CHAPTER VI

SUMMARY

According to the results discussed in Chapter III, IV and V, the finding of this study led to the following conclusions:

1) Two optimal fitting potential functions have been constructed based on *ab intio* closed shell Hartree-Fock MO SCF calculations with ECP/DZP basis sets are in the following forms:

(a) Li^+-NH_2OH potential function

$$\Delta E(kcal/mole) = \sum_{i=1}^{5} \frac{q_{Li}q_i}{r_{Li-i}} + \frac{A_{1i}}{r_{Li-i}^4} + \frac{A_{2i}}{r_{Li-i}^7} + A_3 \exp(-A_{4i} r_{Li-i})$$

(b) Cl^--NH_2OH potential function including the counterpoise method

$$\Delta E(kcal/mole) = \sum_{i=1}^{5} \frac{q_{Cl}q_i}{r_{Cl-i}} + \frac{A_{1i}}{r_{Cl-i}^4} + \frac{|A_{2i}|}{r_{Cl-i}^5} + |A_{3i}| \exp(-A_{4i} r_{Cl-i})$$

The parameters of Li^+-NH_2OH and Cl^--NH_2OH potentials, A_{1i}, A_{2i}, A_{3i} and A_{4i}, have been presented in Table 3.5 and 4.3, respectively and the atomic charges have also been collected in Table 3.6 and the atomic charge of and Cl^- equal to -1 au.. Based on these functions, statistical simulation technigues provide a relatively easy and reliable tool to obtain the structural informations, and have been successfully employed already to study the solvation structure in liquid hydroxylamine.

2) On the basis of the finding produced by Monte Carlo Simulation, leading to the conclusions that the structural investigation of one lithium ion in liquid hydroxylamine at 305 K reveals seven solvent molecules solvated the ion, from which two are chelate-coordinated, the others only via the oxygen binding site. From the result of the simulation of one chloride ion in the solvent, it can be observed that Cl^- under the same temperature forms a solvation shell of eight solvent molecules, which is usually coordinated via H_O however H_N can be found in some configurations. The structure of a solution of one LiCl molecule in liquid hydroxylamine described by radial distribution functions corresponds to the solvated structure, $[Li(NH_2OH)_7]^+$ and $[Cl(NH_2OH)_5]^-$ respectively, by introducing Ewald summation and the long-range interaction to the system.

The structures of the first solvation shell of this study illustrated in Figures 6.1 (a), (b) and (c) were built by sampling one of a mllion configuration that used in the evaluation of the characteristic values.

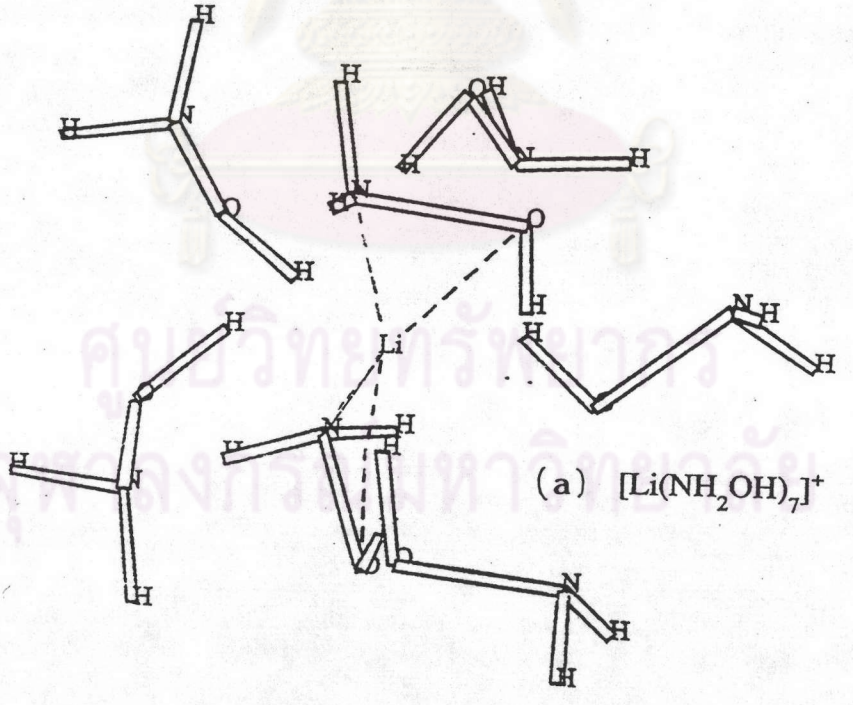
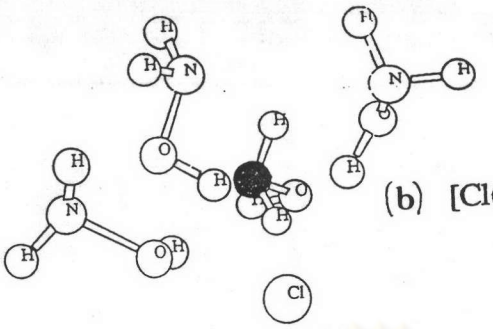


