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Continuum Electrostatics Model for Ion Solvation and Relative Acidity of HCl in Supercritical Water

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Abstract: The free energy of solvation of Cl^-, OH^-, HCl, and H_2O and the relative acidity of HCl versus H_2O are calculated with a continuum electrostatics model and compared with the molecular dynamics free energy perturbation (MD-FEP) simulation. The water densities span gas, liquid, and supercritical conditions. Compared with the simulation data, the simplest continuum model does not predict ion solvation accurately in supercritical water, as it neglects electrostriction, which is persistent to low densities. A generalization including the most basic element of electrostriction is reasonably accurate. However, for the free energy of dissociation of HCl relative to water, the errors are found to cancel between OH^- and Cl^- such that the simple continuum model is quite accurate. Because the reaction is isocoulombic and involves species of similar size, the effects of electrostriction cancel, corresponding entropic contributions are negligible, and the effect of density on the free energy change is small.

1. Introduction

The interest in understanding chemical phenomena in aqueous solutions at elevated temperatures and pressures has grown significantly during the last decade.[1−3] However, fundamental chemical properties, which are well-known in aqueous chemistry at 298 K, are not yet available for supercritical water (SCW) ($T_c = 647.13$ K, $\rho_c = 0.322$ g/cm^3, $P_c = 220.55$ bar) solutions. Examples of such properties include ion solvation and acid−base equilibria, since they play a central role in solvent effects on chemical reaction rate and equilibrium constants, phase equilibria, and corrosion. Practical applications include hydrothermal oxidation of organic wastes in supercritical water (SCW), hydrothermal breeding of crystals, spraying of ceramics, and hydrothermal synthesis reactions, e.g., the commercial hydrolysis of chlorobenzene to produce phenol and dibenzofuran.

Experimental studies of SCW solutions have been challenging, due to high temperature and pressures and corrosion. Some progress has been made by using electrochemical,[4−6] spectroscopic,[7−11] and phase equilibria techniques.[2,3] Recently, the acidity of an organic acid pH indicator, β-naphthol, relative to that of water has been measured spectroscopically to determine its pK_a.[9]

Free energies of ion solvation, ion pairing, and certain chemical reactions have been studied in SCW with molecular models.[12−15] Recently, molecular dynamics-free energy perturbation (MD-FEP)[16,17] simulation has offered a unique opportunity to relate the free energy of solvation of neutral and ionic species to the solvation structure at a molecular level.[18−24] However, these simulations are highly computer intensive, limiting the number of temperature and density state points which can be studied.

In comparison to simulation, continuum electrostatics models for the solvation free energy require far less computer time. These models, which are numerical solutions to Poisson's equation,[25] predict free energies of solvation for various neutral and ionized species in ambient water quite accurately.[26−29] With

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(1) Shaw, R. W.; Brill, T. B.; Clifford, A. A.; Eckert, C. A.; Franck, E. U. *Chem. Eng. News* **1991**, *69*, 26−39.

(2) Tester, J. W.; Holgate, H. R.; Armellini, F. J.; Webley, P. A.; Killilea, W. R.; Hong, G. T.; Barner, H. E. *Supercritical Water Oxidation Technology: A Review of Process Development and Fundamental Research*; Tester, J. W., Holgate, H. R., Armellini, F. J., Webley, P. A., Killilea, W. R., Hong, G. T., Barner, H. E., Eds.; American Chemical Society: Washington, DC, 1993; Vol. 518, pp 35−76.

(3) Gloyna, E. F.; Li, L. *Waste Manage.* **1993**, *13*, 379−394.

(4) Mesmer, R. E.; Marshall, W. L.; Palmer, D. A.; Simonson, J. M.; Holmes, H. F. *J. Solution Chem.* **1988**, *17*, 699−718.

(5) Flarsheim, W. M.; Bard, A. J.; Johnston, K. P. *J. Phys. Chem.* **1989**, *93*, 4234−4242.

(6) McDonald, I. R.; O'Shea, S. F.; Bounds, D. G.; Klein, M. L. *J. Chem. Phys.* **1980**, *72*, 5710−5717.

(7) Pfund, D. M.; Darab, J. G.; Fulton, J. L.; Ma, Y. *J. Phys. Chem.* **1994**, *98*, 13102−13107.

(8) Bennett, G. E.; Johnston, K. P. *J. Phys. Chem.* **1994**, *98*, 441−447.

(9) Xiang, T.; Johnston, K. P. *J. Phys. Chem.* **1994**, *98*, 7915−7922.

(10) Spohn, P. D.; Brill, T. B. *J. Phys. Chem.* **1989**, *93*, 6224−6231.

(11) Green, S.; Xiang, T.; Johnston, K. P.; Fox, M. A. *J. Phys. Chem.* **1995**, *99*, 13787−13795.

(12) Tanger, J. C., IV; Pitzer, K. S. *J. Phys. Chem.* **1989**, *93*, 4941−4951.

(13) Wood, R. H.; Quint, J. R.; Grolier, J.-P. E. *J. Phys. Chem.* **1981**, *85*, 3944−3949. Wood, R. H.; Carter, R. W.; Quint, J. R.; Majer, V.; Thompson, P. T.; Boccio, J. R. *J. Chem. Thermodyn.* **1994**, *26*, 225−249.

(14) Gupta, R. B.; Johnston, K. P. *Ind. Eng. Chem. Res.* **1994**, *33*, 2819−2829.

(15) Smits, P. J.; Economou, I. G.; Peters, C. J.; Arons, J. d. S. *J. Phys. Chem.* **1994**, *98*, 12080−12085.

(16) Mezei, M.; Beveridge, D. L. Free energy simulations. In *Annals New York Academy of Sciences*; Beveridge, D., Jorgensen, W. L., Eds.; New York Academy of Sciences: New York, 1986; Vol. 482, pp 1−23.

(17) Zwanzig, R. W. *J. Chem. Phys.* **1954**, *22*, 1420−1426.

(18) Balbuena, P. B.; Johnston, K. P.; Rossky, P. J. *J. Am. Chem. Soc.* **1994**, *116*, 2689−2690.

