



CHAPTER V

MONTE CARLO SIMULATION OF LITHIUM ION IN 18.45 MOLE % AQUEOUS AMMONIA SOLUTION

Most computer simulations of infinite dilute solution, containing a single ion, have been done with pure aqueous medium (5-20,22-27). The structural properties of an ion in mixed solvents are of much interest since the molecules can be preferentially taken for solvation. The present chapter deals with lithium ion in aqueous ammonia solution. The objectives of this simulation are to investigate the structural properties of the lithium ion surrounded by solvent molecules, in order to compare to those of sodium ion under the same conditions (30). The influence of metal ion on the solvent structure will also be discussed.

5.1 Method of Calculations

Since the present simulation consists of three kinds of particles, namely lithium ion, ammonia and water, five types of potentials are required. The MCY (Matsuoka-Clementi-Yoshimine) potential (41) and the potential developed by Ishida et al. (28) have been employed to represent water/water and ammonia/ammonia interaction energies, respectively. For ammonia/water, the potential function of Tanabe and Rode (29) is employed and the lithium ion/water interactions are described by the function of Clementi et al. (64).

All functions as well as that of lithium ion/ammonia (newly developed and discussed in chapter 3) were obtained based on the ab-initio closed-shell SCF method and well tested by either Monte Carlo or molecular dynamic simulations (28,29,64,72).

The Monte Carlo simulation was carried out for a lithium ion in 18.45 mole % aqueous ammonia solution with periodic boundary condition and Metropolis scheme (3). The system consists of 202 rigid particles, one lithium ion, 37 ammonia and 164 water molecules. The simulation was performed for 20 °C, 1 atm and with the experimental density of 0.9307 g.cm⁻³, corresponding to a box side-length of 18.56 Å, and half of this length was chosen as potential cut-off radius.

One molecule was picked up and displaced randomly on each move. New configurations were randomly generated, translation in all three cartesian directions and rotation about a randomly chosen axis were made. An acceptance rate of roughly 50 % for new configurations was obtained by using ranges of ± 0.1 Å for translations and $\pm 10^\circ$ for rotation. The N-particle configurational energies of the system were calculated under the assumption of pairwise additivity interactions.

5.2 Results and Discussion

In the present Monte Carlo computations, totally 3,200,000 configurations have been generated. After 600,000 configurations temperature was raised shortly to 120 °C and then lowered again to the original value in order to assure that the true equilibrium state has been reached. Final sampling was performed after 2,200,000

configurations for another 1,000,000 configurations. The convergence is shown in figure 5.1 .

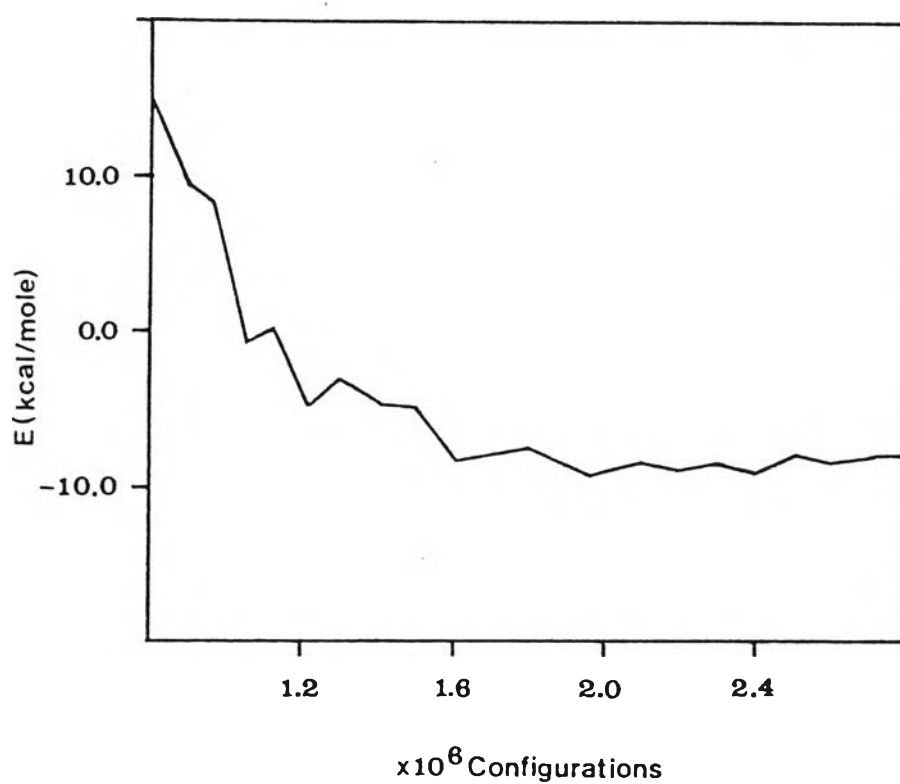


Figure 5.1 Convergence characteristics of the present Monte Carlo simulation for lithium ion in 18.45 mole % aqueous ammonia solution at 20^o C.

After the equilibrium state were established, further 1,000,000 configurations were stored every 500 attempted moves during the MC run, the saved configurations were analyzed to obtain structural data and various distributions.

5.2.1 Radial Distribution Functions

The main features of the solution structure are usually discussed based on a number of radial distribution functions (RDFs) around specified atoms. The solute-solvent structure can be well characterized through partial radial distribution functions for different molecules. The total RDFs were separated therefore, into those of 3 different centers, lithium ion, water and ammonia, to obtain deeper insight into the solvation structure.

All RDFs results are shown in figures 5.2 - 5.7, and their characteristics are summarized in table 5.3.

5.2.1.1 Ion/Molecule Radial Distribution Functions

First, lithium ion was considered as solute surrounded by water and ammonia molecules. Therefore, $\text{Li(I)}/\text{H}_2\text{O}$ and $\text{Li(I)}/\text{NH}_3$ RDFs were calculated.

Lithium Ion/Water Radial Distribution Functions

The Li(I)/H₂O RDFs are shown in figure 5.2, together with the corresponding integration numbers, where one can find the gross population of water molecules surrounding the lithium ion. The functions are characterized by a well pronounced peak at 1.95 Å of Li(I)-O distance, leading to the coordination number of 4.0 up to the minimum at 2.75 Å. This first pronounced peak is rather sharp, symmetric and well separated from the second layer, as can be seen from the truncated of Li(I)-O RDF over quite some distances. In Li(I)-H RDF, the average coordination number of 8.0 hydrogen atoms in the first shell up to 2.50 Å, indicates that all hydrogen atoms point away from the lithium ion. More details related to the molecular orientation will be discussed later in form of angular distributions. The second solvation shell can be recognized at 4.45 Å in Li(I)-O RDF, indicating the average coordination number of 12, integrated up to the second minimum.

Table 5.1 Structural results of the first hydration shell of lithium ion.

Method	R(Li-O)	R(Li-H)	N	Ref.
Monte Carlo	2.10	2.65	6.0	74
molecular dynamics	2.01	2.67	4.1	65
molecular dynamics	2.00	2.70	5.2	66
molecular dynamics	2.04	2.60	6.0	19
molecular dynamics	2.13	2.68	6.1	73
X-ray	1.97	2.57	5.8	76
This work	1.95	2.70	4.0	

N stands for the coordination number. The unit of distance is given in Å.

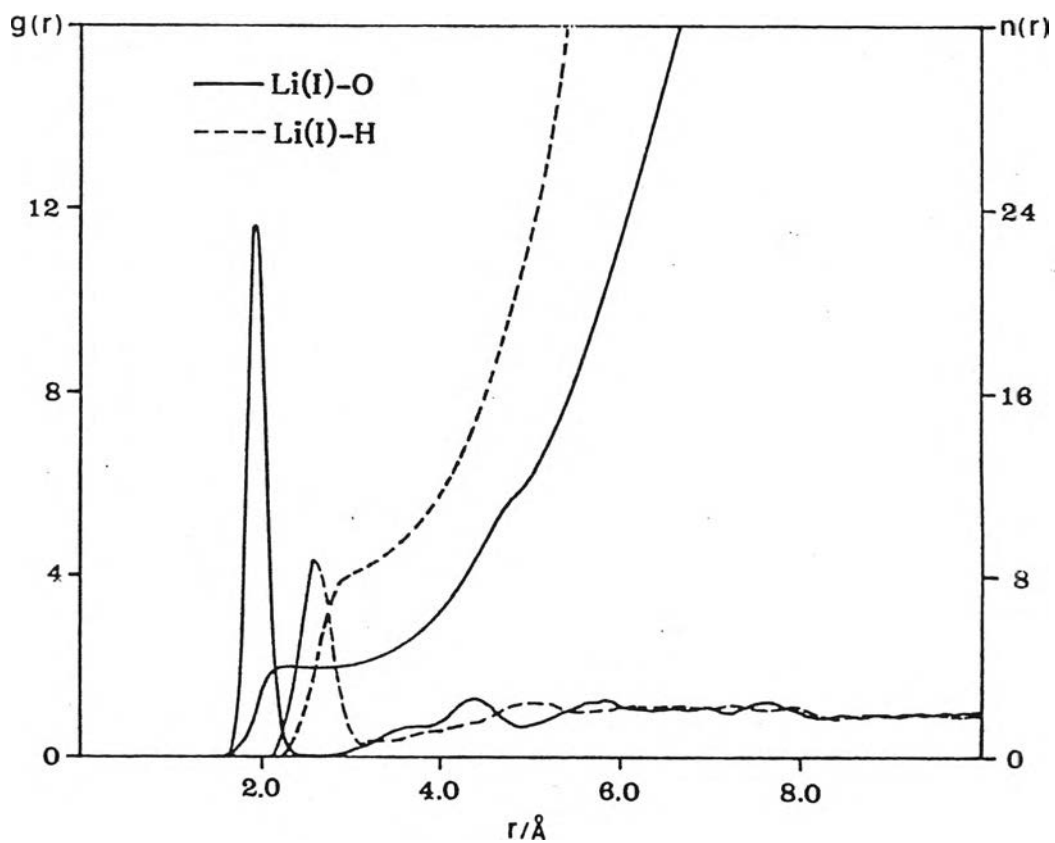


Figure 5.2 Lithium ion/water radial distribution functions and running integration numbers.

Lithium Ion/Ammonia Radial Distribution Functions

The Li(I)-NH_3 RDFs are shown in figure 5.3, the Li(I)-N function shows two separated solvation spheres, but the first layer displays a peculiar structure. Two quite distinct peaks within the area to be attributed to this layer, consisted of 2 ammonia molecules, indicate that the ammonia molecules are located at non-equivalent positions, 25 % about 2.50 Å and 75 % at 3.35 Å far from the lithium ion. The characteristic of the present system has never been observed before in any other ion-solvent simulations, namely that the first layer has two splitting peaks at 2.50 and 3.35 Å. A second peak is located at 4.50 Å, corresponding to the average coordination number of 4.0.

