Understanding the scale of the single ion free energy: A critical test of the tetra-phenyl arsonium and tetra-phenyl borate assumption

Timothy T. Duignan, Marcel D. Baer, and Christopher J. Mundy

Articles you may be interested in

Understanding the scale of the single ion free energy: A critical test of the tetra-phenyl arsonium and tetra-phenyl borate assumption

Timothy T. Duignan,[1,2,a)] Marcel D. Baer,[1,b)] and Christopher J. Mundy[1,3,c)]

[1]*Physical Science Division, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99354, USA*
[2]*School of Chemical Engineering, The University of Queensland, St Lucia, Brisbane 4072, Australia*
[3]*Department of Chemical Engineering, University of Washington, Seattle, Washington 98195, USA*

The tetra-phenyl arsonium and tetra-phenyl borate (TATB) assumption is a commonly used extra-thermodynamic assumption that allows single ion free energies to be split into cationic and anionic contributions. The assumption is that the values for the TATB salt can be divided equally. This is justified by arguing that these large hydrophobic ions will cause a symmetric response in water. Experimental and classical simulation work has raised potential flaws with this assumption, indicating that hydrogen bonding with the phenyl ring may favor the solvation of the TB⁻ anion. Here, we perform *ab initio* molecular dynamics simulations of these ions in bulk water demonstrating that there are significant structural differences. We quantify our findings by reproducing the experimentally observed vibrational shift for the TB⁻ anion and confirm that this is associated with hydrogen bonding with the phenyl rings. Finally, we demonstrate that this results in a substantial energetic preference of the water to solvate the anion. Our results suggest that the validity of the TATB assumption, which is still widely used today, should be reconsidered experimentally in order to properly reference single ion solvation free energy, enthalpy, and entropy. *Published by AIP Publishing.* https://doi.org/10.1063/1.5020171

I. INTRODUCTION

Ionic solvation free energies help determine many important experimental properties such as ionic partitioning coefficients,[1] pKa values,[2] and the electrochemical stability of electrolytes.[3] They are also essential for testing and parameterizing models of electrolyte solutions. If the solvation free energies are not correctly reproduced, then it is unlikely other properties will be correctly predicted. This is supported by the work demonstrating that fitting to reproduce single ion solvation free energies improves the performance of continuum solvent models[4,5] and classical simulation.[6,7]

The solvation free energies of neutral salts can be straightforwardly determined from experiment. Remarkably however, there is still no consensus on what the solvation free energy of individual ions are, namely, there is disagreement regarding the individual contributions of the cation and anion. Knowing these values would help improve our models of electrolyte solution and allow for more accurate predictions of experimental properties. More generally, these quantities are one of the simplest properties of one of the most universal and important substances in the natural world, and our inability to quantitatively model them significantly undermines the confidence we can have in theoretical methods applied to the condensed phase. Determining these values is also necessary to develop a physical understanding of the properties of electrolyte solution. For instance, understanding the charge hyrdation

asymmetry (CHA) has been the subject of significant research.[8–10] The CHA describes the preference for water to solvate an anion over a cation of similar size. Because we do not know what the correct values for the single ion solvation free energies are, the CHA remains elusive. For ions such as potassium and fluoride, the size of this asymmetry varies from ≈75 kJ mol⁻¹ [11] to 170 kJ mol⁻¹ [12] depending on the experimental protocol as shown in Fig. 1.

One challenge for computing single ion solvation free energies within the molecular simulation framework is the choice of the zero of the electrostatic potential. This choice does not matter for neutral ion pairs as the $q\phi$ term will cancel. Confounding the issue, different choices are possible for the zero of the electrostatic potential that result in different definitions of the single ion solvation free energy. There are four key definitions of the single ion solvation free energy: the real, bulk, intrinsic, and Ewald. For a detailed discussion of the aforementioned terminology and the definitions of the surface potentials, we refer the interested reader to the studies of Duignan *et al.*[13] and Remsing *et al.*[14] A textbook on this topic[15] examines the consequences for specific choices of the zero of the potential. In particular, it is argued that the real solvation free energies are experimentally accessible and well determined and correspond to the choice that the zero of the electrostatic potential is in the vapor phase far away from the air-water interface. This choice of zero potential yields a value of −1075 kJ mol⁻¹ for the real solvation free energy of a proton, primarily on the basis of electrochemical measurements.

