Article

# Competitive Ion Pairing and the Role of Anions in the Behavior of Hydrated Electrons in Electrolytes

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**ABSTRACT:** Experiments have shown that in the presence of electrolytes, the hydrated electron's absorption spectrum experiences a blue shift whose magnitude depends on both the salt concentration and chemical identity. Previous computer simulations have suggested that the spectral blue shift results from the formation of (cation, electron) contact pairs and that the concentration dependence arises because the number of cations simultaneously paired with the electron increases with increasing concentration. In this work, we perform new simulations to build an atomistic picture that explains the effect of salt identity on the observed hydrated electron spectral shifts. We simulate hydrated electrons in the presence of both monovalent ($Na^+$) and divalent ($Ca^{2+}$) cations paired with both $Cl^-$ and a spherical species representing $ClO_4^-$ anions. Our simulations reproduce the experimental observations that divalent ions produce larger blue shifts of the hydrated electron's spectrum than monovalent ions with the same anion and that perchlorate salts show enhanced blue shifts compared to chloride salts with the same cation. We find that these observations can be explained by competitive ion pairing. With small kosmotropic cations such as $Na^+$ and $Ca^{2+}$, aqueous chloride salts tend to form (cation, anion) contact pairs, whereas there is little ion pairing between these cations and chaotropic perchlorate anions. Hydrated electrons also strongly interact with these cations, but if the cations are also paired with anions, this affects the free energy of the electron−cation interaction. With chloride salts, hydrated electrons end up in complexes containing multiple cations plus a few anions as well as the electron. Repulsive interactions between the electron and the nearby $Cl^-$ anions reduce the cation-induced spectral blue shift of the hydrated electron. With perchlorate salts, hydrated electrons pair with multiple cations without any associated anions, leading to the largest possible cation-induced spectral blue shift of the hydrated electron. We also see that the reason multivalent cations produce larger spectral blue shifts than monovalent cations is because hydrated electrons are able to simultaneously pair with a larger number of multivalent cations due to a larger free energy of interaction. Overall, the interaction of hydrated electrons with electrolytes fits well with the Hofmeister series, where the electron behaves as an anion that is slightly more able to break water's H-bond structure than chloride.

Ion Pairing in NaCl Results in Both Ions Interacting with $e_{aq}^-$
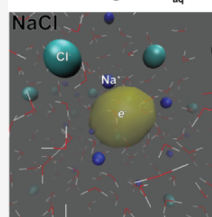
A Lack of Ion Pairing in $NaClO_4$ Results in Only $Na^+$ Cations Interacting with $e_{aq}^-$
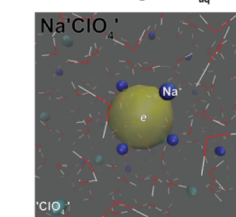
## INTRODUCTION

Despite being the simplest quantum mechanical solute that can be directly studied with both theory and experiment, the hydrated electron ($e_{aq}^-$) is still not well understood at the molecular level. Even though the general consensus is that the hydrated electron is associated with a cavity in liquid water, the size of the cavity, the fraction of the electron that resides in the cavity, and the structure of the water around the cavity are still the subject of debate.[1−7] In addition, there are several experimental observations that are yet to be explained by theory. For example, the hydrated electron's absorption spectrum shifts to the red as the temperature of the solution increases at constant density,[8] something associated with an increase in the electron's radius of gyration,[9] but the electron's molar solvation volume appears to be roughly temperature-independent.[10] Mixed quantum/classical (MQC) simulations only appear to get the temperature dependence correct when employing a non-cavity model of the electron that has the wrong sign of the molar solvation volume.[11−13] DFT-based ab initio simulations capture some of these temperature-depend-

ent trends but also predict an incorrect shape and position of the electronic absorption spectrum.[14,15]

Another property of the hydrated electron that has been less well explored is its behavior in aqueous electrolyte solutions. The nature of excess electrons in the presence of electrolytes is important in radiation chemistry, particularly for atmospheric aerosols and biological systems. Experimentally, what is known is that the absorption spectrum of hydrated electrons undergoes little change in shape but exhibits a small blue shift in the presence of electrolytes.[16] The magnitude of the spectral blue shift increases rapidly at low salt concentrations and then saturates as the electrolyte's solubility limit is
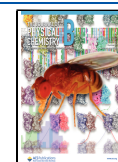
approached.[16] It is also known that di- and tri-valent cations produce larger spectral shifts than monovalent cations when paired with the same anion.[16] Surprisingly, the electrolyte anion also plays a role, as perchlorate salts induce a larger blue shift of the hydrated electron's spectrum than chloride salts with the same cation.[16]

