

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/257460459>

Correspondence Between Cluster-Ion and Bulk Solution Thermodynamic Properties: On the Validity of the Cluster-Pair-Based Approximation.

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · OCTOBER 2013

Impact Factor: 2.69 · DOI: 10.1021/jp408632e · Source: PubMed

CITATIONS

10

READS

39

3 AUTHORS, INCLUDING:



Lukas Vlcek

Oak Ridge National Laboratory

67 PUBLICATIONS 682 CITATIONS

SEE PROFILE

Correspondence between Cluster-Ion and Bulk Solution Thermodynamic Properties: On the Validity of the Cluster-Pair-Based Approximation

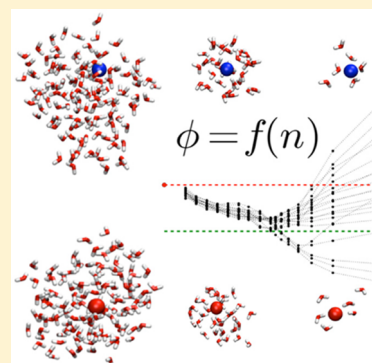
Lukas Vlcek,^{*,†,‡} Ariel A. Chialvo,[†] and J. Michael Simonson[§]

[†]Chemical Sciences Division, Geochemistry & Interfacial Sciences Group, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6110, United States

[‡]Joint Institute for Computational Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6173, United States

[§]Chemical & Engineering Materials Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6475, United States

ABSTRACT: Since the single-ion thermodynamic properties of bulk solutions are not directly accessible from experiments, extrapolations have been devised to estimate them from experimental measurements on small-clusters. Extrapolations based on the cluster-pair-based approximation (CPA) technique (Tissandier et al. *J. Phys. Chem. A* **1998**, *102*, 7787–7794) and its variants are currently considered one of the most reliable source of single-ion hydration thermodynamic data and have been used as a benchmark for the development of molecular and continuum solvation models. Despite its importance, the CPA has not been thoroughly tested and recent studies have indicated inconsistencies with molecular simulations. The present work challenges the key CPA assumptions that the hydration properties of single cations and anions in growing clusters rapidly converge to each other following a monotonous trend. Using a combination of simulation techniques to study the transition between alkali halide ions in small clusters and bulk solution, we show that this convergence is rather slow and involves a surprising change in trends, which can result in significant errors in the original estimated single-ion properties. When these cluster-size-dependent effects are taken into account, the inconsistencies between molecular models and experimental predictions disappear, and the value of the proton hydration enthalpy based on the CPA aligns with estimates based on other principles.



1. INTRODUCTION

The knowledge of single-ion hydration thermodynamic properties is essential for understanding the forces driving many aqueous electrolyte processes, such as selective ion adsorption and separation, formation of the electric double layers at interfaces, diffusion through solutions and membranes, protein denaturation, or transport through ion channels in biological systems.¹ With the increasing importance of computer simulations in the study of atomic-scale phenomena, this knowledge is also critical for the development of intermolecular potential models, either as a means for validating ab initio-based force fields or as the primary reference for empirically based force fields that currently underlie the majority of biochemical and geochemical molecular simulations. Direct experimental measurements of individual cations and anions contributions to bulk thermodynamic properties of dissolved salts are, however, prevented by strong electrostatic interactions between oppositely charged ions. To overcome this limitation, substantial effort has been devoted to estimating the single-ion properties from theoretical and computational models, as well as from extrapolations based on available experimental data.

Historically, the first attempts to determine single-ion solvation properties were based on intuition and simplified theoretical considerations embodied in various extra-thermody-

namic assumptions.² In general, these methods neglect the details of the hydration structure as well as the unknown surface potential of water, both of which influence the behavior of real systems. Despite their simplicity, these approaches still often serve as a basis for the estimation of proton hydration properties that are used as the reference values for the development of intermolecular potential models, and consequently, they impact the outcome of many computer simulations. Probably the most popular of these methods, the so-called TATB, assumes that the hydration properties of the large tetraphenylarsonium (TA) cation and the large tetraphenylborate (TB) anion in bulk water are roughly equal, leading to the proton hydration Gibbs free energy $\Delta G_{\text{aq}}^{\circ}[\text{H}^{+}] = -1056$ kJ/mol and enthalpy $\Delta H_{\text{aq}}^{\circ}[\text{H}^{+}] = -1103$ kJ/mol.^{3–5} (The symbol ‘ \circ ’ refers to the standard state of $P = 1$ bar and $T = 298.15$ K). Another popular method proposed by Schmid and co-workers is based on the assumption of equal hydration entropy of the H^{+} and OH^{-} ions, leading to $\Delta G_{\text{aq}}^{\circ}[\text{H}^{+}] = -1052$ kJ/mol and $\Delta H_{\text{aq}}^{\circ}[\text{H}^{+}] = -1078$ kJ/mol.⁶ While providing useful references, the resulting predictions of hydration free energies and enthalpies based on different extra-thermodynamic assumptions often differ from each other by

Received: August 28, 2013



tens of kJ/mol, i.e., a physically significant magnitude equivalent to the energy of one or more hydrogen bonds.

A more realistic approach to determination of single-ion hydration thermodynamics relies on the increasingly improving accuracy and overall capabilities of quantum chemical and highly realistic molecular simulations. With a perfect representation of interparticle interactions and large computational resources, this method will, in principle, arrive at the correct values. However, since the system size that current practical quantum chemical simulations can handle is limited, the determination of bulk solution properties still must rely on computational approximations and assumptions about the long-range behavior of water, which cannot be treated explicitly in the calculations. While quantum chemical calculations have been used to estimate ion hydration properties,^{7,8} they are still in their earlier stages of development. Studies with realistic polarizable models, which may include long-range effects including water surface potential contributions, have been carried out and provide another source of more accurate estimates.^{9,10}

An alternative approach to estimating single-ion hydration thermodynamics is based on the experimentally accessible properties of small ion–water clusters (known as cluster-ions). The method relies on data from electrospray mass spectrometry experiments that measure the distribution of cluster sizes (number of water molecules solvating a single ion) as a function of temperature and water vapor pressure.¹¹ The cluster-size statistics is then readily converted to free energies, entropies, and enthalpies of hydration. Since these experiments provide information about hydration in small clusters involving typically less than 10 water molecules, only the first hydration shell is directly probed, and therefore, extrapolations are required to estimate the corresponding bulk solution properties. Currently, the most frequently used extrapolation method relies on the cluster-pair-based approximation (CPA),¹² which is considered to provide the most accurate proton hydration free energies and enthalpies.^{13–16} While new variations of this approximation have been developed,^{17,18} they are based on the same underlying assumptions as the original method that the hydration properties of growing cation and anion clusters rapidly converge to each other following a monotonous trend.

In the following sections, we will restrict our discussion to the original CPA method that predicts $\Delta G_{\text{aq}}^{\circ}[\text{H}^+] = -1104.5$ kJ/mol and $\Delta H_{\text{aq}}^{\circ}[\text{H}^+] = -1150.1$ kJ/mol.¹² One of the most distinctive predictions of the CPA, as pointed out by its authors, is that the proton hydration enthalpy is ~ 50 kJ/mol more negative than other contemporary estimates.^{5,6,19} Because these extrapolated values have been used as a benchmark for the development of a wide range of molecular^{15,20,21} and continuum^{14,22} solvation models, they influence the outcome of a vast number of studies using these models. It is therefore surprising that the assumptions underlying the CPA have not been more closely examined. There have been numerous studies of small and medium size ion–water clusters,^{23,24} but none of them addressed the question of the extrapolation of small cluster properties to bulk by straightforward modeling of the transition. The most direct attempts to study the transition were conducted by Peslherbe and co-workers,²⁵ who used a liquid drop model to augment simulated small clusters, and by Coe,²⁶ who used medium-size cluster simulations of ion solvation based on the Stockmayer model for the solvent (consisting of a van der Waals repulsive sphere and a point dipole). Unfortunately, neither of these studies considered the

implications of the nonzero quadrupole moment of water and its related asymmetrical charge distribution. The charge asymmetry (relative to charge reversal, i.e., $q_i \leftrightarrow -q_i$) is known to be responsible for the development of surface potential²⁷ and can significantly influence hydration of ions in clusters. An indication of possible problems caused by those factors is the impossibility of molecular models to reproduce simultaneously hydration free energies and entropies (or enthalpies) as predicted by the CPA.²⁰

In the context of the above observations, the present manuscript pursues three related goals: (i) to investigate the growth of cationic and anionic ion–water clusters over the full range of cluster sizes, (ii) to test the validity of the underlying CPA approximation and the accuracy of single-ion hydration properties derived from this approach, and (iii) to discuss the implications of items (i) and (ii) for the development of intermolecular force fields for the accurate and realistic atomistic simulation of aqueous electrolytes.