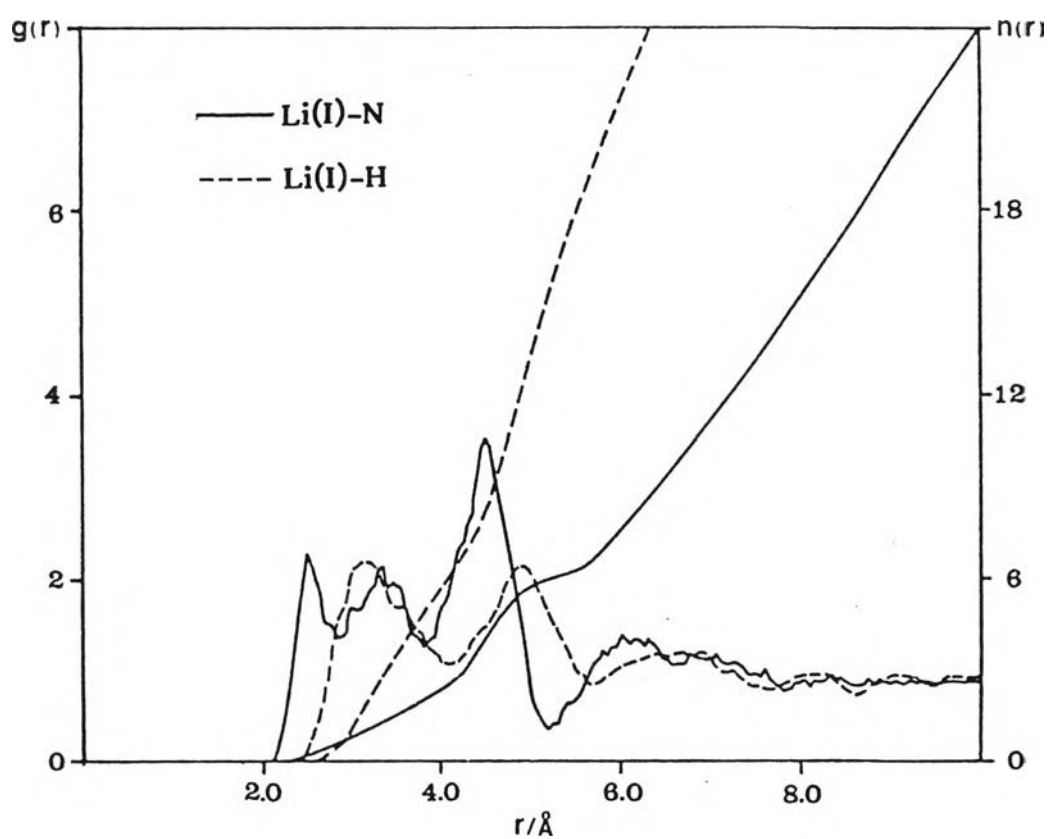


Figure 5.3 Lithium ion/ammonia radial distribution functions and running integration numbers.

Summarizing both averaged lithium/water and lithium/ammonia coordination numbers, a total coordination number of 5.9 is obtained for the lithium ion in 18.45 mole % aqueous ammonia solution. This value is quite similar to the average coordination number of lithium ion in pure water (19,65,73-74) and pure ammonia (28) for an infinite dilute solution. For the second solvation sphere of the ion consists of 12 solvent units, four ammonia and eight water molecules. The fully solvated lithium ion in 18.45 mole % aqueous ammonia can be characterized by $\text{Li}[(\text{H}_2\text{O})_4(\text{NH}_3)_2]^{\text{I}}[(\text{H}_2\text{O})_8(\text{NH}_3)_4]^{\text{II}}$, whereas in the case of sodium ion, characterized by $\text{Na}[(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{\text{I}}[(\text{H}_2\text{O})_7(\text{NH}_3)_2]^{\text{II}}$ (30), the first solvation sphere was dominated by ammonia and the second one by water, lithium ion is preferentially solvated by water in both shells. This is in good agreement with the qualitative concept of the relatively "harder" lithium ion preferring the "harder" oxygen as coordination center compared to the "softer" sodium ion.

It is interesting to note here, therefore, that the Li(I)-O distance obtained from this simulation is shorter than that of any other results for ion in pure water summarized in table 5.1, while alternative situation is found for ammonia. This observation would be described also in terms of preferential solvation discussed above. In pure liquid, solvent molecules in the first hydration shell have to be centered at the equivalent distance far from central ion due to their identical interactions with ion, computed from solute-solvent pair potential. In the case of mixed solvents water molecules will be able to adopt themselves to approach more close to lithium ion according to the soft and hard concept. Such circumstance would lead simultaneously to a longer Li(I)-N distance relative to lithium ion in pure

liquid ammonia. In addition this description also valids for the alternative behaviour of sodium ion in pure an mixed water/ammonia solvents (30).

5.1.1.2 Molecule/Molecule Radial Distribution Functions

First, water molecule was considered as solute, and the surrounding consisting of other water and vice versa for ammonia molecules were investigated. Then, radial distribution functions for different type of molecules will be evaluated. Structural properties obtained for the surrounding of water molecule are listed in table 5.3 as well.

Water/Water Radial Distribution Functions

The water/water RDFs are shown in figure 5.4 , the function pattern is quite identical to pure water (table 5.2). In the O-O RDF, the first maximum is encountered at 2.85 Å and its integrations give 4.5 water molecules up to the first minimum at 3.60 Å. The water-water hydrogen bond structure can be recognized from the peak in O-H(H₂O) RDF at 1.95 Å, integrating as 1.6 hydrogen atoms per oxygen atom.

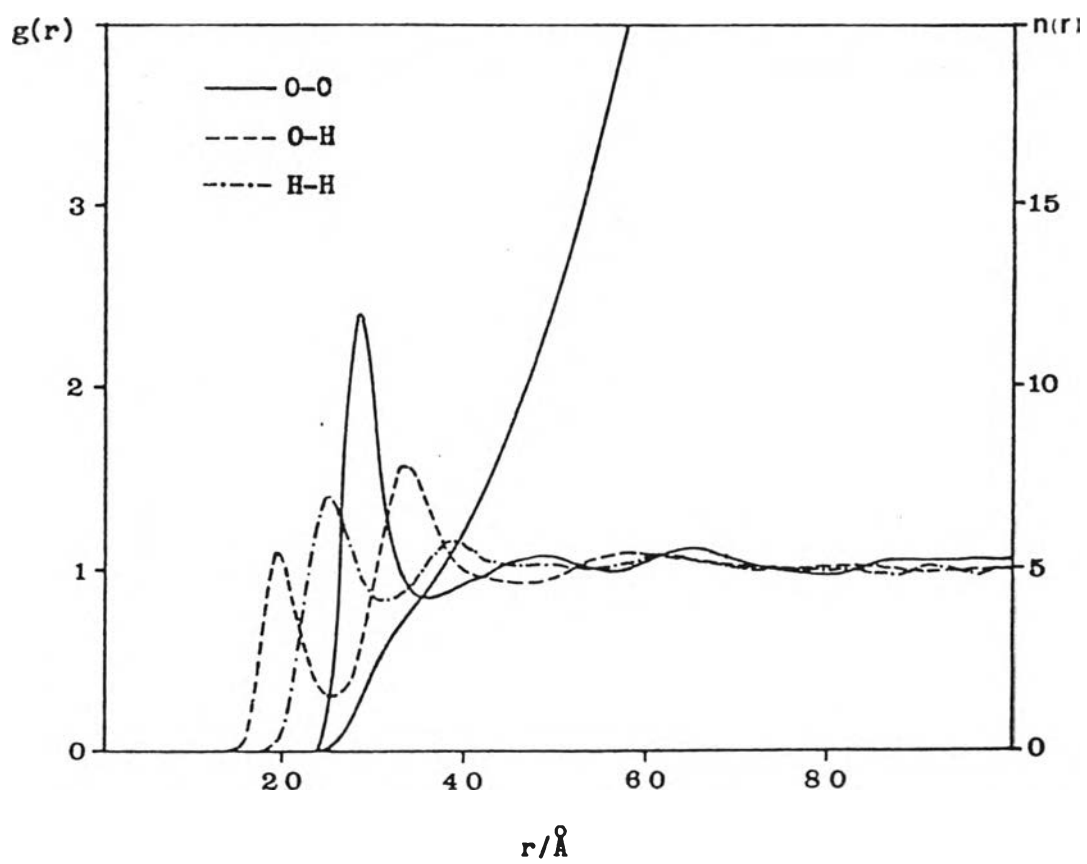


Figure 5.4 Water/water radial distribution functions and running integration numbers.

Table 5.2 Structural properties of liquid water.

	$M_1/\text{\AA}$	$m_1/\text{\AA}$	n_1	$M_2/\text{\AA}$	$m_2/\text{\AA}$	Ref.
O-O						
MCY-CI	2.83	3.53	4.2	4.30	5.60	64
ST2	2.85	3.36	4.9	4.60	5.80	67
STO-3G	2.61	3.34	4.6	4.42	5.30	68
TIP4P	2.78	3.45	5.1	4.50	5.61	67
Exp.	2.85	3.40	4.5-5.5	4.60	5.70	69
O-H						
MCY-CI	1.85	2.50				64
ST2	1.88	2.53	4.1			67
STO-3G	1.90	2.40	3.8			68
TIP4P	1.79	2.45	3.9			67

M_i , m_i and n_i stand for the distance up to the i^{th} maximum, the distance of the i^{th} minimum and the integration numbers up to the i^{th} minimum, respectively.

Ammonia/Ammonia Radial Distribution Functions

The structure of ammonia/ammonia RDFs are given in figure 5.5. Both N-N and N-H functions are flat and broad. The N-N RDF shows the first peak extended from about 3.2 Å to 5.2 Å, and the more pronounced second peak at about 5.8 Å ;integration up to 5.2 Å yields 2-3 ammonia molecules. The average integration numbers under both peaks are about 2-3 and 12 molecules, respectively. The detailed values of structural properties around ammonia are summarized in table 5.3 as well.

Comparision of both water and ammonia RDFs to pure solvents (28,64,67-72), one can clearly see that water structure remains the same, in changing from pure liquid state to its ammonia mixture, while the structural properties of liquid ammonia is completely destroyed by the dominance of water.

