Cluster Formation in a Concentrated Lithium-Liquid Ammonia Solution. A Monte Carlo Study

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Results of a Monte Carlo study of a lithium-liquid ammonia solution at 240 K are reported. The basic cube contained 135 Li^+ and 1025 NH_3. With an experimental density of 0.554 g/cm^3 a side-length of 37.89 Å resulted. The pseudopotential theory is employed, which permits the exclusion of the electrons from an explicit consideration. The structure of the solution is described by various site-site radial distribution functions. The six ammonia molecules in the first solvation shell of the lithium ion are arranged octahedrally. Clusters are formed which consist almost exclusively of two solvated Li^+ which have simultaneously either one ammonia molecule or an octahedral edge or an octahedral plane in common. About one third of the ammonia molecules belong to the bulk phase.

1. Introduction

In [1] an approach has been suggested for the investigation by computer simulation of systems which contain free electrons. Through the application of the pseudopotential theory, renormalized effective interatomic potentials are derived through which electrons can be excluded from explicite consideration and classical computer simulation methods can be employed. The usefulness of this method has been demonstrated by the calculation of structural properties of concentrated metal ammonia solutions. Preliminary results have been presented for two different concentrations with lithium mole fractions $x_{\mathrm{Li}} = 0.118$ and 0.1958.

Although metal ammonia solutions are of great interest from various points of view, there is a serious lack of information on their structural and dynamical properties because of experimental difficulties. Computer simulations cannot only fill this gap but can additionally contribute to a better understanding of the macroscopic properties of such systems on a molecular level.

During the course of the simulations of the lithium ammonia solutions with the potentials reported in [1], we realized that an improvement of both contributions – the direct and indirect ones – to the total potential

$$V_{\mathrm{tot}}^{ij}(R) = V_{\mathrm{ind}}^{ij}(R) + V_{\mathrm{dir}}^{ij}(R) \tag{1}$$

is needed. For the improvement of $V_{\mathrm{dir}}^{ij}(R)$, new *ab initio* calculations have been performed and during the newly performed fitting procedure the charges were not considered to be free parameters. It could be shown that it is a unique feature of metal ammonia solutions that indirect contributions are not only functions of metal concentration but also of temperature [2]. With the new potential, a Monte Carlo (MC) simulation of a lithium-liquid ammonia solution with a lithium mole fraction $x_{\mathrm{Li}} = 0.1164$ has been performed.

In the next section the improved potential will be presented, and details of the simulation will be given. The structure of the solution will be discussed in the following section on the basis of radial distribution functions, the orientation of the ammonia molecules, their geometrical arrangement in the solvation shells of the ions, and the formation of clusters consisting of solvated lithium ions.

2. Potential Functions and Details of the Simulation

A rigid ammonia model is employed in the simulation with an N-H distance of 1.0124 Å and an N-H-N angle of 106.67 ° [3]. The partial charges of 0.2674 |e| and −0.8022 |e| on the hydrogen and the nitrogen atoms, respectively, are taken from SCF calculations of the ammonia molecule [4].

The direct ammonia-ammonia potential is the same as described in [5] while the lithium-ammonia and

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lithium-lithium potentials have been newly derived from *ab initio* calculations using the DZP basis set of Dunning [6] and the HONDO 7 program [7]. They are presented now by

$$V_{\mathrm{LiN}}(R) = -\frac{1115}{R} - \frac{3516}{R^4} + 120417\exp(-3.31\,R), \quad (2\mathrm{a})$$

$$V_{\mathrm{LiH}}(R) = \frac{372}{R} + \frac{49.31}{R^4} + 2241\exp(-2.61\,R), \quad (2\mathrm{b})$$

$$V_{\mathrm{LiLi}}(R) = \frac{1390}{R} - 18.71\exp(-1.62\,R), \quad (2\mathrm{c})$$

where the energies are given in kJ/mol and R in Å.

