CHAPTER VI

SUMMARY

6.1 $Li(I)/NH_3$ Analytical Intermolecular Pair Potential

The intermolecular potential function for $Li(I)/NH_3$ has been constructed based on ab-initio closed shell SCF with DZP basis set , 100 interaction energies were used for the curve fitting procedure. The analytical potential function consists of Coulomb interaction terms , expotential and $1/r^6$ terms, given as :

$$\Delta E(r) = \sum_{i=1}^{4} [-A_{im}/r_{im} + B_{im} \exp(-C_{im} r_{im}) + Dq_i q_j/r_{im}]$$

The function was tested and the standard deviation of 1.32 $kcal.mol^{-1}$ was obtained. The result of interaction-energies in the most stable configuration computed from this function and from SCF scheme were, respectively -40.0 and -40.5 $kcal.mol^{-1}$, and no artificial minima was found in the function.

6.2 Monte Carlo Simulation of a Lithium Ion in 18.45 mole % Aqueous Ammonia Solution

The Monte Carlo simulation for a lithium ion in 18.45 mole % aqueous ammonia solution has been performed for 20 °C and 1 atm. The results show that : i) In contrast to sodium ion, lithium ion is preferentially solvated by water molecules, the exchange process to take place rather via ammonia than water molecules. The first shell of the ion contains 4 water and 2 ammonia molecules, the second solvation sphere consists of 12 solvent units, namely 8 water and 4 ammonia molecules. The fully solvated lithium ion in 18.45 mole % aqueous ammonia can be characterized hence by $Li[(H_2O)_4(NH_3)_2]^{I}[(H_2O)_8(NH_3)_4]^{II}$. Lithium ion is preferentially solvated by water in both shells, whereas in the case of sodium ion, characterized by $Na[(H_2O)_2(NH_3)_4]^{I}[(H_2O)_7(NH_3)_2]^{II}$, the first solvation sphere is dominated by ammonia and the second one by water. ii) Water and ammonia point with the lone pairs site mostly towards the ion, however, the angular orientation of water and ammonia varies significantly due to the influence of other neighbouring molecules. iii) In changing from lithium to sodium ion, the solvation radius is increased as expected. iv) The solvent structure of 18.45 mole % aqueous ammonia is not influenced significantly by the presence of one lithium or sodium ion.