CHAPTER V

THE SIMULATION OF ONE LiCl MOLECULE IN LIQUID HYDROXYLAMINE

Unfortunately, the limitation of this study has been encountered because liquid hydroxylamine is very easily decomposed at room temperature when it is a pure solvent, and a salt like LiCl will enhance this decomposition [36, 37]. There will, therefore, not be much use to simulate a higher salt concentration such as 1 M of LiCl in this solvent. Due to the decomposition, the experimental density of liquid hydroxylamine, one of the solvent properties needed to be handled for the simulation step like the two former systems performed in chapter III and IV, cannot be used at this high concentration. Moreover, experimental structural investigations of electrolyte solutions by means of x-rays and/or neutron diffraction seem hardly feasible and have never been attempted so far. Hydroxylamine, however, is usually handled in aqueous solution, or one of its salts, since these are more stable than free NH_2OH. Hence, the recommendation for the further investigation would be the simulation for mixtures of NH_2OH and H_2O with LiCl.

The system of one LiCl molecule in NH_2OH is studied as a model simulation only. The simulation with just one LiCl molecule (1 M LiCl consists of six LiCl molecule in 216 NH_2OH) has been performed for the methodical reasons, (i) because the influence of a counter-ion can be seen, (ii) because the system become an electroneutral system and can be performed Ewald correction for all molecules (also solvent), which cannot be done for a non-neutral system as Li^+-NH_2OH or Cl^--NH_2OH the same applies for epsilon corrections.

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Monte Carlo Simulation

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The simulation was carried out for 1 Li^+ + 1 Cl^- + 216 NH_2OH at the same conditions *e.g.* density (1.204 g cm^{-3}) and temperature (305 K) *etc.* as in the Li^+-NH_2OH (chapter III) and Cl^--NH_2OH (chapter IV) systems. The Li^+-Cl^- potential model was taken from Bopp P. *et al.* [44]. The cut-off radius for short-range interactions was the half of box-length corresponding to the density and amount of particles in the simulation. The Ewald summation of all $1/r$ interactions (ion-ion, ion-dipole *etc.*) was introduced to the simulation. The experimental dielectric constant of

hydroxylamine solvent outside boxes for energy-correction was used (ε = 77.7). Two million configurations, this system reached to the energetic equilibrium, and then one million configurations were kept to evaluate the characteristic values of the simulation.

Solvation structure of LiCl in NH_2OH

For results of simulation, structural informations have been collected from the sampled configurations in the form of RDFs and their running integration. Their characteristic data are collected in Table 5.1 and the most relevant RDFs, Li^+-O, Li^+-N, , Li^+-H_O, Li^+-H_N, Cl^--O and Cl^--H_O are displayed in Figures 5.1(a)-(f), respectively.

Table 5.1 Characteristic values of 1 LiCl RDFs (first coordination shell).

RDF	r_{max}	r_{min}	n
Li^+-O^{**}	2.00	2.15(5.0)	*
	2.30	2.50(0.0)	7.0
Li^+-N	*	3.45(0.0)	7.0
Li^+-H_O	1.60	1.70(0.0)	7.0
Li^+-H_N **	2.95	*	*
	*	4.3(0.1)	7.0
Cl^--O	3.19	3.9(0.0)	5.0
Cl^--H_O	2.30	3.00(0.0)	5.0

