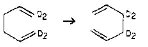
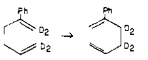
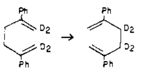
Table VI. Calculated and Observed SDKIEs[a] in Cope Rearrangements

		SDKIE[a]			
	temp	forward reaction[b]		reverse reaction[c]	
reaction	(K)	calcd	obsd	calcd	obsd
	512	1.15	1.129 ± 0.019[d]	1.00	1.07 ± 0.025[d]
	448	1.28	1.295 ± 0.003	1.01	1.09 ± 0.02
	328	1.51	1.57 ± 0.035	1.07	1.07 ± 0.024

[a] Secondary deuterium kinetic isotope effect. Experimental values from ref 14. [b] K_D/K_H. [c] K_H/K_D. [d] Experimental values for monomethyl derivatives.

to large changes in the SDKIE.

Quantitative interpretations of SDKIEs should therefore be based on comparisons with theoretical calculations. Since values were available[15] for three of the reactions studied here, i.e., the rearrangements of **6**, **11**, and **15**, we accordingly calculated the corresponding SDKIEs, using AM1. While AM1 has not previously been applied to SDKIEs, there are good reasons for believing that the results should be satisfactory. Earlier work[43] here has shown that MINDO/3 gives good estimates of deuterium kinetic isotope effects for reactions, as would be expected in view of the satisfactory results obtained from calculations of molecular vibration frequencies,[44] including the changes that take place on deuteriation.[45] Since studies of a number of molecules have shown that AM1 gives generally better estimates of vibration frequencies than MINDO/3, as would be expected in view of the general superiority of MNDO,[46] AM1 should give at least equally good estimates of kinetic isotope effects.

The isotopic rate ratios were estimated (see ref 43) from the differences in enthalpy and entropy of activation calculated for the parent and deuteriated species, these being determined by standard procedures from the vibration frequencies and moments of inertia calculated for the reactants and TSs. The calculations were carried out for **6**, **11**, and **15** and for the deuteriated species (see Table VI) studied by Gajewski and Conrad.[15] No accurate measurements seem to be available for **1**. Table VI compares the calculated and observed isotopic rate ratios.

Our calculations reproduce closely the experimental values for the forward reactions, which cover a wide range, and also for the reverse reaction of **11**. Our calculations predict smaller rate ratios for the reverse reactions of **6** and **15** than for **11** whereas the values reported by Gajewski and Conrad are almost the same for all three. The differences are, however, small, being respectively four and three times the reported standard deviations. They are certainly within the limits set by the accuracy of the experiments and calculations. There is therefore no reason to suppose that the SDKIE data are not consistent with our conclusions concerning the mechanisms of these reactions.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Grant No. AFOSR 86-0022), the Robert A. Welch Foundation (Grant F-126), and the National Science Foundation (Grant CHE82-17948).

Registry No. 1, 592-42-7; **6**, 7399-52-2; **9**, 1076-66-0; **10**, 63779-63-5; **11**, 7283-49-0; **13**, 56644-04-3; **15**, 1541-33-9; **17**, 7736-22-3; O_2, 7782-39-0.

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Ionic Solvation in Nonaqueous Solvents: The Structure of Li^+ and Cl^- in Methanol, Ammonia, and Methylamine

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Contribution from the Chemistry Division, National Research Council of Canada, Ottawa, Canada K1A 0R6. *Received May 6, 1986*

Abstract: Molecular dynamics calculations have been performed on dilute solutions of Li^+ and Cl^- ions in methanol, ammonia, and methylamine. The simulations have been carried out with potentials parametrized, in part, to ab initio molecular orbital calculations. In these solvents Li^+ has a well defined dipole ordered first solvation shell of four molecules with additional structure evident in the second solvation shell. In all three solvents Cl^- has a well defined bond ordered first solvation sheath. The solvation number for Cl^- in methanol is about 5, which is smaller than that in aqueous solution. These findings accord well with the available experimental information.