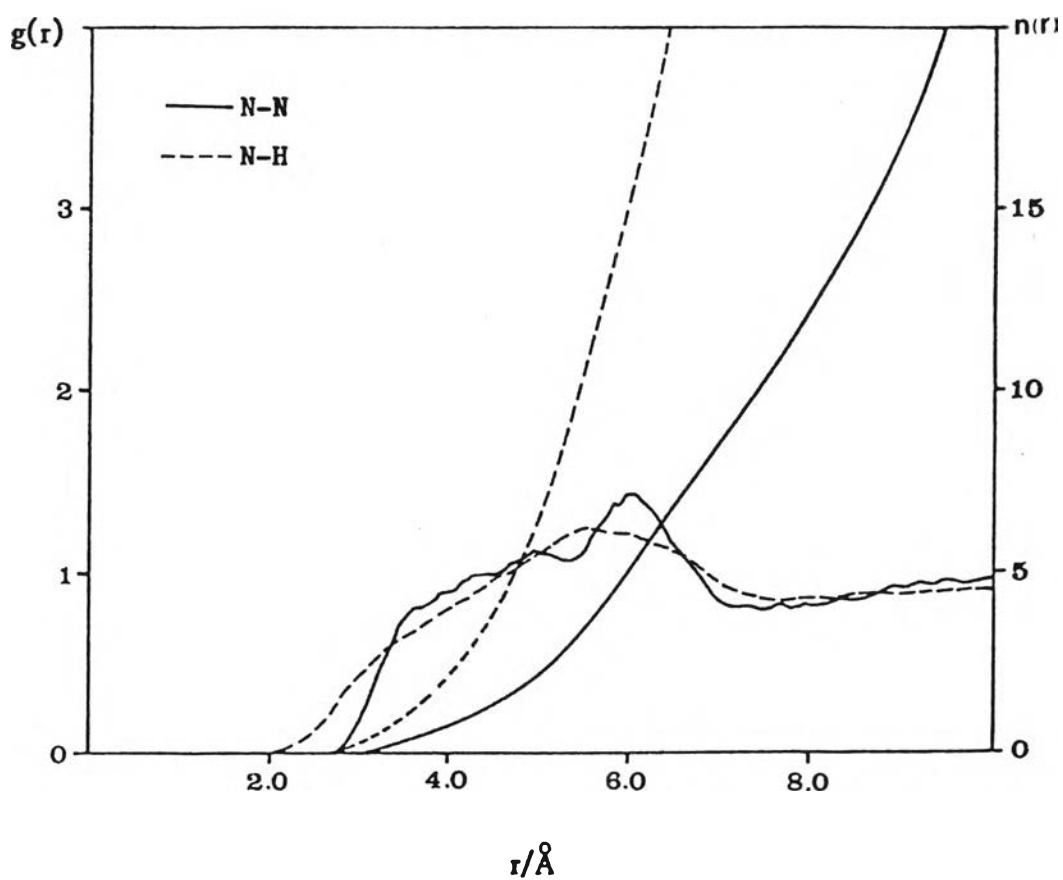


Figure 5.5 Ammonia/ammonia radial distribution functions and running integration numbers.

Water/Ammonia Radial Distribution Functions

Considering water as a central molecule, water-ammonia RDFs (figure 5.6) show the first maximum at 3.20 \AA in O-N RDF and the running integration number up to the first minimum (4.70 \AA) indicates that there are 2.9 ammonia molecules. The hydrogen bond configuration can be recognized by the shoulder peak around 2.2 \AA with 0.9 hydrogen atom in the O-H(NH_3) RDF.

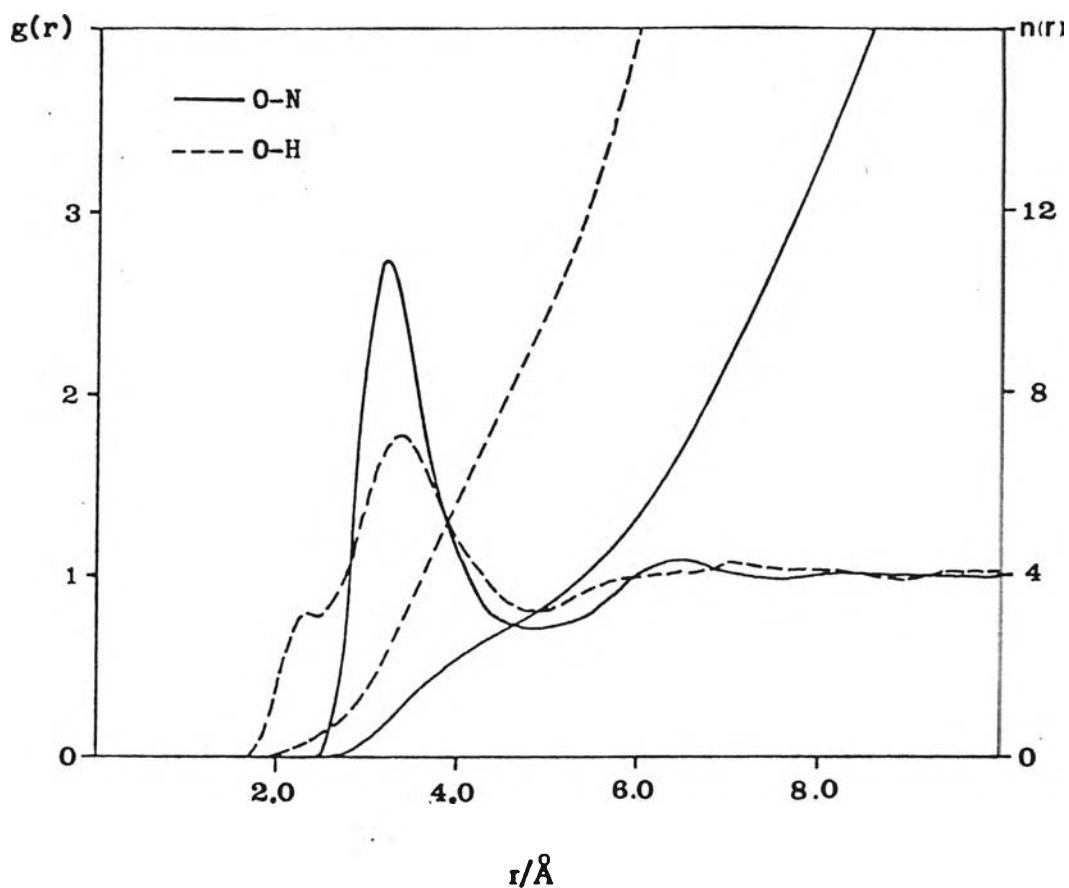


Figure 5.6 Water/ammonia radial distribution functions and running integration numbers.

Ammonia/Water Radial Distribution Functions

In figure 5.7, ammonia is considered to be the central molecule. The O-N and N-O RDFs, representing the distribution of N around O and O around N, respectively shown in figures 5.6 and 5.7, are identical according to the definition of the radial distribution function given in chapter 2. Only the average integration numbers, depending on the density of the surrounding particles, are different. The first maximum of N-O RDF centered at 3.20 \AA leads to the average integration number of 12.5 water molecules around ammonia up to the first minimum at 4.70 \AA . The N...H(H₂O) hydrogen bonding is represented clearly by the peak occurred in form of a shoulder in the N-H(H₂O) RDF around 2.10 \AA , and average integration number of 1 hydrogen atom is obtained. The more pronounced N-H(H₂O) shoulder (figure 5.7) compared to O-H(NH₃) one (figure 5.6) indicates a stronger N...H(H₂O) hydrogen bond than O...H(NH₃), agreement well with Na(I)-NH₃/H₂O results (30).

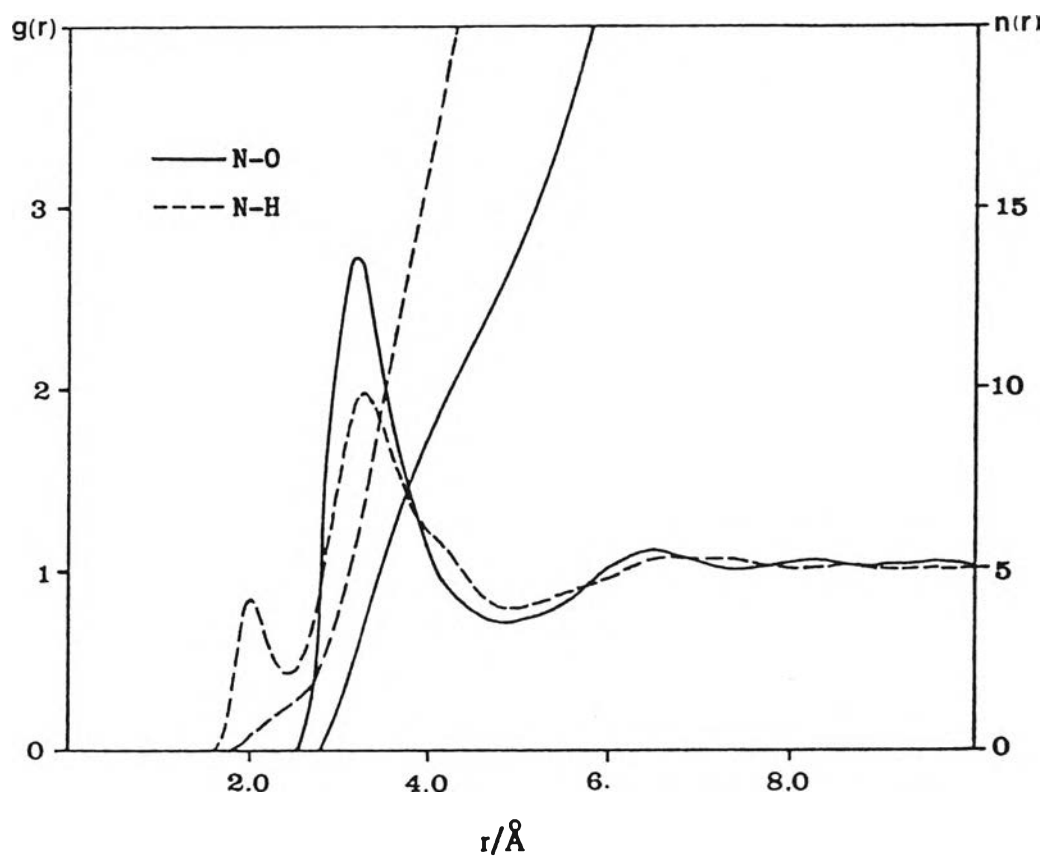


Figure 5.7 Ammonia/water radial distribution functions and running integration numbers.

Table 5.3 Characteristic values of the radial distribution functions for lithium ion in 18.45 mole % aqueous ammonia solution, $i^{\text{th}}\text{Max}$, $i^{\text{th}}\text{Min}$ and n_i are the i^{th} maximum, the i^{th} minimum and the integration numbers up to the i^{th} minimum, respectively.

