ION ASSOCIATION IN HIGH-TEMPERATURE AQUEOUS HCl SOLUTIONS. A MOLECULAR SIMULATION STUDY

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The profiles of the potential of mean force for the $Cl^- - H_3O^+$ pair, as predicted by two *ab initio* models, are determined by constraint molecular dynamics simulation at a near-critical condition. The corresponding association constants are then determined and compared with that from conductance measurements to test the reliability of the current simulation models for HCl.

INTRODUCTION

The characterization of hydrothermal fluids in equilibrium with solid phases requires the analysis of the mass action constants for the solubility and ionization processes [1]. The dissociation of HCl is of particular significance since it is involved in most aqueous chloride mineral solutions found in nature (hydrothermal systems) and in industrial processes (including power-station generators and supercritical water oxidation reactors). The dissociation of HCl in aqueous solutions has been studied over a wide range of state conditions by different experimental methods, including calorimetric techniques [2], electrical conductance [3-5], and solubility measurements [6-8]. Yet, the thermodynamic properties of aqueous solutions of hydrochloric acid, especially those at high temperatures and low densities, are still the matter of some debate.

The obvious corrosive nature of the system [3] makes the experimental study of high temperature of aqueous HCl solutions extremely challenging, and highlights the need for alternative approaches for its investigation. Molecular-based approaches to ion association have already shown great potential in the quest for a fundamental understanding of ion solvation and in the evaluation of the association constant of simple electrolytes at high temperature [9, 10]. As part of a wider ongoing investigation on the thermodynamics of high-temperature ion solvation, here we briefly discuss ion-pair association in model supercritical aqueous hydrochloric acid solutions. This study encompasses the molecular-based determination of the ion-pair association constant via potential of mean-force calculations, and the direct comparison with conductance data. With that purpose our first goal is to test the reliability of two current *ab initio* ion-water potentials in describing ion association in aqueous hydrochloric acid solutions, through a direct comparison between simulation results and conductance measurements at high temperature [3, 5]. This analysis is currently

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complemented with the explicit determination of the individual limiting ion-conductivity, and will be reported in more detail elsewhere [11].

POTENTIAL OF MEAN FORCE AND ASSOCIATION CONSTANT

Provided that we can assume no formation of neutral polyionic cluster [12], we can view the association process in a dilute aqueous solution as the chemical reaction between the free anion A and cation C, that results in the possible associated neutral pair CA configurations of a 1:1 salt as follows,

$$\begin{array}{ccccccccc} & & K_1 & & K_2 & & K_3 & & \\ C & + & A & \Leftrightarrow & CA & \Leftrightarrow & C|A & \Leftrightarrow & C\|A \\ \text{free} & & \text{ions} & & \text{CIP} & & \text{SSHIP} & & \text{SSIP} \end{array} \tag{1}$$

where SSIP, SSHIP, and CIP represent solvent-separated, solvent-shared, and contact ion pairs, respectively. Thus, the equilibrium association constant can be expressed as [9],

$$K_a(T,\rho) = K_1(1 + K_2 + K_2K_3) \cong K_1(1 + K_2) \tag{2}$$

and interpreted microscopically in terms of the anion-cation radial distribution function for the infinitely dilute system [9],

$$K_a = 4\pi \int_0^{r_2} g_{AC}^{\infty}(r) r^2 dr \tag{3}$$

where ∞ denotes an infinite dilution property, and r_2 indicates the position of the second valley of the $g_{AC}^{\infty}(r)$ (*i.e.*, it encompasses the CIP and SSHIP configurations). Therefore, the evaluation of the association and equilibrium constants via molecular simulation requires the non-trivial determination (based on the corresponding potential of mean force (PMF) $\omega(r)$) of the anion-cation radial distribution function at infinite dilution.

As discussed elsewhere [9, 13], the PMF calculation is performed by constraint dynamics involving the spherically-symmetric Cl^- ion and the four-site H_3O^+ ion. In order to obtain a meaningful $\omega(r)$, *i.e.*, an orientational-averaged quantity, we need to constrain the center-to-center distance of the ion-pair and simultaneously allow for the rotation of the H_3O^+ around its center of mass.

