The Born model can accurately describe electrostatic ion solvation.

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Abstract

Accurate models of the free energies of ions in solution are crucial for understanding and modelling the huge number of important applications where electrolyte solutions play a crucial role such as electrochemical energy storage. The Born model, developed to describe ion solvation free energies, is widely considered to be critically flawed as it predicts a linear response of water to ionic charge, which fails to match water's supposed intrinsic preference to solvate anions over cations. Here, we demonstrate that this asymmetric response observed in simulation is the result of an arbitrary choice that the oxygen atom should be the centre of a water molecule. We show that an alternative and reasonable choice, which places the centre 0.5 Å towards the hydrogen atoms, results in a linear and charge symmetric response of water to ionic charge for a classical water model consistent with the Born model. This asymmetry should therefore be regarded as a property of the short range repulsive interaction not an intrinsic electrostatic property of water. We also show that this new water centre results in a more reasonable neutral cavity potential.

Introduction

Free energies of ions in solvent play an important role in a huge range of important applications. They determine the chemical potential, which in turn directly determines chemical equilibria and chemical reaction rates. They can also be related to many other properties of electrolyte solutions that are important for practical applications such as conductivities and rates. Rational design of new electrolytes for practical applications, such as electrochemical energy storage, therefore depends critically on accurate predictive models of these quantities. For example, the most basic and fundamental ionic free energy, the solvation free energy, can be correlated with the rate of transport processes at the electrode/electrolyte interface in batteries.[1] Solvation free energies are also important for determining the distribution of ions in nano-porous materials as desolvation can be necessary for the ion to enter these pores.[?]

The original model of ion solvation free energies is the Born model,[2] which is an application of dielectric continuum theory (DCT) which treats the ion as a charge inside a dielectric cavity. Models that employ the DCT approximation are referred to as continuum solvent models (CSMs).

It has long been accepted wisdom that the Born model fails badly at describing ion solvation because it predicts a linear response of water to solute charge, which contradicts the so-called charge hydration asymmetry (CHA) property of water.[3–11] This refers to the observation that water appears to have an intrinsic preference to solvate negative charges over positive charges, assuming other properties such as size are kept constant. This property is often used used as evidence to argue that models of solutes in water need to include an explicit treatment of the molecular scale details of water and so CSMs, such as the Born model, must be too simple to be of use for quantitatively modelling water.

Despite this foundational issue at the heart of the DCT approach, several CSMs have been developed and successfully applied to many applications.[12,13] The most obvious example being the generalised Born model.[14] It is therefore crucial to critically examine the evidence for the CHA and reassess whether the critiques of the Born model are justified. If it were the case that DCT could be rigorously applied to predict electrostatic solvation thermodynamics of ions it would be very advantageous by firstly, potentially allowing expensive and time consuming explicit solvent molecular simulations to be bypassed. Secondly, it could clarify our understanding of other fundamental and important properties of electrolyte solutions such as chemical potentials, and surface potentials where the electrostatic contribution to ion-ion[15] and ion-surface free energies[10,16] interactions are crucially important.

There are two key pieces of evidence that indicate water has a substantial CHA. One piece is based on experiment, i.e., the potassium cation and the fluoride anion are similar in size based on their Pauling crystal radii and yet the fluoride anion has a substantially more negative solvation energy. This is obviously only indirect evidence at best for a CHA of water as there are many other relevant differences between these two ions, which could

also contribute to a difference in solvation free energy. In particular, fluoride is an anion meaning its electrons are more weakly bound giving it a higher polarisability and so has a larger induction interaction and dispersion interaction with the surrounding water molecules. Additionally, its electron cloud will be more diffuse resulting in larger exchange repulsion energy for fluoride than for potassium.[17] In fact, there is substantial evidence that the difference in the size of the dispersion interaction alone is sufficient to explain the gap in solvation free energy between potassium and fluoride.[18,19] The importance of these non-electrostatic effects in charge solvation is demonstrated by the fact that some cations a such as monovalent copper and silver have anomalously large solvation free energies for their size compared with other cations, which obviously cannot be explained by CHA but is consistent with a dispersion interaction mechanism.[20]

The second piece of evidence is based on calculations of the solvation free energies of idealised solutes in water using Molecular Dynamics (MD) simulation. The solutes are either Lennard-Jones or hard sphere cavities where only the charge on the ion is varied. This supposedly provides a clear estimate of CHA as there are no differences in the non-electrostatic interactions. These calculations clearly show a consistent preference of water for negative charges over positive ones.[4–6,8,10] This method requires a repulsive cavity to be formed in water for the charge to occupy. A centre of the water molecule on which the repulsion acts must be chosen. The universal choice for this centre is the oxygen atom of the water molecule. The method of carving out this cavity has previously been considered to be unimportant and is often not even made explicit.

