

## CHAPTER V

### Simulation of ZnCl<sub>2</sub> Solutions

#### 5.1 Results for Zn<sup>2+</sup>-Chloride Function Including NNLC

In order to compare simulation results to more experimental data, simulation had to be performed for "real" solutions, i.e. solutions with a known concentration of salts of the ion. In this case the chloride was chosen for this purpose. For the simulation one needs to construct a potential function used for describing the interaction between Zn<sup>2+</sup> and Cl<sup>-</sup>. For the zinc(II) ion - chloride potentials the same approximate 3-body corrections were employed as for the zinc(II) ion-water potential.

For the zinc(II) - chloride potential, the nearest neighbour ligand correction could be performed in exactly the same manner as for the zinc(II) - water potential, calculating the energy surface for a chloride ion in the field of a Zn<sup>2+</sup> carrying already one hydration water molecule. The Cl<sup>-</sup> - O distance then becomes the relevant geometrical parameter for the NNL correction term. The orientations for Cl<sup>-</sup> were almost the same as mentioned in the previous chapter except the substitution of the second water molecule with Cl<sup>-</sup>. The ab initio calculations were then performed for numerous different points using HONDO (7.0) program (40).

The energy data were then fitted to a function of the type :

$$\Delta E = \sum \left[ \frac{q_{Zn} q_{Cl^-}}{r} + A_1 \exp(-A_2 r) \right] + NNLC$$
$$NNLC = \sum_N (4.0 - r)^2 A_3 \exp(-A_4 R_{Cl^- O})$$

r ..... Zn<sup>2+</sup> - Cl<sup>-</sup> distance

N ..... number of neighbour ligand within selected spherical area

R<sub>Cl<sup>-</sup>O</sub> ..... distance of chloride ion and oxygen



where 4.0 is the cut-off limit, up to which the correction algorithm is invoked during the fitting procedure and later, during the simulation.

The resulting final parameters for the functions was :

$A_1$ :	60995.2
$A_2$ :	3.40713
$A_3$ :	5526.58
$A_4$ :	2.50965

The difference between NNL correction for water-water and chloride-water as neighbour ligands is visualized in figure 5.1 . It shows that in the case of chloride ligand, the function extend to somewhat larger distance than the case of two waters ligands.

Besides of zinc(II) - water and zinc(II) - chloride potential functions, there are additional potential functions, also needed in the simulation of aqueous  $ZnCl_2$  solutions. Some of these functions

- 1) water - water : MCY potential (27)
- 2) water - chloride : KPC potential (51)
- 3) zinc(II) ion - zinc(II) ion

can be suitably obtained from literature where potential 3) was constructed on the basis of ab initio calculations with the same DZV-ECP basis sets as used in the previous chapter, fitting the SCF energy data to the functional form :

$$\Delta E = \sum \left[ \frac{q_{Zn} q_{Zn}}{r} + \frac{A_1}{r^6} + \frac{A_2}{r^{12}} \right]$$

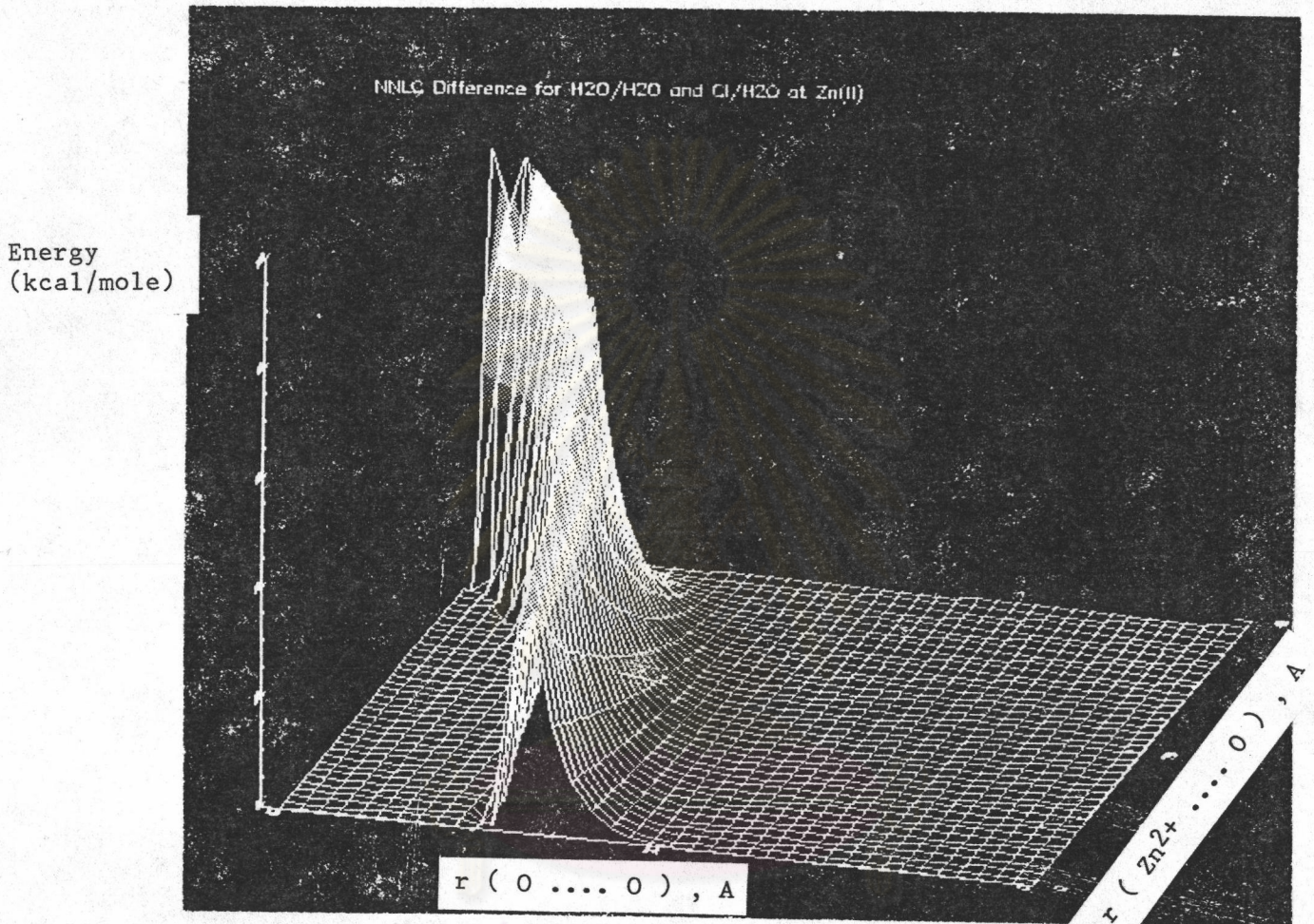
The final parameters are :

$A_1$ :	3531.2
$A_2$ :	669607.3

After having all potential functions, the simulations for zinc chloride solution in different concentrations could be carried out.



Figure 5.1 : Difference between NNL correction for water-water and chloride-water as neighbour ligands.



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## 5.2 Simulation of 1 M Aqueous $ZnCl_2$ Solution

For the simulation, the density of a one molal  $ZnCl_2$  solution was measured at the temperature 25 °C. From this density, the elementary box length for a simulation representing such a solution, consisting of 222 water molecules, 4 metal ions and 8 chloride ions, was evaluated to be 18.947 Å. The three molal and five molal  $ZnCl_2$  solutions used in the later simulations were also measured at the same temperature and these densities are given in table 5.1 including the elementary box lengths. In the Monte Carlo simulations, starting from random configurations, the Metropolis sampling algorithm (24) and periodic boundary conditions were employed. A spherical cut-off for exponential terms of half of the box length was introduced, and Ewald corrections were performed for all long-range interactions. The simulation temperature was set to 25 °C.

The simulations were performed on the DEC 3100 RISC workstation using the MC90 Monte Carlo programme(52).

Table 5.1 : Densities and elementary box lengths for  $ZnCl_2$  solution at different concentrations.

Conc. $ZnCl_2$	$Zn^{2+}$	$Cl^-$	$H_2O$	Density ( $g/cm^3$ )	Box Length (Å)
1	4	8	222	1.10844	18.9472
3	12	24	222	1.29519	19.3265
5	20	40	222	1.47708	19.6226



### Results of 1 M ZnCl<sub>2</sub> solution

It took over 4 million configurations, until the average energy started fluctuating around a stationary value, indicating thermal equilibrium. During the sampling process it became clear that there exist several energetically almost identical configurations for the first shell of ligands around zinc ion. Exchange processes occur only after a large number of configurations so that sampling was performed over 5 million configurations to obtain a good picture of the average structure distribution.

The average number of nearest neighbours considered in the NNL correction was 3.12. For zinc chloride, not only water - water, but also chloride - water corrections are significant, the corresponding energies being 28.0 and 10.0 kcal/mole, respectively. As in the case of zinc(II) ion at infinite dilution, considerable differences were observed in the structures formed around the cations also in one molar chloride solution. The RDFs in figure 5.2 illustrate some of these features and in table 5.2 some of the characteristic values for these RDFs are listed.

Table 5.2 : Characteristic values for the radial distribution functions  $g_{\alpha\beta}(r)^*$  and the running integration number  $n_{\alpha\beta}$  of 1 M ZnCl<sub>2</sub>.

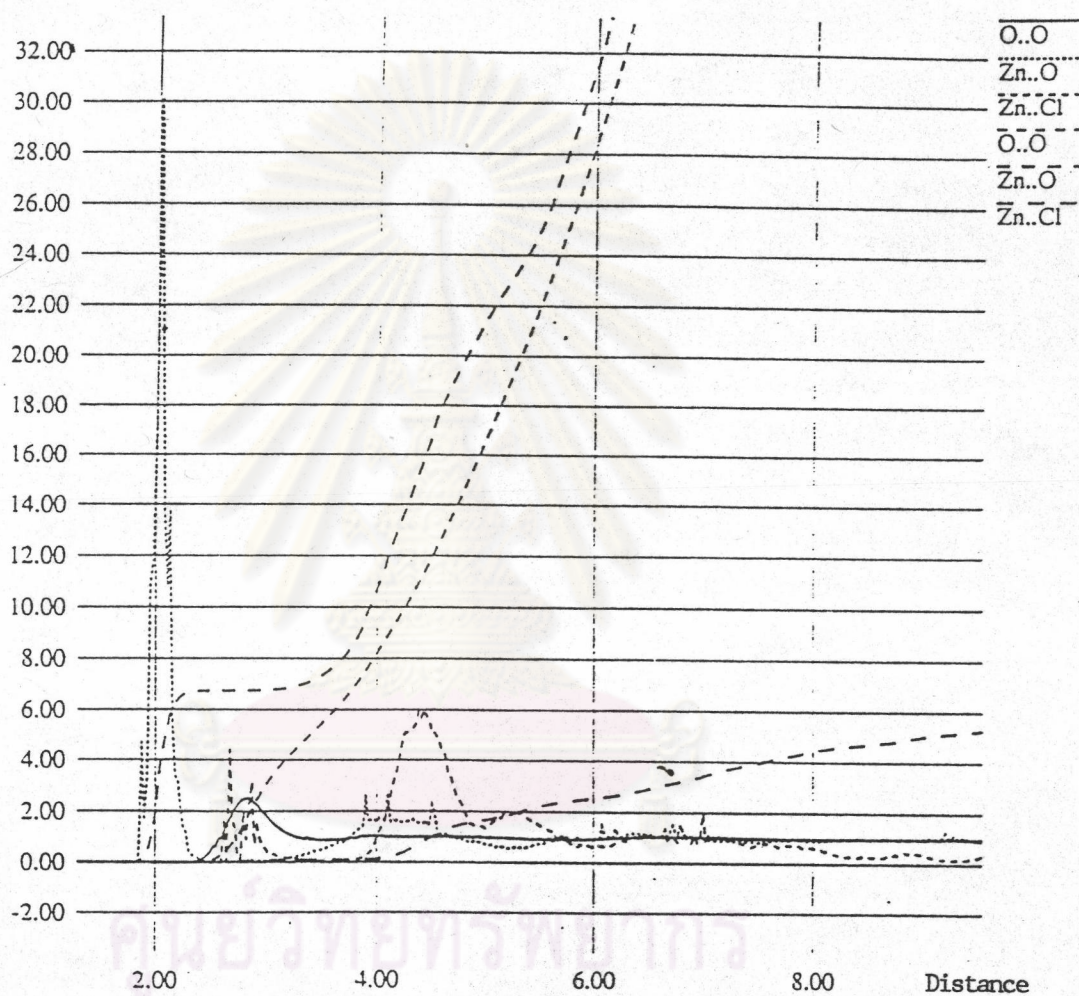
$\alpha$	$\beta$	$r_{M1}$	$r_{m1}$	$n_{\alpha\beta}(r_{m1})$	$r_{M2}$	$r_{m2}$	$n_{\alpha\beta}(r_{m2})$
Zn <sup>2+</sup>	O	2.05	2.40	6.8	4.80	4.80	16.7
Zn <sup>2+</sup>	Cl <sup>-</sup>	2.60	3.20	0.1	4.50	5.90	2.5

\*  $r_{Mi}$  and  $r_{mi}$  are the distances in Å where for the  $i$ th time  $g_{\alpha\beta}(r)$  is a maximum and a minimum, respectively.  $n_{\alpha\beta}(r_{mi})$  is the average coordination number of the  $i$ <sup>th</sup> coordination shell up to the distance of  $r_{mi}$ .