It is useful to define a single ion solvation free energy that does not depend on the properties of the distant air-water

a)Electronic mail: t.duignan@uq.edu.au
b)Electronic mail: marcel.baer@pnnl.gov
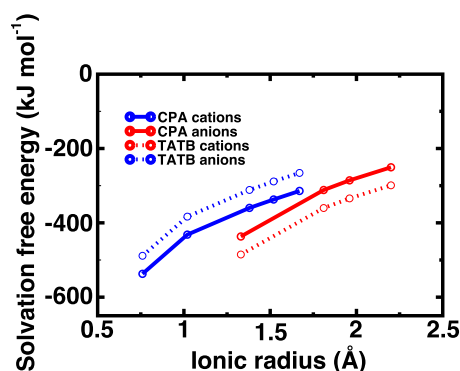c)Electronic mail: chris.mundy@pnnl.gov

FIG. 1. Solvation free energies of the alkali halide ions with the CPA approximation in comparison to the TATB approximation.

interface. One such choice is the intrinsic solvation free energy and differs from the real solvation free energy by the removal of potential due to the distant air-water interface, namely, the dipolar surface potential term.[13,14] The only problem with the intrinsic solvation free energy is that it was shown to depend on the choice of the origin of the water molecule and thus is inherently somewhat arbitrary.[16,17] Another useful definition of the single ion solvation free energies is the bulk solvation free energies as defined by Beck[18] following Harder and Roux.[19] The bulk solvation free energy corresponds to setting the electrostatic potential to be zero at the center of an uncharged cavity in water. This choice of the zero of potential corresponds to the Born model of ion solvation.[13,18] Ambiguities of the bulk solvation free energy are encountered as they depend on both the methods used to create the cavity and its size. The final type of single ion solvation free energy is the Ewald definition. The Ewald solvation free energies corresponds to the values that are determined using Ewald summation with no corrections other than for finite size effects. The Ewald quantity is commonly reported in the literature and corresponds to setting the average electrostatic potential of the cell to be zero. Ewald values have a strong dependence on the water model.[13,14]

Connecting the theoretical definitions and constructs to experiments that can measure the single ion free energies requires the so-called "extra-thermodynamic assumptions." Molecular simulation is a powerful tool to determine if these assumptions are reliable and if so, to determine the definition of the solvation free energy to which they correspond. The cluster pair approximation (CPA)[11,20] is one of the most widely known "extrathermodynamic assumptions." This method determines single ion solvation free energies using experimental formation free energies of ion-water clusters with $n = 1$-6 water molecules. It is apparent that very small clusters do not have the same dipolar surface potential as the bulk air-water interface and this estimate cannot correspond to the real solvation free energy. Hünenberger and Reif[15] argue that the CPA instead gives intrinsic solvation free energies. That would require the CPA values to correspond to a dipolar surface potential of zero, which is a reasonable assumption. Theoretical work has demonstrated that there is a shift in the single ion solvation free energy if the cluster pair method is extended

to large cluster sizes.[21,22] This is evidence that the dipolar surface potential is converging to the bulk surface value as the cluster size increases. Indeed, the intrinsic solvation free energy calculated using *ab initio* molecular dynamics (AIMD) by Duignan *et al.*[16] agrees with the CPA values if the center of nuclear charge is chosen for the center of the water molecule.

The other widely known "extra-thermodynamic hypothesis" and the focus of this current study is the tetra-phenyl arsonium and tetra-phenyl borate (TATB) assumption.[23,24] This assumption states that for two large hydrophobic ions the water response will be symmetric with respect to the charge, namely the positive tetra-phenyl arsonium (TA$^+$) cation should have the same solvation thermodynamics as the negative tetra-phenyl borate anion (TB$^-$). This assumption implies an equal split of the TATB solvation free energy into a cationic and anionic part which straightforwardly allows for the determination of the single ion solvation free energy of all the other ions. The solvation free energies tabulated by Marcus are based on this assumption. Moreover, the TATB values are among the most widely cited in the community. It is therefore crucial to understand the molecular origins of the assumption to provide additional clarity regarding the precise solvation free energy the TATB method is estimating. A depiction of these ions and representative snapshots of the solvating water molecules is shown in Fig. 3.

It is known that the structuring of water around a solute in water can create an electrostatic potential at the position of that solute.[14,18,25] This potential in the center of a hard sphere solute has been studied by many researchers and is referred to as the net potential when it is properly referenced to the vapor phase and it is represented by ϕ_{np} by Beck[18] or Φ_{HW} by Remsing *et al.*[14] This aqueous response to a *neutral* hard sphere solute can create a zeroth order preference for the solvation free energy of the cation versus anion. Indeed, a necessary condition for the TATB assumption to give real solvation free energies is a negligible net potential. If the net potential is non-negligible, the TATB assumption could still be correctly estimating the *bulk* solvation free energies. This is because the bulk solvation free energies have the net potential removed.[13,18] This would require the net potential to be independent of the nature of the solute as otherwise the bulk solvation free energies will require an ion-specific correction to be converted to real solvation free energies.

