Theoretical Calculation of the Water Ion Product K_W

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Abstract: A dielectric solvation model is applied to the prediction of the equilibrium ionization of liquid water over a wide range of density and temperature with the objective of calibrating that model for the study of ionization in water of organic acids, *e.g.*, proteins and nucleic acids. The model includes an approximate description of the polarizability of the dissociating water molecule. The calculated pK_W are very sensitive to the value of the radii that parametrize the model. The radii required for the spherical molecular volumes of the water molecule in order to fit the experimental ion product are presented and discussed. These radii are larger than those commonly used. They decrease with increasing density as would be guessed but the rate of decrease is slight. They increase with increasing temperature, a variation opposite to what would be guessed if radii were strictly viewed as a distance of closest approach. The molecular theoretical principles that might provide an explanation of the thermodynamic state dependence of these radii are discussed.

1. Introduction

The chemical reaction $H_2O = HO^- + H^+$ is of central importance to a variety of practical problems including those associated with chemical processes in aggressive aqueous environments such as supercritical water.[1,2] It has been considered the most important chemical reaction in aqueous solution.[3]

The equilibrium point of this process is often discussed on the basis of the ion product $K_W = [HO^-][H^+]$. Measurements of K_W for water at densities below about twice the critical density are not available though convincing model estimates of this property have been given for the higher temperatures and pressures characteristic of supercritical water processes.[4,5] Moderately high temperatures are required in order to examine K_W over a continuous and extended domain of thermodynamic states, including densities lower than those liquid densities most commonly encountered.

This report gives theoretical calculations of K_W over a wide range of thermodynamic states. The calculations here employ a dielectric solvation model similar to that used by Pitzer and collaborators.[4,5] As an "equation of state" model the present results are not expected to improve upon that prior work. But the present contribution is helpful for several reasons that focus on the basis of the theory. The model used here is simple and the connection with molecular theory is simple too.[6-10] Thus the results here will facilitate direct molecular-scale verification of a number of intermediate quantities. This topic is of recent theoretical interest;[11-14] we expect comparable molecular-scale theory and results to be available in the near future.

Since the model we exploit is common in studies of the charge states of protein and nucleic acid molecules in aqueous solutions, the molecular scale verifications are expected to improve our understanding of those biophysical problems too.[15-23]

A concern with dielectric solvation models is the assignment of cavity radii or volumes. Cavity volumes should depend on the thermodynamic state.[8,10,24,25] This is important to the extent that derivatives of the solvation free energy with respect to thermodynamic state, *i.e.* temperature, pressure, and composition, are required. The molecular theoretical principles upon which those radii might be determined have been identified.[7,8,10] However, this issue can also be studied empirically by analyzing the solvation free energy computed on the basis of the dielectric solvation model over a sufficiently wide range of thermodynamic conditions. The data on the chemical equilibrium that are studied in this report are more extensive than for most reactions in aqueous solutions. The water self-ionization

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reaction is thus suitable for the principal motivation of this work: the delineation of the region where the model works satisfactorily and a calibration of the radii required to describe ionization of organic acids.

The next section gives technical details of the theoretical issues and methods. We then present the results and a discussion.

2. Methods

The dielectric solvation model used here is formulated from the following physical ingredients. Attention is focused on a solute of interest and a solute volume is defined. For liquid water under the most common conditions it is known that the van der Waals volume of the molecule is a reasonable initial choice for the molecular volume. Partial charges describing the solute electric charge distribution are positioned within this volume. The solvent is idealized as a continuous dielectric material with the measured dielectric constant ϵ. The solvent is considered to be excluded from the solute volume and that molecular volume is assigned an internal dielectric constant ϵ_m; when $\epsilon_m > 1$ the model thereby includes an approximate representation of the molecular polarizability.[26] In all the calculations below we have used $\epsilon_m = 2.42$, which corresponds approximately to the known polarizability of the water molecule (1.44 Å^3) when a spherical molecular volume of radius 1.65 Å is assumed. Note, however, that when adjustments of the radii are considered below the value for ϵ_m is not adjusted.