	$1^{\text{st}}\text{Max}/\text{\AA}$	$1^{\text{st}}\text{Min}/\text{\AA}$	n_1	$2^{\text{nd}}\text{Max}/\text{\AA}$	$2^{\text{nd}}\text{Min}/\text{\AA}$	n_2
Li(I)-H₂O						
Li(I)-O	1.95	2.75	4.0	4.45	4.95	12.1
Li(I)-H	2.60	3.10	8.2	-	-	-
Li(I)-NH₃						
Li(I)-N	2.50	2.85	0.5	4.50	5.20	5.9
(splitting						
of 1^{st} peak)	3.35	3.80	1.9	-	-	-
Li(I)-H	3.15	4.20	6.5	-	-	-
H₂O-H₂O						
O-O	2.85	3.60	4.5	-	-	-
O-H	1.90	2.55	1.6	-	-	-
NH₃-H₂O						
N-O	3.20	4.70	12.5	-	-	-
N-H	2.10	2.75	1.2	-	-	-
H₂O-NH₃						
O-N	3.20	4.70	2.9	-	-	-
O-H	2.20	2.40	0.9	-	-	-
NH₃-NH₃						
N-N	3.2	5.2	2-3	-	-	-

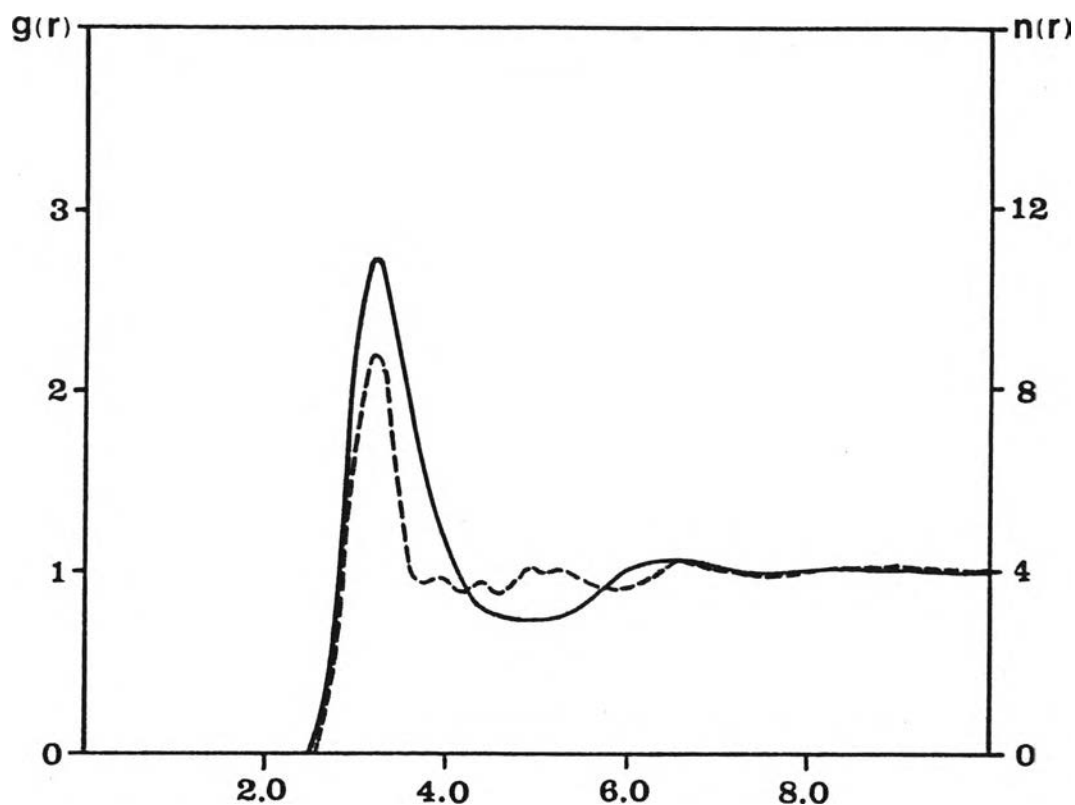


Figure 5.8 Comparison of N-O radial distribution functions. for 18.42 mole % aqueous ammonia solution. Solid line and dashed line show computed RDF and RDF obtained from X-ray scattering, respectively.

Figure 5.8 shows the N-O RDF from the simulation and X-ray results. The N-O RDF computed from this simulation gives quite good agreement with Narten's (77). The first pronounced peak is exactly centered at the same distance. However, the RDF derived from X-ray scattering is more structured than that from the simulation.

5.2.2 Distribution of Coordination Numbers

Since average solvation numbers in the first hydration shell determined by integration of radial distribution functions up to the first minimum do not give informations about solvent exchange, therefore, distribution of coordination numbers has been evaluated. For the coordination number analysis, the "first shell cut-off" was chosen at the first minimum of the radial distribution functions, (RDFs), and all configurations were then investigated for the coordination numbers being realized. The computations have been done only for the well-defined pairs, indicated by the pronounced RDF's peaks.

Figure 5.9 and 5.10 show distribution of coordination numbers for the neighbouring water and ammonia molecules in the first shell of lithium ion, respectively. The coordination number for water in the first shell is almost exclusively 4. A wider range of variation is observed for distribution of ammonia molecules, fluctuated from 1 to 3 with dominant number of 2. In addition, distribution of both solvents indicates that exchange processes in this shell should dominantly involve ammonia molecules rather than water. This observation is strongly confirmed by the character of the Li(I)-O RDF which is truncated at 2.75 \AA , while the minimum of the Li(I)-N RDF is still higher than unity.

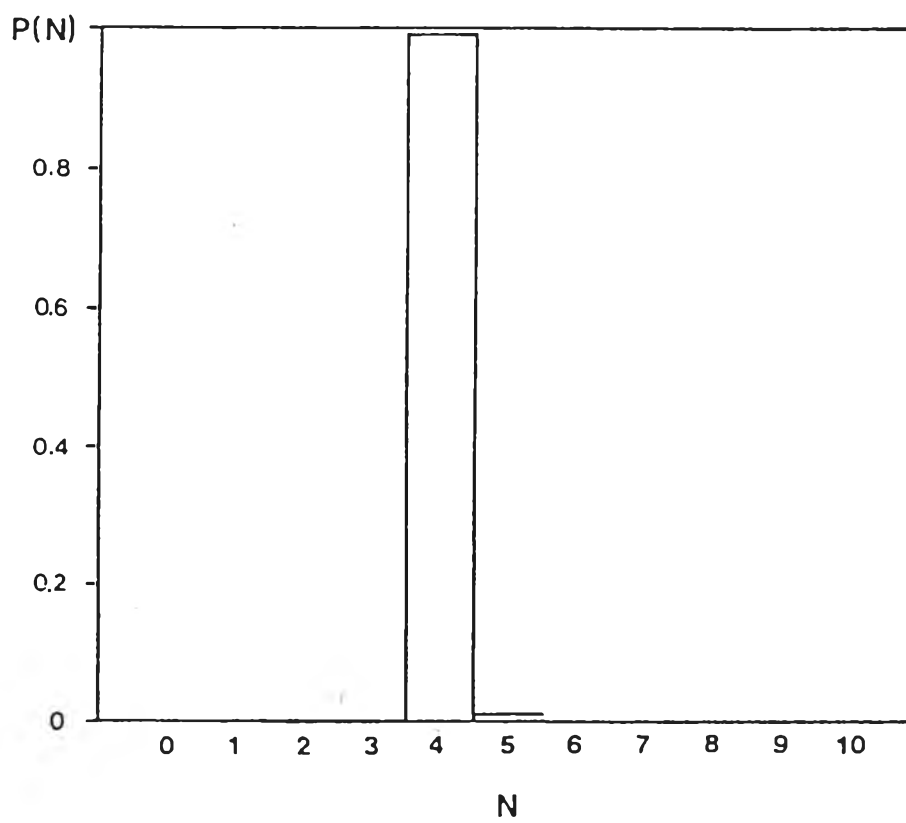


Figure 5.9 Distribution of coordination numbers for water in the first solvation sphere of lithium ion.

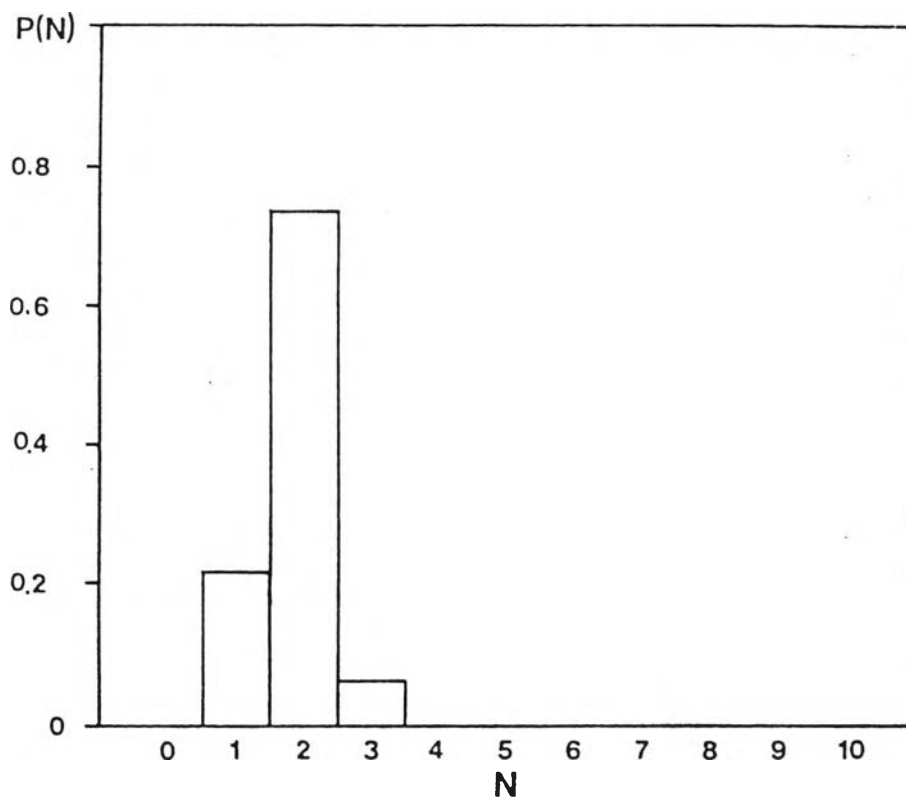


Figure 5.10 Distribution of coordination numbers for ammonia in the first solvation sphere of lithium ion.

The total distribution of coordination numbers around lithium ion has been illustrated in figure 5.11. The coordination numbers fluctuate from 5 to 7, the dominant number is 6 and the average number 5.9 .