Over the past decade or so, a considerable effort has been devoted to understanding the nature of ionic solvation in aqueous solution. One of the most significant developments has been the determination of solvent sheath structures with neutron diffraction techniques.[1] In addition, important insights have been gained from the use of Monte Carlo[2-4] and molecular dynamics[5] calculations based upon simple potential models for the water-water and ion-water interactions. Although considerable theoretical effort has been directed to aqueous solvation, by contrast, relatively little work has appeared on nonaqueous solvents; the work of

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(1) For a review of structural studies see, for example: (a) Neilson, G. W.; Enderby, J. E. *Annu. Rep. Progr. Chem., Sect. C* **1979**, *76*, 1985. (b) Enderby, J. E.; Neilson, G. W. *Rep. Prog. Phys.* **1981**, *44*, 38.

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0002-7863/87/1509-5900$01.50/0

Jorgensen and co-workers[6] being a notable exception. Nonaqueous solvents play an important role in chemistry, and it is surprising therefore that their study has so far received relatively little attention from theoreticians.

A large body of experimental information on ionic solvation in nonaqueous solvents already exists. As an example, we cite the work of Symons and co-workers,[7] who have obtained evidence for a difference between the aqueous and methanolic solvation of anions. In the case of Cl^- they found that the solvation number in water was about 6 compared to only 4 in methanol. The experimentally determined methanolic solvation numbers are believed to be sufficiently reliable to be of use in assessing computer calculations and this, in part, is the motivation for our work.

Methanol is not the only nonaqueous solvent of interest. The study of metal ammonia solutions has a long and venerable history.[8] Although the nature of the solvated electron and the metal-insulator transition are the primary concerns, cation solvation likely also plays a role.[9] The physical properties of alkali metal ammonia solutions are often contrasted with those of alkali metals in methylamine.[9,10] While structural information on lithium-ammonia solutions has emerged recently from an analysis of neutron diffraction measurements,[11] no comparable data are available for methylamine. Here, computer calculations based upon model potentials can provide the first clues to the behavior of this solvent.

In view of the foregoing remarks we have carried out molecular dynamics calculations on dilute solutions of Li^+ and Cl^- in the solvents methanol, ammonia, and methylamine. The interest in simulating Cl^- in the latter two solvents is due to the fact that it is roughly the same "size" as an electron in a polar fluid and thus provides a classical model with which to compare electron solvation calculations.[12]

The outline of the paper is as follows. We first discuss the potential functions to be used in the calculations. The solvent potentials for ammonia and methanol have been taken from the literature,[13-16] but the potential for methylamine is new. The ion-solvent potentials have been derived in much the same way as those of Jorgensen et al.[2] Next, we present the results and compare our findings with the available experimental data for solvation in methanol[7] and ammonia.[11] The article, which is solely concerned with structural properties, ends with a brief summary.

Potential Functions

(a) Solvent Interactions. A number of effective pair potentials have been proposed which reproduce the essential features of the structure of water. The simplest models consist of a Lennard-Jones (12-6) oxygen-oxygen (but *no* hydrogen-hydrogen) potential plus electrostatic interactions between three charge sites on each molecule.[13,14] The simplicity of these models should not obscure the fact that they do remarkably well in reproducing experimental properties. An analogous model has been proposed for ammonia.[15] Here, there are four charge sites, one on each hydrogen atom and the fourth (M) on the molecular symmetry axis, 0.156 Å from the nitrogen toward the hydrogen atoms, plus a nitrogen-nitrogen Lennard-Jones (12-6) potential.

Table I. Potential Parameters

solvent/ ion	atom/ group	q, e	$10^{-3}A^2$, kJ·Å^{12}/mol	C^2, kJ·Å^6/mol
CH_3OH	CH_3	0.297	33270	10040
	O	−0.728	2510	2156
	H	0.431	0	0
NH_3	N	0	11070	7170
	H	0.462	0	0
	M	−1.386	0	0
CH_3NH_2	CH_3	0.25	25780	8563
	N	−1.05	4743	3673
	H	0.40	0	0
Li^+	Li	1.00	1.6	418
Cl^-	Cl	−1.00	108800	14600

In the case of methanol it appears that a reasonable model can also be obtained without explicitly treating the methyl group hydrogen atoms.[16] The proposed model consists of methyl-methyl and oxygen-oxygen Lennard-Jones (12-6) potentials plus three charge sites located on carbon, oxygen, and the hydrogen atom of the OH group, respectively.