(19) Balbuena, P. B.; Johnston, K. P.; Rossky, P. J. *J. Phys. Chem.* **1995**, *99*, 1554−1565.

(20) Balbuena, P. B.; Johnston, K. P.; Rossky, P. J. *J. Phys. Chem.* **1996**, *100*, 2706−2715.

(21) Balbuena, P. B.; Johnston, K. P.; Rossky, P. J. *J. Phys. Chem.* **1996**, *100*, 2716−2722.

(22) Flanagin, L. W.; Balbuena, P. B.; Johnston, K. P.; Rossky, P. J. *J. Phys. Chem.* **1995**, *99*, 5196−5205.

(23) Cui, S. T.; Harris, J. G. *Chem. Eng. Sci.* **1994**, *49*, 2749−2763.

(24) Guillot, B.; Guissani, Y. *J. Chem. Phys.* **1993**, *99*, 8075−8094.

(25) Bockris, J. O. M.; Reddy, A. K. N. *Modern Electrochemistry*, 1st ed.; Plenum Press: New York, 1970; Vol. I.

(26) Simonson, T.; Brünger, A. T. *J. Phys. Chem.* **1994**, *98*, 4683−4694.

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the calculation of the free energy of solvation, other properties such as relative acidities, reaction rates, and equilibrium constants may be determined from classical thermodynamics.

Recently, continuum electrostatics models were used to model the free energy for the hydrolysis of anisole in supercritical water[30] and the ionization constant of water over a wide range of temperature and density.[31] Previously, we investigated the use of a continuum electrostatics model for the free energy of solvation of a model reaction in SCW[32] by comparing the results with MD simulation.[18,19,22] The reaction was the S_N2 nucleophilic substitution reaction of $Cl^- + CH_3Cl$. It was found that the change in ΔA from the reactants to the transition state complex is in reasonable agreement with MD simulation at high and low densities in SCW.[32] However, in the mid-density region, the continuum model underpredicts the MD simulation results for ΔA. The difference between the molecular and continuum methods provides a more direct indication of the effects of local solvation about the reactants and transition state than previous methods. This local density enhancement is also termed clustering or electrostriction. The prevalence of clustering in this region is further supported by radial distribution functions in the simulation studies [19,22] and spectroscopic studies of solvatochromic shifts of acetone and benzophenone in SCW[8] and X-ray absorption fine structure (XAFS) studies.[7] It has also been seen in other supercritical fluids such as CO_2 both spectroscopically[33−40] and by computer simulation.[41,42]

Although acid−base behavior plays a fundamental role in aqueous chemistry, little is known about properties such as pH in SCW. Two acid dissociation reactions have been studied electrochemically,[4] that of HCl

$$HCl \rightleftarrows H^+ + Cl^- \qquad (1)$$

and water

$$H_2O \rightleftarrows H^+ + OH^- \qquad (2)$$

The relative acidity of HCl versus water is the difference between these reactions

$$HCl(aq) + OH^- \rightleftarrows Cl^- + HOH \qquad (3)$$

Unlike the above acid dissociation reactions, eqs 1 and 2, the relative acidity reaction does not involve a proton, whose solvation can be extremely complex. This isocoulombic reaction has been studied both microscopically and from a thermodynamic perspective by MD-FEP techniques, and it was found that the free energy change remains essentially constant between 0.29 and 0.087 g/cm^3 for temperatures from 673 to 768 K.[20,21]

Our objective here is to test the ability of a continuum model to calculate (1) ΔA^{solv} of various ions and molecules, (2) the relative ΔA^{solv} of Cl^- versus OH^- and H_2O versus HCl, and, thus, (3) the relative acidity of HCl versus H_2O. In each case, continuum model results will be compared with recent[20,21] and new MD-FEP simulation results. This approach offers perhaps the best indication of how microheterogeneous solvation or electrostriction (which is not included in the simplest continuum models) affect thermodynamic properties. Whereas it is known that electrostriction influences properties such as ΔA^{solv} of Cl^-,[20] we wish to learn to what extent, if any, it influences the relative solvation and acidity properties listed above. The final section compares the effects of electrostriction and solvent density on the relative acidity of HCl, ion pairing of Na^+ and Cl^-, and the S_N2 reaction of $Cl^- + CH_3Cl$, leading to general guidelines for the applicability of continuum models in SCW.

2. Method

The calculation of the relative acidity of HCl versus water is based on the following thermodynamic cycle in which A is either Cl or OH

$$\begin{tikzcd}
\text{gas} & HA \arrow[r, shift left, "\Delta A_{HA}^{diss}(gas)"] \arrow[d, "\Delta A_{HA}^{solv}"] & H^+ \arrow[l, shift left] \arrow[d, "\Delta A_{H^+}^{solv}"] & + & A^- \arrow[d, "\Delta A_{A^-}^{solv}"] \\
\text{solution} & HA \arrow[r, shift left, "\Delta A_{HA}^{diss}(aq)"] & H^+ \arrow[l, shift left] & + & A^-
\end{tikzcd} \qquad (4)$$

for HCl or H_2O dissociation, respectively. This cycle provides a means to determine $\Delta A_{HA}^{diss}(aq)$ given $\Delta A_{HA}^{diss}(gas)$ and free energies of solvation for transfer from the gas phase to solution as follows:

$$\Delta A_{HA}^{diss}(aq) = 2.3RT\text{p}K_a^* = \Delta A_{HA}^{diss}(gas) + \Delta A_{H^+}^{solv} + \Delta A_{A^-}^{solv} - \Delta A_{HA}^{solv} \qquad (5)$$

Because both the MD simulation and the continuum model are applied at constant T and V, a Helmholtz free energy and not a Gibbs free energy is obtained. The necessary conversions from ΔG to ΔA are discussed in great detail elsewhere.[20,43] To describe the equilibrium concentrations of the reacting species, it is more convenient to use pK_a^* than $\Delta A_{HA}^{diss}(aq)$. Here we define pK_a^* in eq 5 based on the ΔA of dissociation, instead of the ΔG. By writing eq 5 for HCl and H_2O and subtracting, we obtain the free energy relationship for the relative acidity reaction shown in eq 3.

$$\Delta\Delta A^{diss}(aq) = \Delta A_{HCl}^{diss}(aq) - \Delta A_{HOH}^{diss}(aq) = +(\Delta A_{HCl}^{diss}(gas) - \Delta A_{HOH}^{diss}(gas)) + (\Delta A_{Cl^-}^{solv} - \Delta A_{OH^-}^{solv}) + (\Delta A_{HOH}^{solv} - \Delta A_{HCl}^{solv}) \qquad (6)$$

Equation 6 shows that $\Delta\Delta A^{diss}$ depends upon $\Delta\Delta A$(gas) and two relative values of ΔA^{solv}. The relative values of ΔA^{solv} can be computed by either molecular dynamics (MD) simulation or a continuum model.