INTERMOLECULAR POTENTIALS AND SIMULATION METHODOLOGY

Throughout this investigation water is described by the SPC/E model [14] for which we know its critical conditions [15]. For the pair of ion-water interactions we have chosen two sets of potential models, that we will denote as the Gertner-Hynes' and the Kusaka *et al.*'s models. The Gertner-Hynes model [16] is based on *ab initio* calculations for the ions H_3O^+ and Cl^- in $TIP4P$ water. Since the $TIP4P$ and the SPC/E water models give essentially the same representation for the behavior of water at high temperature [10, 17], we do not attempt any re-parameterization to account for the difference between water models. The hydronium ion is described by a non-planar four-site geometry with a bond length $l_{OH} = 1.009\text{Å}$, an HOH angle of 108.5°, with the partial charges $q_O = -0.62e$ and $q_H = 0.54e$.

The ion-water interactions are represented by Lennard-Jones interactions between the water's oxygen and either the hydronium's oxygen or the chloride ion, plus the corresponding electrostatic interactions between all charged sites, *i.e.*,

$$\phi_{wi}(r_{wi}) = 4\varepsilon_{wi}\left[\left(\frac{\sigma_{wi}}{r_{wi}}\right)^{12} - \left(\frac{\sigma_{wi}}{r_{wi}}\right)^{6}\right] + \sum_{\alpha,\beta}^{3,4} \frac{q_w^{\alpha} q_i^{\beta}}{r_{wi}^{\alpha\beta}} \tag{4}$$

where the subscripts w and i refer to water and ion, respectively; while α and β denote the corresponding charged sites. In table 1 we display the size and energy parameters for the Lennard-Jones ion-water interactions, which obey the Lorentz-Berthelot combining rules.

Table 1: Lennard-Jones potential parameters for the Gertner-Hynes model [16]

interaction	$\varepsilon_{wi} / k\ (K)$	$\sigma_{wi}(\AA)$
$w - H_3O^+$	2172.9	2.529
$w - Cl^-$	248.3	3.563

The second hydronium model was developed by Kusaka and co-workers [18] to study the behavior of H_2SO_4 in SPC/E water. This hydronium model is based on the geometry of Rodwell and Radom [19], *i.e.*, $l_{OH} = 0.973\AA$, an HOH angle of $111.6\AA$, with partial charges $q_O = -0.248e$ and $q_H = 0.416e$. Here we supplement their water-hydronium pair potential with the parameterization of Smith and Dang [20] for the chloride-SPC/E interactions. As for the first model, the pair potential is described by equation (4), even though, the Lennard-Jones parameters for the hydronium-water interactions are all given by the Lorentz combining rule, *i.e.*, the geometric mean.

Table 2: Lennard-Jones potential parameters for the Kusaka *et al.*'s model [18]

interaction	$\varepsilon_{wi} / k\ (K)$	$\sigma_{wi}(\AA)$
$w - H_3O^+$	103.9	3.030
$w - Cl^{-\#}$	62.75	3.783

From Smith and Dang [20]

We performed the simulation of the rigid-body dynamics of water and hydronium at isothermal-isochoric conditions, using a quaternion approach for the rotational degrees of freedom [21]. To achieve isothermal conditions we implement three independent Nosé thermostats for the translational (water), rotational (water and hydronium) and the ion-pair translational degrees of freedom, respectively. In addition, we use a Gear predictor-corrector algorithm [22], to fifth order for the translational degrees of freedom and fourth order for the rotational as well as Nosé's dynamical variables, to integrate the equations of motion with a time-step of 1.0 femto second.