Understanding the underlying causes of the CHA has been the subject of much research. For example, it has been shown that this property depends sensitively on the charge distribution of the water molecule. For instance, it is very large for revPBE-D3 quantum mechanical water[9] but much smaller for TIP5P water.[7] The treatment of the lone pair electrons is particularly important.[11]

Many attempts to develop simple models that include an accounting of this effect have

been made. Most commonly different definitions of the cavity size for anions vs cations are used.[3] This approach is supported by simulations which show that a piecewise linear model appears to describe solvation free energies relatively well.[6] Another option is to create models that separate the charge symmetric linear response which can be described with DCT from the asymmetric non-linear term. One approach to doing this is to fit the solvation free energy to a higher order polynomial where one of the terms corresponds to the charge symmetric DCT term and the other terms capture the deviations from this theory.[10] An alternative is to use the Quasi Chemical Theory (QCT),[21,22] which splits the ion-solvation process into an inner-shell term and an outer shell term. The outer shell term can be described with DCT, whereas the inner shell term requires a more complex treatment. Similarly, Remsing and Weeks[23] break the ion solvation process into an initial step of solvating a Gaussian charge distribution, which can be described with a DCT and a second step of collapsing that Gaussian charge distribution down to a point charge in a cavity, which cannot be described with DCT.

However, to the best of our knowledge no researchers have questioned the underlying view that water has a substantial inherently non-linear response to a charge at the atomic scale that cannot be described with DCT and that therefore there is no way to provide a fully accurate model of ion-solvation without the use of explicit solvent simulation.

Here, we question this view by showing that the CHA observed in classical simulation depends sensitively on how the repulsive centre of the solute-water interaction is chosen even reversing sign with a reasonable choice. This demonstrates that the CHA observed with MD simulations should be considered to be a property related to the arbitrary details of the short-range repulsive solute-water interaction rather than an intrinsic electrostatic property of bulk water. Additionally, we show that the problem of the non-linear response of water can be resolved by choosing a centre for water that removes the CHA allowing for excellent agreement with the linear Born model of solvation free energies establishing the applicability of this model even for atomic sized ions. We also show that this choice also effects the surface

potential contribution to solvation free energies.

Theory

Surface potential

When discussing the topic of solvation free energies of single ions, it is crucial to understand the subtleties of the different definitions of this quantity. As there are several contributions to the CHA that need to be disentangled and their contribution depends on what definition is used for the single ion solvation free energy. A brief overview is provided in this section but more comprehensive discussions are provided elsewhere.[8,9,24,25] The central complication is that the solvation free energy of a single ion requires a choice for the zero of the electrostatic potential. Often this choice is not made explicit but is always implicit. The most rigorous choice is for the zero to be infinitely far away from the system of interest in vacuum. When this choice is used the solvation free energies are referred to as the 'real' solvation free energies. A second type of solvation free energies is the Ewald solvation free energies. These are the values determined by using standard Ewald summation. This corresponds to setting the zero of the electrostatic potential to be the average value in bulk water. The average potential inside pure water is determined by the internal structure of the water molecules and its true value is a very large positive value (3–5 V)[26–28] this leads to very unusual solvation free energies when the correct quantum mechanical value is used for this reference. It results in cations being massively favoured as the potential inside the cavity the ion occupies is very negative relative to this large positive reference.[9] This immediately shows how important it is to have a very careful understanding of the details of the electrostatics when considering the CHA. For classical models the incorrect potential in the internal part of the water molecules near the point charges leads to an unphysical negative value for this potential.[29] This leads to a substantial anion preference, which is unphysical both because this is not a relevant reference and because it has the wrong value for classical water in any case. However, even

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when the surface potential is included to correct for this problem and compute real solvation free energies, standard classical water models still appear to show a preference for negative charges.[8]

Another definition of the solvation free energy is the intrinsic solvation free energy. These attempt to define an estimate of the solvation free energy that is referenced to vacuum but where it is assumed that the contribution from the orientation of dipoles at the air-water surface is zero. However, it can be rigorously shown that it is impossible to define such a quantity without making an arbitrary choice for the centre of a water molecule.[9,30] This immediately shows that for the intrinsic solvation free energies the CHA is not a true property of water but depends significantly on an arbitrary choice for the origin of the water molecule.

