CHAPTER IV

DETAIL OF CALCULATIONS

Investigated Systems

Four different mixtures of water and hydroxylamine containing 4.5, 25.0, 50.0 and 75.2 weight % of NH_2OH have been considered. The corresponding numbers of hydroxylamine + water molecules are 5+195, 31+169, 71+129 and 125+75. In all cases, 2 Li^+ and 2 Cl^- have been introduced into the systems leading to the concentration of LiCl in the range of 0.42 - 0.54 M. The density of the pure mixtures (10), based on experimental data, was assumed to be maintained also for these low salt concentrations.

Interaction Potential Functions

In order to describe interactions of all species in the $LiCl/H_2O/NH_2OH$ system, a total of 10 potential functions which have been obtained from the following sources, have to be employed :

1. Li^+-Li^+ (24)
2. Cl^--Cl^- (24)
3. Li^+-Cl^- (24)
4. H_2O - H_2O (25)
5. NH_2OH -NH_2OH (26)

6. NH_2OH - H_2O (27)

7. Li^+ - H_2O (24)

8. Cl^- - H_2O (24)

9. Li^+ - NH_2OH (28)

10. Cl^- - NH_2OH (29)

All of these functions are derived, based on *ab initio* calculations of the corresponding interaction energy surfaces corrected for basis set superposition error where necessary, but not including electron correlation contributions, and they do not contain 3-body or higher terms. The reasons, why this simplified approach to the interactions in the solution can be accepted, have been discussed in the references given above (24-29) and can be assumed valid also for the simulations presented in this work.

Details of Simulations

The basic box lengths for the 4 systems at 32 °C result from the densities (1.00, 1.053, 1.109, 1.166 cm^{-3}) are 18.377, 18.708, 19.231 and 19.936 Å, respectively. A cut-off of half of these box lengths was applied for the evaluation of exponential terms and r^{-n} terms with $n \geq 6$. Monte Carlo simulations were performed with periodic boundary conditions using the minimal image convention (30) and long-range forces were taken into consideration by Ewald summation (3). The Metropolis algorithm (22) was applied, keeping the acceptance ratio at a value of 1/3 by continuous adaptation of shift and turn parameters.

Equilibration needed 4 to 9 million configurations, a further million configurations was used for investigation the results. The total amount of computation time for one simulation thus ranked between 200 and 400 hours on the IBM RISC 6000/530 workstation of the Austrian-Thai Centre for Computer-Assisted Chemical Education and Research Chulalongkorn University. All simulations were performed with the program MC92 (31).

Evaluation of the simulation was performed through radial distribution functions (RDF) and their integration and coordination number distributions obtained through a more detailed analysis of the history files and species interaction energies of each simulation run.