In order to test the TATB hypothesis, it is necessary to determine whether water has a net preference for either the cation or anion and then show that this preference is not purely driven by the net potential or to demonstrate that the net-potential for TATB ions is dependent on specific non-electrostatic properties of the solute. The single ion solvation free energies determined with the TATB assumption differ by ≈ 50 kJ mol^{-1} from the CPA values as shown in Fig. 1. This suggests that the preference for the anion is approximately twice as strong using the TATB assumption as compared to the CPA. This question has been examined recently using spectroscopic measurements[26] that probe the hydrogen bonding interaction of the water molecules with the phenyl rings of the TB$^-$ molecules. This mechanism was originally suggested by Schurhammer and Wipff.[27] Classical MD[27,28] was also used

to investigate this topic. Many different charge sets for the solute were derived from charge partitioning schemes. This work demonstrated that the preference for the anion vs. the cation switched depending on what treatment of the electrostatic interaction was used. This work argued that a standard Ewald reference was best and therefore concluded that the anion was strongly preferred. However, it has more recently been demonstrated that free energies estimated from the Ewald reference are not physically meaningful as this reference takes on a severe model dependence.[13,29] It is also unlikely that classical MD using standard charge partitioning schemes can reproduce the correct hydrogen bonding interaction with the phenyl ring as determined by spectroscopy.[26] A number of simple models have been developed to address this question.[30] These models have concluded that the anion is preferred over the cation, but the size of this preference depends on the model.

Herein, we focus on testing the TATB assumption from a molecular perspective using AIMD. The use of quantum density functional theory (DFT) within the generalized gradient approximation to understand the water structure around hydrophobic ions has recently been demonstrated.[31] DFT has also been demonstrated to reliably model the air-water interface, where the inclusion of dispersion corrections is a key advance.[32,33] Here, we set out to confirm the spectroscopic observations of Scheu *et al.*[26] by simulation of the TA$^+$ and TB$^-$ ions in water in addition to the neutral tetra-phenyl carbon (TC^0) solute. To this end, we establish connection with recent spectroscopic experiments in addition to computing average ion-water binding energies and net potentials demonstrating that there are substantial charge asymmetries between the TB$^-$ and TA$^+$ providing strong evidence that the TATB approximation is not reliable. This analysis neglects considerations of changes in the conformational flexibility of the solute in water compared to the gas phase. It is possible that these effects could provide an additional source of asymmetry between the cation and anion.

II. RESULTS AND DISCUSSION

The radial distribution functions (RDFs) of the hydrogen and oxygen atoms around the tetraphenyl arsonium (TA$^+$), tetraphenyl borate (TB$^-$), and tetraphenyl carbon (TC^0) molecules are shown in Figs. 2(a) and 2(b). It is clear that the RDFs between the water oxygens and the central solute atoms appear to be qualitatively similar for all three solutes. The water hydrogen RDF with the central solute atom demonstrates that the first shell solvation water molecules are reorienting due to the solute charge as expected.

However, there are non-trivial structural differences as a function of the solute charge. Scheu *et al.*[26] use the red shifted vibrational signature of the first solvation shell water molecules to argue that there is preferential hydrogen bonding with the phenyl rings leading to stronger interactions of the water with the anion over the cation. This specific interaction is supported by the RDFs. At about 2.5 Å in the phenyl-carbon to water hydrogen RDF [see Fig. 2(c)], a small peak in the anionic RDF is present that is not observed in the cationic case and only weakly observed in the neutral case of TC^0. We can also
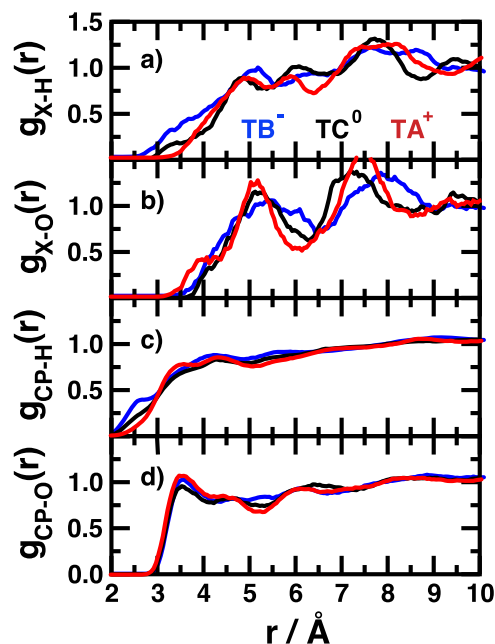