The final type of solvation free energy that is important is the bulk solvation free energy. This corresponds to setting the potential inside a neutral cavity in water to be zero. The usefulness of this definition can be observed by writing the solvation free energy of charging an ion in a cavity in solvent with a non-polarisable model as:

$$\mu_Q = \int_0^Q \langle\phi\rangle_q \, dq = \langle\phi\rangle_0 \, Q + \int_0^Q (\langle\phi\rangle_q - \langle\phi\rangle_0) dq \tag{1}$$

Where $\langle\phi\rangle_0$ is the potential at the centre of a cavity with no charge referenced to vacuum. For the bulk solvation free energies the first term in this expansion is zero by definition. The CHA of the bulk solvation free energies therefore represents the true CHA of the response of water to a charge. This is useful as the other definitions of solvation energy contain contributions to the CHA from both this effect and from the surface potentials of the cavity and bulk interface, which give rise to $\langle\phi\rangle_0$. The CHA of these two terms is often opposite,[8] i.e., for real solvation free energies with the extended simple point charge (SPC/E) water model the first term has a cation preference because SPC/E has a negative net potential. The bulk solvation free energies are particularly relevant if water has a linear response to ionic charge, i.e., $\langle\phi\rangle_q - \langle\phi\rangle_0 = kq$ as then we can write $\mu_Q = Q \langle\phi\rangle_0 + \frac{1}{2}kQ^2$ which can be directly mapped onto the Born equation for the solvation free energy: $\mu_Q = \frac{(Qe)^2}{8\epsilon_0 R_{\text{cav}}}\left(1 - \frac{1}{\epsilon_w}\right)$ meaning the bulk

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solvation free energies are the best values to compare with the Born model. This assumption of linear response can be shown to be equivalent to assuming Gaussian fluctuations in the potential at the centre of the cavity.[31,32]

An issue with this quantity is that bulk solvation free energies rely on the arbitrary choice of the cavity size and it is known that the potential inside a cavity varies significantly with cavity size so this is not an ideal reference.[27] However, it seems that the bulk solvation free energies are free from the arbitrariness that the intrinsic solvation free energies suffer as they do not depend on the choice of the oxygen atom as the centre of the water molecule. However, as we show here this is not the case due to the necessity to create a cavity in water for the ion to occupy.

Results & Discussion

MD simulations

Figure 1 gives the electrostatic potential of a 2.8 Å hard sphere solute in water as a function of charge at its centre for two choices of the centre of the hard sphere repulsion. The centre is shifted by a distance c towards the two hydrogen atoms along the line bisecting the HOH angle as shown in Figure 2. $c = 0$ Å is the universal choice of the oxygen atom as the centre. With this choice a strong non-linearity is observed with a preference to solvate negative charges. The linear fit is constrained to pass through the potential in the neutral cavity. These results are consistent with previous work which show a preference of the SPC/E water to solvate anions.[4–6,8,10] Normally modifications to the Born model are developed to attempt to fit this data such as a piecewise linear model, which is equivalent to using a charge dependant Born radii.[6]