The indirect interaction as a function of the interatomic distance, R, can be derived from the Fourier transformation of the model pseudopotential, $w_i(q)$, where $i, j = \mathrm{H}$, N and Li^+:

$$V^{ij}_{\mathrm{ind}}(R) = \frac{\Omega}{\pi^2}\int_0^\infty F_{ij}(q)\,\frac{\sin qR}{R}\,q\,\mathrm{d}q \quad (3)$$

with

$$F_{ij}(q) = \frac{\Omega q^2}{8\pi}\,w_i(q)\,\frac{1-\varepsilon(q)}{\varepsilon(q)}\,w_j(q), \quad (4)$$

where

$$w_i(q) = -\frac{4\pi z_i}{\Omega q^2}\cos(q\,r_{c,i}) \quad (5)$$

and the dielectric function

$$\varepsilon(q) = 1 + \frac{4\pi}{q^2}\,\Pi(q) \quad (6)$$

with

$$\Pi(q) = \frac{k_{\mathrm{F}}}{\pi^2}\,\frac{f(x)}{1-(4\mu^2/x^2)\,G(x)\,f(x)} \quad (7)$$

and

$$x = \frac{q}{k_{\mathrm{F}}}, \quad \mu^2 = \frac{1}{\pi k_{\mathrm{F}}}, \quad k_{\mathrm{F}} = \left(\frac{3\pi^2 z_m N_m}{\Omega}\right)^{1/3}, \quad (8)$$

$$f(x) = \frac{1}{2} + \frac{4-x^2}{8x}\ln\left|\frac{2+x}{2-x}\right|, \quad (9)$$

$$z_{\mathrm{N}} = -0.8022, \quad z_{\mathrm{H}} = 0.2674, \quad z_{\mathrm{Li}} = 1.0. \quad (10)$$

The effective radii of the ions were chosen to be

$$r_{c,\mathrm{N}} = 1.51, \quad r_{c,\mathrm{H}} = 0.0, \quad r_{c,\mathrm{Li}} = 1.28. \quad (11)$$

Ω is the volume of the system, N_{Li} and z_{Li} are the number of metal ions and their charges, respectively. For further details the reader is referred to [1].

In the course of our investigations we realized that, different from pure metals, in metal-ammonia solutions the indirect contributions to the potentials are strong functions of the temperature of the electron gas, which leads to a temperature dependence of the dielectric function. It is very difficult to describe this effect analytically. Therefore, the temperature effect has been evaluated numerically. For details see [2].

In [1, 2] the Geldart-Vosko approach was employed for the local field function $G(x)$. This approach resulted in very strong screening effects which had led to potentials which were not able to reproduce the density correctly. Therefore, we used in this investigation the Ishimaru local field function [8] leading to a modification of the indirect site-site potentials. In this approach

$$G(x) = A x^4 + B x^2 + C \quad (12)$$
$$+ \left[A x^4 + \left(B + \frac{8}{3}A\right)x^2 - C\right]\left(\frac{4-x^2}{4x}\ln\left|\frac{2+x}{2-x}\right|\right)$$

with

$$B = \frac{9}{16}\gamma_0 r_s - \frac{3}{64}[1-g(0)] - \frac{16}{15}A, \quad (13)$$

$$C = -\frac{3}{4}\gamma_0 r_s + \frac{9}{16}[1-g(0)] - \frac{16}{15}A, \quad (14)$$

$$g(0) = \frac{1}{8}\left(\frac{Y}{J(Y)}\right)^2, \quad (15)$$

$$A = 0.029, \quad Y = 4\left(\frac{\lambda r_s}{\pi}\right)^{1/2} = 4\sqrt{1/\pi\,k_{\mathrm{F}}},$$
$$r_s = \left(\frac{9\pi}{4}\right)^{1/3}/k_{\mathrm{F}}, \quad (16)$$

where $J(Y)$ is a modified Bessel function.

The new total and direct potentials for the ammonia-ammonia as well as the lithium-ammonia interactions are depicted in Figure 1. The full lines show that the new *ab initio* calculations lead to deeper minima compared with the previous ones [1]. The screening affects the two different interactions now in a similar way. The minima of both direct potentials are reduced by about 10% by the indirect contributions. A more detailed picture results from the site-site potentials which are presented in Figure 2.

