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Electrolyte Effects in a Model System for Mesoporous Carbon Electrodes

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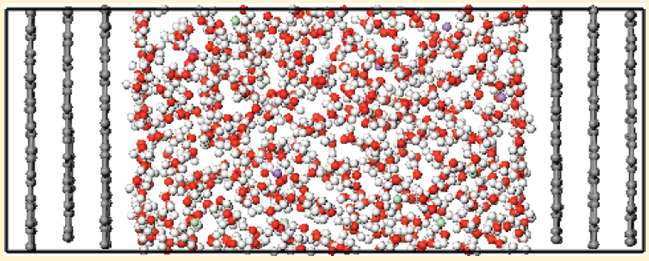
ABSTRACT: In this paper, a variety of alkali halide aqueous electrolyte solutions in contact with planar graphite slit pores are simulated using classical molecular dynamics. Size trends in structure and transport properties are examined by varying the choice of ions. The intermediate atomic weight ions within each group are found to diffuse faster than the larger or smaller ions. System dynamics are driven by changes in water hydration behavior and, specifically, by variations in the number of hydrogen bonds per water molecule. Both the cation and the anion sequences demonstrate that confinement effects can significantly alter the expected trends of alkali halide electrolytes.



INTRODUCTION

One of the key questions for designing electrical energy storage devices with high energy and power density is the choice of electrolytes. In particular, the use of high-surface-area electrodes with meso- and micropores has placed the focus on electrolytes that can diffuse rapidly in confined environments. Aqueous electrolytes, such as alkali halide brines, are appealing because they are inexpensive and display low impedance and high power resulting from the reduced viscosity of the brine.

In bulk solution, alkali halides are distinguished only by subtle changes induced by size. Trends, such as ion pairing, have been well-characterized.[1−4] Generally, these track well with models corresponding to the solvation of Na and Cl salts.[3] When confined, alkali halides have been shown to possess properties that deviate from the expected molecular trends. In addition to reducing solubility, confinement effects can amplify differences between different alkali ions that would be largely indistinguishable in bulk. One such difference is the emphasis on solvent separated ion pairing.[5] It has been established that alkali halides undergo ion-specific effects under confinement, specifically changes in density distributions and horizontal mobilities.[6] In particular, potassium has been shown to have an unusual enhancement in time-dependent capacitance, or, in effect, conductivity.[7] Its role in creating differential capacitance within micropores has been credited with increasing microporous conductivities,[8] which may be useful in the design of future supercapacitor applications. However, there is a need for a study of the systematic trends of alkali halide behavior under confinement by a hydrophobic surface or at a hydrophobic interface.

In this work, the systematic determination of alkali halide properties, such as diffusivities and ion pairing, is investigated. These properties are studied using molecular dynamics in a 4 nm slit pore with atomistically smooth graphene surfaces. The purpose is to compare different alkali halide solutions to determine which possess more desirable characteristics than NaCl as a confined electrolyte for a supercapacitor system.

METHODS

In this study, classical molecular dynamics (MD) was used to determine the qualitative properties of an aqueous, alkali halide brine in contact with mesoscopic slit pores, represented here as graphene sheets, in carbon electrodes. This study used the program Lammps.[9] For the alkali cations (Li, Na, K, Rb, and Cs), the slit size was 4 nm, the concentration was 1 M, and Cl was the counterion. There were a total of 1200 carbon atoms, 555 water molecules, and 10 ions. Similarly, for the halide anions (F, Cl, Br, and I), the slit size was 4 nm, the concentration was 1 M, and Na was the counterion. The pore size was chosen based upon our previous results for a NaCl solution under varying degrees of confinement, which showed an enhancement in diffusivity in 4 nm slit pores.[10] This enhancement was the primary reason for the pore size examined here, as an objective was to maximize the ion diffusivities under confined conditions. The surfaces were left uncharged in this study to provide a baseline for future studies on structure and dynamics at a charged interface.