All simulations were performed with a total of 256 particles using an Ewald sum to account for the electrostatic interactions, with a convergence parameter $\alpha \approx 5.6/L$, and a maximum k

in the reciprocal space such that $k^2 \leq 27$. The simulation length for the constraint dynamics was 200 pico-seconds for each constrained distance after the corresponding equilibration. To run the constraint dynamics for the center of mass of the ion-pair we implemented a SHAKE-like approach [23] to constraint molecular dynamics to study ion-pair association between spherical and non-spherical ions, *i.e.*, by allowing the rotation of the hydronium while keeping it at a fixed distance from the chloride ion. The radial profiles of the ion-pair potential of mean force were determined by constraint dynamics in the "blue-moon ensemble" [24], and the ion-pair constants were obtained in terms of the corresponding integrals over the potential of mean force [9]. More detail on the simulation methodology are given elsewhere [11].

SIMULATION RESULTS AND DISCUSSION

In order to anchor the potential of mean force according to the standard procedure (dielectric attenuated ion-ion potential), we determined the dielectric constant of the water model at $T_r = T/T_c = 1.05$ and $\rho_r = \rho/\rho_c = 1.0$ to be 5.9 ± 0.3.

From the profiles in Figures 1 and 2 it becomes clear that, although the two models exhibit similar features, they predict rather different magnitude for the $Cl^- - H_3O^+$ mean force. Especially significant is the large difference between the actual mean force and the corresponding prediction from that of a continuum dielectric for the Kusaka *et al.*'s model. While the Gertner-Hynes' and Kusaka *et al.*'s models give essentially the same location for the minimum, the Kusaka *et al.*'s model also predicts a clear maximum while the Gertner-Hynes' model exhibits only a change in curvature.

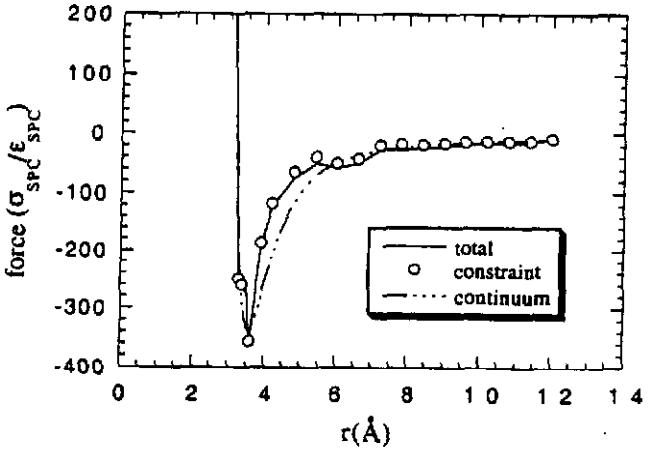

Figure 1. $Cl^- - H_3O^+$ mean force calculation for the Gertner-Hynes' model in units of $\varepsilon_{SPC} = 78.23k$ and $\sigma_{SPC} = 3.166\,Å$. Comparison between constraint dynamics results and the prediction of a continuum model.

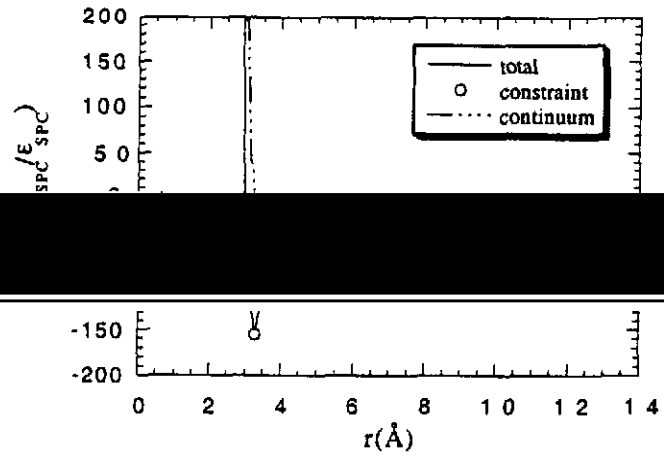

Figure 2. $Cl^- - H_3O^+$mean force calculation for the Kusaka *et al.* s' model in units of $\varepsilon_{SPC} = 78.23k$ and $\sigma_{SPC} = 3.166\,\mathring{A}$. Comparison between constraint dynamics results and the prediction of a continuum model.