However, we see that when the centre of the water molecule is shifted to $c = 0.5$ Å, as shown in red in Figure 1, the asymmetric non-linear response is removed and a linear fit gives an excellent description of the electrostatic potential and therefore the solvation free
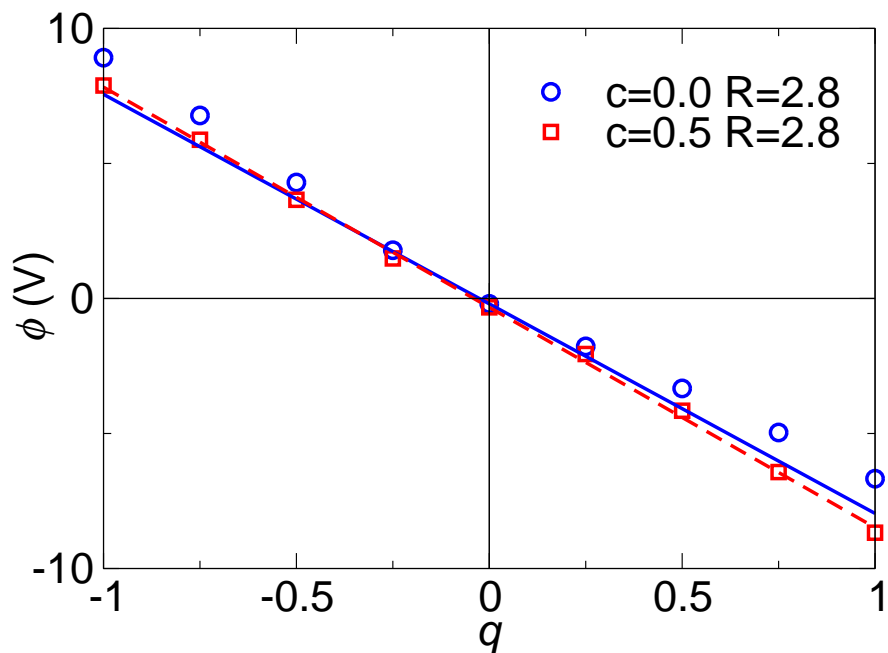
Figure 1: Electrostatic potential at the centre of a $R = 2.8$ Å sized cavity in water with the oxygen centre chosen to be on the oxygen (Blue) or 0.5 Å towards the hydrogens. (Red) Linear best fits are shown for comparison showing good linearity for red.
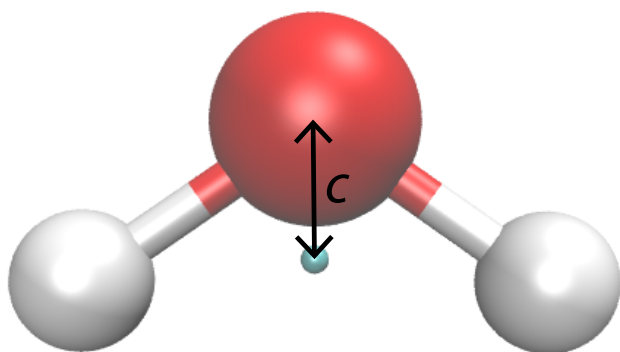

Figure 2: Depiction of the new centre of the water molecule and the c parameter.

energies. Crucially, the water-water interaction is not altered, which still acts on the oxygen atom. This new water centre is only used for the definition of the hard sphere repulsion interaction.

An estimate of the bulk solvation free energies of these ions can be determined by using a linear fit to the electrostatic potential in the positive and negative regions separately where the linear fit is constrained to pass through the cavity potential. The gradient of these linear fits k can be converted to the bulk solvation free energy by $\frac{1}{2}ke$. Table 1 provides the bulk solvation free energies of 2.8 Å sized ions studied.

Table 1: Bulk solvation free energies in kJmol^{-1} of 2.8 Å charged hard spheres with varying c values.

	$q = +e$	$q = -e$
$R = 2.8$, $c = 0.000$ Å	−321	−445
$R = 2.8$, $c = 0.500$ Å	−393	−394
$R = 2.8$, $c = 0.577$ Å	−408	−384

For a centre exactly halfway between the two hydrogen atoms ($c = 0.577$ Å) a preference for cations is actually produced. This demonstrates the strong dependence of the CHA on the arbitrary choice of the centre of the water molecule where the repulsive potential acts. This establishes that the CHA is not an intrinsic property of the electrostatic response of water but rather the result of an arbitrary and unjustified assumption about the nature of the short-range repulsive interaction between solute ions and water.

Figure 3 and Table 2 show that the choice of $c = 0.5$ Å as the centre results in a linear and charge symmetric response of water for various different cavity sizes. This establishes that this response is not unique to the 2.8 Å sized solute. For the solute around 2 Å the linear response does begin to break down. This shows that this linearity is not guaranteed and that there is a size range below whicht the linear response of water breaks down. However, it is worth noting that this 2 Å sized ion is smaller than essentially any real ion would be for instance the ion-oxygen distance is 1.7 Å for cations and 2.2 Å for anions, which are both smaller than the ion-oxygen separation values for lithium and fluoride, which are 2.1