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(27) Jean-Charles, A.; Nicholls, A.; Sharp, K.; Honig, B.; Tempczyk, A.; Hendrickson, T. F.; Still, W. C. *J. Am. Chem. Soc.* **1991**, *113*, 1454−1455.

(28) Mohan, V.; Davis, M. E.; McCammon, J. A.; Pettitt, B. M. *J. Phys. Chem.* **1992**, *96*, 6428−6431.

(29) Sitkoff, D.; Sharp, K. A.; Honig, B. *J. Phys. Chem.* **1994**, *98*, 1978−1988.

(30) Tucker, S. C.; Gibbons, E. N. Theoretical model of anisol hydrolysis in supercritical water: understanding the effects of pressure on reactivity. In *Structure and reactivity in aqueous solutions*; Truhlar, D. G., Cramer, C. J., Eds.; American Chemical Society: Washington, DC, 1994; Vol. 568; pp 196−211. Luo, H.; Tucker, S. C. *J. Am. Chem. Soc.* **1995**, *117*, 11359−11360.

(31) Tawa, G. J.; Pratt, L. R. *J. Am. Chem. Soc.* **1995**, *117*, 1625−1628.

(32) Bennett, G. E.; Johnston, K. P.; Rossky, P. J. *J. Phys. Chem.* **1995**, *99*, 16136−16143.

(33) Kajimoto, O.; Futakami, M.; Kobayashi, T.; Yamasaki, K. *J. Phys. Chem.* **1988**, *92*, 1347−1352.

(34) Kim, S.; Johnston, K. P. *AIChE J.* **1987**, *33*, 1603−1611.

(35) Knutson, B. L.; Tomasko, D. L.; Eckert, C. A.; Debenedetti, P. G.; Chialvo, A. A. Local Density Augmentation in Supercritical Solutions: A Comparison Between Fluorescence Spectroscopy and Molecular Dynamics Results. In *ACS Symposium Series*; Bright, F. V., McNally, M. E. P., Eds.; American Chemical Society: Washington, DC, 1992; Vol. 488, pp 60−72.

(36) Bright, F. V.; Betts, T. A. *Appl. Spectrosc.* **1990**, *44*, 1203−1209.

(37) Sun, Y.-P.; Fox, M. A.; Johnston, K. P. *J. Am. Chem. Soc.* **1992**, *114*, 1187−1194.

(38) Sun, Y.-P.; Bennett, G.; Johnston, K. P.; Fox, M. A. *J. Phys. Chem.* **1992**, *96*, 10001−10007.

(39) Randolph, T. W.; O'Brien, J. A.; Ganapathy, S. *J. Phys. Chem.* **1994**, *98*, 4173.

(40) Carlier, C.; Randolph, T. W. *AIChE J.* **1993**, *39*, 876−884.

(41) Debenedetti, P. G.; Petsche, I. B.; Mohamed, R. S. *Fluid Phase Equilib.* **1989**, *52*, 347−356.

(42) O'Brien, J. A.; Randolph, T. W.; Carlier, C.; Ganapathy, S. *AIChE J.* **1993**, *39*, 1061−1071.

(43) Ben-Naim, A. *Solvation Thermodynamics*; Plenum Press: New York, 1987.

Table 1. Cavity Radii and Partial Charges Used To Describe Cl^-, OH^-, HCl, and HOH in the Standard Continuum Model

compd	atom	cavity radius R (Å)	charge q (e)
Cl^-	Cl	2.128	−1.00
OH^-	O	1.918/1.723[a]	−1.30
	H	1.000	0.30
HCl	H	1.000	0.180
	Cl	2.280	−0.180
HOH	H	1.000	0.424
	O	1.777	−0.848

[a] Modified oxygen radius to obtain experimental free energy of solvation for OH^- in ambient water.

The relative acidity in the gas phase may be obtained from experiment or by ab-initio quantum mechanics. We use experimental data.[44]

The electrostatic solvation free energy contributions for the ionic and neutral species in eq 6 are calculated in a similar manner as done previously for the free energy of an S_N2 reaction.[32] In a continuum model, the electrostatic potential $\phi(\vec{r})$ is calculated numerically from Poisson's equation:

$$\nabla\cdot\epsilon(\vec{r})\nabla\phi(\vec{r}) + 4\pi\rho(\vec{r}) = 0 \tag{7}$$

A charge distribution $\rho(r)$ is defined inside a solute cavity. The solute cavity is imbedded in a solvent continuum that is represented by a (possibly spatially varying) dielectric constant $\epsilon(\vec{r})$. Here, we primarily use the numerical solution to the electrostatic potential from Poisson's equation as conveniently implemented in the Del-Phi program.[45,46] The functions in the Poisson's equation, $\epsilon(\vec{r})$, $\phi(\vec{r})$, and $\rho(\vec{r})$, are approximated by values on a discrete 3-dimensional grid. $\epsilon(\vec{r})$ is prescribed as a fixed characteristic bulk value in solvent-accessible regions and a lower constant value inside the solute surface. The grid is constructed out of a fixed number of nodes located inside a cubic box. In our calculations the number of nodes is fixed at 65.

