Hydration and Transport Properties of Cesium Hydroxide and Mixed Cesium Hydroxide -Sodium Nitrite Aqueous Solutions

Jacob G. Reynolds*[2], Emily T. Nienhuis[1], Trent R. Graham,[1], Ashley Kennedy[1], Sebastian T. Mergelsberg[1], J. David Bazak[1], Carolyn I. Pearce[1,3]

[1]Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA, USA

[2]Central Plateau Cleanup Company, P.O. Box 850, Richland, WA, USA

[3]Department of Crop and Soil Sciences, Washington State University, Pullman, WA, USA

*Author Contact: jacob_g_reynolds@rl.gov

Abstract

This study explores the hydration and transport properties of aqueous cesium hydroxide (CsOH) solution, with or without 1 molar (M) sodium nitrite ($NaNO_2$). Historic studies of electrolyte solutions indicate that Cs^+ ions decrease viscosity and increase diffusion rates, whereas OH^- ions have the opposite effect. Here, the influence of OH^- was dominant in CsOH solutions, leading to increased viscosity and reduced diffusion rates. There was a linear relationship between diffusion coefficients and water activity, emphasizing the significant role of ion-water interactions in determining transport properties. This may be because the interaction between Cs^+ and the anions is weak even when they are in direct contact with each other. The weakness of the ion-pairing was established through thermodynamic analysis. The findings suggest that ion-pairing is not the only important interaction controlling transport properties when ion-pairing is weak. Nonetheless, ion-pairing or obstructions did result in more sluggish transport properties as electrolyte concentrations increased. Overall, the research enhances the understanding of the complexities underlying ion interactions in multicomponent solutions.

Introduction

In the early 20th century, scientists discovered that aqueous electrolytes containing low charge density ions lowered the viscosity of water.[1-3] These electrolytes were described as *depolymerizing water*.[4] They were later classified as chaotropic, i.e. *structure breakers,* because they presumably decreased the hydrogen bonding between water molecules.[3,5,6] The same electrolytes that decreased the viscosity also increased the self-diffusion rate of water, consistent with the conclusion that they decreased hydrogen bonding between water molecules.[5] Many cesium-bearing electrolytes decrease viscosity and increase the diffusion rate of water.[1,2,6,7,8] Today, this phenomenon is understood in terms of the Lewis acidity or basicity of ions relative to water. Ions displace hydrogen bonds between water molecules when the ions dissolve, and cations that are a weaker acid than water decrease viscosity and increase water diffusion rate.[9] Likewise, anions that are a weaker base than water also decrease viscosity and decrease the water diffusion rate.[9] The relative acidity and basicity to water control the strength of water binding to the ions, which in turn influences the electrolyte viscosity.[10,11]

Aqueous solutions of intermediate concentration (> 0.5 molal but less than 6 molal), also have low number of water molecules per ion. The formation of contact ion pairs or larger clusters of ions in these intermediate solutions depends on the identity and concentration of the ions,[12] with higher concentrations of ions the more likely to be in contact with each other through formation of ion pairs. Ion-pairing decreases diffusion rates of ions and increases viscosity of aqueous solutions.[13-16]

Studying the extent of clustering and ion-pairing in relatively concentrated electrolytes is of relevance to retrieval and processing of alkaline radioactive waste at the Department of Energy's legacy nuclear site, Hanford.[17-22] Understanding ion clustering may provide insight into the composition dependence of physical properties, like diffusion coefficients and viscosity, as well as solubility. Mixtures of electrolytes show interesting regularities, such as the linear relationship between diffusion coefficients and water activity in mixtures and consistent relative impacts of background electrolytes on salt solubilities.[23,24]

Hanford nuclear waste contains a large concentration of nitrite (NO_2^-) and hydroxide (OH^-).[25,26] NO_2^- and OH^- aqueous solutions exhibit nonclassical transport properties. OH^- diffuses via multiple mechanisms under alkaline conditions, including Grotthuss transport (proton hopping) and vehicular translocation.[27,28] Nitrite does not adhere to the Stokes-Einstein relationship, which states that the diffusion coefficient of a small molecule in a fluid is inversely proportional to the fluid's viscosity and directly proportional to the temperature.[19,29]

In a recent study, the self-diffusion coefficient of water in aqueous mixtures of NaOH and $NaNO_2$ was explained by the relative strength of binding of water by the ions, where OH^- binds water more strongly than NO_2^-.[23] It is therefore of interest to contrast the behavior of the $NaOH-NaNO_2-H_2O$ system with the $CsOH-NaNO_2-H_2O$ system, because Cs^+ binds water weaker than water binds to itself in aqueous solutions.[30]

Solutions containing Cs^+ also behaved differently during the photolysis of nitrite in alkali hydroxide solutions, which was studied as an analogy to radiolysis in nuclear waste.[31] The study found that the quantity of reactive nitrogen and oxygen photolysis products increased with alkali ion size for solutions containing Li^+, Na^+ and K^+, but solutions with Cs^+ did not follow the trend. The anomalous clustering of Cs^+ was also highlighted in an X-ray scattering study, showing that ion-clusters formed in mixtures of CsOH and $NaNO_2$ were different from those in the individual electrolyte solutions.[32] In the present study, the influence of this different clustering behavior on transport properties in aqueous mixtures of $NaNO_2$ and CsOH is studied.