the height of the peak are shown in parenthesis

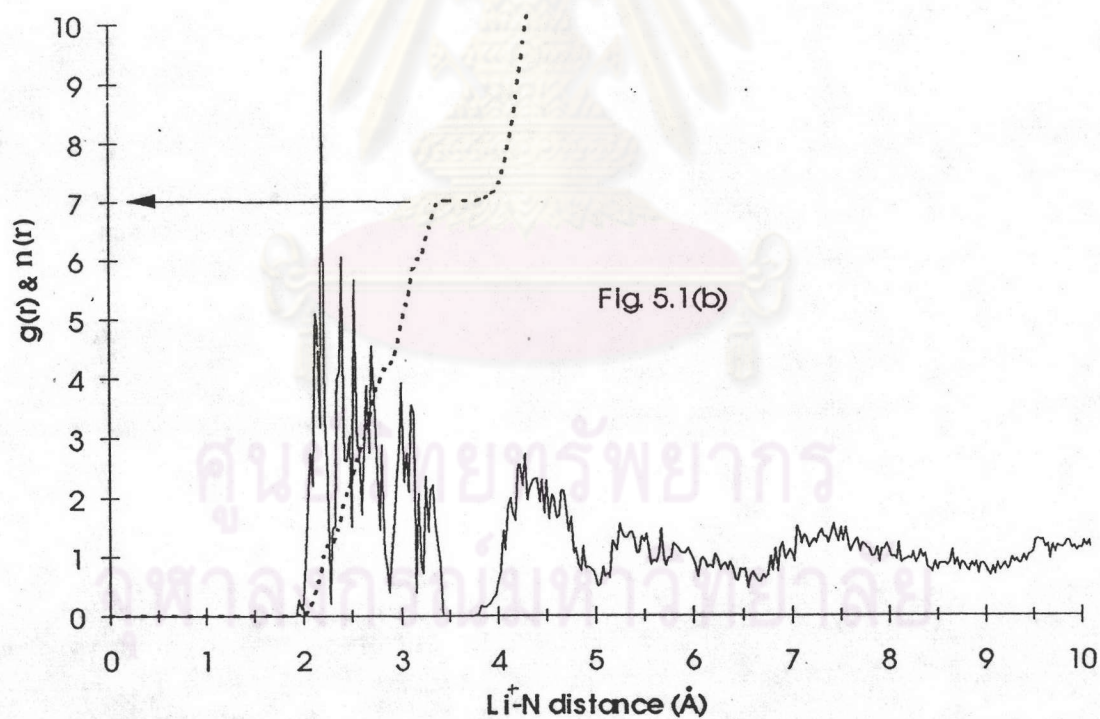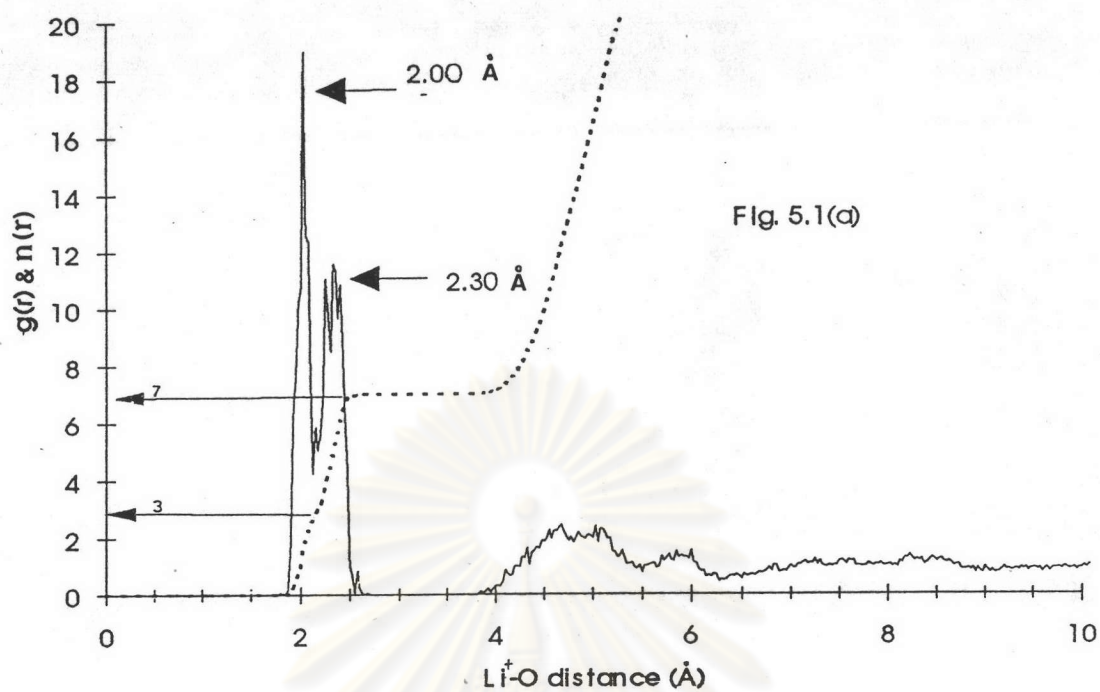*) The RDF location is not clearly defined,   **) split peak

