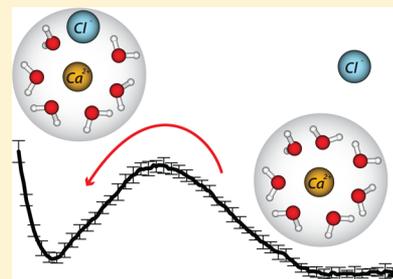


Local Aqueous Solvation Structure Around Ca^{2+} During $\text{Ca}^{2+}\cdots\text{Cl}^-$ Pair Formation

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ABSTRACT: The molecular details of single ion solvation around Ca^{2+} and ion-pairing of $\text{Ca}^{2+}\cdots\text{Cl}^-$ are investigated using *ab initio* molecular dynamics. The use of empirical dispersion corrections to the BLYP functional are investigated by comparison to experimentally available extended X-ray absorption fine structure (EXAFS) measurements that probe the first solvation shell in great detail. Besides finding differences in the free-energy for both ion-pairing and the coordination number of ion solvation between the quantum and classical descriptions of interaction, there were important differences found between dispersion corrected and uncorrected density functional theory (DFT). Specifically, we show significantly different free-energy landscapes for both coordination number of Ca^{2+} and its ion-pairing with Cl^- depending on the DFT simulation protocol. Our findings produce a self-consistent treatment of short-range solvent response to the ion and the intermediate to long-range collective response of the electrostatics of the ion–ion interaction to produce a detailed picture of ion-pairing that is consistent with experiment.



■ INTRODUCTION

Although the importance of the free-energetics of solvation and ion-pairing has been known for decades, the unique molecular scale signatures that give rise to the measured free-energies of solvation and activity have yet to be established.^{1,2} Moreover, our modern theoretical understanding of solvation comes from two distinct points of view. The continuum theory, or Born model in its simplest formulation, is based in linear-response theory. Nevertheless, it is well-accepted that the subtle structural nonlinearities and asymmetries in the solvation process are contained in the definition of the Born radius. Another successful theory of solvation is the so-called quasichemical theory (QCT).^{3–6} QCT views partitioning the free-energy of solvation as coming from two distinct length scales in a thermodynamic cycle: the short-range where the molecular detail informs our understanding, and the remaining long-range (mean-field or linear response) that is determined by long-range slowly varying dielectric fluctuation.⁷ QCT demonstrates that the details of the local hydration structure and its interaction with the solvent are decisive. The complexities involved in identifying those structures, by using information from *ab initio* simulations of aqueous solutions, have been examined recently.^{8–11} Nevertheless, the subtle question of the relationship between the proper level of molecular interaction to determine both the correct population of structures for isolated ions in the condensed phase and the collective intermediate- to long-range response that is responsible for ion-pairing is a subject of great interest.¹²

Moreover, it is only recently that the direct connection between simulation and experiment regarding the precise molecular structure of aqueous electrolytes has been made.^{13,14} To this end, our focus is on the aqueous solvation structure of Ca^{2+} , an ion that plays a significant role in disparate fields ranging from biology to geology. For the purposes presented

herein, Ca^{2+} is chosen because of its stable oxidation state under aqueous conditions and the experimentally determined property that it does not undergo ion-pairing with Cl^- until higher concentrations.¹⁵ Thus, it is an excellent candidate to test the simulation protocol under nearly ideal solution conditions.

Herein, we will investigate both the molecular details of single ion solvation and ion-pairing of CaCl_2 . One of the most remarkable findings will be regarding the flexible nature of the solvation shell of Ca^{2+} defined as the populations of coordination numbers that are accessible within thermal fluctuations. Earlier pioneering work by Ikeda et al. addressed the question of Ca^{2+} hydration using *ab initio* molecular dynamics simulations in conjunction with free-energy sampling of the coordination number.¹⁶ The local solvation structure, as measured by the radial pair distribution function, has long been controversial as discussed in many experimental^{15,17–33} and theoretical studies.^{12,16,33–38} Although the local structure around Ca^{2+} has been resolved using EXAFS in conjunction with *ab initio* molecular dynamics using density functional theory (DFT) as the description of molecular interactions,³³ there is still the need to be able to compare and contrast the flexibility of the solvation shell, as defined previously, as determined by using different simulation protocol. Most *ab initio* studies discussing the details of the Ca^{2+} solvation structure have been performed using standard generalized gradient corrected (GGA) density functionals.^{18,34–38} An additional study performed with a hybrid functional³³ is in

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good agreement with the GGA studies indicating that the structure is not obviously affected by the description of exchange. The disparity in reported coordination numbers in these earlier studies is likely a result of multiple minima in the coordination number free-energy. We will show below that transitions between different coordination numbers can be considered rare events, and therefore, the starting structures and the time-scale limitation of *ab initio* simulation could lead to differences between the DFT studies.

