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ARTICLE

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Non-ideal aqueous electrolyte solutions have been studied since the start of the application of thermodynamics to chemistry in the late 19th century. The present study examines some of the most extreme non-ideal behavior ever observed: solubilities of alkali and NH_4^+ nitrate salts in water that appear to behave the opposite of how the Law of Mass Action would predict. A literature review discovered that the solubilities of NH_4NO_3 and many alkali nitrate salts increases when another nitrate-bearing electrolyte is added to solution. These occurrences were in concentrated solutions with insufficient water to provide all ions their preferred hydration number without sharing waters between ions. This water deficit results in the formation of contact ion-pairs as well as larger ion-clusters. These ion-clusters may be favored when there is more than one type of monovalent cation present.

Introduction

Alkali and NH_4^+ nitrates have wide use in industry and are widely present in soils and natural waters.[1] Many monovalent metal nitrates are highly soluble in water. For instance, Eysseltova et al. reports that the solubility of $NaNO_3$ in water is 10.79 molal.[2] Given the large solubilities of these nitrates, the solubility of other salts can be measured over very wide concentration ranges, helping to understand water dynamics in highly concentrated solutions and the impact of specific interactions between ions in solutions.[3-5]

An example of industrially important highly concentrated nitrate solutions are the millions of liters radioactive waste stored at the Hanford and Savannah River Sites in the United States.[6] There are many unexplained impacts of nitrate in these wastes, such as the large effect of nitrate on aluminum solubility, and the large incompatibility between dissolved nitrate and hydroxide ions.[7-10]

In an effort to understand the complexity of many-component nitrate-rich radioactive waste, a previous

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study evaluated solubility of thirteen Na^+-bearing salts in aqueous solutions of NaOH, NaCl, $NaNO_2$, and $NaNO_3$.[5] The Na^+ from these dissolved electrolytes would be expected to suppress the solubility of Na^+-bearing salts via the common ion effect in the Law of Mass Action. The Law of Mass Action indicates that if a reaction is at equilibrium, and additional reactant is added, the equilibrium is shifted away from the reactant. Reynolds found that the solubility of these Na^+-bearing salts depended on the anion of the background electrolyte.[5,11] Every Na^+-bearing salt was more soluble in aqueous $NaNO_3$ solution than NaOH solution of the same Na^+ molality.[5] This regularity helped explain the solubility trends observed in many-component alkaline nuclear waste. Nonetheless, there are unexplained observations that deserve further attention. For instance, Reynolds noted that the solubility of NaF was insensitive to the concentration of $NaNO_3$ at high concentrations, contrary to the expectations of the Law of Mass Action.[5]

Other more dramatic apparent failures of the Law of Mass Action for aqueous nitrate solutions have been reported. For instance, KNO_3 precipitates from aqueous solution via the reaction in Equation 1. The Law of Mass Action would indicate that if a nitrate-bearing electrolyte were added to a solution saturated with KNO_3, more KNO_3 would precipitate because the nitrate would push Equation 1 to the right. Nonetheless, Wrobel-Kaszanek et al. recently reported that adding NH_4NO_3 to saturated KNO_3 solution increased the solubility of KNO_3.[12] This indicates that adding the common ion nitrate via NH_4NO_3 did not precipitate KNO_3 via the common ion effect and actually enhanced the solubility of KNO_3, an apparent reversal of the Law of Mass Action! The present study asks a simple question – does this apparent reversal in the Law of Mass Action in aqueous NH_4NO_3 and KNO_3 solutions occur in other aqueous nitrate systems? The attributes of nitrate solutions that might contribute to this reversal are also investigated.

$$K^+_{(aq)} + NO^-_{3(aq)} \Leftrightarrow KNO_{3(s)}$$

Equation 1

Mutual Solubility of Cesium Nitrate and Ammonium Nitrate in Water

Figure 1 graphically presents the solubility of NH_4NO_3 salt in water as a function of added $CsNO_3$, data measured recently by Li et al.[13] The NH_4NO_3 solubility decreased with increasing $CsNO_3$ concentration, indicating that $CsNO_3$ suppresses NH_4NO_3 solubility. Ammonium nitrate and $CsNO_3$ both have the nitrate ion in common, so it is not surprising that adding a nitrate source ($CsNO_3$) to saturated NH_4NO_3 solution would precipitate NH_4NO_3 via the common ion effect. Little $CsNO_3$ was required to precipitate much NH_4NO_3; adding 2 moles of $CsNO_3$ precipitated 10 moles of NH_4NO_3! This result would imply a substantial antagonistic effect of Cs^+ on NH_4^+. Sharma et al. measured the electrical conductivity of highly concentrated NH_4NO_3 solutions, and found that it dropped substantially by adding small amounts of $CsNO_3$.[14] The implication is that there is some sort of interaction between $CsNO_3$ and NH_4NO_3 in solution.

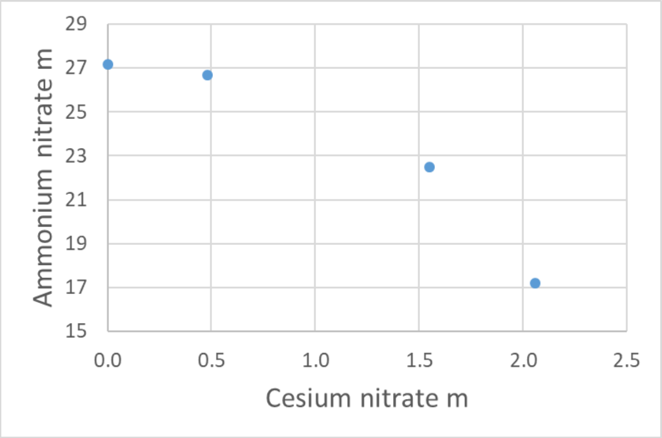

Figure 1. Solubility of Ammonium Nitrate as a Function of Added Cesium Nitrate at 25 °C (data from Reference 13).

