The Primary Solvation Number of Magnesium(II) in Liquid Ammonia

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Abstract: Through application of proton magnetic resonance spectroscopy the primary solvation number of Mg^{2+} was determined to be 5.0 ± 0.2 in anhydrous liquid ammonia for both the nitrate and perchlorate salts over a range of concentrations. A check on this result was obtained through the study of a liquid ammonia solution containing both Co^{3+} and Mg^{2+}. Evidence is presented against the existence of strong magnesium anion complexes and in favor of the species $Mg(NH_3)_5{}^{2+}$. The results were used to formulate an important conclusion concerning the solvation of rare gas configuration cations.

It has been shown in recent years that through the application of nuclear magnetic resonance techniques definitive solvation numbers may be obtained for certain metallic cations in such solvents as water,[1] methanol,[2] N,N-dimethylformamide,[3] and dimethyl sulfoxide.[4] Such determinations are of considerable importance since they provide a solid base of experimental facts upon which theories of ion solvation can be devised and tested.

A particularly interesting group of cations are those with rare gas electronic configurations since this includes Na^+, K^+, Mg^{2+}, and Ca^{2+}, ions of some biological importance in their aqueous solution behavior. These ions are also special since their solvation numbers in aqueous solution cannot be determined through use of the magnetic resonance techniques mentioned above.[1-4] Water molecule exchange between the primary solvation spheres of each of these four ions and the solution bulk is too rapid to permit any *magnetic distinction* between the water molecules in the two environments. The observables such as line widths and chemical shifts are inseparable averages of the appropriate quantities for each of the two environments.[5-7]

There are, however, quite definite *thermodynamic and kinetic distinctions* which can be made between water molecules in the two types of environment. This has been recognized for some time, but the problem has been in the devising of suitable experiments to take advantage of these known or anticipated distinctions.

Recently in this laboratory such a technique[5] was devised in which proton magnetic resonance was employed to study the kinetics of a simple water exchange reaction and hence indirectly the kinetic and thermodynamic distinctions between the various water molecules. These kinetic studies became the basis for an empirical technique for the determination of the primary solvation numbers of such ions as Mg^{2+} and Ca^{2+} among others.

Since the technique is only empirical at present, the results obtained are naturally open to some question for those ions whose solvation numbers are not known by independent measurements. One such ion is Mg^{2+}. This ion is a particularly useful one to center on since it represents a borderline case. It cannot be studied in aqueous solution by the quite definitive separate signal nmr techniques,[1-4] but solvent exchange is sufficiently slow in methanol at low temperatures that separate proton magnetic resonance signals have been observed for bound and unbound methanol.[2]

The definitive result of the magnesium–methanol study is that there are approximately six methanol molecules associated with each magnesium ion in the primary solvation sphere. This number contrasts sharply with the four water molecules per magnesium ion determined through use of our empirical technique.[5] The question which naturally arises concerns the extent to which solvation studies in one solvent can be carried over to similar solvents.

One might well reason that if ion–dipole electrostatics constitute by far the most important factor in the formation of the primary solvation sphere of Mg^{2+} in solution the primary hydration number would be at least as large as the methanol solvation number based on the relative sizes and polarities of the water and methanol molecules. If, on the other hand, other important factors are involved, such as the solvent–solvent and solvent–anion interactions, such simple extrapolations from solvent to solvent are not valid and each solvent must be studied separately.

Because the ammonia molecule is similar to water both in size and polarity, we undertook the determination of the primary ammoniation number of Mg^{2+} in anhydrous ammonia in order to see if the result could be correlated with the results of the methanol study[2] or the aqueous solution study.[5]

Experimental Section

Anhydrous solutions of $Mg(NO_3)_2$ and $Mg(ClO_4)_2$ in liquid ammonia were prepared from reagent grade $Mg(NO_3)_2 \cdot 6H_2O$ and $Mg(ClO_4)_2 \cdot 6H_2O$ with the drying accomplished by a method previously outlined[8] involving repeated distillation of the solvent ammonia in and out of a potassium–ammonia solution. The drying was assumed to be complete when several further distillations in and out of the potassium solution failed to produce a detectable pressure of hydrogen gas.