Nevertheless, open questions remain regarding how the role of the thermodynamic state point of water, which is known to be sensitive to DFT simulation protocol, can affect the local solvation structure around ions.³⁹ To date, there has not been a DFT simulation performed at constant pressure to investigate the influence on the solvation structure near ambient state points of dilute electrolytes. Herein, we use a robust approach by placing the ion of interest in the middle of a water slab in a standard liquid–vapor interface geometry. In previous studies, we have shown that this simulation protocol reasonably reproduces the thermodynamic condition of mass density of liquid water that is relevant for studies at near-ambient conditions. Under bulk periodic boundary conditions for pure water in the presence of anions, including water's self-ions, the use of an empirical dispersion correction introduced by Grimme⁴⁰ is imperative and provides an excellent description of the solvation of a variety of ions as compared to EXAFS experiments.^{13,41–44}

An additional aspect of this study is to contrast the differences in the aqueous solvation structure and ion-pairing between different representations of molecular interaction. At the level of single ion solvation, it has been demonstrated that the solvent response to an ion using quantum-based potentials can be significantly different than that obtained by classical empirical potentials.^{41–43,45} In fact, a recent DFT study has examined the effects of simulation protocol on the aqueous solvation structure of ions where significant differences in aqueous structure for Na⁺ and K⁺ were reported under concentrated solution conditions.⁴⁶ Given the advances in the efficiency of DFT methods, researchers are now computing potentials of mean force (PMF) using non-Boltzmann methods for the ion-pairing process.^{13,47–51}

Understanding the relationship between the single ion solvation and the ion-pairing process was clearly shown in a recent study where the free-energy of ion-pair formation Ca²⁺...Cl⁻ is strongly correlated to the flexibility of the solvation shell around the Ca²⁺.⁴⁷ The balance between ion–water and ion-pairing interactions for doubly charged cations has been recently revisited with classical empirical interaction potentials to describe the fidelity of the aqueous structure of the first solvation shell as determined by EXAFS and to obtain the measured ion-pair statistics determined by neutron scattering.^{15,52,53} The research presented herein builds on the aforementioned empirical studies and provides a self-consistent picture of how local solvation structure impacts solution thermodynamics.

DESCRIPTION OF METHODS

Herein, four different system sizes and compositions are studied. For all simulations, the Born–Oppenheimer *ab initio* molecular dynamics simulations within the NVT ($T = 300$ K) ensemble using periodic boundary conditions are performed within the CP2K simulation suite (<http://www.cp2k.org>). *Ab initio* calculations were performed with the *QuickStep* module

using density functional theory (DFT) as the theory for the electronic structure.⁵⁴ We followed a similar protocol as in ref 50, using a double- ζ basis set that has been optimized for the condensed phase⁵⁵ in conjunction with GTH pseudopotentials⁵⁶ and a 400 Ry cutoff for the auxiliary plane wave basis. A Nosé–Hoover thermostat was attached to every degree of freedom to ensure equilibration.⁵⁷ The Becke exchange⁵⁸ and correlation due to Lee, Yang, and Parr (LYP)⁵⁹ is utilized in addition to the dispersion correction (D2) put forth by Grimme⁴⁰ with a 40 Å cutoff.

The first system is composed of a single Ca²⁺ solvated by 64 water molecules, in a periodic cubic box of length 12.56 Å (water density of 0.97 g/cm³). The second simulation is a larger system containing one Ca²⁺ ion and 96 water molecules in a periodic cubic box of length 14.3 Å (water density of 0.98 g/cm³). The third system closely follows the approach of hard sphere solvation in water,⁴⁵ where we choose to model the systems with two buffering liquid–vapor interfaces containing 338 water molecules, and one Ca²⁺ that is counterbalanced with two OH⁻ anions that are initially placed near the two independent surfaces. Cell dimensions for the slab system are 20 × 20 × 50 Å³, and periodic images were screened by using a two-dimensional wavelet Poisson solver.⁶⁰ During the simulation no ion-pair formation is observed.

The fourth system was constructed to compute the free-energy of ion-pairing between Ca²⁺ and Cl⁻ under bulk periodic boundary conditions using umbrella sampling. This system contains a single Ca²⁺ and Cl⁻ and 110 water molecules in a 15.198 × 15.198 × 15.198 Å³ supercell yielding a system density of 0.99 g/cm³. Umbrella sampling windows for the Ca²⁺...Cl⁻ distance ranging from 2.4 to 5.6 Å were equally spaced by 0.2 Å employing harmonic umbrella potentials of the form $V(r) = k(r_0 - r)^2$ with a force constant k of 95.6 kcal mol⁻¹ Å⁻². To ensure sufficient sampling in the barrier region for the Ca²⁺, additional windows with stiffer force constants were added ranging from 3.2 to 4.5 Å equally spaced 0.1 Å apart with a force constant of 334.6 kcal mol⁻¹ Å⁻². In each umbrella window a trajectory of at least 50 ps was collected after 5 ps of equilibration. The weighted histogram analysis method (WHAM) was employed to extract a free-energy profile from these histograms.⁶¹ We also compared our results of ion-pairing and ion solvation to two recent classical empirical interaction potentials: a polarizable model⁵² and a charge scaled model.⁵³ The potential of mean force for Ca²⁺...Cl⁻ binding and the free-energy in coordination space around a single Ca²⁺ are calculated using the same system sizes and force constants as discussed for the BLYP-D simulations outlined above. All classical simulations are performed using CP2K suite (<http://www.cp2k.org>).

