Density and Temperature Dependences of Hydration Free Energy of Na$^+$ and Cl$^-$ at Supercritical Conditions Predicted by ab Initio/Classical Free Energy Perturbation

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The ab initio/classical free energy perturbation (ABC−FEP) method proposed previously by Wood et al. [*J. Chem. Phys.* **1999,** *110,* 1329] combines the free energy calculated from a classical simulation of an approximate model with the free energy of perturbing the approximate solute−solvent interactions to ab initio interaction energies. This method was used to calculate the hydration free energies of Na$^+$ and Cl$^-$ at a variety of high-temperature state points (973 K with 0.0101, 0.0935, 0.2796 g/cm^3 and 723 K with 0.0098, 0.0897, 0.5113 g/cm^3). The classical simulations were done with an approximate model, previously derived by fitting ab initio results at 973 K and 0.535 g/cm^3. These were followed by perturbation to a QM/MM model in which the interactions of Na$^+$ with H$_2$O and Cl$^-$ with H$_2$O are calculated by an ab initio method, while the interactions of H$_2$O with H$_2$O are calculated by the fluctuating charge TIP4P−FQ model. The pairwise ion−water interaction energies are obtained at the MP2/6-311++G(3df,3pd) level and multibody interactions at the B3LYP/6-311++G(3df,3pd) level for Na$^+$ and B3LYP/aug-cc-pVDZ level for Cl$^-$. Estimates of the accuracy of the ab initio methods and of the sampling errors indicate that these results are more reliable than previous predictions and can be used as benchmarks to assess the accuracy of molecular dynamics simulations or empirically parametrized equations of state. Extrapolations using various semiempirical models were not very accurate at the state points studied. The model of Tanger and Pitzer, which interpolates between gas-phase mass spectroscopic results and high-density predictions, was very accurate. Born models failed at the low-density state points, while compressible continuum models were much better. Interpolation or extrapolation of the present results indicates that previous simulations of two different Lennard−Jones plus charge models have substantial errors at most state points. The approximate models used in the present work performed reasonably well at all state points, with differences from the ABC−FEP corrected results ranging from 0 to 22 kJ/mol.

1. Introduction

The thermodynamic properties of ions or ion pairs in steam at high temperatures and pressures have an important role in many geological processes as well as in steam power generation.[1−4] In hydrothermal systems, ions and ion pairs affect the dissolution, migration, and formation of minerals. Although the solubility of salts in steam is low, it is enough to result in the transport of large quantities of these salts through the steam turbines in electric power plants. Understanding and controlling this transport is a crucial step in mitigating its undesirable consequences, such as stress corrosion cracking, pitting, and metal corrosion in steam cycles.

The hydration free energies of ions are unknown except for some ions in very low pressure steam (<1 bar), where measurements can be made by mass spectrometric techniques. Pitzer[5] and Tanger and Pitzer[6] have used mass spectrometric data to estimate the free energy of hydration of ions in high-temperature steam. In addition, some other semiempirical predictive methods for high-temperature aqueous solutions have been developed. These models have been based on the Born model,[7] the compressible continuum model,[8−10] stepwise association models with Born terms,[6] Langmuir adsorption models

with Born terms,[11] hard-sphere plus charge models,[12] and direct correlation function integral models.[13−15] The accuracy of these predictive models is very hard to assess a priori. It was our hope to perform calculations that are accurate enough to serve as benchmarks for assessing the accuracy of the semiempirical models and to allow development of improved models.

Molecular dynamics (MD) and Monte Carlo (MC) simulations have played a major role in developing a detailed, molecular-level picture of aqueous ions at extreme conditions, because they offer a direct route from intermolecular forces to macroscopic properties. Using these techniques it is, in principle, quite easy to calculate the hydration free energy of any Hamiltonian model of the solvent plus ions. The difficult part is finding an appropriate Hamiltonian model for the forces and energies in the system. While approximate potential models are easily calculated, the inaccuracy of the interaction energy is large and unknown. In the case of ab initio MD, the calculations are so time-consuming that accurate ab initio methods cannot be used for large systems. In either case it is difficult to assess the accuracy of predictions of real aqueous solutions. Extensive discussions of the problems with these methods are available in a number of recent papers[16−25] or the review by Chialvo and Cummings.[26]

The calculations described here use the ab initio/classical free energy perturbation (ABC−FEP) method to calculate the free

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energy of hydration of models of solutes at infinite dilution.[27-30] The method combines the free energy calculated from a classical simulation of an approximate model with the free energy of perturbing the approximate solute−solvent interactions to ab initio interaction energies. In contrast to traditional molecular dynamics, the accuracy of the results is not limited by the accuracy of the approximate potential. In contrast to ab initio MD, it is only necessary to determine ab initio energies at a small number of configurations, taken from the simulation with the approximate model. Similar methods have been developed by other workers. Akhmatskaya et al.[31] and Vaughn et al.[32] used Boltzmann re-weighting of several thousand independent configurations from a simulation of an approximate model to calculate the structure of ab initio models of small clusters, $(H_2O)_5$ and $F^-(H_2O)_4$. They pointed out that this method could also be used to calculate the difference between the free energy of approximate and ab initio models of the cluster. Warshel and co-workers calculated solvation free energies at infinite dilution using approximate models and then applied free energy perturbation to find the free energy of quantum models.[33,34] These early calculations were limited by the very approximate quantum models used. More recently, they applied these methods to free energy changes along solution-phase reaction paths using more accurate ab initio methods.[35-37] However, they have only been able to include a small number of water molecules in the ab initio calculations, and difficulties with ensemble sampling have prevented convergence of the perturbation calculation. In our calculations, large numbers of water molecules (up to 60) can be readily included, and converged perturbation calculations can be achieved with a modest number of configurations (50−100).[30]

This paper is part of a continuing series from our laboratory using the ABC−FEP method to calculate free energies of hydration of models of aqueous solutes. Previous work[27] introduced the ABC−FEP method and tested it on water as a solute in water.[28,29] In our last paper,[30] it was shown that the method was applicable to ions and that it could predict the well-known value for the free energies of hydration of Na^+ and Cl^- at 573 K and 0.725 g/cm^3 within 4 kJ/mol (-657 ± 7 kJ/mol vs the experimental value of -661 kJ/mol). The method was expected to have essentially the accuracy of the ab initio method for solute−solvent energy, which we estimated at about 4 kJ/mol for each ion. The success of this test encouraged us to perform calculations at a series of supercritical state points that would allow predictions and comparisons with literature estimates by interpolation of our results. We avoided calculations near the critical point of water to avoid problems with long-range density fluctuations. In this paper we report calculations at 723 and 973 K at water densities from 0.0098 to 0.5113 g/cm^3. Methods of interpolating our results as a function of temperature and density are briefly explored and used to assess the accuracy of previous methods of estimating hydration free energies.

