Sodium chloride-water clusters in steam: classical, quantum chemical and thermodynamic computational approach.

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Solubility of NaCl in steam can be explained by introducing fugacities of the components or, alternatively, by a successive hydration model [1]. The purpose of our study is to investigate to which extent we can reduce the number of adjustable parameters to adequately describe solubility of NaCl in supercritical water using the cluster approach.

Clusters, important building blocks in thermodynamic models for the bulk water, have recently attracted much attention in both fundamental and applied science. A well known pitfall in ab initio studies of polyatomic systems is a strong tendency to get stuck in local minima during the process of energy minimization. Moreover, the computational cost of such calculations grows very fast with the increasing number of atoms in a cluster. On the contrary, the combination of effective potentials with the efficient search algorithms for global optimization can be a very attractive tool in the quest for the most stable cluster geometry.

To explore the potential energy surface of small sodium chloride-water clusters, we have applied genetic algorithms based on principles of natural evolution [2,3]. The predicted clusters were relaxed to their closest minimum by ab initio minimisation methods. Gibbs free energy of formation, enthalpy of formation, heat capacities and entropy of the clusters were calculated *ab initio*. The derived thermodynamic data for the sodium chloride-water clusters, combined with thermodynamic data for halite and water, were used to model the solubility of sodium chloride in supercritical water (400–550°C, <400 bar). The results, obtained by the Gibbs free energy minimisation technique implemented in the HCh software [4], show an excellent fit of the major consistent sets of experimental data.

References

[1] Pitzer, K. and Pabalan, R. (1986) *GCA* **50**, 1445-1454.
[2] Holland, J. (1975) *Adaptation in Natural and Artificial Systems*. University of Michigan Press, Ann Arbor, MI.
[3] Mitchell, M. (1998) *An Introduction to Genetic Algorithms*. MIT Press, Cambridge, MA.
[4] Shvarov, Yu. and Bastrakov, E. (1999) *AGSO Record* **1999/25**.