A similar study highlighted antagonistic effect in saturated sodium hydroxide solution when nitrate was added.[10] In that case, the large antagonistic effect was attributed to dissolved sodium hydroxide ion-clusters that could not incorporate nitrate into their structure, similar to how a crystal cannot form solid solutions with highly dissimilar ions.[10] The extended sodium hydroxide ion clusters were caused by the extremely high electrolyte concentration in that system leaving insufficient water to dissolve individual ions or ion-pairs.[10,15] A similar mechanism is plausible here, noting that a 27 molal saturated solution of NH_4NO_3 has only about one water molecule per ion. Mosallanejad et al. indicate that highly concentration NH_4NO_3 solution has a repeating pattern of ions emulating a crystal structure.[16] Thus, it is plausible that Cs^+ could simply not fit into the structure of highly concentrated NH_4NO_3 solution and this incompatibility was relieved by precipitation of NH_4NO_3 salt.

While the quantity of NH_4NO_3 precipitated by adding $CsNO_3$ was not expected by the present author, the direction of the effect was expected because it was consistent with the Law of Mass Action. With that in mind, see Figure 2, which is the other side of this system, the solubility of $CsNO_3$ salt as a function of NH_4NO_3 addition. When the first 2.4 moles of NH_4NO_3 is added to saturated $CsNO_3$ solution, $CsNO_3$ responds the direction that the Law of Mass Action indicates it would go. Namely, adding a nitrate source (NH_4NO_3) to a saturated solution of $CsNO_3$ lowers the solubility from 1.4 to 1.3 molal. Something less expected happens when more than 2.4 moles of NH_4NO_3 are added: adding more NH_4NO_3 actually dissolves more $CsNO_3$. This is the opposite of what the Law of Mass Action would predict would happen via the common ion effect. Indeed, $CsNO_3$ is more soluble in 5 molal NH_4NO_3 solution than in pure water. This result indicates that NH_4^+ has a cooperative effect on $CsNO_3$ solubility at high NH_4NO_3 concentration, so cooperative that it reverses the Law of Mass Action. What is even more interesting is that this cooperative effect of NH_4NO_3 on $CsNO_3$ solubility occurs even as $CsNO_3$ highly suppresses NH_4NO_3 solubility. To humanize it, it would appear that $CsNO_3$ likes ammonium nitrate but NH_4NO_3 does not like $CsNO_3$.

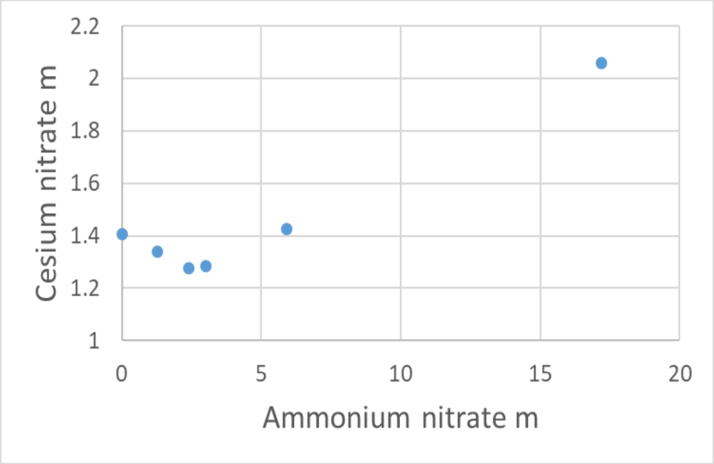

Figure 2. Solubility of Cesium Nitrate as a Function of Ammonium Nitrate Concentration at 25 °C (data from Reference 13).

While the highly antagonistic effect of $CsNO_3$ on NH_4NO_3 solubility deserves a molecular explanation, the present study will focus primarily on the nitrate systems that seem to reverse the Law of Mass Action. While Figure 2 shows that $CsNO_3$ appears to reverse the Law of Mass Action, this observation is based on only three data points. With only three data points supporting this conclusion, one could assume that this is just bad data. Therefore, in the next section a large number of monovalent nitrate solutions is evaluated.

The Solubility of Ammonium and Alkali Nitrates in Aqueous Solutions of Other Nitrates

Figure 3 shows the solubility of NH_4NO_3 salt in aqueous solutions of the alkali nitrates. As noted earlier, NH_4NO_3 solubility decreases rapidly with increased concentration of $CsNO_3$. A similar decrease in solubility occurs in $RbNO_3$ solution, with almost vertical drop above 3.8 molal $RbNO_3$. Ammonium nitrate precipitates as a solid solution in $RbNO_3$ solution rather than as the pure NH_4NO_3 salt.[17] Ammonium nitrate solubility also decreases in KNO_3 solution with increasing nitrate as expected from the Law of Mass Action. In $NaNO_3$ solution, however, the solubility of NH_4NO_3 is little impacted by the addition of $NaNO_3$ even at concentration greater than five molal. In $LiNO_3$ solutions, NH_4NO_3 salt initially precipitates with increasing $LiNO_3$ concentration but solubility increases with increasing $LiNO_3$ above a minimum concentration somewhere between 6.8 and 10.2 molal $LiNO_3$. Thus, at very high $LiNO_3$ concentrations, NH_4NO_3 solubility is the opposite of what would be expected from the Law of Mass Action. Thus, this is a second example of a nitrate solution that appears to reverse the Law of Mass Action, like $CsNO_3$ solubility in aqueous NH_4NO_3 solutions discussed earlier.

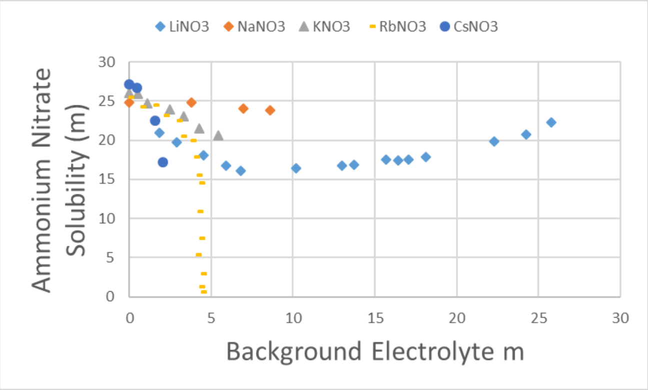

Figure 3. Solubility of Ammonium Nitrate in Alkali Nitrate Solutions at 25 °C. Data from References 17-20.

