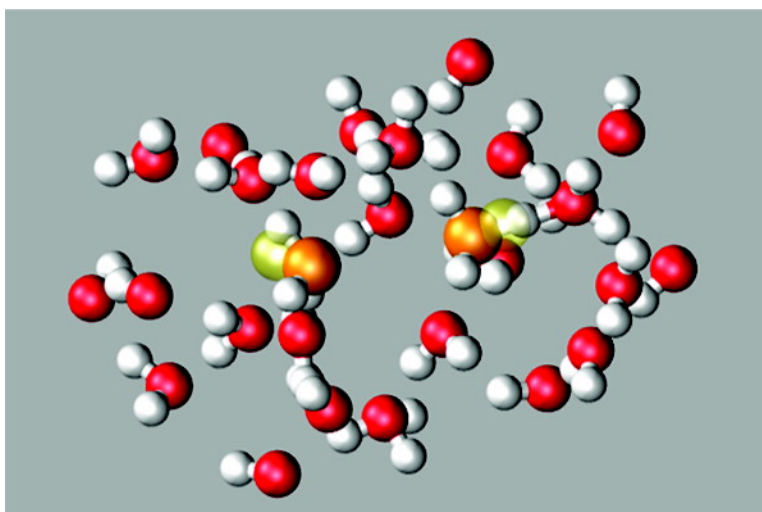


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Unusual “Amphiphilic” Association of Hydrated Protons in Strong Acid Solution

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Abstract: The solvation structure of the hydrated excess proton in concentrated aqueous HCl solution is studied using the self-consistent iterative multi-state empirical valence bond method. At 0.43–0.85 M concentrations, hydronium cations are found to form unusual cation pairs. This behavior is consistent with our earlier finding that hydronium cations can have an “amphiphilic” character due in part to the asymmetric nature of their hydrogen bonding to nearby water molecules. The existence of these hydronium amphiphilic pairs is further supported by a Car–Parrinello ab initio molecular dynamics simulation at 1.0 M HCl concentration. It is also found that the hydronium cation pairs are stabilized by a delocalization of the hydrated excess proton charge defects involving additional water molecules. At the higher concentrations of 1.68 and 3.26 M, the abundance of such hydronium pairs decreases, and the analysis of the radial distribution functions indicates the possible formation of an aggregate structure with longer-ranged order.

Introduction

Proton solvation and transport in aqueous acid solutions is a fascinating fundamental problem that has been studied for more than 200 years.^{1–10} Indeed, aqueous excess protons are essential in many areas of chemistry, biology, and materials science. It has been widely accepted that it is impossible to identify a proton with a unit positive charge in aqueous solution. Even the model of a unit positive charge carried by a hydronium cation is not correct (though oddly enough, this model is often employed in classical molecular dynamics (MD) simulations based on empirical potential energy functions). For example, Figure 1 depicts the excess charge distribution of a H_9O_4^+ cluster in an environment of implicit water molecules treated using the PCM method.¹¹ Both the geometry optimization and the electron density analysis were done using the aug-cc-pvdz basis set¹² at the QCISD level of theory.¹³ The partial charges were deter-

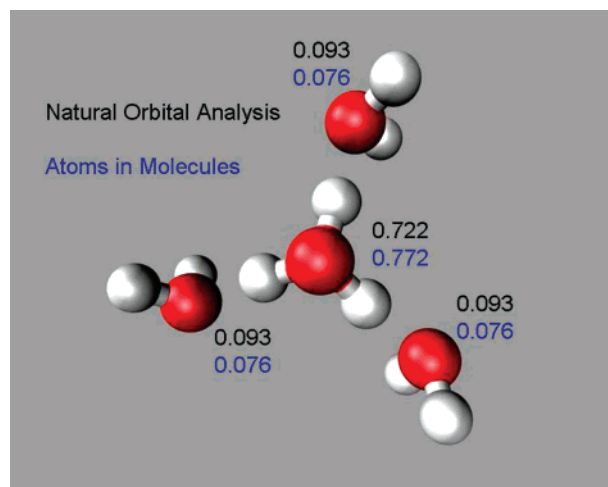


Figure 1. Ab initio partial charges on hydronium and first solvation shell water molecules as determined using the natural orbital analysis and Bader’s atoms in molecules method. This structure represents the Eigen cation, H_9O_4^+ , surrounded by a polarizable continuum model (PCM) boundary to represent the aqueous environment in the electronic structure calculations. The excess proton charge is seen to be significantly delocalized over the four water molecules constituting the Eigen cation.

mined using both the natural orbital analysis method¹⁴ and Bader’s atoms in molecules method.¹⁵ It is apparent from Figure 1 that the charge carried by the excess proton is delocalized over several water molecules, in agreement with the generally accepted picture for aqueous proton solvation.^{7–10} This charge