First, a 100 ps equilibration NVT (NVT: constant number, volume, and temperature) was run. When an MD simulation was performed, the temperature was gradually increased from 0 to 300 K. A 200 ps NPT (NPT: constant number, pressure, and temperature) simulation was then performed at 0 GPa ($P \sim 1$ bar) and 300 K. For all of the simulations, the box had the approximate x and y dimensions of 24.67 and 21.37 Å in the directions of the carbon plane and 56.67 Å perpendicular to it. Although all three boundaries were allowed to vary (<1 Å), the

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Table 1. Force Field Parameters for the Ions

element	mass/amu	charge/e$^-$
Na	22.99	1.00
Cl	35.453	−1.00
Li	6.941	1.00
K	39.0983	1.00
Rb	85.4678	1.00
Cs	132.9055	1.00
F	18.9984	−1.00
Br	79.904	−1.00
I	126.9045	−1.00

	pair coefficients	
Lennard-Jones 12-6 parameters	ε/kcal mol^{-1}	σ/Å
Na	0.1301	2.3502
Cl	0.1000	4.4000
Li	0.1650	1.5050
K	0.1000	3.3310
Rb	0.1000	3.5270
Cs	0.1000	3.8830
F	0.1800	3.1170
Br	0.1000	4.5390
I	0.1000	5.1670

rigidity of the carbon sheets prevented significant variation in the x and y directions. This allowed the water in the simulation cell to reach a density appropriate to the surface conditions. Finally, a 10 ns NVT simulation (T = 300 K) was performed of which 3 ns was used for supplemental equilibration. For the remainder, the position data were sampled and analyzed. The carbon atoms were frozen during this portion of the simulation.[11] Although it is possible to do the calculation with all atoms free, the motion of the carbon prohibitively increases the uncertainties in the calculation of the diffusivities. For details on the simulation methodology, including force field parameters for Na, Cl, H, O, and C, see refs 10 and 12 (and references therein). Parameters for Li, K, Rb, Cs, F, Br, and I ions were taken from papers referenced in the ClayFF work.[13,14] All of these parameters have been summarized in Table 1. Secondary effects, such as the effective charge of electrolyte behavior with decreasing slit size or increased confinement in structures like nanotubes, have not been analyzed specifically here but can be extrapolated from the sodium chloride behavior considering the changes in ion size.[8,10]

RESULTS

Within the two sequences, the differences between the ions were primarily a function of size and hydration. As expected, water−water hydrogen bonding is reduced under confinement, as indicated by the decreased values of the integrated radial density profile between oxygen atoms compared to bulk (Table 2, first column). Under confinement, hydration trends among the ions become clearer and more conspicuous. For example, increasing the size of the cation decreases the hydration of the chloride (Table 2, third column), whereas increasing the size of the anion increases the hydration of the sodium (column 2).

The halide sequence showed a clear trend of decreased ion pairing with increasing anion size, as determined from radial distributions (see Table 2, last column). Ion pairing is reported

Table 2. Integrated Values of the Radial Distribution Profiles and Percentage of Ion Pairing[a]

	O−O	M−O	An−O	An−H	M−An (%)
bulk LiCl	4.742	4.176	7.627	6.780	0.4
bulk NaCl	4.566	5.714	7.587	6.614	12.2
bulk KCl	4.609	8.101	7.286	6.371	27.4
bulk RbCl	4.734	9.487	7.343	6.380	31.1
bulk CsCl	4.480	9.187	6.985	6.168	51.7
bulk NaF	4.738	5.493	5.803	5.738	35.9
bulk NaCl	4.566	5.714	7.587	6.614	12.2
bulk NaBr	4.656	5.703	7.952	6.814	9.4
bulk NaI	4.646	5.791	8.840	7.133	4.2
4 nm slit with LiCl	4.312	4.015	7.354	6.510	5.2
4 nm slit with NaCl	4.282	5.438	7.326	6.391	19.1
4 nm slit with KCl	4.255	7.502	6.816	5.990	42.7
4 nm slit with RbCl	4.239	8.647	6.821	6.022	42.8
4 nm slit with CsCl	4.249	8.914	6.824	6.093	53.1
4 nm slit with NaF	4.296	4.851	5.139	4.943	99.7
4 nm slit with NaCl	4.282	5.438	7.326	6.391	19.1
4 nm slit with NaBr	4.293	5.556	7.647	6.635	10.9
4 nm slit with NaI	4.331	5.685	8.368	6.949	2.9

[a] The integration cutoff is determined by the first minima of the differential radial distribution function. M refers to the alkali metal ion, and An refers to the halide anion.

here as a percentage of the counterions within a radius corresponding to an inner-sphere coordination. The trend is consistent with experimental data, which show an increase in solubility as the anion size is increased. Confinement within a slit pore increases ion pairing for all anions except iodide, which decreases approximately 1%. Note that this small variation is well within the error of the calculations. The confinement effect is quite drastic for NaF, which is almost completely ion-paired, showing an increase of 64%. The solubility of NaF in water is ∼1 M (the concentration used here), so it appears that confinement within a pore significantly facilitates precipitation. The combination of high ion pairing for fluoride and sodium, coupled with the fact that fluoride is a weak base, indicates that NaF is unlikely to provide a sufficient number of free ions to be a useful charge conductor at these concentrations. Correspondingly, the low ion pairing for bromide and iodide is an advantage for these two ions.