The direct contributions to the ammonia-ammonia potential have not been changed compared with the previous ones [1, 5]. The indirect contributions to the N-H interaction differ significantly. The reduced

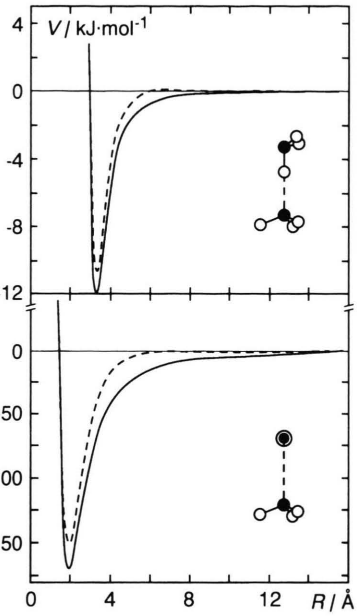

Fig. 1. Ammonia-ammonia (top) and lithium-ammonia (bottom) pair potentials as a function of nitrogen-nitrogen and lithium-nitrogen distances for orientations as shown in the insertion and at a temperature of 240 K with a lithium mole fraction of 0.1146. The full and dashed lines denote the direct and the total potential, respectively.

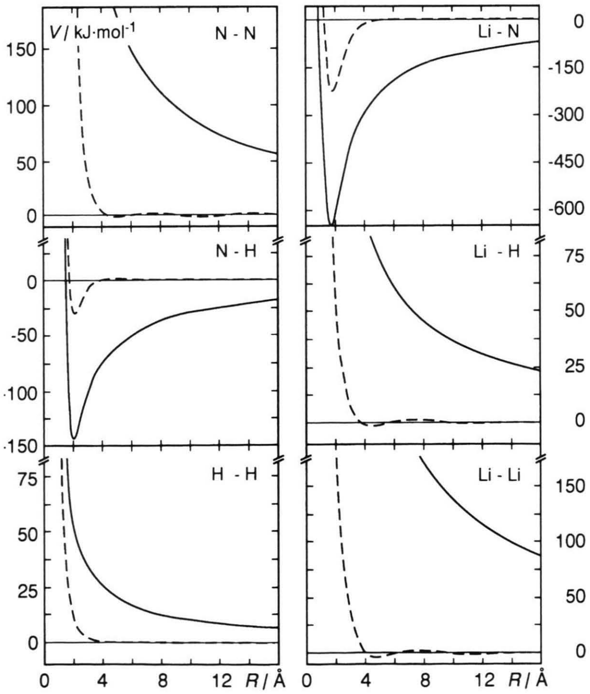

Fig. 2. Site-site potentials for the six different interactions in the lithium-liquid ammonia solution. The denotations are the same as in Figure 1.

screening is responsible for the lower minima. Although there are significant differences in the site-site potentials, the molecule-molecule interaction remains almost unchanged because of the mutual compensation of the changes in the direct and indirect contributions (Figure 1).

The improved Li-N, Li-H and Li-Li direct contributions – resulting from the new *ab initio* calculations – differ significantly from the older ones [1, 5]. They are generally weaker. But the minimum in the lithium-ammonia potential is by about 20% deeper because of a smaller mutual compensation. With the modifications of the pseudopotential theory described above the screening becomes stronger in the case of the Li-N and Li-H interactions. Similar to the direct contributions, the mutual compensation of the site-site potentials leads again to a lower minimum in the total lithium-ammonia potential compared to the older one [1]. Differently, the screening of the Li-Li interactions is less pronounced and the minimum in the total Li-Li potential has become much shallower.

The Metropolis Monte Carlo method [9] was employed. The basic cube contained 135 lithium ions and 1025 ammonia molecules. With an experimental density of 0.554 g/cm^3 at 240 K and 1 atm, a sidelength of the periodic cube of 37.89 Å resulted. Due to the strong screening of the Coulombic interactions by the indirect contributions (see Fig. 2), a cut-off of the total site-site potentials at 15 Å was justified, which saved a significant amount of computer time compared with the Ewald method. The starting configuration was randomly generated. The simulations were carried out for 40 million configurations in order to equilibrate the system. The next 3 million configurations were employed for the evaluation of the structural properties of the solution.