The examples of solubilities that appear to reverse the Law of Mass Action in this study discussed so far have had NH_4NO_3 in solution. Ammonium is somewhat different than the alkali cations in concentrated aqueous nitrate solutions. The shifts in the Raman nitrate bands in aqueous alkali nitrate solutions have been attributed to contact between the alkali ions with nitrate, contact that increases with increasing nitrate concentration.[21] In NH_4NO_3 solutions, however, Vollmer showed that the nitrate Raman bands are essentially independent of concentrations even at very high concentrations where there must be contact between NH_4^+ and nitrate.[22] Vollmer believed that this is because the hydrogen bond strength between NH_4^+ and nitrate in solution is approximately the same as the hydrogen bond strength between water and nitrate in solution.[22] In contrast, the alkali ions accept greater charge from the nitrate ion when they contact nitrate than water does in forming hydrogen bonds with nitrate.[22] Ammonium binds less water and has more structured water in its hydration sphere than K^+, even though they both have roughly the same ionic radius.[23] To ensure that reversing the Law of Mass Action is not simply related to the properties of NH_4^+, other nitrate solutions without NH_4^+ are investigated next.

Figure 4 shows the solubility of $CsNO_3$ salt as a function of alkali nitrate background electrolyte concentration for two electrolytes. From the plot, it is clear that $RbNO_3$ suppresses the solubility of $CsNO_3$, as expected from the Law of Mass Action. In the $CsNO_3$-$RbNO_3$-H_2O system, a solid solution of (Cs,Rb)NO_3 precipitates rather than pure $CsNO_3$ salt.[25] In aqueous $NaNO_3$ solution, the solubility of $CsNO_3$ salt is increased by increasing nitrate concentration after going through a minimum solubility. This is another example of a system that reverses the Law of Mass Action after going through a minimum solubility. None of these electrolytes contain NH_4^+, demonstrating that reversing the Law of Mass Action is not solely due to some property of NH_4^+.

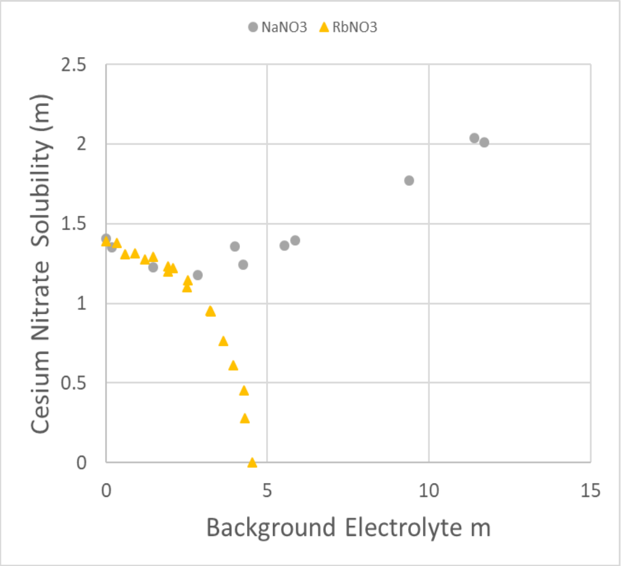

Figure 4. Solubility of Cesium Nitrate or Cesium Nitrate Containing Solid Solution in Aqueous Alkali Nitrate Solutions at 25 °C. Data from References 24 and 25.

Figure 5 shows the solubility of $RbNO_3$ salt or solid solution as a function of added nitrate-bearing electrolyte concentration. Rubidium nitrate precipitates as a solid solutions with KNO_3 and $CsNO_3$ over the entire composition region plotted in Figure 5.[25,26] $RbNO_3$ solubility in aqueous $CsNO_3$ solution follows the Law of Mass Action by decreasing the solubility of $RbNO_3$ with increasing concentration of $CsNO_3$. The solubility of the $RbNO_3$ increases with addition of KNO_3 and $NaNO_3$, reversing the Law of Mass Action.

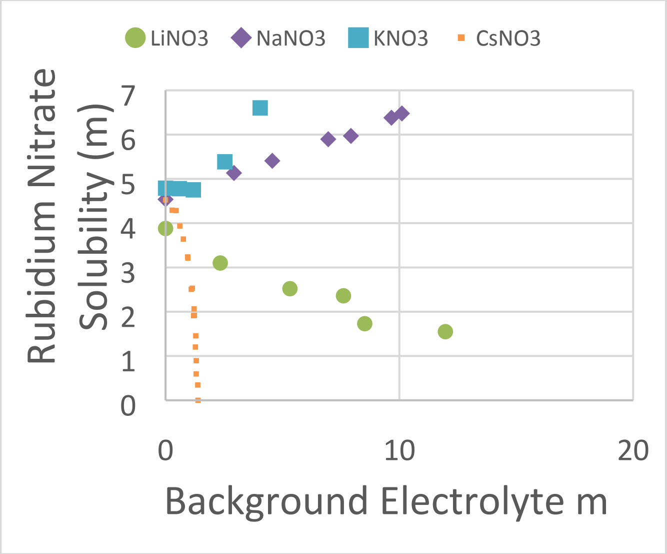

Figure 5. Solubility of Rubidium Nitrate or Rubidium Nitrate Containing Solid Solution in Aqueous Alkali Nitrate Solutions at 25 °C. Data from references 19 and 25-27.

Figure 6 shows that the solubility of KNO_3 increased with increasing concentration of the alkali nitrate electrolyte for all electrolytes with available data over at least part of the concentration range. In $LiNO_3$ solution, the solubility of KNO_3 initially decreases with increasing electrolyte concentration, but it eventually reversed and increases with increasing concentration (Figure 6). In $RbNO_3$ solution, KNO_3 solubility undergoes an oscillating patter, increasing and then decreasing and then increasing again with increasing $RbNO_3$ concentration.[26] Only the first of this repeating pattern for KNO_3 solubility in $RbNO_3$ solution is shown in Figure 6 so that it is easier to see the behavior of other electrolytes, but the pattern does repeat itself.[26] It is not clear if this pattern is the real behavior or if there is just lots of scatter in that dataset that resembles the oscillating pattern. Wrobel-Kaszanek et al. previously showed that KNO_3 solubility increases with increasing concentration of NH_4NO_3.[12]

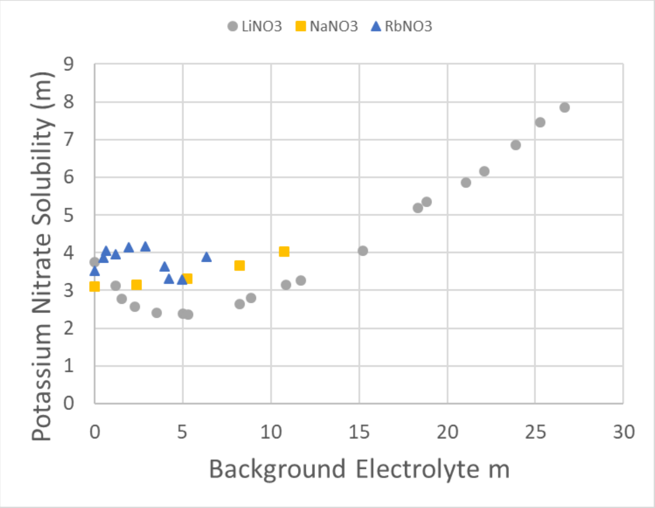

Figure 6. The Solubility of Potassium Nitrate and Associated Solid Solutions in Aqueous Alkali Nitrate Solutions at 25 °C. Data from References 2, 26, and 28.