Figure 5.2 : Radial distribution functions and their integration for 1 M zinc chloride solutions.

### RDFs and INTEGRATION





The sharp peak in the  $\text{Zn}^{2+}\text{..O}$  RDF, located at 2.05 Å, contains a very significant shoulder peak at 2.15 Å. Integration to different limits of the peak leads to the following values : 2.10 Å / 5.0, 2.15 Å / 6.0, 2.5 Å / 6.75. Similar to the case of infinite dilution, 6 seems to be the preferred but not "ideal" hydration number for the first shell. The result is a "compromise", where some first-shell hydration waters are always in non-ideal position not far from the equilibrium distance, thus forming the shoulder peak in the RDF. For water molecules in the first shell, the coordination numbers are distributed as shown in the bar chart given in figure 5.3 where the values are :

up to 2.10 Å (local minimum)

3 water molecules : 4.8 %

4 water molecules : 22.7 %

5 water molecules : 39.7 %

6 water molecules : 32.1 %

7 water molecules : 0.5 %

up to 2.50 Å (separation between the first and the second shell)

6 water molecules : 25.1 %

7 water molecules : 74.9 %

The solvent-separated ion pairs are clearly represented by the large peak at 4.5 Å of the  $\text{Zn}^{2+}\text{..Cl}^-$  RDF in figure 5.2 . Analysing the number of chloride ions contained in this peak up to 4.5 Å, the following coordination number distributions results :

0 chloride ion : 38.5 %

1 chloride ion : 48.6 %

2 chloride ions : 12.8 %

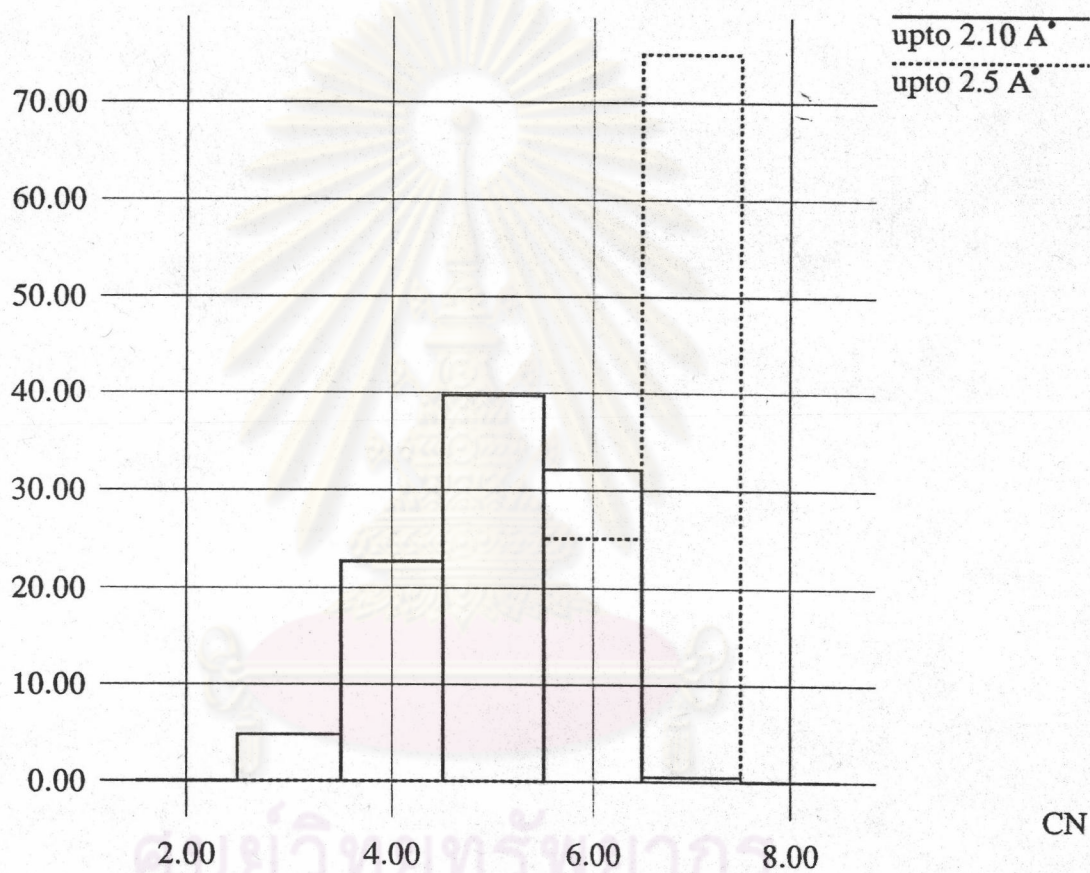
the bar chart illustrating this result is shown in figure 5.4 .



Figure 5.3 : Distribution of water coordination numbers (CN) in 1st hydration shell of  $Zn^{2+}$ , for 2 different limits (cf.text).

### Coordination Number Distribution Zinc Chloride 1M

Percent



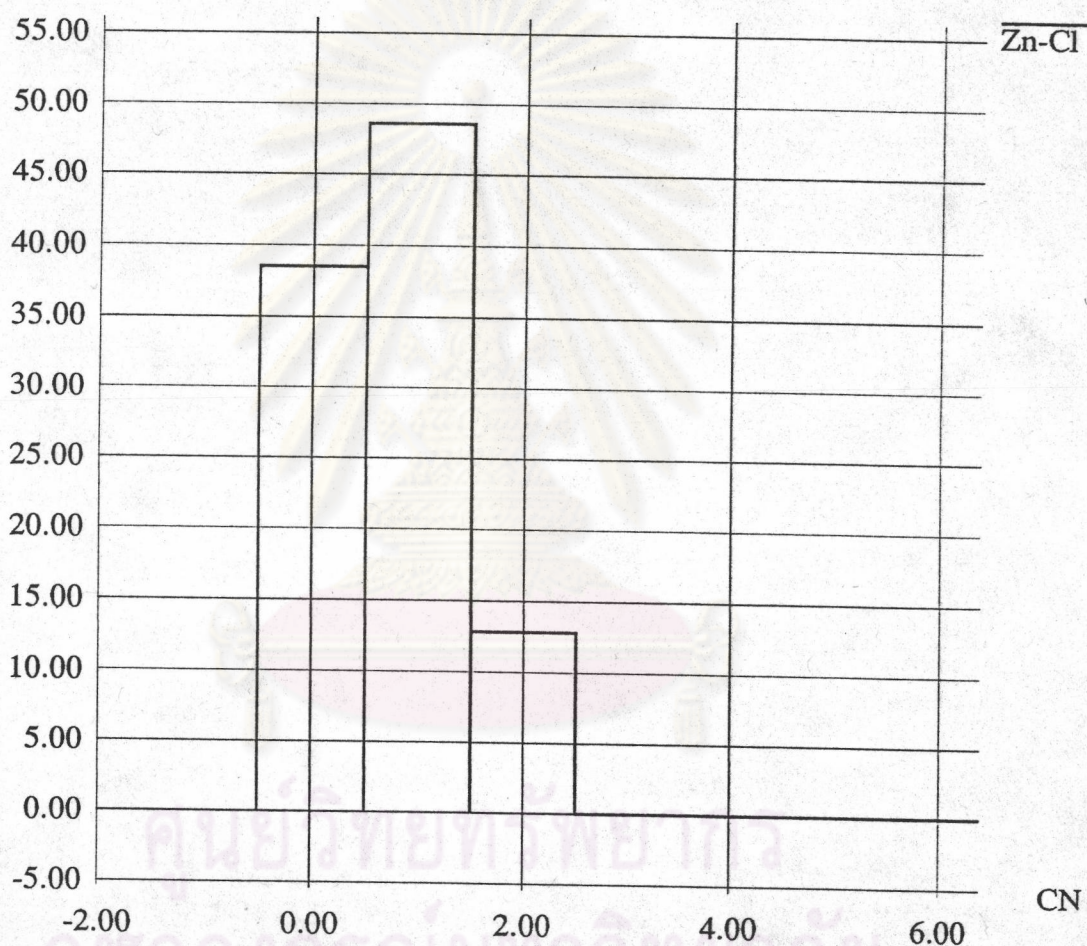
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Figure 5.4 : Distribution of chloride coordination numbers (CN) in 1st solvation shell of  $Zn^{2+}$  within limit 4.5 Å

### Coordination Number Distribution Zinc Chloride 1M

Percent





### 5.3 Simulation of 3 M Aqueous ZnCl<sub>2</sub> Solution

For these simulations, the density of three molal ZnCl<sub>2</sub> solutions used was 1.29519 g/cm<sup>3</sup> leading to the evaluated elementary box length 19.3265 Å as given in table 5.1. In the Monte Carlo simulations, the same conditions as the previous section were mentioned, i.e. starting from random configuration, Metropolis sampling algorithm (24) and periodic boundary conditions were employed. A spherical cut-off for exponential terms of half of the box length was introduced, and Ewald corrections were performed for all long-range interactions. The simulation temperature was set to 25 °C. The system consisted of 12 Zn<sup>2+</sup>, 24 Cl<sup>-</sup> and 222 water molecules.

The simulation was performed on the DEC 3100 RISC workstation using the MC90 Monte Carlo programme(52).

#### Results of 3 M ZnCl<sub>2</sub> Solution

The simulation was performed until the average energy reached the thermal equilibrium and then the sampling procedure was done for another 3 million configurations to obtain a good picture of the average structure distribution. The average number of nearest neighbours resulting in the NNL correction was 1.88 and the correction energies for Zn<sup>2+</sup> - H<sub>2</sub>O and Zn<sup>2+</sup> - Cl<sup>-</sup> were 12.9 and 4.7 kcal/mol, respectively. The Zn<sup>2+</sup>-O and Zn<sup>2+</sup>-Cl<sup>-</sup> radial distribution functions (RDFs) for 3 M ZnCl<sub>2</sub> are shown in figures 5.5 and 5.6, together with the corresponding running integrations, and the characteristic values of RDFs and average coordination numbers are listed in table 5.3.



Table 5.3 : Characteristic values for the radial distribution functions  $g_{\alpha\beta}(r)^*$  and the running integration number  $n_{\alpha\beta}$  of 3 M  $ZnCl_2$ .

