

CHAPTER VI

SUMMARY

The scope of the work presented here was originally to extend the application of Monte Carlo simulation studies to the transition metal ion zinc and its chloride, in order to see structural differences of aqueous solutions of this salt in comparison to alkaline and alkaline earth chloride solutions, which have been well investigated in the past.

However, when the first conventional pair potential for Zn^{2+} interaction with water was constructed by means of ab initio calculations and implemented in a Monte Carlo simulation of an infinitely dilute solution of Zn^{2+} in water, it became clear that the usual simulation procedure, based on the assumption of pairwise additivity of interaction energies, is not capable of describing Zn^{2+} in water, as it leads to the coordination number 8 in contradiction to all experimental findings. This meant that inclusion of 3-body terms should be considered, which actually would imply ab initio calculations of a large number of $H_2O..Zn^{2+}..OH_2$ clusters for zinc-water interactions and $H_2O..Zn^{2+}..Cl^-$ clusters for the zinc-chloride energy surface, respectively.

In order to avoid this enormous computational effort, another algorithm was developed to correct the pair potentials with respect to the positions of other ligands in the metal ion's neighbourhood. This "Nearest Neighbour Ligand Correction", based on the calculation of energy surfaces for zinc monohydrate interacting with water and chloride, respectively, proved successful and allowed a simulation of Zn^{2+} in water without significant time increase compared to the uncorrected pair potential approach and with a resulting structure of the hydrated ion in full agreement with experimental data.

Based on this new algorithm, simulations were performed then for zinc chloride solutions with 1 M, 3 M and 5 M salt concentration. Evaluations were carried

out with respect to radial distribution functions (RDF) and coordination number distributions, leading to a detailed structural picture of these solutions and to species distributions as a function of concentration.

Experimental data known from x-ray diffraction studies are reproduced well by the simulation, and a comparison of experimental $\text{Zn}^{2+}/\text{Cl}^-$ complexation constants with equilibrium constants accessible via the species distribution in the simulated solutions could also be performed. This comparison not only showed good agreement for the first step constant for the reaction $\text{Zn}^{2+} + \text{Cl}^- \rightarrow \text{ZnCl}_2^+$, but proved also helpful in the interpretation of some potentiometric data.

The hydration structure of Zn^{2+} in all solutions has been presented in the form of ligand distribution plots. These pictures clearly reveal a breakdown of a more or less regular octahedral structure, prevailing until 3 M solution, at high ZnCl_2 concentrations. In addition to the detailed data for the relative abundance of various $\text{ZnCl}_n(\text{H}_2\text{O})_m^{(2-n)+}$ species in the solutions, the plots also allowed to conclude that in dichlorozincate complexes the second chloride ligand almost exclusively occupies a trans position with respect to the first one.

Finally, these results have been compared with some very recent simulation data for analogous solutions of CuCl_2 in water, showing that Zn^{2+} displays significant structural and chemical differences to Cu^{2+} . The reasons for the differences in chemical behaviour can be understood on the basis of the molecular structures and species distributions revealed by the Monte Carlo simulations presented in this work.