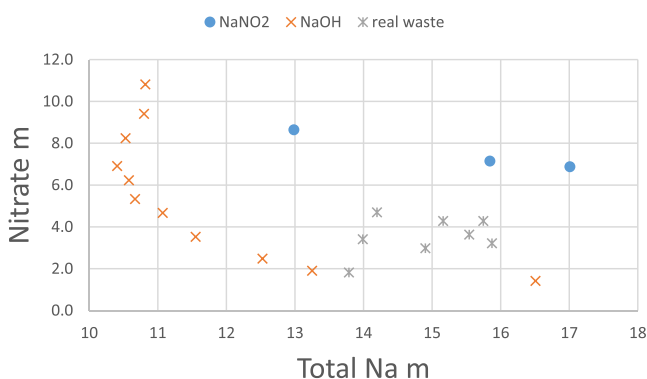


Figure 16. Comparison of NaNO_3 solubility in the Hanford waste to simple NaNO_2 and NaOH solutions (data from TWINS database as well as refs 50 and 51).

NaOH . These results indicate that the Hofmeister series can be used to explain the order of solubility for salts of interest in the Hanford waste.

CONCLUSIONS

While the specific interactions ordered by the Hofmeister series have long been associated with the nonelectrolyte solubility and with the coagulation of colloids and biomolecules, this study shows it is equally applicable to the “salting-out” of salts as well. The distinction between specific interactions caused by the anions and the common ion effect could be readily seen by plotting the solubility of a given salt as a function of sodium molality for different electrolytes. The solubility of the salts at constant total sodium molality always followed the relative order $\text{NaNO}_3 > \text{NaNO}_2 > \text{NaCl} > \text{NaOH}$ for the four background electrolytes studied here. This trend can be used to explain the salt solubility behavior in many-component alkaline nuclear waste as demonstrated here for $\text{Na}_2\text{C}_2\text{O}_4$ and NaNO_3 .

AUTHOR INFORMATION

Corresponding Author

*E-mail: reynoldsjacob@hotmail.com.

ORCID

Jacob G. Reynolds: 0000-0001-6091-8540

Notes

The author declares no competing financial interest.

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