The equation to be solved for the model is

$$\nabla \cdot \epsilon(\mathbf{r}) \nabla \Phi(\mathbf{r}) = -4\pi \varrho_f(\mathbf{r}) \qquad (1)$$

where $\varrho_f(\mathbf{r})$ is the density of electric charge of the solute molecule, the function $\epsilon(\mathbf{r})$ gives the local value of the dielectric constant, and the solution $\Phi(\mathbf{r})$ is the electric potential. To solve this equation, we first cast it as an integral equation, *e.g.*, when all of the free sources are inside the molecular volume

$$\Phi(\mathbf{r}) = \Phi^{(0)}(\mathbf{r})/\epsilon_m + \int_V G^{(0)}(\mathbf{r},\mathbf{r}')\left(\frac{\nabla'\epsilon(\mathbf{r}')}{4\pi\epsilon(\mathbf{r}')}\right)\cdot\nabla'\Phi(\mathbf{r}')d^3r' \qquad (2)$$

Here $G^{(0)}(\mathbf{r},\mathbf{r}')$ is the Green function for the Poisson equation with $\epsilon(\mathbf{r}) = 1$ and $\Phi^{(0)}(\mathbf{r})$ is the electrostatic potential for that case. This equation is correct both for a localized distribution $\varrho_f(\mathbf{r})$ and zero boundary data on a surface everywhere distant and for periodic boundary conditions on a cell of volume V. $G^{(0)}(\mathbf{r},\mathbf{r}')$ is different in those two cases as is $\Phi^{(0)}(\mathbf{r})$. For the unbounded cases treated here $G^{(0)}(\mathbf{r},\mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'|$. This equation is not the only such form that can be solved, but it is the basis for the most popular boundary element approaches for numerical solution of this physical model.[27-33] Because of this we defer a more detailed discussion of integral formulations of eq 1.

The integrand of eq 2 is concentrated on the interface between the solute volume and the solvent. The interpretation of the integral of eq 2 is that it superposes contributions to the electrostatic potential due to charge induced on the surface. We can then use boundary element ideas to solve it. We have used sampling methods, here principally those based upon quasirandom number series,[34-36] to evaluate the

surface integral rather than more specialized methods. Advantages of such approaches are that they are simple, yet permit systematic studies of numerical convergence and exploitation of systematic coarse-graining. The geometries considered here are particularly simple, so these applications are not a stringent test of numerical methods. But an elegant statement of the advantages of boundary element approaches in this context can be found in a paper of Yoon and Lenhoff.[30]

In this application we solved eq 2 for the molecule in the liquid with the experimental dielectric constant and in isolation with the external dielectric constant assigned a value of $\epsilon = 1$. The solutions for these cases are denoted by $\Phi_l(\mathbf{r})$ and $\Phi_v(\mathbf{r})$, respectively. Remember that the "internal" dielectric constant parameter is fixed at $\epsilon_m = 2.42$ throughout. Then we construct

$$\Delta\mu = \left(\frac{1}{2}\right)\int_V \varrho_f(\mathbf{r})(\Phi_l(\mathbf{r}) - \Phi_v(\mathbf{r}))d^3r \qquad (3)$$

the standard chemical potential difference used below. This difference involves only the indirect contributions of eq 2, *i.e.* an infinite self-energy is eliminated by this subtraction. Here $\varrho_f(\mathbf{r})$ is a sum of partial charges. Therefore the integral in eq 3 is a sum over those partial charges.

With applications of such an *ad hoc* model, some arbitrariness is practically unavoidable. For these calculations the most important features of the method that are arbitrary are (i) the chemical equilibrium and chemical species that are treated, and (ii) the intramolecular volumes assigned.

The chemical reaction that we study in order to calculate K_W is

$$2H_2O = H_3O^+ + HO^- \qquad (4)$$
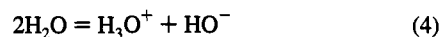
This arbitrary choice is made on the basis of the physical guess that observation of a "free" proton would be less likely than the case where an excess proton is associated with an oxygen atom in roughly the same circumstances that an H−O atom pair is configured in the water molecule. Atoms more distant from an "excess" proton than the nearest oxygen should be of secondary importance. We then consider the equilibrium ratio

$$K = \frac{[H_3O^+][HO^-]}{[H_2O]^2} \qquad (5)$$

We express this quantity as

$$K = K^{(0)}(T) \exp\{-(\Delta\mu_{HO^-} + \Delta\mu_{H_3O^+} - 2\Delta\mu_{H_2O})/RT\} \qquad (6)$$

where $K^{(0)}(T)$ is the equilibrium constant in the absence of intermolecular interactions, *i.e.* for the ideal gas.[11,12] Accounting for the mass balance of eq 4 we then find

$$K_W \equiv [H_3O^+][HO^-] = \varrho^2 K\left[\frac{1 - 2K^{1/2}}{1 - 4K}\right]^2 \qquad (7)$$

where ϱ is the formal density of the water.