The fact that a given number of distillations does produce an essentially anhydrous solution was checked by mixing one of the dried Mg^{2+}–ammonia solutions and the potassium solution used

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[3] N. A. Matwiyoff, *Inorg. Chem.*, **5**, 788 (1966).
[4] S. Thomas and W. L. Reynolds, *J. Chem. Phys.*, **44**, 3148 (1966).
[5] T. J. Swift and W. G. Sayre, *ibid.*, **44**, 3567 (1966).
[6] S. Meiboom, *ibid.*, **46**, 410 (1967).
[7] T. J. Swift and W. G. Sayre, *ibid.*, **46**, 410 (1967).
[8] T. J. Swift and H. H. Lo, *J. Am. Chem. Soc.*, **88**, 2994 (1966).

Table I. The Solvation Number of Mg^{2+} in Liquid Ammonia Solutions of $Mg(NO_3)_2$ and $Mg(ClO_4)_2$

		$Mg(NO_3)_2$		
$(Mg^{2+})/(NH_3)$	7.48×10^{-3}	4.68×10^{-3}	3.31×10^{-3}	2.45×10^{-3}
Solvation no.	5.0 ± 0.2	4.9 ± 0.2	4.9 ± 0.2	5.1 ± 0.2
		$Mg(ClO_4)_2$		
$(Mg^{2+})/(NH_3)$	4.40×10^{-3}	3.60×10^{-3}	2.58×10^{-3}	1.38×10^{-3}
Solvation no.	5.2 ± 0.2	5.0 ± 0.2	5.1 ± 0.2	5.0 ± 0.2

for drying. No detectable pressure of hydrogen was formed, indicating in this particular case that the mole ratio of H_2O to Mg^{2+} was less than 0.01 and the drying procedure is a quite acceptable one for these systems.

A small amount of NH_4NO_3 or NH_4ClO_4 was added to each solution to be studied by means of proton nmr to ensure that a singlet would be obtained as the bulk ammonia signal rather than a triplet. This was done to facilitate the signal integration. Proton spectra were recorded with a Varian A-60A spectrometer equipped with a V-6040 temperature controller.

After the spectra were recorded the solutions were analyzed in the following manner. The sample tube content was frozen in liquid nitrogen and the tube was broken. The broken tube was introduced into a glass vessel holding a known amount of standardized HCl solution. The vessel was closed and the sample tube content was allowed to warm up and react. The resulting solution was titrated with standard NaOH and then with EDTA to determine the magnesium content. Sample analyses carried out in this way were found to be reproducible within 1%.

Results

The proton spectrum at −78° of a $Mg(NO_3)_2$ solution in which $(Mg^{2+})/(NH_3)$ is 7.48×10^{-3} is given in Figure 1. This concentration is nearly that of the saturated solution at this temperature. The two relatively well-resolved Lorentzian signals were integrated by taking the product of each peak height times the signal width at one-half maximum intensity. At temperatures above −78° the smaller signal broadens due to exchange, and above *ca.* −60° only a single large peak is observable.

For the solution whose spectrum is shown in Figure 1 the primary solvation number of Mg^{2+} was calculated to be 5.0. This determination was repeated at several concentrations of both $Mg(NO_3)_2$ and $Mg(ClO_4)_2$, and the results are shown in Table I.

The solvation number of five was quite unexpected. One possible explanation which occurred immediately is that the Mg^{2+} is really six coordinated with the coordination sphere consisting of five ammonia molecules and a nitrate or perchlorate ion. These complexes would have to have rather high stability constants since the concentrations of Mg^{2+} given in the table are not large and there is no significant change in the solvation number as a function of concentration, although it must be admitted that, because of the low intensity of the peak for bound ammonia at low Mg^{2+} concentrations, the concentration range studied was not as large as we might hope to study.