This subtle difference in the mean force profiles translates into more pronounced differences between the actual potential or mean force and the values predicted by the continuum models as indicated in Figure 3 and 4.

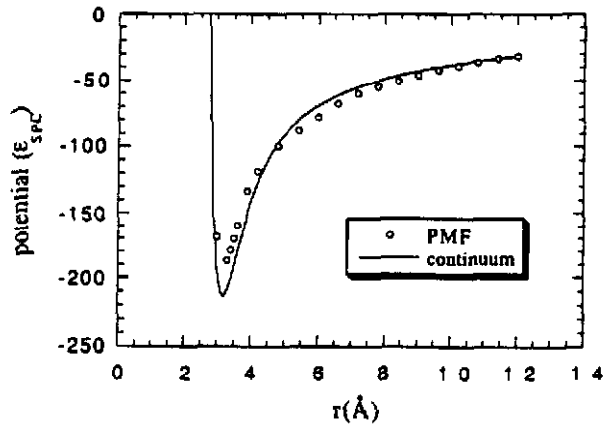

Figure 3. $Cl^- - H_3O^+$ pair potential of mean force for the Gertner-Hynes' model in units of $\varepsilon_{SPC} = 78.23k$. Comparison between constraint dynamics results and the prediction of a continuum model.

More specifically, note that, while the Gertner-Hynes' model predicts a shallower PMF minimum than the continuum model, the trend reverses for distances beyond the CIP configuration. In contrast, the Kusaka *et al.*' s model exhibits no change of trend, but a close agreement with the continuum behavior beyond the CIP configuration.

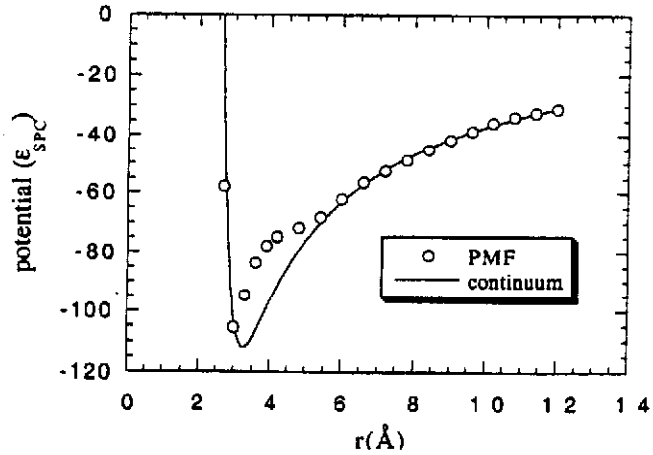

Figure 4. $Cl^- - H_3O^+$ pair potential of mean force for the Kusaka *et al.* s' model in units of $\varepsilon_{SPC} = 78.23k$.. Comparison between constraint dynamics results and the prediction of a continuum model.

In Figures 5 and 6 we show the resulting radial distribution function $g^{\infty}_{Cl^- - H_3O^+}(r)$ and its volume integral which defines the molar association constant $K_a(l/mol)$. For comparison with experiment, we use the regressed expression given by Frantz and Marshall [3-5], which gives a value of $\log K_a(l/mol) \cong 6.8$.