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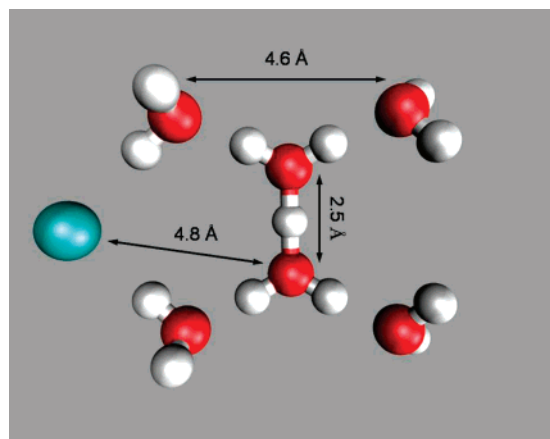


Figure 2. Schematic picture showing the structural motif responsible for the $\text{HCl}\cdot(\text{H}_2\text{O})_6$ structure. The bond lengths shown are estimates based on the RDFs from the SCI-MS-EVB simulation. The blue sphere is a Cl^- anion.

delocalization in turn leads to interesting solvation and transport features that are impossible to model using traditional MD based on nondissociable empirical potentials.^{8–10}

HCl solvation structures have been studied by experimentalists and theoreticians alike.^{16–21} While at least 10 and 13 water molecules are needed to “solvate” one and two HCl molecules, respectively, in the gas phase,¹⁸ HCl dissolves in liquid water up to a 1:3 molar ratio of acid to water.^{19,20} In fact, experimental measurements for HCl solutions ranging from the concentrated 1:3 mixture to infinite dilution have been performed.¹⁶ Figure 2 shows a structural motif that is capable of solvating one HCl molecule by six water molecules. It has been proposed that such a structure polymerizes at a 1:6 concentration and instead forms a long-range ordered structure.¹⁹ This long-range order is not only in agreement with experimental X-ray measurements but also consistent with the observation of a drop in experimental proton diffusion constants at higher concentrations.²² By contrast, at concentrations far below the 1:6 molar ratio but higher than infinite dilution, a clear picture of the microscopic solvation structure of HCl has not yet been established and this will be the focus of the current study. Surprising results are indeed found concerning a unique ion pairing behavior of the hydrated protons.

MD simulations have been routinely employed as an important supplement to experimental studies on the structural and dynamical properties of various systems, helping in associating average atomic arrangements with peaks in the experimental radial distribution functions (RDFs). However, the application of MD simulations to proton solvation and transport has its own well-documented challenges. Simulations based on traditional empirical force fields typically lack the ability to describe the above-mentioned charge delocalization of hydronium cations. More importantly, a hydrated proton, often referred to as a hydronium cation, can move from one water solvation shell to another via Grotthuss shuttling of the partial charge distribution

and bonding arrangement of the neighboring water molecules. Such dynamic charge and bonding topology redistribution corresponds to valence bond rearrangements and atom identity shifts in the molecular dynamics picture that are missing from a treatment using traditional empirical force fields. The inability of such force fields to capture the charge redistribution phenomena can in turn lead to unphysical intermediates in the solvation structure and may confuse assignments of peaks in RDF functions. The dynamics of the proton transport will also not be properly captured.

In order to enable a force-field-based approach to simulate proton solvation and translocation, several groups have designed extensions to traditional force fields in order to capture the charge delocalization and Grotthuss shuttling phenomena.^{8,9,23–41} The multi-state empirical valence bond (MS-EVB) model^{8,9,23,26–28,31–33,36–41} is a deterministic MD method that incorporates these phenomena. It has been extensively validated and applied to numerous systems.^{8,9} The MS-EVB method treats proton solvation and transport by diagonalizing matrices in which each bonding connectivity (topology) in a classical picture is a “basis state”, referred to as an EVB state. The lowest eigenvalue of the EVB matrix for any given configuration of the nuclei gives the total energy, and its eigenvector reflects the likelihood of each of the bonding topologies. The latter can be interpreted as providing the probability that the excess proton is bonded to any given water molecule (the “most probable” hydronium), when in reality the true system is an instantaneous mixture of various bonding topologies with the excess proton being associated with multiple water molecules through Grotthuss shuttling and charge delocalization. The derivatives of the lowest eigenvalue with respect to the coordinates provide the forces for the MS-EVB MD algorithm. The self-consistent iterative multi-state empirical valence bond (SCI-MS-EVB) method⁴⁰ is a generalization of the MS-EVB model that allows for the treatment of solvation and the transport of *multiple* excess protons under intermediate to high acid concentrations at an affordable computational cost. The method is not only computationally efficient but it also scales linearly with the number of protons in the simulation box. The SCI-MS-EVB method will be extensively utilized in the present study.

Another method frequently used for describing proton solvation¹⁰ is the Car–Parrinello MD (CPMD) method.⁴² CPMD

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solves the Kohn–Sham equation on the fly using an extended Lagrangian approach and is in principle capable of capturing the above-mentioned proton charge delocalization and shuttling behavior. If a sufficiently accurate exchange correlation density functional could be found and employed, the CPMD simulation would also produce accurate results. However, the CPMD method is far more expensive than the SCI-MS-EVB method, so obtaining statistically converged results for either structural or dynamical properties of complex systems can be very challenging. As a result, in this paper CPMD simulations are used to provide supporting results for our primary SCI-MS-EVB simulations.