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Å and 2.7 Å respectively.[18] The electrostatic solvation free energy of ions of this size (-630 and -748 kJmol^{-1}) are also far larger than the solvation free energies of the real lithium and fluoride ions. (-436 and -537kJmol^{-1}) The 2.4 Å sized cavity is a much better analogue for these two smallest monoatomic monovalent ions. This demonstrates that linear response of water can be considered to hold for all monoatomic monovalent ions.
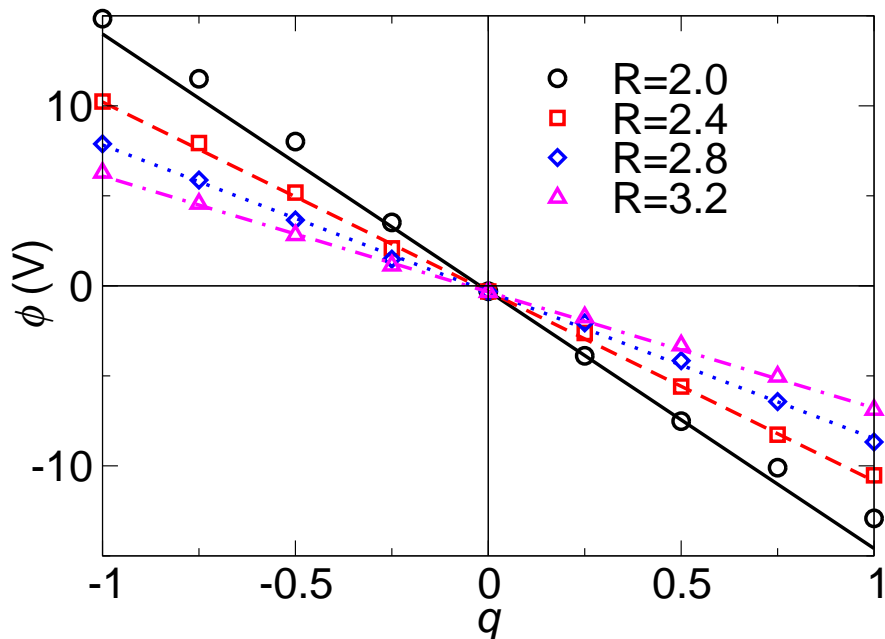

Figure 3: Electrostatic potential at the centre of a cavity of various sizes in water with the centre chosen to be on 0.5 Å from the oxygen. Linear best fits are shown for comparison showing good linearity.

Table 2: Bulk solvation free energies in kJmol^{-1} of charged hard spheres of varying size with $c = 0.5$Å.

	$q = +e$	$q = -e$
$R = 2.0$ Å	-630	-748
$R = 2.4$ Å	-499	-516
$R = 2.8$ Å	-393	-394
$R = 2.3$ Å	-306	-315

Figure 4 shows that with a $c = 0.5$ Å value the cavity potential is quite constant with

less than half as much variation compared with the $c = 0.0$ Å case and around a quarter as much variation if we remove the unphysically small 2 Å cavity for the $c = 0.5$ Å case. This is a significant as such small variation of the cavity potential means that it is reasonable to discuss the bulk solvation free energy in an ion independent way. The value observed here of ≈ -0.34 V is approaching the value proposed by Beck of -0.4 V.[17,31,33,34] This cavity potential is believed to play an important role in driving ion adsorption to the interface and so its clarification should simplify our understanding of that process as well. There is some evidence from a comparison between TA$^+$ and TB$^-$ ions that there is a substantial negative potential that drives adsorption of the anion to the interface.[34,35]
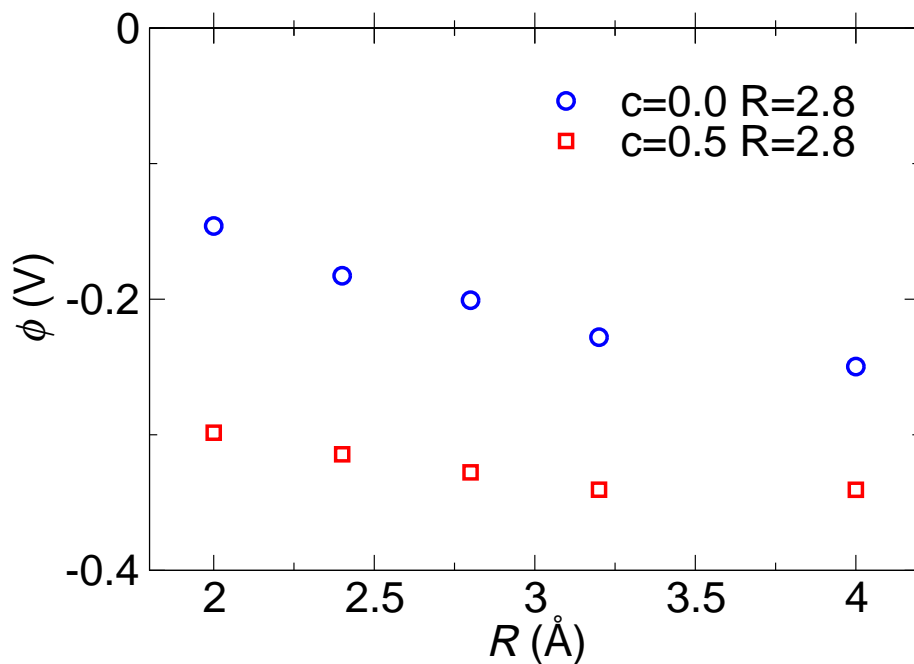