$\alpha$	$\beta$	$r_{M1}$	$r_{m1}$	$n_{\alpha\beta}(r_{m1})$	$r_{M2}$	$r_{m2}$	$n_{\alpha\beta}(r_{m2})$
$Zn^{2+}$	O	2.00	2.05	5.5	4.75	5.00	14.5
$Zn^{2+}$	$Cl^-$	2.65	3.20	0.7	4.60	5.80	3.2

\*  $r_{Mi}$  and  $r_{mi}$  are the distances in Å where for the  $i$ th time  $g_{\alpha\beta}(r)$  is a maximum and a minimum, respectively.  $n_{\alpha\beta}(r_{mi})$  is the average coordination number of the  $i$ th coordination shell up to the distance of  $r_{mi}$ .

The  $Zn^{2+}..O$  RDF displays a very sharp peak for the first hydration shell of the ion, centred around 2.0 Å. Integration over this peak leads to a number of 5.5 water molecules. For water molecules in this first shell, the coordination numbers are distributed as following :

4 water molecules : 8.33 %

5 water molecules : 45.33 %

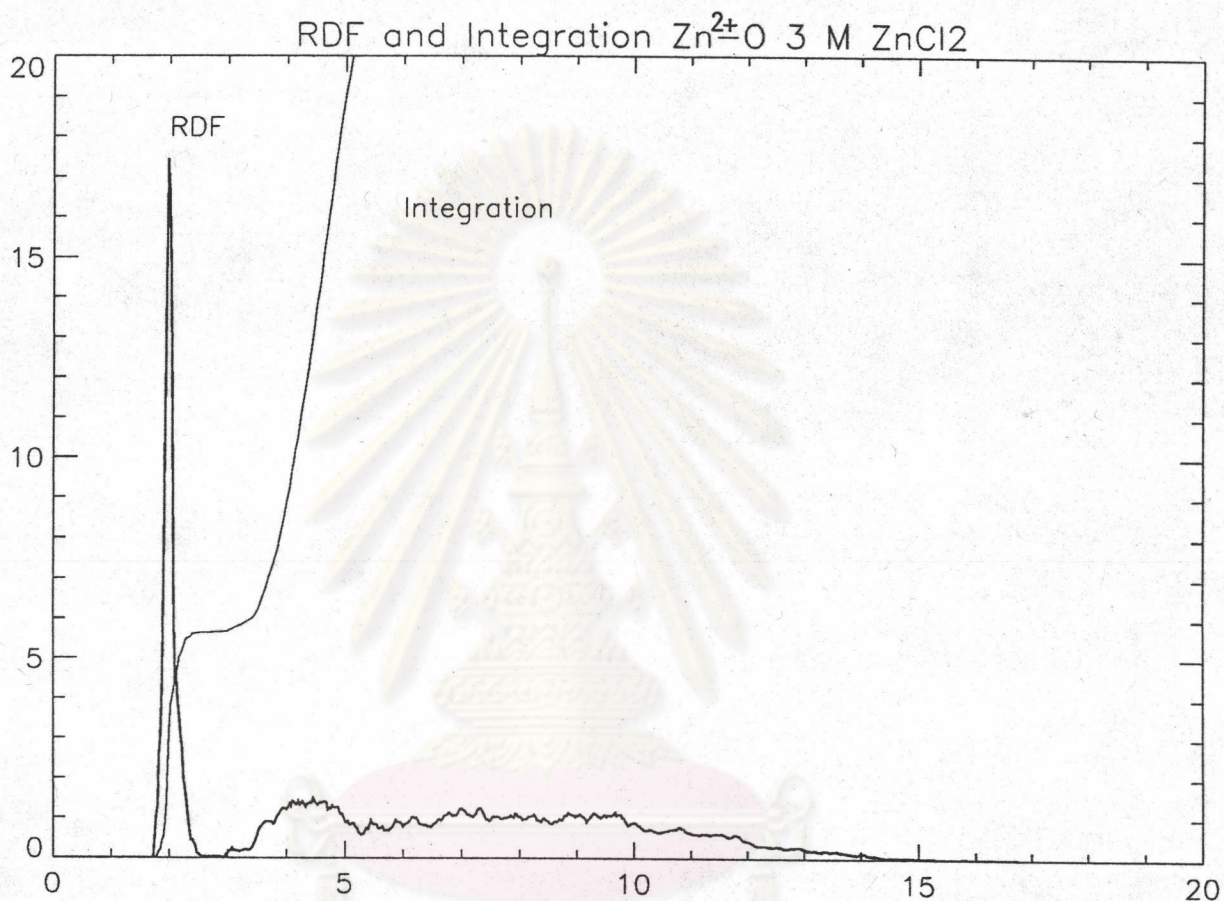
6 water molecules : 21.33 %

7 water molecules : 25.00 %

the bar chart illustrating this result is shown in figure 5.7 .



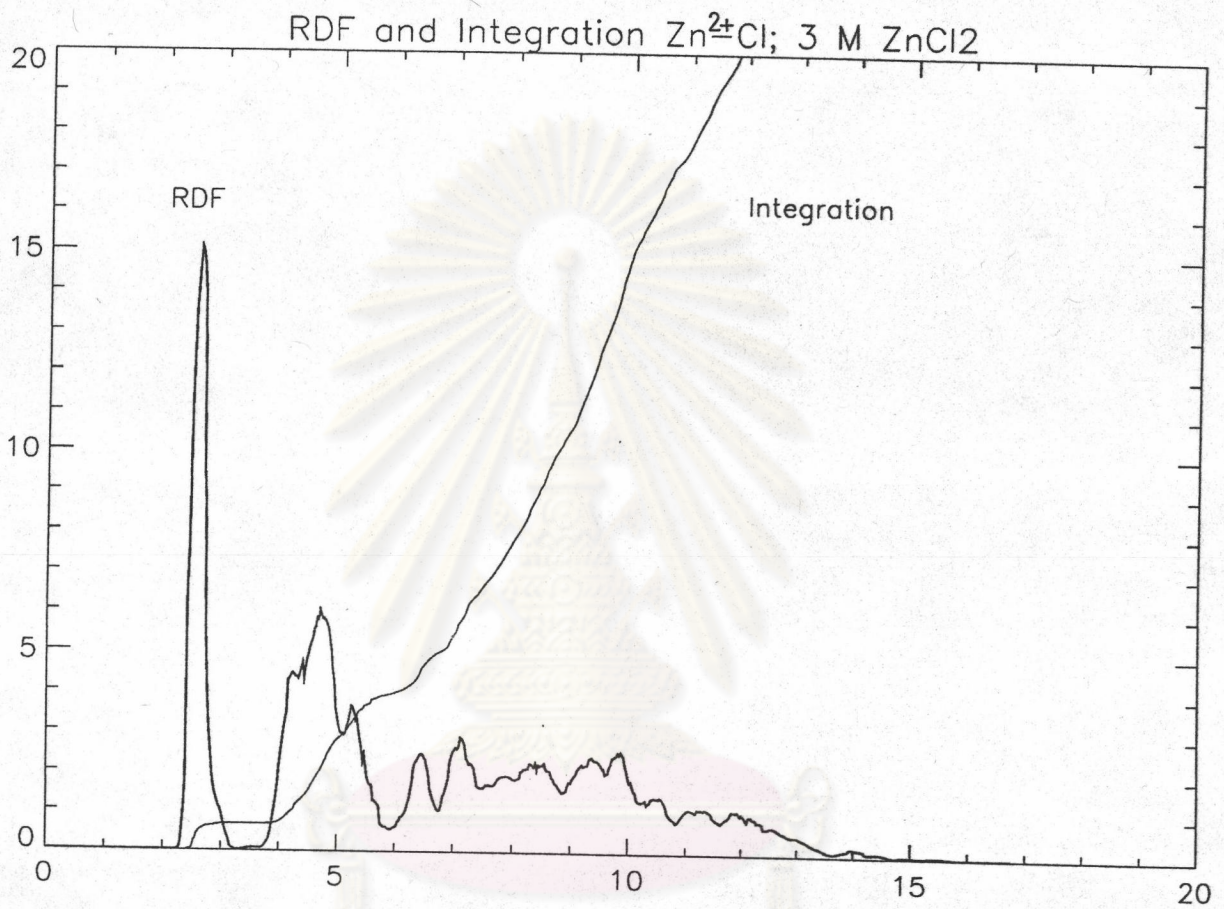
Figure 5.5 : Zn-O radial distribution functions and its running integration for 3 M ZnCl<sub>2</sub> solution.



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Figure 5.6 :  $\text{Zn}^{2+}\text{-Cl}^-$  radial distribution functions and its running integrations for 3 M  $\text{ZnCl}_2$  solution.



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The  $\text{Zn}^{2+} \dots \text{Cl}^-$  RDF shows a sharp peak at 2.65 Å . Integration over this peak up to 3.20 Å leads to the coordination number 0.7 . Analysing the number of chloride ions contained in this peak up to 3 Å gives the following coordination number distribution results :

0 chloride ion : 42.65 %

1 chloride ion : 49.02 %

2 chloride ions : 8.33 %

the bar chart illustrating this result is also shown also in figure 5.7 .

In order to illustrate the structure of the first coordination sphere of  $\text{Zn}^{2+}$  , ligand distribution plots were produced from the simulations' history files by normalizing all ligand positions to the origin, transformation of one water ligand to the positive x axis and analogous relocation of all other ligand positions within a radius of 3.5 Å around the central ion. For the plots, the oxygen positions in the xy-, xz- and yz- planes within a thickness of 0.5 Å were searched, and the probability to find another ligand is shown in the 3-D figures 5.8-5.11 , in which the  $\text{Zn}^{2+}$  lies in the center of the displayed plane.

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Figure 5.7 : Distribution of water and chloride ion coordination numbers (CN) in the 1st solvation shell of  $Zn^{2+}$  (water limit 2.5 Å., chloride ion limit 3 Å)