FIG. 2. Radial distribution functions for water hydrogen with respect to (a) the central atom for TB$^-$ (blue), TC^0 (black), and TA$^+$ (red) and (c) the phenyl-ring carbon atoms, and water oxygen with respect to (b) the central atom for TB$^-$ (blue), TC^0 (black), and TA$^+$ (red) and (d) the phenyl-ring carbon atoms.

examine the orientational structure of the water molecules around the solutes. This is shown in Fig. 3 depicting the differing orientations of the closest water molecules due to the charge on the solutes. Interestingly, the TC^0 solute structure is much more similar to the TB$^-$ anion than to the TA$^+$ cation. This is due to the hydrogen bonding with the phenyl rings that are similar for both of the TC^0 and TB$^-$ solutes. Interestingly, the solvation of the TA$^+$ cation appears to closely resemble the solvation around a neutral hard sphere hydrophobic molecule
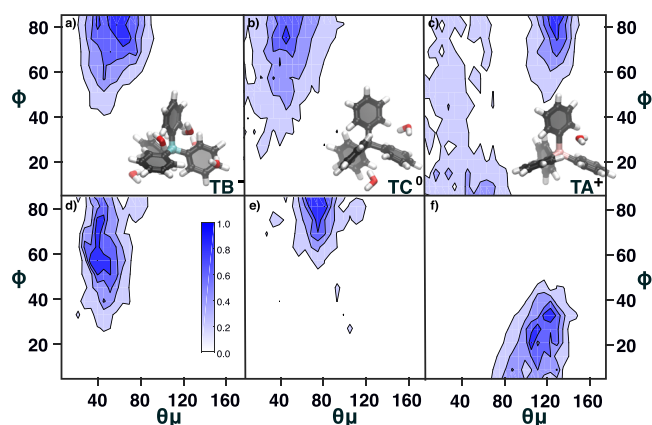

FIG. 3. Orientational structure distribution functions of the first water around the solutes. The upper row (a)–(c) is with respect to the phenyl ring and second row (c)–(f) is with respect to the central atom. Also included are some representative snapshots of the TA$^+$, TB$^-$, and TC^0 solutes with the closest solvating water molecules. The analysis presented consists of examining the orientational distribution of the closest solvating water molecule averaged over the entire trajectory. Here Θ_μ and Φ are the orientations of the water dipole and the angle of rotation about the dipole with respect to the O-solute vector, respectively. Details of the orientational analysis are provided in by Remsing *et al.*[14]

of similar size.[14] This provides additional evidence that hydrogen bonding with the phenyl rings leads to significant ion specific effects for these solutes.

To make direct contact with the experimentally observed vibrational frequency shift of about 70 cm^{-1}, we compute the vibrational density of states (VDOSs) using the mass weighted autocorrelation function of the velocity over 4 ps long windows. The resulting spectra were smoothed by a Gaussian convolution kernel of 10 cm^{-1} standard deviation.[34] In Fig. 4, the VDOS for the whole system (solute and solvent) calculated for the TB$^-$ simulation is shown as grey shaded area. Comparing the full spectrum, there are significant differences in the OH-stretch spectral region between the three different simulations. Focussing solely on water molecules that have a hydrogen that is within 3.0 Å of any of the phenyl carbons reveals ion-specific spectral signatures. The anion shifts the "free-OH" blue by 70 cm^{-1} with a maximum around 3588 cm^{-1} compared to the cation at 3657 cm^{-1}. The pure hydrophobic solute lies in between at 3620 cm^{-1}. These frequency shifts are consistent with the shift observed spectroscopically by Scheu et al.[26]

The structural and spectroscopic results provide some evidence that the water is not responding symmetrically to the positive and negative solutes. This casts some doubt on the TATB assumption. However, from the structural data alone, it is not possible to draw definitive conclusions regarding the solvation thermodynamics. It is still possible that the structural asymmetries are not significant enough to alter the energies. To more directly probe the validity of the TATB assumption, it is necessary to compute interaction energies directly. The computational demands of using DFT to compute solvation free energies with the methods detailed by Duignan et al.[13,16] for these large hydrophobic ions are at present formidable.

It is straightforward however to compute the average binding energy of the solute to the water: $\langle U_{\text{bind}} \rangle$. This binding energy is defined as
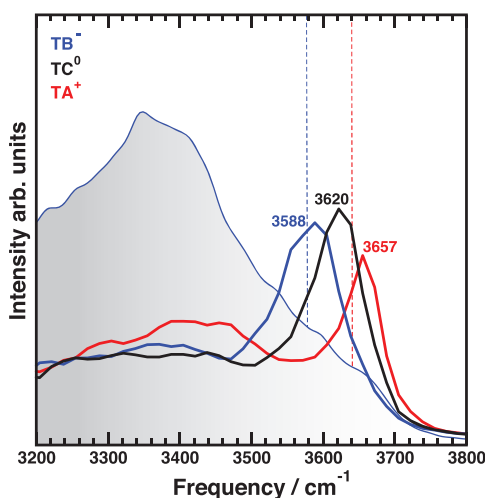
$$U_{\text{bind}} = U_{\text{XS}} - U_{\text{S}} - U_{\text{X}}. \quad (1)$$