The alkali sequence, paired with Cl, displays the opposite trend in ion pairing with respect to cation size. In general, as the size of the cation decreases, ion pairing also decreases. As one would expect, ion pairing increases when the system is confined to a slit pore. This is especially true for the K and Rb ions, which display the largest increases in ion pairing upon confinement with 15% and 12%, respectively. Pairing for LiCl is curiously low even in the confined environment of the slit pore (5.2%), which could indicate its potential utility. The global trends in ion pairing do not strictly follow solubility, which could be the result of a force-field problem similar to one observed for alkaline earth metals.[15] Specifically, the experimental bulk solubility data would suggest an upward trend in ion pairing going from Li to K, where solubility is a minimum. The continuing increase in Rb and Cs ion pairing data indicates that the possible force-field issue is limited to these two heavier ions.

All of the vertical (normal to the graphene sheets) profiles are qualitatively similar to those shown in Figure 1. None of the ions

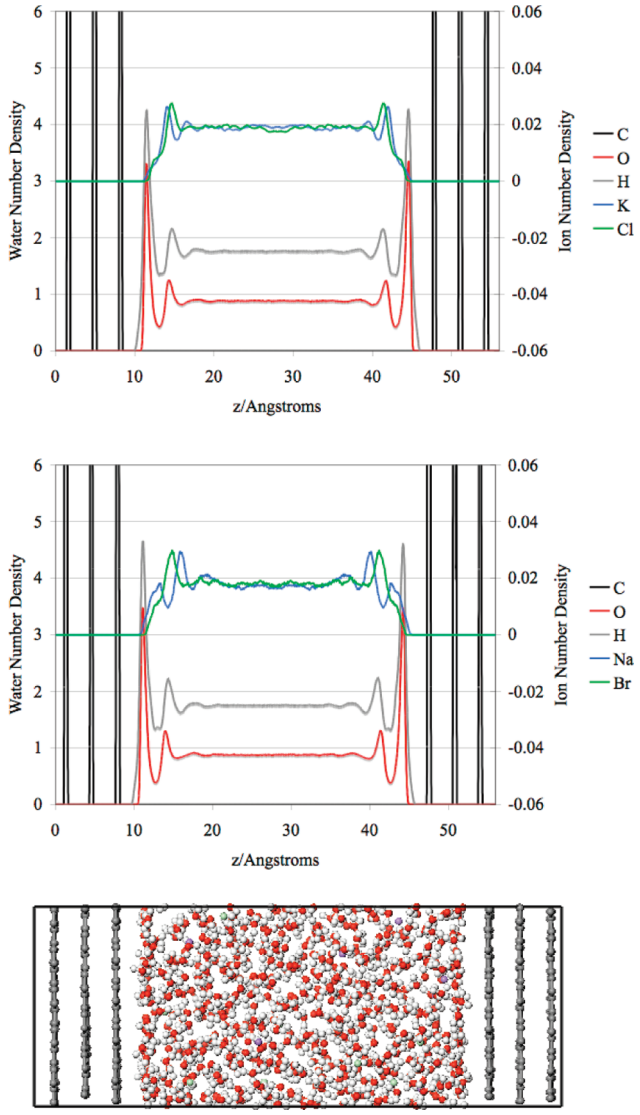

Figure 1. Atomic snapshot of NaCl (bottom) and vertical profiles (top and middle) for the systems investigated. Here, solutions of KCl (top) and NaBr (middle) are shown, which are representative of the two sequences studied. The left axis is for the water, and the right axis is for the ions.