3. Results and Discussion

a) Radial Distribution Functions

The solvent-solvent, ion-solvent and ion-ion RDFs and the corresponding running integration numbers are presented in Figure 3. Their characteristic values as well as those obtained for a single lithium ion in 215 ammonia molecules [5] are summarized in Table 1. The coordination numbers are defined as the running integration numbers at the positions of the first minima of the RDFs.

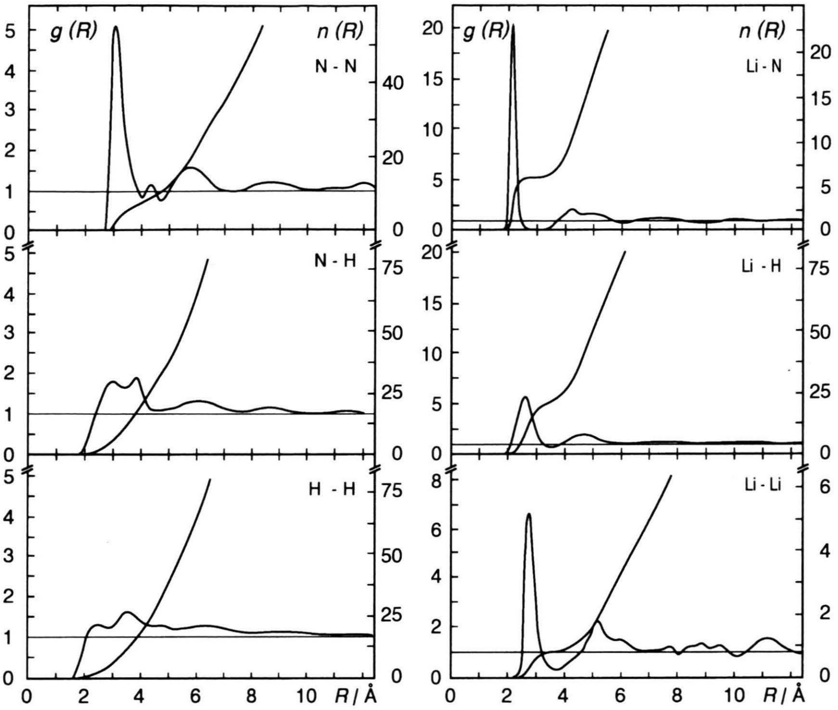

Fig. 3. Partial radial distribution functions and running integration numbers.

Table 1. Characteristic values of the radial distribution functions $g_{xy}(R)$. R_i, and R_{Mi} and R_{mi} are the distances in Å, where for the ith time $g_{xy}(R)$ is unity, has a maximum and minimum, respectively. The values for the dilute solution, $x_{Li} = 0.0046$, are also given for comparison.

xy	$x_{Li} \cdot 100$	R_1	R_{M1}	$g_{xy}(R_{M1})$	R_2	R_{m1}	$g_{xy}(R_{m1})$	R_{M2}	$g_{xy}(R_{M2})$	$n_{xy}(R_{m1})$
NN	11.98	2.80	3.04/4.32	5.1/1.2	3.88	4.06/4.68	0.9/0.7	5.92	1.6	8.1/10.7
	0.46	3.04	3.38	2.2	4.29	5.0	0.7	6.64	1.2	12.8
NH	11.98	2.40	3.00/3.82	1.8/1.9	–	4.48	1.1	6.00	1.4	28.6
	0.46	3.11	3.62	1.3	4.47	4.9–5.3	0.8	–	–	34.2–43.4
HH	11.98	2.04	2.38/3.56	1.3/1.6	–	–	–	–	–	–
	0.46	3.07	3.82	1.2	4.56	5.0–5.5	0.9	–	–	36.5–47.6
LiN	11.98	1.95	2.16	20.0	2.50	2.88	0.2	4.30	2.1	6.0
	0.46	2.01	2.29	15.9	2.53	2.80	0.0	4.38	2.9	6.0
LiH	11.98	2.13	2.64	5.6	3.27	3.46	0.7	4.64	1.9	20.6
	0.46	2.54	2.87	6.5	3.16	3.40	0.0	5.00	1.9	18.0
LiLi	11.98	2.51	2.74	6.6	3.25	3.72	0.3	5.24	2.3	0.8
	0.46	–	–	–	–	–	–	–	–	–

Significant changes in the solvent structure can be observed by the comparison of the N-N, N-H and H-H RDFs for the two different concentrations. In the simulation with the single lithium ion, these RDFs are nearly the same as in pure ammonia [5]. The pseudopotential theory has not been employed in this case. Consequently, there exists no indirect contribution to the total potential.