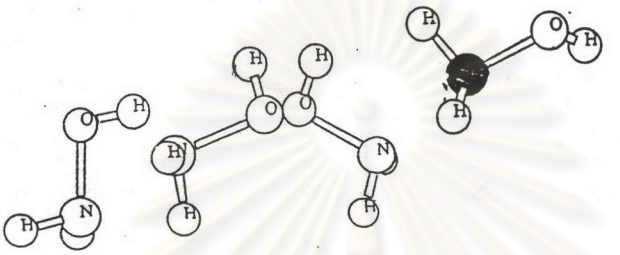
Figure 6.1 The first solvation structure :

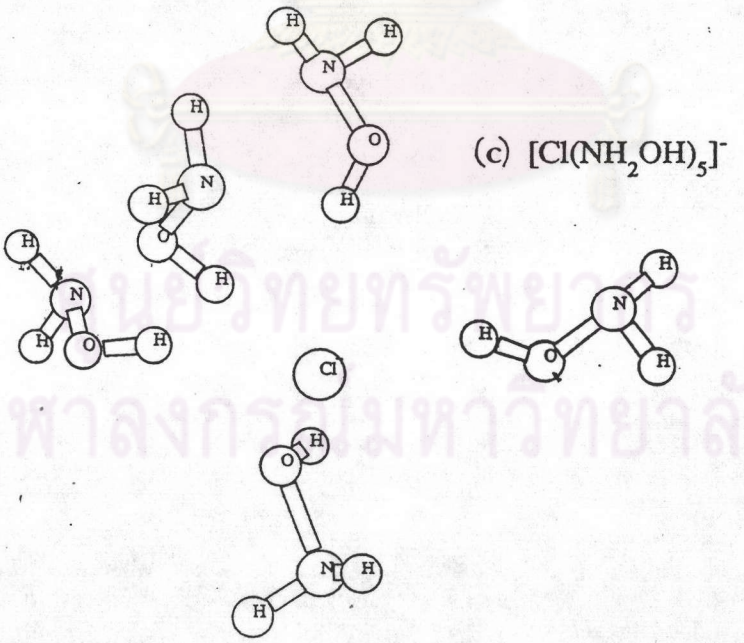
(a) $[Li(NH_2OH)_7]^+$, (b) $[Cl(NH_2OH)_8]^-$ and (c) $[Cl(NH_2OH)_5]^-$

Figure 6.1 (continue)



(b) $[Cl(NH_2OH)_8]^-$.





(c) $[Cl(NH_2OH)_5]^-$

Lastly the thesis provides comments that since liquid hydroxylamine is soluble in water, the structure of its salts in the mixture of these 2 solvents would be an interesting subject for the further study. Although the experimental structural studies of this solution by mean of x-rays or neutron diffraction have not been existed during this time, the simulations of ions in this mixture would be a very useful information for comparing to this studies which can lead to an explanation how ions are solvated by the solvent molecules in highly concentrated electrolyte solutions and how counter ion pairs are formed. Moreover, the effect of the intramolecular relaxation for correcting the unfavourable location of OH hydrogens around the lithium ion in the first solvation shell, the geometry optimization of hydroxylamine and the ions-hydroxyalmine at higher level Hartree-Fock such as MP2 calculation for testing the basis set are expected to supply more detailed informations of this study and would be worthwile further investigations.