Experimental

Solution Preparation

$NaNO_2$ and CsOH stock solutions were prepared by dissolving the appropriate amount of $NaNO_2$ (>99%, Sigma-Adrich) and CsOH (50 wt% in H_2O, Sigma-Alrich) into deionized (DI) water. To prepare the concentration series of aqueous CsOH and $NaNO_2$ – CsOH, the prepared stock solutions were mixed and diluted volumetrically with DI water. Stock solutions and the solution concentration series were prepared in a N_2 glovebox to avoid CO_2 and water adsorption to the reagent stocks. Concentrations are reported as molarity, M, moles of solute per liter of solution.

Densimetry and Viscometry

An Anton Paar DMA 4500 M oscillating u-tube instrument was used to conduct all density measurements, with the harmonic response calibrated to both dry air and ISO 17034-certified water. Bubble-free injection of samples was confirmed using the onboard camera. The densimeter was connected in-line to an Anton Paar Lovis 2000 ME viscometer module for dynamic viscosity measurements via the rolling-ball technique. A 1.59 mm I.D. capillary with a gold-plated ball was used for all viscosity measurements, and the run times were again calibrated using the reference water standard. A level adjustment to ensure forward/reverse reproducibility was performed prior to the calibration. During the measurements, the instrument's internal run time accuracy criteria were used for automatic inclination angle selection. The temperature was regulated to 20°C for the density and viscosity determinations.

Multinuclear Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectra were acquired at a magnetic field strength of 11.7467 T. For ^{1}H and ^{23}Na, spectra were collected on an Agilent/Varian spectrometer equipped with a 5 mm broadband probe. Spectra of ^{17}O and ^{133}Cs were recorded on a Bruker spectrometer, also utilizing a 5 mm broadband probe. At 11.7467 T, the Larmor frequencies are approximately 500.13 MHz for ^{1}H, 132.33 MHz for ^{23}Na, and 65.62 MHz for ^{133}Cs. The spectrometer temperature of 20 °C was calibrated with the ^{1}H chemical shifts of ethylene glycol.[33] Diffusion experiments for the listed nuclei employed pulsed-field gradient stimulated echo (PFGSTE) methods with convection compensation. Pulse widths as well as gradient strength and duration were optimized for each sample and nucleus. Diffusion coefficients were determined by fitting the signal attenuation curves. Diffusion coefficients were referenced to that of deionized H_2O at 25 °C.[34]

Modeling

Marcus has argued that the strength of interaction between water and monovalent electrolytes is proportional to water activities.[35] Water activity has thus been used as an indicator of the strength of water bound by ions.[36-38] The water activity (a_w) of a multicomponent solution can be estimated from solution composition using Zavitsas' model, as modified for multicomponent solutions and shown in Equation 1.[39]

$$a_w = \frac{55.509 - \left(\sum_{j=1}^{q} m_j H_{d(j)}\right)}{55.509 - \left(\sum_{j=1}^{q} m_j H_{d(j)}\right) + \left(\sum_{j=1}^{q} m_j i_{e(j)}\right)} \qquad \textbf{Equation 1}$$

Here, 55.509 is the number of moles of water in a kilogram of water, m is the molality of electrolyte 'j', q is the number of electrolytes in the mixture, while H_d and i_e are electrolyte specific parameters representing the electrolyte hydration number and extent of dissociation. The water activities used later were calculated using **Equation 1**.

Equation 1 has been used successfully to predict activities in multicomponent aqueous solutions previously.[39-41] The model is mathematically equivalent to Zdanovskii's rule, a rule that has been shown to widely apply to aqueous electrolyte mixtures.[42-44] Thus, it is likely that this model accurately predicts the water activity of $CsOH$-$NaNO_2$-H_2O mixtures here.