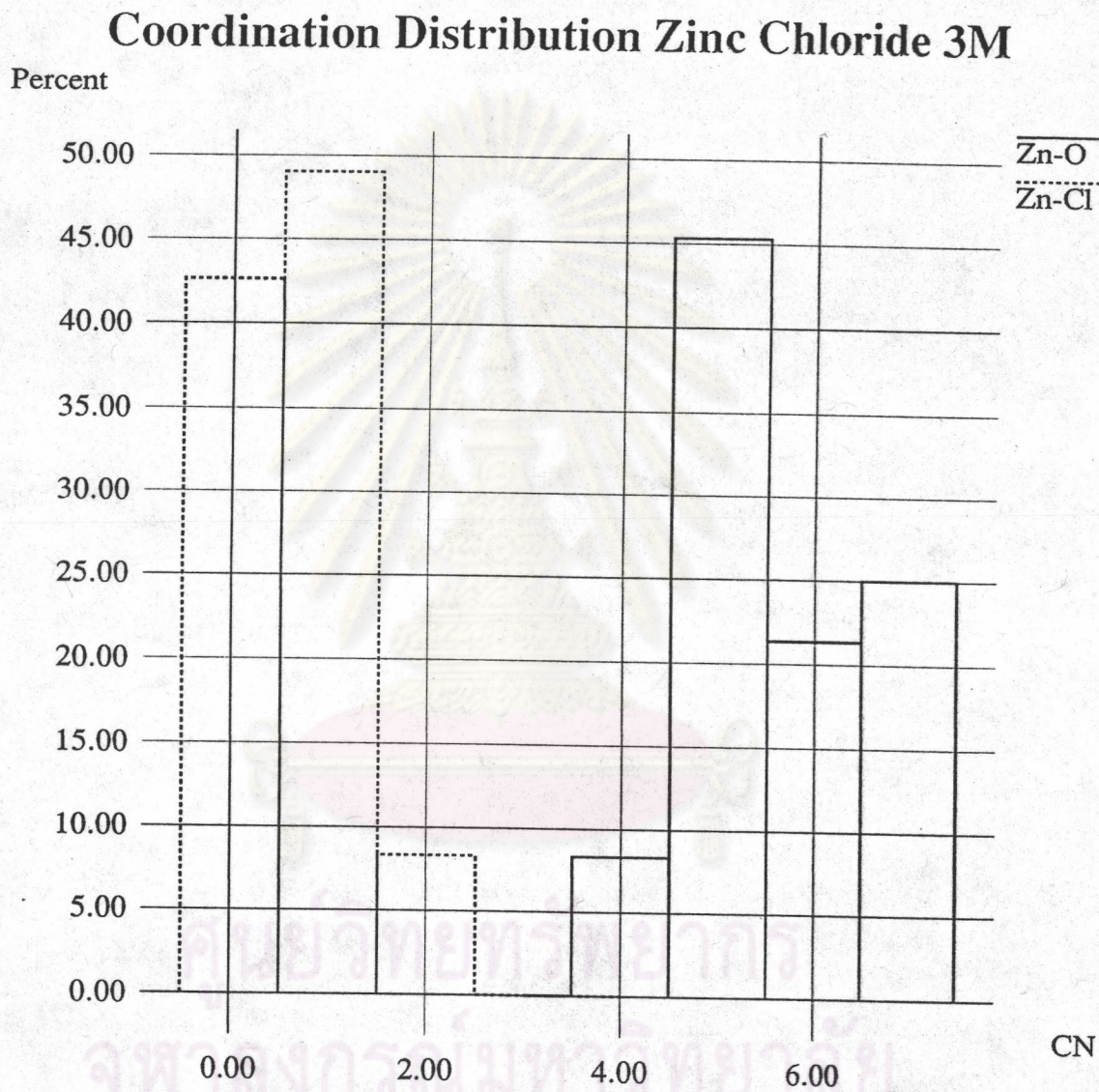
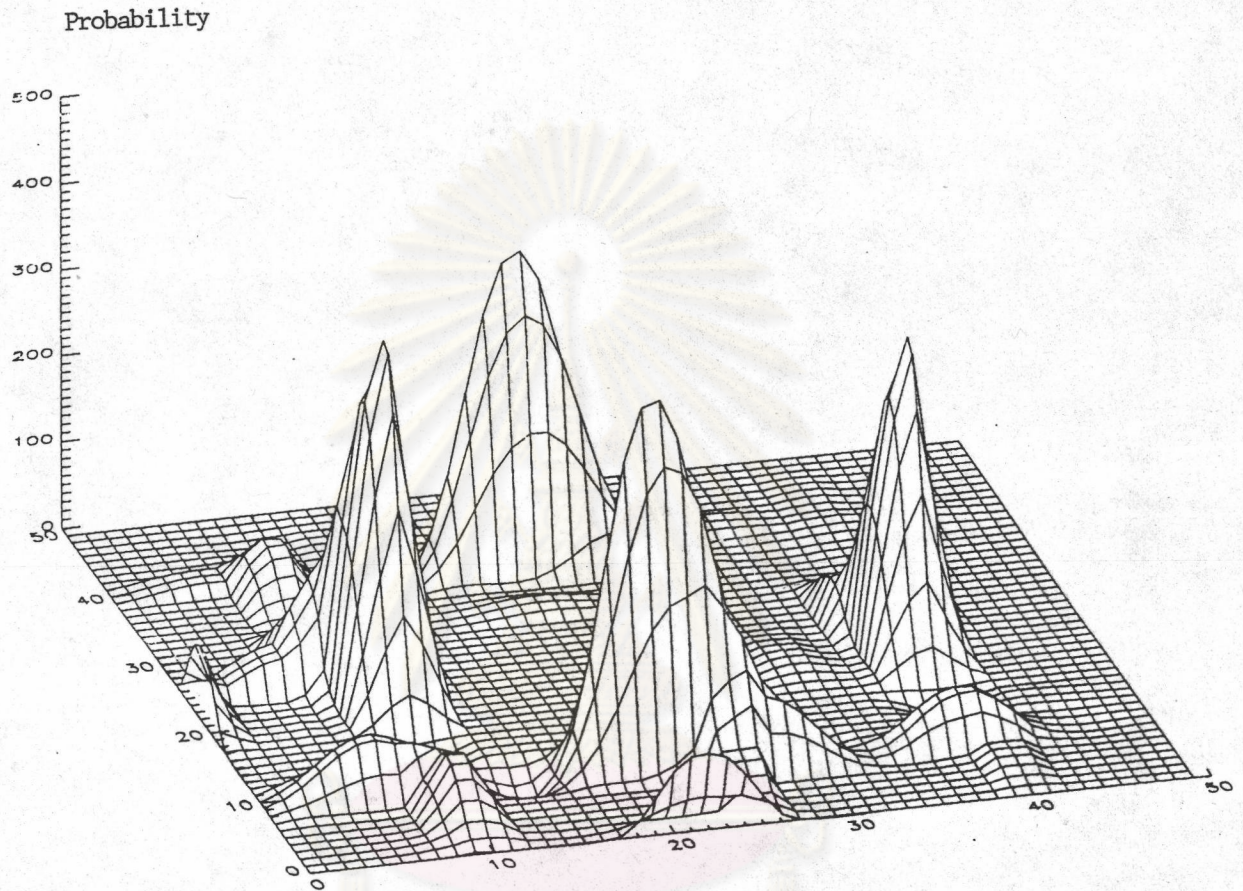




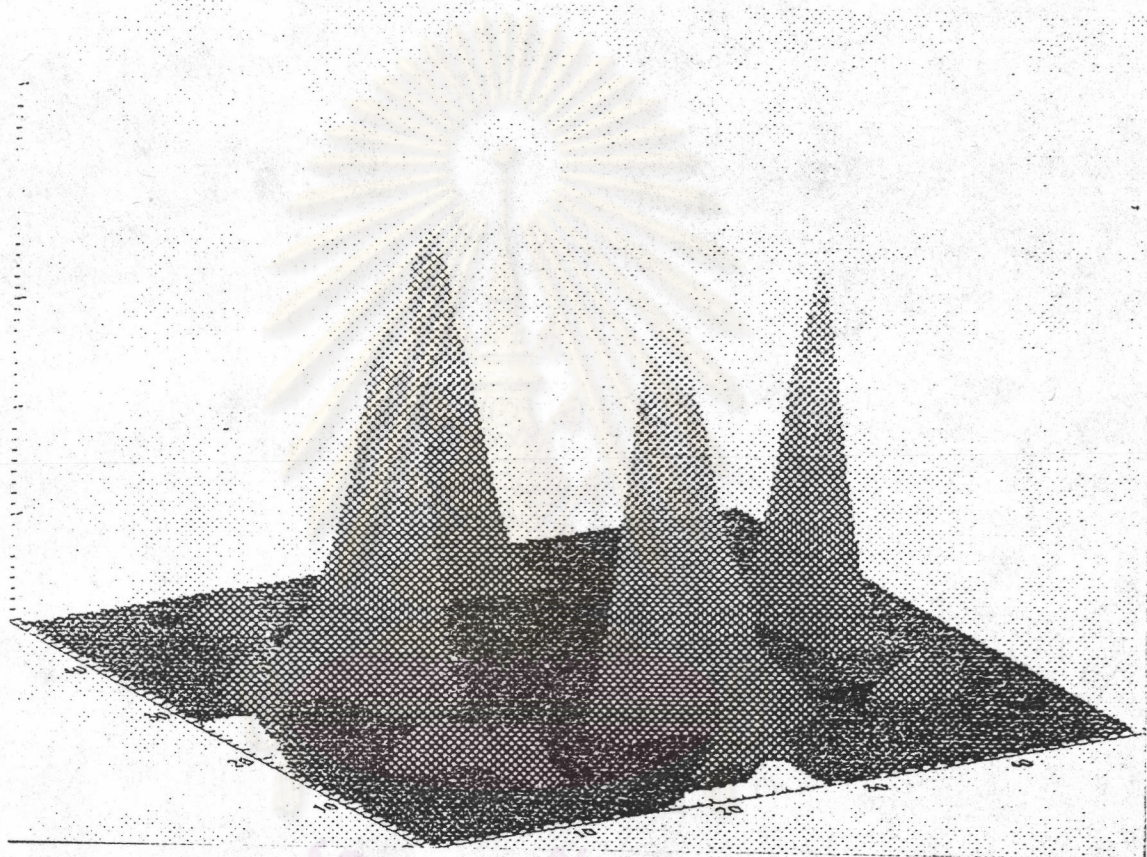
Figure 5.8 : Combined xy/xz/yz plane probability plots for water ligand positions in the first coordination sphere around  $Zn^{2+}$ , whose position is in the center of the displayed plane. (for 3 M  $ZnCl_2$  solution)



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Figure 5.9 : Combined  $xy/xz/yz$  plane probability plots for water ligand positions in the first coordination sphere around  $Zn^{2+}$ , whose position is in the center of the displayed plane. (for 3 M  $ZnCl_2$  solution)



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Figure 5.10 : Probability plots for water ligand in the first coordination sphere. The uppermost part shows plot contours, the middle part the 3-dimensional plot and the lower part areas of high probability (light) and low probability (dark). (for 3 M  $\text{ZnCl}_2$  solution)

