CHAPTER IV

THE SIMULATION OF ONE CHLORIDE ION IN LIQUID HYDROXYLAMINE

For this chapter, an analytical potential function of the 2-body interaction energy surface for Cl^--NH_2OH based on *ab initio* MO SCF calculations corrected by basis set super position error estimation has been constructed, and then the simulation of one chloride ion in 216 hydroxylamine molecules has been performed employed by this function.

Methods

4.1 Potential Function

4.1.1 Performance of ab initio calculations

From previous works [31-33, 37], ECP/DZP basis set has been proposed to serve for *ab initio* calculations in the study of computer simulations by which hydroxylamine molecules have played an important role as a pure solvent. For the *ab initio* energy evaluated by computational calculations, not only an acceptable compromise between computational effort and accuracy is considered but also an analogous work would also be concerned. During all SCF calculations on this work, therefore, the ECP/DZP basis set for hydroxylamine was followed through chapter III and the basis set for chloride was gotten from Steven et al [22].

The fully geometrical optimization was performed with the basis set mentioned above. The hydroxylamine geometry was taken from Tsunekawa [35]. By regarding about the molecular structure and chemical interaction, both H_O and H_N can bind with Cl^- and give an unequally minimum energy depending on atomic charges, +0.405 and +0.301 respectively, obtained by Mulliken population analysis [25]. Because results from the optimization can be used to interpret and imply the first solvation structure from the simulation. In this case, two Cl^--NH_2OH geometries (see position (a) and (b) in Figure 4.1) were optimized

The results are collected in Table 4.1 and compared to the corresponding values for hydroxylamine itself.
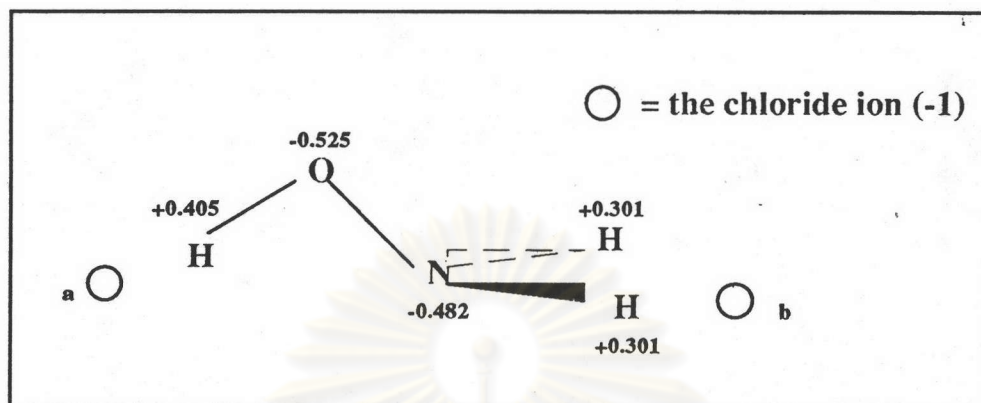

Figure 4.1 Atomic charges of NH_2OH and two positions of Cl^-(a & b) for optimization

Table 4.1: Fully optimized geometrical parameters (Å & degree) for NH_2OH

and $Cl^- - NH_2OH$ (a and b are the directions defined in Figure 4.1)

N-H	N-O	O-H	$Cl-H_O$	$Cl-H_N$	HNH	E (Hartree)	Note
1.017	1.453	0.962	---	---	107.1	---	Expt. [35]
1.005	1.406	0.946	---	---	106.9	-27.052	ECP/DZP [31]
							this work
1.008	1.398	0.976	2.142	4.610	106.2	-41.7823	(a)
1.009	1.424	0.946	4.818	2.401	101.5	-41.7778	(b)

From Table 4.1, results indicated that Cl^- coordinated to H_O gave the minimum energy. This can be explained due to strong bonding interaction. Therefore, within the first solvation shell, Cl^- should prefer to bond with H_O than H_N.