Figure 5.1 Radial distribution functions and its integration (dotted line)
(a)-(d) Li^+-O, Li^+-N, Li^+-H_O, Li^+-H_N
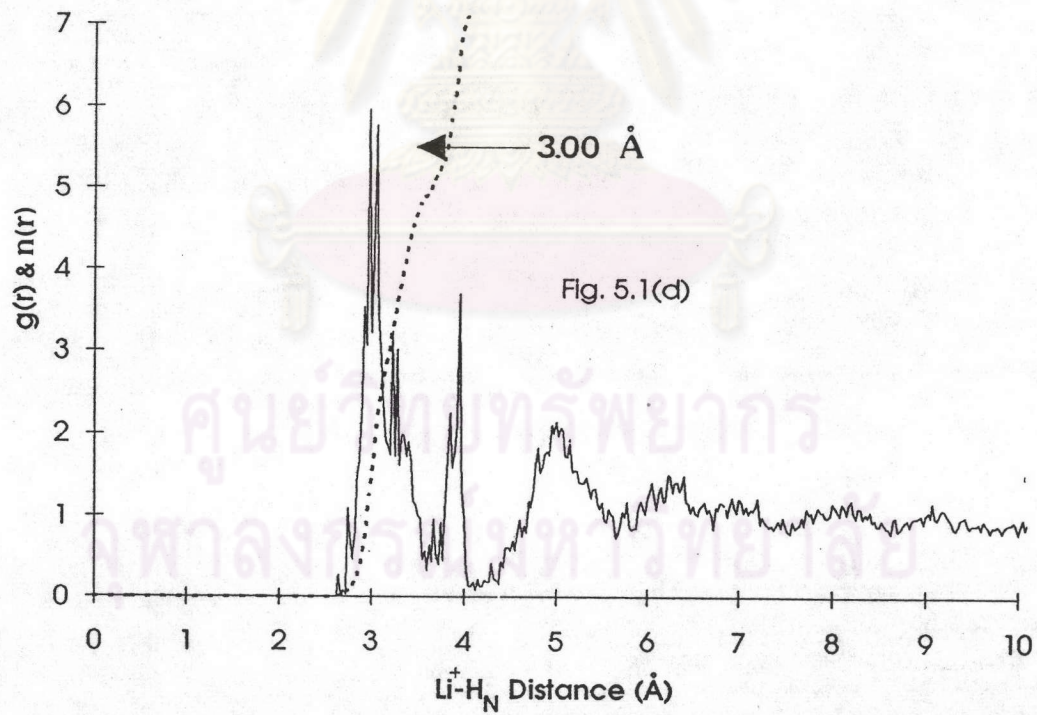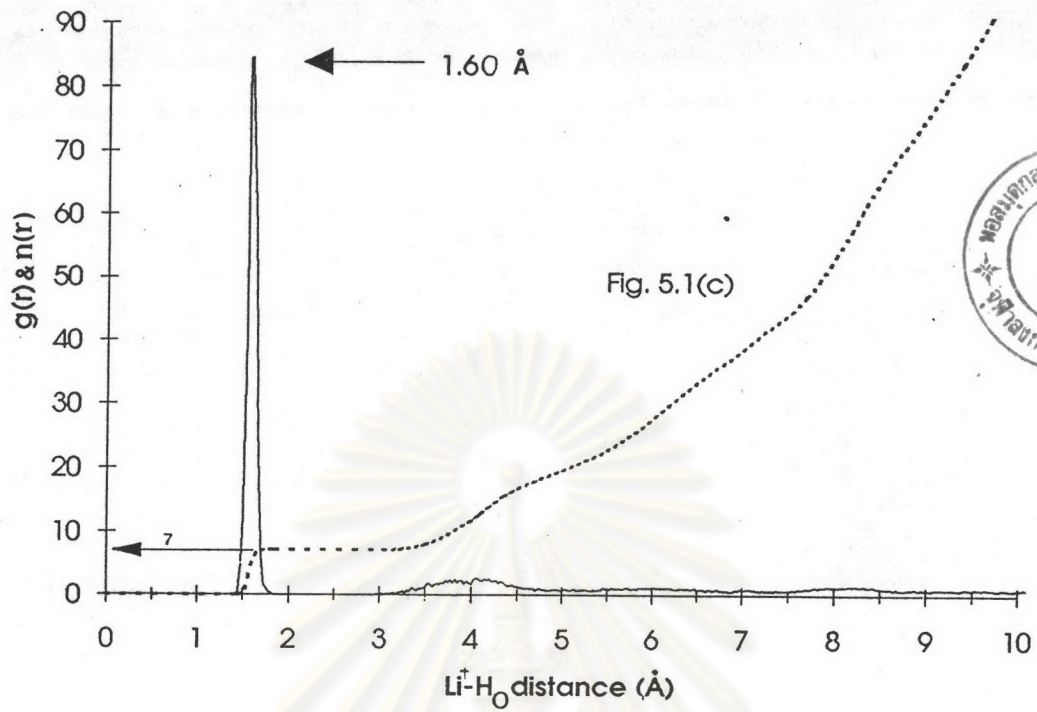