Here U_{XS} is the total energy of the solute (X) and solvent (S). U_{S} is the energy of the solvent alone and U_{X} is the energy of the solute in the gas phase. This average binding energy is crucially important for computing the single ion solvation free energies which for a rigid solute can be written explicitly following Ben-Amotz et al.[35] as

$$\mu = -k_{\text{B}}T \ln \left\langle \exp^{-\beta U_{\text{bind}}} \right\rangle = \langle U_{\text{bind}} \rangle + k_{\text{B}}T \ln \left\langle \exp^{\beta \delta U_{\text{bind}}} \right\rangle. \quad (2)$$

It is therefore clear that if $\langle U_{\text{bind}} \rangle$ shows substantial charge hydration asymmetries, then there will be substantial asymmetries in the single ion solvation free energy as well and the TATB hypothesis cannot be considered reliable.

It has been previously established that the energies need to be corrected to account for the surface potential as we initially computed this binding energy using Ewald summation. There is also a finite system size correction required. These corrections are explained in Sec. III. Table I gives the resulting binding free energies. It is clear that there is a very large asymmetry of ≈180 kJ mol^{-1}, with the anion being strongly preferred over the cation consistent with the structural information. This provides compelling evidence that the TATB assumption is not reliable. It is of interest to point out that although it is unlikely that linear response theory can be applied for the ions studied herein, the linear response estimate of the charging contribution to the solvation free energy will be approximately half of the difference in interaction energy between the charged and uncharged states.[35]

Given that we have established an asymmetry in both the structure and energy, it is of interest to understand the sources of this asymmetry. The net potential at the center of an uncharged solute in water will preferentially solvate an anion or cation depending on its sign. In the unphysical limit of very small charges, the net potential would be the dominant term in the free energy of solvation. Table I provides the net potentials for the three solutes studied that are computed at the central atom of the solute calculated with that solute removed. The net potential is corrected by the appropriate terms, (e.g., the mean inner potential or the surface potential) for proper reference to the vapor phase and a finite size term (see Sec. III). Our results demonstrate that the neutral solute has a significant positive potential at its center. This is a result of the hydrogen bonding with the phenyl rings creating a preferred orientation of the water molecules around the solute. This net potential alone would create a preference of ≈150 kJ mol^{-1} for the anion. This is large enough to explain 85% of the total asymmetry (≈180 kJ mol^{-1}). Moreover, this potential is much larger than is observed for a similarly sized hard sphere in water. It has been shown that a 6 Å size hard sphere with BLYP-D2 water

FIG. 4. Vibrational density of states for the water molecules in the first solvation shell around the phenyl carbon atoms for TB$^-$ (blue), TC^0 (black), and TA$^+$ (red) compared to the full spectrum (grey shaded) for the TB simulation. Solvation shell water molecules are defined based on the g(r); see Fig. 2 for the phenyl-ring carbon atoms to water hydrogen atoms. The VDOS is calculated based on a window function of 2 ps. The dashed lines give the experimental values determined by Scheu et al.[26]

TABLE I. Net potentials and average binding energies for the three solutes.

Solute	$\langle U_{\text{Bind}} \rangle$ (kJ mol^{-1})	Net potential (V)
TC^0	−269	0.8
TA$^+$	−465	−2.4
TB$^-$	−644	3.6

has a net potential of -0.025 V.[14] As outlined by Marcus,[24] for the TATB assumption to be reliable, these ions must closely resemble hard spheres with inert peripheries. This significant difference in electrostatic potential created by the TC^0 solute and a hard sphere of similar size demonstrates that these ions do not meet these criteria.

An additional and common source of the CHA is that water may respond asymmetrically to the presence of a positive or negative charge. This effect is captured in the Born model framework by assuming different Born radii definitions for cations and anions. It is assumed that this effect will become negligible for large hydrophobic ions, hence the TATB assumption. This study suggests that this is not the case. By examining the shift in the net potential going from the neutral solute to the ion, Table I depicts a slightly larger shift for the cation than for the anion. This indicates that the water response is more favorable to the positive ion than to the negative ion and is the opposite behavior to what is observed for small charged hard spheres.[13] This effect will counteract the net potential and is roughly -20% of the solvation asymmetry.