For each of the polyatomic solute molecules present in the dissociation reaction, eq 3, a set of atomic radii with corresponding point charges must be specified and located on the grid. In Table 1 we present the values used for the atoms of the various molecules. The cavity radii are generally obtained from the Lennard-Jones diameters, σ. These are taken directly from the solute/solvent optimized potentials for liquid simulations (OPLS) force fields that are used in the MD simulation,[20,21] following the suggestion by Honig et al. for Del-Phi calculations,[29] with radii of $2^{-5/6}\sigma$. Also, we use the recommended hydrogen atom cavity radius of 1.0 Å.[26,29]

For the chloride ion, with the theoretical cavity radius obtained from the OPLS values, the free energy of solvation in ambient water computed with the continuum model just described is relatively close to the experimental value. A suggested value for the cavity radius used with the continuum model for chloride ion is also reported by Honig et al.;[47] this cavity radius is adjusted to give the experimentally determined enthalpies of solvation in ambient water.[20,21] For the hydroxide ion, another cavity parameter set was also considered here, since the OPLS derived radii gave poor agreement with experiment in ambient water. With the OPLS based radii, ΔA^{solv} is −88.0 kcal/mol, whereas the average experimental value[20,21] is −99.3 kcal/mol. In the alternative set, the cavity radius for the oxygen atom in OH^- was adjusted in order to fit to the average of experimentally observed values of ΔA^{solv} in ambient water.[20,21] This radius causes the ΔA^{solv} of OH^- to be, correctly, noticeably more negative than that of Cl^- (see Table 2).

In addition to the solute cavity radius, a solvent probe radius of 1.4 Å for water was specified.[26] The solvent probe radius corrects for regions of space near the solute cavity which become inaccessible to the solvent molecules. As a result, greater accuracy is achieved in treating the solute/solvent dielectric boundary on the grid.[45,48]

Once the solute is placed on the grid, the dielectric function $\epsilon(r)$ is constructed and is represented by a three-dimensional step function. For the grid locations that lie inside the solute cavity, the dielectric constant of the grid is set here to unity. For the locations that lie outside the solute cavity, the dielectric constant is set to the solvent bulk dielectric constant. We will refer to this prescription as the standard continuum model.

Since this continuum model will be compared with simulation, here we use the bulk dielectric constant which was fit to simulation data for the extended simple point charge (SPC/E) model of water.[49] The values were constructed from simulation data for temperatures between 500 and 2500 K and for densities less than or equal to 1.0 g/cm^3. The dielectric function is given as a function of T (in K) and ρ (in g/cm^3) in eq 8

$$\begin{aligned} \epsilon(\rho) &= 1 + B(\rho)/T + C(\rho)/T^2 \\ B(\rho) &= b_1\rho + b_2\rho^2 + b_3\rho^3 \\ C(\rho) &= c_1\rho + c_2\rho^2 + c_3\rho^3 \end{aligned} \tag{8}$$

where $b_1 = 3690.27$, $b_2 = 5346.95$, $b_3 = -1269.30$, $c_1 = 2.39747\text{E}6$, $c_2 = 4.02446\text{E}6$, and $c_3 = -923962$. Equation 8 is used for all cases, except for ambient water (AW), where the experimental value of ϵ was used.

To solve the Poisson's equation, Coulombic boundary conditions were used with a cubic box size of edge length 64 Å corresponding to a grid fineness of 1.0 grid/Å. Subsequent calculations were then performed on a finer grid, using as boundary conditions information from the previous calculations. This method of increasing the grid fineness, and therefore the resolution of the dielectric boundary of the solute, is termed focusing.[45] The calculations were performed in order of increasing grid fineness starting at 1.0 grids/Å to 2.0, 3.0, 4.0, and finally 5.0 grids/Å.

3. Results and Discussion

3.1. Free Energy of Solvation for Ions and Neutral Molecules. The results of the continuum electrostatics model described above for ΔA^{solv} of the ions and molecules in eq 6 are shown in Table 2. In ambient water, ϵ is 80; it ranges from 20 to 2 in SCW at the densities of interest. The function $(1 - 1/\epsilon)$ serves as a macroscopic measure of the medium polarity as is evident in the Born equation

$$\Delta A^{\text{solv}} = -\frac{e^2q^2}{4\pi\epsilon_0 R}\left(1 - \frac{1}{\epsilon}\right) \tag{9}$$

for a point charge q located inside a spherical cavity of radius R. For a spherical ion which can be described by a single-point charge, like Cl^-, the solvation free energy derived from the Poisson's equation reduces to the Born value. For OH^-, described by a two-point-charge model, we use the numerical solution to Poisson's equation. For OH^-, ΔA^{solv} from Poisson's equation is not linear in $(1 - 1/\epsilon)$, as in the Born equation, but the deviation from linearity is small.

For both Cl^- and OH^-, as the dielectric constant decreases, with a decrease in density or increase in temperature, ΔA^{solv} given by the standard continuum model or by simulation becomes less negative (Table 2). In fact, a given ϵ does not uniquely specify density and temperature. Of the three variables, T, ρ, and ϵ, specification of any two fixes the third. Therefore, many T and ρ thermodynamic states map to the same

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(44) Bartmess, J. E.; McIver, R. T., Jr. The Gas-Phase Acidity Scale. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, pp 87−121.

(45) Gilson, M. K.; Sharp, K. A. *J. Comput. Chem.* **1987**, *9*, 327−335.

(46) Sharp, K. A. *Del-Phi*, 3.0 ed.; Sharp, K. A., Ed.: Columbia University, 1988.

(47) Rashin, A. A.; Honig, B. *J. Phys. Chem.* **1985**, *89*, 5588−5593.

(48) Lee, B.; Richards, F. M. *J. Mol. Biol.* **1971**, *55*, 379−400.

(49) Neumann, M. Computer Simulation of Water and The Dielectric Equation of State. In *Physical Chemistry of Aqueous Systems*; White, H. J., Sengers, J. V., Neumann, D. B., Bellows, J. C., Eds.; Begell House, Inc.: New York, 1995.