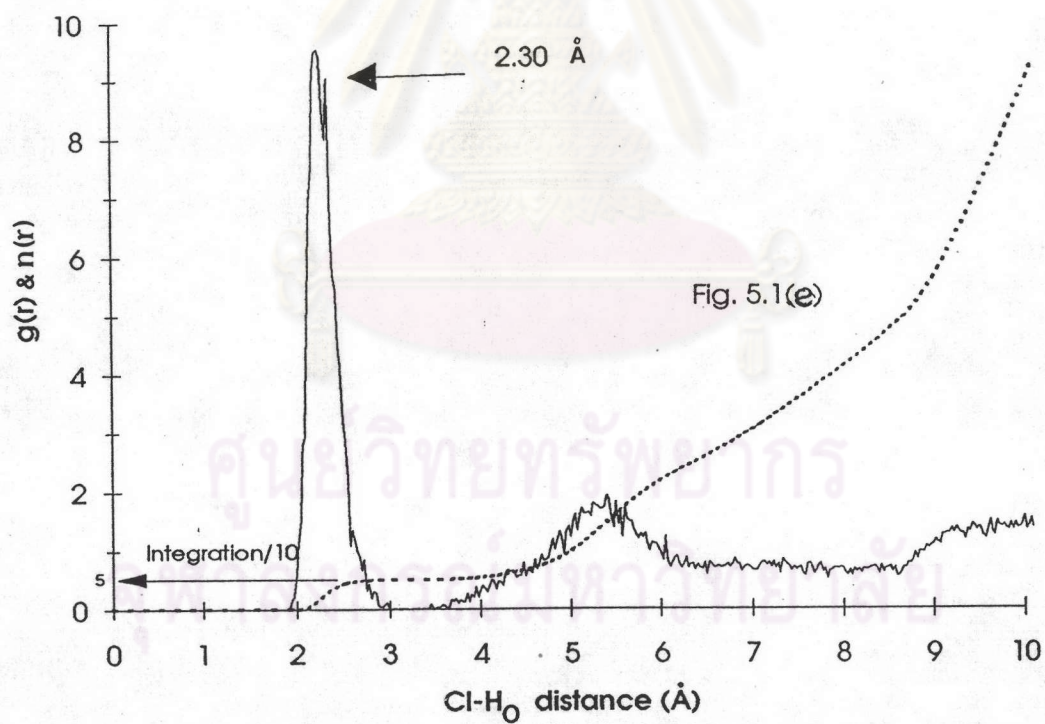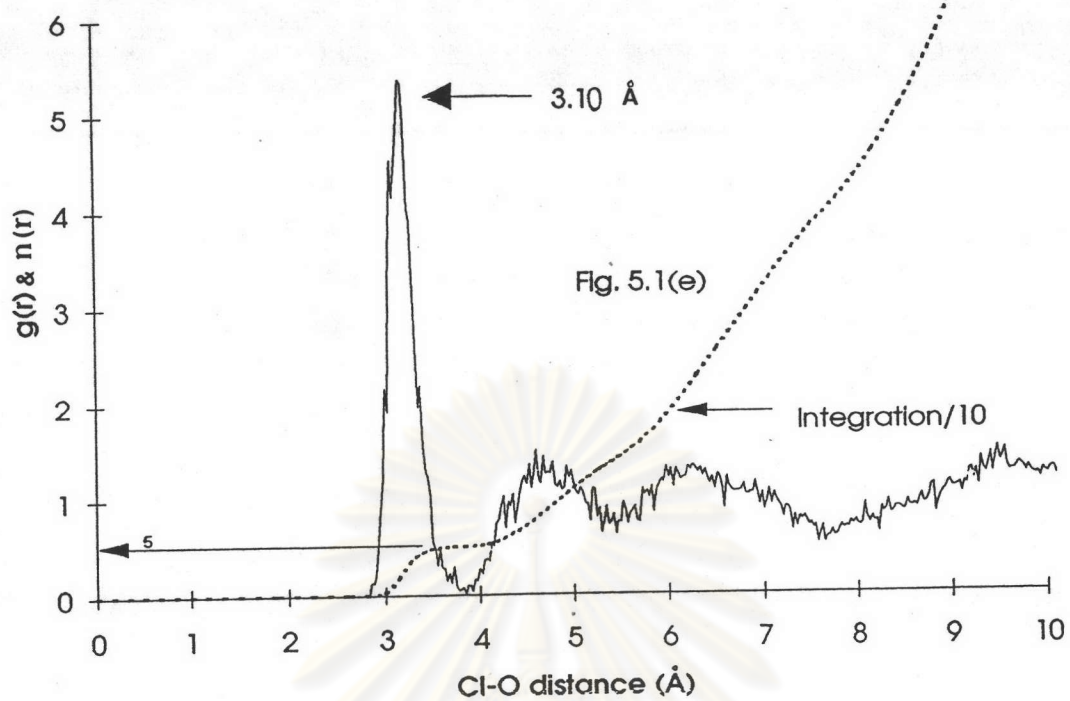(e)-(f) Cl^--O, Cl^--H_O