The organization of this paper is as follows. Section 2 describes the methodology used in the classical simulations and ABC−FEP technique for aqueous Na^+ and Cl^-. In section 3, we present a summary of the ABC−FEP predictions for the hydration free energies of the ions, and section 4 compares and discusses these results with those of other methods. Some conclusions are drawn in section 5.

2. Methodology

2.1. Molecular Dynamics Simulation with Approximate Models. The molecular dynamics simulations with our ap-

TABLE 1: Model Potential Parameters for Cl^-−H_2O and Na^+−H_2O Interactions (eqs 1 and 2)

model	a	b	A_{XO} (kJ mol^{-1} Å^a)	B_{XO} (kJ mol^{-1} Å^b)	A_{XH} (kJ mol^{-1} Å^a)	B_{XH} (kJ mol^{-1} Å^b)
Cl^--H_2O	9	6	669636.27	22010.82	2319.16	
Na^+-H_2O	6	4	7341.56	719.97	1627.21	285.78

a Please provide footnote. *b* Please provide footnote.

proximate models were performed using the DL-POLY MD package[38] with some modifications to include the fluctuating charge TIP4P−FQ water model[39] using Ewald sums. This water model is polarizable but has a rigid geometry. The hydrogen and oxygen charges were constrained to prevent them from going toward infinity, which otherwise occurs occasionally in high-temperature simulations. The model potentials used for the ion−water interactions had the form

$$U_{X,O} = \frac{A_{XO}}{r_{XO}{}^a} - \frac{B_{XO}}{r_{XO}{}^b} + \frac{q_X q_O}{r_{XO}} \qquad (1)$$

$$U_{X,H} = \frac{A_{XH}}{r_{XH}{}^a} - \frac{B_{XH}}{r_{XH}{}^b} + \frac{q_X q_H}{r_{XH}} \qquad (2)$$

where the interaction parameters A, B, a, and b for the approximate models are listed in Table 1.

The charges on the ions, q_X, are $\pm 1.0e$, while the charges on O and H are determined by the fluctuating charge model for water, with polarization due to the solute and other water molecules.[39] These approximate models were derived in a previous study[30] by fitting ab initio results for configurations taken from a simulation at 973 K and 0.535 g/cm^3. The ion (Cl^- or Na^+) was held fixed at the center of a cubic box containing 200 TIP4P−FQ water molecules. The calculations were done in two steps, first growing a point mass into an uncharged particle and then charging the particle. The reverse process was also calculated to check that the hysteresis was small and verify that our equilibration time was sufficient.[40] The Ben−Naim and Marcus definition of hydration was used (solute concentration is the same in the gas phase and in solution).[41] The conversion to the usual standard states of ideal gas and 1 *m* solution, $\Delta_h{}^m G$, is given by $\Delta_h{}^m G = \Delta G + RT$ ln$[RTm^\theta \rho^0/p^\theta]$, where ρ^0 is the pure solvent density, $p^\theta = 1$ bar, and $m^\theta = 1$ mol/kg.

2.2. Summary of ABC−FEP Method. A detailed discussion of the ABC−FEP method has been given[27] and will not be repeated here. Briefly, the ABC−FEP method allows calculation of the free energy of a quantum mechanical (i.e., a pure ab initio or QM/MM hybrid) model without the computer-intensive simulation of that model. This allows the use of more sophisticated quantum models than would be feasible if the full simulation were done with that model. The main idea is to calculate the hydration free energy of solute (X) in solvent (S) as the sum of the hydration free energy of an approximate model ($\Delta G[\bullet \rightarrow A]$) plus the free energy of transforming the approximate solute−solvent interactions to the quantum model interactions ($\Delta G[A \rightarrow Q]$)

$$\Delta G = \Delta G[\bullet \rightarrow A] + \Delta G[A \rightarrow Q] \qquad (3)$$

In this work, $\Delta G[\bullet \rightarrow A]$ were obtained using thermodynamic integration. The key to the ABC−FEP method, $\Delta G[A \rightarrow Q]$, was calculated by free energy perturbation

$$\Delta G[A \rightarrow Q] = -RT \ln \langle \exp[-(U_{XS}{}^Q - U_{XS}{}^A)/RT] \rangle_A \quad (4)$$

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Here, $U_{XS}{}^A$ and $U_{XS}{}^Q$ indicate the approximate and quantum solute−solvent interaction energies, respectively. The brackets with subscript A indicate an average over N_{conf} configurations generated in a classical simulation with the approximate potential.

2.3. Ab Initio Interaction Energies. To evaluate $\Delta G[A \rightarrow Q]$, the difference between the ab initio and approximate solute−solvent interaction energies, $\Delta U = U_{XS}{}^Q - U_{XS}{}^A$, are required at each of the sampled configurations (see eq 4). We calculated ΔU only for the interaction of the solute with the nearest n water molecules. This assumes that the approximate model is accurate enough for the more distant water molecules and reduces the cost of calculating $U_{XS}{}^Q$.

We further approximate the interaction energies of the solute with the nearest n solvent molecules as a sum of n pairwise interaction energies and the multibody interaction energy of solute with the nearest m solvent molecules

$$U_{XS} = U_{XS,n}[\text{pair}] + U_{XS,m}[\text{multi}] \qquad (5)$$

Here, the pairwise interaction energy, $U_{XS,n}[\text{pair}]$, is the sum of all n solute (X)−solvent (S_i) pair interaction energies, $U_{XS,n}[\text{pair}] = \sum_{i=1}^{n} u_{X,S_i}$. The multibody interaction energy, $U_{XS,m}[\text{multi}]$, is the difference between the pairwise and total interaction energies of a cluster with m solvent molecules, $U_{XS,m}[\text{multi}] = U_{XS,m} - U_{XS,m}[\text{pair}]$. The full solute−solvent interaction energy for this cluster, $U_{XS,m}$, is obtained by taking the total energy of the cluster and subtracting the energies of isolated X and the energy of the cluster with the solute particle removed (keeping the solvent molecules in exactly the same positions). This approach allows substantial savings in computational effort for a given level of accuracy. We find that the multibody interactions can be calculated with m much less than n and that less demanding ab initio methods can be used to calculate the multibody interactions.[30] Of course, when m and n are large enough, $\Delta U = U_{XS}{}^Q - U_{XS}{}^A$ does not appreciably change with increasing n or m. Values of n were chosen by plotting the average value of ΔU as a function of n to determine where the difference between the approximate and quantum models has converged. Values for m were chosen from previous experience and from test calculations with different values of m. For each state point, we compared calculations with at least two different m. This test indicated that the multibody interactions had converged to within 1 or 2 kJ/mol in all cases. To calculate ΔU, we use eq 5 for $U_{XS}{}^Q$ and $U_{XS}{}^A$ with the same m and n so that multibody electrostatic effects outside the nearest m waters will partially cancel. To avoid surface free energy effects in the outer shell of water molecules, the choice of water molecules included in the cluster is based on distances from the solute to a point equidistant from the three atoms in the water molecules.[42]