To date, there has been only limited simulation work aimed at understanding the interaction between hydrated electrons and aqueous electrolytes. Most such work has focused on the interaction between the hydrated electron and a single $Na^+$ cation in an effort to understand the nature of the salt-induced blue shift.[17,18] These MQC simulations have shown that hydrated electrons form contact pairs with electrolyte cations that are stabilized by several $k_BT$ of free energy.[17,18] In particular, work from our group found that there exists a delicate balance between the way the cation is solvated and the $Na^+-e_{aq}^-$ interaction: small changes in the simulated cation/water interaction have a large effect on the calculated stability of the ($Na^+$, $e_{aq}^-$) contact pair.[17] MQC simulations predict a salt-induced spectral blue shift that is exaggerated by nearly an order of magnitude,[17,18] an effect that we have argued arises from non-pairwise additivity in the pseudopotentials employed in such simulations.[19]

Our group also has used MQC simulations to study the behavior of excess electrons as a function of salt concentration.[19] We found that the calculated spectral blue shift increases with increasing salt concentration because the hydrated electron can simultaneously interact with multiple cations to form ($nNa^+$, $e_{aq}^-$) contact pairs, where $n$ = 1, 2, or 3. Each additional cation is responsible for an enhanced spectral blue shift, with the effect saturating once three cations are involved. The concentration-dependent blue shift is then explained by the fact that the number of cations involved in ($nNa^+$, $e_{aq}^-$) contact pairs increases with increasing salt concentration.[19]

Despite all this previous work, there still is no theoretical explanation of the role that either the cation or anion plays in the spectroscopy and contact pair formation of hydrated electrons in electrolyte solutions. Thus, in this paper, we use MQC simulations to investigate the behavior of hydrated electrons and their contact pairs in the presence of different electrolytes at the same concentration. We explore the role of the cation by simulating both $Na^+$ and $Ca^{2+}$ salts. The role of the anion is explored by comparing salts of both cations with $Cl^-$ and $I^-$. We note that the interaction of hydrated electrons with iodide salts has not been studied experimentally, but as mentioned above, there are experiments using perchlorate salts,[16] which have a similar degree of ion pairing with $Na^+$ and $Ca^{2+}$ as $I^-$, as seen by the similar position of $I^-$ and $ClO_4^-$ on the Hofmeister series.[20,21] Thus, we view our model of $I^-$ as a spherical anion that equivalently represents the solvation properties of perchlorate, allowing our simulations to be directly compared to the experiments in ref 16. To make the comparison to experiment as clear as possible, we will label this anion "$ClO_4^-$" throughout the rest of this work.

With the simulations in hand, we find that rather than the direct electronic interaction between the hydrated electron and mono- and di-valent cations being important, it is the number of cations that coordinate with the electron that is sensitive to the cation valency: divalent cations have a higher average coordination number than monovalent cations at the same concentration. We also see that the anion plays a role because salts that better dissociate in solution produce larger blue

shifts. This is because of competitive ion pairing: it is harder for hydrated electrons to replace anions that are stably paired with cations and easier for hydrated electrons to associate with cations that are solvated independently of their counterions. We find that our simulations are able to reproduce the cation- and anion-dependent experimental spectral trends and that the nature of the competitive ion pairing matches well with what is expected from the Hofmeister series.

## ■ METHODS

We simulated the ground-state dynamics of an excess electron in concentrated aqueous NaCl, Na"$ClO_4$", $CaCl_2$, Ca("$ClO_4$")$_2$ solutions using MQC molecular dynamics simulations to directly examine the interactions responsible for the salt-induced blue shift of the hydrated electron's absorption spectrum. We chose the salts for this study to isolate both the effect of the cation's charge and the extent of ion association on the magnitude of the blue shift of the hydrated electron's spectrum in the presence of electrolytes. In particular, we chose $Ca^{2+}$ as a divalent cation both because it has been studied experimentally[16] and because of its tight hydration sphere. We selected iodide/perchlorate because this anion also has been studied experimentally[16] and because it does not have strong ion association with either aqueous $Na^+$ or $Ca^{2+}$ compared to the corresponding chloride salts.

We chose to study the hydrated electron in these electrolytes via MQC simulation because the system sizes and simulation time scales required are computationally out of reach for ab initio methods, including those based on DFT. In our simulations, the electron/water interactions were modeled with the widely accepted cavity-forming pseudopotential developed by Turi and Borgis,[1] while the cation/electron and anion/electron interactions were described with one-electron Phillips–Kleinman[22,23] pseudopotentials developed in-house[19,24] using the procedure described in the Supporting Information (SI). Long-range electrostatic interactions were treated using the Ewald summation method with a 10 Å cut-off.

As summarized in Table 1, each simulation consisted of a periodic box filled with a varying number of flexible single-

**Table 1. Setup for Hydrated Electron/Aqueous Electrolyte MQC Simulations**

| solution | waters | electrolyte ions | simulation box length (Å) | basis set grid length (Å) |
|---|---|---|---|---|
| 0.0 m NaCl | 499 | 0 | 24.65 | 17.93 |
| 3.8 m NaCl | 439 | 30 | 24.34 | 17.70 |
| 3.8 m Na"$ClO_4$" | 439 | 30 | 24.39 | 17.74 |
| 4.1 m $CaCl_2$ | 409 | 30 | 24.04 | 17.49 |
| 4.1 m Ca("$ClO_4$")$_2$ | 409 | 30 | 24.71 | 17.97 |

point-charge classical water molecules,[25] Lennard-Jones (LJ)-type classical ions, and a single quantum mechanical electron represented in a 24 × 24 × 24 plane-wave basis set. The size of the simulation box was chosen to replicate the experimental density of the electrolyte solution under standard temperature and pressure conditions. The length of the cubic grid spanned by the basis set used to described the quantum subsystem was constrained to be ~73% the length of the simulation box.