In the following section we explain the theoretical underpinnings of the CPA and outline our approach to testing its assumptions and resulting predictions. In Section 3 we describe our choice of intermolecular potential models and simulation methods. In Section 4 we present and discuss our results, while in the final section we summarize our findings and highlight their implications for various fields of research.

2. THEORETICAL BACKGROUND

2.1. Note on Terminology. To avoid potential terminological confusion among the available literature, we felt compelled to explicitly define several common qualifiers attached to single-ion hydration properties, namely ‘conventional’, ‘real’, ‘intrinsic’, and ‘absolute’. We are aware of two definitions of ‘conventional’ properties: one expresses these quantities relative to the proton hydration properties (i.e., based on the transfer of a proton from gas to solution),⁶ while the other describes them relative to the proton formation properties in a solvent (i.e., according to the formation of a proton in a solution from its standard state, $1/2\text{H}_2$).¹² Since the latter convention was used in the original CPA development, we are adopting it in this article.

The qualifier ‘real’ is consistently used for quantities that include solvent surface (phase) potential (i.e., those pertaining to processes that can be realized in real systems), while ‘intrinsic’ is consistently used for quantities excluding the surface potential (see section 2.3 below). Finally, the term ‘absolute’ is typically used as synonymous to ‘intrinsic’,^{10,28} but it is also used to describe the results of cluster experiments,^{12,17,18} which naturally include the cluster surface potential²⁸ and have been extensively considered to measure ‘real’ properties.^{10,13,15,20} In summary, our study addresses the CPA extrapolations of ‘real’ cluster properties that seamlessly transition to bulk ‘real’ properties, but are called ‘absolute’ in the original literature.¹²

2.2. Cluster-Pair-Based Approximation.¹² The CPA approach is based on the notion that the difference between the real standard hydration thermodynamics of a cation, $\text{A}^+(\text{H}_2\text{O})_n$, and an anion, $\text{B}^-(\text{H}_2\text{O})_n$, comprising n water molecules tends to zero as the cluster size increases,²⁹ i.e.,

$$\lim_{n \rightarrow \infty} \{\Delta X_{\text{aq}}^{\circ}[\text{A}^+(\text{H}_2\text{O})_n] - \Delta X_{\text{aq}}^{\circ}[\text{B}^-(\text{H}_2\text{O})_n]\} = 0 \quad (1)$$

where $\Delta X_{\text{aq}}^{\circ}[\dots]$ stands for either real standard hydration Gibbs free energy, $\Delta G_{\text{aq}}^{\circ}[\dots]$, or enthalpy, $\Delta H_{\text{aq}}^{\circ}[\dots]$.

This relationship can be further rearranged to express the proton formation thermodynamic properties, $\Delta X_f^\circ[\text{H}^+(\text{aq})]$, as a difference between the sums of stepwise cluster cation and anion hydration, $\Delta X_n^\circ[\dots] = \sum_{i=1}^n \Delta X_{i-1,i}^\circ[\dots]$, and corresponding conventional properties, $\Delta X_{\text{aq}}^{\circ,\text{con}}[\dots]$, as follows:¹²

$$\frac{1}{2} \left\{ \lim_{n \rightarrow \infty} (\Delta X_n^\circ[\text{A}^+] - \Delta X_n^\circ[\text{B}^-]) - (\Delta X_{\text{aq}}^{\circ,\text{con}}[\text{A}^+] - \Delta X_{\text{aq}}^{\circ,\text{con}}[\text{B}^-]) \right\} = \Delta X_f^\circ[\text{H}^+(\text{aq})] \quad (2)$$

where the values for the stepwise sums are obtained from electrospray mass spectrometry experiments,¹¹ and the relationship between real and conventional properties is defined as¹²

$$\Delta X_{\text{aq}}^\circ[\text{I}^z] = \Delta X_{\text{aq}}^{\circ,\text{con}}[\text{I}^z] + z \Delta X_f^\circ[\text{H}^+(\text{aq})] \quad (3)$$

where z is the formal charge of ion I^z .

Since the $\Delta X_n^\circ[\dots]$ values are only known for small clusters, the estimate for increasingly larger and infinite clusters is achieved by scaling the first term in eq 2

$$\frac{1}{2} \left\{ \frac{\Delta X_n^\circ[\text{A}^+] - \Delta X_n^\circ[\text{B}^-]}{c_{n,n}(\text{A}^+, \text{B}^-)} - (\Delta X_{\text{aq}}^{\circ,\text{con}}[\text{A}^+] - \Delta X_{\text{aq}}^{\circ,\text{con}}[\text{B}^-]) \right\} = \Delta X_f^{\circ,\text{CPA}}[\text{H}^+(\text{aq})] \quad (4)$$

where

$$c_{n,n}(\text{A}^+, \text{B}^-) = \frac{\Delta X_n^\circ[\text{A}^+] + \Delta X_n^\circ[\text{B}^-]}{\Delta X_{\text{aq}}^{\circ,\text{con}}[\text{A}^+] + \Delta X_{\text{aq}}^{\circ,\text{con}}[\text{B}^-]} \quad (5)$$

Note that this quantity includes only sums of cation and anion contributions and therefore can be determined unambiguously.

According to the original publication, the extrapolation will be most accurate for ion pairs (real or hypothetical) whose prediction of $\Delta X_f^{\circ,\text{CPA}}[\text{H}^+(\text{aq})]$ is constant in the experimentally accessible range of clusters.¹² The assumption that this constancy will hold as the cluster size increases is central for the validity of the CPA. The ideal cluster pair can be identified by a procedure described by Tissandier et al.¹² and further discussed in section 4.2.

In essence, the CPA effectively assumes that the cluster-size dependence of the hydration thermodynamics observed for small clusters will extrapolate monotonically into the not sampled region of larger cluster sizes and consequently relies on the absence of surprises in the range between small clusters and bulk (i.e., infinite-size cluster).¹²

2.3. CPA Estimate of the Surface Potential. As discussed by Asthagiri and co-workers,²⁸ the estimates of ion hydration based on cluster experiments naturally include a liquid–vapor surface potential, which adds opposite canceling contributions to the real hydration properties of cations and anions. However, this interfacial contribution is not included in the intrinsic hydration properties, which by definition represent a theoretical construct assuming a water phase with no boundaries. While impossible to attain in real systems, this condition is fulfilled in computer simulations under periodic boundary conditions and the Ewald summation treatment of long-range Coulombic interactions;³⁰ this theoretical observation has been confirmed via computer simulations of ion transfer through vapor–liquid interfaces.³¹

Thus, the conversion between real, $\Delta X_{\text{aq}}^\circ[\dots]$, and intrinsic, $\Delta X_{\text{aq}}^{\circ,\text{int}}[\dots]$, properties requires inclusion of a surface potential contribution, ϕ_X^{sp} , i.e.,

$$\Delta X_{\text{aq}}^\circ[\text{I}^z] = \Delta X_{\text{aq}}^{\circ,\text{int}}[\text{I}^z] + ze\phi_X^{\text{sp}} \quad (6)$$

where e is the unit of electrostatic charge. As a consequence of the formal equivalence between eqs 3 and 6, the expression in eq 2 can be transformed by replacing conventional properties with intrinsic properties, where the right-hand side of the equation corresponds to the estimated surface potential, i.e.,

$$\frac{1}{2} \left\{ (\Delta X_n^\circ[\text{A}^+] - \Delta X_n^\circ[\text{B}^-]) - (\Delta X_{\text{aq}}^{\circ,\text{int}}[\text{A}^+] - \Delta X_{\text{aq}}^{\circ,\text{int}}[\text{B}^-]) \right\} = e\phi_X^{\text{sp}}(n) \quad (7)$$

The difference between estimated values of $\Delta X_f^\circ[\text{H}^+(\text{aq})]$ and ϕ_X^{sp} as a function of n (eqs 2 and 7) results in a vertical shift given by the difference between the conventional and intrinsic properties, but it does not change the shape of the curves because neither conventional nor intrinsic values depend on n . This redefinition of the original eq 2 allows us to calculate the limiting value of $\phi_X^{\text{sp}}(n)$ for $n \rightarrow \infty$, which in this case corresponds to the surface potential of a planar vapor–liquid interface. Moreover, it follows from eqs 2 and 7 that any trends and deviations detected in the estimation of ϕ_X^{sp} will be present in the consequent estimate of $\Delta X_f^\circ[\text{H}^+(\text{aq})]$.