The model coefficients for $NaNO_2$ were published previously and are $H_d = 0.819$ and $i_e = 2.000$.[45] The coefficients for CsOH were determined here by fitting the model using the method of reference[46] to the CsOH solution water activity data published by Hamer and Wu[47], which is based on measurements by Harned and Schupp[48]. Those parameters for CsOH are: $H_d = 1.4358$ and $i_e = 2.000$. The H_d parameter is interpreted as the time-averaged number of water molecules held so strongly by the electrolyte that they act as part of the electrolyte rather than part of the solvent. The i_e is the number of particles that the electrolyte breaks into. An i_e value of 2 means that there is no ion-pairing between the electrolytes. "No ion pairing" in the contest of the model means that there are no ion-pairs that act thermodynamically like a distinct species, but it says nothing about the proximity of the ions to each other. Previous studies have shown that Na^+ and NO_2^- are in direct contact with each other in concentrated solutions but do not behave thermodynamically like a distinct species.[17,21,45] The model is consistent with results from Sipos et al. who reported negligible ion-pairing in aqueous CsOH solutions in a potentiometric study.[49]

Results

When ions such as Cs^+, Na^+, NO_2^-, and OH^- dissolve in water, they displace hydrogen bonds between water molecules with bonds between water and the ions. Many studies have shown that the diffusion rate of water and electrolyte in water is influenced by the strength of interaction between water and the electrolyte.[8,50-52] The viscosity of aqueous electrolyte solutions is also expected to be influenced by the strength of interaction between the ions and water.[53,54] The Na^+ and NO_2^- are expected to have similar Lewis acidity as water and are experimentally observed to increase solution viscosities and decrease water and ion diffusion rates when added as $NaNO_2$.[17,19,54] Hydroxide binds water molecules and has been observed to increase solution viscosity and decrease diffusion rates of water at both high and low concentrations.[55-57] Cs^+, in contrast, binds to water molecules weaker than water molecules bind to each other, resulting in a decrease in diffusion viscosity and increase in diffusion rates at low concentrations.[1-3,9,58,59] At higher concentrations, Cs^+-bearing electrolytes start to increase in viscosity and diffusion rates decrease due to obstruction by slower diffusing species.[52] The present study examines an electrolyte that has both Cs^+ and OH^- in it, two ions that are expected to have opposite effects on transport properties.

The measured density and dynamic (or absolute) viscosity are reported in **Table 1.** The viscosity is plotted in **Figure 1,**where it is also compared to the viscosity of aqueous $NaNO_2$ solution data from reference[54]. Viscosity slowly increases with increasing CsOH, both with and without 1 M $NaNO_2$. Where concentration ranges overlap, the data is consistent with existing data on the viscosity of aqueous CsOH solutions,[57] supporting the assertion that this new data is accurately measured. The solutions with 1 M $NaNO_2$ have slightly higher viscosities than those of the same CsOH concentration without $NaNO_2$, indicating that $NaNO_2$ increases the viscosity relative to water, consistent with earlier studies with only $NaNO_2$.[54] At constant total electrolyte molality, however, the solutions without $NaNO_2$ have higher viscosities. Given that Cs^+ tends to lower viscosity of aqueous solutions,[1,2] OH^- is likely responsible for the larger impact of CsOH on viscosity than $NaNO_2$. This increase in viscosity caused by OH^- overrides the viscosity lowering effect of Cs^+.

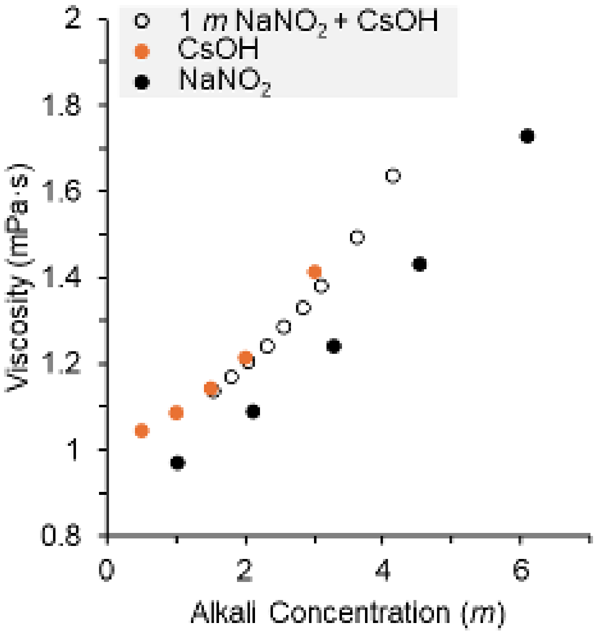

Figure 1. Viscosity (η) of aqueous CsOH, NaNO$_2$, and 1 M NaNO$_2$ + CsOH solution as a function of electrolyte molality.