The coordination number (n) is computed using the same functional form as that in a previous study.¹⁶

$$n = \sum_i^{N_o} \frac{1 - \left(\frac{r_i}{r_0}\right)^p}{1 - \left(\frac{r_i}{r_0}\right)^q} \quad (1)$$

Here, p and q are integers, usually $p = 16$ and $q = 32$; r_i is the distance between the Ca²⁺ and oxygen i , and $r_0 = 3.0$ Å. The free-energy is computed using the umbrella sampling technique. Sampling windows for n ranged from 4.9 to 8.1 and were equally spaced by 0.1 Å apart employing harmonic umbrella potentials of the form $V(r) = k(r_0 - r)^2$ with a force constant k of 956 kcal mol⁻¹. In each umbrella window a trajectory of at least 50 ps was collected after 5 ps of equilibration. The

weighted histogram analysis method (WHAM) was employed to extract a free-energy profile from these histograms.⁶¹

EXAFS spectra are calculated using the MD-EXAFS approach, where spectra are calculated from randomly sampled structures along the trajectory and averaged.⁶² To ensure that the subset converges to the ensemble spectra, we compare the radial distribution function to the full ensemble average. The calculations are done using the FEFF9 code⁶³ with the same settings as in ref 33.

RESULTS AND DISCUSSION

We start with discussing the local solvation structure around a single Ca^{2+} solvated with 64 water molecules at a fixed density (water density of 0.95 g/cm^3) using DFT with the BLYP functional both with and without an empirical dispersion correction. As pointed out above, all DFT simulations for Ca^{2+} to date except for one have used standard generalized gradient corrected functionals without an empirical dispersion correction. Figure 1 shows the pair distribution function (PDF) of

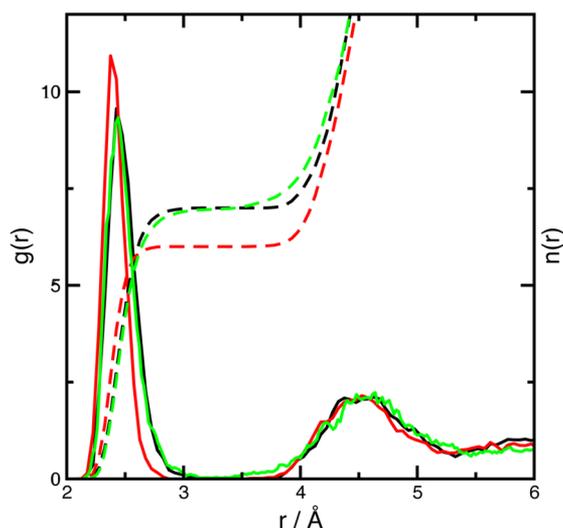


Figure 1. Calcium–oxygen pair distribution function (—), $g(r)$, and running coordination number (---), $n(r)$, computed with BLYP and BLYP-D under periodic bulk solvation (single Ca^{2+} in 64 water molecules at density 0.97 g/cm^3) shown in red and black, respectively, compared with the slab geometry in green computed with BLYP-D.

water oxygen atoms around the Ca^{2+} ion in conjunction with its running coordination number. The solvation structure obtained in this study using BLYP corresponds well with structures from other published *ab initio* data for single ion and CaCl_2 simulations using a similar box size and simulation protocol resulting in a coordination number of 6.^{16,34,36,38,47} When the dispersion correction is added, the so-called BLYP-D protocol, the Ca^{2+} ion becomes seven-fold coordinated in excellent agreement with recent EXAFS experiments that estimate a coordination number of 6.7.³³ We make an ansatz, that for a system with a single divalent cation, the dispersion correction will be largely manifest in the important water–water interactions. This is further corroborated by studies that have shown that the density of water at 300 K shows a significant difference between BLYP and BLYP-D simulations. It is now accepted that uncorrected BLYP predicts a much less dense liquid phase of water ($\approx 0.85 \text{ g/cm}^3$) than BLYP-D that is consistent with the experimental density at 300 K.^{44,64,65} The extent to which empirical dispersion corrections to DFT yield

consistently better results for ion solvation is still a matter for future research.^{66,67}

To investigate the density effect on the coordination number of Ca^{2+} , we use the slab configuration that has proven to be a good proxy to the NpT ensemble^{44,65,68} in conjunction with BLYP-D that is known to give the correct water density in the center of the slab (see [Description of Methods](#) section for details). The resulting PDF from a 20 ps simulation is shown in Figure 1. The salient point is that the coordination number is seven for the Ca^{2+} under the approximate NpT conditions afforded by the slab geometry and is almost identical to the results from the fixed density periodic simulation. The only noticeable difference occurs at the onset of the second solvation shell.

We further analyze the simulations by directly comparing them to the EXAFS measurements using all three different protocols as is shown in Figure 2a–c. The BLYP-D simulation performed at a water density of 0.95 g/cm^3 at 300 K reproduces the experiment and the DFT simulations using hybrid functionals with dispersion very well.³³ It can clearly be seen in Figure 2b that the experiment can distinguish between six- and seven-fold coordination around Ca^{2+} . It is also interesting to note that the average Ca^{2+} –oxygen distance as measured by EXAFS is well-reproduced by all simulations.