SCI-MS-EVB Simulation Details

There are currently three different parameterizations of the MS-EVB model, denoted MS-EVB1,^{26,28} MS-EVB2,³⁸ and MS-EVB3.⁴¹ The recently developed MS-EVB3 parameterization is based on a more accurate underlying water model⁴³ and is the most successful at conserving the total system energy in an MS-EVB simulation. In this study, the MS-EVB3 parameterization was therefore employed.

Cubic simulation boxes containing 256 water molecules and 2, 4, 8, and 16 HCl pairs were used to model aqueous HCl solution at concentrations of 0.43, 0.85, 1.68, and 3.26 M, respectively. The volumes of the boxes were adjusted to reflect the experimental density at all the concentrations studied. The bound molecular HCl EVB state was not included in the SCI-MS-EVB treatment since the presence of these states is assured to be negligible even for the most concentrated strong acid system simulated in this study.⁴⁴ The Cl[−] anion was modeled as a negatively charged van der Waals sphere with its parameters taken from our previous study.⁴⁰ Since the MS-EVB3 potential has Lennard-Jones interactions between hydronium hydrogens and the other ions, a Lennard-Jones potential is also added between the hydronium hydrogen and Cl[−], such that $\sigma_{\text{HH-Cl}^-} = 2.650 \text{ \AA}$ and $\epsilon_{\text{HH-Cl}^-} = 0.028 \text{ kcal/mol}$.

These parameters were chosen so as to make HCl a strong acid while allowing a negligible amount of Lennard-Jones interaction between hydronium hydrogen and Cl[−] beyond the first solvation shell. This choice of parameters reproduces the experimental RDF between hydronium hydrogen and Cl[−]. The Ewald summation method was employed in all cases. Each system was equilibrated for 500 ps at 298 K in the canonical (constant NVT) ensemble using a Nosé–Hoover thermostat⁴⁵ with a relaxation time of 0.5 ps. Then, results were obtained from microcanonical (constant NVE) simulations following the same procedure described in our previous study.⁴⁰ The length of the constant NVE SCI-MS-EVB simulation was chosen such that the simulation time in nanoseconds multiplied by the number of excess protons in the system was no less than 8 ns. A 0.5 fs MD time-step was used in all cases.

In an MS-EVB simulation, the excess proton is shared by multiple water molecules simultaneously and a water oxygen atom within that complex typically has no more than a 65% chance of being protonated as a classical hydronium-like structure. For a single excess proton simulation, identification of the instantaneous hydronium-like oxygen (the oxygen with the largest EVB amplitude) is an acceptable approach. However, such an approximation is no longer valid for a multiple excess proton simulation. For a system containing four excess protons, the state in which each hydronium oxygen is identical to the “most probable” hydronium oxygen only gets a $(65\%)^4 = 18\%$ weight. This complication makes it more difficult to calculate an RDF for a system containing more than one excess proton. One must instead calculate the state-averaged RDFs. In doing so, an RDF for each state is

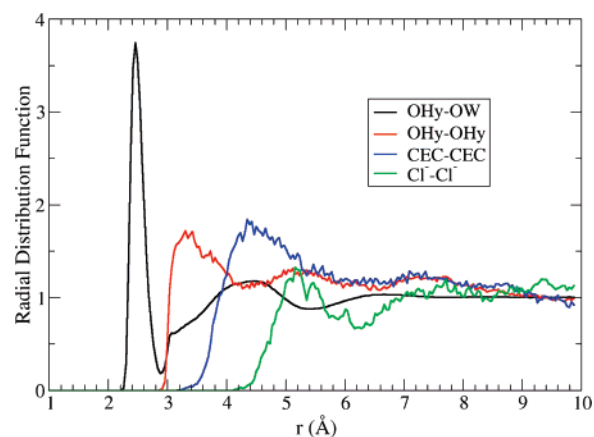


Figure 3. OHy–OW, OHy–OHy, CEC–CEC, and Cl[−]–Cl[−] RDFs from the 0.43 M HCl simulation using the SCI-MS-EVB method. OHy denotes hydronium oxygen atoms, OW denotes water oxygen atoms, and CEC is the hydrated proton center of excess charge. See text for more details.

calculated and a linear combination taken of all the RDFs with the weight of each RDF being the same as the weight of the corresponding state. The inclusion of all possible EVB states is a daunting task, since each proton on average contributes to 23 states. An RDF for 2 protons will need to include 529 states, and an RDF for 16 protons will need to include 6.1×10^{21} states. Thus, only the most important states (the states with highest weight) are included in the RDF averaging. For the 2 proton simulation, the most important 8 states were included; for the 4 proton simulation, 16 states were included; and for the 8 proton simulation, 64 states were included. For the 16 proton simulation, 8 of the 16 protons were randomly picked for the purpose of calculating RDFs and only 64 states were included. We chose the number of states as above so that for the 2 and 4 excess proton systems, the relative weight of the least important state included over the most important state was 10%. For the 8 excess proton and 16 excess proton systems, that relative weight was less than 15%.

Excess Proton Solvation Structure at 0.43 M HCl Concentration.