Figure 7 demonstrates that the solubility of $NaNO_3$ salt increases with increasing concentration of all of the alkali nitrates except $LiNO_3$. Thus, all of the alkali nitrate solutions with a cation larger than Na^+ enhanced rather than suppressed $NaNO_3$ solubility. Gupta and Ismail showed that the electrical conductivity of concentrated $NaNO_3$ and KNO_3 mixtures was lower than the end member solutions of the same concentration.[30] This may indicate stronger ion-pairing in the mixture than in the solutions with a single type of cation.

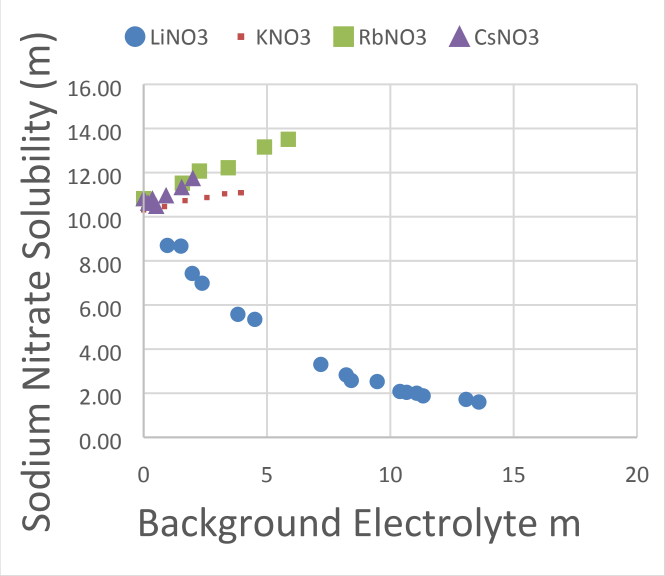

Figure 7. The Solubility of Sodium Nitrate in Aqueous Alkali Nitrate Solutions at 25 °C. Data from References 2, 27, 29, and 30.

$LiNO_3$ precipitates as either a tri-hydrate ($LiNO_3{\cdot}3H_2O$) or as an anhydrous species depending on the ionic strength of solution (Equations 2 and 3).[19] The solubility of the tri-hydrate will depend on the activity of water to the third power, where the solubility will increase when the water activity is lowered. When the water activity is sufficiently low, anhydrous $LiNO_3$ is stable instead of $LiNO_3{\cdot}3H_2O$.

$$3H_2O + Li^+_{aq} + NO^-_{3(aq)} \leftrightarrow LiNO_3 * 3H_2O_{(s)} \qquad \text{Equation 2}$$

$$Li^+_{aq} + NO^-_{3(aq)} \leftrightarrow LiNO_{3(s)} \qquad \text{Equation 3}$$

The background electrolytes not only add nitrate, they also lower the activity of water.[31] Consequently, adding any background electrolyte will push the reaction in Equation 2 to the left by lowering the water activity even as any nitrate added will push the reaction to the right. Therefore, a simple plot of background electrolyte concentration versus $LiNO_3{\cdot}3H_2O$ solubility does not determine whether the Law of Mass Action is followed.

Equation 3 indicates that there is no water in the reaction to create anhydrous $LiNO_3$, so the water is not consumed in the reaction so does not show up in the equilibrium expression. Consequently, the solubility of the anhydrous $LiNO_3$ is evaluated rather than $LiNO_3{\cdot}3H_2O$ to avoid having to determine water activity in the mixtures. The only alkali metal nitrate solutions with data available that precipitates anhydrous $LiNO_3$ instead of $LiNO_3{\cdot}3H_2O$ is KNO_3 (Figure 8). The solubility of anhydrous $LiNO_3$ in aqueous KNO_3 and NH_4NO_3 solution is also plotted in Figure 8, and shows that both systems reverse the Law of Mass Action because the solubility of anhydrous $LiNO_3$ increases with increasing KNO_3 and NH_4NO_3 concentration.

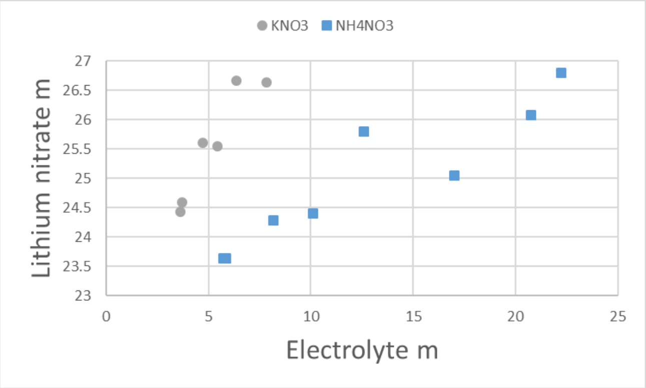

Figure 8. Solubility of Anhydrous $LiNO_3$ in Aqueous KNO_3 and NH_4NO_3 Solutions at 25 °C. Data References 2 and 28.

The solubility of an alkali nitrate salt sometimes increases with increasing nitrate concentration if the nitrate is added as an alkali immediately above or below it on the periodic table. However the nitrate salt solubility will almost always increase with increasing background nitrate concentration if it is dissolved in an alkali nitrate solution that is more than one row away on the periodic table. The only exception in the data collected here is the solubility of $RbNO_3$ in aqueous $LiNO_3$ solution. Many of the solubilities initially decrease with increasing nitrate concentration but reach a minimum and then increase with increasing nitrate concentration.

