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Osmotic pressure of aqueous electrolyte solutions via molecular simulations of chemical potentials: Application to NaCl

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ABSTRACT

The osmotic pressure, Π, is an important thermodynamic property of aqueous electrolyte solutions, which is intimately related to the activity of the water solvent, and is sensitive to the details of the force field used in molecular simulations of such systems. Its calculation in the most important case of discrete water models has received scant attention in the literature; the only existing method involves a special-purpose molecular dynamics approach implementing virtual semi-permeable membranes separating solution and solvent phases. Here, we develop and demonstrate a new thermodynamically based approach utilizing simulation results for the salt chemical potential, μ_s, and for the solution specific volume, v_m. The methodology may also be used in principle to calculate the activity of water and of the electrolyte from simulation data for Π and v_m. We demonstrate our approach in the case of aqueous NaCl solutions at ambient conditions by calculating new results for both Π and the related osmotic coefficient property, ϕ, from simulation data for μ_{NaCl}. We compare with experimental data the predictions of two polarizable force fields (AH/BK3 and AH/SWM4-DP) and of a typical non-polarizable force field (JC). We find that AH/BK3 produces results in good agreement with experiment for both Π and ϕ over the entire experimentally accessible concentration range, and that the AH/SWM4-DP results are generally poor. The JC results are very good at concentrations below about 3 molal, but deteriorate rapidly at higher concentrations.

1. Introduction

Aqueous electrolyte solutions are one of the most important components of environmental, geochemical and biological systems, and the ability to understand and predict their thermodynamic properties is of considerable interest and importance. Advances in computational technology have rendered it feasible for molecular-level simulation methodologies based on molecular dynamics (MD) and Monte Carlo (MC) techniques to provide useful property predictions and microscopic insight for many fluid systems, including those involving aqueous solutions [59,5,60,9,36,39,12]. Biocomputing simulations are an important application area for these methodologies, within which aqueous electrolytes play a crucial role as the molecular environment for the protein or other biological molecules of interest. Molecular simulations can be used either to predict properties directly, or to generate pseudo-experimental data that can be used to fit the parameters of macroscopic thermodynamic models.

The requirements for molecular simulation methodology to provide accurate predictions for a particular fluid property for a given class of systems are: (1) the model should accurately describe the interactions among the system's molecules; (2) an appropriate algorithm must be available for the property's calculation; and (3) the algorithm must be carefully implemented in computer code.

Concerning requirement (1), information concerning the molecular description is encapsulated in a force field (FF), a mathematical model of the molecular interactions implemented within the simulation algorithm. In view of the special nature of water, FFs for its molecular description have long been of interest and many models have been proposed, at various levels of molecular-level realism, ranging from dielectric continuum to non-polarizable and polarizable descriptions [17,61,30,6]. The electrolyte FF used for aqueous solutions must be tailored to that of water, creating many possibilities. A goal has been to develop a general class of electrolyte models tailored to the best available water FF, members of which

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are transferable to broad thermodynamic parameter ranges and to aqueous environments involving multiple electrolytes.

In general, it is becoming increasingly recognized that FFs based on the assumption of pairwise additivity are inadequate, both for pure water and for its solutions. A recent study [44] showed that electrolyte FFs based on the widely used simple charged Lennard-Jones model with Lorentz–Berthelot combining rules and tailored to the commonly used SPC/E water FF [7] are unable to provide quantitatively accurate predictions of important higher concentration aqueous solution properties. One possibility of incorporating many-body effects is to add polarizability to the model, which mimics some of the effects of multi-body molecular interactions. Many such FFs have been developed for pure H_2O (see, for example the review of Guillot [17]). Two recent promising proposals of this type are those of Lamoureux and Roux (SWM4-DP) [30] and of Kiss and Baranyai (BK3) [25]; aqueous alkali halide FFs tailored to them have also been developed (AH/SWM4-DP [31] and AH/BK3 [26], respectively). The former mimics polarizability using a point-charge-on-spring (Drude) model and the latter uses a Gaussian-charge-on-spring distribution model.

The parameters of aqueous electrolyte FFs have typically been determined by fitting simulation results to approximate high-level ab initio computational data or to various types of experimental data, including the infinite dilution properties of hydration free energy, enthalpy and entropy for single ions [22,10,19], chemical potential derivatives related to experimental values of the solution compressibility and density at a single concentration in conjunction with Kirkwood–Buff integrals [63,58,16], low-concentration densities [11], and solid salt properties such as lattice constants [22,63]. FFs determined by these means have frequently been unable to satisfactorily predict more complex and composition-dependent thermodynamic properties, and thus the composition dependence of solution chemical potentials [44], and the osmotic pressure, [35,24,34,56], Π, have recently been used as alternative approaches to fit FF parameters.