Table 4.2 Basis set superposition errors (Δe) for the two lowest lying

directions (a) and (b)

$r_{Cl^--H_i}$ (Å)	Δe (kcal/mole)	
	(a) Cl^--H_O	(b) Cl^--H_N
2.00	4.77	5.79
2.20	4.34	5.13
2.34*	4.09	-
2.45**	-	4.12
2.50	3.67	4.24
2.80	2.63	3.08
3.00	2.09	2.50
3.70	0.66	0.87
4.20	0.16	0.30
5.20	0.02	0.02
7.20	0.00	0.00

* the global minimum for direction (a) ** the global minimum for direction (b)

However, possible errors due to using the limited basis sets have been determined by performing basis set superposition error estimations. The results showing in Table 4.2 reveal that the interaction energies calculated by using this basis set gave a rough estimate of BSSE. The lowest stabilization energy ($\Delta E_{(a)}$) without BSSE correction calculated in this work is -14.81 kcal/mol, while the BSSE performed by the counterpoise correction proposed by Boys and Bernardi [24] about 27 % of $\Delta E_{(a)}$ was observed. This result indicated that an overestimated interactive energy in the SCF calculation could not be neglected, the counterpoise correction proposed must

be performed to improve energies for *ab initio* calculations. From this analysis, it could be expected that the corrected energy hypersurface of the Cl--NH2OH interaction would be more reasonable as an aspect of accuracy, and hence give a reliable intermolecular potential function.

In this work, about 508 *ab initio* corrected energies for the representative of the Cl^{-}-NH_2OH interactions have been generated by the geometrical selection regarding chemically representative conformations. An intermolecular pair potential function for this interaction has been derived based on these energies.

4.1.2 Fitting of the Intermolecular Pair Potential

The interaction energies ΔE_{SCF} , including BSSE corrections, have been fitted to an analytical potential of the form

$$\Delta E = \sum_{i=1}^{5} \frac{q_{Cl}q_i}{r_{Cl-i}} + \frac{A_{1i}}{r_{Cl-i}^{m}} + \frac{|A_{2i}|}{r_{Cl-i}^{n}} + |A_{3i}|\exp(A_{4i}r_{Cl-i}) \qquad (4.1)$$

where q denotes the partial charges of the atoms obtained by Mulliken population analysis, r the distances between Cl^{-} and the ith atom of hydroxylamine, and A_{1i}-A_{4i} the final fitting parameters. For various values of m and n, fitting have been performed by a non-linear Marquard-Levenberg algorithm, minimizing the squared differences between fitted and corrected SCF interaction energies. Weight factors have been introduced to give special emphasis to values near the global and local energy minima, values above 30 kcal/mole have been excluded. The best resulting function has been tested according to the procedure of Beveridge et al., through which additional SCF points have been included in the fitting procedure until the standard deviation remained constant and sufficiently small

4.2 Monte Carlo Simulation

A simulation was carried out by the program MC91 for a system consisting of one chloride ion and 216 hydroxylamine molecules at 305°C. Corresponding to the density of pure hydroxylamine of 1.204 g.cm^{-3} at this temperature, the elementary box length was set to be 21.464 Å, and half of this distance was chosen as cut-off radius for exponential terms. The starting configuration was chosen randomly, and equilibration was achieved after two million configurations. Other two million configurations were used for evaluating the structural informations in order to investigate the structure of the solution of this system.

Results and Discussion

4.3 Potential Function

According to the iterative procedure outlined in the previous topic, the best fit of the analytical corrected function of the form

$$\Delta E_{FIT} = \sum_{i=1}^{5} \frac{q_{Cl}q_i}{r_{Cl-i}} + \frac{A_{1i}}{r_{Cl-i}^4} + \frac{|A_{2i}|}{r_{Cl-i}^5} + |A_{3i}|\exp(A_{4i}r_{Cl-i}) \qquad (4.2)$$

was obtained. The standard deviation was about 10 %. The final fitting parameters of the function are summerized in Table 4.3.