The ideal gas contribution $K^{(0)}(T)$ can be obtained from standard formulae and information on the molecular structures of the species considered. The information used here is collected in Table 1.[37-39]

What remains is the evaluation of the excess chemical potentials appearing in eq 6 for the equilibrium ratio K. This brings us to the second arbitrary feature of our calculation, the assignment of molecular volumes. Here we assumed that each molecular volume is a sphere centered on the oxygen atom and that the radii of the spheres for all species were equal. This constraint is not necessary. However, some fitting to the experimental results will be required and limiting the number of fitting parameters seems prudent. It might be hoped that the fitted radii would validly describe ionization of organic acids too;

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Table 1. Properties Used in the Calculation of Molecular Partition Functions

property	H_2O^a	$H_3O^{+\ b}$	$HO^{-\ b}$
σ^c	2	1	1
$\Theta_{v1}{}^d$	2679.48	2067.21	7603.99
Θ_{v2}	5641.60	2694.40	
Θ_{v3}	5796.13	2736.17	
Θ_{v4}		4267.23	
Θ_{v5}		4304.29	
Θ_{v6}		4315.57	
$\Theta_A{}^e$	13.6745	8.3841	33.9547
Θ_B	20.9686	13.4501	
Θ_C	39.1187	13.9630	
$E_g{}^f$	-1032.98	-1203.55	-643.127

^{a} Geometry from ref 38. ^{b} Geometry from ref 39. ^{c} Rotational symmetry number. ^{d} Vibrational temperatures as defined in ref 37, in kelvin. These properties were calculated using SCF approximation, a 6-31g* basis set, and the geometries of refs 38 and 39. ^{e} Rotational temperatures as defined in ref 37, in kelvin. These properties were calculated in the same way as the vibrational temperatures were. ^{f} Electronic ground state energies from ref 39 relative to the energies of the separated isolated atoms, in kcal/mol.
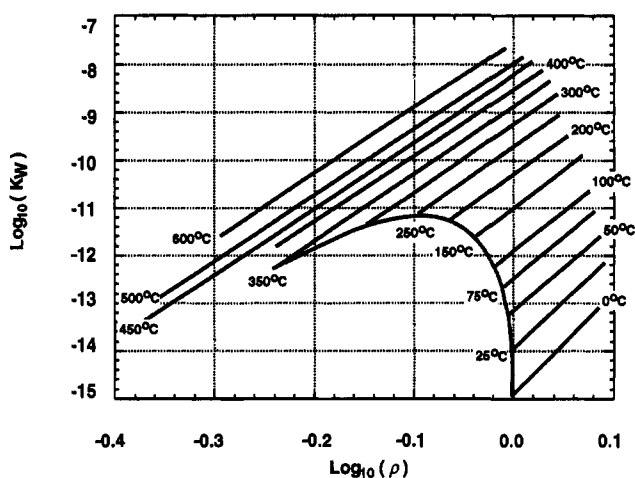
Figure 1. The water ion product K_W ([mol/L]^2) as a function of density ϱ (g/cm^3) and temperature over a range of liquid thermodynamic states. The region underneath the dome-shaped curve is the liquid–vapor coexistence region.

if the radii of protonated and deprotonated oxygen atoms were not transferrable to different but similar chemical environments with acceptable accuracy much of the usefulness of the model would be lost. In addition, the molecular underpinnings of the dielectric solvation model have been clarified over recent years; for solute species with spherical short-ranged (non-electrostatic) interactions with the solvent, we can hope that sufficient molecular information will become available to make applications such as this more geniunely predictive.[7,8,10]

We note the precedent for cations to be assigned slightly larger radii than the isoelectronic anions;[40,41] several explanations of this have been offered.[8,40,41] Here we assume that such complications are sufficiently slight that we can ignore them.

Finally we must specify the charge distribution $\varrho_f(\mathbf{r})$ of the chemical species treated and the dielectric constant. For the former quantity we used atom centered partial charges following the method of Breneman and Wiberg.[42] The dielectric constant utilized was that given by the empirical equation of Quist and Marshall.[43]
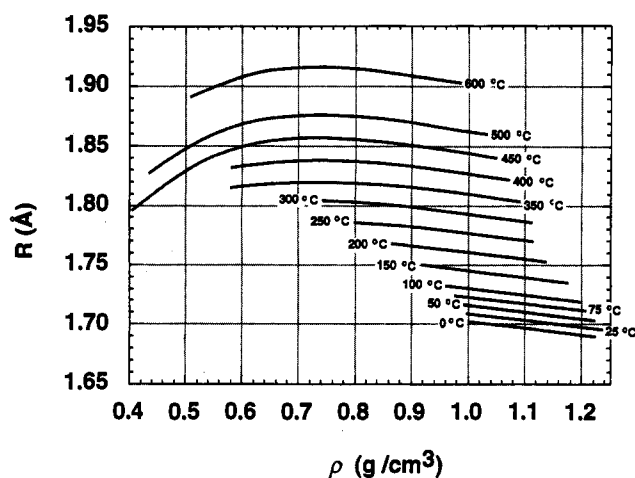
3. Results and Discussion

Our results for K_W are shown in Figure 1. The densities treated range over a factor of 3 including the triple point density.