Previous experience has shown that MP2 calculations with a 6-311++G(3df,3pd) basis set are adequate for Na$^+$−H$_2$O and Cl$^-$−H$_2$O pair interactions.[30] Multibody interactions were calculated with DFT using the B3LYP functional[43,44] with the aug-cc-pVDZ basis set for Cl$^-$ and the 6-311++G(3df,3pd) basis set for Na$^+$.[30] Corrections for basis set super position error (BSSE) were calculated by the counterpoise method[45] for every water−solute pair interaction in all configurations at each temperature and pressure. The BSSE for the multibody interactions were found to be negligible in previous work at 973 K and 0.535 g/cm^3. In this work, the multibody BSSE was calculated at 0.0101 g/cm^3 and 973 K and also found to be negligible, so the BSSE was neglected for all multibody interactions.

2.4. Criteria for N_{conf}. The calculated free energy would be exact if an infinite number of configurations were used in eq 4. In previous work, we found that if the approximate solute model is reasonably accurate, then 50−100 configurations are enough to obtain an accurate free energy. Such a small sample of configurations can be sufficient because, with a good approximate model, the FEP term (eq 4) is a small fraction of the total free energy. Then, even a rather large relative uncertainty in this term (∼10%) contributes only a small uncertainty to ΔG. Our criteria for an accurate approximate model are that the peak in the distribution of $\exp[-\Delta U/kT]$ is sampled by 50−100 configurations and that the bootstrap error estimate[46] for $\Delta G[A \rightarrow Q]$ is small (<1.5 kJ/mol). The bootstrap technique gives a reasonably accurate estimate of the uncertainty due to the limited number of configurations. The boostrap error estimate is calculated by using many random choices of N_{conf} configurations from the sample of N_{conf} independent configurations selected from a simulation. In each of these random choices, some configurations may be duplicated and others not included. This method assesses the probable error due to picking only a single set of N_{conf} configurations. Estimates of the systematic error introduced by our finite sample size indicate it is negligible for the approximate models used here.[47] If these criteria for an accurate model are not satisfied, more configurations must be included in the average or the approximate model must be reparametrized to obtain a better model. Recently Murdock et al.[48] used the cumulant expansion technique to check the convergence of quantum−classical free energy differences. Using this method results in negligible changes in the present calculations.

Our goal in this work is to achieve predictions with overall accuracy only a little larger than the accuracy of the ab initio method (∼4 kJ/mol). Thus, we required sampling errors (as estimated with the bootstrap method) in the ABC−FEP calculations to be less than 1.5 kJ/mol and the thermodynamic integration errors to be less than 3.5 kJ/mol.

3. Predicted Hydration Free Energies with ABC−FEP Method

We started with the approximate Na$^+$−H$_2$O and Cl$^-$−H$_2$O models in Table 1 (see eqs 1 and 2) in our predictions of the free energy of Na$^+$ and Cl$^-$ at six state points (973 K with 0.0101, 0.0935, and 0.2796 g/cm^3 and 723 K with 0.0098, 0.0897, and 0.5113 g/cm^3). For each of these conditions, we chose 50 independent configurations ($N_{conf} = 50$) from molecular dynamics simulations, except for $\rho = 0.5113$ g/cm^3 at 723 K where $N_{conf} = 100$. The pairwise interaction energies were converged with $n = 15$ for $\rho \approx 0.01$ g/cm^3, $n = 30$ for $\rho \approx 0.1$ g/cm^3, $n = 50$ for $\rho \approx 0.3$ g/cm^3, and $n = 60$ for $\rho \approx 0.51$ g/cm^3. The multibody interaction energies were converged with $m = 7$ for $\rho \approx 0.01, 0.1$ g/cm^3 and $m = 9$ for $\rho \approx 0.3$ g/cm^3 and $\rho \approx 0.51$ g/cm^3. The difference in the multibody interaction energies with different m varied from 0.5 to 1.8 kJ/mol. The predicted hydration free energies of the individual ions are listed in Table 2. In every case, the bootstrap error estimate of $\Delta G(A \rightarrow Q)$ was within our criterion (<1.5 kJ/mol; see footnote d of Table 2) for a good approximate model. Histograms of $\exp[-\Delta U/kT]$ showed that the peak in the distribution was reasonably well sampled. We believe these predictions are accurate because the uncertainty is ultimately limited by the first-principles calculations which have no empirical parameters. Moreover, at 573 K we compared our results for hydration free energy of the ions to accurate experimental results and directly verified their accuracy[30] (see below).

TABLE 2: Hydration Free Energies (kJ/mol) of Na$^+$ and Cl$^-$ at 973 and 723 K with Various Densities