Table 4.3 Final fitting parameters of the Cl⁻-NH₂OH potential function

i	A_1 (kcal.Å⁴. mol⁻¹)	A_2 (kcal.Å⁵. mol⁻¹)	A_3 (kcal mol⁻¹)	A_4 (Å⁻¹)
Cl⁻-H$_N$	-1421.366	1826.340	1281.625	2.01397
Cl⁻-N	-2849.103	8625.442	137.119	0.61021
Cl⁻-O	-2142.729	6523.416	0.73468	0.30704
Cl⁻-H$_O$	-898.081	1569.668	-0.4327	0.02244
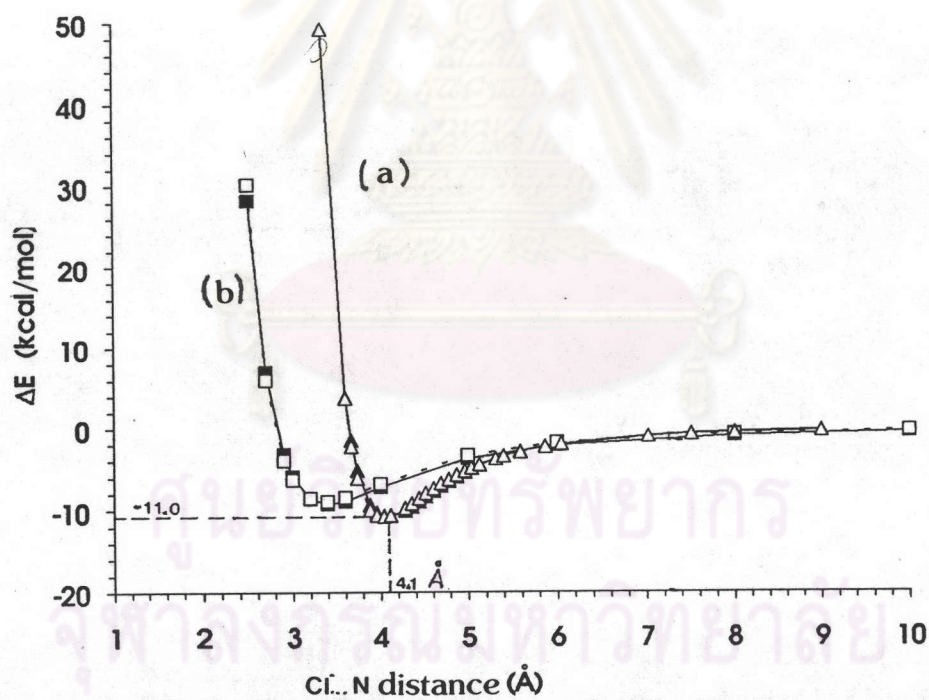