Nitric acid is another monovalent nitrate solution, and Figure 9 shows the solubility of alkali nitrate salts in aqueous nitric acid. Lithium nitrate salt solubility decreases with increasing concentration of HNO_3. All of the other alkali nitrate salt solubilities initially decrease with increasing HNO_3 concentration until reaching a minimum solubility. The minimum is salt specific. Above that minimum, the solubility of the alkali salts increase with increasing HNO_3 concentration (Figure 9). The HNO_3 concentration in the $LiNO_3$ solubility study only extends up to 15.5 molal HNO_3. It is possible that the $LiNO_3$ solubility would eventually reach a minimum and then increase with increasing HNO_3 concentrations if larger HNO_3 concentrations were studied. The minimum solubility of the nitrate salts of the largest alkalis (K^+, Rb^+, Cs^+) is at much lower HNO_3 concentration than the smaller $NaNO_3$ (Figure 9). Note that the highest nitric acid concentration in Figure 9 in the K^+, Rb^+, and Cs^+, solutions is not the highest studied, it is the highest soluble concentration. At higher concentrations in the solutions of the heavier alkali, double salts formed that had nitric acid in them; $KNO_3{\cdot}HNO_3$, $RbNO_3{\cdot}HNO_3$ and $CsNO_3{\cdot}HNO_3$.[32,34]

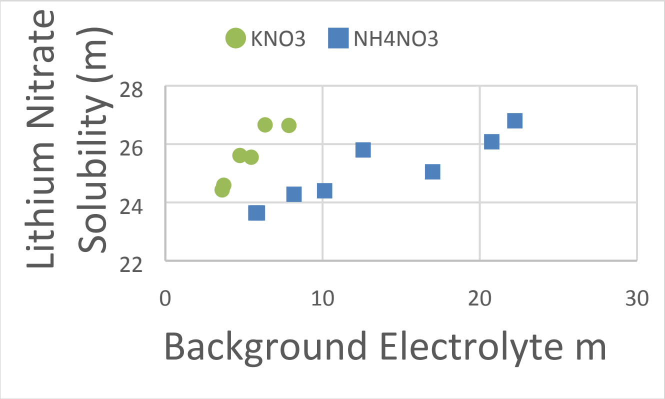

Figure 9. Solubility of Alkali Nitrate Salts in Nitric Acid at 25 °C. Data from References 19, and 32-34.

This study focused mainly on nitrate solutions of monovalent cations, but an obvious question is if this reversal of the Law of Mass Action can occur in nitrate solutions of divalent cations. A limited literature review showed that the answer is at least occasionally yes. Figure 10 shows that the solubility of KNO_3 and $CsNO_3$ increases with increasing $Sr(NO_3)_2$ concentration, reversing the Law of Mass Action in a solution of a divalent cation.

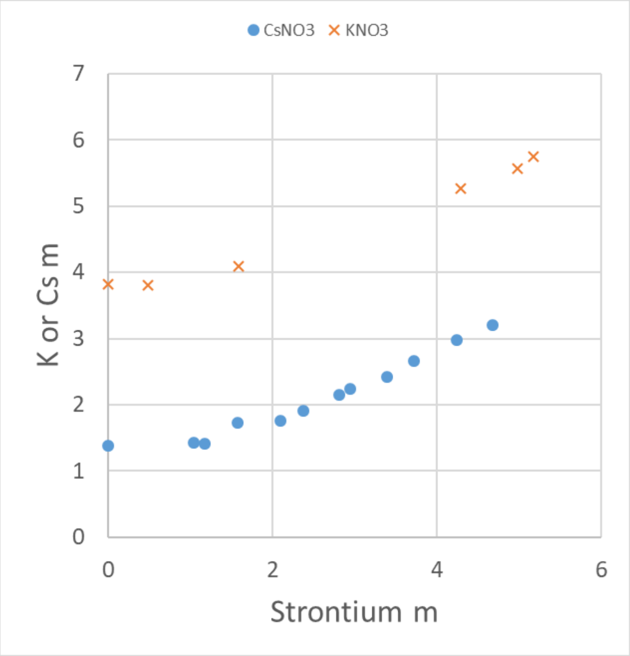

Figure 10. The solubility of Potassium and Cesium Nitrate Salts in the presence of Dissolved Strontium Nitrate at 25 °C. Data from Reference 35.

Hydration, Hydrogen Bonding, and Ion-Pair Formation

These results show that many alkali and NH_4^+ nitrate solubilities appear to reverse the Law of Mass Action. This appearance comes from the assumption that a nitrate-bearing electrolyte in concentrated aqueous solution dissociate into free nitrate that would suppress the solubility of other nitrate salts. Clearly, alternative species can be proposed to explain this behavior, such as ternary nitrate-cation-nitrate complexes.[36] The presence of such species could be used to explain why the solubility of some nitrate salts increase when another nitrate-bearing electrolyte is added. Gruszkiewicz, et al.[37] have successfully modelled solubilities in the $NaNO_3$-KNO_3-H_2O system using the Mixed Solvent Electrolyte model of Wang et al.[38] for liquid phase activities. Franke et al. was similarly able to model the solubility of most alkali nitrates in aqueous HNO_3 solution with the Pitzer model.[39] Neither of them reported the solution phase species they used nor any of their model coefficients, so we cannot use their results for guidance on potential ternary or higher order species. While the present study focused at 25 °C data, Voigt and Voigt noted that solubility in the $LiNO_3$-KNO_3-H_2O system reverse the Law of Mass Action at 100 °C as well, and they developed a thermodynamic model for that system.[40] They did not include ternary species in the model, but added empirical mixing terms to account for the curvature in the solubility data.[40] What these modelling studies show us is that it is empirically possible to model systems that reverse the Law of Mass Action, even if we do not understand the underlying reasons why they behave that way. To better understand nitrate solution behavior, we will look at the structure of aqueous nitrate solutions.