Table 2. Comparison of Continuum Model and MD Simulation Results for Solvation Free Energy (kcal/mol) of the Ionic and Neutral Species in Ambient and Supercritical Water

thermodynamic state			$\Delta A^{\mathrm{solv}}_{\mathrm{Cl^-}}$		$\Delta A^{\mathrm{solv}}_{\mathrm{OH^-}}$		$\Delta A^{\mathrm{solv}}_{\mathrm{HCl}}$		$\Delta A^{\mathrm{solv}}_{\mathrm{HOH}}$	
T (K)	ρ (g/cm^3)	ϵ	Del-Phi	simulation	Del-Phi	simulation	Del-Phi	simulation	Del-Phi	simulation
673	0.087	2.06	−40.2	−51.0	−51.2	−63.23	−0.4	0.5	−4.0	−2.3
768	0.290	4.65	−61.3	−49.4	−78.5	−65.26	−0.8	2.2	−7.0	−3.4
673	0.290	5.44	−63.8	−53.0	−81.6	−70.51	−0.8	0.9	−7.4	−4.2
298	1.000	80.0	−77.2	−73.4	−99.1	−95.96	−1.1	−0.5	−9.7	−10.2

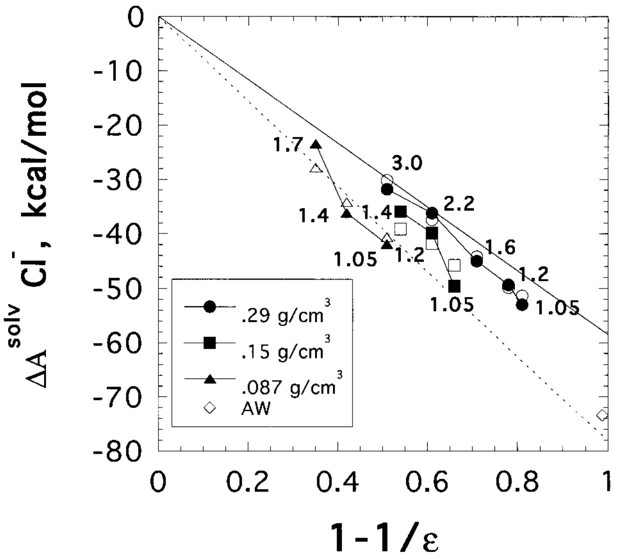

Figure 1. Comparison of the continuum electrostatics Born model (eq 9; ion radius: 2.128 Å, dashed line; 2.8 Å, solid line); modified continuum model (see text)[52] (open symbols) and MD simulation (filled symbols connected by lines) for the free energy of solvation of the chloride ion from ambient to supercritical conditions. (The point labels represent temperatures reduced with respect to T_c of the model, 640 K.)

value of ϵ. However, once ϵ is fixed, the standard continuum model does not depend upon density or temperature. Consequently, once the radius is chosen, the standard continuum model results cover many possible combinations of densities and temperatures for Cl$^-$ in water as ϵ is varied.

In order to examine the effect of the molecularity of the solvent, we have performed MD-FEP simulations for a chloride ion at infinite dilution in SPC/E[50] water. Several additional state points have been added to an earlier study[20] using the same methods. The simulation results are shown by filled symbols in Figure 1 for three isochores (points connected by lines) at supercritical temperatures. At constant density, $|\Delta A^{\mathrm{solv}}|$ decreases as temperature increases, as expected, due to a decrease in attractive molecular interactions.

Considering the data of Figure 1 from an isothermal perspective also yields insight, demonstrating, in particular, clear evidence for the marked effects of electrostriction on the simulated values. At 673 K ($T_r = 1.05$), as the density is lowered from 0.29 to 0.087 g/cm^3, ΔA^{solv} of Cl$^-$ is found from simulation to be nearly constant despite a change in bulk dielectric constant from 5.4 to 2.1. According to the standard continuum model, this decrease in ϵ would be expected to decrease $|\Delta A^{\mathrm{solv}}|$ of Cl$^-$ by about 37% (see Table 2). As shown by simulation, the coordination number of water in the first solvent shell of Cl$^-$ does not decrease much from ambient water to 673 K ($T_r = 1.05$) and 0.087 g/cm^3 due to the strong ion−water hydrogen bonds.[19,20,22] This local density augmentation in the first coordination sphere, also called clustering or electrostriction, is analogous to well-known behavior for physical adsorption of gases on surfaces,[22,51] and thus the isothermal behavior here exhibits behavior analogous to Langmuir adsorption. That is, starting from low gas-phase densities, as the bulk density is increased, water molecules occupy preferred positions about the ion until the first shell is filled up. As the density is further increased, the isotherm becomes flat. Finally as the density is further increased, solvation from solvent in the outer shells causes $|\Delta A^{\mathrm{solv}}|$ to again increase. The large contribution from the first shell to ΔA^{solv} is clearly evident in simulation.[20]

These effects become weaker at higher temperatures as thermal energy overcomes attractive interactions. As is evident in Figure 1, 673 K ($T_r = 1.05$) does not yet correspond to a "high" temperature in this context. At 773 K ($T_r = 1.2$), ΔA^{solv} becomes considerably weaker as the density is decreased. Here, the fact that desolvation takes place in the first shell can be clearly seen in the coordination number from simulation.[20,21]

The dashed line in Figure 1 represents the predictions of the Born model (eq 9), using an ion radius (2.128 Å) which yields reasonable agreement with experiment for ambient conditions (see Table 2). As is evident in the figure and from the corresponding data in Table 2, this Born result reproduces the simulated data in SCW only roughly and in an average sense. In particular, it is striking that this model fails to correctly predict the simulated results in the high-temperature limit. In this limit, the continuum model should be most accurate, since the local solvent homogeneity is nearly correct. Considering the clear evidence in simulation for strong effects due to inhomogeneous solvent density (electrostriction) and the failures of the Born model just discussed, we next consider briefly the simplest generalization of that model which includes the effects of electrostriction. Results obtained from generalized continuum models will be discussed in more detail in a later paper.