As was shown for the uncorrected BLYP functional in an earlier study,¹⁶ the solvated Ca^{2+} has multiple coordination numbers that are accessible within a few $k_B T$, with six being the most probable state. This finding is reconfirmed herein although there are no transitions observed into the neighboring coordinating states for a free, unrestrained run. On the other hand, the BLYP-D simulation only explores the seven-fold coordinated state. To understand these differences it is instructive to compute the underlying free-energy in coordination space using the umbrella sampling approach. To this end, similar to a recent study using classical empirical potentials,³⁸ we directly compare the 64 water molecule system for BLYP and BLYP-D and an additional larger BLYP-D system with 96 water molecules all under bulk periodic boundary conditions to explore the effect of system size on the free-energy landscape. Figure 3a depicts the free-energy of the Ca^{2+} oxygen coordination number (n) in aqueous solution as described by the aforementioned three different simulation protocols. The BLYP results correspond well with the work of Ikeda et al.¹⁶ with Ca^{2+} in a six-fold coordinated state and a barrier to the seven-fold state of roughly 3 kcal/mol that is roughly 1 kcal/mol less stable. The eight- and five-fold coordinated states reside much higher in free-energy differences of 5 and 8 kcal/mol, respectively. The results of the BLYP-D simulations with different supercell size are the same within the error bars of our calculations. Specifically, BLYP-D predicts the most stable coordination state for Ca^{2+} to be seven. The six-fold coordinated state is destabilized by about 1 kcal/mol and separated with a 3 kcal/mol barrier independent of the size of the supercell. Not surprisingly, the largest differences between all of the simulations presented are in the regions of higher coordination number. The eight-fold state is 2 kcal/mol more stable with the BLYP-D protocol. Increasing the system size from 64 to 96 water molecules has a small but statistically discernible effect in reducing the barrier from 4 to 3 kcal/mol. As a self-consistent check, we estimated the free-energy in coordination space from an unrestrained simulation in the slab geometry using BLYP-D. The free-energy surface computed by inverting the population, $P(n)$, to obtain a free-energy defined

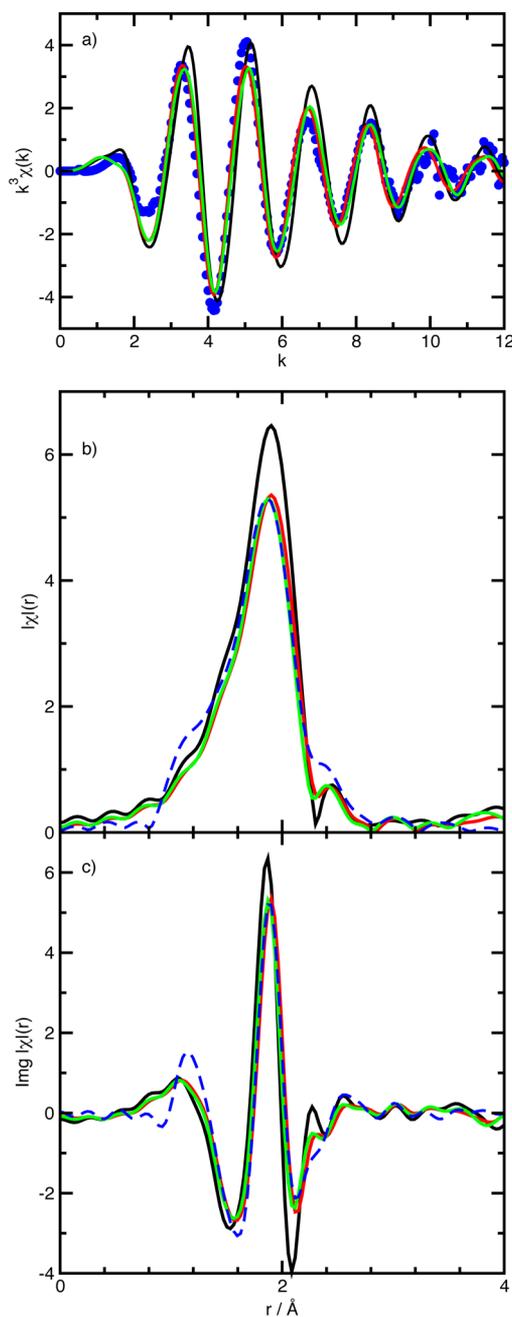


Figure 2. Comparison of the experimental Ca K-edge XAFS spectra (blue ---)^{15,33} with the simulated spectra using the MD-EXAFS approach. (a) Experiment in blue, BLYP (black), BLYP-D (red), and BLYP-D (both single Ca^{2+} in 64 water molecules at a density 0.97 g/cm^3) and in the slab configuration (green). The corresponding Fourier transform (radial structure factor) yielding (b) the real $|\chi(r)|$ and (c) its imaginary part $|\text{Im}\chi(r)|$.