The classical LJ parameters used to simulate the $Na^+$ and $Cl^-$ ions were taken from ref 26, while those for the $Ca^{2+}$ ion

were taken from ref 27. As discussed further below, the key difference between chloride and perchlorate salts is that the latter generally have less ion-pairing with kosmotropic cations than the former. Developing a classical simulation model for $ClO_4^-$ and corresponding pseudopotential for use in MQC simulations, however, is beyond the scope of this work. Thus, to understand the role that pre-existing ion pairing plays when hydrated electrons are introduced into aqueous electrolytes, we approximated the behavior of perchlorate anions by simulating them as large spherical anions that do not strongly ion pair with either sodium or calcium cations in water. The particular simulation parameters we chose were originally designed to mimic iodide,[28] and throughout we refer to this anion in our simulations as "$ClO_4^-$" because of its general behavior, as discussed further below. All of the classical LJ parameters we use are summarized in Table 2.

**Table 2. Classical LJ Parameters Used to Describe Water/Water, Water/Ion, and Ion/Ion Interactions**[a]

| atom | $\sigma$ (Å) | $\epsilon$ (kJ/mol) |
|---|---|---|
| $Na^+$ | 2.350 | 0.544 |
| $Ca^{2+}$ | 2.361 | 1.882 |
| $Cl^-$ | 4.400 | 0.419 |
| "$ClO_4^-$" | 5.400 | 0.292 |
| O | 3.166 | 0.650 |

[a]The parameters for $Na^+$ and $Cl^-$ were taken from ref 26. The parameters for $Ca^{2+}$ and "$ClO_4^-$" were taken from refs 27 and 28, respectively.

The initial configuration for each MQC simulation of the excess electron in a concentrated electrolyte solution was extracted from an entirely classical (i.e., without the quantum mechanical electron) microcanonical $(N, V, E)$ simulation of the corresponding system in the absence of an excess electron at roughly room temperature. These all-classical simulations were propagated for a total of 800 ps at room temperature using a 1 fs time step. To initiate each hydrated electron simulation, we added the quantum mechanical electron to a configuration extracted out of the classical simulation's end point. Each MQC system with the hydrated electron was simulated for a total of 480 ps in the $(N, V, E)$ ensemble at ~300 K using a 0.5 fs time step. The velocity Verlet algorithm[29] was used to propagate all dynamics, with the quantum mechanical forces computed via the Hellman–Feynman theorem.[30]

Potentials of mean force (PMFs) between the quantum electron and classical ions were constructed using the coupled-perturbed quantum umbrella sampling method.[31] To calculate the PMFs in the different simulated solutions, we restrained the distance between the hydrated electron's center of mass and a single $Na^+$ or $Ca^{2+}$ ion using a quantum harmonic umbrella potential with a 1.5 eV/Å $^2$ force constant. Twenty-five 60 ps long simulation windows were computed in the canonical $(N, V, T)$ ensemble as the target electron/cation distance was varied from 0 to 6 Å in 0.25 Å increments. In addition, we also calculated the quantum mechanical PMF for a bulk hydrated electron interacting with a single $Na^+$ cation, while a $Cl^-$ anion was held a fixed distance $R = 2.5$ or 2.8 Å from the cation to examine the role of $(Na^+, Cl^-)$ pairing on the stability of $(Na^+, e_{aq}^-)$ contact pairs; these anion distances were chosen because 2.8 Å is the most stable distance of the $(Na^+, Cl^-)$ contact pair, while 2.5 Å is a bit closer in distance

and ~2 $k_BT$ less stable, as discussed further below. Twenty-nine windows were simulated for these systems, and a classical harmonic potential with a 1.5 eV/Å $^2$ force constant was used to restrain the $Na^+$–$Cl^-$ distance. The first 21 windows simulated 60 ps of dynamics and spanned $e_{aq}^-$–$Na^+$ distances from 0 to 5 Å in 0.25 Å increments, while the remaining 30 ps long windows were used to extend the PMF up to a $e_{aq}^-$–$Na^+$ distance of 9 Å in 0.5 Å increments. The velocity Verlet algorithm[29] was used to propagate the dynamics with a 0.5 fs time step, while the temperature was held at 300 K using the Nosè–Hoover[32] chain thermostat. The multi-state Bennet acceptance ratio method[33] was implemented to construct all the PMFs using uncorrelated configurations extracted every 200 fs following a 10 ps long equilibration period.