In all cases the potential parameters were chosen to give roughly the correct molecular dipole moments (slightly enhanced as a crude allowance for induction effects) and also the correct liquid density and binding energy. It is in this sense that the models should be regarded as *effective* pair potentials.

To the best of our knowledge no such potentials exists for methylamine. Accordingly, in analogy with the derivation of the methanol potential we employed a four-site model with methyl-methyl and nitrogen-nitrogen Lennard-Jones (12-6) potentials plus four charge sites on carbon, nitrogen, and the two hydrogen atoms of the amine group, respectively. An initial set of parameters was taken from studies on related systems,[17] although minor adjustments were necessary to ensure the correct liquid density and binding energy.[18]

As mentioned above, the interaction potentials are the sum of Coulombic terms between charge sites and Lennard-Jones terms of the form[2]

$$V_{ij}(r_{ij}) = A_iA_j/r_{ij}^{12} - C_iC_j/r_{ij}^{6} \qquad (1)$$

The solvent atom or group potential parameters and their associated charges are listed in Table I.

(b) Ion-Solvent Potentials. The potential parameters for the lithium and chloride ions listed in Table I were taken from previous studies on aqueous solutions without modification.[2] We recall that these parameters were chosen to reproduce experimental interaction energies and calculated geometries of ion-water and ion-methanol complexes.[19] These ion-ion parameters, which are used to construct the ion-solvent potentials, were not constrained to fit existing data on ion-ammonia or ion-methylamine complexes.[19] They nevertheless give a good account of the available information.

Simulation of Dilute Solutions

Constant volume molecular dynamics calculations[20] have been performed on the pure solvents and solutions containing a single ion and either 107 ammonia or 127 methanol or methylamine molecules in a cube with periodic boundary conditions. The ion

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(15) Impey, R. W.; Klein, M. L. *Chem. Phys. Lett.* **1984**, *104*, 579.

(16) (a) Jorgensen, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 335, 341. (b) Jorgensen, W. L.; Madura, J. D. *J. Am. Chem. Soc.* **1983**, *105*, 1407.

(17) Jorgensen, W. L.; Swenson, C. J. *J. Am. Chem. Soc.* **1985**, *107*, 569.

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(19) Smith, S. F.; Chandrasekhar, J.; Jorgensen, W. L. *J. Phys. Chem.* **1982**, *86*, 3308.

(20) All calculations were carried out with the program MDPOLY written by R. W. Impey.