The final contribution to the solvation energy is due to the specific quantum mechanical interactions of the ion with the water molecules. This effect is not reflected in the net potential as it does not have an electrostatic origin. It has been demonstrated that anions will have a larger dispersion interaction with water, which is a plausible explanation for the CHA.[36] This has been confirmed with symmetry adapted perturbation theory (SAPT) calculations.[10] Although these calculations also demonstrate a large exchange repulsion term that acts in the opposite direction mitigating the CHA.[37] In the case of TB^- and TA^+, it is difficult to estimate the dispersion interaction of these large ions with the water due to the inaccurate assumption of a point polarizability.[38] For TB^- and TA^+ ions, hydrogen bonding of the waters with the phenyl rings introduces an additional potential source for the asymmetry. For example, Schurhammer and Wipff[27] demonstrated that there is a ≈ -40 kJ mol^{-1} hydrogen bond formed between the phenyl ring of TB^- and a water molecule in the gas phase, whereas the short-range interaction energy between the TA^+ and a water molecule is much smaller. We leave it as a conjecture that this is the source of the remaining 35% of the solvation asymmetry.

We have argued above that the TATB assumption neglects a preference of water for the anion. This view gives rise to a puzzle. The puzzle is that the values for the solvation properties determined using the TATB assumption already show a strong preference for the anion. In fact this preference for the anion is stronger than almost all other estimates of the single ion solvation properties.[15] It is therefore implausible that this preference is even larger than the TATB assumption predicts. A potential resolution of this puzzle can be identified if the original experimental values for the TATB solvation properties are reassessed. Marcus arrives at an "experimental value" of 2×47 kJ mol^{-1} for the solvation enthalpy of the TATB salt.[23] However, this value depends on a model to determine the lattice formation enthalpy of the crystalline tetraphenyl salts.[23] It is plausible that this model may not be applicable to the tetraphenyl salts for a variety of reasons. In particular, it again ignores the specific interactions with the phenyl rings.

We therefore advocate that values for the single ion solvation properties based on the TATB assumption no longer be considered reliable.

III. CONCLUSION

In summary, we have demonstrated that there are small, but significant structural differences around the TA^+ cation and the TB^- anion. The electronic complexity of the TA^+ and TB^- necessitates the use of high quality interaction potential based on quantum mechanics to distinguish the aqueous structural response between TA^+ and TB^-. Specifically, hydrogen bonding with the phenyl rings is observed through our simulations for the TB^- anion but not for the TA^+ cation, and the experimentally observed vibrational shift associated with this hydrogen bonding is reproduced. We then perform direct calculation to confirm that the water is preferentially interacting with the anion and consequently identify the large positive net potential as the dominant source of this preference. These calculations and simulations presented herein suggest a significant ion specific effect for the single ion free energy of the TA^+ and TB^- solutes and calls into question the validity of this assumption that is widely used in the community to determine single ion solvation free energies as given by Marcus.[12] Given that we have demonstrated that the TATB approximation has been demonstrated to be unreliable, it is crucial that new methods for determining single ion solvation free energy are developed that are known to be reliable. Various exciting new attempts to address this problem are currently being developed.[16,39–41]

IV. COMPUTATIONAL DETAILS

A. *Ab initio* simulations

Born-Oppenheimer *ab initio* molecular dynamics simulations within the NVT (at 300 K) ensemble using periodic boundary conditions are performed within the CP2K simulation suite (http://www.cp2k.org) containing the *QuickStep* module for the DFT calculations.[42] We followed a similar protocol as in Ref. 43, using a double zeta basis set that has been optimized for the condensed phase[44] in conjunction with GTH (Goedecker-Teter-Hutter) pseudopotentials[45] using a 400 Ry cutoff for the auxiliary plane wave basis. A Nosé-Hoover thermostat was attached to every degree of freedom to ensure equilibration.[46] The Becke exchange[47] and correlation due to Lee, Yang, and Parr (LYP)[48] is utilized in addition to the dispersion correction (D2) put forth by Grimme[49] with a 40 Å cutoff. The TX simulation cell consisted of one solute molecule in 497 water molecules in a cubic box with the edge length of 24.955 Å. Production simulations of 45 ps were conducted for TX molecules.

B. Charged system corrections

These simulations and energy calculations all use periodic boundary conditions with Ewald summation to treat the electrostatics. There are numerous technical challenges associated with correcting free energies calculated using Ewald summation. Approximate methods to perform these corrections have been outlined and discussed extensively elsewhere.[40,50] We

draw on this work to apply the following corrections to the energies and potentials presented above.

With Ewald summation the zero of the electrostatic potential is chosen so that the average electrostatic potential of the cell is zero. This is a result of setting the $k = 0$ term to 0 in the k-space sum. This means that the energies of systems with a net charge need to be corrected as otherwise the solvation free energies will depend on the arbitrary internal properties of the water molecules.