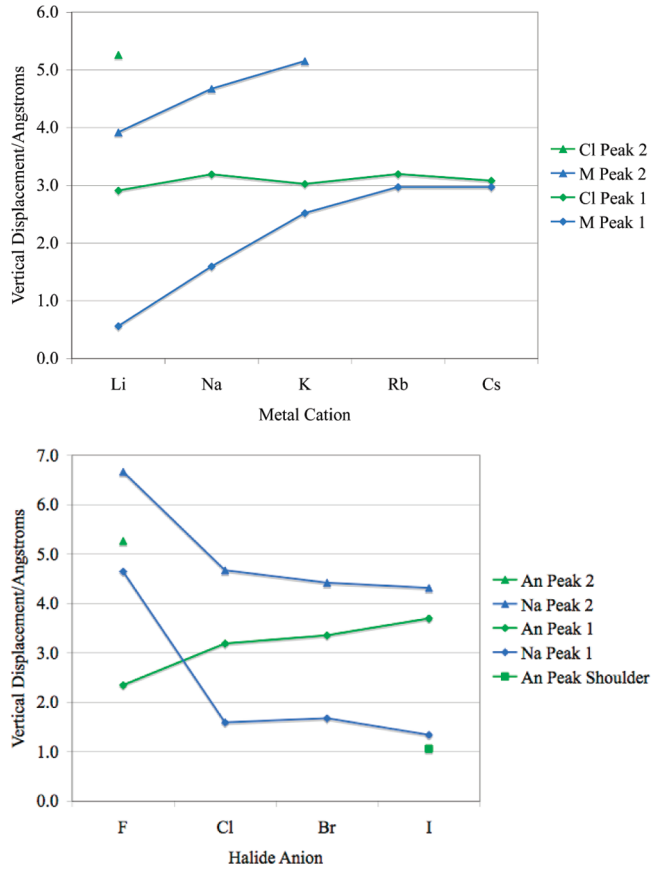

Figure 2. Summary of ion peak positions measured relative to the beginning of the water layer (cations, top; anions; bottom). The differences between Li and F from the other ions are consistent with their role as structure promoters. In general, sodium and chloride peak positions are insensitive to the choice of counterions, excluding ion pairing.

like to inhabit the surface of the brine; ion peaks were all inward (further away from the carbon surface) of the first layer of water atoms. There were differences, however, in terms of the number and placement of the ion peaks relative to the water peaks, indicating the importance of hydration in the formation of ion, structured layers. Figure 2 displays the peak maxima of all electrolytes. The primary driver of peak position was ion size, where the trend is for larger ions to move further away from the surface when the counterion is kept constant. Furthermore, there was generally more vertical structure for the smaller ions than the larger ones. The Na ion was able to fit snugly between the peaks of water molecules, which may be the reason that there was slightly more vertical structure for the sodium halides than the alkali chlorides. Excluding the effects of ion pairing, changing the alkali ion had almost no effect on the peak position of the chloride ion (top), or vice versa, changing the halide had little effect on the position of the Na ion (bottom). Looking specifically at the halide graph, fluoride is the exception to this where two clear sets of ion pairs drastically shift the position of the sodium peaks. There are other properties of fluoride that could be expected, such as its role as a structure promoter, but the ion pairing masks these. In the other systems, the effect of ion pairing on the vertical profile is much less pronounced. As an aside, in NaCl, increasing concentration increases the number of structured peaks. There is a second chloride peak, which appears at 4 M beyond the second sodium peak, as was the case with fluoride. There is a prominent shoulder present in iodide, which occurs before the first chloride peak. This is feature also exists for both chloride and bromide, but to a lesser extent. As the anion increases in size, it moves outward, allowing for more ions to inhabit the first water peak, a position that is less favored than the second water peak. Overall, for many of the larger ions, the amount of charge separation of ions at the interface is significantly reduced relative to their smaller counterparts.

The diffusion profiles in a 4 nm slit pore for both the alkali and the halide ions are shown in Figure 3. In all cases, these diffusivities are driven primarily by horizontal motion with the vertical components (perpendicular to the carbon surface) being significantly smaller and similar for all ions. Chloride's diffusivity did not change substantially with the choice of alkali ion (top-left panel). Interestingly, potassium shows a significant rise in diffusivity relative to the other cations, which corresponds to a