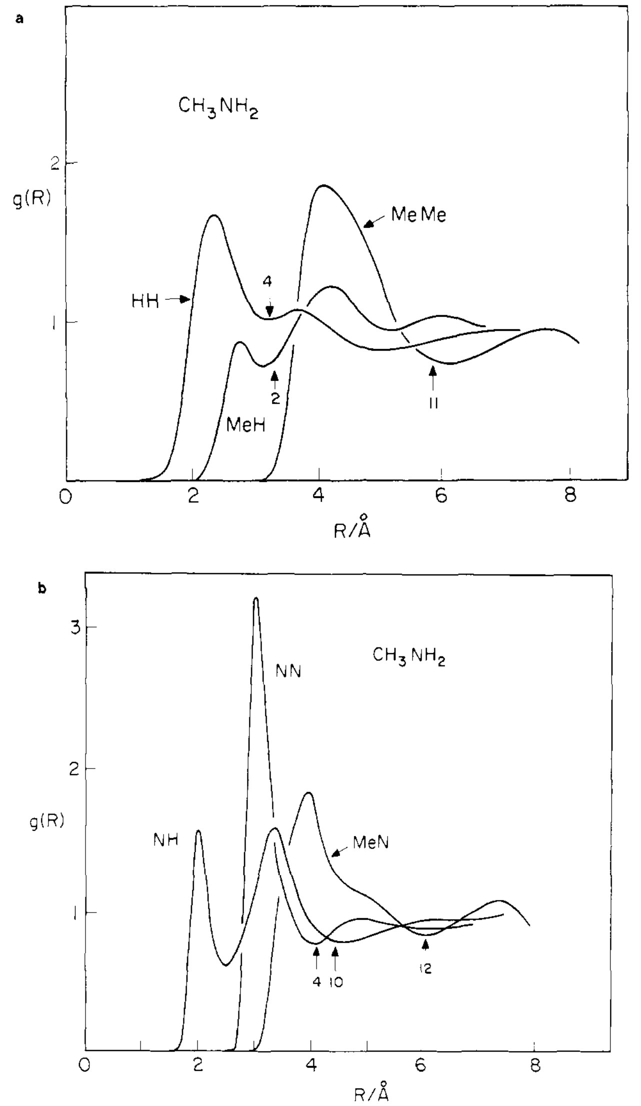

Figure 1. Atom–atom radial distribution functions for methylamine at $T = 263$ K and $V = 44.4$ cm^3/mol. Coordination numbers are indicated by arrows and arabic numerals.

and solvent molecules interacted with potentials derived from parameters listed in Table I. For the smaller system the potentials were truncated at 8 Å, but for the larger system a 9 Å cutoff was employed. An Ewald method was used to handle the long-range Coulomb interactions. The solvent molecules were held rigid via the following constraints on the interaction site separations: d(NH) = 1.0124 Å and d(HH) = 1.6243 Å for ammonia; d(NH) = 1.0330 Å, d(HH) = 1.6324 Å, d(MeH) = 2.1826 Å, and d(MeN) = 1.4560 Å for methylamine; and d(OH) = 0.9450 Å; d(MeH) = 1.9482 Å, and d(MeO) = 1.4300 Å for methanol. The MD calculations employed a time step of 1 fs and a Gear algorithm[21] for integrating the equations of motion. In all cases two independent runs of about 10 ps were carried out, the last 6 ps of which were used to compute structural data.

Results and Discussion

(a) Thermodynamics and Solvent Structures. The thermodynamic quantities evaluated during the molecular dynamics calculations are given in Table II. The data for pure methanol and ammonia are essentially identical with those of previous workers.[15,16] However, the results for methylamine are new and Figure 1 shows the site-site radial distribution functions (rdf's) for this system. The Me–Me, Me–N, and Me–H rdf's are very reminescent of the corresponding functions in methanol.[16] Moreover, the N–H and H–H rdf's yield coordination numbers of 4 rather than 2 found for O–O and H–H in methanol. On the basis of the height of the N–H rdf, it appears that the hydrogen bonding in methylamine is somewhat weaker than that in methanol.