We consider the modification proposed by Beveridge and Schnuelle,[52] where the continuum solvent is represented by two concentric solvent regions with different dielectric constants. The modified model has two adjustable parameters, an inner and an outer radius defining the inner concentric region. However, reasonable values for these can be obtained from simulated structural data. For the inner radius, we use the value of $R = 2.8$ Å corresponding to the value where the ion−water pair distribution function first rises rapidly from zero.[20] A similar value ($R = 2.9$ Å) was found to be the best in a continuum model representation of solvation of the chloride ion in AW by Ichiye et al.[53] The present model is relatively insensitive to the choice of the outer radius; we have used 4.75 Å, coinciding with the minimum after the first peak in $g_{\mathrm{ClO}}(r)$.[20] The dielectric constant of the inner solvent shell is taken to be the bulk value, evaluated at the average local density of this shell (2.8 Å < R < 4.75 Å) obtained from the simulation and the corresponding temperature, using Neumann's correlation

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(50) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. *J. Phys. Chem.* **1987**, *91*, 6269−6271.

(51) Subramanian, R.; Pyada, H.; Lira, C. T. *Ind. Eng. Chem. Res.* **1995**, *34*, 3830−3837.

(52) Beveridge, D. L.; Schnuelle, G. W. *J. Phys. Chem.* **1975**, *79*, 2562−2565.

(53) Hyun, J.-K.; Babu, C. S.; Ichiye, T. *J. Phys. Chem.* **1995**, *99*, 5187−5195.

for the dielectric constant.[49] The solid line shown in Figure 1 gives the results for the standard Born model, with uniform dielectric constant, but now using the ionic radius of 2.8 Å, corresponding to the inner radius of the modified continuum model. As can be seen, in the high-temperature, low-density limit, the model is now reasonably consistent with the simulations. A desirable feature of the model is that the inner and outer radii are temperature independent in the supercritical region.

Under conditions other than these extremes, the simulation results exhibit deviations from the simple Born line. The modified continuum model should provide the simplest estimate of those deviations which are associated with electrostriction alone. The results of the modified model are indicated by empty symbols in Figure 1. The modified model is, in fact, in very good agreement with the simulation values for the high and intermediate density lines, although it becomes worse for the lowest density case, where the ratio of local-to-bulk densities is the highest, becoming nearly 20 at 673 K.[20] It is noteworthy that this decrease in accuracy at the lowest densities occurs for state points that are increasingly further from the critical point; hence, it is not a reflection of any special aspect of near-critical behavior. The comparisons in Figure 1 thus demonstrate that including electrostriction in the supercritical region significantly improves the continuum approximation, and that the use of the radius that is successful under ambient conditions gives only rough estimates within the Born model.

Another alternative for introducing electrostriction into a continuum framework for spherical ions[13] as well as polyatomic ions[30] is to determine the local solvent density at each point in space by taking into account the effects of solvent compressibility on the electrostatics. Although this approach includes electrostriction, the observed radial range of the local solvent density enhancement is much longer than that found from simulation,[18−22] at least at the conditions considered in this work, which are never in very close proximity to the critical point. In the future, it will be informative to compare free energies from this type of model with those from models which mimic the shorter ranged local density variation observed in the simulations.

Despite the considerations above, an enormous advantage of the standard continuum model over MD simulation is that $\Delta A^{\rm solv}$ may be calculated at numerous conditions of T and ρ, due to the small computational requirements. No simulation data are required, and the most qualitative features are correct, as evidenced by Figure 2. Figure 2 shows both isochores and isobars for Cl^- and OH^- at subcritical and supercritical conditions, with the standard model and the parameters given in Table 1. The isobar at 250 bar is very close to the liquid branch of the coexistence curve up to the critical temperature. The shapes of the individual curves for the two ions look very similar, although the smaller OH^- ion is more solvated, as expected. At supercritical conditions, the large changes in ΔA along isobars are due primarily to the large decreases in ρ with T.

The continuum model results for $\Delta A^{\rm solv}$ of the neutral molecules H_2O and HCl are shown in Table 2, along with previous MD simulation results.[20] The cavity radii are given in Table 1. In each case the magnitude of $\Delta A^{\rm solv}$ is far less than that for ions as expected. The solvation is much stronger for water than HCl, since H_2O is more polar. For both neutral molecules, $\Delta A^{\rm solv}$ in ambient water from the continuum model is close to that of the MD simulation. At the other conditions, the $\Delta A^{\rm solv}$ is about 2−3 kcal/mol more negative for the standard continuum model. The differences between the standard continuum model and MD simulation in SCW for both neutral molecules therefore follow the same general trends seen in the case of the ions.

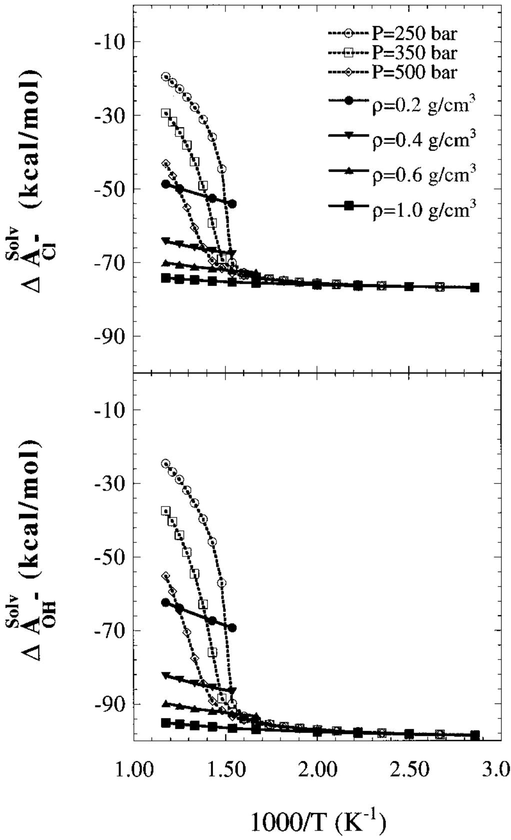

Figure 2. Isochores and isobars for the free energy of solvation of chloride and hydroxide ions, calculated via the standard continuum solvent model.