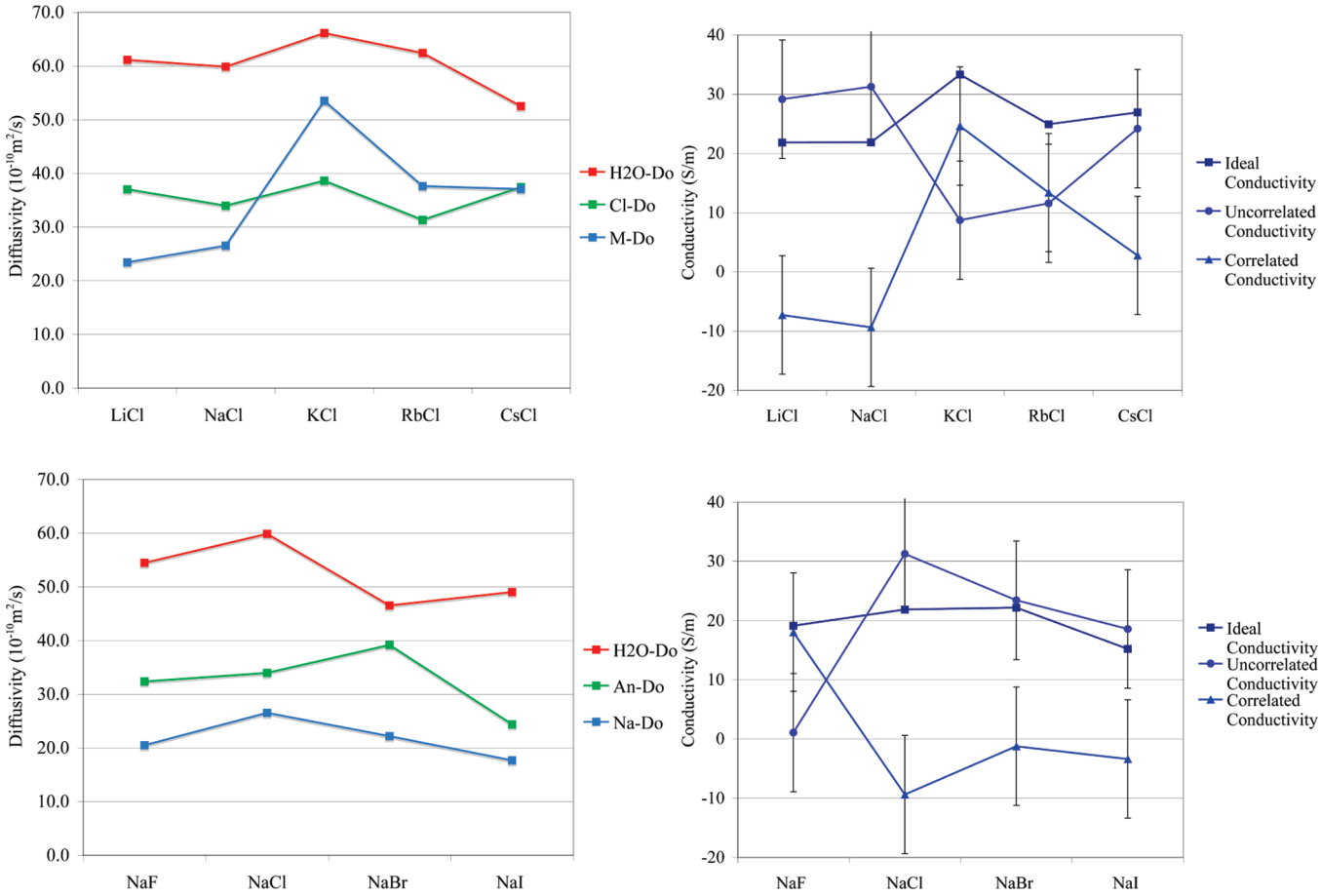

Figure 3. Diffusivity (left) and conductivity (right) profiles by ion in a 4 nm slit pore (top, cations; bottom, anions). The error bars associated with the diffusivity calculations are smaller than the data points.

minimum of chloride hydration (Table 2, fourth column). It also correlated with a lowering of water−water hydrogen bonds relative to the sodium chloride solution in the slit (Table 2, first column). These two properties have already been shown to correlate for sodium chloride under confinement.[10,16] Increased conductivity has been confirmed experimentally in a comparison of time-dependent capacitance of cations in nanoporous carbon structures, which shows an enhancement of current for KCl in pores around 0.7 nm in diameter.[7] This experiment also reports the anomalous behavior of potassium relative to the other alkali metals found here.

