

# ION-PAIR ASSOCIATION IN HYDROTHERMAL SOLUTIONS BY CONDUCTANCE EXPERIMENT AND MOLECULAR SIMULATION

## WHAT HAVE WE LEARNED AND WHAT CAN WE EXPECT?

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Knowledge of the properties of supercritical aqueous mixtures is essential to the understanding of the dissolution, transport, and precipitation of salts in many natural environments and industrial processes. The characterization of these hydrothermal systems requires knowledge of the equilibrium constants for the solubility and ionization processes. In particular, the thermodynamic description of many natural and industrial processes including volcanic vapors, hydrothermal vents, steam power generation and supercritical water oxidation, relies on the availability of accurate data for the thermodynamic behavior of aqueous electrolyte solutions.

The dissociation of MX in aqueous solutions (where M includes  $\text{H}_3\text{O}^+$ ,  $\text{Cu}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$ , and X includes  $\text{Cl}^-$ ,  $\text{OH}^-$ ) has been studied extensively by calorimetric techniques, electrical conductance, and solubility measurements (Mesmer et al., 1991). Yet, the thermodynamic properties of these aqueous solutions, especially those at high temperatures and low densities, are still the matter of some debate, in that the dissociation constants determined from solubility data appear to be at odds with those from conductivity measurements (Chialvo et al., 2000; Ho et al., 2000a; Ho et al., 2000b). These discrepancies highlight the intrinsic challenges behind the accurate measurements of electric conductivity in low-density, dilute, and extremely corrosive aqueous systems, the likely existence of additional species not taken into consideration in the treatment of solubility data, and consequently, the need for improved experimental methods and more sophisticated modeling techniques. The fundamental driving force for speciation reactions in the competition between solvent-solute and solute-solute interactions in solution. Molecular-based approaches to ion solvation show great potential in the quest

for a fundamental understanding of ion solvation, by guiding the interpretation of experimental data, assisting in the assessment of their consistency, and connecting the microscopic and macroscopic properties of interest in a rigorous, unambiguous fashion (Chialvo and Cummings, 1999).

As part of a wider ongoing investigation on high-temperature ion solvation and complexation, in this work we focus our attention on ion-pair association in hydrothermal systems. We report on our latest molecular-based studies of ion-pair association at precisely the same corresponding states as those from our own conductance experiments with a flow-through cell. This comparison allows us to test the reliability of the intermolecular potentials involved, before we proceed with the simulation studies at conditions unattainable by current experimental methods, such as at lower density and higher temperature. The knowledge of the ion association behavior under these experimentally inaccessible conditions is becoming one of the most important goals of high temperature aqueous chemistry, because this region can yield fundamental information regarding ion-pair solvation that is essential for the proper modeling of these mixtures (Sverjensky et al., 1997).

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