Table 1. Densities and viscosities of solutions of 1 M NaNO$_2$ + 0.25 – 3 M CsOH and solutions of 0.5 – 3.0 M CsOH

Solution Name, units in Molarity (M; mol/L)	CsOH molality (mol/Kg)*	NaNO$_2$ molality (mol/Kg)*	Density (g·cm^3)[b]	Dyn. Viscosity (mPa·s)	Shear Rate (s^{-1})	Var. Coeff. (%)[c]
1 M NaNO$_2$	-	1	1.03392	1.064	513.3	0.0146
0.5 M CsOH	0.50	-	1.07350	1.045	516.2	0.0100
1.0 M CsOH	1.00	-	1.15019	1.086	485.7	0.0140
1.5 M CsOH	1.50	-	1.22441	1.143	505.7	0.0771
2.0 M CsOH	2.00	-	1.29986	1.214	470.7	0.0306
3.0 M CsOH	3.01	-	1.44506	1.414	395.0	0.0764
1 M NaNO$_2$ + 0.50 M CsOH	0.5133	1.0266	1.11802	1.136	517.4	0.0828
1 M NaNO$_2$ + 0.75 M CsOH	0.7702	1.0269	1.15523	1.169	499.7	0.0707
1 M NaNO$_2$ + 1.00 M CsOH	1.0267	1.0267	1.19291	1.206	481.6	0.0002
1 M NaNO$_2$ + 1.25 M CsOH	1.2859	1.0287	1.22847	1.241	465.5	0.0121
1 M NaNO$_2$ + 1.50 M CsOH	1.5430	1.0287	1.26596	1.286	446.6	0.0069
1 M NaNO$_2$ + 1.75 M CsOH	1.8030	1.0303	1.30195	1.331	429.2	0.0101
1 M NaNO$_2$ + 2.00 M CsOH	2.0615	1.0308	1.33896	1.38	411.6	0.0126
1 M NaNO$_2$ + 2.50 M CsOH	2.5859	1.0343	1.41056	1.493	376.2	0.0534
1 M NaNO^2 + 3.00 M CsOH	3.1094	1.0365	1.48352	1.638	338.9	0.0798

*Calculated from the measured density and as-prepared molarities

[b] The uncertainty in the density data is a constant 0.00005 g/cm^3.

[c] The fractional variation coefficient for the viscosity data.

Table 2. Measured Self-Diffusion Coefficients and Estimated Water Activities for Aqueous CsOH and CsOH + 1 M $NaNO_2$ Solutions.

CsOH molality*	$NaNO_2$ molality*	Cs Diff. Coef. (10^{-10} m^2s^{-1})	Na Diff. Coef. (10^{-10} m^2s^{-1})	H Diff. Coef. (10^{-10} m^2s^{-1})	Predicted water activity	Bound water molecules/Kg of water
0	1	-	10.85±0.3	19.01±0.06	0.979	0.84
1.027	1.027	13.71 ± 0.095	9.77± 0.18	17.23± 0.03	0.928	2.32
2.062	1.031	11.65± 0.037	8.59± 0.12	15.33± 0.02	0.893	3.80
3.109	1.036	9.61± 0.030	7.28± 0.17	13.20± 0.02	0858	5.31
0.990	0	15.31± 0.067	-	18.92± 0.07	0.964	1.43
1.999	0	12.92± 0.069	-	16.99± 0.05	0.929	2.87
3.014	0	10.96± 0.045	-	15.07± 0.02	0.895	4.33

*Calculated from the measured density and as-prepared molarities

Self-diffusion coefficients were determined with pulsed field gradient ^{1}H, ^{23}Na, and ^{133}Cs NMR spectroscopy, and reported in Table 2. Reported values and uncertainties are from the standard error of the fit of the Stejskal-Tanner relationship of the integrated signal intensity using a single component. Self-diffusion coefficients define the rate of diffusion in an equilibrium solution, meaning that diffusion is not driven by a concentration gradient.[60] The diffusion of protons was faster than the diffusion of Cs^+, which in turn was faster than the diffusion of Na^+, as indicated by the size of the diffusion coefficients (Figure 2A). This is consistent with other studies of the diffusion of water and alkali ions in aqueous systems with other anions.[60] The diffusion coefficients for all three elements changed approximately linearly with increased electrolyte concentration over this concentration range (Figure 2A). The diffusion coefficient of Na^+ was the least sensitive to the total electrolyte concentration, as indicated by the shallowest slope of the diffusion coefficient versus electrolyte concentration line (Figure 2A). Molecular dynamics studies indicate that Cs^+ accelerates the mobility of water molecules in its hydration sphere.[61,62] Proton diffusion is more likely attributed to H_2O than OH^- diffusion because of the greater abundance of water than OH^-.