by $W(n) = -k_B T \ln(P(n))$, where k_B is Boltzmann's constant and at a temperature, $T = 300 \text{ K}$, is shown in Figure 3a. The result is nearly identical with the larger BLYP-D system size of 96 waters. Moreover, a dependence on the underlying free-energy in coordination space on the system size is observed for higher coordination numbers. The good overall agreement between the larger BLYP-D and slab simulation, namely, a single Ca^{2+} solvated by 96 and 338 water molecules, respectively, suggests that the finite size effects are largely

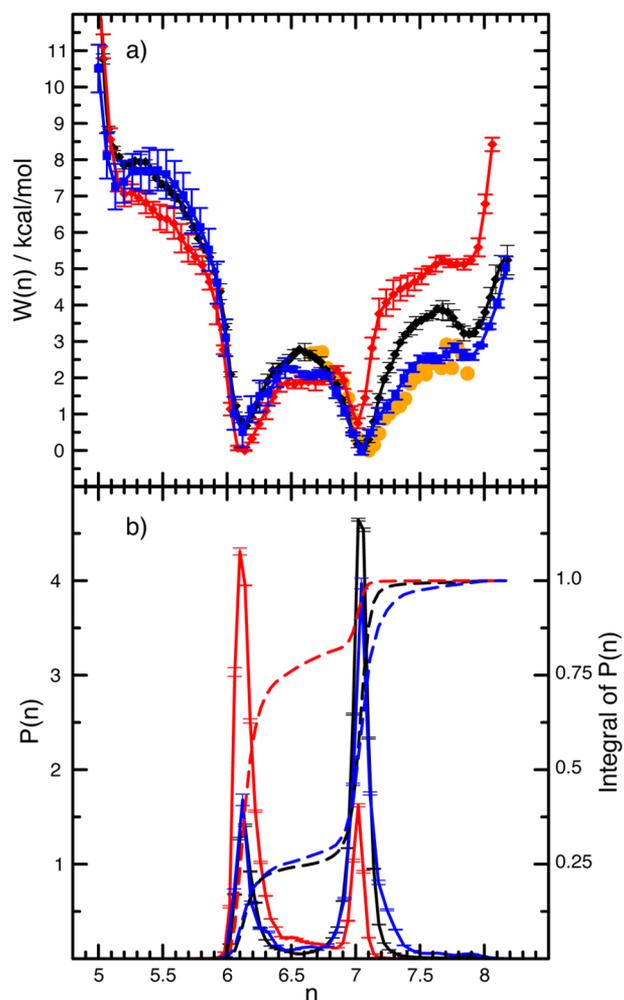


Figure 3. (a) Free-energy of the Ca^{2+} oxygen coordination number (n) in aqueous solution obtained from umbrella sampling for BLYP (red), BLYP-D (black) for the small system containing 64 water molecules, and BLYP-D (blue) for a system with 96 water molecules. Orange circles indicate the free-energy, $W(n) = -k_B T \ln P(n)$, with $P(n)$ estimated from the slab simulation where k_B is Boltzmann's constant and at a temperature $T = 300 \text{ K}$. (b) Normalized probability distribution, $P(n)$ (solid curves), and the integral of $P(n)$ (dashed curves).

absent for the 96 water BLYP-D simulation under bulk periodic boundary conditions.

Instead of only focusing on the free-energy it is also instructive to compare the resulting population $P(n)$ computed at 300 K as shown in Figure 3b. As foreshadowed in the free-energy, the populations for BLYP and BLYP-D are reversed. For the BLYP simulation at equilibrium, a significant majority of 75% of the Ca^{2+} ions would be solvated by six water molecules and about 25% by seven water molecules. Coordination numbers of Ca^{2+} that are higher than seven and lower than five do not show any significant population in any of the simulations. Both BLYP-D simulations are in agreement with 75% of the Ca^{2+} in a seven-fold coordinated state and 25% being six-fold coordinated. These computed populations lead to average coordination numbers of 6.3 and 6.7 for BLYP and BLYP-D, respectively.

Thus, far, we have established the role of both the simulation protocol and the necessity for a high-quality interaction potential to describe the local solvation structure around

Ca^{2+} . We continue by pursuing and understanding the subtle balance between the aforementioned short-range solvent response to the ion, and the collective intermediate to long-range electrostatics needed to describe the ion-pairing of CaCl_2 .¹² The free-energy of CaCl^+ ion-pair formation was one of the first published using DFT simulations in conjunction with the uncorrected BLYP functional.⁴⁷ This study suggested that the resulting free-energy is highly dependent on the coordination number that is found around the Ca^{2+} . As shown above, our present results show significant differences for the free-energy in coordination space for the isolated Ca^{2+} depending on the use of dispersion corrected and uncorrected BLYP. We extend our studies beyond the single Ca^{2+} and compute the potential of mean force (PMF) of ion-pairing for CaCl^+ along the Ca^{2+} – Cl^- radial distance. The supercell size for the ion-pairing calculation requires almost doubling the number of water molecules from 64 to 110 as compared to the earlier study.⁴⁷ Figure 4 depicts the PMF of CaCl^+ ion-pairing