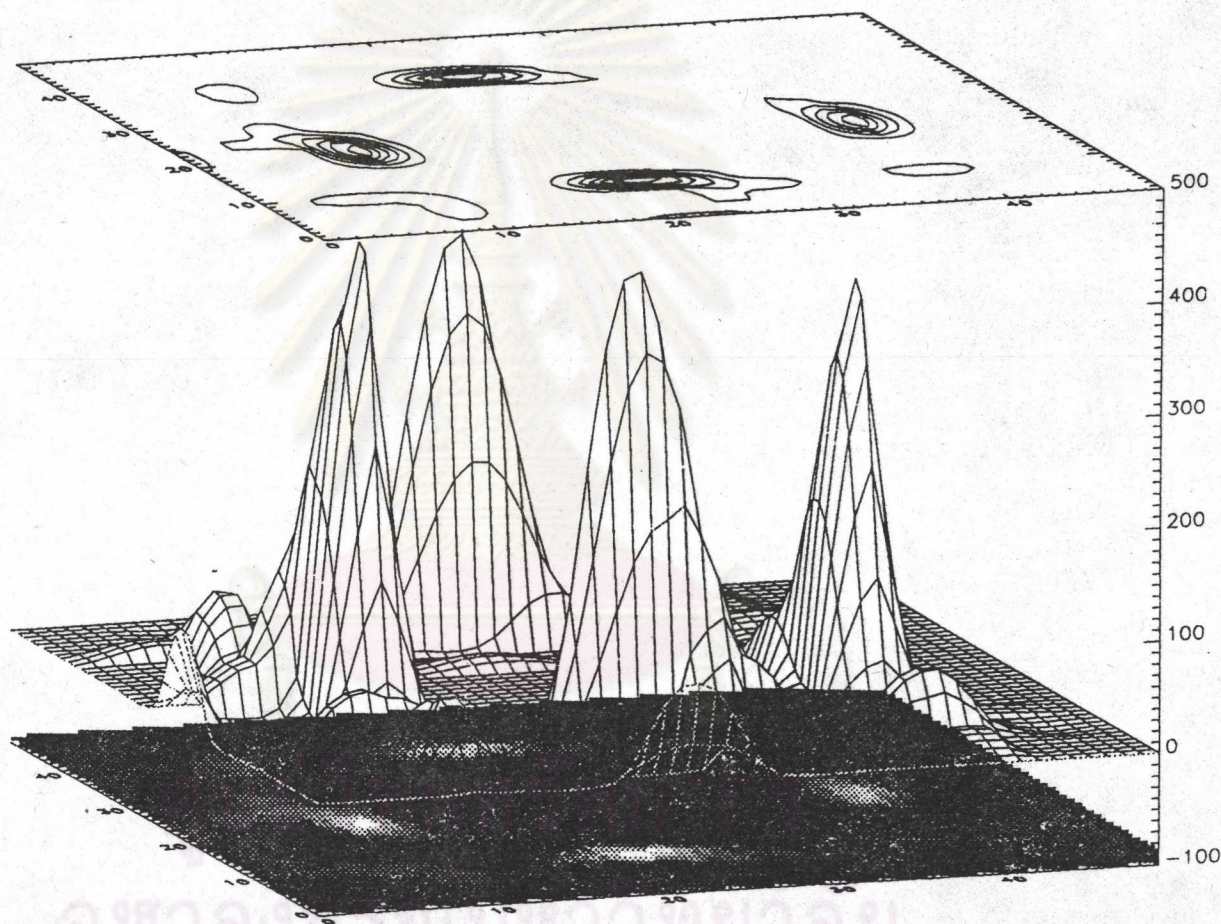
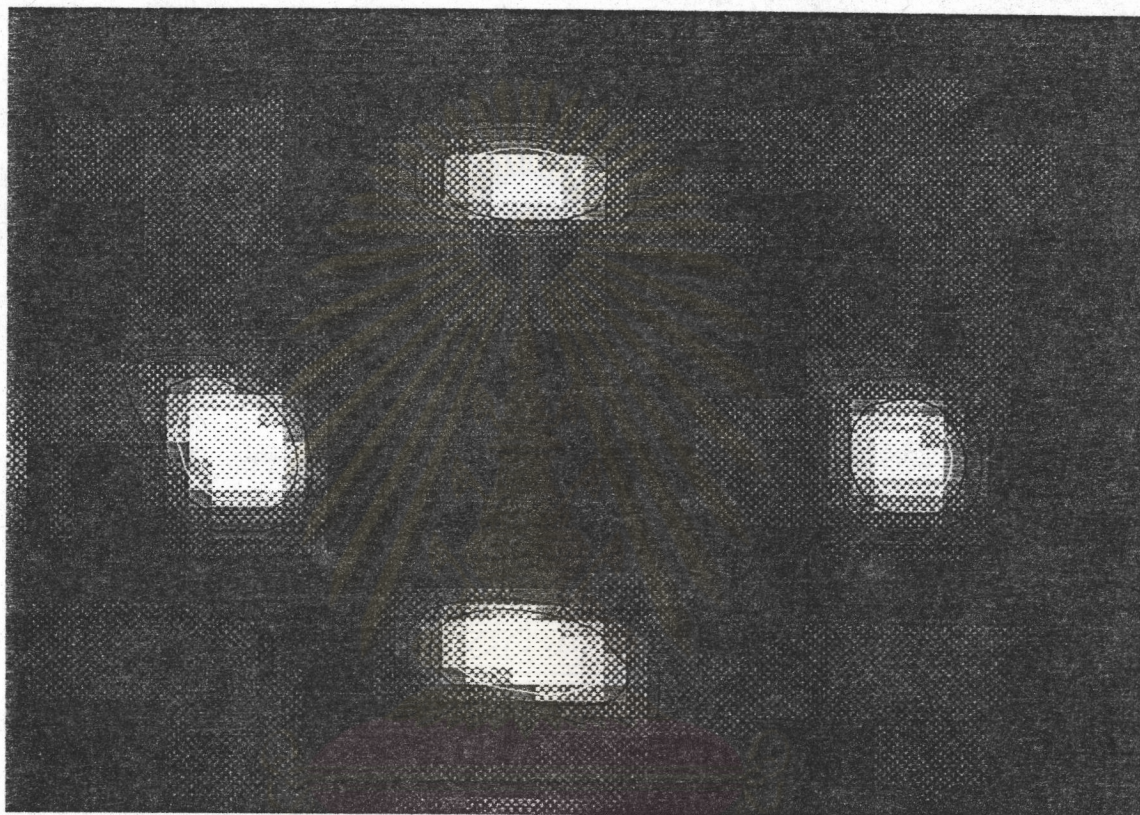




Figure 5.11 : The contour plot of probability of water ligands around  $Zn^{2+}$  whose position is in the center. (for 3M  $ZnCl_2$  solution)



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#### 5.4 Simulation of 5 M Aqueous ZnCl<sub>2</sub> Solution

In this simulation, the system consisting of 20 Zn<sup>2+</sup>, 40 Cl<sup>-</sup> and 222 water molecules was treated at the same conditions as in the previous section. The elementary box length was 19.6226 Å., the simulation temperature 25 °C. The simulation was also performed on the DEC 3100 RISC workstation using the MC90 Monte Carlo programme(52).

#### Results of 5 M ZnCl<sub>2</sub> Solution

The simulation was performed until the average energy reached the thermal equilibrium and then the sampling procedure was done for another 5 million configurations to obtain a good picture of the average structure distribution. The average number of nearest neighbours found in the NNL correction was 1.94 and the correction energies for Zn<sup>2+</sup> - H<sub>2</sub>O and Zn<sup>2+</sup> - Cl<sup>-</sup> are 16.38 and 6.52 kcal/mol, respectively. The Zn<sup>2+</sup>-O and Zn<sup>2+</sup>-Cl<sup>-</sup> radial distribution functions (RDFs) for 5 M ZnCl<sub>2</sub> were shown in figures 5.12 and 5.13, respectively, together with the corresponding running integrations, and the characteristic values of RDFs and average coordination numbers are listed in table 5.4 .

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Table 5.4 : Characteristic values for the radial distribution functions  $g_{\alpha\beta}(r)^*$  and the running integration number  $n_{\alpha\beta}$  of 5 M  $ZnCl_2$ .

$\alpha$	$\beta$	$r_{M1}$	$r_{m1}$	$n_{\alpha\beta}(r_{m1})$	$r_{M2}$	$r_{m2}$	$n_{\alpha\beta}(r_{m2})$
$Zn^{2+}$	O	2.00	2.40	5.1	(4.80)	(5.20)	(12.8)
$Zn^{2+}$	$Cl^-$	2.60	3.20	1.0	4.70	5.80	4.0

\*  $r_{Mi}$  and  $r_{mi}$  are the distances in Å where for the  $i$ th time  $g_{\alpha\beta}(r)$  is a maximum and a minimum, respectively.  $n_{\alpha\beta}(r_{mi})$  is the average coordination number of the  $i$ th coordination shell up to the distance of  $r_{mi}$ . Parentheses indicate uncertainty in assignment.

In the Zn-O RDF, the first hydration shell of  $Zn^{2+}$  is represented by a sharp peak at 2.0 Å. Integration over this peak up to 2.40 Å leads to coordination number 5.1. Evaluation of the  $Zn^{2+}$ -O coordination number distribution up to 2.50 Å gave the following results :

4 water molecules : 20.00 %

5 water molecules : 42.47 %

6 water molecules : 32.53 %

7 water molecules : 5.00 %

the bar chart illustrating this result is shown in figure 5.14 .

The  $Zn^{2+}..Cl^-$  RDF shows a sharp peak at 2.60 Å, accompanied by a smaller at 2.80 Å. Integration over both peaks up to 3.20 Å leads to coordination number 1.0. Analysing the number of chloride ions contained in this peak up to 3 Å gives the



following coordination number distribution results :

0 chloride ion : 24.97 %

1 chloride ion : 50.83 %

2 chloride ions : 24.20 %

the bar chart illustrating this result is also shown in figure 5.15 .

Figure 5.12 :  $Zn^{2+}$ -O radial distribution function and its running integration for 5 M  $ZnCl_2$  solution.

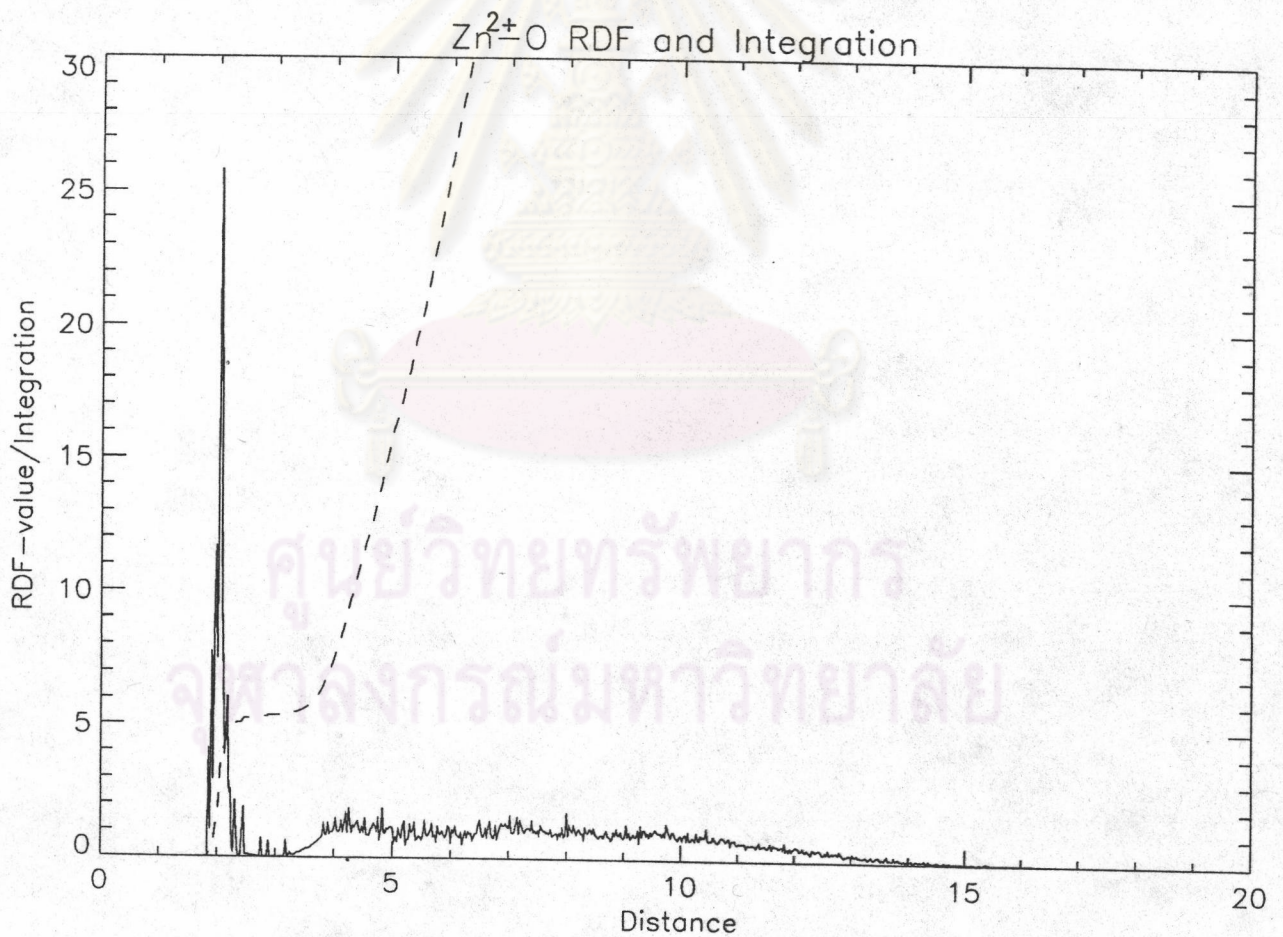
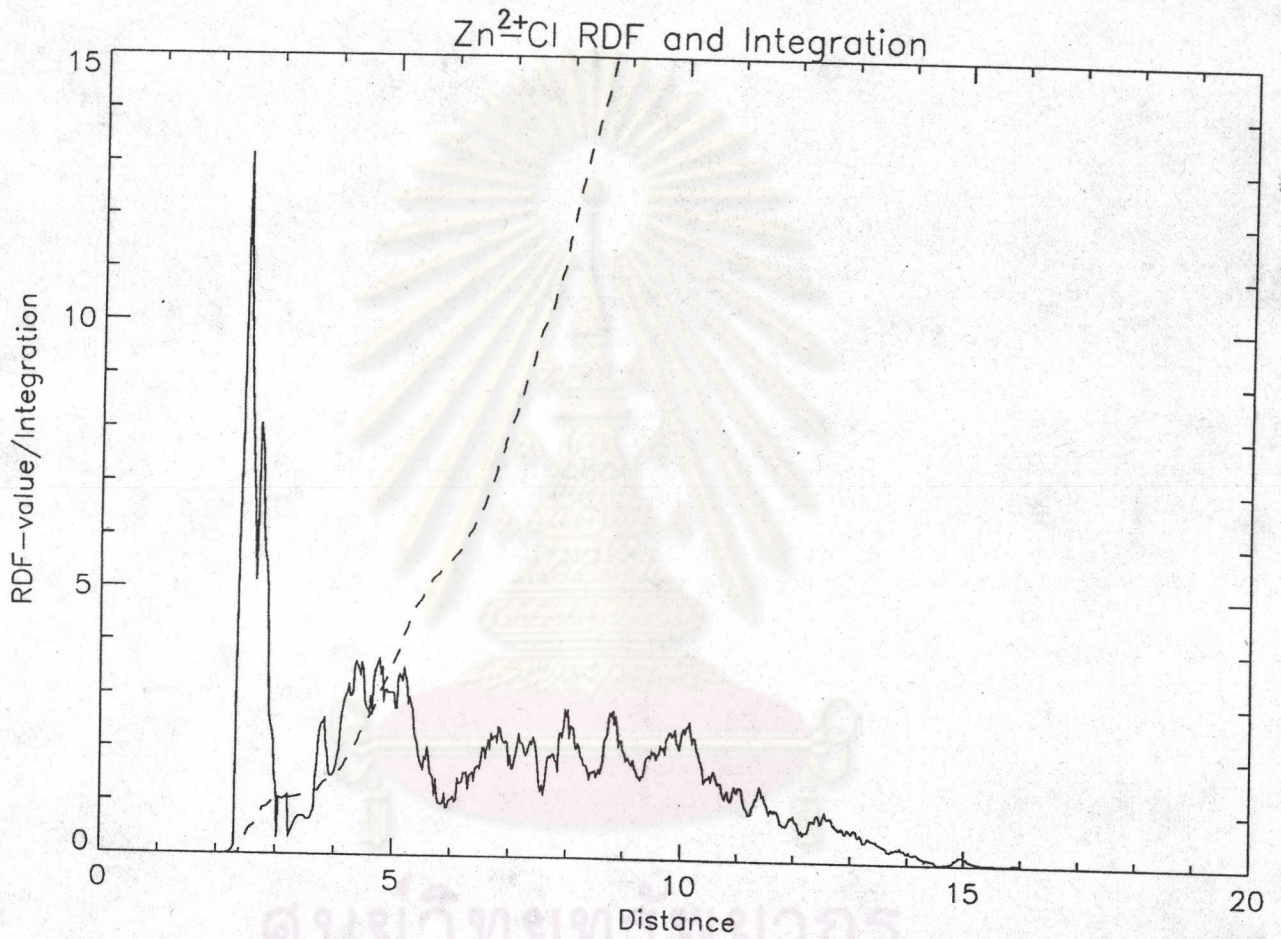