Bond-valence is extensively used in crystallography to understand relative bond strength.[41] Brown[42] showed that the concept of bond-valence is effective at describing complexes in aqueous solutions, and Bickford et al.[43] showed that water itself follows the bond valence rules. Though water molecules have a net neutral charge, they are polar and form hydrogen bonds with each other. In the average tetrahedral structure of water, each oxygen atom in water forms two hydrogen bonds with other water molecules and each water proton forms one hydrogen bond with another water molecule.[44] Bickmore et al.[43] indicates that an average of 0.43 valence units of charge are transferred from the water oxygen to other water molecules via hydrogen bonds, which means that each hydrogen bond transfers an average of (0.43/2) = 0.22 valance units. There is expected to be large variability around this value, especially for water molecules in the coordination sphere of ions.[42]

While Bickford et al.[43] determined the quantity of charge transferred from hydrogen bonding via quantum mechanics, the bond-valences below are determined using the classic approximation used in Pauling's bond strength formula. That approximation is that the bond-valance between an ion and each counter ion coordinating it is equal to the formal charge on the ion divided by the coordination number, shown in Equation 4.[41] Pauling used the term bond strength but it is more commonly referred to as bond-valence today.[41]

$$Bond\ Valence = \frac{formal\ charge}{coordinaiton\ number} \qquad \text{Equation 4}$$

Ammonium and the alkali ions are coordinated by between 4 and 10 water molecules in dilute solution, Li^+ with 4 at the low end and Cs^+ with 10 at the high end.[16,23,45-48] When one positive charge on the cations is divided by four water molecules, then 0.25 valence units is accepted per water molecule by the cations on average. When one positive charge is divided by 10 water molecules, an average of 0.1 valence units occur per coordinating water molecule, which is less than most waters exchange with each other in bulk solution.

Nitrate is a planer multi-atom ion, so coordination number is not as easily defined. Computational and diffraction studies indicate that there is between 6 and 11 water molecules surrounding nitrate.[49-52] Most of the water molecules are sitting off the edge of the plane and are hydrogen bonded to one of the oxygens, with a lower density of water immediately above and below the nitrogen atom in dilute solutions.[52,53] Different computational models indicate different numbers of hydrogen bonds are formed between the oxygens on nitrate and the surrounding water molecules, with Vchirawongkwin et al.[54] indicating that each oxygen forms an average of 1.8 hydrogen bonds and Banerjee et al.[55] indicating each oxygen forms 2-3 hydrogen bonds. If the nitrate ion's one charge is divided by 5 to 10 hydrogen bonded water molecules it is determined that nitrate has an average of 0.1 to 0.17 valence units per water molecule. This is less than the charge traded between water molecules in bulk water and is consistent with Yadav et al.'s computational study indicating that water forms stronger hydrogen bonds with other water molecules than with nitrate.[52] Thus, water molecules are weakly held to and have short lifetimes around nitrate, as verified by vibrational spectroscopy.[52-57]

Using the lowest estimated nitrate hydration number (6) and the monovalent cation with the smallest number of coordinating water molecules (4), the minimum number of water molecules coordinating a mole of electrolyte in this study is ten. A kilogram of water is about 55.5 moles. If 55.5 water molecules is divided by the 10 water molecules required to completely hydration the dissociated ions, it comes to 5.55 moles of electrolyte that can be hydrated by a kilogram of water. Thus, any time the total alkali or NH_4^+ nitrate concentration is greater than 5.55 molal, there is not enough water molecules for the ions to fully dissociate and each ion to have a complete hydration sphere without having to share water molecules with other ions. The larger cations with 10 coordinating water molecules would have to start sharing waters above 3.5 molality by the same logic. It is expected that specific interactions would be important in solutions where there is not enough water to fully hydrate all of the ions so the water molecules have hydrogen bonds with more than one ion. Ions that are in direct contact with another ion would exchange charge with the neighboring ion rather than water. Likewise, the water molecules that are being shared by ions will alter the number or strength of the hydrogen bonds that they form with the molecules surrounding them.[16,23,46,46,52,55] Similarly, nitric acid solution undergoes a major structural change, where ion-paired nitric acid becomes a major species above approximately four molar concentration.[58]

All of the systems evaluated where the Law of Mass Action was reversed were in solutions with insufficient water to provide all ions their preferred hydration number without sharing water molecules. Some of the solutions evaluated in this study have total electrolyte molalities greater than 28, which is less than one water molecules per ion. Consequently, there must be significant contact between ions, called “contact ion pairing”.[59,60] Extensive experimental evidence shows alkali nitrates form ion-pairs in aqueous solution.[21,49-51,61-69] While diffraction data for the alkali nitrate solutions indicate that there is direct contact between the cations and nitrate,[49-51] measures of the strength of ion-pairs indicates that they are not strongly held together.[22,59,62-66] For instance, the stability constant for the sodium-nitrate ion pair has been reported to be 0.7 by Shilov and Lyashchenko[68] or 1 by Wachter et al.[66]. Similarly, stability constants for the potassium-nitrate and rubidium-nitrate ion-pairs have been reported to be 1.1 and 0.8, respectively.[62,69]

Concentrated nitric acid solution is the prototypical example of counter ions in direct contact with each other yet not strongly held. The proton forms contact-ion pairs with nitrate to form the nitric acid molecule in concentrated aqueous solution.[58,70,71] As evidenced by the fact that nitric acid is a very strong acid in water, this proton cannot possibly be held to the nitrate strongly. When a base is added, it will readily dissociate and react with the base.[72,73] Wren and Donaldson indicate that the proton and nitrate solution associate in concentrated solution primarily because there is insufficient water to hydrate both ions rather than because of an inherent attraction.[74]

Ion-Cluster Formation

One of the systems reported that reverse the Law of Mass Action without nitrate is the KCH_3COO-$Co(CH_3COO)_2$-H_2O system.[75] Lyashchenko noted the reversal of the Law of Mass Action occurred in the KCH_3COO-$Co(CH_3COO)_2$-H_2O system when the electrolytes formed ion-clusters in solution that are larger than just two ions.[75] Therefore, review of the literature on cluster formation in alkali nitrate solutions may be informative.

Several studies have claimed to observe Na^+-nitrate clusters in concentrated aqueous solutions using Raman spectroscopy.[61,76] They were able to divide the nitrate peaks in the Raman spectra into multiple peaks using curve fitting software, and attributed the high energy peaks to Na^+-nitrate ion-clusters.[61,76] There are other potential interpretations of these different bands, including different types of ion-pairing.[54,67,77] Thus, additional lines of evidence for clusters is desirable. Many computational studies of Na^+-, K^+- and NH_4^+-nitrate solutions support the observation of ion-clusters in these solutions.[16,49,78-81] Rubidium and Cs^+ nitrate solutions have not been studied by methods to identify clusters at high concentrations.[36,82]

In Ghadar et al.’s study of $NaNO_3$, only about 2% of the ions are ion-paired in 1 M solution whereas about 21% of ions are ion-paired in 10 M.[79] They found that about 6 % of the ions in 10 M $NaNO_3$ existed in clusters with four or more ions.[79] Other studies of Na^+, K^+, and NH_4^+ nitrate solutions provide qualitatively consistent results, albeit over different concentrations ranges and with computational models of different levels of fidelity, and differing levels of detail reported in the manuscripts.[16,49,78-81] These results are thus consistent with the conclusion that there are ion-clusters in concentrated nitrate solutions.