## ■ RESULTS AND DISCUSSION

How should the presence of salts with different cations and anions affect the properties of a hydrated electron? It might make sense that multivalent cations would have stronger interactions with excess electrons than monovalent ions because of their higher electron affinities, but multivalent cations also are more strongly solvated by water, and stronger ion solvation is associated with a decreased interaction between the ion and a hydrated electron.[17] The fact that anion identity also affects hydrated electron behavior[16] indicates that ion pairing plays an important role in determining the interaction between excess electrons and aqueous electrolytes. This leads to the critical questions that we address in this work: what types of ion-pairing are hydrated electrons involved in? Do hydrated electrons behave like conventional anions? If so, where would they lie on the Hofmeister series?[20] If not, how does their quantum mechanical nature influence the way they compete with conventional anions during competitive ion pairing with a particular cation?

It is well known that ions of opposite charge and similar size tend to associate in aqueous solutions.[34] Small cations tend to pair with small anions because the close proximity of oppositely charged point charges results in strong Coulombic interactions that more than compensate for the energetic penalty associated with the dehydration that accompanies ion pairing. For large cations and anions, where the electrostatic interactions are relatively weak, ion pairing is driven by the formation of water/water interactions that are more favorable than the separate ion/water interactions. These ideas underlie the Hofmeister series,[20] which predicts that the tendency for a given cation to undergo ion association increases as the anion's ability to disrupt the hydrogen bonding network of water increases. The Hofmeister series puts anions' H-bond disruptive tendency in the order $Cl^- \gg I^- \geq ClO_4^-$,[21] suggesting that it is reasonable to approximate the ion-pairing behavior of perchlorate with a simulation model of iodide because monatomic ions are much less computationally expensive to implement in MQC simulations, as mentioned above.

Figure 1 shows how our simulated ions pair in the absence of excess electrons by examining pair distribution functions, $g(r)$, for the arrangement of anions around a given cation. Figure 1A compares the anion distribution for 4.1 m aqueous solutions of $Ca^{2+}$ ions with either $Cl^-$ or "$ClO_4^-$" counterions, while Figure 1B shows the same for 3.8 m solutions for the corresponding $Na^+$ salts. For both cations, it is clear that the first-shell anion peak is significantly reduced for "$ClO_4^-$"
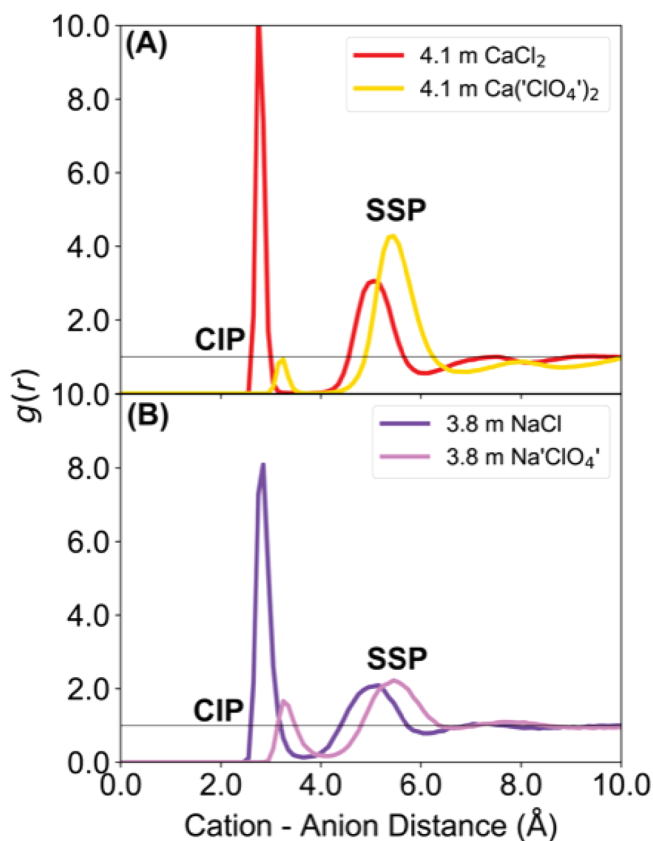
**Figure 1.** Radial distribution functions, $g(r)$, for classically simulated 3.8 m NaCl, 3.8 m Na"ClO$_4$", 4.1 m CaCl$_2$, and 4.1 m Ca("ClO$_4$")$_2$ aqueous solutions without an excess electron. As expected from their positions on the Hofmeister series, the Cl$^-$ salts show a much stronger degree of contact ion pairing with the small cations than the corresponding "ClO$_4^-$" salts, while the "ClO$_4^-$" salts show a slightly enhanced degree of SSP formation compared to the Cl$^-$ salts.

compared to Cl$^-$, indicating a large decrease in direct cation−anion contact ion pairs (CIPs). Instead, the "ClO$_4^-$" salts show a slightly enhanced second shell peak, indicating that these salts have a slightly preferred tendency to make solvent-separated pairs (SSPs) compared to their Cl$^-$ counterparts, but the enhancement in SSPs is much less significant than the decrease in direct CIP formation. Thus, the classical ions in our simulations reproduce the expected Hofmeister ion pairing behavior.