In the following discussion, the hydronium oxygen will be abbreviated as OHy, the water oxygen as OW, and the hydrated proton center of excess charge²⁶ as CEC. The CEC is an important quantity that characterizes the instantaneous location of the center of the delocalized excess proton charge, much in the same way that a center of mass variable characterizes the location of a distribution of masses. The CEC may also be treated as a “coordinate” for the excess proton charges, and hence, statistical distributions such as RDFs for this coordinate may be calculated.

Figure 3 shows the OHy–OHy, OHy–OW, CEC–CEC, and Cl[−]–Cl[−] RDFs for 0.43 M HCl solution. The first striking feature of Figure 3 is that the most prominent peak in the OHy–OHy RDF is at 3.3 Å, whereas the first peak in the Cl[−]–Cl[−] RDF is at 5.2 Å, coinciding with the second peak in the OHy–OHy RDF. A strong peak at 3.3 Å is quite interesting considering that the first peak (the close contact peak) in the OHy–OW RDF is at 2.5 Å and the second peak (the water-solvent-separated peak) in the OHy–OW RDF is at 4.6 Å. The separation of 3.3 Å is therefore nearer to the close contact peak in the OHy–OW RDF than the water-separated peak, thus indicating that there is not enough space for even one water molecule to be between the two hydronium cations in that region. This finding is quite surprising, considering the strong electrostatic repulsion that would act between a pair of point charges at this separation.

It is also interesting that the onset in Figure 3 of the first OHy–OHy peak at 3.3 Å immediately follows a depression in the OHy–OW RDF. Since the hydronium cation has positive partial charge, it is energetically unfavorable for the hydronium oxygen to be a proton acceptor. This makes it energetically unfavorable for water to be at the oxygen lone pair side of the hydronium. The origin of the depression

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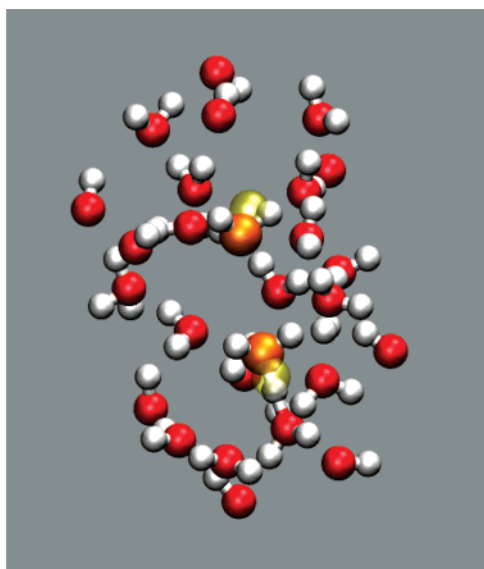


Figure 4. Representative configuration from the 0.43 M SCI-MS-EVB simulation showing two hydronium cations joining their hydrophobic regions together behind their oxygen atoms (orange spheres) to form an amphiphilic ion pair. The two excess proton CECs (semitransparent yellow spheres) move away from each other so as to minimize the electrostatic repulsion.

in the OHy–OW RDF has been attributed to this being the “hydrophobic” side of the hydronium,⁴⁶ so the hydronium cation can be considered to be an “amphiphilic” cation.⁴⁶ This concept has led, for example, to the prediction that hydronium cations may be enriched at the boundary of an acidic aqueous solution with a low dielectric medium such as the water–vapor interface.⁴⁶ In turn, this suggests that the surface of acidic aqueous solution has an effectively lower pH than the bulk region,⁴⁶ a result that has been revisited several times through additional simulations using more primitive classical hydronium models.^{47,48} Recent experimental support has also been provided for the surface enhancement of hydrated protons in acidic solution.^{49–52} Our prediction of an effectively lower interfacial pH has also recently been extrapolated to the surface of neutral water by Buch et al.,⁵³ although the latter authors utilized indirect computational modeling that remains to be validated.

The onset of the 3.3 Å peak in the OHy–OHy RDF from the present simulations indicates that a hydronium cation is occupying the hydrophobic oxygen side of another hydronium, thus forming an unusual contact ion pair (CIP) between two cations. Moreover, since the CIPs are formed by joining the hydrophobic sides of the hydronium cations together, such an arrangement is actually a coalescence of two amphiphilic (albeit positively charged) species in aqueous solution. Figure 4 shows a snapshot that is representative of such configurations, and clearly the hydronium cations have their “hydrophobic” oxygen sides facing each other, thus supporting this conclusion.