For $LiNO_3$ solutions, Han[83] did not literally say that there were clusters of $LiNO_3$, but that may be because their study focused on just the water in solution. Han[83] calculated that only about 60 % of the water was bound to an ion in 20 M $LiNO_3$ even though there was less than three water molecules per ion and Li^+ ions typically bind four water molecules per mole in dilute solutions.[47,84,85] That result is consistent with the formation of ion-clusters with little water in them at high concentrations. Similarly, no study was specifically found that showed that nitric acid forms clusters in solution at high concentration. Nitric acid is completely miscible in water.[86] Thus, there must be a water content where there is still water in solution and some nitric acids completely surrounded by other nitric acids in solution.

Summary of Attributes of Nitrate Solutions that Reverse the Law of Mass Action

Until this point in the discussion we have established some attributes of concentrated nitrate solutions:

- The solutions are so concentrated that there is not enough water to provide all ions their full hydration number without sharing water molecules.
- Given how concentrated the solutions are, there is direct contact between cation and anion in solution.
- Despite their being direct contact between cation and anion, the strength of the ion pairs formed are weak in solutions with a single cation.
- The ions crowd together to create ion-clusters that are larger than just two ions.

From these attributes, we can speculate how they contribute to the reversal of the Law of Mass Action. To understand this hypothesis, we will return to the bond-valence concept, and show how it can be used to explain nitrate solution solubilities in water. Ion pairing is frequently described in terms of Collin's Law of Matching Water Affinities.[87] In that Law, ion-pairs occur in aqueous solution between counter-ions that have similar affinity of water. Collins used hydration enthalpies to develop his law,[87] which are unavailable for most of the nitrate solutions evaluated here at relevant concentrations. Collin's Law is related to Person's Hard-Soft Acid Base Principal, which is related to the concept that ions with matching Lewis basicity and Lewis acidity form stable complexes.[88,89] Average bond-valence is one of the more convenient ways to estimate Lewis basicity, and the information to do so is readily available, so it is used here.[41,90,91] Collins noted that ions with similar affinities for water may not just form ion-pairs and stay dissolved, they may precipitate from solution.[87] Lithium and fluoride, having similar affinity for water, have very low water solubility as LiF. In contrast, cesium and fluoride, having very dissimilar attraction for water, has very high water solubility as CsF.[87] Using bond valence, a similar relationship can be observed with the nitrates. The solubility of the alkali and ammonium nitrates in water is shown in Figure 11, showing that the cations with high nitrate solubility have higher average bond valences per coordinating ion. The bond valence for each alkali cation is the average bond valence from many crystal structures reported by Gagné and Hawthorne.[90] For NH_4^+, the bond valence in water was used, assuming that NH_4^+ binds to four water molecules strongly.[46] The solubility of $NaNO_3$ in water form reference[2] was used, and the estimated metastable solubility of anhydrous $LiNO_3$ from reference[19] was used in Figure 11. The median solubility of KNO_3 from references[20,26,28] was used, and references[25-27] for $RbNO_3$, and references[13,24,25] for $CsNO_3$ solubility in Figure 11. The solubility of NH_4NO_3 from Li et al. was used.[13] Note that nitric acid is not on Figure 11 because it is infinitely soluble in water at 25 °C, but its bond valence is 0.5, so it would be way off the chart to the right.

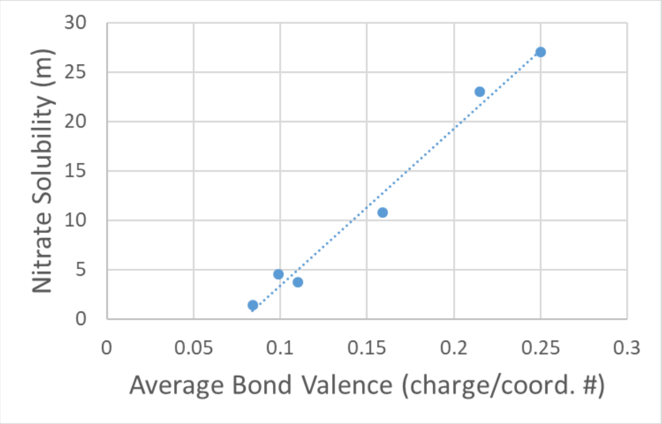

Figure 11. Solubility of Alkali or Ammonium Nitrate as a Function of the Average Bond-valence of the cation.

Hawthorne determined that the average bond valence per nitrate-oxygen atom and coordinating cations in crystal structures is 0.12.[91] Stable crystal structures are most likely to occur when the bond-valence of the cation and anion closely match.[41,91] Therefore, the most stable alkali nitrates are expected to be those with an average bond-valence near 0.12. This is consistent with the three cations with average bond-valences closest to 0.12 (K^+, Rb^+, Cs^+) having the lowest solubility in water. Their solubility is low because they have the most stable solid phases. The proton (H^+) does not form a solid at room temperature with nitrate because its bond-valence is so different from nitrate that nitric acid is more stable as a liquid where it has more flexibility in its coordination number and bond lengths. When nitric acid does precipitate at very cold temperatures, it precipitates with water in its structure where water can mediate the bond valence between the proton and nitrate.[92,93] The solubility of NH_4NO_3, $LiNO_3$, and $NaNO_3$ is high as well because their cations have higher bond valences than nitrate, though not nearly as high as nitric acid.

The relationship between alkali and NH_4^+ nitrate solubilities and cation bond-valence shown in Figure 11 for water is caused by the different stabilities of the solid phases. Others have asserted that the bond-valence model is as applicable to aqueous solutions as it is to crystal structures[42,43] . The cations that form less stable solids with nitrate probably also form unstable ion-pairs in the liquid phase for the same reason when the liquid is so concentrated that the ions must be in contact with each other. Those liquid phase ion pairs do not have to be that stable, to keep from precipitating solids, the liquid-phase ion pairs just must be more stable than the comparable solid. For counterions with very different preferred bond-valences the liquid phase has more potential coordinating numbers and geometries than a crystal. Nitric acid is again the extreme case, where the nitric acid is extremely reactive, despite the fact that the proton and nitrate are highly associated in the liquid phase.