Figure 5.13 :  $\text{Zn}^{2+}$ -Cl radial distribution function and its running integration for 5 M  $\text{ZnCl}_2$  solution.



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Figure 5.14 : Distribution of water coordination numbers (CN) in 1st hydration shell of  $Zn^{2+}$  within limit 2.5 Å. (for 5 M  $ZnCl_2$  solution)

### Coordination Number Distribution Zinc Chloride 5M

Percent

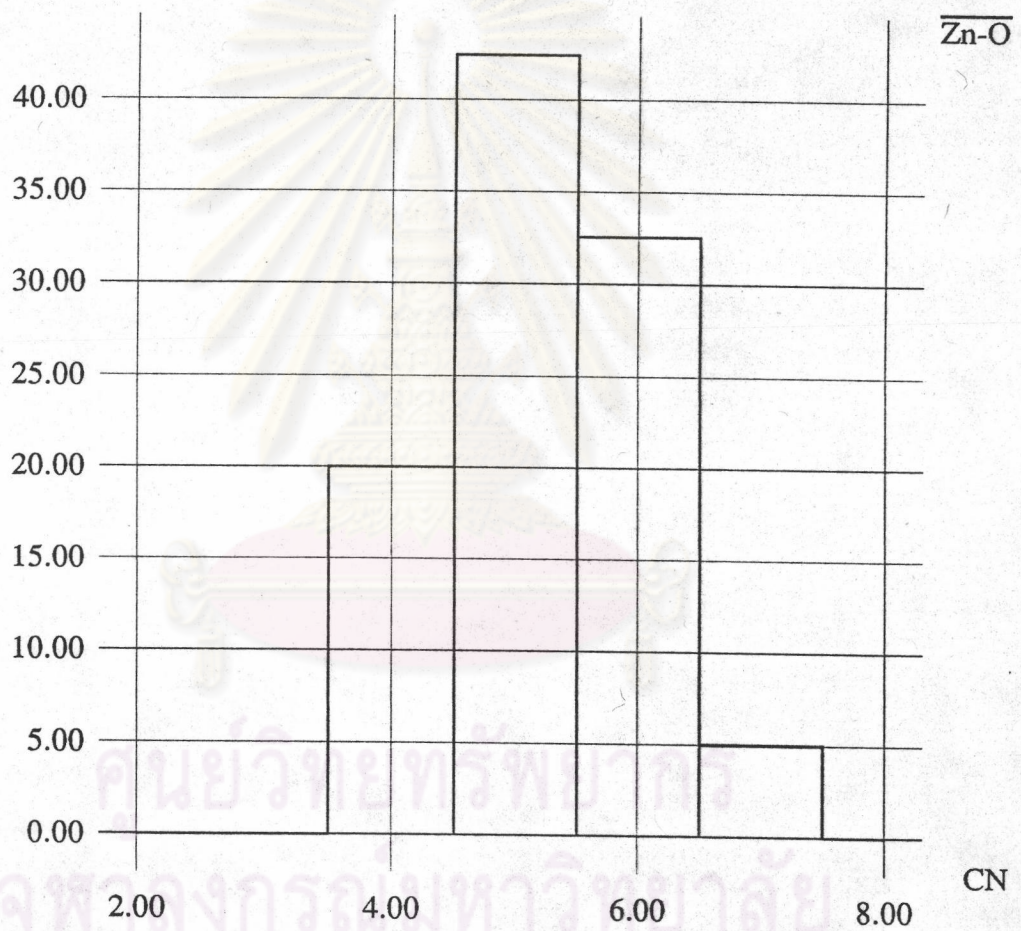
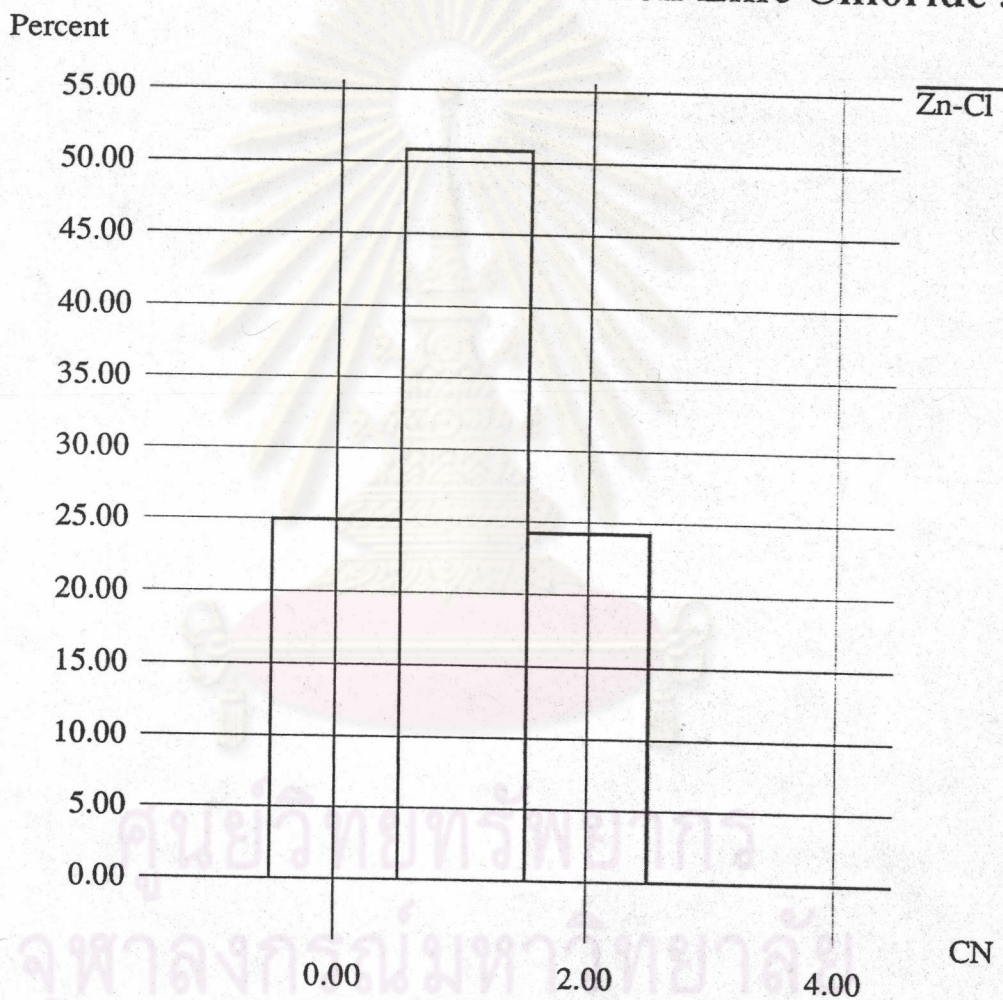




Figure 5.15 : Distribution of chloride coordination numbers (CN) in the 1st solvation shell of  $Zn^{2+}$  within limit 3 Å. (for 5 M  $ZnCl_2$  solution)