Additional Evidence from Car–Parrinello MD Simulation. In order to further confirm the hydronium ion pairing behavior observed in the SCI-MS-EVB simulations, a CPMD simulation was carried out using a plane-wave basis set with an 80 Ry cutoff and the HCTH/120

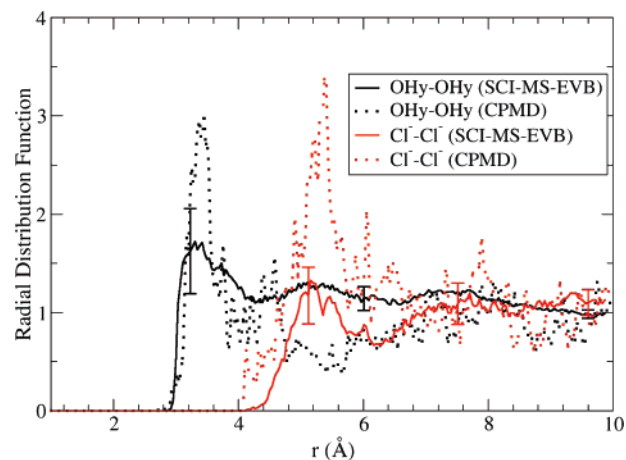


Figure 5. Comparison of the OHy–OHy and Cl[−]–Cl[−] RDFs calculated using the SCI-MS-EVB and CPMD methods, respectively.

exchange correlation functional.⁵⁴ The fitting set for this functional includes hydrogen-bonded complexes that increase the reliability of the condensed phase simulations of the hydrogen-bonded liquids.^{55,56} The system was integrated with a time step of 3 au.

In the CPMD simulation, the excess protons were identified using a geometry-based method best described as a “water molecule elimination process”. In this procedure the oxygens were picked one by one and then were eliminated together with their two closest hydrogens. At the end of this procedure two protons were left, and these protons were identified as excess protons. The oxygen that was closest to an excess proton was identified as the instantaneous hydronium oxygen in the CPMD simulation.

Due to the high cost associated with CPMD simulations, it was not practical to start from an arbitrary configuration and run CPMD for an extended period of time to sample all configurations having amphiphilic hydronium pairs. The CPMD simulation was therefore started from an SCI-MS-EVB configuration in which the hydronium pair had been formed. Additionally, simulation of the 0.43 M HCl concentration would require a box containing at least 256 water molecules, which is very large for a CPMD simulation, so a cubic box containing 110 water molecules, two excess protons, and two chlorine anions was simulated instead at a 1.0 M HCl concentration. The CPMD simulation was equilibrated for 5 ps using a simple velocity rescaling method to maintain the target ionic temperature of 300 K. The production run was then carried out in the microcanonical ensemble for 72 ps. The average ionic temperature during the microcanonical simulation was $T = 303$ K. Monitoring of the distance between the hydronium oxygens during the 72 ps period indicates that the ion pair dissociated and reassociated several times, thus ruling out the possibility of the system being completely trapped in a single hydronium pair arrangement. The dissociation and reassociation events were signified by jumps in the hydronium oxygen separation between first and second solvation shells of more than 2 Å. The average lifetime of the ion pairs was 15 ps. This is a rough estimate given the relatively short length of the CPMD trajectory, but it is to be compared with the lifetime of approximately 1 ps for excess proton hopping (translocation events) between two water molecules in CPMD simulations of a single excess proton in water.

Figure 5 compares the OHy–OHy and Cl[−]–Cl[−] RDFs calculated using the CPMD method at 1.0 M concentration with the SCI-MS-EVB result at 0.43 M concentration. The location of the peaks is in excellent agreement. The intensities of the peaks, on the other hand, do not agree as well, but this is expected given the sizable error bar

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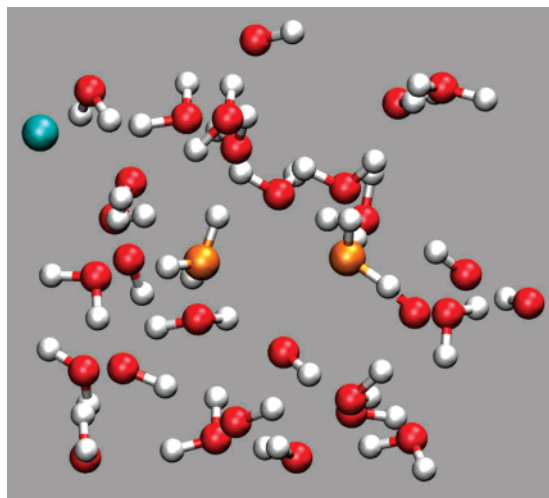


Figure 6. Representative configuration from the 1.0 M CPMD simulation showing two hydronium cations joining their hydrophobic regions together behind their oxygen atoms (orange spheres) to form an amphiphilic cation pair. The blue sphere is a Cl^- anion.

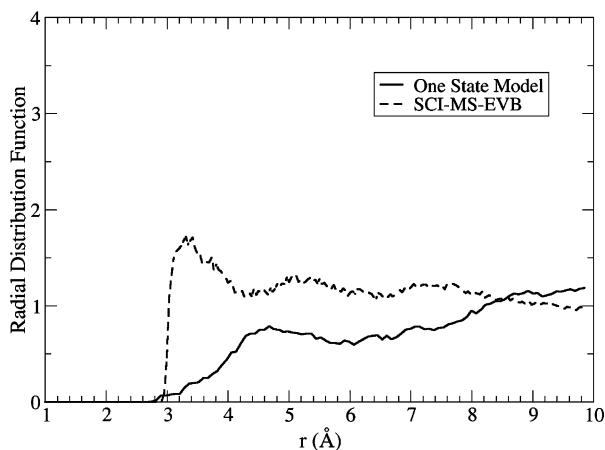


Figure 7. OHy–OH_y RDF for 0.43 M HCl solution from a simulation using a one-state EVB (classical hydronium) model, in which excess proton charge delocalization is impossible. The dashed line is the corresponding result obtained from the SCI-MS-EVB calculation.

associated with even the SCI-MS-EVB simulation, which was 4 ns long. The error bar on the 72 ps CPMD RDF could not be reliably estimated but is certainly larger. The CPMD simulation also shows a higher peak intensity because it was started from a paired initial configuration, so the simulation likely did not spend as much time sampling the configurations in which the two hydroniums are well-separated.

