

# TOWARD A MOLECULAR-BASED UNDERSTANDING OF HIGH-TEMPERATURE SOLVATION PHENOMENA IN AQUEOUS ELECTROLYTE SOLUTIONS

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## INTRODUCTION

The theoretical treatment of the solvation phenomenon of simple ions in aqueous solutions has been rather difficult, despite the apparent simplicity of the system. Long-range solvent-screened electrostatic interactions, coupled to the large variation (with state conditions) of the dielectric permittivity of water, give rise to a variety of rather complex solvation phenomena including dielectric saturation, electrostriction, and ion association. Notably, ion solvation in high-temperature/pressure aqueous solutions plays a leading role in hydrothermal chemistry, such as in the natural formation of ore deposits, the corrosion in boilers and reactors, and in high-temperature microbiology.

Tremendous effort has been invested in the study of hydrothermal solutions to determine their thermodynamic, transport, and spectroscopic properties with the goal of elucidating the solute-solvent and solute-solute interactions over a wide range of state conditions. It is precisely at these conditions where our understanding and predictive capabilities are most precarious, in part, as a result of the coexistence of processes with two rather different length scales, i.e., short-ranged (solvation) and long-ranged (compressibility-driven) phenomena (Chialvo and Cummings 1994a). The latter feature makes hydrothermal systems extremely challenging to model, unless we are able to isolate the (compressibility-driven) propagation of the density perturbation from the (solvation-related) finite-density perturbation phenomena (Chialvo and Cummings 1995a).

## METHOD

To tackle such difficulties we have developed a solvation formalism that discriminates the disparate length-scale phenomena, i.e., solvation from compressibility-driven phenomena, through the splitting of the species total correlation functions into their

direct and indirect contributions according to the Omstein-Zemike equation (Chialvo, Cummings et al. 1999). Therefore, we describe the solvation of a single ionic solute (salt) in a pure solvent in terms of a *thought experiment*, one that creates a *non-ideal solution* infinitely dilute solution from the corresponding *ideal solution* (in the sense of the Lewis-Randall rule (Chialvo 1993)).

The main goal of this formalism is to connect the microscopic changes of the solvent structure around the solute species with the macroscopic (thermodynamic) properties which best characterize the solvation process. This connection is achieved in essentially four equivalent ways by interpreting the driving force of the solvation process, from either a microscopic or a macroscopic perspective. Initially, we take the neutral ionic solute as a hypothetical “molecular” entity in order to derive the solute properties that are usually measured experimentally. Then; we derive the corresponding individual-ion contributions to the neutral ionic solute properties, and make contact with the actual solvent environment around the individual ions. According to this formalism, the salt partial molar properties can be defined in terms of their individual ion counterparts, *i.e.*, in terms of the relative structuring of the solvent environment around individual species. Consequently, the solvation properties of the individual ions are linked unambiguously to the solvent’s electrostriction around the species in solution, as well as to the coefficients of the Helmholtz free energy expansion for dilute mixtures.

In order to make contact between model predictions and experimental results, we use the formalism to interpret the solvation behavior of simple salts in high-temperature aqueous solutions, according to the integral equation calculations, and recent experimental data from Wood and co-workers (Gruskiewicz and Wood 1997; Sedlbauer, Yezdimer et al. 1998). More specifically, we make a molecular-based interpretation for the success of the underlying ideas behind the recently proposed regression approach for the solute partial molar volumes (Gruskiewicz and Wood 1997; Sedlbauer, Yezdimer et al. 1998). The chosen combination of quantities exhibits a rather intriguing weak temperature-dependence in the range of  $550 < T(K) < 725$  (O’Connell, Sharygin et al. 1996; Sedlbauer, Yezdimer et al. 1998), that makes it very attractive for the development of engineering correlations. With that purpose, we performed integral equation calculations for a few alkali halides at infinite dilution aqueous-type solutions, along three supercritical isotherms (643K, 673K, and 703K), and within the density range of  $0.0136 \leq \rho(g / cm^3) \leq 0.81$ . In the present calculations the systems are defined as charged hard sphere ions immersed in a model aqueous-like solvent, described as a hard sphere with embedded point polarizability and permanent electrostatic multipole moments (including quadrupole and

octupoles). The calculations were carried out by solving the reference hypemetted-chain (RHNC) equations with solvent polarization effects treated at the self-consistent mean-field (SCMF) level as described elsewhere (Kusalik and Patey 1988; Kusalik and Patey 1988).

## RESULTS AND DISCUSSION

The resulting comparison, based on the solvation formalism, indicates that the weak temperature-dependence of the regressed experimental data for high-temperature aqueous electrolyte solutions is a manifestation of the behavior of the corresponding solvation (as opposed to compressibility driven) phenomena (Chialvo, Cummings et al. 1999; Chialvo, Kusalik et al. 1999). In addition, these results not only confirm the well-behaved nature of the true solvation properties, but also the ability of the formalism to pinpoint the most adequate set of macroscopic (measurable) properties (and their unambiguous microscopic counterparts) to be used in a successful correlation approach. Bearing in mind the ultimate goal of these molecular-based studies, we finally discuss some theoretical implications concerning the modeling of high-temperature aqueous-electrolytes solutions, and some suggestions on what properties may be better suited for correlation purposes toward the development of engineering correlations.

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