Experimentally, all we know about the way hydrated electrons interact with salts is the way ion pairing affects the hydrated electron's absorption spectrum. Hydrated electrons in pure water have a broad absorption spectrum with a Gauss−Lorentzian shape that peaks near 720 nm.[35] In the presence of salts, the electron's spectrum blue-shifts, with the magnitude of the blue shift dependent on the salt concentration and the identities of the cation and anion.[16] Thus, to understand if our MQC simulations correctly reproduce the experimental behavior, we show the calculated absorption spectrum, $I(E)$, of our simulated hydrated electrons in different aqueous salt solutions in Figure 2A. The spectra were computed in the inhomogeneous limit by binning oscillator strengths ($\mu_{0,i}$) for the three lowest electronic transitions for uncorrelated configurations extracted out of the equilibrated MQC trajectories every picosecond and then sorting them into
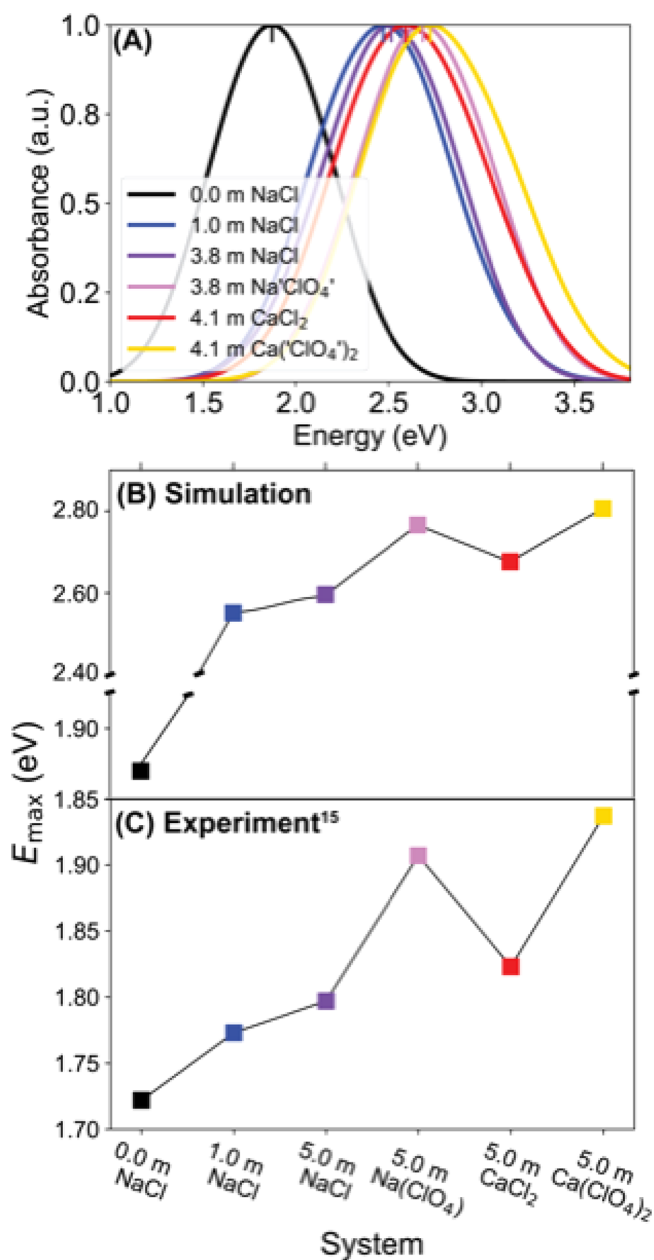


**Figure 2.** Spectroscopy of the hydrated electron in different aqueous electrolyte solutions. (A) Simulated absorption spectra of the hydrated electron in 3.8 m NaCl, 3.8 m Na"ClO$_4$", 4.1 m CaCl$_2$, and 4.1 m Ca("ClO$_4$")$_2$ aqueous solutions. (B) Energy at which the simulated absorption spectrum peaks ($E_{max}$) as a function of salt identity and concentration.(C) Experimental $E_{max}$ data adapted from ref 16. Although the absolute magnitudes of the simulated spectral shifts are too large for the reasons described in ref 19, the relative spectral shifts with different cation/anion combinations are in excellent agreement with experiment.

0.01 eV-wide bins based on the corresponding transition energies ($\Delta E_{0,i}$) according to

$$I(E) = \sum_{i=1}^{3} |\mu_{0,i}|^2 \, \Delta E_{0,i} \delta(E - \Delta E_{0,i}) \tag{1}$$

where $\delta(E)$ is the Dirac $\delta$-function. The "stick-spectra" generated this way were then convoluted with a Gaussian of width $\sigma = \frac{1}{4\sqrt{2}}$ eV.