Despite the above caveats, inspection of the CPMD configurations responsible for the CIP peak at 3.3 Å in Figure 6 again reveals a similar amphiphilic association of two hydronium ions as seen in Figure 4 from the SCI-MS-EVB simulation. Although the peak height in the CPMD RDF is not converged, the CPMD simulation did indicate that appreciable stability is associated with the hydronium ion pairs. This behavior is thus not likely to be an artifact caused by the SCI-MS-EVB method or the MS-EVB3 model parameterization.

Role of Protonic Excess Charge Delocalization. Both the SCI-MS-EVB and CPMD simulations indicate that the unusual hydronium pair stabilization somehow overcomes the repulsion between the positive charges of the cations. It is important to determine whether this effect is simply a classical hydrophobic effect due to the asymmetry of the hydronium cation and its resulting perturbation of the underlying water structure⁴⁶ or whether nonclassical delocalization of the excess protonic charge defects plays an additional stabilizing role. This question

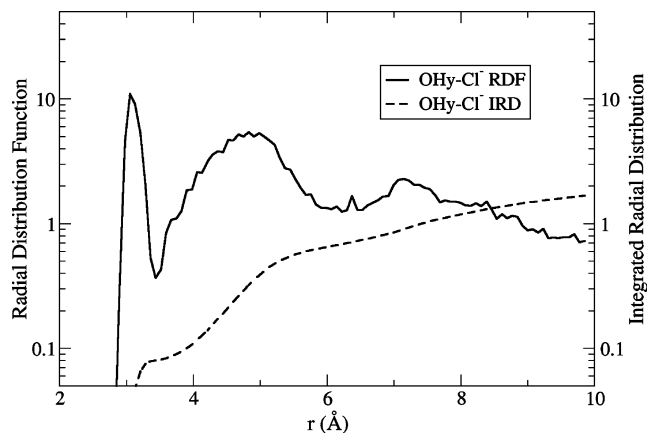


Figure 8. OH_y–Cl[−] conditional RDF (solid line) for configurations calculated with OH_y–OH_y separations below 4 Å. The dashed line plots the integrated radial distribution (IRD) number of OH_y–Cl[−] pairs as a function of separation.

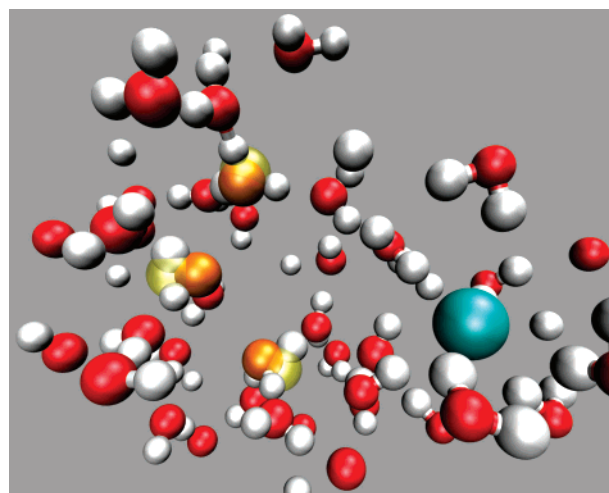


Figure 9. Snapshot from the 0.85 M SCI-MS-EVB simulation showing three hydronium cations forming a three-hydrated proton cluster. The semitransparent yellow balls are the positions of the three CECs, which again arrange themselves to minimize their electrostatic repulsion. The blue sphere is a nearby Cl^- anion.

was addressed by calculating the OH_y–OH_y RDF using a one-state MS-EVB model where charge delocalization is suppressed (i.e., a classical hydronium model). This is identical to a simulation using a traditional empirical force field that is unable to capture the charge delocalization and Grotthuss hopping phenomena of a solvated hydronium species, as is often done.^{47,48,53} Figure 7 shows the RDF calculated using such a classical hydronium model. Although there is still a finite probability of seeing two hydronium cations get as close as 3.3 Å, it is much less probable compared with the full SCI-MS-EVB results. The inability of a classical hydronium model to delocalize the excess protonic charges must therefore significantly reduce the stability of amphiphilic hydronium cation pairs. Indeed, as shown in Figure 3, the first peak in the CEC–CEC RDF (as opposed to the OH_y–OH_y RDF) is actually around 4.3 Å in the full SCI-MS-EVB simulations, rather than 3.3 Å, which corresponds to the first peak in the OH_y–OH_y RDF. It has been shown in previous studies³⁸ that the position of a single excess proton CEC in water is usually very close to the position of the hydronium oxygen. However, as shown in Figure 4 by the semitransparent yellow balls (CEC locations), when a CIP is formed between two hydronium cations the separation between the CECs is shifted to be approximately 1 Å larger than the separation between the hydronium oxygens and hence the electrostatic repulsion is effectively reduced. The unusual hydronium cation pairing observed in the present work is