Figure 4: Electrostatic potential at the centre of a neutral cavity of various sizes in water with the oxygen centre chosen to be on the oxygen (Blue) or 0.5 Å towards the hydrogens. (Red)

Of course it is still a topic of debate whether SPC/E is accurately estimating the value of ≈ -0.34 V obtained here for the potential. It should be possible to much more accurately obtain this value using this same method with more sophisticated descriptions of water such

as MB-pol[36] or quantum mechanical MD simulations.[37] SPC/E is too negative relative to DFT-MD[29] but there is some evidence that the surface dipolar potential of DFT-MD is too positive relative to MB-pol.[25]

Continuum solvent model comparison

The Born solvation free energy model gives the solvation free energies with the following expression.

$$\mu_Q = \frac{(Qe)^2}{8\epsilon_0 R_{\text{cav}}}(1 - \frac{1}{\epsilon_w}) \tag{2}$$

The cavity size parameter is the distance to where the dielectric constant reaches its effective value of 78.3. In reality the dielectric constant will vary as a function of distance. However, as Ref. 38 shows, at the planar interface it is reasonable to approximate this with a sharp step function. The beginning of this layer will be a distance away from the centre of the water molecule, i.e., $R_{\text{cav}} = R_{\text{HS}} - R_{\text{Adj}}$. Where R_{Adj} is a fitted parameter adjusted to reproduce the potential at the centre of the charged cavity. A value of $R_{\text{Adj}} = 1.0$ Å provides a best fit to the data and seems reasonable given it is the size of the OH bond but a value anywhere from 0.5 to 1.4 Å could be possible as 0.5 Å is the distance to the oxygen atom and 1.4 Å is the average size of a water molecule in bulk.

Figure 5 compares this Born model estimate with bulk solvation solvation free energies determined from MD simulation with $c = 0.5$ Å and shows excellent agreement for cavities of 2.4 Å and larger.

Intuitive explanation

Above, we have used explicit MD simulations to demonstrate the importance of the choice of origin on the CHA for water. But it is also worth considering a simple thought experiment to build the intuition around the importance of the molecular origin. Imagine a solvent made of two opposite charges on a stick. The only natural choice of the origin of this molecule is
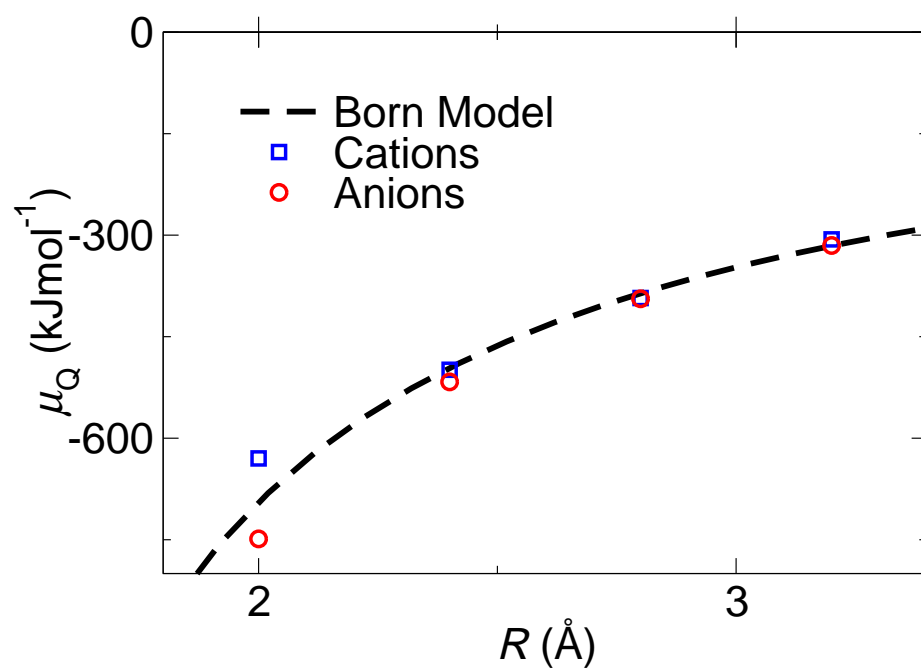
Figure 5: Comparison of Born model predictions with calculations of the bulk solvation free energies of cations and anions of different sizes using $c = 0.5$ Å.

