Understanding the properties of salt-H\textsubscript{2}O mixture is of great significance to biochemistry, separation technology, and CO\textsubscript{2} geologic sequestration. Molecular simulation is a promising approach to provide predictions for the physical and chemical properties of salts and their mixtures with H\textsubscript{2}O, but the accuracy of these predictions depends sensitively on the quality of the underlying intermolecular potential models. There have been concerted research efforts in developing force fields for salts, especially for NaCl and its aqueous solutions.\textsuperscript{1}–\textsuperscript{10} Prior studies have shown that non-polarizable NaCl force fields do not represent accurately the properties of the NaCl+H\textsubscript{2}O mixture over a wide range of conditions.\textsuperscript{11,12} Polarizable force fields have also been developed for this system.\textsuperscript{13–18} Even though inclusion of polarizability may improve the model performance, the computational cost of polarizable force fields is generally 5-10 times higher than their non-polarizable counterparts.

Recently, Leontyev, and Stuchebrukhov showed that polarizable force fields can be approximated by nonpolarizable ones with scaled charges.\textsuperscript{19} Using this idea, Fuentes-Azcatl and Barbosa developed a force field for NaCl, namely NaCl/\epsilon, using screening factors in the Coulombic interactions to account for the effect of polarization.\textsuperscript{20} The resulting NaCl/\epsilon force field, in conjunction with the TIP4P/\epsilon\textsuperscript{21} and SPC/\epsilon\textsuperscript{22} water force fields, was parameterized to density and radial distribution function of the NaCl crystal as well as density and dielectric constant of the NaCl+H\textsubscript{2}O mixture at salt concentration of 4 mol/kg. The NaCl/\epsilon force field yields accurate calculation for properties of pure NaCl, including density and surface tension, as well as properties for the NaCl+H\textsubscript{2}O mixture including solution density, dielectric constant, ion solvation structure, shear viscosity, and diffusion coefficient. Using direct coexistence molecular dynamics (MD) simulation, Fuentes-Azcatl and Barbosa calculated the solubility of NaCl in H\textsubscript{2}O and found it to be in good agreement with experimental data at 298.15 K. In this work, we obtain the activity coefficients for the NaCl/\epsilon and TIP4P/\epsilon (and SPC/\epsilon) H\textsubscript{2}O force field combinations from 298.15 K to 473.15 K, quantities which have not been obtained previously. We also estimate the solubility of NaCl/\epsilon force field by calculating the electrolyte and crystal chemical potentials in bulk systems without interfaces present.

The mean ionic activity coefficient of NaCl, which is related to electrolyte chemical potential, was obtained from MD simulations in the isothermal-isobaric ensemble, and the electrolyte chemical potential of NaCl was estimated from the free energy change of adding a pair of Na\textsuperscript{+} and Cl\textsuperscript{−} ions into the system, as in prior work.\textsuperscript{24,25} The solubility of NaCl was estimated by finding the salt concentration where the electrolyte chemical potential is equal to the crystal chemical potential, which was obtained using the Einstein molecule method.\textsuperscript{23,24}

The mean ionic activity coefficients for the NaCl/\epsilon and TIP4P/\epsilon force fields are given in Figure 1 and compared with the prediction from the SPC/\epsilon+SD force fields. We confirmed the thermodynamic consistency of the mean ionic activity coefficient from Gibbs-Duhem calculation of the water activity; the details of such calculation are given in the supplementary material.\textsuperscript{26} As shown in the Figure 1, the combination of NaCl/\epsilon and TIP4P/\epsilon force fields underestimates the activity coefficients at all temperatures studied. The activity coefficients predicted by the NaCl/\epsilon+TIP4P/\epsilon force fields decrease almost linearly with salt concentration, failing to follow the experimental trend. Although the dielectric constant of NaCl+H\textsubscript{2}O mixture at high salt concentration (4 mol/kg) was included in the model development, the prediction of activity coefficient from intermediate to high salt concentration is not improved compared to the SPC/\epsilon+SD models, which suggests that inclusion of dielectric constant in the parametrization is not sufficient for reproducing the activity coefficients. We also calculated the activity coefficients using the NaCl/\epsilon and SPC/\epsilon force fields (results given in the supplementary material\textsuperscript{26}), and found a similarly inadequate representation of the activity coefficients and their temperature dependence.

The solubility of NaCl in H\textsubscript{2}O from the NaCl/\epsilon and TIP4P/\epsilon force fields is given in Figure 2 and compared to the results from the SPC/\epsilon+SD force fields. Both the TIP4P/\epsilon+NaCl/\epsilon and SPC/\epsilon+SD force fields underestimate the solubility at all temperatures investigated. Fuentes-Azcatl and Barbosa reported a NaCl solubility of 6 mol/kg for the TIP4P/\epsilon+NaCl/\epsilon force fields at 298.15 K using direct coexistence MD simulation; however, our free energy based calculation yields a solubility around 0.1 mol/kg, which is significantly lower than the experimental data. It is recognized that the solubility of salt calculated from direct coexistence simulation differs from the results obtained from free energy based calculation.\textsuperscript{27,28} The reason of the discrepancy is not clear at this point and is the subject of ongoing research. Although the solubility of NaCl is underestimated, the NaCl/\epsilon and TIP4P/\epsilon force fields predict correctly an increase in
The NaCl/\(\varepsilon\) force field gives accurate description for many mixture and crystal properties, it is unable to represent the activity coefficient and solubility of NaCl in H\(_2\)O, and its performance is not improved relative to the SPC/E+SD force field. The unsatisfactory representation of activity coefficient and solubility from NaCl/\(\varepsilon\) force field suggests that it may be inadequate to develop an ion force field by only including simple properties such as density and dielectric constant in the model parameterization. This coincides with a similar conclusion in the recent review of Nezbeda et al.\(^{28}\)

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