Figure 4.2 The corrected ΔE_{SCF} (solid line) and ΔE_{FIT} (dashed line) curves for the two lowest lying attractive forces (a) Cl⁻-H$_O$ and (b) Cl⁻-H$_N$
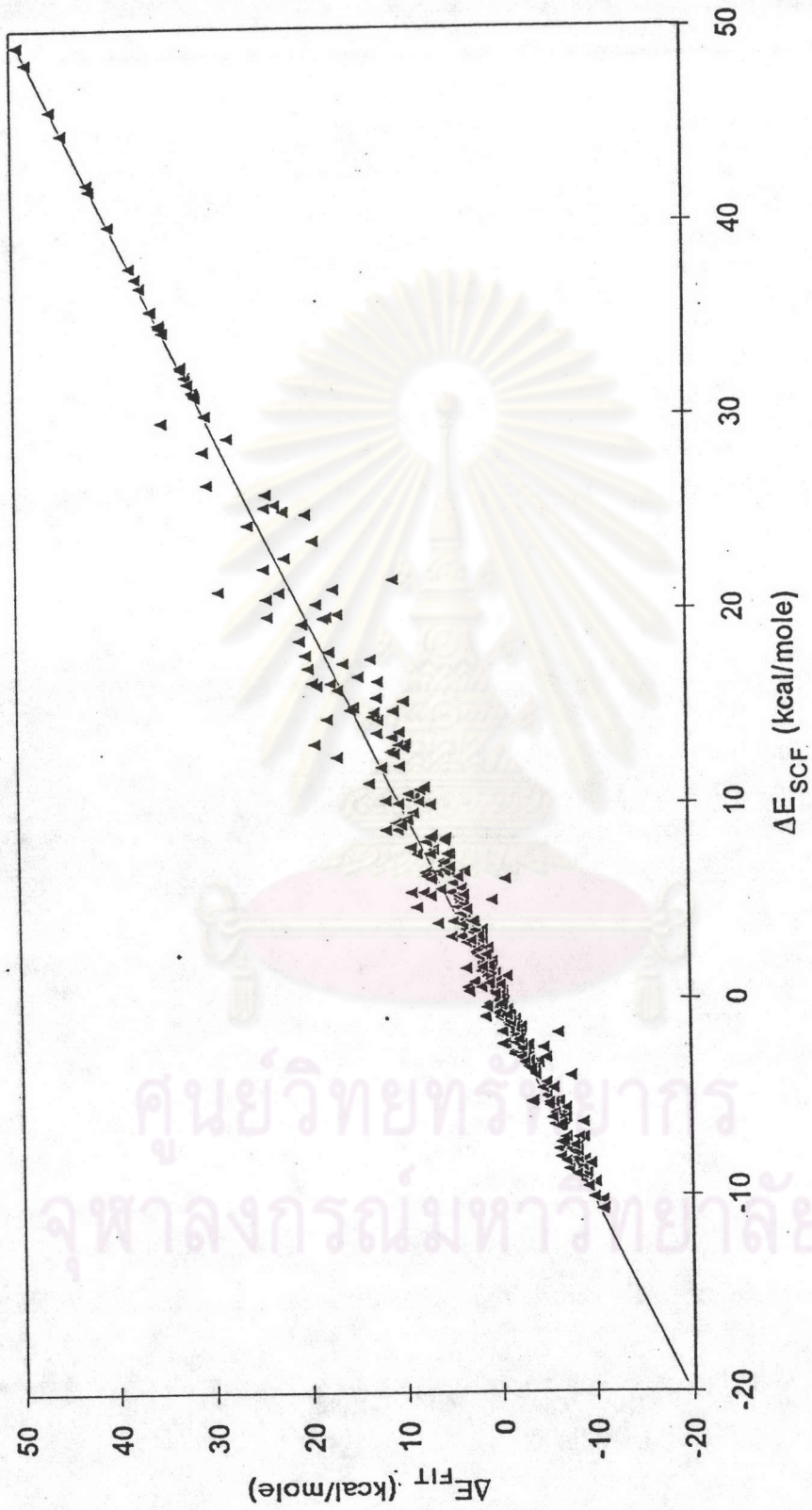
Figure 4.3 Comparison of interaction energies: potential fitted values (ΔE_{FIT}) versus *ab initio* calculated (ΔE_{SCF}) for all points in the set.