### Coordination Number Distribution Zinc Chloride 5M





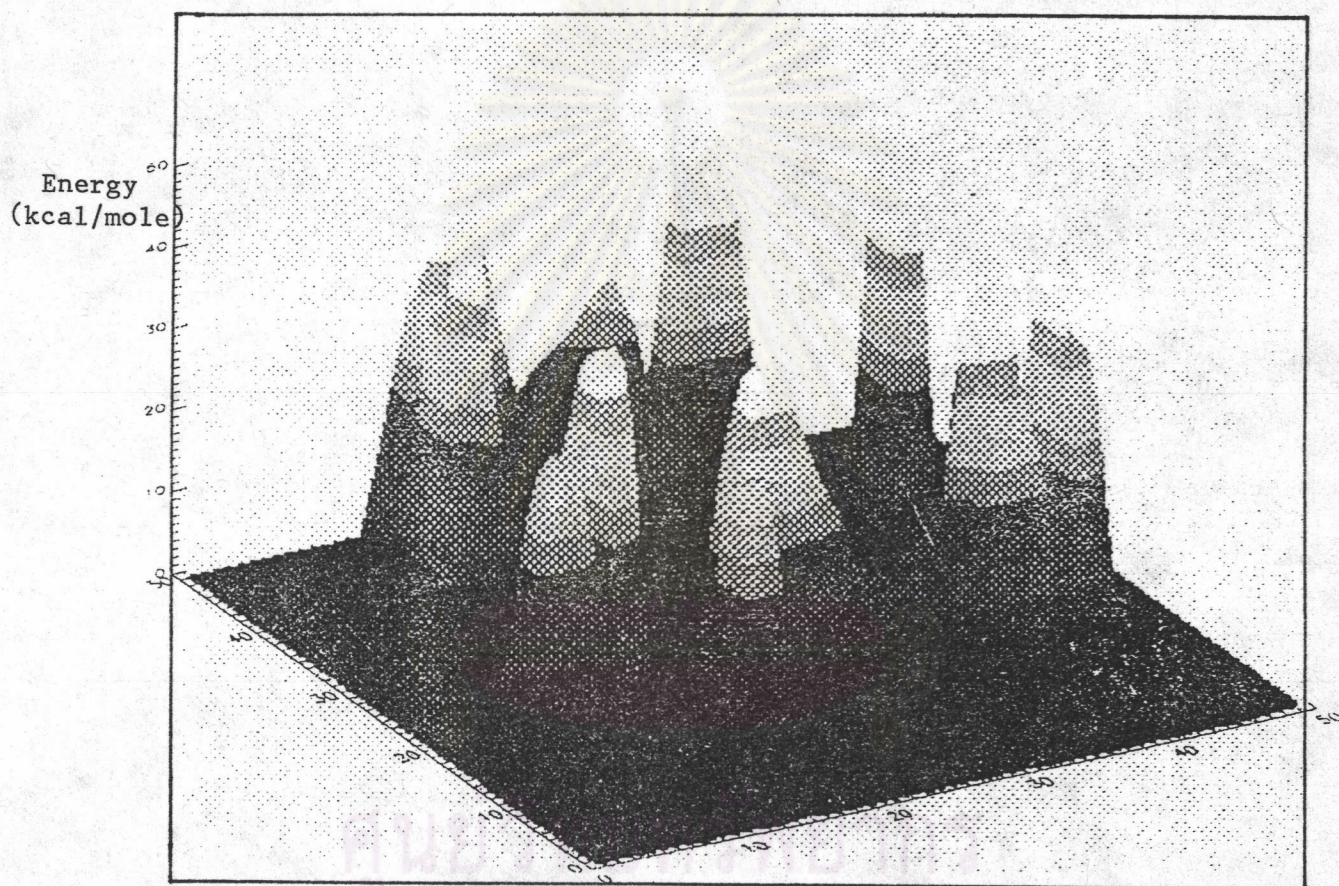
Ligand distribution plots were also produced by the same procedure as outlined for 3 M  $\text{ZnCl}_2$  in order to illustrate the structure of the first coordination sphere of  $\text{Zn}^{2+}$ . These picture are displayed in figures 5.16 and 5.17 .



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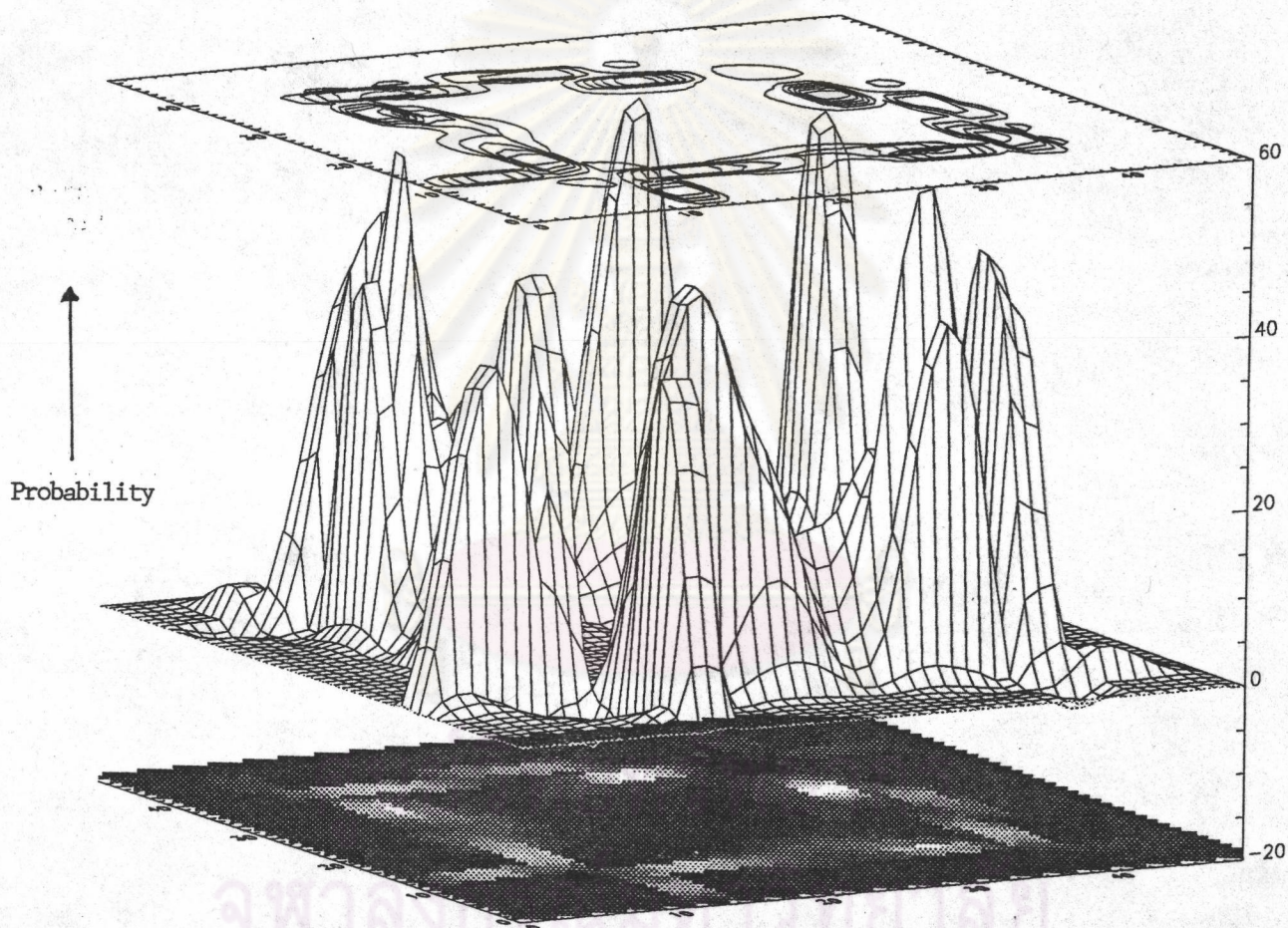
Figure 5.16 : Combined  $xy/xz/yz$  plane probability plots for water ligand positions in the first coordination sphere around  $Zn^{2+}$ , whose position is in the center of the displayed plane. (for 5 M  $ZnCl_2$  solution)



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Figure 5.17 : Probability plots for water ligand in the first coordination sphere. The uppermost part shows plot contours, the middle part the 3-dimensional plot and the lower part areas of high probability (light) and low probability (dark). (for 5 M  $\text{ZnCl}_2$  solution)





## 5.5 Comparison of Solutions at Different Concentrations with Respect to Experimental Data

### Structural Data

For comparison, the characteristic values of RDFs and average coordination numbers for 1 M, 3 M and 5 M solutions are listed in table 5.5 .

Table 5.5 : Characteristic values for the distribution functions  $g_{\alpha\beta}(r)^*$  and running integration numbers  $n_{\alpha\beta}$ . (For 1 M, 3 M and 5 M  $ZnCl_2$  solutions)

$\alpha$	$\beta$	Conc.	$r_{M1}$	$r_{m1}$	$n_{\alpha\beta}(r_{m1})$	$r_{M2}$	$r_{m2}$	$n_{\alpha\beta}(r_{m2})$
$Zn^{2+}$	O	1.0	2.05	2.40	6.8	4.80	4.80	16.7
		3.0	2.00	2.50	5.5	4.75	5.00	14.5
		5.0	2.00	2.40	5.1	(4.80)	(5.20)	(12.8)
$Zn^{2+}$	$Cl^-$	1.0	2.60	3.20	0.1	4.50	5.90	2.5
		3.0	2.65	3.20	0.7	4.60	5.80	3.2
		5.0	2.60	3.20	1.0	4.70	5.80	4.0

\*  $r_{Mi}$  and  $r_{mi}$  are the distances in Å where for the  $i$ th time  $g_{\alpha\beta}(r)$  is a maximum and a minimum, respectively.  $n_{\alpha\beta}(r_{mi})$  is the average coordination number of the  $i$ th coordination shell up to the distance of  $r_{mi}$ . Parentheses indicate uncertainty in assignment.

The  $Zn^{2+}$ -O distance is in excellent agreement with the experimental (46) value of 2.08 Å obtained for  $Zn(H_2O)_6^{2+}$ , which is the dominant species in 1 M  $ZnCl_2$  solution. The  $Zn^{2+}$ -H RDF (not displayed in the figures) with a first peak 0.6-0.7 Å beyond the first  $Zn^{2+}$ -O peak proves the dipole-oriented arrangement of the 1st hydration shell water molecules.



The  $\text{Zn}^{2+}$ -Cl RDFs display a very distinct peak for chloride ions directly bound to the metal ion, and a second, more diffuse but still well separated peak representing anions bound via a water molecule to  $\text{Zn}^{2+}$ . These "outer-sphere" complexes are apparently more important in chloride solutions of this metal ion than for aqueous solutions of  $\text{CuCl}_2$  (53)

From the probability plots mentioned in the previous section (figures 5.8-5.10, 5.16 and 5.17) one can recognize basic octahedral-like structures (as deduced also from experiment (46,54) ). This octahedral-like structure is clearly visible for 3 M solution, although not the same well ordered as in the case of  $\text{Cu}^{2+}$ (53). This is due to the larger contributions of species  $\text{Zn}(\text{H}_2\text{O})_n^{2+}$  with  $n = 4, 5$  and 7 (details see below). When the salt concentration reaches 5 M (figures 5.16 and 5.17), this octahedral-like structure is strongly disturbed, and ligands are so widely scattered around the "ideal" positions, that one can state a real "breakdown" of the regular hydration structure. A picture comparing 3 M and 5 M probability plots is provided in figure 5.18.

With increasing salt concentration, dichlorozincate species are forming to a considerable extent. In order to obtain more information about the structure of such species, the same procedure as outlined before for water ligands has been performed for chloride ligands. The result, displayed in figure 5.19, where the large peak represents the first chloride ligand as reference, clearly indicates that the second ligand is located in a trans-position to the first one. Vicinal ligands -still significantly present in  $\text{CuCl}_m^{(2-n)+}$  species (53)- are almost not detected.



Figure 5.18 : Combined  $xy,xz,yz$  plane probability plots for water ligand positions in the first coordination sphere around  $Zn^{2+}$ , whose position is in the center of the displayed plane; 3 M (lower part of figure) and 5 M (upper part of figure)  $ZnCl_2$  solution.