973 K	Na$^+$				Cl$^-$			
ρ (g/cm^3)	0.010	0.035	0.2796	0.535[a]	0.0101	0.0935	0.2796	0.535
$\Delta_h{}^m G(\rightarrow A)$[a]	−57.8 (3.5)	−161.8 (2.7)	−236.3 (1.6)	−267.8 (2.6)	−40.0 (3.2)	−112.1 (2.4)	−212.1 (2.1)	−253.1 (2.1)
$\{N_{conf}, n, m\}$[b]	{50,15,7}	{50,30,7}	{50,50,9}	{100,60,9}	{50,15,7}	{50,30,7}	{50,50,9}	{80,60,10}
$\Delta U_{multi}{}^{DFT-FQ}$[c]	5.9 (4.5)	21.9 (7.8)	30.5 (11.3)	38.4 (13.0)	−0.2 (2.8)	−0.1 (5.0)	3.0 (7.0)	2.0 (8.8)
$\Delta U_{pair}{}^{MP2}$[c]	−19.8 (10.6)	−34.2 (9.8)	−34.3 (15.1)	−38.5 (17.4)	0.2 (2.9)	−0.1 (4.6)	−2.9 (5.1)	−9.0 (5.1)
$U_{pair,BSSE}{}^{MP2}$[c]	7.5 (3.5)	15.2 (2.6)	19.8 (3.2)	26.8 (3.0)	5.6 (3.7)	16.4 (4.2)	22.8 (4.1)	28.5 (3.9)
$\Delta G(A \rightarrow Q)$[d]	−17.4 (1.3)	−15.2 (1.2)	−8.6 (1.3)	−6.2 (1.3)	−0.5 (0.5)	−1.5 (0.7)	−2.6 (1.3)	−10.9 (1.2)
$\Delta_h{}^m G$[e]	−75.2 (5.4)	−177.0 (4.9)	−244.9 (4.5)	−274.0 (4.9)	−40.5 (5.1)	−113.6 (4.7)	−214.7 (4.7)	−264.0 (4.7)

723 K	Na$^+$			Cl$^-$		
ρ (g/cm^3)	0.0098	0.0897	0.5113	0.0098	0.0897	0.5113
$\Delta_h{}^m G(\rightarrow A)$[a]	−105.6 (3.5)	−223.2 (2.7)	−303.6 (1.7)	−54.7 (2.8)	−150.0 (3.1)	−281.6 (2.3)
$\{N_{conf}, n, m\}$[b]	{50,15,7}	{50,30,7}	{100,60,9}	{50,15,7}	{50,30,7}	{50,60,9}
$\Delta U_{multi}{}^{DFT-FQ}$[c]	18.1 (7.1)	31.1 (9.9)	46.2 (12.3)	0.1 (2.9)	0.6 (6.5)	−0.1 (8.3)
$\Delta U_{pair}{}^{MP2}$[c]	−38.2 (8.9)	−41.5 (12.7)	−41.9 (16.6)	0.6 (3.7)	−0.4 (3.9)	−1.3 (4.5)
$U_{pair,BSSE}{}^{MP2}$[c]	14.3 (2.4)	18.6 (2.7)	26.3 (2.9)	10.6 (3.4)	19.5 (2.8)	31.5 (3.9)
$\Delta G(A \rightarrow Q)$[d]	−22.4 (0.8)	−14.4 (1.4)	−4.3 (1.5)	−0.2 (0.5)	−2.4 (1.1)	−4.9 (0.6)
$\Delta_h{}^m G$[e]	−128.0 (5.4)	−236.4 (4.9)	−307.9 (4.5)	−54.9 (4.8)	−152.4 (5.1)	−286.5 (4.6)

[a] Figures in parentheses are the estimated 67% confidence limits. The conversion of ΔG to $\Delta_h{}^m G$ is described in the text. $\Delta_h{}^m G(\bullet \rightarrow A)$ includes the infinite lattice correction (see ref 58). The result at 973 K and 0.535 g/cm^3 is from ref 30. [b] Parameters used in the most accurate calculations. [c] Figures in parentheses are the standard deviation of the values of ΔU or BSSE. The range of ΔU or BSSE gives an estimate of the range of errors in the approximate model at the equilibrated configurations for this temperature and density. [d] The figure in parentheses is the uncertainty due to limited sampling, estimated by Bootstrap resampling (the error in the ab initio method is not included). [e] ΔG is calculated from eq 3. Figures in parentheses are the estimated uncertainty including our estimate of the uncertainty of the ab initio method as 4 kJ/mol.

In addition to final values for $\Delta_h{}^m G$, the contributions and uncertainty of each free energy term in the calculations are listed in Table 2. Average values and standard deviations of the pair, multibody, and BSSE contributions to ΔU are also reported. These values show that there are substantial multibody interactions for Na$^+$, as might be expected given the small radius of this ion. The importance of many-body contributions implies that it will not be possible to develop an effective pairwise interaction model of Na$^+$−H$_2$O interactions that is accurate over a wide range of density. For Cl$^-$, the ab initio corrections are much smaller for Cl$^-$ than those for Na$^+$, demonstrating that the approximate chloride pair model is reasonably accurate at all the state points considered here.

Figure 1 shows the ABC−FEP predictions for the sum of the free energies of hydration for the two ions, $\Delta_h{}^m G$[Na$^+$ + Cl$^-$]. As discussed below, this sum facilitates comparison to other methods. Results from these calculations are shown at 973 and 723 K as a function of water density, together with previously reported results[30] at 973 K with 0.535 g/cm^3 and 573 K with 0.725 g/cm^3. We find that $\Delta_h{}^m G$[Na$^+$ + Cl$^-$] shows a much more pronounced variation with water density than with temperature over the range considered. Presumably this reflects the sensitivity of the dielectric constant to density changes.

4. Comparison to Other Methods and Discussion

Because we believe the present estimates are the most accurate available, in the following discussion we compare our results to predictions from other methods.

4.1. Comparison with Semiempirical Results. Table 3 summarizes our results and several semiempirical predictions of $\Delta_h{}^m G$[Na$^+$ + Cl$^-$] at these state points. The comparisons are shown graphically for the results at 973 K in Figure 2 and at 723 and 573 K in Figure 3. Our theoretical predictions of individual ions do not include the surface dipole moment of a large water drop, and in some cases it is not clear whether such effects are included in the data used to parametrize semiempirical models.[5,6] For consistency, we compare predictions of the sum of the free energies of hydration of Na$^+$ and Cl$^-$ so the surface dipole moment corrections for the two ions cancel.
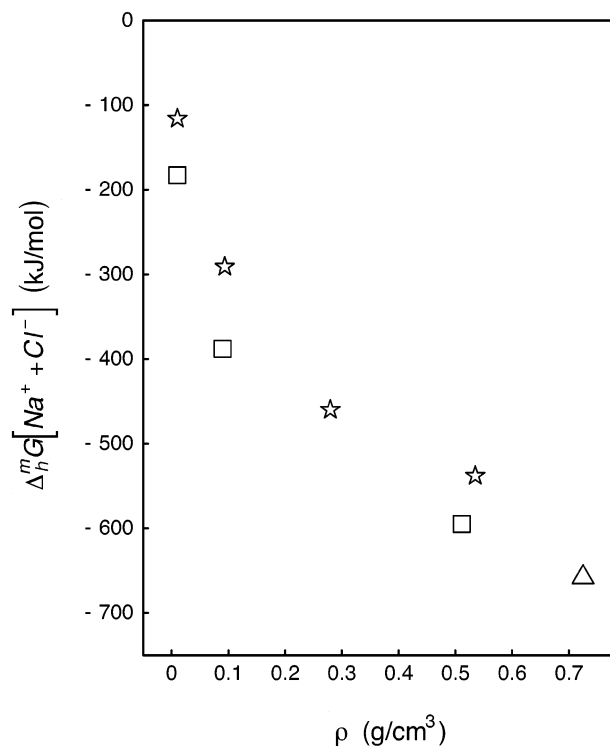

Figure 1. Predicted hydration free energies from the ABC−FEP method for $\Delta_h{}^m G$[Na$^+$ + Cl$^-$] at 973 and 723 K with various water densities as well as a previously reported result at 573 K: (☆) 973 K; (□) 723 K; (△) 573 K.