The best choice for the zero of the electrostatic potential is to be zero in the vapor phase very far away from the interface. This choice corresponds to real solvation free energies. The total surface potential is equal to the difference between the average potential in water and the average potential in the vapor phase far from the interface. We therefore need to subtract the total surface potential from these energies to correct them. The total surface potential can be given in terms of the dipolar surface potential plus the Bethe potential. The dipolar surface potential is a property of the interface and we use a value of 0.480 V as calculated by Remsing *et al.*[14] There is a significant uncertainty associated with this quantity, for instance, Hünenberger and Reif[15] recommend a value of 0.13 V. This corresponds to an uncertainty of at least 35 kJ mol^{-1} in the values of the binding free energies calculated here. The Bethe potential needs to be recalculated for the system here, by using the Wannier centers as described by Remsing *et al.*[14] and Duignan *et al.*[13] This results in values of 3.47 V for the TA$^+$ simulations and 3.53 V for the TB$^-$ simulations and 3.35 V for the calculations where no solute was present.

The calculations of the energies of the isolated solute molecules were also performed in PBC for consistency. This means that these energies also need to be corrected for by the Bethe potential of the cell. The dipolar surface potential does not contribute as this term is 0 for the gas phase. The Bethe potential with only the ion present was 0.12 V for TA$^+$ and 0.18 for TB$^-$. The version of Eq. (1) including corrections is

$$U_{\text{bind}} = \left(U_{\text{XS}} + q\phi_D + q\phi_{\text{Bethe}}^{\text{XS}}\right) - U_S - \left(U_X + q\phi_{\text{Bethe}}^{X}\right) + U_{\text{FSC}}. \tag{3}$$

No correction terms are required for the pure solvent energy as this system is charge neutral. It is also necessary to include a finite size correction term,[51,52] which is necessary to account for the fact that the ion is only solvating the finite number of water molecules in the cell, which will differ from the case of an infinitely large cell. This correction is given by[52]

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

where $\xi_{\text{Ew}} = -2.837$ and the ion size (R_I) is 5 Å. There is a corresponding correction to the net potentials, which is calculated from the above by dividing by the solute charge. This correction is included in the values given in Table I. This finite size correction is charge symmetric, so it is not relevant for testing the TATB assumption, but it is important to get the absolute values correct.

[1] Y. H. Zhao and M. H. Abraham, J. Org. Chem. **70**, 2633 (2005).
[2] K. S. Alongi and G. C. Shields, *Annual Reports in Computational Chemistry* (Elsevier Masson SAS, 2010), Vol. 6, pp. 113–138.
[3] A. Urban, D.-H. Seo, and G. Ceder, npj Comput. Mater. **2**, 16002 (2016).
[4] T. T. Duignan, D. F. Parsons, and B. W. Ninham, J. Phys. Chem. B **118**, 8700 (2014).
[5] T. T. Duignan, D. F. Parsons, and B. W. Ninham, Phys. Chem. Chem. Phys. **16**, 22014 (2014).
[6] D. Horinek, S. I. Mamatkulov, and R. R. Netz, J. Chem. Phys. **130**, 124507 (2009).
[7] D. Horinek, A. Herz, L. Vrbka, F. Sedlmeier, S. I. Mamatkulov, and R. R. Netz, Chem. Phys. Lett. **479**, 173 (2009).
[8] J. P. Bardhan, P. Jungwirth, and L. Makowski, J. Chem. Phys. **137**, 124101 (2012).
[9] A. Mukhopadhyay, A. T. Fenley, I. S. Tolokh, and A. V. Onufriev, J. Phys. Chem. B **116**, 9776 (2012).
[10] T. T. Duignan, D. F. Parsons, and B. W. Ninham, Chem. Phys. Lett. **608**, 55 (2014).
[11] M. D. Tissandier, K. A. Cowen, W. Y. Feng, E. Gundlach, M. H. Cohen, A. D. Earhart, J. V. Coe, and T. R. Tuttle, J. Phys. Chem. A **102**, 7787 (1998).
[12] Y. Marcus, *Ion Properties* (CRC Press, Jerusalem, 1997).
[13] T. T. Duignan, M. D. Baer, G. K. Schenter, and C. J. Mundy, J. Chem. Phys. **147**, 161716 (2017); e-print arXiv:1702.05203.
[14] R. C. Remsing, M. D. Baer, G. K. Schenter, C. J. Mundy, and J. D. Weeks, J. Phys. Chem. Lett. **5**, 2767 (2014).
[15] P. Hünenberger and M. Reif, *Single-Ion Solvation: Experimental and Theoretical Approaches to Elusive Thermodynamic Quantities* (The Royal Society of Chemistry, 2011).
[16] T. T. Duignan, M. D. Baer, G. K. Schenter, and C. J. Mundy, Chem. Sci. **8**, 6131 (2017).
[17] M. A. Kastenholz and P. H. Hünenberger, J. Chem. Phys. **124**, 124106 (2006).
[18] T. L. Beck, Chem. Phys. Lett. **561-562**, 1 (2013).
[19] E. Harder and B. Roux, J. Chem. Phys. **129**, 234706 (2008).
[20] C. P. Kelly, C. J. Cramer, and D. G. Truhlar, J. Phys. Chem. B **110**, 16066 (2006).
[21] L. Vlcek, A. A. Chialvo, and J. M. Simonson, J. Phys. Chem. A **117**, 11328 (2013).
[22] T. P. Pollard and T. L. Beck, J. Chem. Phys. **140**, 224507 (2014).
[23] Y. Marcus, J. Chem. Soc., Faraday Trans. 1 **83**, 339 (1987).
[24] Y. Marcus, J. Chem. Soc., Faraday Trans. 1 **83**, 2985 (1987).
[25] H. S. Ashbaugh, J. Phys. Chem. B **104**, 7235 (2000).
[26] R. Scheu, B. M. Rankin, Y. Chen, K. C. Jena, D. Ben-Amotz, and S. Roke, Angew. Chem., Int. Ed. **53**, 9560 (2014).
[27] R. Schurhammer and G. Wipff, J. Phys. Chem. A **104**, 11159 (2000).
[28] R. Schurhammer and G. Wipff, J. Mol. Struct.: THEOCHEM **500**, 139 (2000).
[29] M. M. Reif and P. H. Hünenberger, J. Phys. Chem. B **120**, 8485 (2016).
[30] J. Schamberger and R. J. Clarke, Biophys. J. **82**, 3081 (2002).
[31] M. D. Baer, V.-T. Pham, J. L. Fulton, G. K. Schenter, M. Balasubramanian, and C. J. Mundy, J. Phys. Chem. Lett. **2**, 2650 (2011).
[32] M. D. Baer, C. J. Mundy, M. J. McGrath, I.-F. W. Kuo, J. I. Siepmann, and D. J. Tobias, J. Chem. Phys. **135**, 124712 (2011).