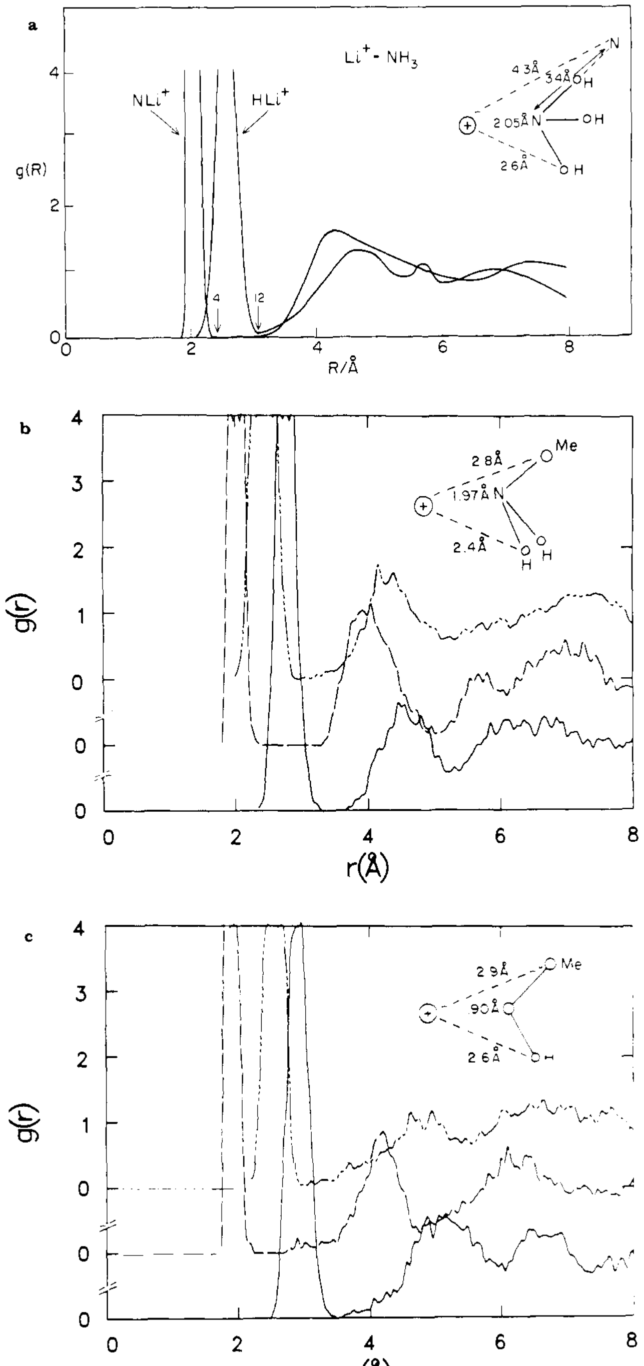

Figure 2. (a) Atom–atom radial distribution functions for lithium ion solvation in ammonia. Inset is the rough structural model (see text). (b) Atom–atom radial distribution functions for lithium ion solvation in methylamine. Top curve, Li–H; middle curve, Li–N; and bottom curve, Li–Me. Inset is the rough structural model (see text). (c) Atom–atom radial distribution functions for lithium ion solvation in methanol. Top curve, Li–H; middle curve, Li–O; and bottom curve, Li–Me. Inset is the rough structural model (see text).

Since the molecular dynamics calculations were all performed at constant volume rather than constant pressure we cannot discuss the enthalpy change associated with the solvation process.[2] Nevertheless, it is clear from the data in Table II that the changes in potential energy on solvation of Li^+ and Cl^- in these nonaqueous solvents are quite comparable to those found in aqueous solution.[2]

(b) Solute–Solvent Structures. Radial distribution functions

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(21) Gear, G. W. *Numerical Initial Value Problems in Ordinary Differential Equations*; Pretice-Hall: Englewood Cliffs, NJ, 1971.

Table II. Thermodynamic Results from Molecular Dynamics Calculations

system	V, cm^3/mol	N^a	T, K	$\langle U\rangle$,^{b} mJ/mol	P,^{c} kbar
CH_3NH_2	44.4	128	263	-3.60	0.2
CH_3NH_2/Li^+	44.4	127	250	-4.30	-0.1
CH_3NH_2/Cl^-	44.4	127	259	-3.93	-0.2
CH_3OH	40.5	128	301	-4.51	1.0
CH_3OH/Li^+	40.5	127	305	-5.02	1.0
CH_3OH/Cl^-	40.5	127	304	-4.72	1.0
NH_3	26.5	108	260	-2.02	-0.1
NH_3/Li^+	26.5	107	247	-2.57	-0.5
NH_3/Cl^-	26.5	107	270	-2.37	-0.6

[a] The number of solvent molecules used. [b] Potential energy of the system. The statistical uncertainty is typically 0.01 mJ/mol. [c] The statistical error in the pressure is less than 0.1 kbar.