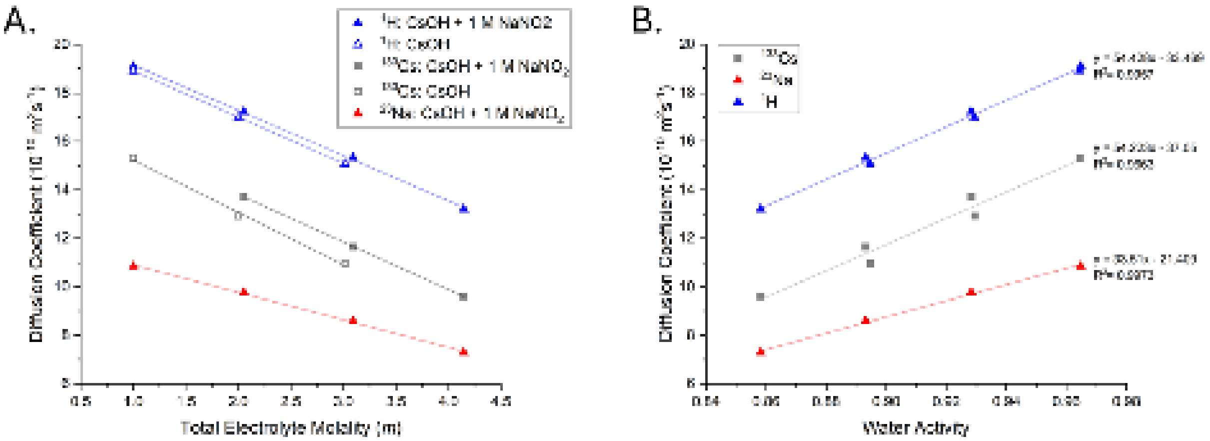

Figure 2. Pulsed field gradient NMR-derived diffusion coefficients as a function of (A) total electrolyte molality and B) estimated water activity. Linear best fit lines are shown and R^2 values reported.

The diffusion coefficients for ^{133}Cs, ^{23}Na, and ^{1}H as a function of the water activity are shown in **Figure 2B** for solutions that contain CsOH or 1 M $NaNO_2$ + CsOH. There is a small difference in the diffusion coefficients of ^{1}H and ^{133}Cs in the solutions that have 1 M $NaNO_2$, as indicated by the small offset (increase) in the diffusion coefficients for samples that have nearly identical water activities. There is a strong correlation between the diffusion coefficient of all three ions and the water activity, as indicated by the R^2 values for linear fits greater than 0.95 (**Figure 2B**). For monovalent ions, Marcus[35] found that the strength that ions bind water is proportional to the impact of the ions on water activity, where ions that lower the water activity will bind water more strongly. The lower the water activity, the stronger the water molecules are bound to the ions, which results in smaller proton diffusion coefficients (**Figure 2B**). An earlier study showing the strong correlation between diffusion coefficients and water activity asserted that the most important specific interaction effecting diffusion is the interaction between the ions and water.[23] The stronger binding of water by Na^+ than Cs^+ has previously been used to justify the faster diffusing rate of Cs^+ ions in water than Na^+, which is seen in **Figure 2B** for mixtures with both ions (Figure 2b).[63]

Figure 3 shows that there is a linear correlation between the viscosity and the diffusion coefficients, as expected from the Stokes-Einstein relationship.[64] Like the correlation between diffusion coefficients and water activity, the slope of the diffusion coefficients versus viscosity lines are essentially identical for ^{133}Cs and ^{1}H (**Figure 3**). This strong correlation between diffusion coefficients, viscosity, and water activity suggests that there is a common origin for the effects of electrolytes on all three. Earlier studies have attributed the relative impact of different electrolytes on viscosity to the relative strength that ions bind water.[3,9,53,54] Hence, the correlation between diffusion coefficients and water activity as well as diffusion coefficients and viscosity indicate that the interaction of the ions with water is a major contributor to the transport properties.

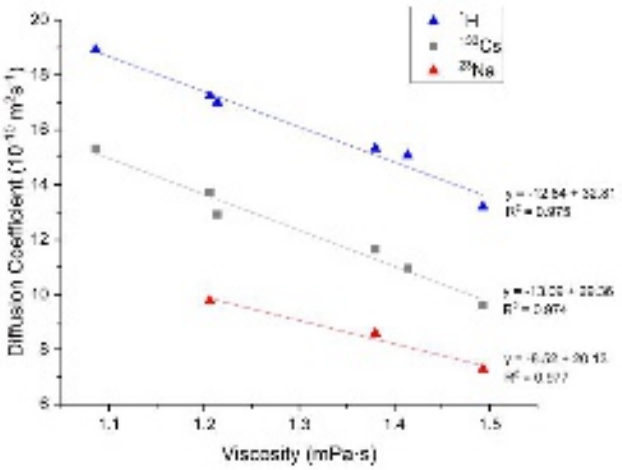

Figure 3. Pulsed field gradient NMR-derived ^{1}H, ^{23}Na, and ^{133}Cs diffusion coefficients as a function of solution viscosity. Linear best fit lines are shown and R^2 values reported.