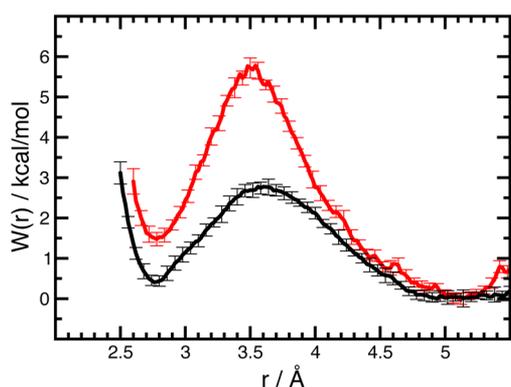


Figure 4. Comparison of Ca^{2+} and Cl^- ion-pairing free-energy using umbrella sampling for BLYP-D (black) and BLYP (red).

process. The uncorrected BLYP exhibits a solvent separated ion-pair (SSIP) that is about 2 kcal/mol more stable than the contact ion-pair (CIP) and separated by a 6 kcal/mol barrier going from SSIP to CIP. The addition of the dispersion correction (BLYP-D) reduces the stability of the CIP by 1.5 kcal/mol relative to the SSIP, but more noticeably, the barrier for ion-pair formation is reduced to 3 kcal/mol. Our results suggest that the differences in simulation protocol have only a minor effect on the relative stability between the CIP and the SSIP, but the change in barrier height between the two states is dramatic, and will have consequences for the kinetics of ion-pair formation.⁶⁹

Experimentally, no long-lived ion-pairing is seen for CaCl^+ for concentrations as high as 6 M, but clear signatures of the formation of stable SSIPs are detected.¹⁵ Similarly, both the chlorine K-edge and calcium K-edge EXAFS spectra show no sign of ion-pairing.¹⁵ On the basis of the PMF for BLYP-D shown in Figure 4, the formation of the CIP should be very low, likely below the detection limit of the EXAFS experiment. As a self-consistent test of our simulation protocol, we investigate the difference in the EXAFS signatures of both Ca^{2+} and Cl^- in both the CIP and SSIP states and compare it to the EXAFS spectra generated from the BLYP-D calculations of the isolated ions in water. Our findings depicted in Figure 5a,b are in excellent agreement with the EXAFS data. Both the Ca^{2+} and Cl^- in the SSIP behave as isolated ions. However, for Ca^{2+} , the CIP configuration, there are clear deviations from the

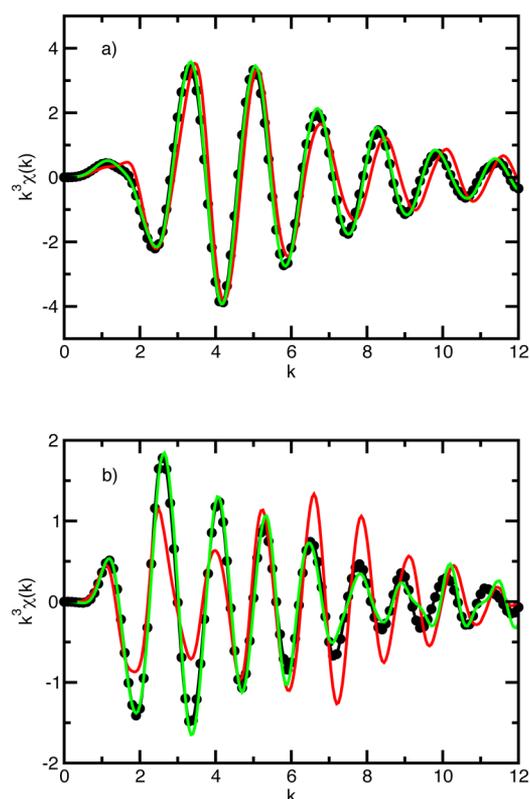


Figure 5. Comparison of the simulated Ca (a) and Cl (b) K-edge XAFS spectra. For Ca, the isolated ion BLYP-D (black), ensembles of configurations from the CIP (red), and SSIP (green) are shown. The Cl experimental reference is taken from 2.5 M NaCl (black) from ref 13 and compared to ensembles of configurations from the CIP (red), and SSIP (green).

isolated spectra for $k > 6$. The same trend is observed for the Cl^- . For the case of Cl^- the CIP displays much larger deviations from the isolated solvated ion. This suggests that the SSIP, regardless of whether it is probed through the Ca^{2+} and Cl^- K-edge, is not distinguishable from the simulations of the isolated ion. Therefore, our results suggest that the CaCl^+ system is best described as either a CIP (or bound) or isolated (not associated) ions.

Finally, we compare the free-energy in coordination space and the PMF of ion-pairing between the BLYP-D case that is the best representation to the experimental EXAFS and two classical empirical interaction potentials that have recently weighed in on the ion-pairing of CaCl^+ .^{52,53} Both classical representations of interaction are improvements on older force fields where it was found that the ion–ion Lennard-Jones was reparameterized in the case of Dang and co-workers (Dang model) and the charges of the ions were rescaled in line with the electronic continuum correction (ECC model); also, Lennard-Jones values were reparameterized (ECCR model) as discussed in detail by Kohagen and co-workers.⁵³ It should be noted that a recent study has also pursued the consistency of describing the short-range structure and its relationship to the long-range collective behavior of CaCl_2 and MgCl_2 solutions.¹² Through a more complex empirical model in conjunction with a physically motivated charge partitioning scheme, this study also reports good agreement of the local structure and long-range collective response as determined by osmotic pressure. Here, we build on these concepts and examine the ion-pairing PMF for CaCl^+ using the original and modified Dang model and