halfway between the two charges. This liquid can have no CHA in this case as the molecule is entirely symmetric. However, it is possible to make a different choice for the centre of this molecule and place the centre on the negative charge on the stick. Now imagine a charged hard sphere is solvated in this liquid. The hard sphere repulsion acts on the 'centre' of the molecule, which is chosen to be the negative charge. In this case the liquid will appear to have a large preference for anions as the positive charges do not feel the hard sphere repulsion and can approach closer to the solute. This solvent will also appear to behave strongly non-linearly. Essentially, the problem is that as the negative solute charge increases the effective size of the cavity decreases. But this should not be considered a true feature of this liquid as it is entirely an artefact of selecting the negative charge to be the centre. Comparatively, most common models of water only differ minimally from this simple model in that the positive charge is split onto two separate charges but otherwise it has a very similar structure and so the same argument applies. Looked at from this perspective it is entirely unsurprising that classical MD shows an anion preference CHA. This is an inevitable and predictable result of placing the repulsion on the negative charge (the oxygen) of this molecule. The fact that classical MD shows this CHA is therefore not good evidence that it is a true property of water as it is entirely a result of a direct and unquestioned assumption in the model.

An additionally interesting insight can be gleaned from this model. The air-solvent interface will create an electrostatic potential due to the orientation of dipoles at it. For our toy model this property again must be 0 if halfway point between the two charges is chosen as the centre of the molecule by symmetry. However, it is known that the size of this dipolar surface potential also depends on the choice of the origin of the water molecule as described by the following equation:

$$\phi_{\mathrm{D}}^{\mathrm{shift}} = -\frac{\rho_w \langle \boldsymbol{\mu} \cdot \boldsymbol{d} \rangle}{3\epsilon_0} \tag{3}$$

If we shift our origin to the negative charge of the molecule, which we take to be the

distance $0.5 \cos\left(\frac{109.47}{2}\right) = 0.29$ Å as this is the distance to halfway between the oxygen and hydrogen charges on an SPC/E water molecule and assume the same dipole moment and density as SPC/E water we determine a surface potential of $+0.28$ V very similar to the calculated surface dipole potential of water with SPC/E with the oxygen atom as the centre $(+0.26\text{V}).$[29] This highlights how much of the supposed asymmetry of the water molecule is purely a result of assuming the oxygen atom to be the centre of the molecule.

We can also recalculate the surface dipole potential of water with the centre of $c = 0.5$ Å as the value which gives a linear response of water. This gives a surface dipole potential for water of -0.23 V. Interestingly this is a lot closer to the net potential at the centre of the empty cavity. ($-.30$ V with 2.0 Å cavity and $c = 0.5$ Å). This implies that the Bulk and intrinsic solvation free energies are much closer to each other when a linear response centre is chosen for the water molecule in contrast to the case of the oxygen centre where these two solvation energies are in opposite directions from the real solvation free energies.

Counter argument

One potential counter argument to the point of view outlined in this work is to argue that the choice of oxygen for the centre of the molecule is not arbitrary and reflects some inherent property of the water molecule. One justification of this argument could be to point to the fact that many properties of water can be reproduced with simple models that make this assumption like SPC/E. But this is not convincing evidence as these models have been fitted to reproduce these values by varying parameters such as the charges and Lennard-Jones parameters and this choice has not been demonstrated to be the best one based on a rigorous examination of all the choices or comparison with quantum mechanical calculations. Additionally, even if this choice is best for describing the properties of pure water this does not necessarily mean it is also true for ions which have very different electronic structure to pure water and will therefore likely repel water in different ways. In fact, it is not even clear that one choice of the centre of a water molecule will work best for both real cations and

anions or even that it is possible to identify such a 'centre of repulsion' concept for them. Real ions will have complex and specific short-range quantum mechanical interactions with water. It is not reasonable to assume that all ions are best described with a simple oxygen centred repulsive term. In fact symmetry adapted perturbation theory calculations show[17] that the fluoride ion's exchange repulsion interaction with surrounding water molecules is roughly four times larger than potassium's even though these two ions have very similar ion-oxygen distances. This highlights the inaccuracy of an oxygen centred repulsion.

It is obviously not possible for a simple electrostatic continuum solvent model to directly account for all of the complexities associated with the short range quantum mechanical inter-actions. That is the reason additional terms such as dispersion solvation energy and surface area dependent correction terms are used in combination with a continuum electrostatics model to achieve experimental agreement.[20] The question about how best to model these terms remains debatable although significant progress has been made.