The diffusivity of NO_2^- can also be derived from the width of the nitrite Raman bands.[65,66] The width of nitrate (NO_3^-) Raman bands is proportional to the vibrational relaxation of NO_3^- and, given the similar structure, it has been assumed that the vibrational relaxation of NO_2^- is also proportional to the Raman band width, and empirically correlated to diffusion rates.[23,67] Nienhuis et al.[32] measured Raman spectra of solutions at a constant $NaNO_2$ concentration of 1 M, but with increasing concentrations of CsOH. The full width at half max (FWHM) for the ν_1 nitrite bands is shown in **Figure 4** as a function of increasing CsOH concentration, along with similar data on NaOH solutions for comparison. At lower concentrations, the ν_1 Raman bands were broader and the diffusion coefficients were higher for most species (comparing **Figures 3** and **Figure 4**), The ν_1 Raman bands are narrower for the NaOH solutions than the CsOH solutions at lower concentrations, which may be related to differences in ion-paring noted by Nienhuis et al.[32], and likely indicates slower NO_2^- diffusion coefficients in the Na^+ system than in the Cs^+ system. The ν_1 Raman band FWHM decreases for both the Na^+ and the Cs^+ solutions at higher concentrations, which may indicate that the nitrite vibrational relaxation decreases at higher concentrations, consistent with the proton, Na^+, and Cs^+ diffusion coefficients shown in Figure 3.

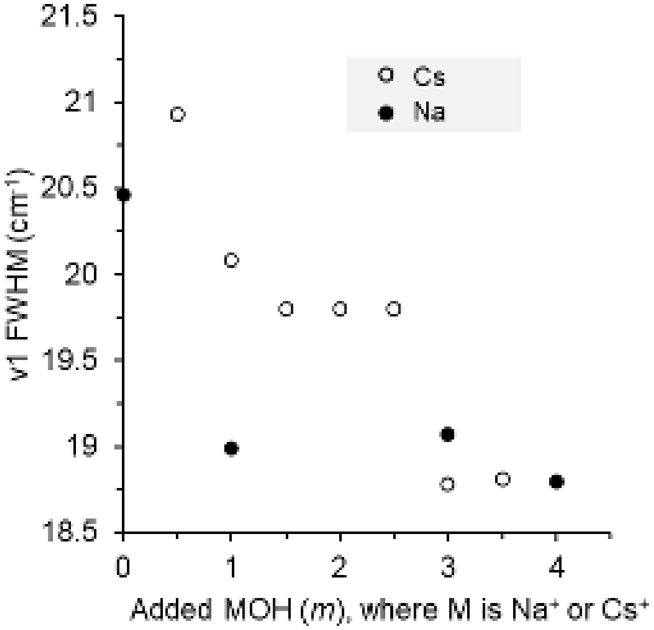

Figure 4. The FWHM of the ν_1 (total symmetric stretch stretch) nitrite Raman band as a function of CsOH concentration with constant 1 molar $NaNO_2$ concentration.

Discussion

A recent small-angle X-ray scattering study of the $NaOH$-$NaNO_2$-H_2O system determined that there was only a small difference in the ion-clustering upon mixing NaOH and $NaNO_2$ solutions together, confirming they were close to a mechanical mixture.[32,68] However, for the $CsOH$-$NaNO_2$-H_2O system, substantially different clustering was observed when CsOH and $NaNO_2$ solutions were mixed, and there are likely clusters that contained a mixture of OH^- and NO_2^- ions.[32] Quantitatively, the diffusive behaviors and viscosity of the $CsOH$-$NaNO_2$-H_2O and $NaOH$-$NaNO_2$-H_2O system were different. Qualitatively, however, they had similar trends with concentration.

In the $NaOH$-$NaNO_2$-H_2O system, the diffusion rates were not linearly proportional to the total electrolyte concentration,[69] whereas in the $CsOH$-$NaNO_2$-H_2O system, the diffusion coefficients are linearly related to the total electrolyte concentration (**Figure 2A**). The $CsOH$-$NaNO_2$-H_2O system, which had the more complicated ion-clustering as shown by X-ray scattering data,[32] had the simpler relationship between diffusion rates and total electrolyte concentration. The lack of linear correlation for the $NaOH$-$NaNO_2$-H_2O system prompted a plot of the diffusion rates as a function of water activity for that system, with water activity used as an indicator of the strength electrolytes interacted with water.[23,35]