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Figure 2. Empirical radii R, as a function of density and temperature, required for the dielectric solvation model to fit the experimental results.

The lowest density shown is approximately 0.4 g/cm^3. Temperatures encompass all of the traditional liquid range from the triple temperature to above the critical temperature. Figure 2 shows the empirical radii that resulted from fitting the model result to experimental values given by Marshall and Franck.[2] The magnitudes of these radii are reasonable but they are significantly larger than would be most commonly guessed.[41] For the upper part of this density range, the radii are decreasing functions of density at constant temperature. But the variations of the radii with density at fixed temperatures are slight; the decreases in the radii are 3–7 times smaller than the rule $\delta R/R \approx -\delta\varrho/3\varrho$ motivated by the Onsager estimate of the radius, $4\pi R^3 \varrho/3 = 1$.[24,44] The variation observed for R with temperature at fixed density is not accounted for by this rule. Moreover, a natural guess for the variation of R with temperature at constant density is not so clear; if R were identified as a distance of closest approach of the solvent molecules to the solute then R would be expected to decrease with increasing temperature at fixed density.

The sensititivity to the parameter R is an important issue for applications of the model. In the present case, pK_W can change by 1 unit if the value of R is changed by 1% from the value that fits the experiment. A change of 2% in R from the optimum value can lead to a change of more than 3 units in pK_W. Computational searches for a set of three radii (R_{H_2O}, $R_{H_3O^+}$, R_{HO^-}) that could satisfactorily fit the whole behavior in Figure 1 without thermodynamic state dependence were unsuccessful. For example, consider the isotherm at $T = 0$ °C of Figure 1 for which the total change in pK_W is about 1.7. The set of three density independent radii that we found to give the best fit to those data still lead to errors of $+0.57$ and -0.55 at the beginning and the end, respectively, of the isotherm shown. The set of three thermodynamic state independent radii that produced the best fit to the data over the whole of Figure 1 lead to typical errors in pK_W greater than 4 and those radii were not chemically reasonable.

How the model corresponds most naturally to molecular theory is known,[7,8,10] and this correspondence provides an avenue for theoretical determination of R. The corresponding molecular theory is the second-order cumulant approximation

$$\Delta\mu \approx \Delta\mu_0 + \langle\sum_j \varphi(j)\rangle_0 - \frac{\beta}{2}\langle(\sum_j \varphi(j) - \langle\sum_k \varphi(k)\rangle_0)^2\rangle_0 \quad (8)$$

Here $\varphi(j)$ is the electrostatic interaction potential energy

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coupling the solute to solvent molecule j. The brackets, $\langle ... \rangle_0$, indicate the thermal average in the absence of those electrostatic couplings, and $\Delta\mu_0$ is the excess chemical potential of the solute at infinite dilution again in the absence of electrostatic interactions. When the solute is an infinitely dilute second component this molecular approximation is perturbation theory through second order in the electrostatic interactions. When the molecule is not literally an infinitely dilute second component the "infinite dilution" restriction means that one molecule is distinguished for the purposes of calculation. This is still a natural theory but the medium now contains a non-zero concentration of molecules mechanically identical to the "solute". The medium properties non-perturbatively reflect that fact. From the perspective of this molecular theory, the dielectric solvation model application neglects the zeroth- and first-order terms, makes an estimate of the second-order term, and neglects all succeeding contributions.

Careful calculation on a molecular basis of the terms in eq 8 would be a helpful next step for clarification of these theoretical models. Jayaram et al.[45] and Rick and Berne[46] have tested dielectric solvation models by computer experiment. Their results provide, in principle, the information requested here but they were not analyzed from the point of view of the present goals for this system. Those results together suggest that hydrogen-bonding interactions are borderline cases for dielectric solvation models. Although the present application and its motivation in ionization of organic acids is of wide interest, it is likely a severe test for these models. Thus the empirical radius R determined here probably subsumes other errors that would have been encountered had the molecular theory been implemented.

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