The screening in the concentrated solution strongly reduces the repulsion for the N-N and H-H interactions (Fig. 2) and leads, therefore, to more pronounced first peaks in the corresponding RDFs at significantly shorter distances compared with the very dilute solution (Table 1). In spite of the fact that the potential minimum for the N-H interaction is also strongly reduced by the screening, the first peak in $g_{NN}(R)$ is more pronounced. The reduction in the N-N and H-H repulsion overcompensates this effect, as can be seen from the total ammonia-ammonia potential depicted in Fig. 1, where the indirect contributions reduce the potential minimum by only about 10%.

In the concentrated solution, where 7.5 ammonia molecules are available for each lithium ion, the N-N RDF is in accordance with the formation of clusters where two solvated Li^+ have one, two or three ammonia molecules in common (see below). In such a cluster, where the six NH_3 molecules in the first solvation shell of lithium are octahedrally arranged (Table 1 and Fig. 4), one would expect about eight nearest neighbor nitrogen atoms around a central one at a distance of about 3 Å (first peak in $g_{NN}(R)$) and another two at about 4.3 Å, twice the Li-N distance (small intermediate peak) in agreement with the coordination numbers, $n_{NN}(R_{m1})$, given in the last column of Table 1. In keeping with this picture, both the first maximum and the first minimum in pure ammonia are found at distances longer by about 0.3 Å [5], resulting in a coordination number larger by about three than in the concentrated solution. Roughly speaking, the two Li^+ in the cluster are replaced by two ammonia molecules, and additional contributions come from the ammonia molecules in the bulk phase.

In accordance with the cluster formation, the second nearest ammonia neighbors would appear at about 6 Å (second peak in $g_{NN}(R)$; 0.7 Å shorter than in the dilute solution). This maximum is formed by the more than 30% ammonia molecules outside of the first solvation shells of the lithium ions.

The cluster formation in the concentrated solution leads – similar to $g_{NN}(R)$ – also in $g_{NH}(R)$ and $g_{HH}(R)$ to more pronounced first peaks at shorter distances than in pure ammonia [5]. The broad maxima there are splitted now. But it seems to be quite difficult to assign definite structures to the characteristics of these RDFs. Also the long range parts of all three solvent RDFs differ significantly for the two concentrations, which is again a consequence of the cluster formation.

The screening effect of the electrons leads to a slightly shorter distance of the first peaks in $g_{LiN}(R)$ and $g_{LiH}(R)$ when compared with the very dilute solution (Table 1). Although the coordination number does not change, the first peak in $g_{LiN}(R)$ is slightly higher and that in $g_{LiH}(R)$ slightly lower in the concentrated solution. Both first minima are less pronounced. The larger coordination number for hydrogen, $n_{LiH}(R)$, is expected to result either from a less strong orientation of the solvation shell ammonia molecules because of screening effects, or from the undefined orientations of the ammonia molecules common to two lithium ions (see Figure 5).

The small effect of the lithium concentration on the structure of the solvation shell is in accordance with the only 10% decrease in the potential minimum of the lithium-ammonia interaction by the indirect contributions (Figure 1). The rather rigid solvation shell structure is confirmed by the finding that in 90% of all cases the coordination number is six while in only 5% each it is 5 or 7 (see also Figure 4).