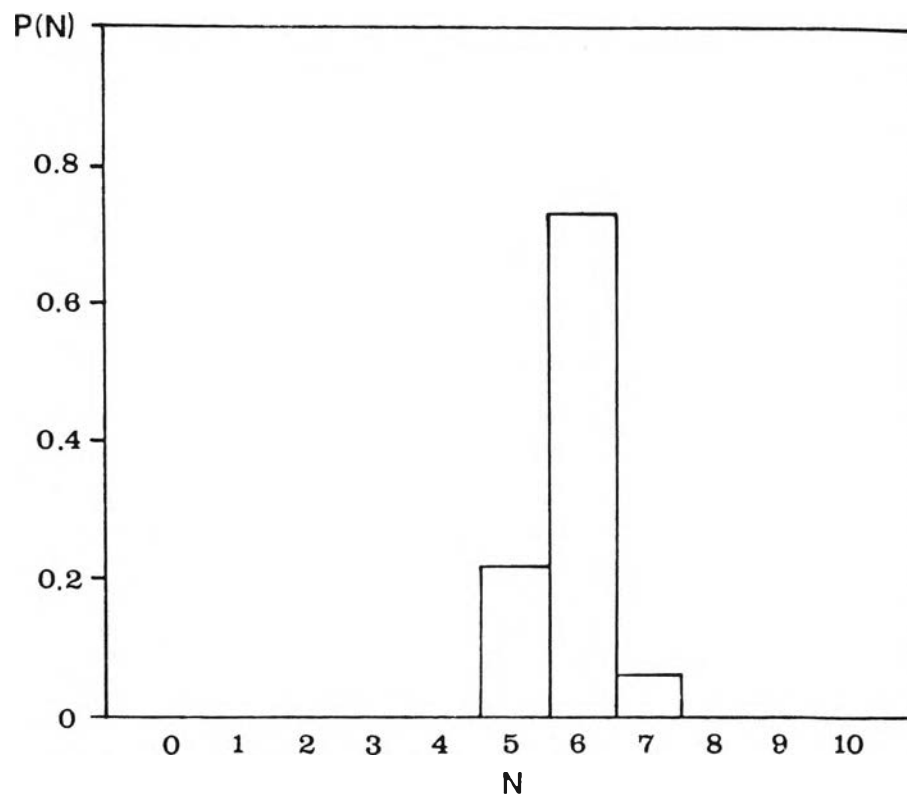


Figure 5.11 Total distribution of coordination numbers in the first solvation sphere of lithium ion.

Molecule/Molecule Distribution of Coordination Numbers

The distribution of ammonia around water in form of N and H atoms of ammonia with respect to O atom is shown in figures 5.12 and 5.13, respectively. The coordination numbers fluctuate from 1 to 7 in figure 5.12 with the most probable coordination number of 2. The wide range fluctuation is due to the weak interaction between water and ammonia molecule. For the distribution of H (of ammonia) around O, shown in figure 5.13 the hydrogen bonded neighbours is prominently found to be 1.

For water around ammonia, a large fluctuation of distribution is observed, ranging from 3 to 15 (figure 5.20). The hydrogen bonded distribution shows the most probable of 1 (figure 5.15). The narrow range of distribution of the hydrogen bonding, $H(NH_3)$ around O compared to $H(H_2O)$ around N, agrees well with the above conclusions drawn from RDF data.

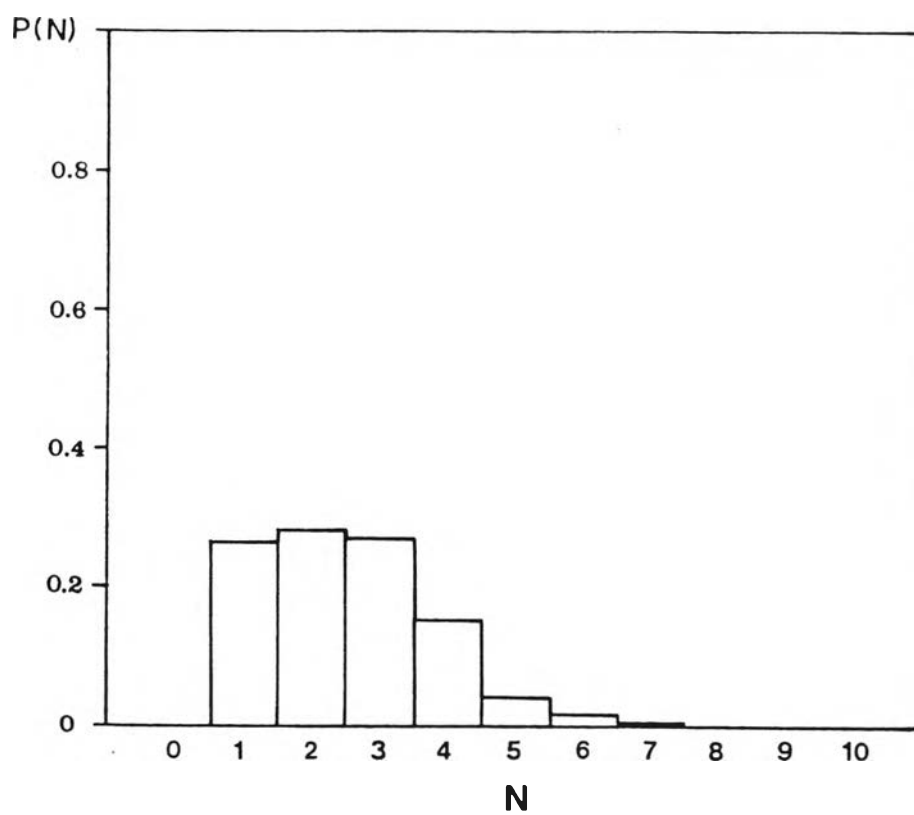


Figure 5.12 Distribution of coordination numbers for ammonia in the first solvation sphere of water.

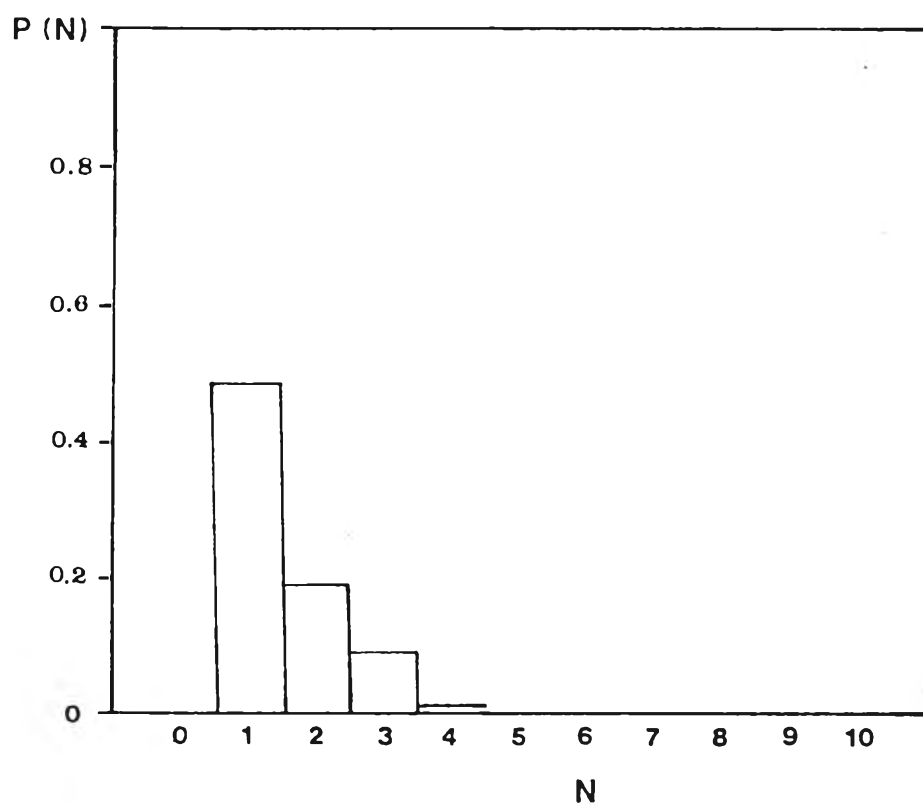


Figure 5.13 Distribution of coordination numbers for hydrogen neighbours of water.

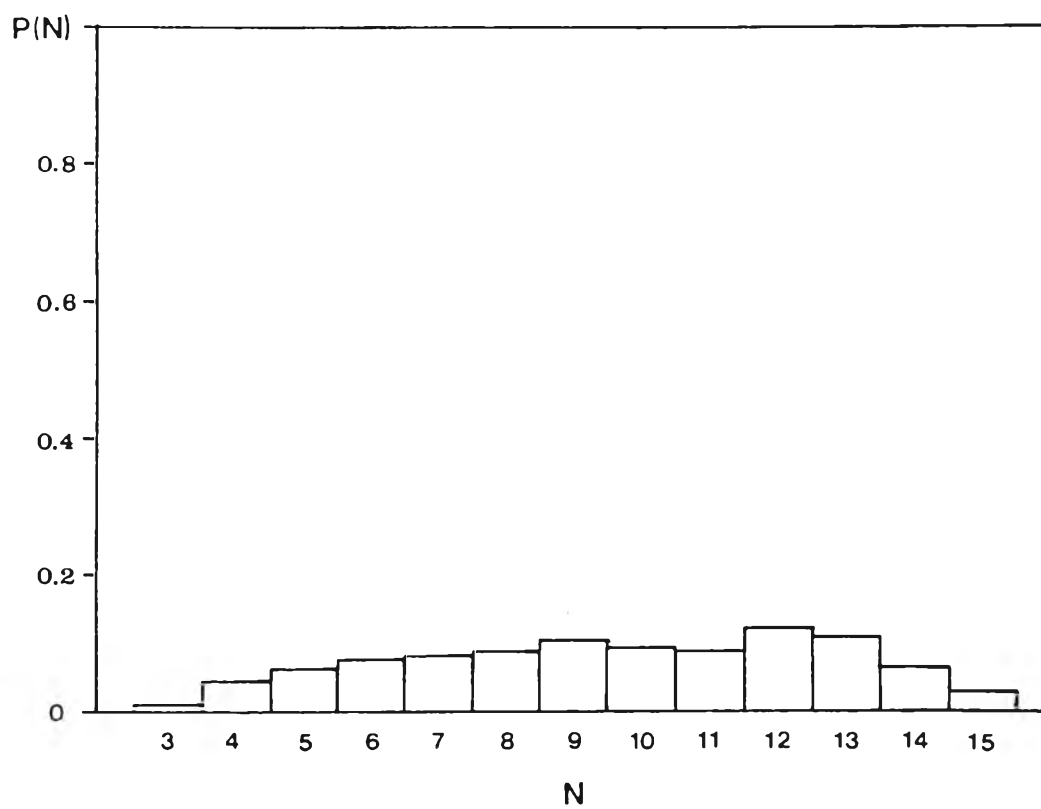


Figure 5.14 Distribution of coordination numbers for water in the first solvation sphere of ammonia.