3.2. Dissociation of Hydrogen Chloride Relative to Water in AW and SCW. It was seen above that, because the continuum model does not account for solvent compressibility or microheterogeneous solvation, $\Delta A^{\rm solv}$ for the individual ionic species and neutral molecules do not agree closely with MD simulation in SCW. Despite this limitation, the continuum model agrees beautifully with simulation for the difference in $\Delta A^{\rm solv}$ for the ions, Cl^- and OH^-, and for the neutral molecules HCl and H_2O. This is clearly shown in Figure 3. This cancellation of errors suggests that the neglected microheterogeneous solvation, in particular electrostriction in the continuum model, influences each of the ions and each of the neutral species in a similar manner. This result is not surprising in hindsight, given the similar charges and sizes for the atoms in each pair. The behavior in Figure 3 can be explained physically in terms of the sizes and charges on the atoms of the various species. As ϵ increases from 1 to 80, $\Delta A^{\rm solv}_{\rm Cl^-} - \Delta A^{\rm solv}_{\rm OH^-}$ increases as solvation favors the smaller ion OH^- over Cl^-. (Each ΔA is negative.) Additionally, $\Delta A^{\rm solv}_{\rm HOH} - \Delta A^{\rm solv}_{\rm HCl}$ becomes more negative as solvation of HOH exceeds that of HCl, because of water's larger dipole moment and smaller size. We note that the change in this term is noticeably smaller than the change in $\Delta A^{\rm solv}_{\rm Cl^-} - \Delta A^{\rm solv}_{\rm OH^-}$. By favoring the solvation of OH^-, the equilibrium for the relative acidity reaction $HCl + OH^- = Cl^- + HOH$ moves to the left with increasing ϵ, indicating the relative acidity decreases due to solvation forces.

Because the continuum model agrees with simulation for the relative free energy of solvation of the ions and of the neutral

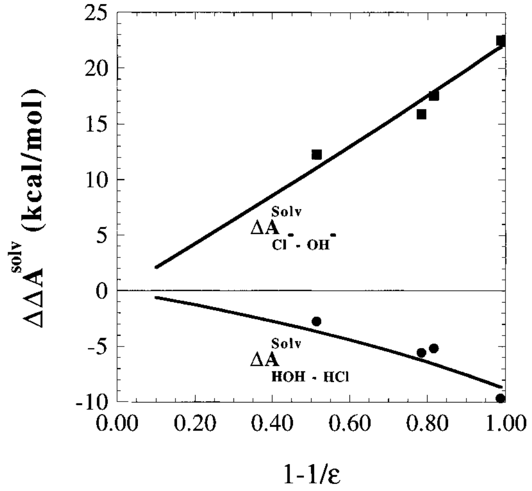

Figure 3. Relative solvation free energies of the ionic and neutral species (parameters of Table 1) that appear in the reaction $HCl + OH^- = Cl^- + H_2O$ (lines: standard continuum model, symbols: MD simulation[20,21]).

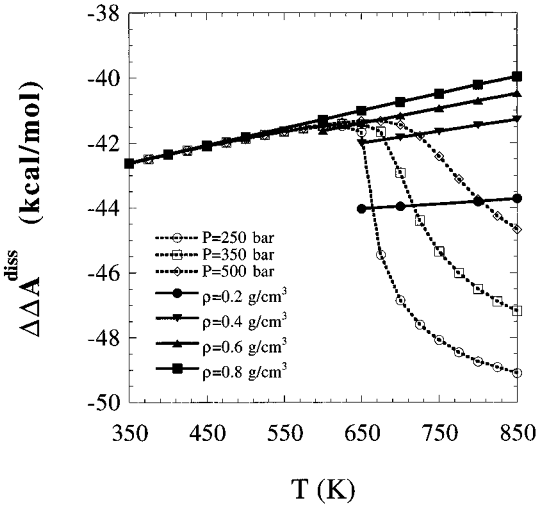

Figure 4. Relative free energy of dissociation of hydrogen chloride versus water along various isochores and isobars from the standard continuum model.

species, it must predict accurately the simulated relative acidity of HCl versus water. For other isocoulombic reactions where similar ions and similar neutral molecules are present, the standard continuum model may also be expected to perform well.

The good agreement between the standard continuum model and MD simulations for relative solvation, and thus relative acidity, provides justification for extending these continuum calculations to a large number of temperatures and densities. Examples are given in Figure 4 which follow the same states discussed previously in Figure 3. In the gas phase at 298 K, the dissociation reaction of HCl is strongly favored relative to HOH, i.e. $\Delta\Delta A^{\text{diss}} = -56.0$ kcal/mol. In aqueous solution, the relative acidity decreases due to the stronger solvation of OH^- versus Cl^-, as discussed above. However, the effect is small. Consider a range in $1 - 1/\epsilon$ from 1 to 0.8, which corresponds to a change from ambient water to SCW. The increment in $\Delta A^{\text{solv}}_{\text{Cl}^-} - \Delta A^{\text{solv}}_{\text{OH}^-}$ and the increment in $\Delta A^{\text{solv}}_{\text{HOH}} - \Delta A^{\text{solv}}_{\text{HCl}}$ are not very different in magnitude, so that the overall solvation free energy varies very little. Despite the extremely wide range in T and ρ in Figure 4, $\Delta\Delta A^{\text{diss}}$ varies by only 2 kcal/mol, down to 0.2 g/cm^3.

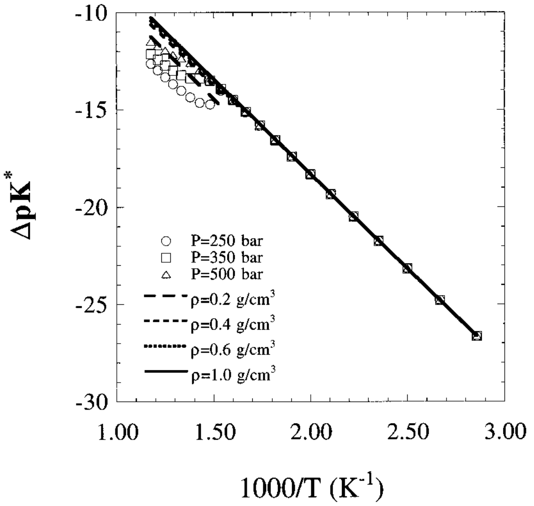

Figure 5. ΔpK* (eq 11) for the dissociation of hydrogen chloride versus water along various isochores and isobars from the standard continuum model.