In both the Na^+ and Cs^+ systems, the proton and alkali cation diffusion coefficients were linearly correlated to the water activity as calculated by Equation 1 (Figure 2b and Graham et al.[69]). The slopes of those lines were different, however, with the $CsOH$-$NaNO_2$-H_2O system being more sensitive to water activity. The slope of the proton diffusion coefficient versus water activity was 38.8 for the $NaOH$-$NaNO_2$-H_2O system but was 54.4 for the $CsOH$-$NaNO_2$-H_2O system (Figure 2b; and Reynolds et al.[23]). Similarly, the slope of the Na^+ diffusion coefficient versus water activity line was 21.1 for the $NaOH$-$NaNO_2$-H_2O system but was 33.5 for the $CsOH$-$NaNO_2$-H_2O system. For the $NaOH$-$NaNO_2$-H_2O system, it was asserted that the linear relationship between water activity and the diffusion coefficients indicated that the interaction between the ions and water had a larger impact on diffusion rates than the ion-pairing,[23] a conclusion that also holds for the Cs^+ system.

A recent NMR study of the $NaOH$-$NaNO_2$-H_2O system showed that all NMR active nuclei (^{23}Na, ^{1}H, ^{15}N, ^{17}O) exhibited deshielding as the concentration of NaOH increased, indicating decreasing electron density for all species, which would mean electrons are increasingly delocalized in the system with increasing concentration.[32] This was also true for ^{133}Cs, ^{17}O and ^{23}Na in the $CsOH$-$NaNO_2$-H_2O system, but there was increased shielding on the ^{1}H shift,[32] indicating higher electron density on the protons in water when Cs^+ was present than when Na^+ was present. The ^{1}H shift for the two systems is compared in Figure 5, showing the downfield shift for the Na^+ system and upfield shift for the Cs^+ system. The only difference between these two systems is the alkali cation, and neither alkali cation would expect to form bonds with the water-proton, which means the difference in the ^{1}H NMR shift must be driven by how Na^+ and Cs^+ bind oxygen, influencing the ^{1}H shift inductively. The Na^+ binds the water oxygen (O_w) stronger than the hydrogen bonds from other water molecules it displaces,[70-72] which would increasingly pull electron density away from the oxygen, which in turn would pull electron density away from the water-proton. In contrast, Cs^+ binds the O_w weaker than the hydrogen bond received from other water molecules, so Cs^+ extracts less electron density from O_w which moves electron density to the proton, better shielding the proton nucleus (Figure 5). Higher proton electron density would then signify weaker hydrogen bonds with neighboring water molecules or anions. These weaker hydrogen bonds then result in Cs^+ decreasing the solution viscosity and increasing the diffusion rates of neighboring water molecules.[9,30,58.62]

Even though the diffusion rate of OH^- itself appears to be faster than other ions as inferred from electrical conductivity,[27,28] OH^- slows the rate of diffusion of neighboring water molecules by binding them strongly[73,74] This increased the viscosity and decreased the diffusion rate of the water proton in CsOH solution despite the presence of Cs^+ (Figures 1 and 2). The Cs^+ ion nonetheless had a viscosity lowering effect, as indicated by the lower viscosity and increased diffusion coefficients of the CsOH system relative to the NaOH system data from reference[75] (Figure 6).

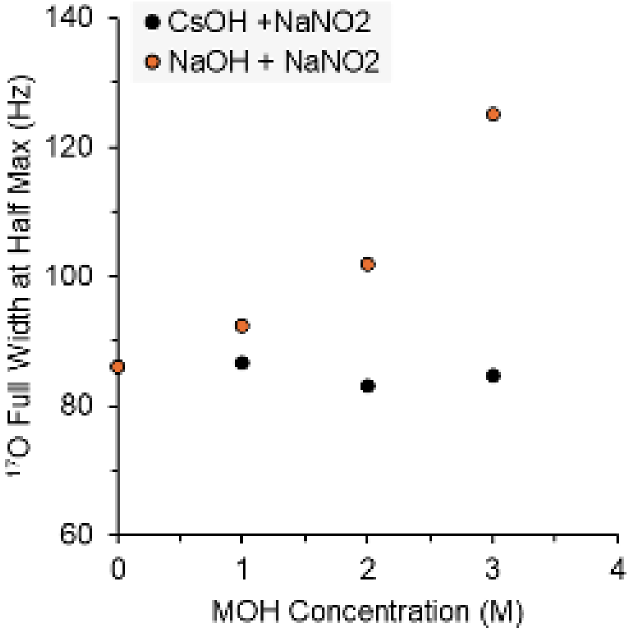

Figure 5. The ^{1}H NMR spectra of 1 M $NaNO_2$ solution containing increasing amounts of CsOH or NaOH. Taken from Nienhuis et al.[32]

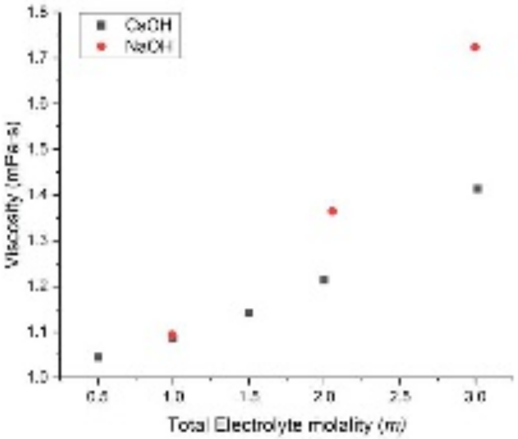

Figure 6. Comparison of the viscosity of aqueous NaOH and CsOH solutions.