The first peak in $g_{LiLi}(R)$ is quite pronounced at 2.4 Å. This distance is much shorter than the flat potential minimum between 4 and 5 Å (Figure 2). The running integration number is one at about 4.5 Å. This leads – as in $g_{NN}(R)$ – again to the conclusion that cluster formation must occur in spite of the fact that

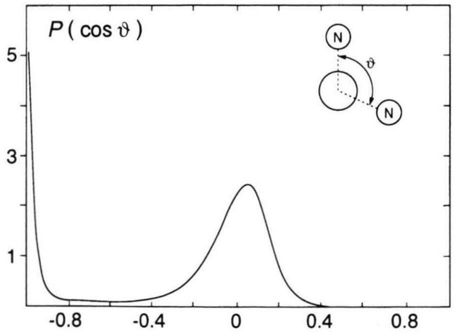

Fig. 4. Distribution of cos ϑ – where ϑ is defined as the nitrogen-lithium-nitrogen angle – calculated for the ammonia molecules in the first solvation shell of the lithium ion.

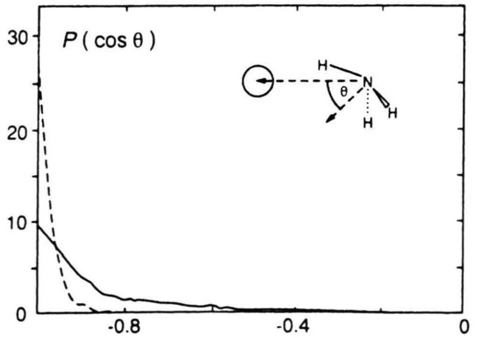

Fig. 5. Normalized distributions of cos θ for the ammonia molecules in the first solvation shells of the lithium ions. θ is defined in the insertion. Full and dashed lines refer to lithium mole fractions of 0.1164 and 0.0046, respectively.

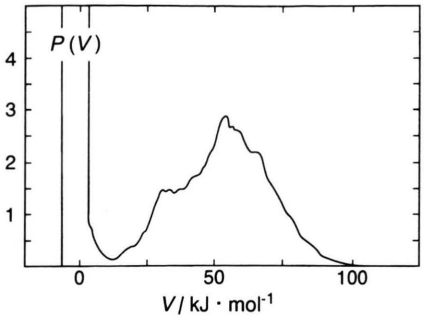

Fig. 6. Lithium-lithium pair interaction energy distribution in arbitrary units.

at least 30% of all ammonia molecules do not belong to a first solvation shell (see below).

The $g_{\mathrm{LiLi}}(R)$ is in accordance with the pair interaction energy distribution, $P(V_{ij})$, shown in Figure 6. The positive energies at about 50 kJ/mol result from the interaction of two Li^+ characterized by the first peak in $g_{\mathrm{LiLi}}(R)$, as can be seen from a comparison with $V^{\mathrm{tot}}_{\mathrm{LiLi}}(R)$ depicted in Figure 2. The negative energies mainly result from those Li^+ which belong to the second peak. At this distance $V^{\mathrm{tot}}_{\mathrm{LiLi}}(R)$ has its flat minimum. The large number of small positive interactions result from Li^+ at distances larger than 6 Å.

b) Solvation Shell Structure

The geometrical arrangement of the ammonia molecules in the solvation shells of the lithium ions can be deduced from the simulation by the calculation of the distribution of cos ϑ, where ϑ is defined as the N-Li-N angle. The result is depicted in Fig. 4, where only the ammonia molecules in the first solvation shells are included in the distribution.

It is obvious from Fig. 4 that the six ammonia molecules are arranged octahedrally around the lithium ion. The integration over the distribution shows that there is one other solvation shell molecule at about 180° and four more at about 90°. It is interesting to note that the maximum is not exactly at $\cos\vartheta = 0$ but shifted slightly to positive values, appearing at 86°. This slight disturbance of the octahedral arrangement might be caused by the cluster formation as discussed below, where one, two or three ammonia molecules belong simultaneously to the solvation shell of two lithium ions.

c) Orientation of the Ammonia Molecules

The orientation of the ammonia molecules in the solvation shells of the lithium ions is described by the distribution of cos θ, where θ is defined as the angle between the dipole moment direction of the ammonia molecule and the vector pointing from the nitrogen atom towards the ion. The normalized distributions are presented in Fig. 5 for the two concentrations with the mole fractions 0.1164 (full) and 0.0046 (dashed).