All of the semiempirical predictions agree at 573 K and 0.725 g/cm^3 because there are experimental results close to this state point which were used to parametrize all of these models. The agreement of our parameter-free ABC−FEP result[30] (−657 kJ/mol) with the fit to this experimental data by Archer[49] (−661 kJ/mol) confirms the accuracy of the method.

The earliest prediction of the free energy of hydration was that of Pitzer.[5] His model was based on equilibrium constants (determined from mass spectroscopic experiments) for the association of the first few water molecules with a sodium or

TABLE 3: Comparison of the Hydration Free Energy (kJ/mol) of Na$^+$ + Cl$^-$ with Semiempirical Predictions at Various Temperatures and Water Densities

T (K)	973 K				723 K			573 K
ρ (g/cm^3)	0.0101	0.0935	0.2796	0.535	0.0098	0.0897	0.5113	0.725
ABC/FEP[a]	−116(7)	−291(7)	−460(7)	−538(7)	−183(7)	−388(7)	−595(7)	−657(7)
Archer[b]								−661
revised HKF[c]				−545			−608	−663
Pitzer[d]	−146	−300	−416		−198	−347		
Tanger−Pitzer[e]	−123	−297	−469	−546	−189	−388	−605	−662
SWOC[f]			−493	−548			−609	−662

^{a} Present results, derived from Table 2. Figures in parentheses are estimated uncertainties. ^{b} From fitting experimental data (see ref 49). ^{c} Revised HKF model predictions (SUPCRT92) (see ref 7). Predictions above 0.35 g/cm^3 only. ^{d} Pitzer prediction using mass spectrometric data (see ref 5). Predictions to 0.3 g/cm^3 only. ^{e} Tanger and Pitzer prediction using mass spectrometric data and revised HKF predictions (see ref 6). ^{f} Sedlbauer et al. predictions (see ref 14). Predictions above 0.2 g/cm^3 only.

TABLE 4: Radii (nm) in the Born and Compressible Continuum (CC) Models that Give the ABC/FEP Result for Na$^+$ and Cl$^-$ at Various Temperatures and Water Densities

R(nm)	973 K				723 K			573 K
ρ (g/cm^3)	0.0101	0.0935	0.2796	0.535	0.0098	0.0897	0.5113	0.725
R[Na$^+$, Born^a]	0.039	0.117	0.175	0.194	0.028	0.107	0.188	0.191
R[Na$^+$, CC^b]	0.193	0.184	0.186	0.189	0.194	0.183	0.185	0.187
R[Cl$^-$, Born^a]	0.073	0.174	0.197	0.200	0.069	0.162	0.201	0.190
R[Cl$^-$, CC]	0.238	0.241	0.208	0.196	0.259	0.252	0.198	0.186

^{a} Born plus continuum cavity model (see ref 8). ^{b} Compressible continuum plus continuum cavity model (see ref 8).

chloride ion in very low pressure water vapor. Pitzer used a Born term for the interaction of the ion−water cluster with outer water molecules and adjusted the radius to fit the association constants of Quist and Marshall[50] at 1073 K and densities above 0.3 g/cm^3. In our predictions from this model, we used the fugacity of water as recommended by Pitzer and Pabalan[51] rather than the pressure. Table 3 and Figure 2 show that Pitzer's predictions are not bad, but they are well outside the estimated uncertainty of our results. The differences range from −15 to −30 kJ/mol at 0.01 g/cm^3, −9 to +41 kJ/mol at 0.1 g/cm^3, with one point (at 0.3 g/cm^3) off by more than 44 kJ/mol. Pitzer did not recommend making predictions at water densities above 0.3 g/cm^3, so our comparisons have been limited to lower densities.

Tanger and Pitzer[6] later revised and extended the model of Pitzer.[5] This new model was again based on the mass spectroscopic experiments at low densities but with the addition of the predictions of the revised HKF model of Tanger and Helgeson at high densities.[52,53] The mass spectroscopic data was used to determine the enthalpy and entropy of association of the first six water molecules, while the predictions at high temperatures were used to determine the 12 adjustable parameters in their model. The result of this is a remarkably accurate prediction of the free energies of hydration of sodium and chloride ions. As seen in Table 3 and Figures 2 and 3, most of the predictions are low by only 4−10 kJ/mol, with one prediction being the same as the ABC−FEP prediction. This is a triumph of the art of semiempirical prediction.

Next we consider the final revised HKF predictions of Shock et al.[53] as embodied in the SUPCRT92 software package.[7] Table 3 and Figure 2 show that at ca. 0.5 g/cm^3 these predictions are quite accurate. The authors did not recommend making predictions below 0.35 g/cm^3, so we do not compare our predictions at lower densities.

Sedlbauer, Wood, and O'Connell[14] based their predictions on an empirical representation of $\bar{V}_2^0/(\kappa RT)$, where $\bar{V}_2^0$ is the partial molar volume of the ion and κ is the isothermal compressibility. This quantity is closely related to the Krichevsky parameter and to the direct correlation function integral.[54] This prediction is quite accurate where experimental data is available, though it deviates further from the ABC−FEP results at low density. Near the critical density, the error (33 kJ/mol) is well outside the estimated uncertainty of our results. Apparently, the extrapolation from experimental results at lower temperatures and higher densities was too long to allow an accurate prediction.

Taken as a whole, many of these predictions are within 20 kJ/mol, which is quite good considering the range of solvation energies and the lack of experimental data. The predictions from Tanger and Pitzer[6] are remarkably accurate, but it was not apparent a priori to the present authors that this should be the best predictive method. The ABC−FEP calculations were necessary to recognize the accuracy of this particular prediction. It is possible that the predictions of Tanger and Pitzer are more accurate because they interpolate between the low-density mass spectrocopic data and the high-density predictions of Tanger and Helgeson,[52] whereas the other predictions are extrapolations from either the low-density or high-density results.