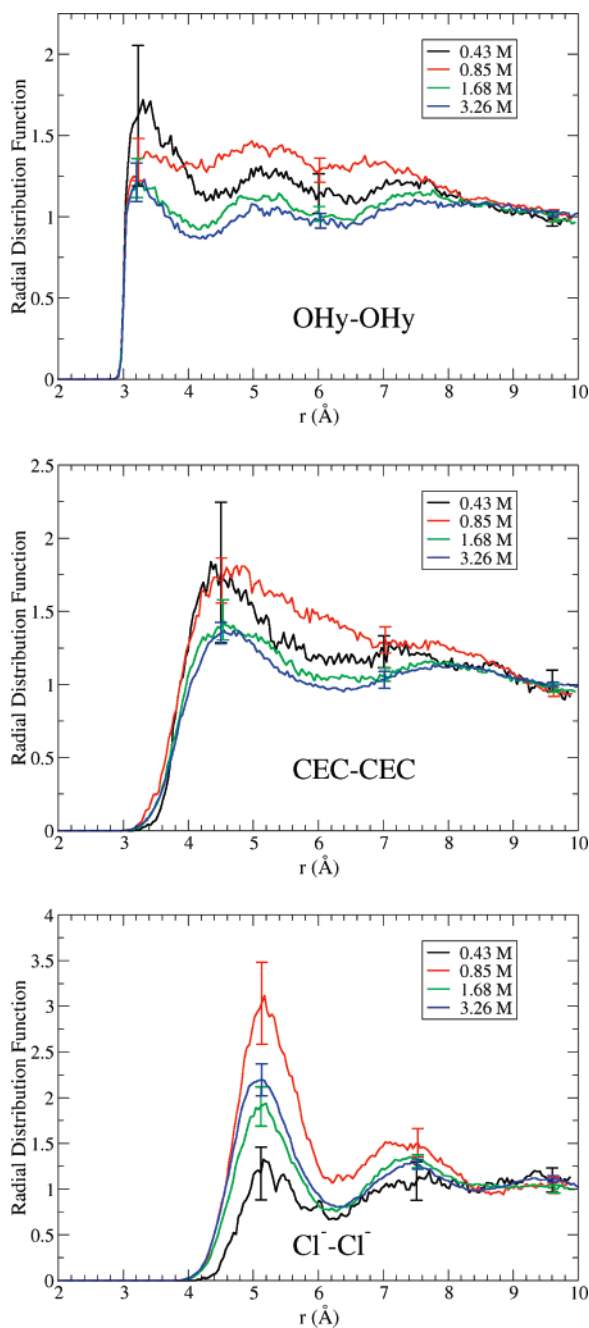


Figure 10. OHy–OHy, CEC–CEC, and Cl[−]–Cl[−] RDFs for 0.43, 0.85, 1.68, and 3.26 M HCl solutions simulated using the SCI-MS-EVB method.

therefore attributed to a unique combination of the hydronium amphiphilic character⁴⁶ and the ability of the excess proton charge defects to delocalize across multiple water molecules, the latter effect being a nonclassical behavior which is essential to the cation pair stability.

Since the hydronium CIP has a positive net charge, Cl[−] ions are enriched in regions close to these pairs and also contribute to their stabilization. Figure 8 shows the conditional OHy–Cl[−] RDF calculated from configurations when a OHy–OHy distance is less than 4 Å. The resulting conditional RDF integrates to give the dashed curve. For each hydronium, there is, on average, found to be 0.6 Cl[−] ions within the distance of the second solvation shell of the hydronium.

The quantum nuclear effect of the hydrogen atoms was ignored in both the MS-EVB and CPMD simulations as these effects have only a minor influence on the RDFs that is smaller than the error bars.³⁸ Nuclear quantum effects are, however, known to delocalize the excess proton to some degree and thus enhance the Zundel-like cation

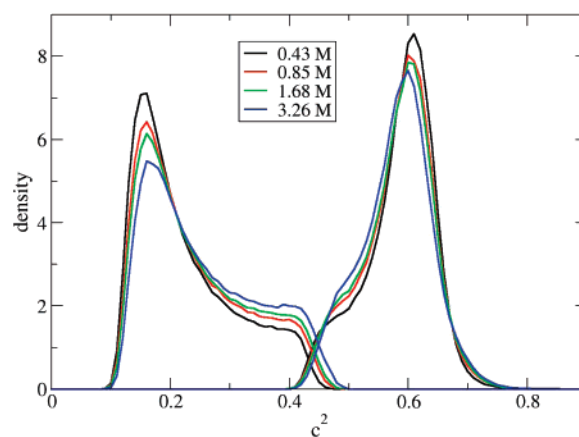


Figure 11. Distribution of the largest two SCI-MS-EVB amplitudes, c_1^2 and c_2^2 , for HCl solutions at concentrations of 0.43, 0.85, 1.68, and 3.26 M.