BLYP-D compared in Figure 6a. The improved parametrization affects the PMF only for distances less than 3.5 Å. The effect of

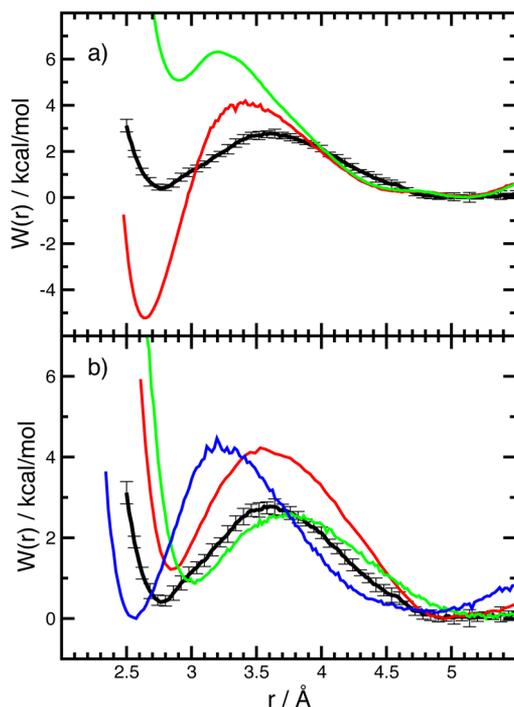


Figure 6. Comparison of Ca^{2+} and Cl^- ion-pairing free-energy obtained with umbrella sampling. (a) BLYP-D (black), the original Dang model (red), and the modified Dang model (green). (b) BLYP-D (black) and OPLS (red), ECC model (green), and ECCR model (blue).

changing the ion–ion Lennard-Jones parameters in the modified Dang model leads to a 10 kcal/mol destabilization of the CIP to a local minimum that is 5 kcal/mol less stable than the SSIP. Moreover, the position of the CIP for the modified Dang model shifts by about 0.2 Å from 2.6 to 2.8, very close to the 2.7 seen for the BLYP-D.

We can also test the agreement between the ECCR model that was shown to better reproduce the long-range structure as measured by neutron diffraction, and improved mobility rates over the original OPLS force field.⁵³ In Figure 6b three different models are compared to the BLYP-D for the PMF of CaCl^+ ion-pairing: the original OPLS model, the ECC (charges of Ca^{2+} and Cl^- are scaled by 0.75), and the ECCR which has additional reparametrized Lennard-Jones values for both ions.⁵³ All three PMFs are very similar to the BLYP-D as shown in Figure 6b. The OPLS model estimates the CIP to be about 1 kcal/mol less stable than the BLYP-D prediction and overestimates the barrier by a factor of 2 from the SSIP to CIP. A straightforward scaling of the charges (ECC model) yields results that are in good agreement with the BLYP-D, namely, an identical barrier from the SSIP to the CIP and only 0.5 kcal/mol in the stability of the CIP. Only the ion–ion distance for the ECC model in the CIP is shifted by 0.3 Å to larger values than that of the BLYP-D. Although additional changes of the Lennard-Jones values (ECCR) give an improvement for the long-range structure for the ion-pair,⁵³ there is a noticeable change for the PMF of ion-pairing. The ECCR produces a barrier from SSIP to CIP that is similar to the original OPLS model. Moreover, ECCR overestimates the

stability for the CIP by 0.5 kcal/mol over the BLYP-D and produces a shift of the Ca–Cl distance to 2.5 Å.

The underlying assumption in the modification of the classical empirical models is that it is the ion-pair interaction that is solely responsible for an accurate representation of the PMF of ion-pairing. We can test this hypothesis by examining the Ca^{2+} –oxygen pair distribution functions depicted in Figure 7a. Significant differences between all models are seen in the