Earlier studies indicate that ion-pairing between Na^+ or Li^+ and OH^- slowed down the diffusion rate of the ions.[15] The thermodynamic analysis here, as well as the potentiometric study by Sipos et al. indicate that CsOH does not form ion-pairs.[49] Similarly, earlier thermodynamic analysis indicates that neither Na^+ nor

Cs^+ form ion-pairs with NO_2^-.[45,76] These thermodynamic studies are in sharp contrast with spectroscopic, computational, and X-ray scattering studies indicating that all these species form both ion-pairs and larger clusters in solution.[17,21,32,68] Hefter has noted that discrepancies are common between ion-pairing constants determined spectroscopically and those determined thermodynamically.[77] We have previously argued that two counter ions in direct contact with each other do not always interact with each other strongly enough to behave thermodynamically as a distinct ion-paired species.[23,45] The difference between the thermodynamic analysis for ion-pairing in $CsNO_2$ and CsOH solutions and the scattering and spectroscopic data indicates that the interaction between Cs^+ and NO_2^- as well as OH^- in solution likewise does not act thermodynamically as a distinct ion-pair species.

This conclusion is consistent with ionic liquids, where ions often act thermodynamically like distinct species despite having counterions in virtually every direction.[78] Indeed, in Colbin et al's review of ion-pairing impacts on electrical conductivity, they argued that ion-pairing mass action equations poorly represents the conducting species precisely because there are multiple interactions between ions in solution in multicomponent solutions.[79]

In solid $CsNO_2$, the interaction between Cs^+ and NO_2^- is so weak that the NO_2 spins within the crystal from thermal vibration, even at ambient temperature.[80.81] Consequently, $CsNO_2$ does not have a well-defined crystallographic position for the N and O atoms.[80,81] Given the interaction between Cs^+ and NO_2^- is weak even in the solid state, it is reasonable to expect that the interaction between Cs^+ and NO_2^- would be too weak to act thermodynamically like a distinct ion-pair species in liquid. Solid anhydrous CsOH also exhibits rotational disorder at ambient temperatures.[82] While the present study evaluated solution concentrations only up to 3 M CsOH, cesium hydroxide is highly soluble at over 27 moles per kilogram of water.[83] This corresponds to less than one water molecule per ion at saturation. Such high concentration ensures contact between counterions in solution.[84] A recent study found that these concentrated solutions do not occur because the ions have a strong affinity for each other, but rather because they lack such affinity. If the ions had a strong attraction, they would precipitate.[85]

Putting the thermodynamic, viscosity, diffusion coefficient and spectroscopic data together thus indicates that CsOH as well as $CsNO_2$ form contact ion-pairs and larger clusters at the intermediate concentrations studied here and by Nienhuis et al.[32], but these contact ion-pairs are held together sufficiently weakly that they do not exhibit thermodynamic behavior characteristic of a distinct species. However, the formation of contact ion-pairs and larger ion-clusters requires correlated motion among the ions, indicating that there is ion-interaction between the ions.[79] The interaction between the ions and water is likely to be more impactful to transport properties in this system.

Conclusions

This study provides critical insights into the hydration and transport properties of CsOH and CsOH-$NaNO_2$ mixed aqueous solutions. Individually, Cs^+ would be expected to decrease viscosity and increase diffusion rates while OH^- would be expected to do the opposite. The results here indicate that the impact of OH^- is greater, because the diffusion rates in CsOH solution decreased and the viscosity increased. The Cs^+ did have an effect, however, because the viscosities are lower than the similar NaOH-based system. The impact of adding a constant concentration of $NaNO_2$ was moderate.

A previous spectroscopic study identified a complex change in solution structure with increasing concentration, yet the transport properties exhibited simple correlation with concentration. The weak interaction identified by the thermodynamic modeling indicates that this may be because the ions are not bound to each other strongly even when they are in direct contact with each other. The linear relationship between diffusion coefficients and water activity further underscores the significant role of ion-water interactions in determining transport properties, despite previous spectroscopic studies indicating extensive contact-ion pairing in this system. Nonetheless, these small interactions noticeably increase with concentration.

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Conflict of Interest Statement

The authors have no conflicts to disclose.

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