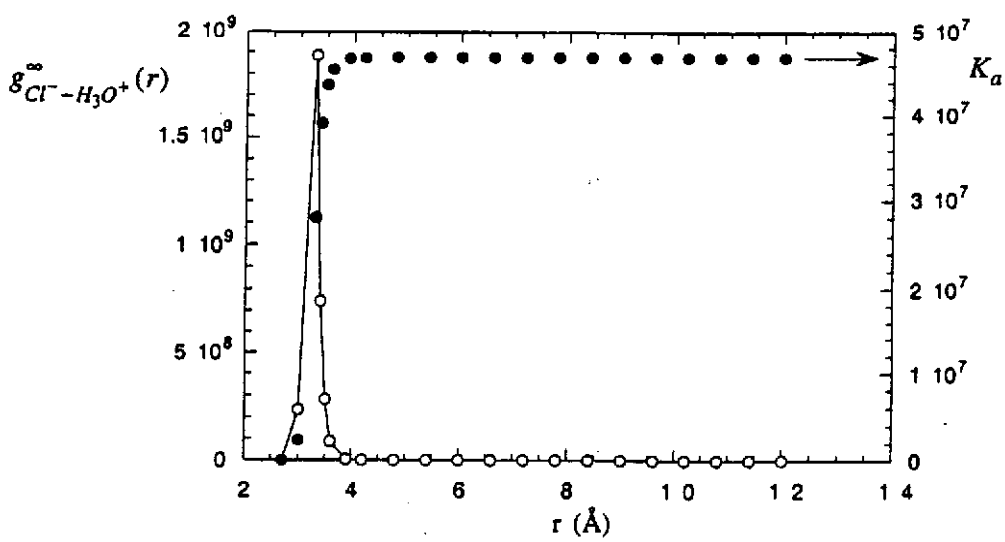

Figure 5. $Cl^- - H_3O^+$radial distribution function (O) and resulting association constant (•) (in units of l/mol) for the Gertner-Hynes' model.

Figure 5 clearly indicates that the association constant for Gertner-Hynes' model is essentially defined within the first peak of $g^{\infty}_{Cl^- - H_3O^+}(r)$, *i.e.*, the one related to the CIP configuration. According to this model, the molar association constant at near critical condition is $\log K_a(l/mol) \cong 7.6$. In contrast, Kusaka *et al.* 's model predicts an association constant with significant contributions from the SSHIP configuration, *i.e.*, its $g^{\infty}_{Cl^- - H_3O^+}(r)$ presents a clear change of curvature (a flat second peak or shoulder) in the range of $4Å < r < 6Å$ which contributes significantly to the volume integral. The resulting value for this constant is $\log K_a(l/mol) \cong 3.8$.

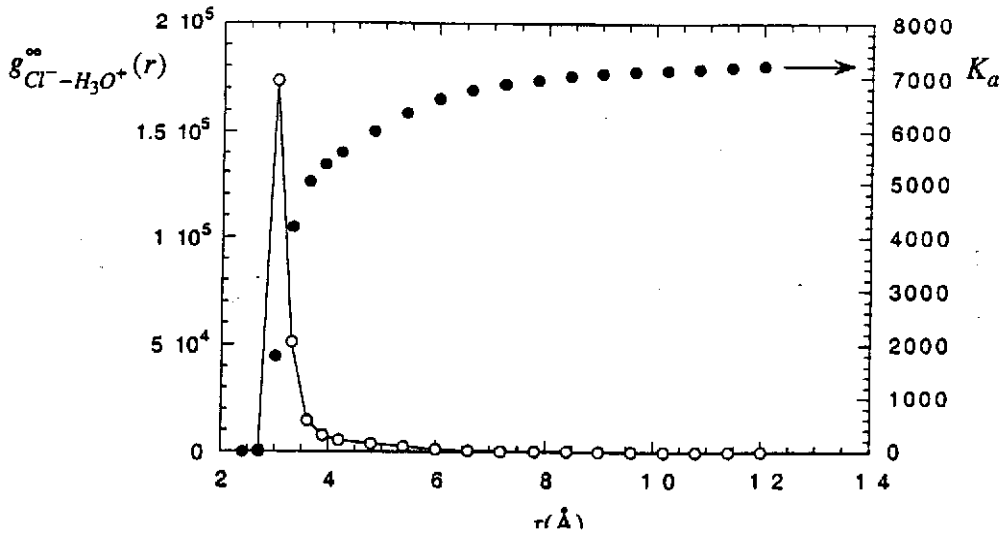

Figure 6. $Cl^- - H_3O^+$ radial distribution function (O) and resulting association constant (●) (in units of l/mol) for the Kusaka *et al.* s' model.