As a means of checking for such complexing and also as a means of calibration of the technique used to obtain the results given in the table an anhydrous liquid ammonia solution was prepared containing Co^{3+} and Mg^{2+} in nearly equimolar concentrations. The Co^{3+} was added in the form of $Co(NH_3)_6(NO_3)_3$.

The proton spectrum of this Co^{3+}–Mg^{2+}–ammonia solution at −78° contains, in addition to the two peaks shown in Figure 1, a third peak 130 cycles to the low-field side of the smaller peak in the figure, and this signal clearly arises from the protons of the ammonia molecules coordinated to Co^{3+}.

Integration of the three peaks yielded 6.0 ± 0.2 as the solvation number of Co^{3+} and 5.0 ± 0.2 as the solvation number of Mg^{2+}. This result shows that the number of 5.0 for Mg^{2+} is quite definitive. In addition, there was no nmr evidence for any of the ammonia molecules bound to Co^{3+} being replaced by nitrate ions even after the solution was allowed to stand in the nmr tube for a long period at room temperature. While this study is not completely conclusive, it seems rather unlikely that the solvation number of 5.0 for Mg^{2+} is a consequence of strong nitrate and perchlorate complexing. An additional argument against such complexing is given in the Discussion. Clearly the existence or nonexistence of such complexes is an important point and must be the subject of further investigation.

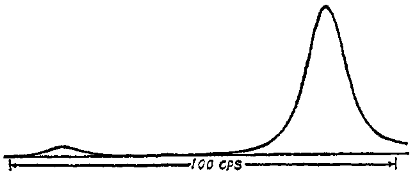

Figure 1. Proton nmr spectrum of Mg^{2+} in liquid ammonia solution at −78°.

Discussion

If it is assumed for the present that the measured solvation number of five does not result from anion complexing, from what factor does it arise? This question is discussed somewhat in the subsequent paragraphs, but clearly it cannot be answered satisfactorily without extensive further study.

One important conclusion is quite clear, however, and that is that the number of five is an unexpected one in light of *both* the methanol and water solvation studies. It would appear that the balance of factors does differ from solvent to solvent and that extrapolation of results of solvation studies from one solvent to another is a questionable procedure even for ions of rare gas electronic configuration.

While the main point of this study was the attempt to find a simple correlation or lack of simple correlation between the solvation numbers of a given ion in similar solvents, several other interesting questions are raised concerning the specific results obtained.

One of these concerns the fact that only one signal was found for ammonia bound to Mg^{2+}. A five-coordinate ion must have nonequivalent ammonias, as must a nitrate or perchlorate complex. A third possibility is that the number five results from an equilibrium between a four-coordinate and a six-coordinate species with an equilibrium constant near 1. In this case also nonequivalent ammonia molecules are present.

Since only one Lorentzian signal was observed for bound ammonia, the signals from the nonequivalent ammonias must have very nearly the same chemical shifts and line widths or, as is more likely, the exchange between the nonequivalent ammonias must be rapid. Such an exchange cannot take place between $Mg(NH_3)_4^{2+}$ and $Mg(NH_3)_6^{2+}$ without involving the bulk solvent, and hence this is an argument against the existence of these two species in equilibrium.

In order that bulk solvent not be involved in the exchange between bound ammonia molecules, the exchange mechanism must be intramolecular. Intramolecular rearrangements in six-coordinate species are in general quite slow[9] and show up typically for complexes in which ligand exchange is also very slow. It is therefore likely that a six-coordinate $Mg(NH_3)_5(NO_3)^+$ species or $Mg(NH_3)_5(ClO_4)^+$ species would give rise to two separate proton signals for bound ammonia.

Intramolecular rearrangement is in general quite facile[10] for five-coordinate species, and it is likely that the ion $Mg(NH_3)_5^{2+}$ would give rise to only one bound ammonia signal. The most important factor in the formation of such an ion may be the rather strong ion pairing known to occur in liquid ammonia. Further studies on this system are currently in progress.

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