Figure 5.1 (continue)

Figure 5.1 (continue)

According to the results of this study, it can be seen that the position of all first maximum peaks (r_{min}) reported in Table 5.1 and Figures 5.1 did not change significantly by comparing with RDFs in Figures 3.3(a)-(b) and 4.4(a)-(d) for Li^+ and Cl^-, respectively. It is implied that the molecular orientation of the solvent around Li^+ and Cl^- within first solvation shell should be conformed to the results of previous chapters. The Li^+-O and Li^+-H_O RDFs in Figures 5.1(a) and (c) is similar to Li^+-O and Li^+-H_O RDF in Figures 3.3(a) and (c) respectively. Two maximum peaks for Li^+-O RDF pronouncing within the first shell are located at 2.0 and 2.3 with which the total running integration number 7 can be seen. This can be implied that the Li^+-O interaction is not influenced by the Cl^--NH_2OH interaction. The unfavorable location of Li^+-H_O in Figure 5.1(c) is still occurred with H_O quite close to the cation. The Li^+-N and Li^+-H_N RDF in Figures 5.1(b) and (d) are not well defined but clearly show that the total integration number is 7. The position of the first maxima of Cl^--O and Cl^--H_O in Figures 5.1(e) and (f) are located at 3.20 and 2.30, respectively. Their corresponding-running integration numbers revealed that Cl^- is solvated by 5 solvent molecules. These occurrences can be explained in term of perturbation of the counter-ion to Cl^- in this simulation which is included by using Ewald summation correction for all long-range interactions, especially ion-ion and ion-dipole interactions.
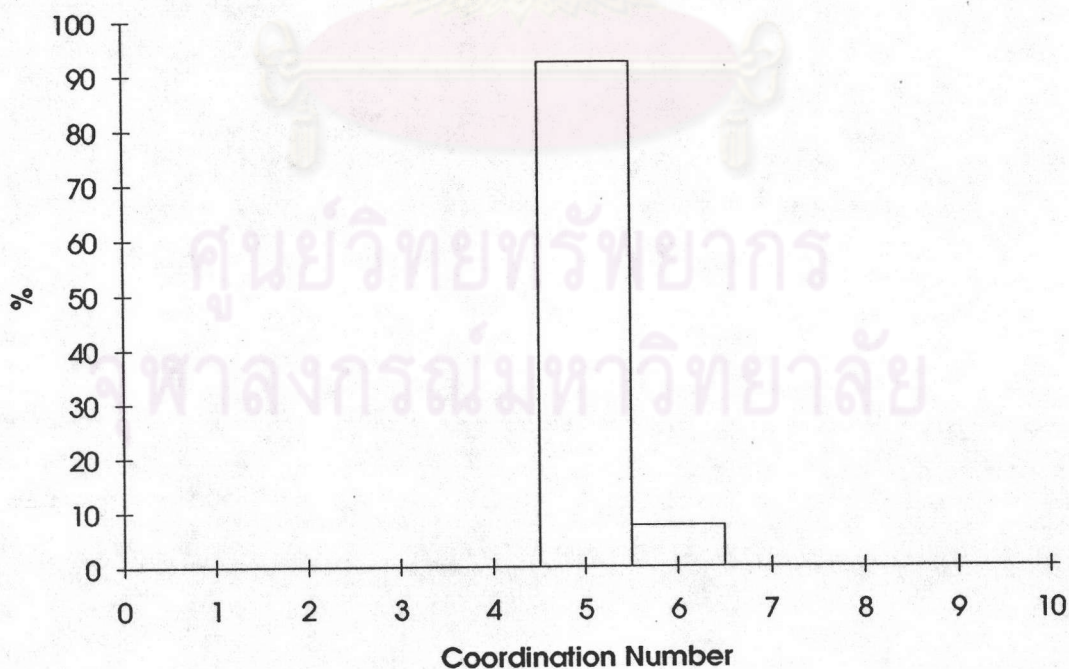

Figure 5.2 Coordination number distribution for Cl^--O up tp 4.0 Å

This explanation can be described by comparing the stabilization energy (ΔE_{FIT}) of Li^+-NH_2OH (-24.0 kcal/mol) and Cl^--NH_2OH (-11.0 kcal/mol) at the minimum energy. It is indicated that the Li^+-NH_2OH interaction is much stronger than the interaction of Cl^--NH_2OH, and thus all NH_2OH molecules of the first shell around Li^+ will not be influenced by Cl^-, on the other hand Cl^--NH_2OH is influenced by Li^+, and therefore leading to the first solvation structure of Cl^- as $[Cl(NH_2OH)_5]^-$. To illustrate the solvation of Cl^-, the coordination number distribution was performed and 5 solvated molecules surrounding the ion are found with more than 90 % of the distribution (see Figure 5.2). The finding of this study , leading to the conclusion that the counter-ion and long-range corrections introduced to the simulation are influenced to this system.