Table 3. Comparison of Solvent Effects on Various Types of Reactions in SCW

reaction	ΔS	local structure	ρ effect
$Cl^- + CH_3Cl = [^{\delta-}Cl\cdots CH_3{}^{\delta+}\cdots Cl^{\delta-}]$	significant	yes	large
$Na^+ + Cl^- = Na^+Cl^-$ (ion pair)	dominant	yes	large
$HCl + OH^- = H_2O + Cl^-$	small	no	small

The entropy change for the dissociation of HCl relative to water, $\Delta\Delta S^{\text{diss}}$, is related to $\Delta\Delta A^{\text{diss}}$ by

$$\Delta\Delta S^{\text{diss}} = -\mathrm{d}(\Delta\Delta A^{\text{diss}})/\mathrm{d}T \qquad (10)$$

Since $\Delta\Delta A^{\text{diss}}$ along isochores varies little with temperature, $T\Delta\Delta S^{\text{diss}}$ is negligible compared with $\Delta\Delta E^{\text{diss}}$. This result is supported further by the analysis of MD simulation results in conjunction with experimental data.[21] It is only for extremely low densities and high temperatures that $\Delta\Delta A^{\text{diss}}$ becomes T and ρ dependent and finally approaches the gas-phase value. The small $T\Delta\Delta S^{\text{diss}}$ can be traced to small values of $T\Delta S^{\text{solv}}_{\text{Cl}^-} - T\Delta S^{\text{solv}}_{\text{OH}^-}$ and $T\Delta S^{\text{solv}}_{\text{HOH}} - T\Delta S^{\text{solv}}_{\text{HCl}}$.[21] The energetics dominate in all of these cases. The small value of $T\Delta\Delta S^{\text{diss}}$ is consistent with our observation[20,21] that the local molecular structure does not have a net influence on $\Delta\Delta A^{\text{diss}}$.

From $\Delta\Delta A^{\text{diss}}$, Δp$K$* can be computed by the relationship

$$\Delta pK^* = \Delta\Delta A^{\text{diss}}/2.3RT \qquad (11)$$

The results for ΔpK* along different isobars and isochores versus inverse temperature are shown in Figure 5. In SCW, the equilibrium constant is reduced substantially compared to AW. Since $\Delta\Delta A^{\text{diss}}$ does not change significantly with changes in density up to about 650 K, the ΔpK* data along different isobars and isochores fall close to each other. At about 650 K the ΔpK* isobars begin to deviate from this linear behavior, as density effects become much more substantial. The change in ΔpK* with temperature is due overwhelmingly to the explicit T dependence in eq 11, as $\Delta\Delta A^{\text{diss}}$ is relatively constant.

A comparison of simulation results for the reaction of $HCl + OH^-$ with other types of reactions provides general insight into solvent effects in SCW (Table 3). For the S_N2 substitution reaction of CH_3Cl and Cl^- to form the symmetric transition state $^{\delta-}Cl\cdots CH_3{}^{\delta+}\cdots Cl^{\delta-}$, the charge dispersal is large. Consequently the solvent density effect on ΔA is large, as is the effect of local solvation structure.[32] The formation of the NaCl ion pair also involves a large change in charge distribution. Again local structure plays a large role, and the density effect is large.[23,54] The entropy gain from removing water of solvation from the ion pair relative to the individual ions drives the reaction. For both of these reactions, continuum models lose accuracy in SCW, because of electrostriction. In contrast, the continuum models can predict $\Delta\Delta A^{\mathrm{diss}}$ accurately for the reaction $\mathrm{HCl} + \mathrm{OH}^- = \mathrm{HOH} + \mathrm{Cl}^-$ since the effects of electrostriction essentially cancel between the pair of ions. Because the reaction is isocoulombic and the ions have similar sizes, the density effect on ΔA is small. Correspondingly, the entropy contribution is small.

4. Conclusions

New simulation results over a wide range in temperature and density indicate electrostriction influences absolute free energies of solvation markedly for Cl^- . The effect of electrostriction may be quantified by comparing simulation with the Born model, if the Born radius is chosen in a physically significant manner. The radius where the ion−water pair distribution first rises rapidly from zero leads to desirable results. The simulated free energies are always more negative than those from the Born model, and they merge at high temperatures where electrostriction becomes small. A simple dual concentric shell continuum model with an average local density in the first shell (obtained from simulation) predicts the simulated free energy quite accurately.

The accuracy of continuum models for reactions in SCW depends strongly upon the importance of electrostriction. Electrostriction is important in ion solvation and reactions with large changes in charge dispersion, such as $\mathrm{S_N2}$ reactions and ion pairing reactions. Consequently, the entropy contribution to ΔA of reaction is significant, and in some cases dominant, and the free energy change is sensitive to density. However, for the relative solvation of similar species, such as OH^- versus Cl^-, the effects of electrostriction nearly cancel. Thus, entropic effects are negligible, and the free energy change with density is small. In these examples, the simplest continuum model is in excellent agreement with simulation, and provides a means to study a large number of densities and temperatures with negligible requirements for computer time.

With changes in thermodynamic conditions from ambient to SCW states, in the range of temperatures from 298 to 853 K and densities from 1.0 to 0.2 g/cm3, $\Delta\Delta A^{\mathrm{diss}}$ remains fairly constant. This observation, previously obtained by MD simulations, has been found to agree with experiment.[21] Because $\Delta\Delta A^{\mathrm{diss}}$ is essentially constant, the change in $\Delta \mathrm{p}K^*$ with temperature is due overwhelmingly to the explicit T dependence in eq 11.

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(54) Gao, J. *J. Phys. Chem.* **1994**, *98*, 6049−6053.