When paired with different halides, sodium ion's diffusivity also shows a slight quadratic dependence (Figure 3, bottom-left). The trend for the anions is relatively muted with only a slight rise for both chloride and bromide versus fluoride and iodide, which can be understood in terms of the opposing trends between water−water hydrogen bonding and ion pairing (Table 2, first and last columns). The water−water hydrogen bonding is only weakly affected by ion choice compared to confinement.[10] Ion pairing is near unity for NaF, so one would expect diffusivities to be lower. At the opposite extreme, ion pairing is extremely low for NaI; however, hydration is at a maximum, leading to decreased diffusivities. In between, chloride and bromide experience moderate amounts of both effects and exhibit slightly higher diffusivities as a result. This highlights the important role that both water−water hydrogen bonding and ion pairing jointly have on ion diffusivity, leading to a quadratic trend for both cations and anions favoring the moderate-sized ions (Na, K, Cl, and Br). Furthermore, both the cation and the anion sequences nicely demonstrate that confinement effects can significantly alter the expected trends in alkali halide behavior.

The trends in conductivity mirror the quadratic trend seen in the diffusivity coupled with ion pairing effects (see Figure 3). There are three types of conductivity calculated here: the first is the ideal or diffusion-based conductivity, the second is the correlated conductivity (the extent to which the cation and anion motion is in the same direction), and the third is the uncorrelated conductivity (the difference between ideal and correlated).[10,17] At 10 ns, the behavior seems to qualitatively track ion pairing. In excess of 40% ion pairing (KCl, RbCl, CsCl, and NaF), much of the conductivity behavior is correlated. This is particularly striking for sodium fluoride, which has ∼100% ion pairing and a similar percentage of correlation. For ion pairs with less than 40% pairing, the correlated results were generally negative and all were within uncertainty of zero, suggesting little correlation. This contrasts with our previous results on sodium chloride for only 2 ns, where we calculated a positive correlation, indicating that behavior over these two time scales appears to be governed by different processes.[10]

The difficulty with calculating correlated conductivity is that, over various time scales, the degree of correlation can vary substantially due to changing influences during the course of the simulation. This variability and time scale dependence is enhanced when under confinement. For long equilibration times,

the result is a fairly large uncertainty in the calculated value of the correlated conductivity, and as a result, the uncorrelated portion of the conductivity as well. The equilibration time for these properties depends on the interacting behavior of both species and can vary significantly from system to system. For example, the equilibration time for Cs was much longer than for the other ions, highlighting some of the difficulties experienced when calculating properties in confined environments. Indeed, we even observe some variation in the value of the diffusivity calculated at 2 and 10 ns, suggesting that the confined dimension is influencing the mean-squared displacement over longer time scales. This is consistent with the hydrologic expectation of diffusion behavior, which, over longer time scales, shows a greater extent of fluid flow perturbation when in contact with a grain boundary than the atomic scale influences seen in these simulations. Exploring these subtleties is a direction of future research.

For the cations, the trend in ideal conductivity mirrors experimental results that have been reported for approximately 1 nm size pores confirming the importance of the electrolyte.[7] Although this is smaller than the pores we studied, the probable absence of counterions will generate a comparable degree of confinement with respect to relative length scales and likely produce qualitatively similar effects. In a small charged pore, counterions will be excluded because of pressure effects,[16] and the observed time-dependent capacitance of a pore should reflect the single ion ideal diffusivity. The anion conductivities show a more muted trend but still possess the same quadratic dependence with intermediate ions displaying higher ideal conductivities. The ions with the highest diffusivity within their sequences, sodium and potassium (excluding Rb and Cs for reasons noted earlier) and chloride and bromide, all show low correlation in their conductivity with the exception of potassium. Potassium has a substantial amount of correlation present due to higher ion pairing, which suggests that both the cation and the ion are diffusing rapidly in concert. The size of the ion is likely to be one driver of this trend, which is coupled strongly to ion pairing. The other driver is likely the water−water hydrogen bonds. Ultimately, these effects are smaller than those of confinement, like changing pore size and shape.

CONCLUSIONS

Many of the ions show distinct behavior relative to the baseline of the NaCl brines. Lithium displays particularly good ion pairing behavior, but because of relatively high water−water hydrogen bonding, does not display a high conductivity. Potassium shows some particularly interesting properties relative to sodium electrolyte brine, and for certain applications, the benefits may outweigh the costs. Fluoride is a particularly bad choice, as it is likely to precipitate fully in the slits under low bias conditions. Bromide is at least as good a conductor as chloride, but iodide displays lower conductivity despite the low ion pairing results. Although the slit pore size employed here is on the cusp of what would be expected for an interfacial system and that of a confined environment, the results are still useful for setting a baseline for supercapacitor systems. Most of the ions show promise as high-power delivery electrolytes for use in an electric double-layer-type supercapacitor.

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