For Figure 4.2, the stabilization energy curves obtained from ΔE_{SCF} and ΔE_{FIT} for some directions are plotted versus the Cl⁻-N distance. A further illustration of the quality of the potential function is shown in Figure 4.3, where ΔE_{SCF} are plotted against ΔE_{FIT}. Perfect agreement would have implied a straight line of unit slope, and the scatter about this line gives a graphical measure of the quality of the function. It is then apparent that the fit is rather good for all important low lying energy points but gets gradually worse, as being moved towords the repulsive energy region.

Three-body effects could be expected not to play an important part due to the relatively weak interaction and the large equilibrium distance between ion and ligands, and have thus not been investigated.

4.4 Solvent structure of Cl⁻-NH₂OH system

The characteristics of the verious radial distribution functions (RDFs) are summerized in Table 4.4. The Cl⁻-O, Cl⁻-N, Cl⁻-H_O and Cl⁻-H_N RDFs are shown together with their corresponding running integration in Figures 4.4 (a), (b), (c), and (d), respectively.

Table 4.4: Characteristic radial distribution functions (first coordination shell)

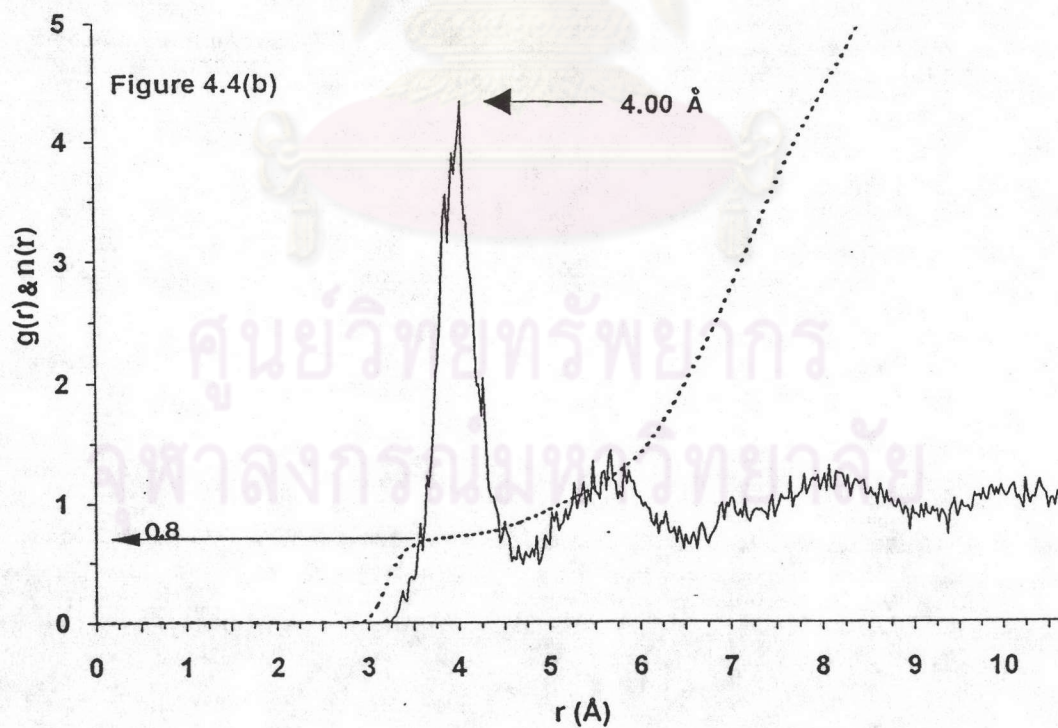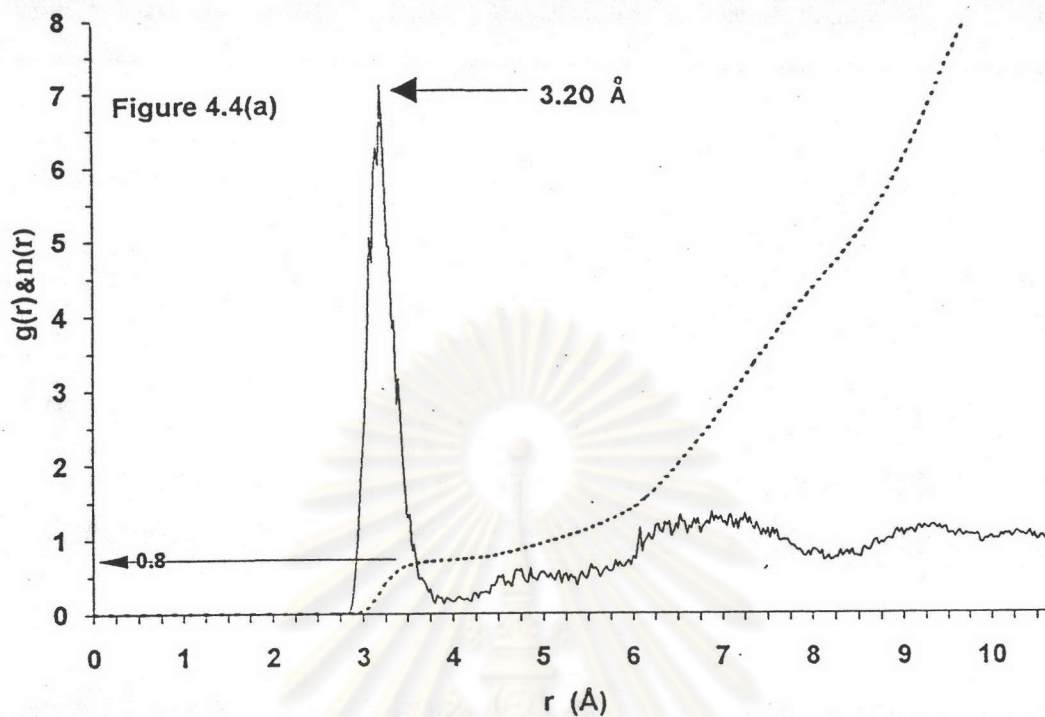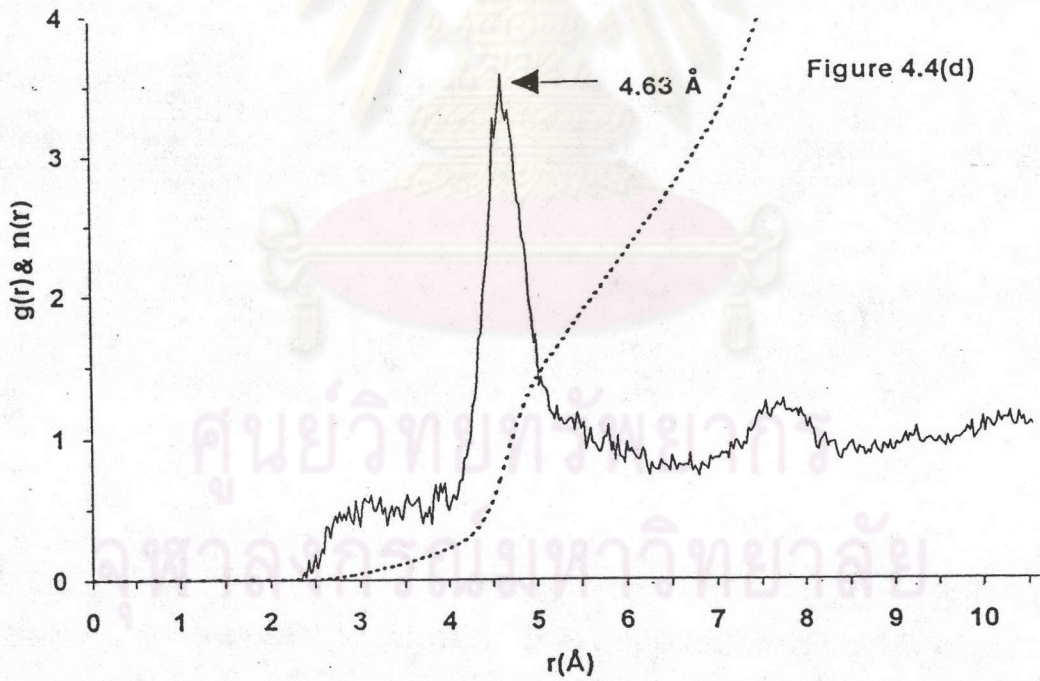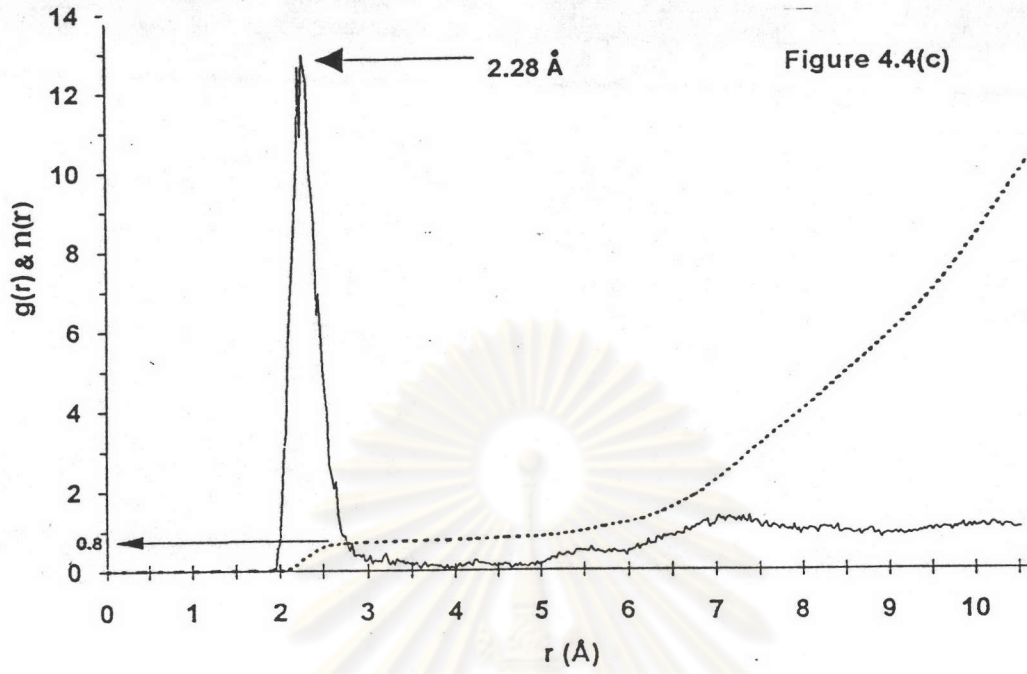| RDF	$r_{max.}$	$r_{min.}$	n
Cl-O	3.20	5.18	8
Cl-N	4.00	4.70	8
Cl-H_O	2.28	5.45	8
Cl-H_N	4.63	6.50	---