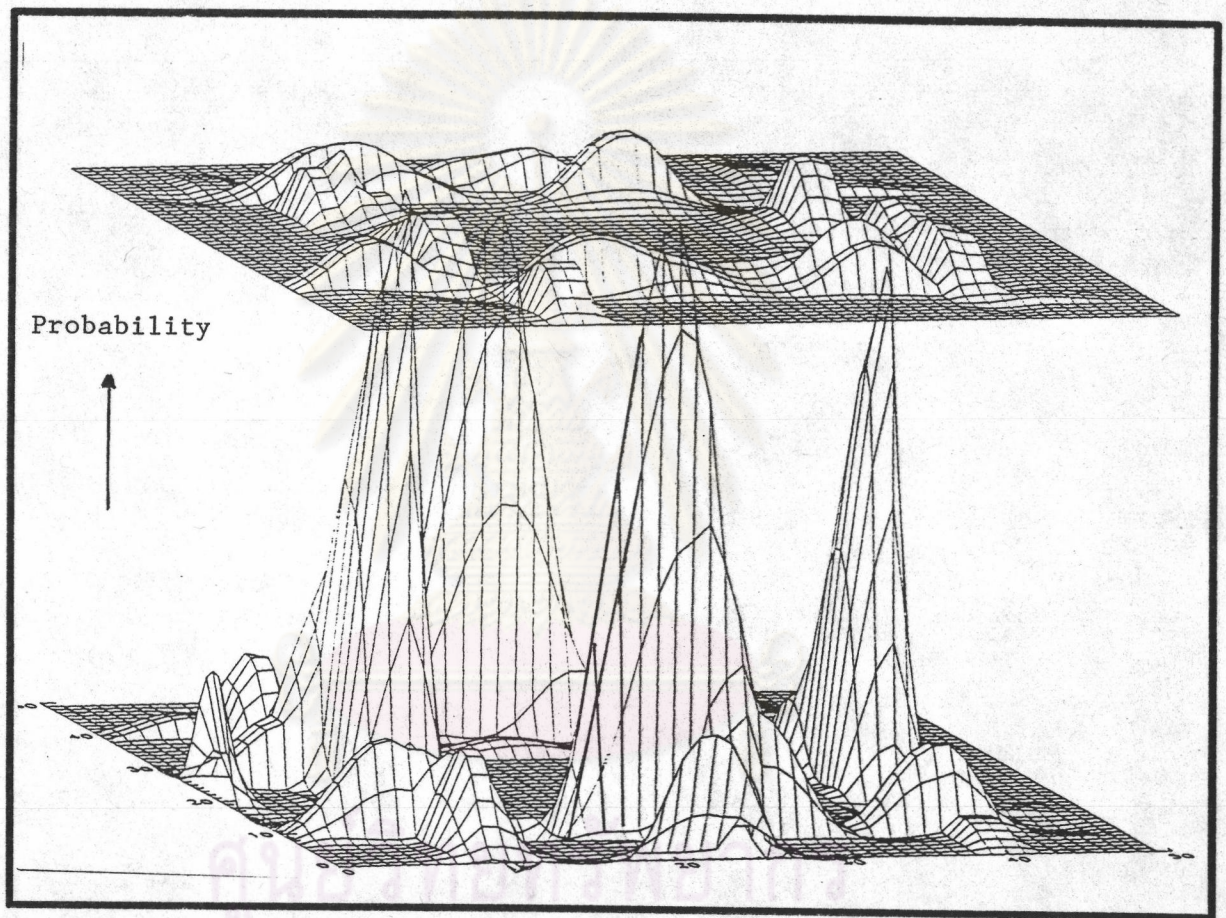
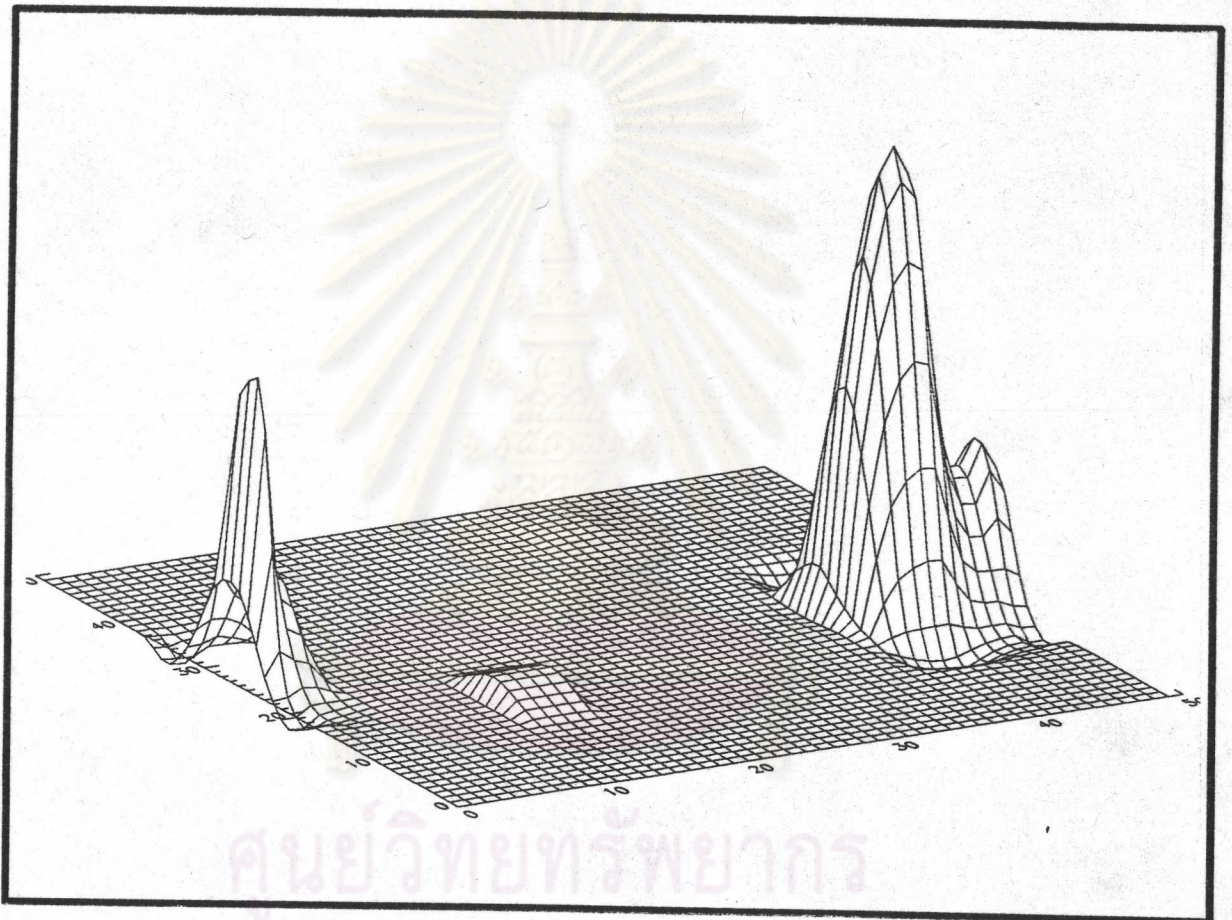




Figure 5.19: Combined  $xy/xz/yz$  plane probability plot for the location of a second chloride coordinated to  $Zn^{2+}$  in 5 M  $ZnCl_2$  solution ( $Zn^{2+}$  position in the center of the plane, large peak represents first  $Cl^-$  ligand)



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### Energy Data

The changes in the structural composition of the  $\text{ZnCl}_2$  solutions with increasing salt concentration are reflected in the interaction energies of the metal ion with water and chloride, respectively. Table 5.6 gives a summary of these data from all simulations, showing the strong concentration dependence of the ion's hydration energy. The increasing formation of direct  $\text{Zn}^{2+}$ -Cl bonds -occurring only for 5 % of the ions in 1 M  $\text{ZnCl}_2$  - at higher concentrations is recognized from a sharp increase in the total zinc-chloride interaction energy.

In the same table, the influence of the approximate 3-body terms introduced by the NNLC algorithm is recorded. The correction energies increase with salt concentration and are of the the same order of magnitude as in the case of the  $\text{CuCl}_2/\text{H}_2\text{O}$  system (53). Although these corrections amount only to a few percent of the hydration energy, they have been shown to be crucial in order to obtain correct coordination numbers.

Table 5.6 : Interaction energies and energy corrections for nearest neighbour ligands from Monte Carlo simulations at different concentrations.

Conc. (molal)	Interaction Energy (kcal/mol)		Energy correction (kcal/mol)		
	$\text{Zn}^{2+} - \text{H}_2\text{O}$	$\text{Zn}^{2+} - \text{Cl}^-$	$\text{Zn}^{2+} - \text{H}_2\text{O}$	% <sup>a</sup>	$\text{Zn}^{2+} - \text{Cl}^-$
0.0	-848.0	-	10.9	1.3	-
1.0	-636.2	-865.0	6.7	1.1	2.4
3.0	-478.2	-2379	12.9	2.7	4.7
5.0	-407.6	-3867	16.4	4.0	6.5

<sup>a</sup> % of hydration energy



Table 5.7 : Coordination number (CN) distribution for water and chloride ligands in aqueous  $ZnCl_2$  solutions of different concentration.

a) water

CN:	4	5	6	7
1 M*	0.0	0.0	25.1	74.9
3 M	8.3	45.3	25.3	25.0
5 M	20.0	42.5	32.5	5.0

\* including a small shoulder peak

b) chloride

CN:	0	1	2
1 M	95.0	5.0	0.0
3 M	42.7	49.0	8.3
5 M	25.0	50.8	24.2

Table 5.8 :  $Zn^{2+}/Cl^-$  complex formation constants from experiments and simulation.

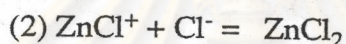
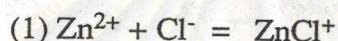
$\beta_1$	$\beta_2$	$\beta_3$	$\beta_4$	Ref.
0.60	----	----	----	54(spectrophotometric)
5.62	3.09	0.64	1.51	55(electrochemical)
4.72	0.65	1.54	3.35	56(electrochemical)
0.48	1.86	0.56	1.41	57(ultrasonic)
0.40	0.09	----	----	this work



### Species Distribution and Equilibria

In order to obtain more detailed insight into the composition of  $\text{ZnCl}_2$  solutions, coordination number distributions for the first shell were evaluated. The results are compiled in Tables 5.7a and 5.7b for water and chloride ligands, respectively. From these data, the main species present in aqueous  $\text{ZnCl}_2$  solutions can be classified as  $\text{Zn}(\text{H}_2\text{O})_{6-7}^{2+}$ ,  $\text{ZnCl}(\text{H}_2\text{O})_5^+$ , and  $\text{ZnCl}_2(\text{H}_2\text{O})_4$ , with increasing presence of the chlorocomplexes at higher salt concentrations. Only small amounts of  $\text{ZnCl}(\text{H}_2\text{O})_6^+$  are found, in agreement with experiment. (54)

From the quantities of  $\text{ZnCl}_n(\text{H}_2\text{O})_m$  species predicted to coexist in 5 M solution, an evaluation of the corresponding consecutive complex formation constants for the reactions



is possible. In the experiments (cf. table 5.8), based on electrochemical (55,56), spectrophotometric (54) and supersonic (57) data, also the steps to form  $\text{ZnCl}_3^-$  and  $\text{ZnCl}_4^{2-}$  are reported. From this simulation, there is no indication towards these species even in 5 M solution. Considering however the distinct peaks for solvent-separated ion pairs and the number of chloride ions associated with such species in the RDFs (cf table 5.5) it seems well possible that such "outer sphere" species are partially registered by the experimental methods as complexes thus producing overestimated formation constants for the "true"  $\text{ZnCl}_n^{(2-n)+}$  complexes. The fact that the potentiometrically evaluated constant (55,56) are considerably larger than experimental and simulation-based constants for the (more stable)  $\text{CuCl}_n^{(2-n)+}$  complexes (53,58-62), and at the same time show an unusual high stability for the tetrachlorocomplex, supports this hypothesis. Considering the good agreement of  $\beta_1$  from spectrophotometric (54) and ultrasonic (57) measurements and this simulation, and of experimental and simulation-based constants in the  $\text{Cu}^{2+}/\text{Cl}^-/\text{H}_2\text{O}$  system (53), the formation constants obtained from this simulation seem to be quite reliable data for chlorozincate ("contact ion pair") complex formation in aqueous solution.