The original CPA expressions given by eqs 4 and 5 can now be rewritten as

$$\frac{1}{2} \left\{ \frac{\Delta X_n^\circ[\text{A}^+] - \Delta X_n^\circ[\text{B}^-]}{c_{n,n}(\text{A}^+, \text{B}^-)} - (\Delta X_{\text{aq}}^{\circ,\text{int}}[\text{A}^+] - \Delta X_{\text{aq}}^{\circ,\text{int}}[\text{B}^-]) \right\} = e\phi_X^{\text{CPA}} \quad (8)$$

where ϕ_X^{CPA} is the CPA estimate of the surface potential contributions to be determined from the common intersections of linear fits of data at each cluster size, and

$$c_{n,n}(\text{A}^+, \text{B}^-) = \frac{\Delta X_n^\circ[\text{A}^+] + \Delta X_n^\circ[\text{B}^-]}{\Delta X_{\text{aq}}^{\circ,\text{int}}[\text{A}^+] + \Delta X_{\text{aq}}^{\circ,\text{int}}[\text{B}^-]} \quad (9)$$

This reformulation also shows that the CPA can only be accurate if the planar liquid–vapor surface potential is equal to the averaged cation and anion surface potentials for small clusters. However, there is no evidence that small clusters forming only the first hydration shell should predict the correct surface potential of pure water. This stems from the fact that in small clusters, used as the basis for the extrapolations, the orientation of water molecules and the corresponding surface potential are dominated by ion–water interactions; consequently, they contain only very limited information about the interfacial structure of pure water, which is solely responsible for the values of ϕ_X^{sp} . Yet, as eq 8 indicates, the CPA makes precisely such an assumption, and therefore, the CPA cannot be generally valid for all systems with the obvious exception of charge symmetric solvents for which $\phi_X^{\text{sp}} = 0$. To check whether the CPA is numerically accurate at least for aqueous systems, we performed molecular simulations that would supply data for experimentally inaccessible values of cluster size n in eq 7.

3. MODELS AND METHODS

3.1. Intermolecular Potential Model. In this study, we consistently use nonpolarizable interaction-site models of water and ions, where the functional form of the site–site potential combines the Lennard-Jones (LJ) and point charge interactions, i.e.,

$$u(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \quad (10)$$

where $u(r_{ij})$ is the potential energy between sites i and j separated by a distance r_{ij} , ϵ_{ij} and σ_{ij} are the Lennard-Jones parameters, q_i is the charge on site i , and ϵ_0 is the permittivity of vacuum. The ion–water force field parameters were optimized by Joung and Cheatham³² for use with the SPC/E model of water³³ and are summarized in Table 1. As we will show later,

Table 1. Force Field Parameters for the SPC/E-Based Ion Models from Joung and Cheatham;³² Cross- Interactions between Unlike Sites Are Determined from the Lorentz–Berthelot Combining Rules: $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$ and $\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}$

site	q_i [e]	σ_{ii} [Å]	ϵ_{ii} [kJ/mol]	site	q_i [e]	σ_{ii} [Å]	ϵ_{ii} [kJ/mol]
O	−0.8476	3.166	0.65	Cs	1.0	3.6010	0.3760
H	0.4238	0.0	0.0	F	−1.0	4.0215	0.0310
Li	1.0	1.4094	1.4089	Cl	−1.0	4.8305	0.0535
Na	1.0	2.1595	1.4755	Br	−1.0	4.9017	0.1128
K	1.0	2.8384	1.7979	I	−1.0	5.2010	0.1790
Rb	1.0	3.0950	1.8623				

the general conclusions of this study are not sensitive to any particular choice of a force field. Our use of simple nonpolarizable models is motivated by their computational efficiency and widespread use, which makes the present results relevant to many current molecular modeling studies. Specifically, the SPC/E model predicts the water dielectric constant in relatively better agreement with experiment than its direct competitors, and it has been used in the majority of electrolyte models recently developed.^{20,21,34–36} It has been also argued that the SPC/E model accurately reproduces the orientational distribution of water molecules near the liquid–vapor interface as obtained from experiments and ab initio simulations.^{13,37,38}

Since the rigid nonpolarizable potential models are not a perfect representation of reality, it is appropriate to outline their limitations. One of their main drawbacks is the inability to respond to external electric fields with an induced dipole moment created by electronic polarization and molecular shape distortion. In the case of the SPC/E model of water, whose dipole moment is optimized for the liquid phase,³³ the lack of polarizability can result in deviations of predicted properties in environments substantially different from liquid water, such as in the lowering of orthobaric vapor pressure³⁹ or limited solubility in nonpolar media.⁴⁰ In principle, one cannot expect correct hydration energetics of individual clusters without additional corrections for electronic polarization in vapor and bulk liquid, as well as under the strong electric fields of small aqueous-ion clusters. However, the construction of the CPA equations (eqs 2 and 7) insures that these effects will be compensated as a result of taking differences between cation and

anion contributions, as well as the additional differences between cluster and bulk hydration properties. Many model imperfections that apply equally either to cations and anions, or to clusters and bulk, will be effectively filtered out. For instance, subtracting cation and anion properties will eliminate deviations from the correct long-range polarization determined by the dielectric constant. Likewise, the deficiencies resulting from the absence of explicit electronic polarization will be substantially reduced because the polarization tensor of a water molecule is nearly isotropic⁴¹ and will respond similarly to cation and anion charges regardless of water molecule orientation in the hydration shell. Consequently, the dominant factor determining the CPA accuracy is the orientation of solvent permanent dipole moments, and while the choice of a water model may influence the details of our analysis, it cannot change the qualitative conclusions.

Moreover, the CPA results are rather insensitive to the choice of ion–water potentials because subtracting the hydration properties of an ion in a cluster from those of the same ion in bulk water eliminates many imperfections of the short-range interactions and, more importantly, because the CPA selects an ideal ion pair independent of specific interactions. This means that the results from the method proposed here do not depend on any specific choice of ion–water interaction parameters.

3.2. Simulation Details. As discussed in section 2, a test of the CPA assumptions requires the knowledge of hydration thermodynamics in systems ranging from small clusters to bulk solutions, as well as the structure of a flat liquid–vapor interface. To investigate these properties, we used a combination of molecular dynamics (MD) and Monte Carlo (MC) simulation techniques as described below.

3.2.1. Bulk (Intrinsic) Hydration Properties. Intrinsic bulk hydration properties were determined from MD simulations in the isobaric–isothermal (NPT) ensemble at $T = 298.15$ K and $P = 1$ bar using a simulation box containing one ion and $n = 511$ SPC/E water molecules. Simulations in larger systems ($n = 1023$) were also performed to test the system-size independence of the calculated bulk hydration properties. Coulombic interactions were computed using an Ewald summation approach with corrections for a charged system and finite-size (B-type) corrections applied.^{30,42} The NPT-MD equations of motion were integrated via velocity Verlet algorithm with the Nose–Hoover thermostat/barostat and a time-step of 1 fs.

The ion hydration enthalpy was calculated from the difference of enthalpies of a box with and without the ion for a fixed n in simulations spanning 10 ns. The Gibbs free energies of hydration were calculated using a two-stage thermodynamic integration (TI).⁴³ In the first stage, non-Coulombic interactions were gradually coupled in 20 steps using the soft LJ potential,⁴⁴ while the Coulombic interactions were coupled in the second stage within another 20 steps, where each TI step spanned 400 ps. These simulations were performed using LAMMPS software with custom additions for charged-system corrections, the soft LJ potential, and functionality necessary for the TI of this potential,⁴⁵ and the outcome of these runs was verified by comparison with values reported in literature.³²

3.2.2. Cluster Hydration Enthalpy. Ion hydration enthalpies in clusters with $n = 1, 2, 3, 4, 5, 6, 7, 8, 11, 16, 23, 37, 64, 125, 296$, and 1000 SPC/E molecules were calculated from the isochoric–isothermal (NVT) MD averages of cluster energies while assuming volume work against near vacuum to be negligible ($PV \approx 0$). The simulation box size of $100 \times 100 \times$

100 Å with pair interaction cutoff $r_c = 50$ Å ensured minimal finite-size and cutoff artifacts. The analysis of particle distributions at r_c showed that the error caused by the atom-based cutoff was less than 0.1 kJ/mol in the calculated enthalpies. Finite-size artifacts were small due to the large box size-to-cluster size ratio and, moreover, effectively compensated by subtracting cation and anion values in the calculation of ϕ_X^{sp} (eq 7). Simulations of smaller clusters ($8 < n \leq 125$) spanned 200 ns, while shorter simulations were performed for larger clusters: 100 ns for 296 and 30 ns for 1000 SPC/E molecules. LAMMPS⁴⁵ was used to perform these MD simulations. NVT-MC simulations using TOWHEE⁴⁶ were also run for the smallest clusters ($n \leq 8$) to eliminate possible thermostatting artifacts caused by large temperature fluctuations in NVT-MD simulations.

3.2.3. Cluster Hydration Free Energy. To avoid introducing potential artifacts caused by artificially fixing the ion position in the center of a water cluster, which might be justified only for large clusters,^{13,24} we calculated the hydration free energies in a manner similar to the actual cluster-ion experiments.¹¹ Series of Grand Canonical Monte Carlo (GCMC)⁴⁷ simulations were performed in which the water chemical potential, $\mu_i(T,V)$, was fixed at different values (corresponding to varying experimental water vapor pressure), and the statistics of cluster sizes was analyzed and combined using the histogram reweighting technique⁴⁸ (for details, see Appendix A).