However, in general it is highly unlikely that an ionic solute will have an ion-water repulsion centred around the correct point for a linear model to be applicable. The question then naturally arises as to whether this linear model is useful for understanding these solutes. The best approach to modelling these real ions we believe is to find the closest model potential to the true potential so that the real hydration structure is matched as closely as possible. This model potential can be composed of a mixture of a charged hard sphere term to describe the long range electrostatics combined with a short range correction term to give the correct local hydration structure. Given this partitioning it is natural that the hard sphere repulsion should act on the $c = 0.5$ Å centre of the water molecule as this will mean that the long range electrostatics can be described with a simple linear model. The correction due to the short range potential can potentially then be treated with a perturbative level of theory and if the similarity is close enough this correction can potentially be estimated using linear theory as well. This is essentially the approach used in Ref. 25. It may be necessary as well to include a relaxation term which corresponds to the relaxation of the hard sphere repulsion. This

term is inherently non-linear but can be kept relatively small if the hard sphere cavity is chosen to minimise it.[25]

Conclusions

In conclusion, we have shown that the apparent CHA of water observed with simulation is caused by attempting to incorporate assumed details of the complex short-range repulsion into the description of the electrostatics and that there is no inherent non-linear CHA in the pure electrostatic response of water to a charge even at the atomic scale. In other words, the apparent CHA of water is not an intrinsic property of bulk water as often argued but is rather a result of the asymmetric short-range repulsive interaction between ions and water arbitrarily assumed in classical simulation models by placing the centre of the water molecule on the oxygen.

Calculation details

Simulations are run using the LAMMPS programme[39] in the constant volume (NVT) ensemble at 300 K with the Nose-Hoover thermostat. 512 water molecules and one ion are placed in a box of dimensions 18.7^3 Å^3 to reproduce the experimental water density. To keep the water density fixed the box size was increased to 18.8^3 Å^3 for the 3.2 Å sized cavity and to 21.8^3 Å^3 with 343 waters for the 4 Å cavity. Calculations are run for 500 ps with a 50 ps equilibration prior to analysis. Structures are output every 50 fs. The Lennard-Jones parameters are kept fixed as the standard SPC/E values for the water-water interaction. An M site is added to the water molecule a distance c from the oxygen atom halfway between the two hydrogen atoms. The HMH angle is given by:

$$2\tan^{-1}\left(\frac{\sin\left(\frac{109.27}{2}\right)}{\cos\left(\frac{109.27}{2}\right) - c}\right) \tag{4}$$

The solute solvent hard sphere modelled using a very sharp exponential repulsion:

$$A \exp\left(\frac{\sigma - r}{\rho}\right) \tag{5}$$

where $A = 84$ kJmol^{-1}, $\rho = 0.5$ Å^{-1} and σ is the hard sphere radius and the repulsion acts on the M-site of the water molecule.

Electrostatic potentials at the centre of the cavity were determined using Ewald summation. The cross check was performed by calculating the electrostatic potentials by integrating out the spherical charge density according to the Poisson equation in spherical coordinates out to the edge of the box. And computing the average potential over the box reference. The following expression is used to correct the solvation free energies and potentials for finite size effects as a function of charge:

$$\mu_{\text{Ew-Corr}} = -\frac{q_I^2}{8\pi\epsilon_0 L}\left(1 - \frac{1}{\epsilon_w}\right)\left(\xi_{\text{Ew}} + \frac{4\pi}{3}\left(\frac{R_I}{L}\right)^2 - \frac{16\pi^2}{45}\left(\frac{R_I}{L}\right)^5\right) \tag{6}$$

This method of computing the electrostatic potential is equivalent to setting the zero of the electrostatic potential in water to be zero. This is an unphysical reference for classical water models. The electrostatic potential should be set to be zero infinitely far into the vacuum accross the air-water surface. The electrostatic potentials are therefore all corrected by the surface potential of SPC/E water. The surface potential of pure SPC/E is $-.59$ V.[27]

See Refs. 9,24,40,41 for a more extensive discussion of these corrections.

Statistical errors were determined through the block averaging and estimating the error in the mean as well as running multiple extra runs and examining the standard deviation. Errors were determined to be ± 0.02 V for the potentials during charging. This corresponds to an error of 1 kJmol^{-1} in the solvation energies. For determining potentials inside the neutral cavities as shown in Figure 4 more precision is needed and runs of 2500 ps were used to reduce the errors to 0.005 V. All errors are smaller than the symbols used in the plots.

Acknowledgements

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