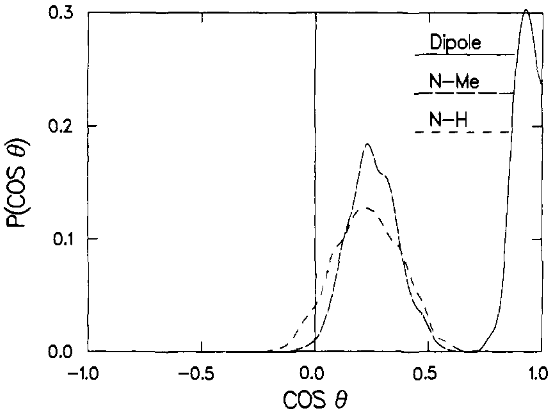

Figure 3. Orientation distribution function for primary solvation sheath molecules. θ is the angle between the Li^+–N vector and various vectors associated with the CH_3NH_2 solvent molecules.

involving the Li^+ and the interaction sites of the solvent molecules are shown in Figure 2. In all solvents Li^+ is strongly solvated by a distinct shell of 4 solvent molecules; the Li–O and Li–N rdf's decay to zero before the second solvation shell begins. In ammonia, the second peak in the rdf Li–N has a height not much less than that of a normal fluid. The position of this secondary peak, at 4.3 Å (see Table III), suggests that the second solvation shell is hydrogen bonded to the first shell. There is also evidence of subsidiary structure around 5.8 Å which suggests that the influence of the Li^+ ion extends quite far into the solvent. The positions of the peaks in the Li–N and Li–H distributions given in Table III accord well with the values gleaned from neutron diffraction studies on the solution $Li-4ND_3$ namely 2 and 2.5 Å, respectively.[11] The fact that we observe a very stable unit $Li-4NH_3$ is especially gratifying since $Li-4NH_3$ is known to form a stable eutectic compound at low temperatures.[8,9]

In the case of methylamine the secondary solvation sheath around the Li^+ ion is well developed, as in the case of ammonia. However, the coordination numbers obtained by integrating the rdf's out to 5 Å suggest a secondary solvation sheath of about 5 molecules. The secondary peak positions are consistent with hydrogen bonding between the first and second shells. Analysis of the peak positions given in Table III implies that both ammonia and methylamine have a *dipole ordered* first solvation sheath. A similar situation obtains for Li^+ in methanol. The deduction based on the rdf's of Figure 2 that Li^+ has a dipole ordered first solvation sheath was confirmed by a direct analysis of the orientational distribution functions for the relevant solvent molecules.

In particular, we monitored the quantity $P(\cos\theta)$, where θ is the angle between a given vector on the solvent molecule (e.g., O–H or N–H bond) and the Li^+–O or Li^+–N vector. Figure 3 shows typical plots obtained for Li^+ in methylamine.

In methylamine and methanol a dipole ordered solvent sheath leaves 8 and 4 hydrogen atoms exposed to the solvent, respectively. It appears that about two-thirds of these are utilized to form the secondary solvation shell.