For all practical purposes, Gibbs and Helmholtz free energies were equated since the PV contributions are negligibly small (equal to volume work against near vacuum) and partially canceled when taking the difference between the properties of cation and anion clusters used in the CPA method ($\Delta F_n^{\circ}[A^+] - \Delta F_n^{\circ}[B^-] \approx \Delta G_n^{\circ}[A^+] - \Delta G_n^{\circ}[B^-]$). This approximation was tested by comparing internal energies and enthalpies of hydration in NVT-MD/MC simulations and showed that the resulting errors lie within the statistical uncertainty of the simulation results. All GCMC simulations were performed using TOWHEE software, where the combined length of the GCMC simulations for each ion was at least 1×10^{10} individual MC moves, and the histogram reweighting was accomplished with an in-house code.

3.2.4. Surface Potential of a Planar Liquid–Vapor Interface. The surface potential of planar liquid–vapor interfaces, $\phi_X^{\text{sp}}(\infty) \equiv \phi_X^{\text{sp}}$, was calculated at temperatures between 278.15 and 318.15 K via NVT-MD with $n = 1000$, which formed a pure liquid water slab with an approximate thickness of 37 Å and a vapor gap of 40 Å. The Coulombic interactions were computed using the Ewald summation. Simulations at each temperature spanned 20 ns with an integration time-step length of 1 fs. The free energy contributions to the surface potential were determined by integration of the averaged charge density profiles,³¹ while the entropic and enthalpic contributions were obtained from the corresponding temperature derivative of the computed ϕ_X^{sp} (for details, see Appendix B).

4. RESULTS AND DISCUSSION

4.1. Cluster-Size Dependence of Hydration Thermodynamics. We have shown in section 2.3 that the CPA can provide accurate extrapolations only if the average surface potential of water surrounding ions in small clusters is equal to the surface potential of a planar liquid–vapor interface of pure water. While qualitative considerations suggest that this is unlikely to happen because different forces drive those

structures, i.e., ion–water interactions vs water–water interactions, it is important to gain a more quantitative insight into the behavior of these systems through direct molecular simulations.

By performing molecular-based MC and MD simulations of ion–water clusters with sizes spanning the full range from small to (effectively) infinite, we are able to test the assumptions involved in the CPA-derived values of $\Delta G_{\text{aq}}^{\circ}[\dots]$ and $\Delta H_{\text{aq}}^{\circ}[\dots]$.^{12,14} For example, Figure 1 shows the plots of the

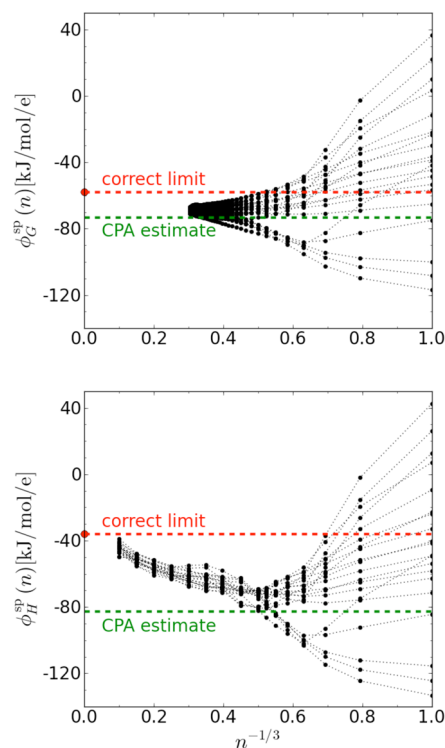


Figure 1. Estimate of surface potential contributions $\phi_X^{\text{sp}}(n)$ and its enthalpic contribution $\phi_H^{\text{sp}}(n)$ as a function of cluster size at $T = 298.15$ K. Black circles, cluster-pair values; red dashed line, planar surface potential ϕ_X^{sp} ; green dashed line, the CPA estimate of the surface potential. The plot may be compared to Figure 1 of Tissandier et al.¹²

surface potential estimates $\phi_X^{\text{sp}}(n)$ ($X = G$ or H) as a function of $n^{-1/3}$, where the estimates were calculated according to eq 7. The data for finite values of n (black dots) were obtained from explicit simulations of ion–water clusters, while the values for the infinitely large clusters (i.e., $n^{-1/3} = 0$; red dots and red dashed lines) were obtained from independent simulations of the planar surface potential of a water slab. The resulting value of the free energy contribution to the planar surface potential, $\phi_G^{\text{sp}} = -57.7$ kJ/mol/e ($-0.598(2)$ V) at 298.15 K, is within the statistical error from a recently published value of $-0.600(1)$ V,³¹ and the enthalpic contribution to the surface potential at 298.15 was determined to be $\phi_H^{\text{sp}} = -36.05$ kJ/mol/e (-0.374 V) as described in Appendix B. The correct convergence of the explicit cluster values of $\phi_X^{\text{sp}}(n)$ to those derived from water-slab calculations for infinitely large clusters can serve as a consistency check.

The most distinctive feature of $\phi_X^{\text{sp}}(n)$ as a function of $n^{-1/3}$ is the decline between $0 < n^{-1/3} < 0.5$, which roughly corresponds to a linear dependence of the surface potential contributions on $1/R$, where $R \approx n^{1/3}$ is the cluster radius, for clusters with a complete first hydration shell. It is clear that the observed $n^{-1/3}$

slope of $\phi_{\text{H}}^{\text{sp}}(n)$ exhibits an insignificant dependence on the specific ion–water interactions, i.e., it mainly reflects the cluster size effect. The same form of strong dependence of surface potential on cluster size, $\phi_{\text{G}}^{\text{sp}}(n)$, has been observed in earlier studies with the SPC water model.^{24,49} Such a behavior does not support the common underlying assumption of extrapolation methods that the slope of the curves should go to zero as $n^{-1/3}$ approaches zero, which was also used as one of the main CPA justifications.¹² For medium size clusters ($16 < n < 1000$), the most negative values of $\phi_{\text{H}}^{\text{sp}}(n)$ correspond to ion pairs involving the iodide anion, which is known to be readily adsorbed at the vapor–liquid interface.³¹ The resulting weaker dielectric interactions of this unevenly hydrated anion then lead to a decreased $\phi_{\text{H}}^{\text{sp}}(n)$ for the given ion pair.

The rise of $\phi_{\text{X}}^{\text{sp}}(n)$ with increasing n corresponds to greater favorability of hydrating anions relative to cations in increasingly larger clusters. From a GCMC simulation perspective, this is seen as broader anion cluster-size distributions skewed toward larger clusters. Several experimental and simulation studies discussed the observed increasingly more favorable hydration of anions in growing clusters in terms of a higher compatibility of anion hydration shells with the surrounding bulk.^{23,50,51} Direct simulation studies of larger clusters then showed that the surface potential contributes to less favorable hydration of cations as the cluster size increases.²⁴ Similar evidence for different hydration of cations and anions in larger clusters was also seen in the studies based on the liquid drop model,²⁵ but the results were discussed from the perspective of the average locations of ions within the clusters and not as a result of changes in the interfacial structure of water. Contradicting conclusions about the hydration of ions in the intermediate range of cluster sizes were reached by Coe;²⁶ however, the discussion was based on simulations performed with a charge-symmetric solvent, and consequently, no differences in the surface potential effects could be expected.

4.2. CPA Estimates. To estimate the deviations between the CPA predictions and the actual bulk hydration properties of our model systems, we followed the procedure described in the original work by Tissandier and collaborators¹² but adapted it for our study (section 2.3). Using simulated $\Delta X_n^{\circ}[I^{\circ}]$ values for small clusters ($n \leq 6$), we plotted the estimated values of $\phi_{\text{X}}^{\text{sp}}$ as a function of the differences $\Delta X_n^{\circ}[A^+] - \Delta X_n^{\circ}[B^-]$ (see eq 8 and Figure 2 of this work, and Figure 2 of Tissandier et al.¹²). The CPA estimates of the surface potential contributions, $\phi_{\text{X}}^{\text{CPA}}$, are determined from the common intersections of linear fits of $\phi_{\text{X}}^{\text{sp}}(n)$ for different cluster sizes ($n \leq 6$).¹²

In Figure 2 we show the $\phi_{\text{X}}^{\text{CPA}}$ values calculated from eq 8 as a function of the differences $\Delta X_n^{\circ}[A^+] - \Delta X_n^{\circ}[B^-]$ for $X = H, G$ along with the corresponding linear fits, whose resulting intersections are at $\phi_{\text{G}}^{\text{CPA}} = -73.2(1.0)$ kJ/mol/e and $\phi_{\text{H}}^{\text{CPA}} = -82.7(4.4)$ kJ/mol/e. Note that the uncertainties given in the parentheses include only the standard deviation of the common intersection; we expect additional uncertainties associated with simulation errors, the specific choice of ion, and the cluster-ion sizes (n) included in the fitting.