For both concentrations there is a strong preference for the dipole moment of the ammonia molecule pointing away from the ion. The distribution is much broader for the concentrated solution. The reason for the significant difference in the widths of the distributions is expected to be connected with the cluster formation (see below). In the case of the single ion (dashed), solely the interaction between solvation shell molecule and the ion determines the orientation because of the relatively weak interactions between the solvation shell molecules and those in the bulk. In the concentrated solution, however, where – because of the cluster formation – one, two or three ammonia molecules belong simultaneously to the solvation shells of two lithium ions, there is a competition between the two ions for the energetically most favorable orientation leading to the broad distribution.

d) Cluster Formation

In order to understand in more detail the different features of the various RDFs depicted in Fig. 3, we have investigated in a first step the distribution of the ammonia molecules between the first solvation shells of the lithium ions and the bulk. An ammonia molecule is considered to belong to the first solvation shell if the Li-N distance is smaller than $R_{\mathrm{m1}} = 2.88$ Å, the position of the first minimum in the Li-N RDF. The coordination number of an Li^+, defined by $n_{\mathrm{LiN}}(R_{\mathrm{m1}})$, is found to be six (Table 1). It has been calculated from the simulation that 33% of all NH_3 belong to the bulk. From the remaining 67% of the molecules, 55% are coordinated to one Li^+ and 12% simultaneously to two Li^+. In the following discussion we shall denote these three kinds of NH_3 molecules by N0, N1, and N2, respectively. It has been mentioned above that the formation of clusters explains the positions of the first as well as that of the small second peak in the N-N RDF. The shoulder at the long distance side of the first peak results from the N-N distances in the bulk, where a broad first maximum exists which is centered at 3.4 Å (Table 1).

The next point of interest is the distribution of the ammonia molecules N1 and N2 in the first solvation shells of the 135 lithium ions in the solution. With the denotation $Li(N1)_m(N2)_{6-m}$, the result is given in Table 2.

Table 2. The fraction in % of the clusters of kind *m*.

m	6	5	4	3	2
%	32	8	16	38	6

The structure of the clusters can be visualized easily. The octahedrally arranged solvation shells of two lithium ions have an NH_3 molecule, an edge and a plane in common for m equal to 5, 4, and 3, respectively. For m2 one can imagine that a central solvated Li^+ has two of his edges in common with two neighboring ones. From the numbers in Table 2 it could not be excluded that clusters with more than 3 Li^+ exist in the solution as e.g. the cluster m2 could be imagined with five Li^+ where four of them are combined with a central one by having one NH_3 molecule each in common. It will be demonstrated in the next paragraph that the probability to find such clusters is very small.

The number of nearest neighbor lithium ions around a central one up to the first minimum of the Li-Li RDF at 3.72 Å, $n_{LiLi}(r_{m1})$, is 0.8, in accordance with the distribution given in Table 3.

Table 3. Percentage of nearest neighbor lithium ions, $n_{LiLi}(R_{m1})$, around a central one.

$n_{LiLi}(R_{m1})$	0	1	2	3
%	40	44	14	2

The Li-Li distances for the clusters m3, m4 and m5 are about 2.8, 3.1 and 4.3 Å, respectively. This means that clusters m5 and m6 do not contribute to the first peak in the Li-Li RDF and consequently $n_{LiLi}(R_{m1}) = 0$, in agreement with Table 2. As there is no peak around 4.3 Å in $g_{LiLi}(R)$ and a shoulder can hardly be recognized, it has to be concluded that the number of clusters m5 is quite small, again in accordance with Table 2. This means also that in the clusters m4, m3 and m2 those with common edges and common octahedral planes are the by far most important ones, excluding contributions to these clusters from m5. The second peak in the Li-Li RDF must consequently almost exclusively result from the independently solvated lithium ions (m6).

Sarkar et al. [10] have deduced recently from a renewed evaluation of older X-ray data by Narten that clusters are formed in pure liquid ammonia at 277 K. This result cannot be related to the cluster formation here.

Acknowledgements

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