In summary, our molecular simulation study of the ion-pair formation at near critical conditions suggests that the Gertner-Hynes' model predict the association constant in better agreement with experiment than the Kusaka *et al.* 's model. In fact, the latter underestimates this constant by about three orders of magnitude. Current simulation studies on the limiting ionic conductivity of these models will shed additional light on the reliability of these models for the accurate representation of this hydrothermal system at low density and high temperature con ditions.

ACKNOWLEDGMENTS

This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, and by the Environmental Management Science Program of the Office of Environmental Management, U. S. Department of Energy at Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corporation for the U.S. Department of Energy under contract DE-AC05-96OR22464. PTC was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy.

REFERENCES

1. Mesmer, R.E., D.A. Palmer, and J.M. Simonson, *Ion Association at High Temperatures and Pressures*, in *Activity Coefficients in Electrolyte Solutions*, K.S. Pitzer, Editor. 1991, CRC Press: Boca Raton. p. 491-529.
2. Simonson, J.M., *et al.*, Journal of Physical Chemistry, 1990. **94**: p. 7675-7681.
3. Franck, E.U.,. Zietschr. Phys. Chemie N.F., 1956. **8**: p. 192-206.
4. Pearson, D., C.S. Copeland, and S.W. Benson, Journal of the American Chemical Society, 1963. **85**: p. 1047-1049.
5. Frantz, J.D. and W.L. Marshall,. American Journal of Science, 1984. **284**: p. 651-667.
6. Chou, I.M. and J.D. Frantz,. American Journal of Science, 1977. **277**: p. 1067-1072.
7. Frantz, J.D. and R.K. Popp,. Geochimica et Cosmochimica Acta, 1979. **43**: p. 1223-1239.
8. Ruaya, J.R. and T.M. Seward,. Geochimica et Cosmochimica Acta, 1987. **51**: p. 121-130.
9. Chialvo, A.A., *et al.*, Journal of Chemical Physics, 1995. **103**: p. 9379-9387.
10. Chialvo, A.A. and P.T. Cummings, *Molecular-based Modeling of Water and Aqueous Solutions at Supercritical Conditions*, in *Advances in Chemical Physics*, S.A. Rice, Editor. 1999, Wiley & Sons: New York. p. 115-205.
11. Chialvo, A.A., *et al.*, 1999. Manuscript in preparation.
12. Oelkers, E.H. and H.C. Helgeson, Science, 1993. **261**: p. 888-891.
13. Chialvo, A.A. and P.T. Cummings, *Supercritical Water and Aqueous Solutions: Molecular Simulation*, in *Encyclopedia of Computational Chemistry*, P.v.R. Scheyer, Editor. 1998, Wiley & Sons. p. 2839-2859.
14. Berendsen, H.J.C., J.R. Grigera, and T.P. Straatsma, Journal of Physical Chemistry, 1987. **91**: p. 6269-6271.
15. Guissani, Y. and B.J. Guillot, Journal of Chemical Physics, 1993. **98**: p. 8221-8235.
16. Gertner, B.J. and J.T. Hynes, Faraday Discussions, 1998. **110**: p. 301-322.
17. Chialvo, A.A. and P.T. Cummings,. Journal of Physical Chemistry, 1996. **100**: p. 1309-1316.
18. Kusaka, I, *et al.* ,. Journal of Chemical Physics, 1998. **108**: p. 6829-6848.
19. Rodwell, W.R. and L. Radom, Journal of the American Chemical Society, 1981. **103**: p. 2865-.
20. Smith, D.E. and L.X. Dang, Journal of Chemical Physics, 1994. **100**: p. 3557-3566.
21. Evans, D.J. and S. Murad,. Molecular Physics, 1977. **34**: p. 327-331.
22. Gear, C.W., *The Numerical Integration of Ordinary Differential Equations of Various Orders*, 1966, Argonne National Laboratory.
23. Ciccotti, G. and J.P. Rychaert,. Computer Physics Reports, 1986. **4**: p. 345-394.
24. Ciccotti, G., *et al.*,. Journal of Chemical Physics, 1990. **93**: p. 7137-7147.