The observed differences between our Figure 2 and Figures 2 and 3 of the original reference¹² reflect imperfections of the simple molecular models and a somewhat different set of ion pairs used in our study (e.g., inclusion of Cs^+ and exclusion of OH^-). However these differences do not influence identification of the ideal (hypothetical) ion pair (i.e., they have negligible effect on the CPA estimate $\phi_{\text{X}}^{\text{CPA}}$), which is correctly

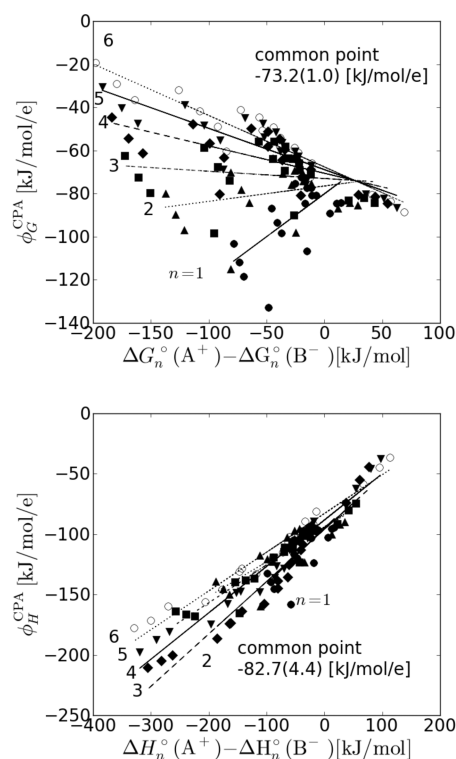


Figure 2. Estimates of the surface potential contributions $\phi_{\text{G}}^{\text{CPA}}$ (top) and its enthalpic contribution $\phi_{\text{H}}^{\text{CPA}}$ (bottom) as a function of the cation–anion difference of cluster-ion hydration free energies and enthalpies, respectively; different symbols correspond to different cluster sizes, and the integer numbers denote the sizes. The resulting values are obtained from the best estimate of the common point of the linear fits. The plots may be compared to Figures 2 and 3 of Tissandier et al.¹²

chosen as a pair with a nearly flat $n^{-1/3}$ dependence of $\phi_{\text{G}}^{\text{sp}}$ and $\phi_{\text{H}}^{\text{sp}}$ for small clusters. As in the original reference, this ideal cluster pair is similar to the $\text{Na}^+ \text{F}^-$ pair.¹²

To further test our results, we also followed a slightly different scheme used by Kelly and co-workers,¹⁴ which derives the limiting value of the surface potential (proton hydration free energy in their context) from the plots of the surface potential estimates against the difference of intrinsic hydration properties of $\Delta X_n^{\circ, \text{int}}[B^-] - \Delta X_n^{\circ, \text{int}}[A^+]$ for $X = G, H$ (see Figure 3). The resulting estimates of the surface potential contributions $\phi_{\text{G}}^{\text{KEL}} = -67.9(1.1)$ and its enthalpic contribution $\phi_{\text{H}}^{\text{KEL}} = -81.1(3.1)$ differ slightly from the corresponding $\phi_{\text{G}}^{\text{CPA}}$ and $\phi_{\text{H}}^{\text{CPA}}$, yet they lead to the same general conclusions about the significant underestimation of the surface potential contributions and the proton's hydration properties $\Delta G_{\text{aq}}^{\circ}[\dots]$ and $\Delta H_{\text{aq}}^{\circ}[\dots]$.

If the differences between the actual and the CPA-derived surface potential contributions are used to correct the experimental CPA estimates of the hydration properties, the resulting corrected (cCPA) values are $\Delta G_{\text{aq}}^{\circ, \text{cCPA}}[\text{H}^+] = -1089.0$ kJ/mol and $\Delta H_{\text{aq}}^{\circ, \text{cCPA}}[\text{H}^+] = -1103.5$ kJ/mol. Such corrections would bring the CPA predictions of $\Delta H_{\text{aq}}^{\circ}[\text{H}^+]$ closer to other literature values, whose majority lies between -1090 kJ/mol and -1135 kJ/mol.^{19,29} The only other $\Delta H_{\text{aq}}^{\circ}[\text{H}^+]$ estimate close to the CPA value of -1150.1 kJ/mol, is -1153 kJ/mol from a study relying on the same assumption of zero slopes of $\phi_{\text{X}}^{\text{sp}}(n)$ for $n^{-1/3}$ approaching zero.⁵² However, our results suggest that this assumption is generally incorrect. We note that

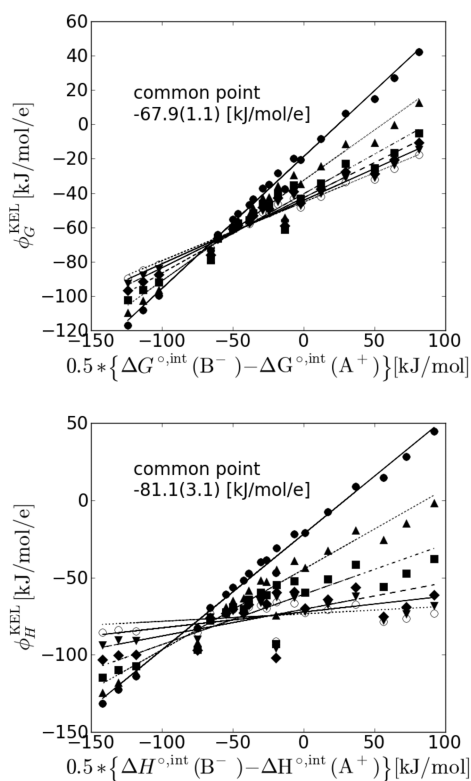


Figure 3. Estimates of the surface potential contributions ϕ_G^{KEL} (top) and its enthalpic contribution ϕ_H^{KEL} (bottom) as a function of the anion–cation difference of intrinsic hydration free energies and enthalpies, respectively. Different symbols correspond to different cluster sizes. The resulting values are obtained from the best estimate of the common point from the linear fits. The plots may be compared to Figure 1 of Kelly et al.¹⁴

even though the deviations between ϕ_X^{SP} and ϕ_X^{CPA} values can be estimated directly from the difference between the actual planar surface potential and its small-cluster predictions ($n \leq 6$), the results obtained from simulations of large clusters allow us to study the details of the gradual transition from small-cluster to bulk hydration.

The relatively smaller shift in ϕ_G^{SP} from its CPA prediction compared to the shift in ϕ_H^{SP} may be one likely reason why the discrepancy between the CPA values and molecular model predictions was not noticed in earlier studies, whose majority focused only on free energies, and consequent lack of interest in investigating further the validity of the assumptions behind the hydration in larger clusters. The significance of these deviations will be further exacerbated by ion charge, whose impact can lead to rather severe errors if used as a basis for theoretical and simulation studies. For instance, a shift of 90 kJ/mol in the hydration entropic terms ($T\Delta S_{aq}^{\circ}$) of Ca^{2+} and CO_3^{2-} ions can completely change our understanding of the interatomic forces and mechanisms driving processes such as adsorption and precipitation involving these ions.⁵³

Given the limitations of our nonpolarizable force fields, these values will have to be further validated and refined according to more realistic classical models or quantum chemical simulations. However, we must point out that the present estimates incorporate more information than the original CPA and more microscopic realism than any extra-thermodynamic assumption. In fact, the cCPA combines experimental data for small clusters and molecular modeling results for the experimentally

inaccessible region of large clusters. Consequently, the cCPA avoids the use of ad hoc models for extra-thermodynamic assumptions, and contrary to the original CPA, cCPA does not neglect the significant cluster-size effects.

4.3. Testing the cCPA Predictions. To test whether the adjusted cCPA values of the real single ion hydration properties are physically reasonable, we investigated their compatibility with molecular simulations. Such an analysis is important because many recent force field parametrizations rely on the CPA estimates.^{15,20,21,34} As mentioned in the Introduction, simple molecular models of the type investigated here are not able to reproduce a typical set of hydration properties (i.e., $\Delta G_{aq}^{\circ}[\dots]$, $\Delta H_{aq}^{\circ}[\dots]$, and $\Delta S_{aq}^{\circ}[\dots]$) based on the CPA.²⁰ However, this inconsistency has not been further analyzed, possibly because empirical force fields are typically optimized to reproduce only a single thermodynamic function (either $\Delta G_{aq}^{\circ}[\dots]$ ^{15,20,21,34} or $\Delta H_{aq}^{\circ}[\dots]$ ⁵⁴).