Figure 2B shows that in all the salt solutions, the magnitude of the hydrated electron's calculated spectral blue shift is about an order of magnitude larger than that observed experimentally, an artifact of non-pairwise additivity of the pseudopotentials employed that do not properly account for partial charge transfer between the water and the cations, as we have discussed previously.[19] Other than this exaggerated magnitude, however, the relative blue shifts in the different salt solutions are in excellent agreement with experiment:[16] the blue shifts associated with the $Ca^{2+}$ salts are larger than those of the $Na^+$ salts, and the blue shifts in the presence of the "$ClO_4^-$" counterion are larger than those associated with $Cl^-$. Also in agreement with experiment is the fact that the blue shift induced by the change in anion is stronger than that induced by the change in cation.[16]

To get a better sense of how well the simulations reproduce the experiments, in Figure 2B,C we directly compare the position of the simulated and experimental hydrated electron's absorption spectral maximum, $E_{max}$, as a function of salt identity and concentration. Figure 2B shows the results from our simulations, while Figure 2C shows experimental results extracted from ref 16. Other than the fact that the simulated spectral maxima are all overly blue-shifted, our simulations perform remarkably well at replicating the experimental trends. This gives us confidence that we can use the molecular information available in the simulations to uncover the reasons why salts with different cations and anions have different interactions with hydrated electrons and thus produce different spectral shifts.

Since we know that hydrated electrons have spectral shifts in electrolyte solutions due to ion pairing, we start by investigating the interactions between excess electrons and different salt ions in water. Figure 3 shows PMFs computed using quantum umbrella sampling[31] along a distance coordinate between the position of a cation and the hydrated electron's center of mass.[17,18] The data show that the hydrated electron forms much more stable contact pairs with $Ca^{2+}$ (Figure 3A) than with $Na^+$ (Figure 3B), providing a first clue as to why the spectrum of the electron is more blue-shifted by calcium salts than sodium salts. Moreover, the PMFs also show that the strength of the $e_{aq}^-$–cation interaction is influenced by the identity of the anion, particularly for the $Na^+$ cation: (cation, $e_{aq}^-$) contact pairs with "$ClO_4^-$" counterions are more stable than those with $Cl^-$ counterions.

Clearly, the identities of the electrolyte's cation and anion and the way they are solvated in water all help to determine how these ions interact with hydrated electrons. To further explore how hydrated electrons interact with both cations and anions, in Figure 4 we investigate the number of cations and anions that reside in the vicinity of free-energetically bound (cation, $e_{aq}^-$) contact pairs. Using the pair distribution functions shown in Figure 1, we define an anion as being in direct contact if it sits within 4.0 Å of a $Ca^{2+}$ or $Na^+$ cation, and using the PMFs in Figure 3, we define the electron as being in contact if its center of mass lies within 4 or 6 Å of a $Na^+$ or $Ca^{2+}$ cation, respectively. Figure 4 shows that with "$ClO_4^-$" salts, hydrated electrons interact with multiple cations and essentially no anions, whereas with $Cl^-$ salts, there are typically two or three anions associated with the cations that strongly interact with the electron.

These results strongly suggest that the hydrated electron behaves like a Hofmeister series anion that is slightly more disruptive to water H-bonding than $Cl^-$. Chloride ions are
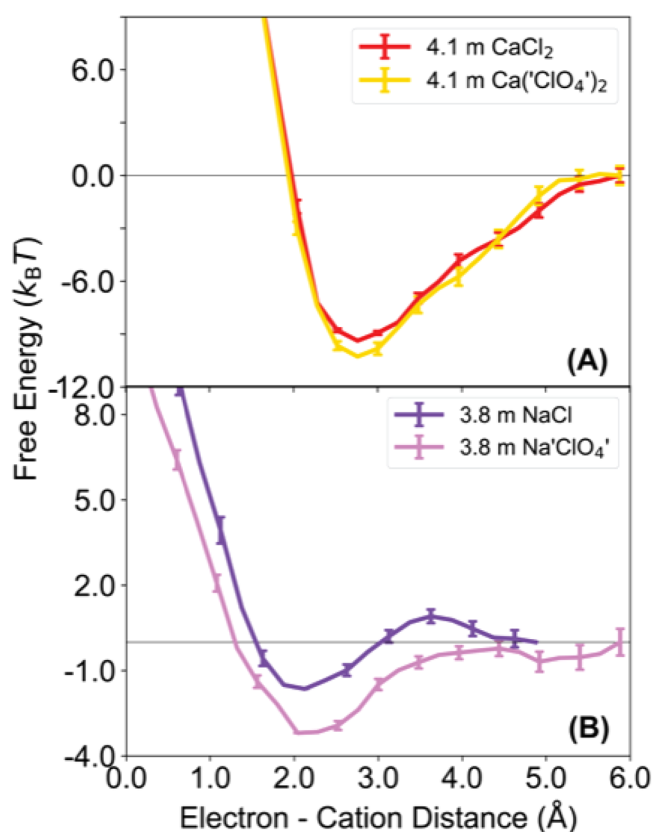