The ion-clusters in nitrate solutions may be stabilized in solution with more than one cation. Nitrate in solution donates charge to several ions simultaneously, and the quantity of charge donated to each ion must be balanced to equal the one negative charge. As noted earlier, the reversal of Law of Mass Action appears to be most common when the alkali ions are more than one row away from the alkali in the salt. Similarly, the minimum solubility of the heavy alkalis (K^+, Rb^+, Cs^+) in nitric acid is at lower concentrations than the smaller $NaNO_3$. The average amount of bond-valence shared between cation and anion would be expected to be lower for the larger alkali ions than the smaller ions because the larger cations have larger coordination number. When nitrate must be in contact with more than one ion, it must share its single negative charge between all of the cations as well as the water molecules still hydrogen bonded to it. It is likely that balancing this bond-valence is more favorable when two cations contacting nitrate have different charge densities than when they have similar charge densities. Thus, it is likely that the larger clusters are stabilized by having more than one cation. As noted earlier, the electrical conductivity of extremely concentrated solutions of mixed cation nitrate solutions were lower than nitrate solutions with just one cation at the same concentrations.[14,30] Decreases in electrolyte solution conductivity are frequently attributed to ion-pair formation.[59] Formation of stronger ion-pairs or clusters with more than one cation would be thus one potential explanation of lower conductivities in the mixed-cation solution. That, in turn, would make the liquid phase nitrate species more stable and increase the solubility of the salts. That may be why the reversal of the Law of Mass Action is most common in solutions of cations with different radii.

Management of charge density around nitrate may also allow the liquid to optimize how hydrated the ions are. Ions of low charge density that bind water weakly (e.g., Cs^+) may facilitate ions that bind water more strongly (e.g. Li^+) to spend more time coordinated by water rather than nitrate when both are in solution together.

The molecular description of how two cations with difference charge densities can help manage the charge density around nitrate is not well defined because of limited spectroscopic studies of mixtures. Nonetheless, the recent study by Mitra et al. may give some indication of how this might occur.[94] Mitra et al. indicate that the nitric acid molecule dissociates in concentrated aqueous clusters when Cs^+ contacts the nitrate ion.[94] This indicates that the proton itself in nitric acid is less strongly held by the nitrate when Cs^+ contacts nitrate. The proton has a very large charge density because of its small size, and nitrate, with a small charge density, is able to push away the proton when it is in contact with Cs^+.[94] The cesium ion-has a small charge density like nitrate. Applicability of the Mitra et al. study to concentrated solutions is limited because they studied small clusters with 8-12 atoms in a vacuum and the clusters were not charge balanced. Nonetheless, the Mitra et al. study shows that having two cations with different charge densities can help nitrate manage the charge density in its immediate vicinity. Ion-clusters with alkali or NH_4^+ may be similar to nitric acid solution. Optimizing the charge density around nitrate in water would make the liquid phase nitrate species more stable and increase the solubility of the salts.

A Historical Perspective Guiding Future Work.

In the early 20th century, many physical chemists were grappling with strong electrolyte solutions that appeared to disobey the Law of Mass Action, including scientists in Arthur Noyes' and Gilbert Lewis' laboratory at The Massachusetts Institute of Technology. They assumed that these failures of the Law of Mass Action were related to uncertainty in the dissociation of the electrolytes, and thus their ignorance of the precise speciation of the electrolytes.[95,96] The failures of the Law of Mass Action they were studying were less severe than those discussed in the present study; they were studying electrolytes whose solubilities were simply imperfectly proportional to mole fraction of reactants. Those discrepancies motivated them to develop the concepts "activities" and "activity coefficients" as empirical tools used in thermodynamic calculations for strong electrolyte solutions without detailed knowledge of the speciation.[96,97] Activities are still used in electrolyte solution thermodynamics, over 100 years later.[98] As noted earlier, empirical activity coefficient models have successfully described nitrate systems that appear to reverse the Law of Mass Action, demonstrating the power of that approach and justifying its continual use.[37,39,40] These studies required fitting the data to models because there is not a way to predict activities a priori in concentrated solutions presently.

Though Noyes' and Lewis' labs were extensively engaged in electrolyte thermodynamics, they also delved into other research areas such as crystal structures and the nature of chemical bonds.[99] Lewis, for instance, developed the concept of a chemical bond as being two electrons shared between atoms.[100] The historian Servos[99] believes they developed these secondary research interests in order to better understand the speciation of concentrated electrolyte solutions to explain the apparent failures of the Law of Mass Action. Lewis developed the "activities" concept when the structure of the atom was still being debated, and thus before quantum mechanics and most spectroscopic methods were available. These modern methods, however, have not yet lead to a complete understanding of non-ideal electrolyte behavior in concentrated solutions, such as the reversal of the Law of Mass Action reported here.

Studying aqueous nitrate mixtures with modern experimental and computational methods may provide clues to the causes of solution non-ideality. Following Lyashchenko, [75] the present study concluded that the reversal of the Law of Mass Action occurs at concentrations where there is ion-association creating ion-clusters. Nonetheless, the binding between cation and nitrate appear to be weak in single electrolyte solutions.[59] Reduced electrical conductivity of mixed solutions[14,30] could be interpreted as stronger binding or larger clusters when more than one cation is present. Whether these ion-clusters are part of the cause of the highly non-ideal behavior or just coincidentally occur at the high concentrations where the Law of Mass Action is reversed is still to be determined, primarily because so few spectroscopic studies have been performed on nitrate solutions with more than one cation.

In an earlier publication, the author argued that studying the very few electrolytes that appear to behave ideally in aqueous solutions may provide insight into the source of non-ideal behavior for other electrolytes.[101] Here, I propose that studying some of the most non-ideal behavior observed in inorganic electrolytes, the apparent reversal of the Law of Mass Action in nitrate solutions, may also provide insight into the causes of non-ideality in concentrated solutions.

Author Contributions

This study was authored by a single person.

Conflicts of interest

There are no conflicts of interest.

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