To illustrate the impossibility of reproducing a set of CPA-derived properties, it is instructive to plot $T\Delta S_{aq}^{\circ}[\dots]$ as a function of $\Delta H_{aq}^{\circ}[\dots]$, Figure 4, to reveal a characteristic

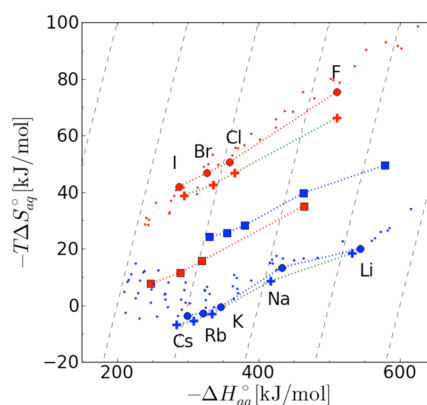


Figure 4. Real bulk single ion hydration entropy ($-T\Delta S_{aq}^{\circ}$) versus enthalpy ($-\Delta H_{aq}^{\circ}$) from molecular simulations (circles, model by Joung and Cheatham³² with our values for the surface potential contributions, ϕ_X^{SP} ; dots, data from Tables III–VI by Horinek and co-workers²⁰ with our values of ϕ_X^{SP}), the CPA (squares¹²), and the cCPA (crosses). Cations are shown in blue, anions in red, and the gray dashed lines denote free energy isolines, $\Delta G_{aq}^{\circ} = \Delta H_{aq}^{\circ} - T\Delta S_{aq}^{\circ}$.

approximately linear relationship between the two quantities. These linear trends, which only break for large cations, have long been recognized^{6,55} and are well reproduced by simple models considered in this work, as clearly evident in the data adapted from the systematic study of Horinek and co-workers²⁰ (dots in Figure 4). Note that while the slope of the lines and their average value (corresponding to one-half of the neutral salt values) are essentially correct, the separation between the cation and anion lines deviates significantly from the CPA values. In passing we should highlight that the separation between cation and anion lines reflects the charge asymmetry of water molecules: any charge-symmetric solvent would solvate the positive and negative ions identically,⁵⁶ and as a result, the corresponding cation and anion trend lines in Figure 4 would coincide. The symmetric but opposite shift between the model-based and experiment-based values for the cation and anion trend lines implies that the observed discrepancy is not the result of a specific choice of ion–water force field parameters but a manifestation of the long-range, ion charge-dependent effect associated with the surface potential. The linear

dependence between entropy and enthalpy also means that once any of the three quantities (G , H , or S) is fixed, the remaining pair becomes determined, leaving little room for further adjustment.

The large systematic differences between the simulated and CPA-derived values of bulk thermodynamic properties are reminiscent of the systematic deviation found in our cluster studies, indicating their common origin. If we assume that the same cluster size-related shifts in the surface potential occur in the experimental systems and then correct the CPA values accordingly, we find that the main systematic discrepancy between cluster-ion experiments and molecular models disappears, as illustrated in Figure 4 under the 'cCPA' label. The agreement between the cCPA trend lines and the simulation predictions is nearly quantitative for cations, while a residual systematic shift in hydration entropies can still be observed for anions. The occurrence of this shift for anions is not unexpected given the strong correlation between hydration entropies and diffusivities,⁵⁷ and the fact that simple models systematically under-predict anion diffusion coefficients.⁵⁸ As Figure 4 illustrates, correcting this residual shift cannot be accomplished by changing anion–water oxygen LJ interaction parameters, but a more substantial change in the interaction model is required. Our preliminary tests indicate that including ion–water hydrogen LJ interactions, which emulate charge penetration effects, can align simulation predictions with cCPA values and, at the same time, correct the anionic diffusion coefficients.

An explanation for such a good match between simulations and the cCPA values may lie in two distinct possibilities: either (A) the models provide a reasonable description of the real hydration properties and the CPA is missing the surprising behavior in the range of medium-sized clusters, or (B) the CPA values are accurate and the model predictions are biased by a significant artifact. While the present study cannot unequivocally decide between these two options (or their combination), there are reasons to believe that option (A) is the most likely scenario. In section 2.3 we pointed out that there is no *a priori* reason for the CPA to be accurate because it relies on reconstructing a pure-water planar surface potential from the average of small-cluster properties driven by interactions with the central ion. Moreover, in section 3.1, we discussed how and why many inaccuracies of simple models are compensated by the CPA equations. For option (B) to be correct, the vapor–liquid interfacial structure predicted by the SPC/E water model would have to be significantly incorrect. However, it has been recently argued that the model is capable of realistic reproduction of water molecule orientations near the interface.¹³ Simulations with more realistic polarizable models by Lamoureux and Roux also show that the SPC/E predictions of the surface potential are in line with the more sophisticated force fields.¹⁰ In fact, the same study, with ion–water interactions optimized to reproduce experimental ion–water dimer enthalpies, arrives at similar unfavorable conclusions about the validity of the CPA. While the authors used a different approach that relies on accurate individual ion–water interactions, whereas ours is independent of such interactions, their estimated value of the hydration free energy is $\Delta G_{\text{aq}}^{\circ}[\text{H}^+] = 1084 \text{ kJ/mol}$, i.e., about 21 kJ/mol more positive than the CPA estimate, and in good agreement with our prediction (1089 kJ/mol).

Regardless of whether either explanation is correct, it becomes clear that the CPA estimates should not be used to

optimize simple molecular force fields; either the CPA values are incorrect or the surface description by simple models is unrealistic enough to prevent accurate calculation of real hydration properties. To the best of our knowledge, the above considerations have been missing in the development of aqueous electrolyte force field parametrizations based on the CPA values, in which the intrinsic hydration properties were converted to the CPA predictions using the surface potential of a flat surface of the corresponding water model.^{15,20,21} As shown in Figure 4, this choice leads to discrepancies between hydration free energies, enthalpies, and entropies of individual ions. Regarding other popular choices of reference data for empirical model development, hydration free energy values derived by Marcus using TATB⁴ and by Schmid⁶ have been used to optimize intrinsic properties.^{32,36} However, if the $\phi_{\text{X}}^{\text{sp}}$ contributions to the surface potential of the SPC/E water are added to derive the corresponding real properties, the resulting values will be close to the corresponding CPA estimates. An indication that both CPA (for real properties) and TATB (for intrinsic properties) estimates of hydration free energies are too negative can be seen in the systematic underestimation of the radius of divalent cations when they are optimized to reproduce hydration free energies.^{34,36} More positive values of $\Delta G_{\text{aq}}^{\circ}[\text{I}^r]$, such as those derived in the present work, result in a radius compatible with experimental data, as verified with the help of the Supporting Information provided by Li and co-workers.³⁶

5. CONCLUSIONS

The present results demonstrate dissimilar effects of cations and anions on their hydration in aqueous clusters. Our molecular simulations of aqueous-ion clusters of varying sizes indicate that the differences between the hydration thermodynamic properties of cations and anions decrease rather slowly with cluster size and are roughly proportional to the inverse radius ($1/R$) of a cluster. Such behavior has direct consequences for the cluster-size distribution as a function of ion charge; for instance it implies a relatively higher probability of larger anionic vs cationic clusters in water vapor. This finding is also critically important for the assessment of the cluster-pair-based approximation, which relies on rapid convergence between cation and anion hydration properties in larger clusters. Our theoretical analysis shows that there is no *a priori* reason for the general validity of such assumptions, and our simulations suggest that the use of the CPA extrapolations may result in physically significant errors (up to tens of kJ/mol) in the estimated single-ion hydration properties.

If the cluster-size dependence of hydration thermodynamics is taken into account, the previously observed inconsistencies between the CPA-derived hydration properties (i.e., $\Delta G_{\text{aq}}^{\circ}[\dots]$, $\Delta H_{\text{aq}}^{\circ}[\dots]$, and $\Delta S_{\text{aq}}^{\circ}[\dots]$) and the predictions of simple molecular models disappear. In addition, the cluster-size-induced effects would reconcile the hydration free energies predicted by simple models with the experimentally determined radii of the first hydration shell and would explain the differences between the CPA-based $\Delta G_{\text{aq}}^{\circ}[\text{I}^r]$ and those derived from realistic polarizable models, as described in the literature.¹⁰ The cluster-size correction would also realign the CPA-based value of $\Delta H_{\text{aq}}^{\circ}[\text{H}^+]$ with the majority of other published estimates.¹⁹ Such observations strongly suggest that the discrepancy between cluster-ion experiments and molecular models stems predominantly from the inaccuracy of the reference values rather than from artifacts of simple force fields.

The theoretical and practical relevance of hydration phenomena in growing aqueous clusters, which have implications for environmental chemistry as well as for hydrophobic confinement of electrolyte solutions, warrants further investigation of aqueous-ion clusters with a more advanced representation of water and ion–water interactions.