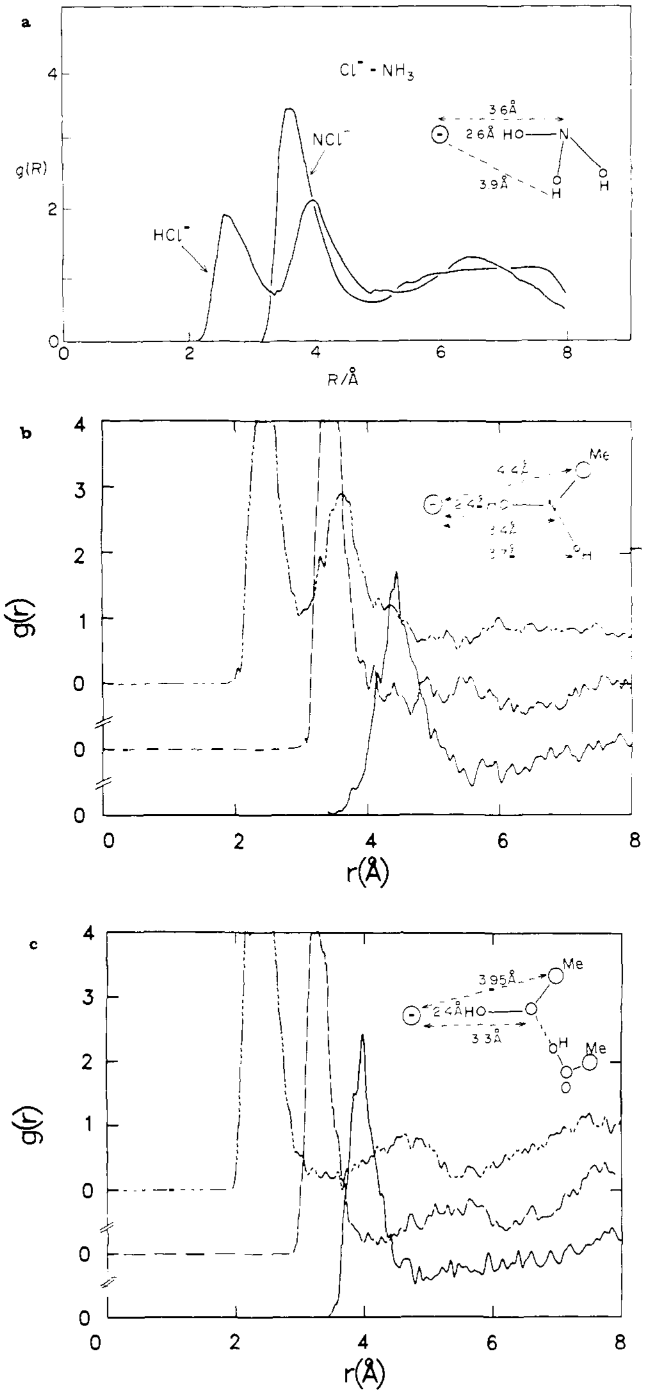

Figure 4. (a) Atom–atom radial distribution functions for chloride ion solvation in ammonia. Inset is the rough structural model (see text). (b) Atom–atom radial distribution functions for chloride ion solvation in methylamine. Top curve, Cl–H; middle curve, Cl–N; and bottom curve, Cl–Me. Inset is the rough structural model (see text). (c) Atom–atom radial distribution functions for chloride ion solvation in methanol. Top curve, Cl–H; middle curve, Cl–O; and bottom curve, Cl–Me. Inset is the rough structural model (see text).

For ammonia a dipole ordered first solvation shell implies that there are 12 hydrogen atoms exposed to the solvent. The secondary and tertiary structures observed in the Li–N rdf suggest that it is not possible to hydrogen bond 12 equidistant ammonia molecules to the Li^+-4NH_3 complex.

The notion of a *secondary* solvation shell for sodium ions in methanol was identified in the Monte Carlo calculations of Jorgensen et al.[6] In this particular calculation the primary and secondary shells each contained 6 methanol molecules which is very similar to the behavior of sodium ions in aqueous solution.[2,5] On the basis of NMR and infrared spectroscopic studies, Symons

Table III. Structural Results for Solvation Shells[a]

ion	solvent	atom	first shell distance, Å	second shell distance, Å
Li^+	NH_3	N	2.05 (4)	4.3 (12)
		H	2.60 (12)	4.8
Li^+	CH_3NH_2	N	1.97 (4)	3.9 (5)
		H	2.40 (8)	4.3 (10)
		C	2.75 (4)	~4.5
Li^+	CH_3OH	O	1.90 (4)	4.2 (4)
		H	2.6 (4)	~4.8
		C	2.9 (4)	~5.1 (9)
Cl^-	NH_3	N	3.6 (12)	
		H	2.6 (9)	3.9
Cl^-	CH_3NH_2	N	3.40 (6–8)	
		H	2.40 (6)	3.7
		C	4.40 (10)	~7.5
Cl^-	CH_3OH	O	3.3 (5)	~5.4
		H	2.4 (5)	~4.6(4)
		C	4.0 (8)	~7.5