**Figure 3.** PMF calculated using the methodology in ref 31, along the electron–cation distance coordinate for hydrated electrons in (A) 4.1 m $CaCl_2$ (red curve) and 4.1 m Ca("$ClO_4$")$_2$ (yellow curve) and (B) 3.8 m NaCl (purple curve) and 3.8 m Na"$ClO_4$" (pink curve) aqueous solutions. Cations with a greater charge result in deeper free energy wells. As the extent of cation/anion pairing decreases (cf. Figure 1), the stability of the (cation, electron) contact pair increases. Thus, the hydrated electron's interaction with aqueous electrolytes is determined by competitive ion pairing.

strongly paired with sodium and calcium ions in liquid water (Figure 1), but hydrated electrons even more strongly prefer to interact with these cations, leading to hydrated electron complexes that contain multiple cations and anions [e.g (3$Na^+$, 2$Cl^-$, $e_{aq}^-$) complexes, as seen in Figure 4B]. Since perchlorate anions do not prefer to associate with either $Na^+$ or $Ca^{2+}$ cations in water, hydrated electrons can strongly associate with these cations without any accompanying anions [e.g (3$Ca^{2+}$, $e_{aq}^-$) clusters, as seen in Figure 4C]. In Figure S1 of the Supporting Information, we also show that the hydrated electron has a larger effect on the way water solvates $Na^+$ in chloride solutions compared to perchlorate solutions. All of this fits well with the standard idea that solvated electrons break water's local H-bonding structure, as also suggested by recent ab initio simulations.[4,14]

Since the number of cations associated with a hydrated electron in the presence of salt is roughly independent of the identity of the anion, the presence or absence of nearby anions must play a direct role in the hydrated electron's spectroscopy. Since anions are repulsive to hydrated electrons, it would make sense that the anions in (cation, anion, $e_{aq}^-$) clusters destabilize the cation/electron interaction. To verify this hypothesis, in Figure 5 we compute the PMF between a single $Na^+$ cation and hydrated electron (dark green curve) and the same PMF in the presence of a $Cl^-$ anion. For the latter calculation, in
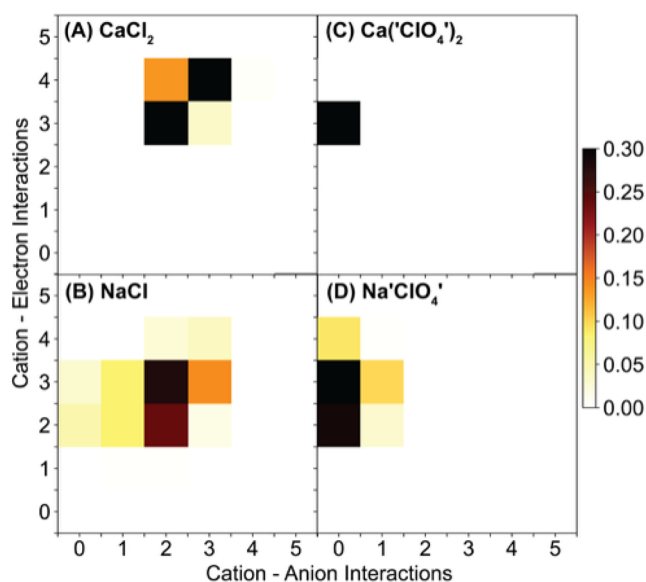
**Figure 4.** Local ionic environment around the hydrated electron in different ionic solutions, characterized by the number of cations near the electron and the number of anions near those cations. Cation/electron cut-off distances of 4.0 and 6.0 Å were used to identify $(Na^+, e_{aq}^-)$ and $(Ca^{2+}, e_{aq}^-)$ contact pairs, respectively. For all cation/anion combinations, whenever a unique anion fell within 4.0 Å of a cation that was part of a $(cation, e_{aq}^-)$ contact pair, it was considered to be part of a (cation, anion) contact pair. The data show that hydrated electrons in $Cl^-$-containing salts (A,B) form simultaneous contact pairs with cations and anions, while electrons in solutions with "$ClO_4^-$" anions (C,D) only pair with cations.
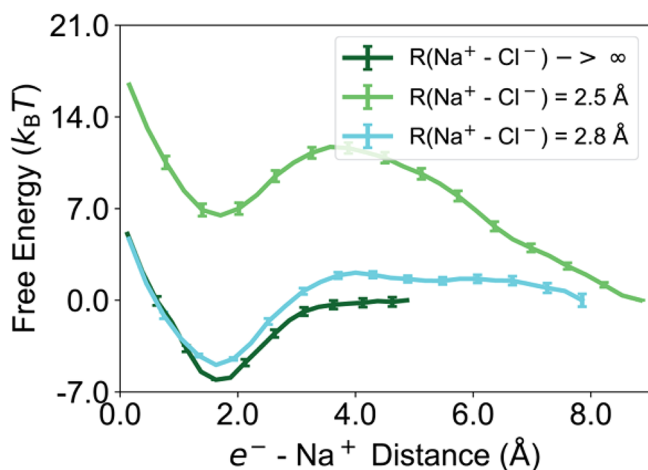