It is informative to examine the predictions of simple electrostatic theories because they demonstrate the great importance of the solvent compressibility at these conditions. Table 4 gives the Born radius that would fit the ABC−FEP data when used with a simple continuum cavity plus Born term.[8] The radius is relatively constant at densities above 0.3 g/cm^3 ($R \approx 1.9$ Å) but drops precipitously at lower densities. The drop is larger for the Na$^+$ ion, reflecting its small radius. This change in effective radii shows that, at low densities, the ions are far more solvated than expected from the Born model. In other words, the hydration free energy predicted with a constant-radius Born model is not negative enough. In contrast to the Born model, when the compressible continuum (CC) model is used for the same calculation,[8] the radius that gives the ABC−FEP result varies slowly with density (see Table 4). Unlike the Born model, the solvent is compressible in the CC model, and the first hydration sphere of the ions is relatively intact even at low densities. For instance, Wood et al. calculated the coordination number of a chloride ion at 723.15 K and 0.01 g/cm^3 in the Born and CC approximations to be 1.46 and 3.01, respectively.[8] Their simulation of an approximate model[8] yielded a coordination number of 3.18. Many investigators using molecular
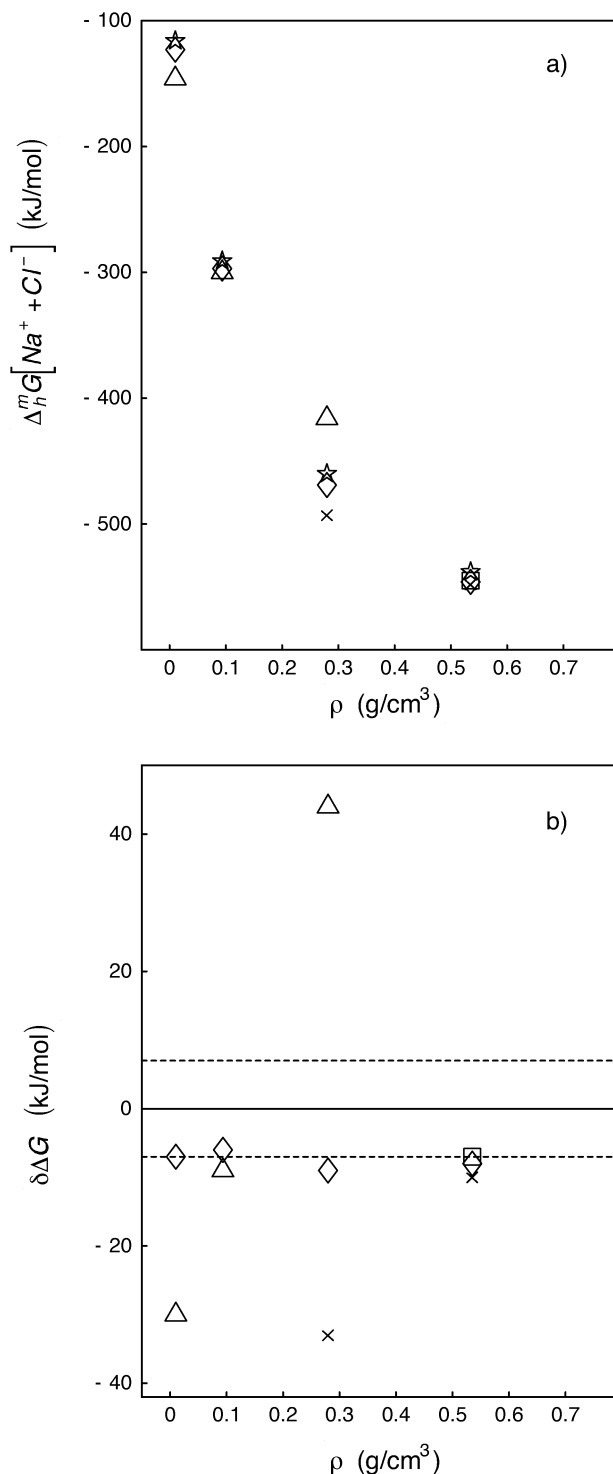
Figure 2. (a) Comparison of hydration free energies from the ABC–FEP method for $\Delta_h^m G$[Na$^+$ + Cl$^-$] at 973 K with various semiempirical approaches. (b) Deviation of semiempirical theory predictions from the ABC–FEP predictions, $\delta\Delta G = \Delta_h^m G$[Na$^+$ + Cl$^-$,Semiempirical] $-$ $\Delta_h^m G$[Na$^+$ + Cl$^-$,ABC $-$ FEP]. Horizontal lines show the uncertainty of ABC–FEP predictions, approximated here as 7 kJ/mol for all state points (actual values are in Table 2): (☆) ABC/FEP prediction; (○) Revised HKF model predictions (SUPCRT92); (△) Pitzer (ref 5); (◇) Tanger-Pitzer (ref 6); (×) Sedlbauer et al. (ref 14).

Figure 3. (a) Comparison of hydration free energies from the ABC–FEP method for $\Delta_h^m G$[Na$^+$ + Cl$^-$] at 723 K (all points except at $\rho = 0.725$ g/cm^3) and 573 K ($\rho = 0.725$ g/cm^3 only) with various semiempirical approaches. (b) Deviation of semiempirical theory predictions from ABC–FEP predictions, $\delta\Delta G = \Delta_h^m G$[Na$^+$ + Cl$^-$,Semiempirical] $-$ $\Delta_h^m G$[Na$^+$ + Cl$^-$,ABC $-$ FEP]. Horizontal lines show the uncertainty of ABC–FEP predictions, approximated here as 7 kJ/mol for all state points (actual values are in Table 2): (☆) ABC/FEP prediction; (□) Revised HKF model predictions (SUPCRT92); (△) Pitzer (ref 5) and (at 573 K and 0.725 g/mol only) Archer (ref 49); (◇) Tanger-Pitzer (ref 6); (×) Sedlbauer et al. (ref 14).

dynamics or Monte Carlo simulation of approximate models have also noted that atomistic models predict more extensive solvation at low density than the Born model.[8,18,55–57] The small (5%) and somewhat irregular variation of R[Na$^+$, CC] in Table 4 at low densities may be due to a change in the coordination numbers of the ions.