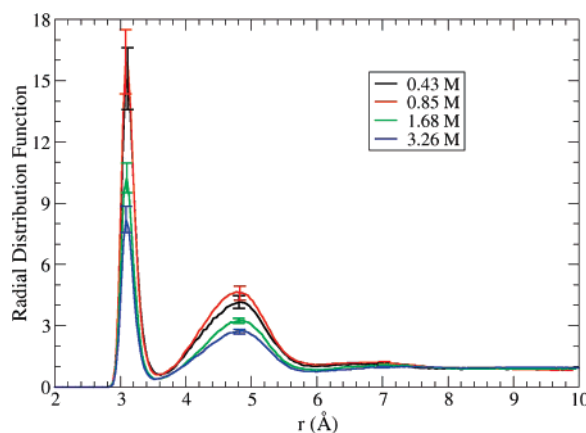


Figure 12. OHy–Cl[−] RDFs for HCl solutions at 0.43, 0.85, 1.68, and 3.26 M concentrations simulated using the SCI-MS-EVB method.

configurations in bulk water.^{8–10,23,27,28} The nuclear quantization might therefore increase the stabilization of the hydronium pairs through additional delocalization of the excess proton CECs beyond the classical limit. This could further reduce the electrostatic repulsion in the ion pairs. However, this is speculation that remains to be validated.

Excess Proton Solvation Structure at Higher Concentrations. Since the hydronium cations can evidently join together to form amphiphilic pockets, a natural question to ask is if such pockets can be formed by more than two hydronium cations. This indeed seems to be the case. Figure 9 shows a configuration obtained from the 0.85 M HCl trajectory that depicts an arrangement in which three hydronium cations are close to each other. Here again the locations of the three CECs (semitransparent yellow balls) are seen to shift away from the hydronium oxygen atoms so as to stabilize the hydrated proton cluster.

At higher concentrations, one might also expect that even larger hydrated proton aggregates could be formed. In order to address this question, the RDFs for HCl at 0.43 M were compared against those at higher concentrations. Figure 10 shows the RDFs for OHy–OHy, CEC–CEC, and Cl[−]–Cl[−] at 0.43, 0.85, 1.68, and 3.26 M calculated from the SCI-MS-EVB simulation. Surprisingly, the height of the first peak is actually decreased for the 1.68 and 3.26 M concentrations. At higher concentrations, the interaction between hydronium and chloride evidently increases to such an extent that the hydronium ion pairs, although they still exist, are less prominent. As argued by Agmon,¹⁹ the solvated HCl starts to form a longer-ranged ordered structure. This is consistent with the finding that the shape of the RDFs at 1.68 and 3.26 M is rather similar at shorter distances but the RDF for 3.52 M solution has more structure at larger separations with a third peak

emerging clearly in the $\text{Cl}^- - \text{Cl}^-$ RDF. This can be interpreted as the growth of aggregates with longer-ranged order, as the concentration increases.

Figure 11 shows the distribution of the weights of the two most important MS-EVB states at various concentrations. The peaks around 0.65 and 0.15 correspond to Eigen-like species, whereas the shoulders around 0.30 to 0.55 correspond to Zundel-like species.^{28,38} It is seen that the Zundel cations become more favorable at higher concentrations beyond 1.68 M, consistent with the gradual appearance of the structure shown in Figure 2, since the excess proton is solvated as a Zundel cation in this structural motif. The Cl^- anion can also form a solvent-separated ion pair with the hydronium oxygen in this structural motif. Figure 12 shows the $\text{OH} - \text{Cl}^-$ RDFs at concentrations from 0.43 to 3.26 M. The second peak in the $\text{OH} - \text{Cl}^-$ RDF increases in intensity as concentrations increase, also in agreement with a gradual formation of the structural motif in Figure 2.

Conclusions

The hydrated proton structures in aqueous HCl solution have been simulated using the SCI-MS-EVB method within the MS-EVB3 parameterization for concentrations of 0.43, 0.85, 1.68, and 3.26 M HCl. Additional simulations were carried out using the CPMD method with the HCTH 120 functional for 1.0 M HCl solution. The SCI-MS-EVB simulations indicate that at the lower concentrations of 0.43 to 0.85 M hydrated protons are found to exhibit a unique cation pairing and clustering behavior consistent with hydronium cations having an amphiphilic character. The existence of these ion pairs was further supported by the CPMD simulations. It was also found that the

cation pairs are stabilized by a nonclassical charge delocalization of the excess proton charge defects over multiple water molecules. At concentrations higher than 1.68 M, the abundance of such “amphiphilic” cation pairs decreases and the simulations instead indicate the possible formation of aggregates with a longer-ranged ordered structure.

While it has been found experimentally that dihydronium ion pair species can exist in crystals,⁵⁷ the present molecular simulation results predict that hydrated excess protons can also form unusual ion pairs in aqueous strong acid solution. Thus, hydrated protons can manifest themselves in ways that are substantially different from the behavior of other, more classical cations. Indeed, such seemingly “simple” systems as concentrated aqueous acid solutions can be much more complex at the molecular level than we might have expected.

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