■ APPENDIX A: CLUSTER HYDRATION FREE ENERGIES FROM THE HISTOGRAM REWEIGHTING TECHNIQUE

The grand canonical probability $p_i(n)$ of finding an ion cluster with n water molecules in a system characterized by the chemical potential of water, $\mu_i(T,V)$ is defined as

$$\frac{\mathcal{H}_i(n)}{\mathcal{H}_i^{\text{TOT}}} = p_i(n) = \frac{Z(n) \exp[\beta\mu_i n]}{\exp[-\beta\Omega_i]} \quad (\text{A1})$$

where, $Z(n)$, is the canonical partition function of a system with one ion and n water molecules in volume V , at temperature T , with $\beta = 1/k_B T$, and k_B being the Boltzmann constant. $\mathcal{H}_i(n)$ denotes the histogram count for n water molecules, $\mathcal{H}_i^{\text{TOT}}$ is the total number of measurements, and Ω_i is the grand potential ($\Omega_i = -P_i V$). The difference between Helmholtz free energies, $\Delta F(n+1, n)$, for ion-clusters with $n+1$ and n water molecules can be then written as

$$\beta\Delta F(n+1, n) = -\ln\left[\frac{Z(n+1)}{Z(n)}\right] = -\ln\left[\frac{\mathcal{H}_i(n+1)}{\mathcal{H}_i(n)}\right] + \beta\mu_i \quad (\text{A2})$$

Individual cluster-size histograms obtained from GCMC simulations characterized by different $\mu_i(T,V)$ values can be combined using the histogram reweighting equations adapted for the grand canonical ensemble.⁴⁸ The canonical partition functions are then obtained by self-consistent iterative solution of the following equations:

$$P(n, \mu_i) = \frac{\sum_{i=1}^R \mathcal{H}_i(n) \exp[\beta\mu_i n]}{\sum_{j=1}^R \mathcal{H}_j^{\text{TOT}} \exp[\beta(\mu_j n + \Omega_j)]} \quad (\text{A3})$$

$$\exp[-\beta\Omega_i] = \sum_n P(n, \mu_i) \quad (\text{A4})$$

where

$$P(n, \mu_i) = Z(n) \exp[\beta\mu_i n] \quad (\text{A5})$$

To simplify notation, here we assume that the samples are statistically independent. In case correlations are present in the data, corresponding weights have to be added to the equations as shown elsewhere.⁴⁸

■ APPENDIX B: THERMODYNAMIC CONTRIBUTIONS TO THE SURFACE POTENTIAL OF THE SPC/E WATER

Thermodynamic contributions to the potential of a planar vapor–liquid interface were obtained from fitting the values of ϕ_G^{SP} at different temperatures (Table B1) with a quadratic polynomial, i.e.,

$$\phi_G^{\text{SP}}(T) = 8.3221 - 0.37033 \times T + 0.00049917 \times T^2 \text{ [kJ/mol]} \quad (\text{B1})$$

Table B1. Surface Potential of a Planar Liquid–Vapor Interface at Different Temperatures for the SPC/E Model of Water

T [K]	ϕ_G^{SP} [kJ/mol/e] (ϕ_G^{SP} [V])	T [K]	ϕ_G^{SP} [kJ/mol/e] (ϕ_G^{SP} [V])
278.15	−56.03 (−0.581)	300.65	−57.88 (−0.600)
283.15	−56.52 (−0.586)	303.15	−57.99 (−0.601)
288.15	−56.97 (−0.590)	308.15	−58.35 (−0.605)
293.15	−57.28 (−0.594)	313.15	−58.68 (−0.608)
295.65	−57.74 (−0.598)	318.15	−59.02 (−0.612)
298.15	−57.69 (−0.598)		

The entropic contribution, ϕ_S^{SP} , was then calculated from the temperature derivative of the polynomial, while the enthalpic contribution was calculated from $\phi_H^{\text{SP}} = \phi_G^{\text{SP}} + T\phi_S^{\text{SP}}$.

■ AUTHOR INFORMATION

Corresponding Author

*(L.V.) E-mail: vlcek11@ornl.gov.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy.

■ REFERENCES

- (1) Fawcett, W. R. *Liquids, Solutions, and Interfaces*; Oxford University Press: New York, 2004.
- (2) Conway, B. E. *Ionic Hydration in Chemistry and Biophysics*; Elsevier: Amsterdam, The Netherlands, 1981; Vol. 12.
- (3) Marcus, Y. The Thermodynamics of Solvation of Ions. 4. Application of the Tetraphenylarsonium Tetraphenylborate (TATB) Extrathermodynamic Assumption to the Hydration of Ions and to Properties of Hydrated Ions. *J. Chem. Soc., Faraday Trans. I* **1987**, 83, 2985–2992.
- (4) Marcus, Y. Thermodynamics of Solvation of Ions. 5. Gibbs Free-Energy of Hydration at 298.15-K. *J. Chem. Soc., Faraday Trans. I* **1991**, 87, 2995–2999.
- (5) Marcus, Y. The Thermodynamics of Solvation of Ions. 2. The Enthalpy of Hydration at 298.15-K. *J. Chem. Soc., Faraday Trans. I* **1987**, 83, 339–349.
- (6) Schmid, R.; Miah, A. M.; Sapunov, V. N. A New Table of the Thermodynamic Quantities of Ionic Hydration: Values and Some Applications (Enthalpy–Entropy Compensation and Born Radii). *Phys. Chem. Chem. Phys.* **2000**, 2, 97–102.
- (7) Zhan, C. G.; Dixon, D. A. Absolute Hydration Free Energy of the Proton from First-Principles Electronic Structure Calculations. *J. Phys. Chem. A* **2001**, 105, 11534–11540.
- (8) Zhan, C. G.; Dixon, D. A. First-Principles Determination of the Absolute Hydration Free Energy of the Hydroxide Ion. *J. Phys. Chem. A* **2002**, 106, 9737–9744.
- (9) Grossfield, A.; Ren, P. Y.; Ponder, J. W. Ion Solvation Thermodynamics from Simulation with a Polarizable Force Field. *J. Am. Chem. Soc.* **2003**, 125, 15671–15682.
- (10) Lamoureux, G.; Roux, B. Absolute Hydration Free Energy Scale for Alkali and Halide Ions Established from Simulations with a Polarizable Force Field. *J. Phys. Chem. B* **2006**, 110, 3308–3322.
- (11) Kebarle, P.; Verkerk, U. H. Electrospray: From Ions in Solution to Ions in the Gas Phase, What We Know Now. *Mass Spectrom. Rev.* **2009**, 28, 898–917.
- (12) Tissandier, M. D.; Cowen, K. A.; Feng, W. Y.; Gundlach, E.; Cohen, M. H.; Earhart, A. D.; Coe, J. V.; Tuttle, T. R. The Proton's Absolute Aqueous Enthalpy and Gibbs Free Energy of Solvation from Cluster-Ion Solvation Data. *J. Phys. Chem. A* **1998**, 102, 7787–7794.