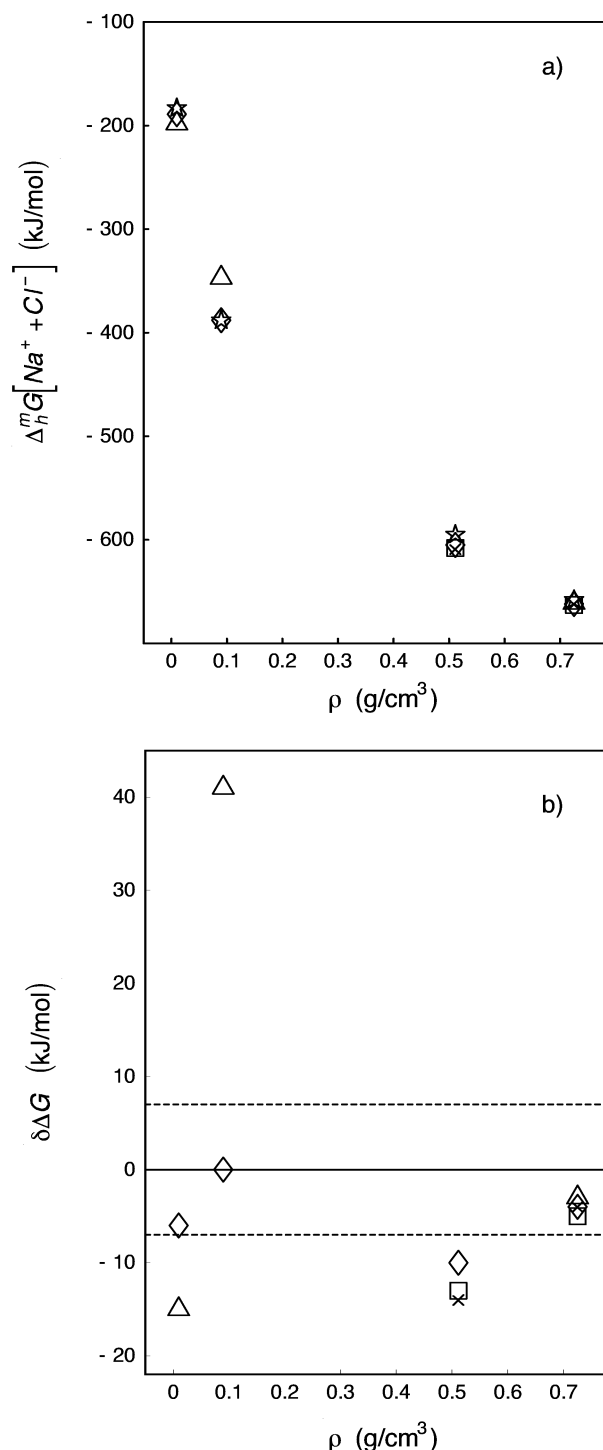**4.2. Comparison with Monte Carlo and Molecular Dynamics Simulations.** In the case of molecular dynamics (MD) and Monte Carlo (MC) simulations, we can make comparisons with the free energies of individual ions because the calculations all are for a water drop without a surface dipole moment. To

TABLE 5: Comparison of the ABC/FEP Results with Molecular Dynamics or Monte Carlo Simulations of Approximate Models

ref	T (K)	ρ (g/cm^3)	ion	model		$\Delta_h{}^mG$ (kJ/mol)	$\delta\Delta G$ (kJ/mol)^a
Balbuena et al. (1996)	673	0.29				−191	52
	768	0.29	Cl$^-$	6-12^b	SPC/E	−172	57
	673	0.087				−180	−15
	673	0.29				−281	27
	768	0.29	Na$^+$	6-12^b	SPC/E	−277	6
	673	0.087				−286	−32
Fernandez-Prini (1998)	623	0.048	Cl$^-$	6-12^c	SPC	−97	46
	623	0.017				−63	25
	623	0.048	Na$^+$	6-12^c	SPC	−164	78
	623	0.017				−137	50
Liu et al. (2002)	723	0.5113				−282	5
	723	0.0897				−150	2
	723	0.0098				−55	0
	973	0.535	Cl$^-$	9-6^d	FQ^e	−253	11
	973	0.2796				−212	3
	973	0.0935				−112	2
	973	0.0101				−40	1
	723	0.5113				−304	4
	723	0.0897				−223	14
	723	0.0098				−106	22
	973	0.535	Na$^+$	6-4^d	FQ^e	−268	6
	973	0.2796				−236	9
	973	0.0935				−162	15
	973	0.0101				−58	17

^{a} $\delta\Delta G = \Delta_h{}^mG(\text{model}) - \Delta_h{}^mG(\text{ABC−FEP})$. ^{b} Cl$^-$−H$_2$O model from Weiner et al. *J. Comput. Chem*. **1986**, 7, 230. Na$^+$−H$_2$O model from Rao and Singh *J. Am. Chem. Soc*. **1990**, 112, 3803. We have used $\Delta_hG[P,T] = \Delta_hA[V,T]$ following Ben-Naim (see ref 41). The $P\Delta_hV$ correction of Balbuena et al. should not be applied. We have corrected for the error in using Ewald sums (see refs 58−60). The corrections are not large (11−21 kJ/mol). ^{c} Na$^+$−H$_2$O and Cl$^-$−H$_2$O model from Pettitt and Rossky J. *Chem. Phys*. **1986**, *84*, 5836 and Laria and Fernandez-Prini *J. Chem. Phys*. **1995**, *102*, 7664. ^{d} Parameters in Table 1. ^{e} Fluctuating charge model of Rick et al. (see ref 39).

compare the present predictions with previous results at different state points, we used our CC model with a radius found by linear interpolation. First, the radii that fit the present predictions at both 723 and 973 K were interpolated with respect to density. Linear interpolation or extrapolation with respect to temperature was then used to find the radius of the CC model at the temperature and density of the prior simulations (see Table 5). The uncertainty of this procedure is estimated as less than ±5 kJ/mol.