**Figure 5.** PMF calculated using the methodology in ref 31, along the electron−cation distance coordinate for hydrated electrons interacting with a single $Na^+$ cation (dark green curve) and a sodium cation that was restrained to be paired with a chloride anion at either the "natural" $Na^+-Cl^-$ contact pair distance of 2.8 Å (light blue curve; cf. Figure 1) or a slightly closer distance of 2.5 Å (light green curve). Clearly, the presence of a nearby anion can strongly affect the interaction of a hydrated electron with a cation.

addition to restraining the distance between the $e_{aq}^-$ center of mass and $Na^+$ using quantum umbrella sampling, we also added a classical restraint to the $Na^+-Cl^-$ distance, $R$, holding it to either the preferred cation−anion contact pair distance ($R$ = 2.8 Å, light blue curve; cf. Figure 1) or to a distance that is slightly closer than the optimal contact pair distance ($R$ = 2.5 Å, light green curve). We found that when the sodium cation is

in a simultaneous contact pair with both a hydrated electron and a chloride ion, the $Na^+-e_{aq}^-$ interaction is slightly destabilized. When the $Cl^-$ anion is forced even closer to the $e_{aq}^-$, there is significant destabilization of the $(Na^+, e_{aq}^-)$ contact pair due to both unfavorable solvation and direct Coulombic repulsion.

All of this explains why hydrated electrons in aqueous perchlorate salts show larger spectral blue shifts than with chloride salts. The presence of multiple nearby cations stabilizes the ground state of the hydrated electron more than the excited states, so $(cation, e_{aq}^-)$ complexes have a blue-shifted absorption spectrum.[19] When the cations are present as perchlorate salts, the anions are separately solvated and do not reside near the electron, so the electron experiences the strongest possible cationic interactions and thus the maximum possible spectral blue shift. With chloride salts, however, there is competitive ion pairing that helps to keep chloride ions near the cations that are in turn interacting with the hydrated electron. The corresponding anion−electron interactions destabilize the $(cation, e_{aq}^-)$ contact pair, negating part of the cation-induced blue shift of the hydrated electron's absorption spectrum.

Finally, the data in Figure 4 also provide an explanation for why the hydrated electron's spectrum shifts by different amounts in the presence of different cations. All the above data suggest that it is not the cation identity alone that determines the spectral shift but the fact that different cations have different propensities to form multiple cation−electron complexes. Figure 4 shows that hydrated electrons prefer to pair with three or four calcium ions but only two or three sodium cations due to the deeper free energy well in the PMF (cf. Figure 3). Thus, it is likely that the presence of the extra paired cation, on average, causes the hydrated electron's spectrum to blue shift more in the presence of $Ca^{2+}$ than in the presence of $Na^+$.

## CONCLUSIONS

In summary, we have explored the way hydrated electrons interact with different aqueous electrolytes by simulating them in concentrated NaCl, Na"$ClO_4$", $CaCl_2$, and Ca("$ClO_4$")$_2$ solutions. We find that the simulated spectral blue shift with the divalent calcium ion is larger than that with monovalent sodium and that the blue shifts with the perchlorate salts are larger than those with chloride salts, in excellent agreement with experiment.[16] We know from previous work that the spectral blue shifts result from the creation of hydrated electron−cation contact pairs that can contain multiple cations interacting with the same electron.[19] Here, we showed that the reason for the ordering of the spectral shifts with different electrolytes is due to competitive ion pairing of the electron and anions with the cations. Chloride anions prefer to stay in contact pairs with small cations so that when hydrated electrons pair with these cations, some of the $Cl^-$ anions come along. This creates ionic complexes that contain multiple cations, a few anions, and a hydrated electron; the repulsive interactions from the anions reduce the net cation-induced blue shift of the electron's spectrum. With perchlorate salts, on the other hand, there is little natural ion pairing with cations, leading to the formation of pure cation−electron contact pairs that experience the full possible cation-induced spectral blue shift.

We also see that the divalent $Ca^{2+}$ ions produce slightly larger spectral blue shifts than $Na^+$ ions not because of their

direct electronic interaction with the hydrated electron but because of their greater free energy stabilization in solution, which leads to a larger number calcium ions simultaneously pairing with the electron than sodium ions with the same anion. The interaction of different electrolytes with hydrated electrons can be well described by invoking the Hofmeister series, where the electron behaves as an anion that is somewhat more able to disrupt water's H-bonding structure than chloride, explaining its role in competitive ion pairing. Overall, hydrated electrons make an excellent probe of the local ionic environment in electrolyte solutions.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcb.2c04463.

Ionic pseudopotentials; pseudo-orbital parameters; cut-off radii and tapering range used for the Steinhauser function; and $Na^+-O$ radial distribution functions for 3.8m NaCl and NaCl"$ClO_4^-$" solutions (PDF)

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### Notes

The authors declare no competing financial interest.

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