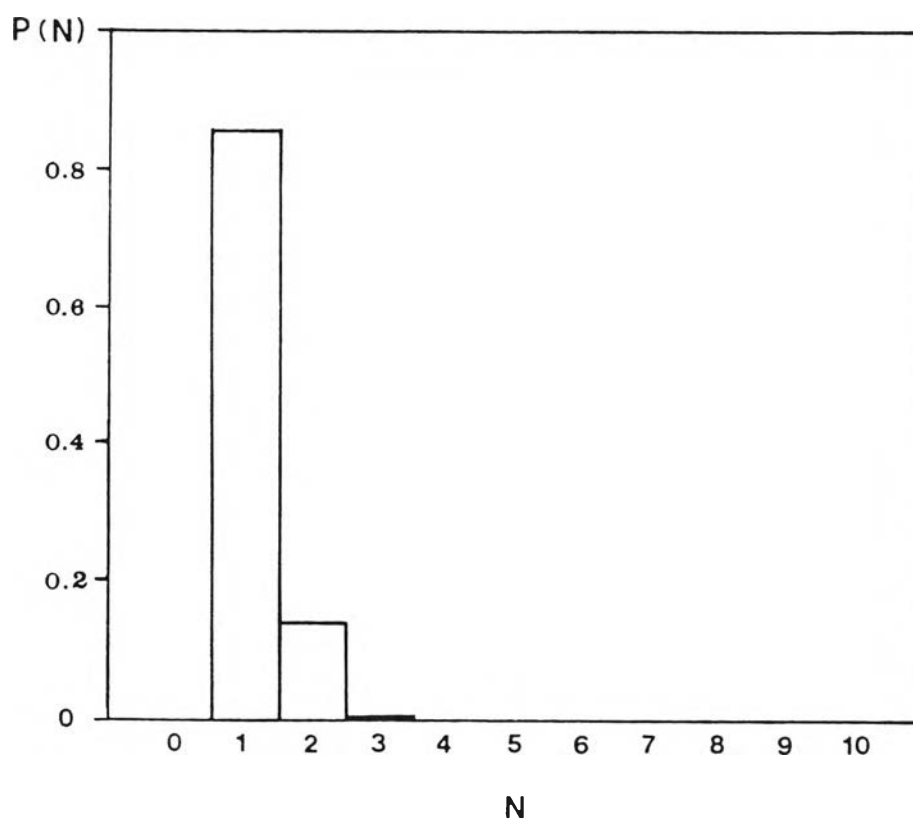


Figure 5.15 Distribution of coordination numbers for hydrogen neighbours of ammonia.

5.2.3 Distribution of Angles

The orientation of solvent molecules in the first solvation shell can be evaluated through the angular distribution functions, which are characterized by the cosine of the angles θ and ϕ representing the angle between ion coordination site vector and the dipole vector of water and ammonia molecules, respectively. The definition of θ and ϕ are illustrated in figure 5.16.

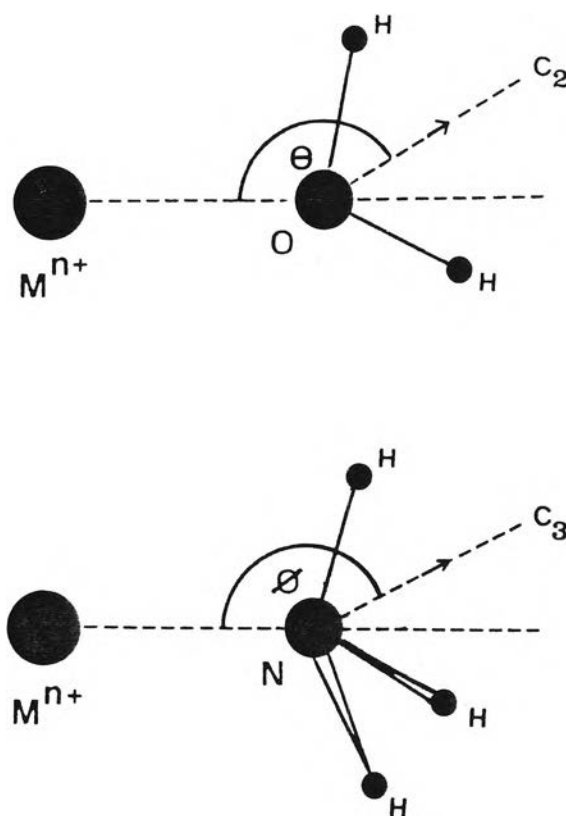


Figure 5.16 Definition of the angle θ and ϕ used in angular distributions.

Molecular orientations in the first solvation shell of lithium ion have been computed and plotted in figures 5.17 and 5.18. The main peak of $\cos \theta$ was -1.0 , indicating the favourable ion - binding configuration along the C_2 axis symmetry of water towards the oxygen's lone pairs. Water molecules are clearly dipole oriented, for ammonia however, two distinct peaks are observed. The larger one at -0.98 (169°), represents also roughly dipole orientation, the smaller one characterizes a deviation of 24 degrees from this "ideal" orientation. In connection with the splitting of the first Li(I)-N RDF peak and varying coordination numbers, this can be interpreted by the presence of ammonia molecules in non-ideal orientations at an elongated distance from the ion, most probable because of steric reasons due to ligand-ligand interactions.

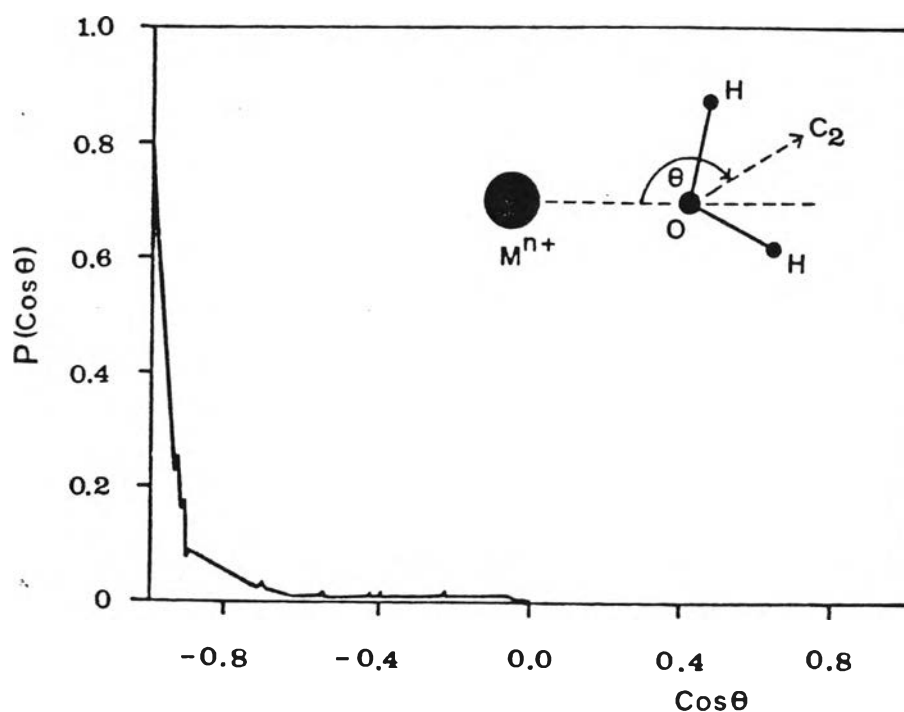


Figure 5.17 Distribution of orientation of water molecules in the first solvation sphere of lithium ion.

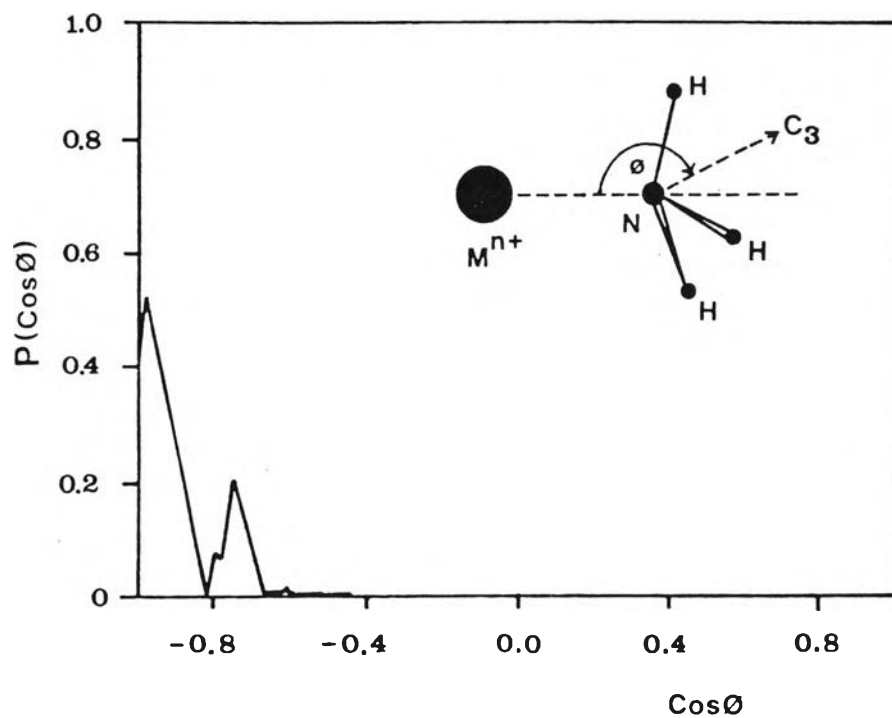


Figure 5.18 Distribution of orientation of ammonia molecules in the first solvation sphere of lithium ion.

5.2.4 Distribution of Interaction Energies

Interaction energy distributions for all pairs are shown in figure 5.19 -5.23. The ordinate gives the probability of molecules (in arbitrary units), while the abscissa shows the pair interaction energy (in kcal.mol^{-1}).

5.2.4.1 Ion/Molecule Energy Distributions

Lithium Ion/Water Energy Distributions

The resulting data for $\text{Li(I)}-\text{H}_2\text{O}$ presented in figure 5.19 shows a large separation of first shell bound waters from others. The minimal energy for $\text{Li(I)}/\text{H}_2\text{O}$ is about $-35.0 \text{ kcal.mol}^{-1}$ which is identical to the optimal value obtained from its pair potential (64).