[a] The coordination numbers for each solvation shell, obtained from integration of the appropriate rdf's, are quoted in parentheses.

et al. were previously led to the notion of well defined primary and secondary solvation sheaths for methanolic solutions.[7] Their conclusions concerning the behavior of sodium ions agreed well with the computer simulation.[6]

Of more immediate interest is the recent conclusion of Robinson and Symons that Cl^- form only four hydrogen bonds in methanol compared to six in water.[7] Experimental and theoretical values for the latter quantity actually scatter over a wide range.[2] However, the essential point is that there seem to be fewer hydrogen bonds for Cl^- in methanol than in water.

Analysis of Figure 4 shows clearly that Cl^- is solvated by a well defined solvent sheath of roughly 5 methanol molecules (see Table III). There is also a weakly defined secondary solvent sheath. The peak positions of the rdf's clearly show that the first solvent sheath is *bond ordered*, the hydrogen atom pointing directly at the chloride ion. The secondary solvent sheath is hydrogen bonded to the primary one. The solvation number we find is smaller than the value of 7 calculated for aqueous solvation.[2] Our findings therefore support the general conclusions of Symons and coworkers concerning methanolic solvation.[7]

The methylamine solvent sheath around the chloride ion also appears to be bond ordered and is composed of about 8 molecules. However, the difference between the coordination numbers for Cl–N and Cl–H suggests that in the first solvent sheath not all molecules are hydrogen bonded to the Cl^- ion.

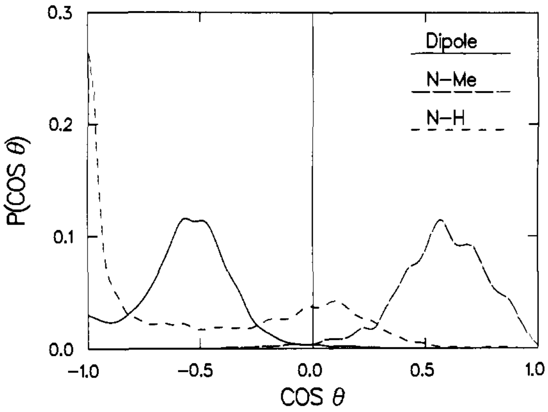

Figure 5. Orientational distribution function for primary solvation sheath molecules. θ is the angle between the Cl^-–N vector and various vectors associated with the CH_3NH_2 solvent molecules.

In ammonia the Cl^- ion is also bond ordered as is evident from the rdf for H atoms. The deductions based on the rdf's in Figure 4 that Cl^- is solvated by bond-ordered solvent molecules is confirmed by detailed analysis of the orientational distribution functions for solvent sheath molecules such as shown in Figure 5.

Conclusion

Simple ion–molecule potentials of the type introduced previously by Jorgensen et al.[2] for ion–water and ion–methanol interactions have been used to investigate the solvation of Li^+ and Cl^- ions in ammonia, methanol, and methylamine.

In all solvents the first solvent shell of Li^+ consists of four strongly bound *dipole-ordered* solvent molecules. However, the secondary structure is more enhanced in the case of ammonia. This finding may have some relevance in explaining the well-known differences in the electronic properties of alkali metals dissolved in these solvents.[8,9] The structure of the Li^+4NH_3 complex which we obtain in the simulation agrees well with an analysis of neutron diffraction data.[11]

The solvation sheath of Cl^- is *bond ordered* in the solvents studied here, and there is little evidence for significant structure beyond the primary solvation shell. The solvation number for Cl^- in methanol is definitely less than the corresponding value in aqueous solution, a conclusion that agrees well with deductions based upon experimental observations.[7]

Registry No. Li^+, 17341-24-1; Cl^-, 16887-00-6; CH_3OH, 67-56-1; NH_3, 7664-41-7; CH_3NH_2, 74-89-5.