

IAPWS Certified Research Need - ICRN

Properties of Salts in Steam

The IAPWS Working Group - Physical Chemistry of Aqueous Solutions has examined the published work in the area of the chemistry of electrolytes in steam.

IAPWS recognizes that there is a requirement for work to be pursued in this field and has prepared this document to assist potential investigators obtain sponsorship. Specifically new experimental or improved techniques are needed for studying the behaviour of salts in steam. The results obtained with these techniques together with simulation results, solubility and volatility data should provide a coherent thermodynamic model.

Although encouraging this work, IAPWS is not able under its statutes to provide financial support. The IAPWS contact can provide any further development information and will liaise between research groups.

Issued by the

**International Association for the Properties of
Water and Steam**

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The chemistry of electrolytes in steam is largely dependent on the physical nature of the solute at the molecular level in terms of the degree of ion association, the extent of hydration of all the species, and the existence of ionic clusters. For example, the interpretation of volatility measurements requires the adoption of a thermodynamic model that must either take into account the speciation in the vapor phase explicitly at the experimental conditions, or make assumptions concerning the species present and their activity coefficients.(1,2) Similarly, future potentiometric measurements to extreme conditions in the laboratory and in the field will rely on speciation information in order to calibrate the electrodes effectively. The general problem is not only one of scientific interest, but also comes into play in the application of experimental data to conditions prevailing in commercial steam generators and turbines, where a critical need exists to understand the process of vaporous carry-over and the subsequent deposition and/or concentration in thin films of corrosive compounds from contaminated steam. The solubilities of a range of salts have been measured to super-critical conditions, but due to the difficult nature of these experiments, the reported values often differ by orders of magnitude. There are a limited number of experimental approaches available to identify speciation in steam and thus far the results are somewhat ambiguous, or at best untested.(3,4) More recently dramatic improvements in computational simulation modeling have shown promise in quantifying speciation in aqueous solutions at ambient conditions, and some efforts are beginning to address the high temperature - low density regime (305 ° - 343 °C, 0.405 - 0.270g/cm³). (5) Clearly these two approaches must proceed in the traditional scientific manner with the experimental evidence providing confirmation of the computational studies. The scientific and industrial needs for understanding the thermodynamics of salts in low density aqueous solutions are three-fold:

1. Develop new experimental techniques and/or improve existing methods for studying the behavior of salts in steam and correlating these results with solubility and volatility data to provide a coherent thermodynamic model.
2. Develop further simulation procedures to study the properties of salts in aqueous solutions at high temperatures over a range of densities (pressures) and relating these predictions to the experimental data base.



3. Correlating the thermodynamic model to industrial situations such as the water/steam cycle of power plants and supercritical waste oxidation treatment plants in order to understand the current problems of corrosion at the metal/metal oxide interface.

Experimental Approaches to Identify and Quantify Salt Speciation in Steam

Simulation studies will provide an important guiding insight into the problem of speciation/hydration of solutes in steam, but ultimately experimental evidence must be the goal of this endeavor. Various experimental techniques are amenable to modification that would allow the properties of salts in low density aqueous solutions to be measured with sufficient accuracy as to be useful for extracting thermodynamic quantities. The most traditional method involves conductance measurements that provide direct information on ion association. Existing high temperature/high pressure conductance data (6,7 - using NaCl as an example) have provided valuable ion association constants for many electrolytes in the condensed phase, but tend to become unreliable as the density of the liquid decreases. However, new experimental developments, such as the conductance cell designed at the University of Delaware, (8) may offer promise for studying salt solutions at low densities, possibly down to steam pressures with good accuracy. Other methods providing structural information, e.g., NMR, X-ray and neutron scattering, etc., together with solubility measurements and mass spectrometry, are possible candidates for studying the speciation and hydration of salt solutions to extreme conditions, although the former are currently restricted to concentrated solutions. This ICRN does not attempt to address the perhaps equally important issue of non-thermodynamic behavior of salts in steam, although any information gained on speciation would have a direct impact on kinetic processes.

References

1. D.A. Palmer and J.M. Simonson, "Behavior of Ammonium Salts in Steam Cycles," Electric Power Research Institute, Palo Alto, CA: EPRI TR-102377, 1993.
2. J. Alvarez, H.R. Corti, R. Fernández-Prini, and M.L. Japas, *Geochim. Cosmochim. Acta*, 58, 2789 (1994).
3. J.K. Fogo, S.W. Benson, and C.S. Copeland, *J. Phys. Chem.*, 22, 212 (1954).
4. P. Kebarle, *Ann. Rev. Phys. Chem.*, 28, 445 (1977).
5. P.T. Cummings, H.D. Cochran, J.M. Simonson, R.E. Mesmer, and S. Karaborni, *J. Chem. Phys.*, 94, 5606 (1991).



6. A.S. Quist and W.L. Marshall, . *Phys. Chem.*, 72, 684 (1968).
7. P.C. Ho, D.A. Palmer, and R.E. Mesmer, *J. Solution Chem.*, 23, 997 (1994).
8. G.H. Zimmerman, M.S. Gruskiewicz, and R.H. Wood, *J. Phys. Chem.*, 99, 11612 (1995).

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