Figure 4.4 Radial distribution functions (solid line) for Cl-O (a), Cl-N (b), Cl-H$_O$ (c) and Cl-H$_N$ (d) and its integration (dotted line) devided by 10

Figure 4.4 (continue)

Figure 4.4(c)

Figure 4.4(d)

As the results displayed in Figure 4.4, the first maximum in Cl^--O and Cl^--N RDFs is located at 3.2 and 4.0 Å, respectively, indicating that binding of the solvent ligands to Cl^- occurs to O of NH_2OH. This is confirmed by the Cl^--H_O RDF, showing a single sharp peak at 2.28 Å. Integration of this peak as well as of the Cl^--O and Cl^--N RDFs leads to 8 NH_2OH molecules located in the first solvation shell of the chloride ion. The Cl^--H_N RDF shows a shoulder first, followed by larger peak extending up to almost 7 Å, where integration already reaches a value above 20. This RDF indicates that the angular orientation of the solvent molecules in the first shell is not uniform so that a few of the H_N can be found within the area of the first shell. The majority of H_N are located at the far side of the anion, where already some H_N of the outer region can be found.

Table 4.5 Comparison of characteristic values of RDFs for chloride ion in various solvents. r_{max} and n denote the positions of the first maxima in the ion-Atom and its integration numbers, respectively.

Ion	Solvent	Method	Atom	r_{max}	n
Cl^-	NH_2OH	MC (This work)	O	3.20	8.0
			N	4.00	8.0
Cl^-	H_2O	MC[38]	O	3.25	8.4
	H_2O	MD[39]	O	3.29	7.2
	NH_3	MD[41]	N	3.60	12.0
	CH_3NH_2	MD[41]	N	3.40	6-8.0
F^-	H_2O	MC[38]	O	2.60	4.1
	H_2O	MD[39]	O	2.67	5.8

The finding of the study in this system is also confirmed by comparing to the characteristic values of the previous reports [38,39,41]. The positions of the first mixima for the Cl⁻-O RDFs in water and in hydroxylamine together with the solvation number for Cl⁻ and F⁻ are compared in Table 4.5 with the results of Monte Carlo calculationes of Mezei and Beveridge [38] and MD simulations of Impey *et al.* [39] and found to be in good agreement although the solvent is different.

A second solvation layer is not well defined, but according to the Cl⁻-N and Cl⁻-O RDFs, nitrogen atoms are closer to the solvent molecules in the first shell than oxygens. Since all NH₂OH-NH₂OH RDFs are identical to those the pure solvent [31-33], this second layer can be considered rather as a perturbation of the bulk structure by the solvate and not as ion-oriented second solvation shell.