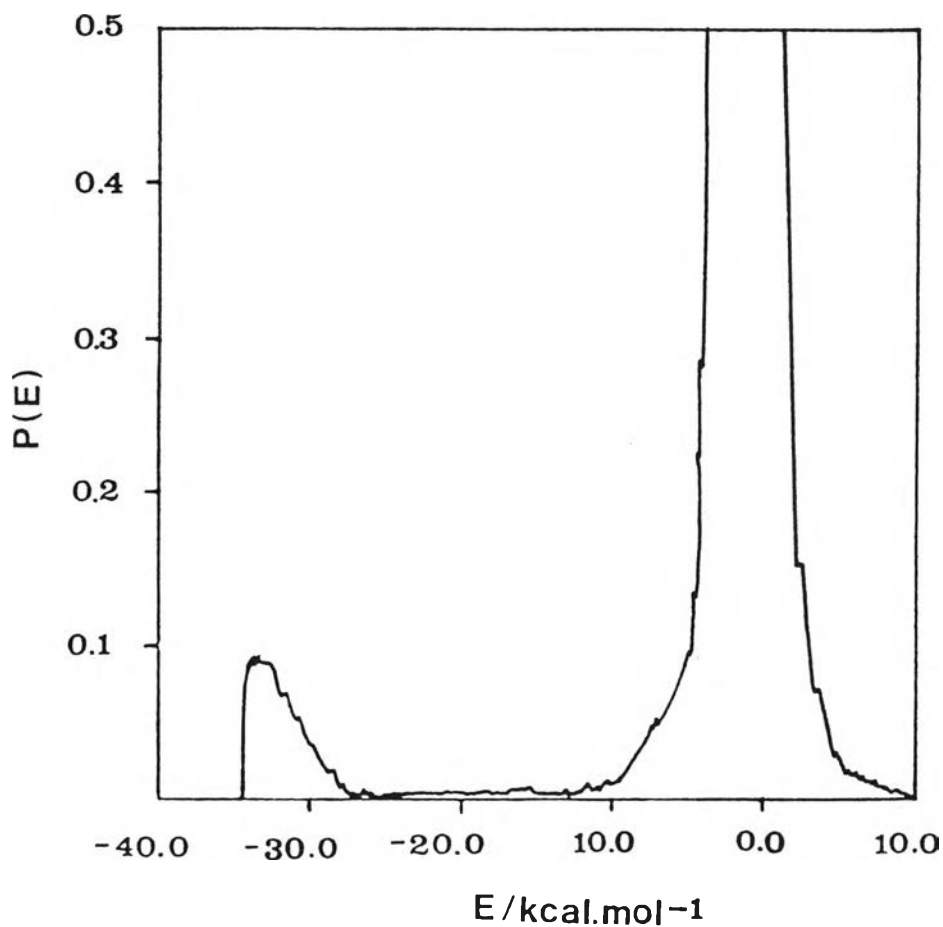


Figure 5.19 Lithium ion/water pair energy distribution functions

Lithium Ion/Ammonia Energies Distributions

As the $\text{Li(I)}/\text{NH}_3$ interaction shown in figure 5.20, the separation of the first shell is by far less clear, indicating once more exchange processes to take place rather via ammonia than water molecules. The minimal $\text{Li(I)}-\text{NH}_3$ interaction energy of $-24.0 \text{ kcal.mol}^{-1}$ indicated in this figure is $16.0 \text{ kcal.mol}^{-1}$ higher than the most stable interaction energy computed from the potential function (see chapter 3).

The decrease of $\text{Li(I)}/\text{NH}_3$ interaction, but not for those $\text{Li(I)}-\text{H}_2\text{O}$, relative to their pair potential functions could be related to either solvent-solvent interactions or to hard and soft ion-solvent interactions. That means, ammonia molecules would be oriented according to the favourable configuration of other species (H_2O and Li(I)) due to (i) the weaker hydrogen bonded of ammonia dimer in relation to ammonia-water and water-water and (ii) as mentioned before, the harder lithium ion prefers the harder oxygen atom as coordination center.

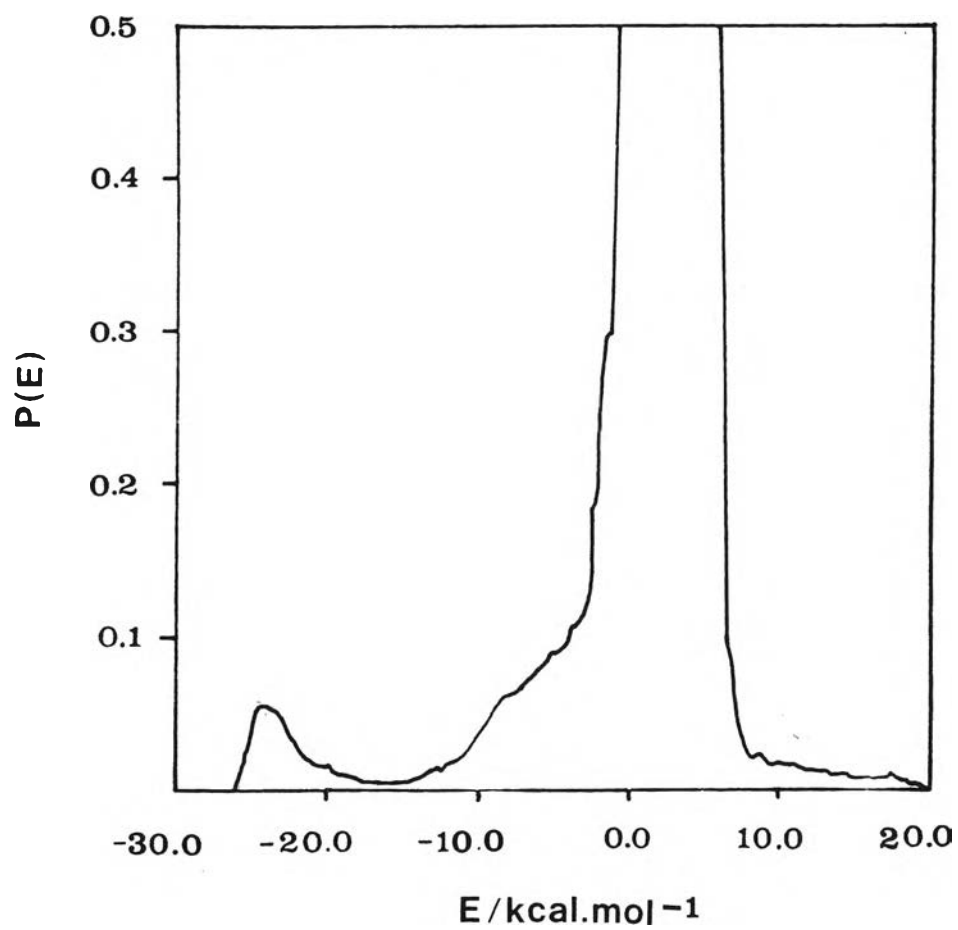


Figure 5.20 Lithium ion/ammonia pair energy distribution functions

5.2.4.2 Molecule/Molecule Energy Distributions

The distribution of dimerization energies for $\text{H}_2\text{O}/\text{H}_2\text{O}$, NH_3/NH_3 and $\text{H}_2\text{O}/\text{NH}_3$ are illustrated in figures 5.21 to 5.23, the minimal dimerization energies are -6.7 , -4.0 and $-13.0 \text{ kcal.mol}^{-1}$, respectively. For all interactions, no maximum is found, indicating rather weak interaction between solvent molecules.