- (13) Beck, T. L. The Influence of Water Interfacial Potentials on Ion Hydration in Bulk Water and near Interfaces. *Chem. Phys. Lett.* **2013**, *561*, 1–13.
- (14) Kelly, C. P.; Cramer, C. J.; Truhlar, D. G. Aqueous Solvation Free Energies of Ions and Ion-Water Clusters Based on an Accurate Value for the Absolute Aqueous Solvation Free Energy of the Proton. *J. Phys. Chem. B* **2006**, *110*, 16066–16081.
- (15) Warren, G. L.; Patel, S. Hydration Free Energies of Monovalent Ions in Transferable Intermolecular Potential Four Point Fluctuating Charge Water: An Assessment of Simulation Methodology and Force Field Performance and Transferability. *J. Chem. Phys.* **2007**, *127*, 064509.
- (16) Camaioni, D. M.; Schwerdtfeger, C. A. Comment on "Accurate Experimental Values for the Free Energies of Hydration of H^+ , OH^- , and H_3O^+ ". *J. Phys. Chem. A* **2005**, *109*, 10795–10797.
- (17) Donald, W. A.; Williams, E. R. An Improved Cluster Pair Correlation Method for Obtaining the Absolute Proton Hydration Energy and Enthalpy Evaluated with an Expanded Data Set. *J. Phys. Chem. B* **2010**, *114*, 13189–13200.
- (18) Tuttle, T. R.; Malaxos, S.; Coe, J. V. A New Cluster Pair Method of Determining Absolute Single Ion Solvation Energies Demonstrated in Water and Applied to Ammonia. *J. Phys. Chem. A* **2002**, *106*, 925–932.
- (19) Grunwald, E.; Steel, C. A Thermodynamic Analysis of the First Solvation Shells of Alkali and Halide Ions in Liquid Water and in the Gas Phase. *Int. Rev. Phys. Chem.* **1996**, *15*, 273–281.
- (20) Horinek, D.; Mamatkulov, S. I.; Netz, R. R. Rational Design of Ion Force Fields Based on Thermodynamic Solvation Properties. *J. Chem. Phys.* **2009**, *130*, 124507.
- (21) Reif, M. M.; Hunenberger, P. H. Computation of Methodology-Independent Single-Ion Solvation Properties from Molecular Simulations. IV. Optimized Lennard-Jones Interaction Parameter Sets for the Alkali and Halide Ions in Water. *J. Chem. Phys.* **2011**, *134*, 144104.
- (22) Chamberlin, A. C.; Cramer, C. J.; Truhlar, D. G. Performance of Sm2 on a Test to Predict Small-Molecule Solvation Free Energies. *J. Phys. Chem. B* **2008**, *112*, 8651–8655.
- (23) Zidi, Z. S. On the Stability of Ion Water Clusters at Atmospheric Conditions: Open System Monte Carlo Simulation. *J. Chem. Phys.* **2012**, *137*, 124107.
- (24) Darden, T.; Pearlman, D.; Pedersen, L. G. Ionic Charging Free Energies: Spherical Versus Periodic Boundary Conditions. *J. Chem. Phys.* **1998**, *109*, 10921–10935.
- (25) Peslherbe, G. H.; Ladanyi, B. M.; Hynes, J. T. Cluster Ion Thermodynamic Properties: The Liquid Drop Model Revisited. *J. Phys. Chem. A* **1999**, *103*, 2561–2571.
- (26) Coe, J. V. Connecting Cluster Anion Properties to Bulk: Ion Solvation Free Energy Trends with Cluster Size and the Surface Vs Internal Nature of Iodide in Water Clusters. *J. Phys. Chem. A* **1997**, *101*, 2055–2063.
- (27) Horvath, L.; Beu, T.; Manghi, M.; Palmeri, J. The Vapor–Liquid Interface Potential of (Multi)Polar Fluids and Its Influence on Ion Solvation. *J. Chem. Phys.* **2013**, *138*, 10.
- (28) Asthagiri, D.; Pratt, L. R.; Ashbaugh, H. S. Absolute Hydration Free Energies of Ions, Ion-Water Clusters, and Quasichemical Theory. *J. Chem. Phys.* **2003**, *119*, 2702–2708.
- (29) Klotz, C. E. Solubility of Protons in Water. *J. Phys. Chem.* **1981**, *85*, 3585–3588.
- (30) Reif, M. M.; Hunenberger, P. H. Computation of Methodology-Independent Single-Ion Solvation Properties from Molecular Simulations. III. Correction Terms for the Solvation Free Energies, Enthalpies, Entropies, Heat Capacities, Volumes, Compressibilities, and Expansivities of Solvated Ions. *J. Chem. Phys.* **2011**, *134*, 144103.
- (31) Arslanargin, A.; Beck, T. L. Free Energy Partitioning Analysis of the Driving Forces That Determine Ion Density Profiles near the Water Liquid–Vapor Interface. *J. Chem. Phys.* **2012**, *136*, 104503.
- (32) Joung, I. S.; Cheatham, T. E. Determination of Alkali and Halide Monovalent Ion Parameters for Use in Explicitly Solvated Biomolecular Simulations. *J. Phys. Chem. B* **2008**, *112*, 9020–9041.
- (33) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. The Missing Term in Effective Pair Potentials. *J. Phys. Chem.* **1987**, *91*, 6269–6271.
- (34) Mamatkulov, S.; Fyta, M.; Netz, R. R. Force Fields for Divalent Cations Based on Single-Ion and Ion-Pair Properties. *J. Chem. Phys.* **2013**, *138*, 024505.
- (35) Jensen, K. P.; Jorgensen, W. L. Halide, Ammonium, and Alkali Metal Ion Parameters for Modeling Aqueous Solutions. *J. Chem. Theory Comput.* **2006**, *2*, 1499–1509.
- (36) Li, P. F.; Roberts, B. P.; Chakravorty, D. K.; Merz, K. M. Rational Design of Particle Mesh Ewald Compatible Lennard-Jones Parameters for +2 Metal Cations in Explicit Solvent. *J. Chem. Theory Comput.* **2013**, *9*, 2733–2748.
- (37) Fan, Y. B.; Chen, X.; Yang, L. J.; Cremer, P. S.; Gao, Y. Q. On the Structure of Water at the Aqueous/Air Interface. *J. Phys. Chem. B* **2009**, *113*, 11672–11679.
- (38) Kuhne, T. D.; Pascal, T. A.; Kaxiras, E.; Jung, Y. New Insights into the Structure of the Vapor/Water Interface from Large-Scale First-Principles Simulations. *J. Phys. Chem. Lett.* **2011**, *2*, 105–113.
- (39) Baranyai, A.; Bartok, A.; Chialvo, A. A. Limitations of the Rigid Planar Non-Polarizable Models of Water. *J. Chem. Phys.* **2006**, *124*, 74507.
- (40) Vlcek, L.; Chialvo, A. A.; Cole, D. R. Optimized Unlike-Pair Interactions for Water–Carbon Dioxide Mixtures Described by the SPC/E and EPM2 Models. *J. Phys. Chem. B* **2011**, *115*, 8775–8784.
- (41) Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press: New York, 1969.
- (42) Bogusz, S.; Cheatham, T. E.; Brooks, B. R. Removal of Pressure and Free Energy Artifacts in Charged Periodic Systems Via Net Charge Corrections to the Ewald Potential. *J. Chem. Phys.* **1998**, *108*, 7070–7084.
- (43) Frenkel, D.; Smit, B. *Understanding Molecular Simulations: From Algorithms to Applications*; Academic Press: New York, 2007.
- (44) Beutler, T. C.; Mark, A. E.; Vanschaik, R. C.; Gerber, P. R.; Vangunsteren, W. F. Avoiding Singularities and Numerical Instabilities in Free-Energy Calculations Based on Molecular Simulations. *Chem. Phys. Lett.* **1994**, *222*, 529–539.
- (45) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular-Dynamics. *J. Comput. Phys.* **1995**, *117*, 1–19.
- (46) Martin, M. G.MCCCS Towhee. towhee.sourceforge.net.
- (47) Norman, G. E.; Filinov, V. S. Investigations of Phase Transitions by a Monte-Carlo Method. *High Temp.* **1969**, *7*, 216–222.
- (48) Ferrenberg, A. M.; Swendsen, R. H. Optimized Monte-Carlo Data-Analysis. *Phys. Rev. Lett.* **1989**, *63*, 1195–1198.
- (49) Kastenholz, M. A.; Hunenberger, P. H. Computation of Methodology-Independent Ionic Solvation Free Energies from Molecular Simulations. I. The Electrostatic Potential in Molecular Liquids. *J. Chem. Phys.* **2006**, *124*, 124106.
- (50) Grossfield, A. Dependence of Ion Hydration on the Sign of the Ion's Charge. *J. Chem. Phys.* **2005**, *122*, 024506.
- (51) Arshadi, M.; Yamdagni, R.; Kebarle, P. Hydration of Halide Negative Ions in Gas Phase 0.2. Comparison of Hydration Energies for Alkali Positive and Halide Negative Ions. *J. Phys. Chem.* **1970**, *74*, 1475–1482.
- (52) Coe, J. V. Connecting Cluster Ions and Bulk Aqueous Solvation: a New Determination of Bulk Single-Ion Solvation Enthalpies. *Chem. Phys. Lett.* **1994**, *229*, 161–168.
- (53) Raiteri, P.; Gale, J. D.; Quigley, D.; Rodger, P. M. Derivation of an Accurate Force-Field for Simulating the Growth of Calcium Carbonate from Aqueous Solution: A New Model for the Calcite–Water Interface. *J. Phys. Chem. C* **2010**, *114*, 5997–6010.
- (54) Peng, T. F.; Chang, T. M.; Sun, X. Q.; Nguyen, A. V.; Dang, L. X. Development of Ions-Tip4p-Ew Force Fields for Molecular Processes in Bulk and at the Aqueous Interface Using Molecular Simulations. *J. Mol. Liq.* **2012**, *173*, 47–54.
- (55) Krestov, G. A. Entropy Changes in the Hydration of Monoatomic Ions. *Teor. Eksp. Khim.* **1965**, *1*, 479–487.
- (56) LyndenBell, R. M.; Rasaiah, J. C. From Hydrophobic to Hydrophilic Behaviour: A Simulation Study of Solvation Entropy and Free Energy of Simple Solutes. *J. Chem. Phys.* **1997**, *107*, 1981–1991.

(57) Krekelberg, W. P.; Pond, M. J.; Goel, G.; Shen, V. K.; Errington, J. R.; Truskett, T. M. Generalized Rosenfeld Scalings for Tracer Diffusivities in Not-So-Simple Fluids: Mixtures and Soft Particles. *Phys. Rev. E* **2009**, *80*, 061205.

(58) Joung, I. S.; Cheatham, T. E. Molecular Dynamics Simulations of the Dynamic and Energetic Properties of Alkali and Halide Ions Using Water-Model-Specific Ion Parameters. *J. Phys. Chem. B* **2009**, *113*, 13279–13290.