Π is an important property of aqueous solutions, both in general and particularly for modeling a range of physiological and physical phenomena (see, *e.g.*, Rösgen et al. [54]). Although it is directly related to the water chemical potential, μ_{H_2O}, this connection has not been computationally exploited in the past in the case of discrete water models, perhaps in part due to challenges in calculating μ_{H_2O} for such systems. The chemical potentials of the water solvent and of the electrolyte itself are arguably the most important thermodynamic properties of aqueous solutions. Their knowledge as functions of the relevant thermodynamic variables enables the determination of all other system thermodynamic properties.

Luo et al. [35,34] recently developed a MD simulation method for directly calculating Π without the need for chemical potential calculations, which has similarities to earlier work of Murad et al. [47,48,51,50]. The methodology simulates aqueous solution and pure water phases separated by virtual membrane walls permeable only to water. Π is calculated in the simulation from the force per unit area on the walls. (See the original paper [35] for details.)

Concerning requirement (2), although many general and well-tested MD simulation packages are readily available, they are not intrinsically well-suited to the calculation of chemical potentials, for which MC methodologies are usually considered to be more appropriate. The calculation of solubility for aqueous electrolytes provides a particularly interesting example of the different MD and MC approaches used. All MC methods determine the solubility by directly calculating the composition at which the electrolyte solution and crystalline solid chemical potentials are equal [15,33,55,42,4,49,45,44,38], whereas MD methodologies determine the solubility indirectly. One MD approach implements a physical configuration in which the solution phase is equilibrated in the presence of solid phases (for example, a “slab configuration” with the solution phase located between two crystalline solid phases), and solubility is determined as the composition of the electrolyte in the solution phase from a sufficiently long simulation run [23,4,13,27]. Another MD-based methodology seeks to determine the solubility by examining the composition at which sufficiently large ion clusters emerge in the course of the simulations [3,2,37]. Since these different approaches are expected to have correspondingly different dependencies on simulation protocols such as system size, length of simulation runs and treatment of long-ranged forces in inhomogeneous systems, it remains unclear at the present time whether all currently available implementations can achieve the same result.

Table 1
Aqueous solubility simulation results by various research groups for NaCl at $T = 298.15$ K and $P = 1$ bar using the Joung–Cheatham SPC/E-compatible FF [22]. m is the NaCl molality in mol kg^{-1} H_2O. A quantity in parentheses denotes the standard uncertainty in the final digits.

Method	Solubility(m)
MD with slab geometry [23]	7.27(7)
MC and thermodynamic integration [4]	4.8(3)
MD with slab geometry [4]	5.5(4)
OEMC [44,45]	3.64(20)
MD with slab geometry [27]	6.20
MD and thermodynamic integration [27]	6.42
MD with MC particle insertion [38]	3.59(4)
Experiment [18]	6.14

Concerning requirement (3), a significant factor is that the relative dearth of general MC software packages may mean that algorithms to calculate chemical potentials must be developed locally, raising potential issues with differences in simulation protocols and in the implementation details of the computer code.

The challenges of requirements (2) and (3) are exemplified by recent solubility studies which, even when using the same water and electrolyte FFs, have produced different results. This is illustrated in Table 1, which shows results obtained by several research groups for the salt solubility at ambient conditions in aqueous NaCl solutions using the non-polarizable Joung–Cheatham FF tailored to SPC/E water (JC) [22] using various MD and Monte Carlo (MC) approaches. As can be seen, only two of the results are in concordance. As discussed elsewhere [46], the NaCl solubility calculation is intrinsically difficult, since (1) the solution salt chemical potential tends to exhibit a small concentration dependence at higher concentrations near the solubility limit; and (2) the solution chemical potentials are extremely sensitive to the details of the simulation procedure employed. These difficulties are reflected in the wide range of calculated solubility values in Table 1.

In a recent study [46] we independently calculated both water and salt chemical potentials, and verified their mutual consistency with respect to the Gibbs–Duhem equation. To our knowledge, this was the first such use of this consistency test in conjunction with simulations, and it provided support for the correctness of our calculation procedures. This is further supported by the mutual agreement of our Osmotic Ensemble Monte Carlo (OEMC) results in Table 1 and the recent calculations of Mester and Panagiotopoulos [38], who used a different methodology.

As noted, solution chemical potentials are important for many purposes. In this paper, we demonstrate their use in calculating Π and the related osmotic coefficient property, ϕ, by developing a new thermodynamically based method relating these properties to molecular simulations of either the water or the electrolyte chemical potential. We demonstrate the approach in the case of aqueous NaCl solutions at ambient conditions and compare with experiment the predictions arising from the representative non-polarizable