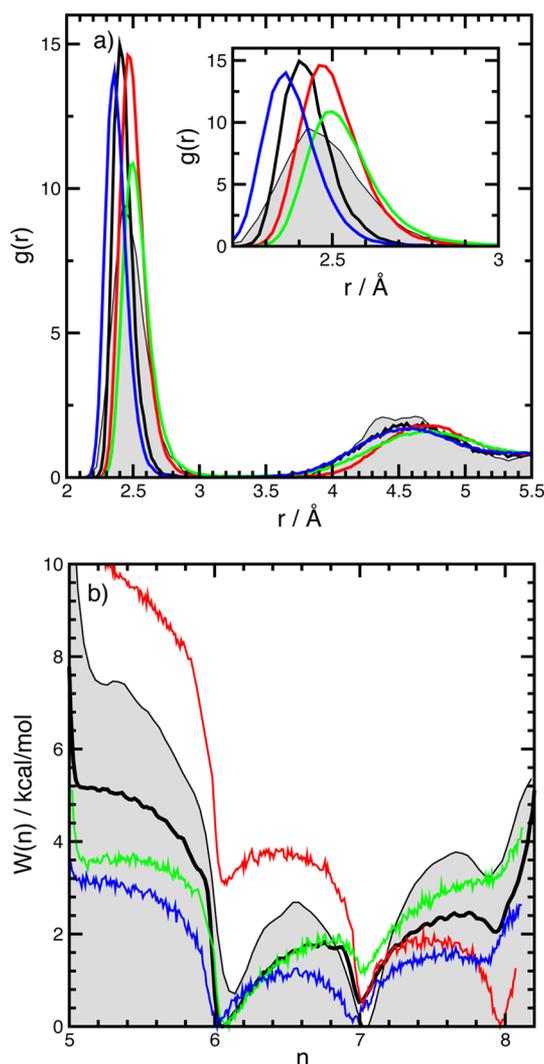


Figure 7. (a) Pair distribution function, $g(r)$, of oxygens around calcium for BLYP-D under bulk solvation (gray shaded area), the Dang model (black), OPLS (red), ECC model (green), and ECCR model (blue). Inset highlights the region of the first maximum. (b) Free-energy in coordination number space, $W(n)$. BLYP-D is depicted as a gray shaded area, the Dang model (black), OPLS (red), ECC model (green), and ECCR model (blue).

distribution (number and distances) of the first solvation shell water molecules. The position of the first maximum is well-reproduced by both the OPLS and Dang model (the modified Dang model and the original Dang model are the same for this interaction), but produce differing coordination number: six for the Dang model and seven to eight for OPLS. Again, the best agreement with BLYP-D is seen for the ECC model, where the ECCR model is shifted almost 0.2 Å to smaller distances. Additionally, in Figure 7b the free-energy in coordination number space for the single solvated Ca^{2+} is compared. The

Dang model overall is very close to the uncorrected BLYP in both the free-energy in coordination number space (see Figure 3a) and the pair distribution function (see Figure 1). What is clear from our study is the difficulty of getting both the correct local solvent response and the intermediate- to long-range collective response encoded in a single parametrization of an empirical model in order to be quantitative about the mechanisms of ion-pairing.

CONCLUSION AND OUTLOOK

In summary, we have shown that the local structure around Ca^{2+} is well-described using the BLYP-D functional as compared to EXAFS experiments. The empirical dispersion correction to DFT is needed to be able to properly describe the short-range structure around this particular set of ions, namely, Ca^{2+} and Cl^- . Discrepancies in the reported number of water molecules in the first solvation shell from different DFT studies using the same functional can be reconciled by considering multiple accessible minima in the free-energy landscape for the coordination number around Ca^{2+} . We find significant changes due to dispersion correction that produces a change in preferred coordination from six- to seven-fold in agreement with EXAFS. Our studies on finite size effects suggest that the population of larger coordination states will be affected likely leading to higher coordinated states for bigger systems. The slab geometry was tested as a good proxy to the NpT ensemble and produced results consistent with bulk periodic boundary condition simulations. Not surprisingly, the effect of dispersion corrected functionals also produces a PMF of ion-pairing between Ca^{2+} and Cl^- that is distinct from uncorrected functionals and leads to a large reduction in the barrier from SSIP to the CIP of CaCl^+ . We have demonstrated in this work that the intrinsic solvation properties validated by EXAFS are encoded in the PMF for ion-pairing of CaCl_2 . The resulting PMF in the dilute limit suggests a picture consistent with reparameterized classical point charge models fit to reproduce concentration dependent collective properties of CaCl_2 as determined by neutron diffraction.⁵³ Future studies will be focused on further validation of the accuracy of the BLYP-D PMF for ion-pairing in the dilute limit by using this important short-range molecular information to compute collective properties of CaCl_2 solutions using methods outlined in numerous studies.^{70–73} Although we cannot directly speculate that there is a connection between the BLYP-D obtained PMF and the observed concentration dependence of ion-pairing, it is interesting to note that the relative populations of the SSIP to the CIP computed using Figure 4 are in near quantitative agreement to the experimental values obtained at higher concentrations.¹⁵ Future investigations will be focused on using rigorous definitions of ion-pairing in conjunction with the PMF as have recently been reviewed in ref 73. Moreover, our simulated EXAFS K-edge spectra for ensembles of structures of Ca^{2+} and Cl^- in the SSIP state predict a solvation structure indistinguishable from the computed spectra from simulations of the isolated ions.

We also tested our understanding of our results generated with DFT by comparison to several modified classical empirical models of the solvation and ion-pairing of CaCl_2 . Overall, the best agreement between BLYP-D and classical models was found to be the ECC model. The ECC charge scaling approach shows better agreement with the BLYP-D over the modified Dang model. Although the reparametrizing of the ion–ion interaction is certain to influence the computed PMF, this

assumes that the short-range local solvent response to the bare ion can be viewed in more simplistic terms, analogous to dielectric continuum theory. The research presented herein is consistent with other theoretical findings for monovalent ions⁷ and has shown that, indeed, the local solvent response is a difficult and important quantity to ascertain. Moreover, we have produced a self-consistent picture suggesting that DFT provides both the accurate solvent response to an isolated ion and the important intermediate- to long-range ion–ion interaction that is needed to explain the experimental data of CaCl_2 ion-pairing.¹⁵

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Notes

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