[33]M. Galib, M. D. Baer, L. B. Skinner, C. J. Mundy, T. Huthwelker, G. K. Schenter, C. J. Benmore, N. Govind, and J. L. Fulton, J. Chem. Phys. **146**, 084504 (2017).

[34]G. Mathias and M. D. Baer, J. Chem. Theory Comput. **7**, 2028 (2011).

[35]D. Ben-Amotz, F. O. Raineri, and G. Stell, J. Phys. Chem. B **109**, 6866 (2005).

[36]T. T. Duignan, D. F. Parsons, and B. W. Ninham, J. Phys. Chem. B **117**, 9421 (2013).

[37]T. P. Pollard and T. L. Beck, Curr. Opin. Colloid Interface Sci. **23**, 110 (2016).

[38]T. T. Duignan, D. F. Parsons, and B. W. Ninham, J. Phys. Chem. B **117**, 9412 (2013).

[39]M. M. Reif and P. H. Hünenberger, J. Chem. Phys. **134**, 144104 (2011).

[40]Y. L. Lin, A. Aleksandrov, T. Simonson, and B. Roux, J. Chem. Theory Comput. **10**, 2690 (2014).

[41]A. Mukhopadhyay, I. S. Tolokh, and A. V. Onufriev, J. Phys. Chem. B **119**, 6092 (2015); e-print arXiv:1504.00414v1.

[42]J. Vandevondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, and J. Hutter, Comput. Phys. Commun. **167**, 103 (2005).

[43]E. Pluharova, M. D. Baer, C. J. Mundy, B. Schmidt, and P. Jungwirth, J. Phys. Chem. Lett. **5**, 2235 (2014).

[44]J. VandeVondele and J. Hutter, J. Chem. Phys. **127**, 114105 (2007).

[45]S. Goedecker, M. Teter, and J. Hutter, Phys. Rev. B **54**, 1703 (1996).

[46]G. J. Martyna, M. L. Klein, and M. Tuckerman, J. Chem. Phys. **97**, 2635 (1992).

[47]A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[48]C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[49]S. Grimme, J. Comput. Chem. **25**, 1463 (2004).

[50]M. A. Kastenholz and P. H. Hünenberger, J. Chem. Phys. **124**, 224501 (2006).

[51]G. Hummer, L. R. Pratt, and A. E. García, J. Phys. Chem. **100**, 1206 (1996).

[52]P. H. Hünenberger and J. A. McCammon, J. Phys. Chem. **110**, 1856 (1999).