Table 5 and Figure 4 compare the ABC−FEP results with those from prior simulations of approximate models. All previous calculations have used Lennard−Jones plus charge models of solute−water interactions ($a = 12$ and $b = 6$ in eq 1) and either the SPC or SPC/E water model. The first predictions of the free energy of hydration of Na$^+$ and Cl$^-$ ions in high-temperature aqueous solutions were made by Balbuena et al.[55] with models previously used at ambient conditions. Before making the comparison, we corrected the results for the difference between a periodic lattice with neutralizing background (Ewald sum) and infinite dilution.[58−60] The results of Balbuena et al. for the Cl$^-$ ion are too positive by 49 and 52 kJ/mol at the state points with 0.29 g/cm^3 and too negative by 7 kJ/mol at 0.087 g/cm^3. For the Na$^+$ ion, the differences range from 27 to −23 kJ/mol. Fernandez-Prini[61] used a different Lennard−Jones plus charge model (previously used at ambient conditions) and found results that were more positive than the present results by 25−78 kJ/mol. There are no apparent a priori reasons for preferring the results of Fernandez-Prini or Balbuena et al. The large differences in results from the models they chose show the importance of accurate models for predicting solvation at high temperatures.

Since our ABC−FEP method requires developing an approximate model, we can compare our final results with those of our own approximate model. This model was parametrized

using first-principles calculations of the energies of 30 configurations for Na$^+$ and 50 configurations for Cl$^-$ at 973 K and 0.535 g/cm^3. Table 5 and Figure 3 show that this model is quite good, especially for the Cl$^-$ ion. The differences between the ABC−FEP results ranged from 0 to 11 kJ/mol for the Cl$^-$ ion, whereas for the Na$^+$ ion the differences ranged from 4 to 22 kJ/mol. Our previous work[30] indicated that the accuracy of our approximate model is primarily a result of parametrization with configurations taken from a high-temperature simulation, but the use of lower exponents is required to achieve this accuracy.

5. Conclusions

The ABC−FEP results reported here represent the first parameter-free theoretical study of the temperature and density dependence of hydration free energies for ions in supercritical conditions. We estimate that the results for individual ions have an uncertainty of about 5 kJ/mol at all state points, making them useful standards for testing the accuracy of semiempirical models and other atomistic simulations. We found that the semiempirical model of Tanger and Pitzer is remarkably accurate over the entire range of densities and temperatures studied here. Other semiempirical models are not nearly as accurate. Comparing our results to electrostatic models shows that solvent compressibility must be accounted for under the conditions studied.

MD or MC simulations of hydration free energies for ions are quite sensitive to the interaction potentials used in supercritical conditions. Pair interaction models parametrized at ambient conditions do not appear to be adequate for calculations in high-temperature aqueous solutions. Our results suggest that fitting a rather small number of configurations from an approximate simulation at high temperature is an effective way of developing new models suitable for supercritical conditions.
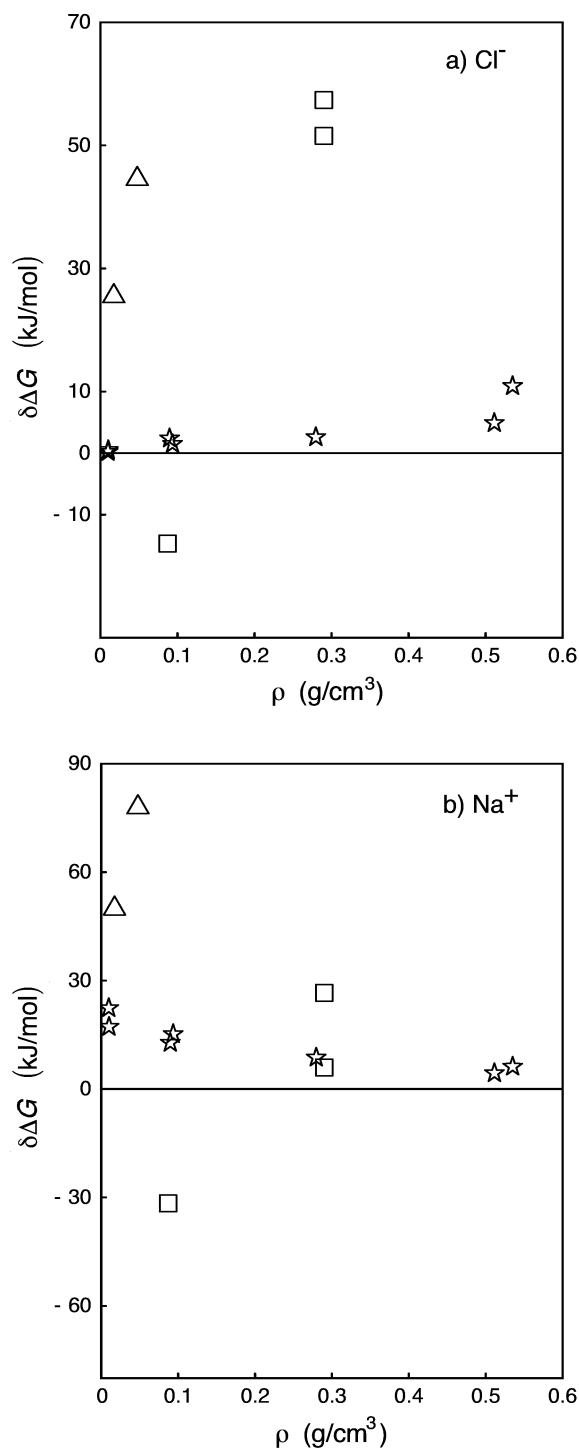
Figure 4. Deviation of hydration free energy from ABC−FEP for (a) Cl⁻ and (b) Na⁺ from simulations with various approximate models; $\delta\Delta G = \Delta_h^m G[\text{Ion, Model}] - \Delta_h^m G[\text{Ion, ABC} - \text{FEP}]$. All of the state points from Table 5 are shown; the temperature corresponding to each density and model can be found in the table: (☆) Present work (Table 1); (□) Balbuena et al. (1996); (△) Fernandez-Prini (1998).

This method (using both energies and the virial in the fitting) was originally recommended by Mezei.[62] The models developed from simulations at a single state point in our previous work have proven adequate for calculations over a substantial range of conditions. In the case of Cl⁻, the approximate model predictions of hydration free energy turn out to be accurate enough for our purposes. The ABC−FEP correction is small and does not substantially modify the free energy at densities of 0.3 g/cm³ or below. In these cases, the ABC−FEP calculation

serves primarily to test the range of validity of the approximate model. On the other hand, the ABC−FEP corrections are significant for Na⁺, even at low density. Multibody interactions are more significant in this case, and a single pairwise interaction model is not adequate for predictions over wide range of conditions. While the approximate model of Na⁺ interactions is adequate for sampling configurations, the ABC−FEP correction is essential for accurate predictions of hydration free energies. The present work thus illustrates how ABC−FEP calculations provide a practical and systematic means for developing new model potentials, validating their predictions and correcting their errors.

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