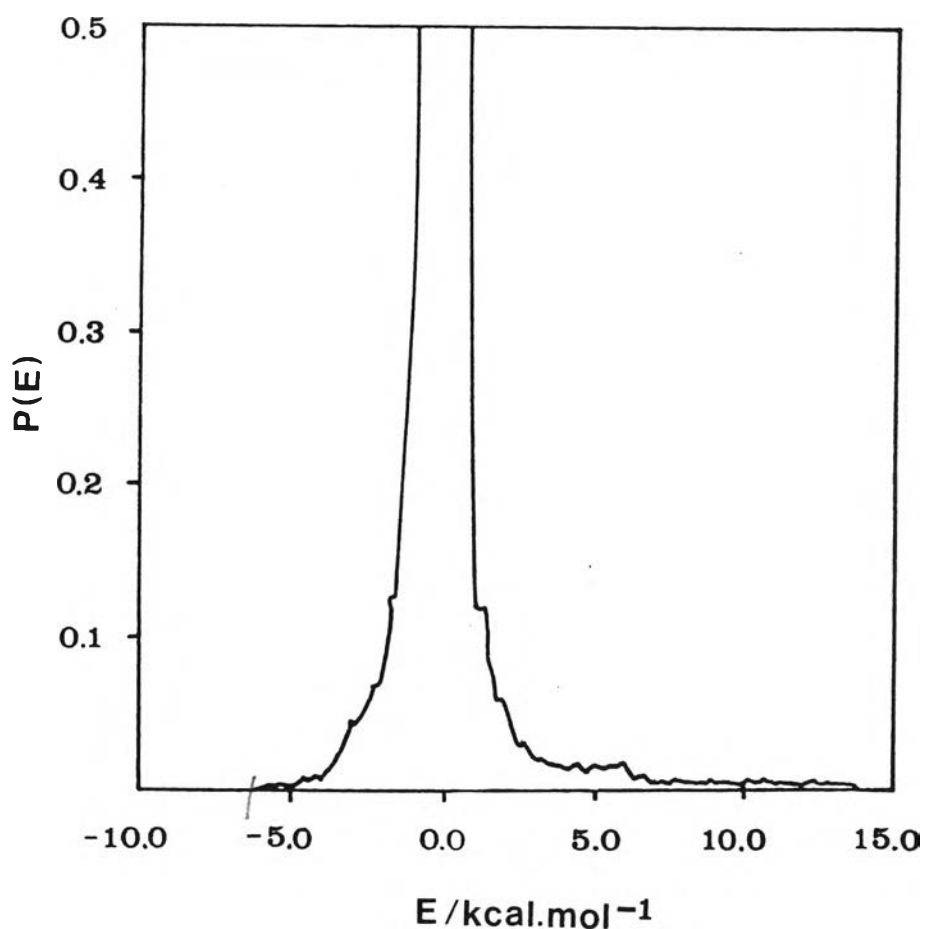


Figure 5.21 Water/water pair energy distribution functions

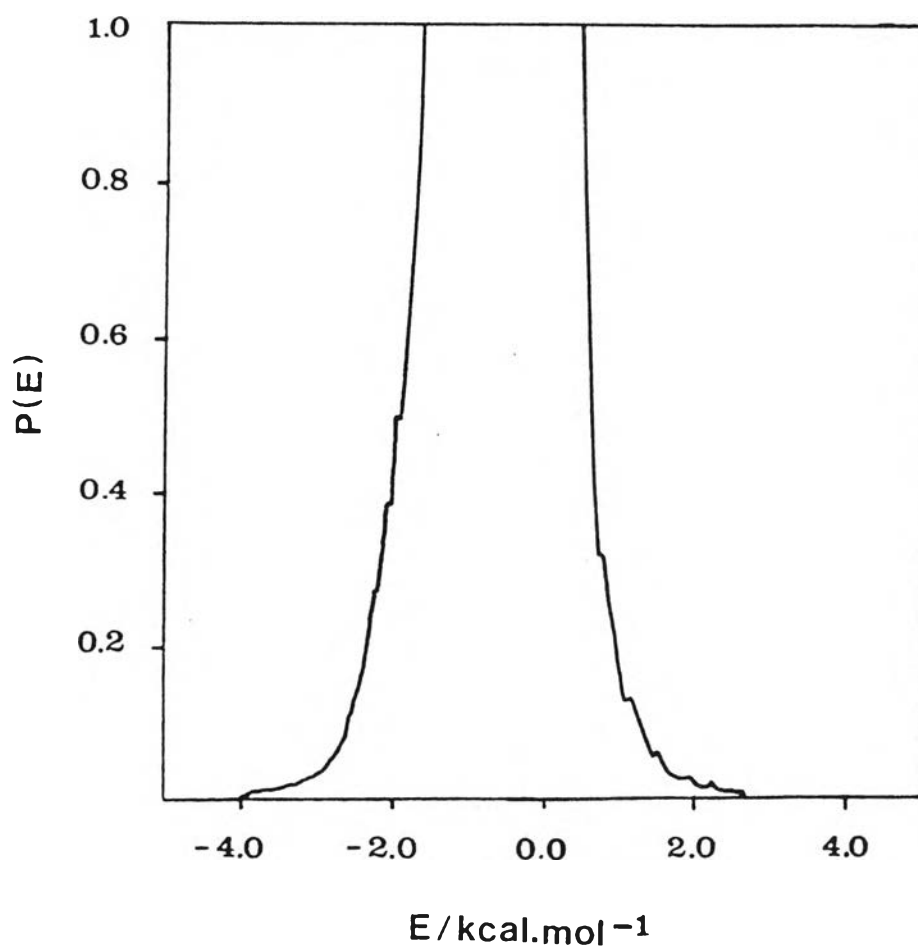


Figure 5.22 Ammonia/ammonia pair energy distribution functions

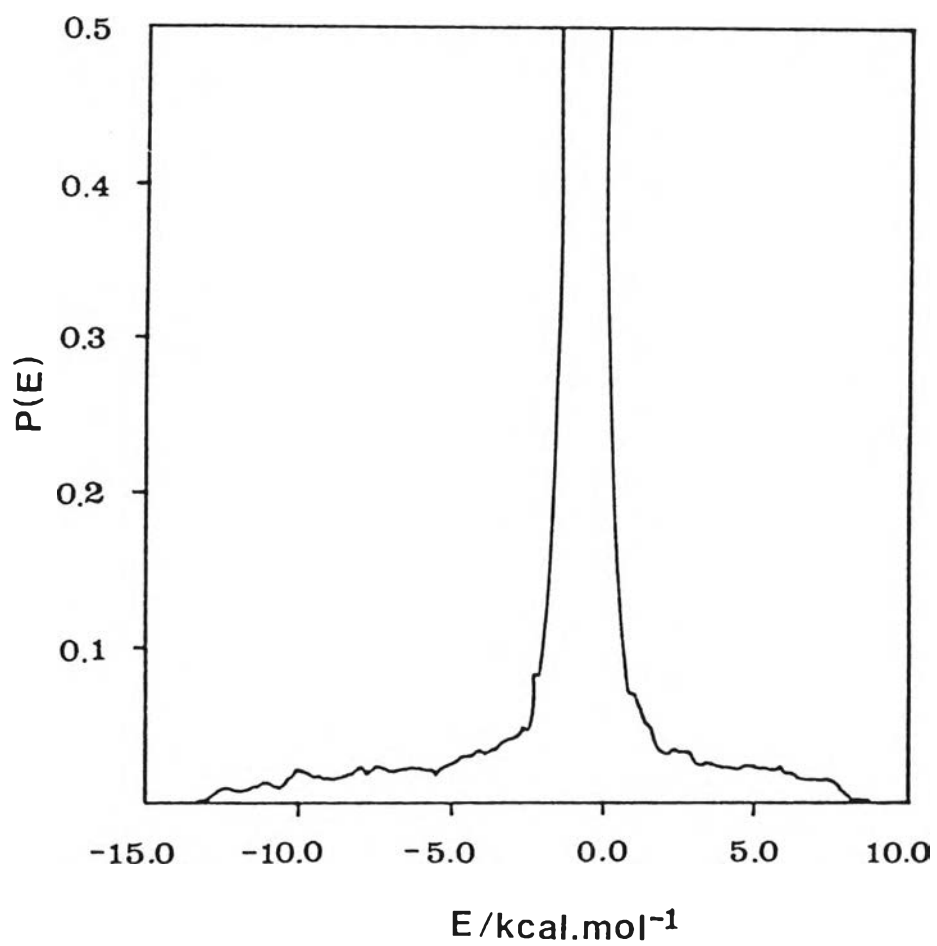


Figure 5.23 Water/ammonia pair energy distribution functions

5.2.5 Solvent Coordinates in the Ion's First Shell

In order to evaluate more details of the exact solvent position around the central ion, the distribution of the cosine angles and the N...N distances of the two ammonias in the first hydration shell of lithium ion have been calculated and plotted in figures 5.24 and 5.25, respectively. The angle β is defined as an angle between two vectors from lithium ion pointing towards each N-atom, i.e. only configurations consisting of two ammonia molecules in the first hydration shell of lithium ion (about 75 %) are taken into account. The definition of β is also given in the insertion of figure 5.19.

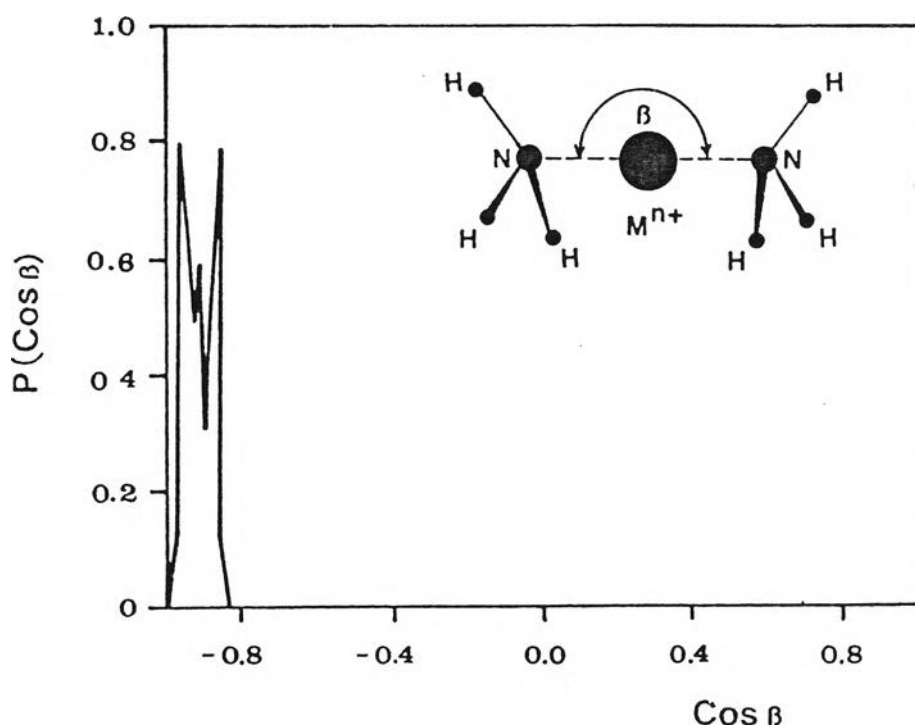


Figure 5.24 Distributions of N-Li(I)-N angles for the two ammonia molecules located in the first solvation sphere.

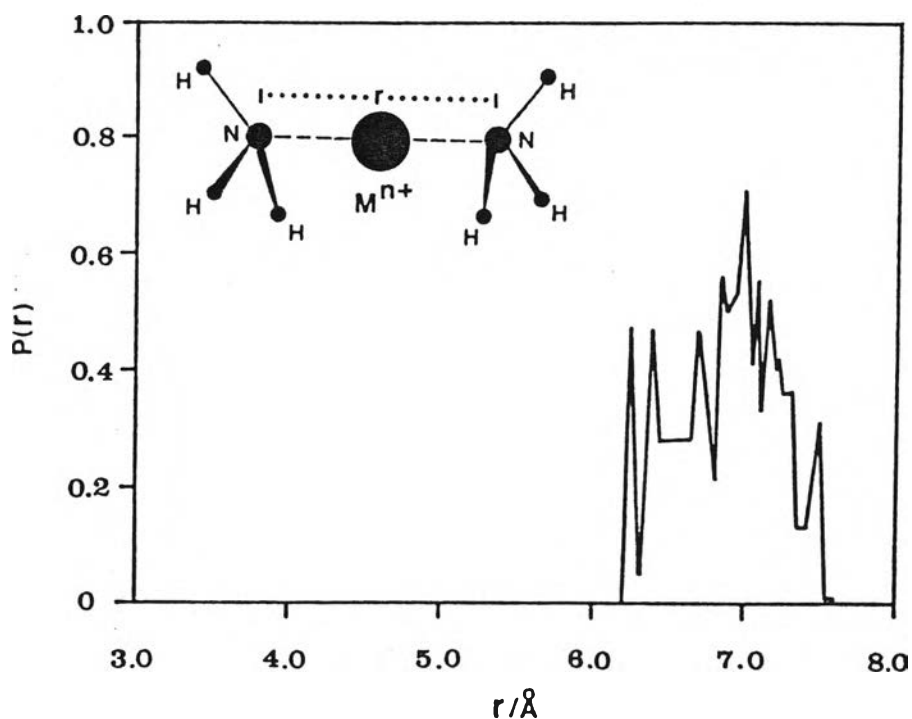


Figure 5.25 Distribution of distances between nitrogen atoms for the two ammonia molecules in the first located solvated sphere.

The distribution of cosine shows, however, two distinct peaks corresponding to the angle of 169° and 153° . This plot indicated that the two ammonia molecules are almost always located in trans position, and hence water ligands in one plane. This suggestion is clearly proved by the distribution of N...N distance varies from 6.2 to 7.6 Å, centered at about 7 Å (figure 5.24) which is nearly two times the value of the Li(I)...N distance indicated by the maximum of the first peak of Li(I)-N RDF (figure 5.3).

Computer-generated representation of one of the 10^6 possible configurations of solvent molecules in the first solvation shell of lithium ion was drawn in figure 5.26. The lithium ion is, however, octahedrally coordinated to the nitrogen and oxygen atom of the two ammonia and four water molecules, respectively. The molecular plot in this figure is in excellent agreement with the results shown in figure 5.24 and 5.25.

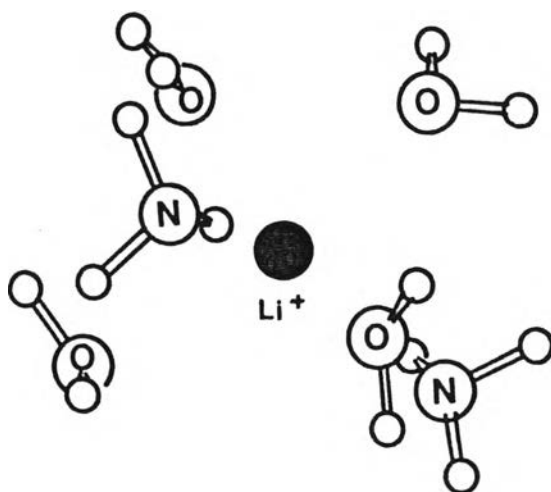


Figure 5.26 Computer-generated representation of one of the 10^6 possible configurations of solvent molecules in the first solvation shell of lithium ion.