AN NMR STUDY OF IONIC SOLVATION OF ALKALINE EARTH CATIONS WITH DIMETHYLSULFOXIDE IN NITROMETHANE SOLUTION

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Abstract

A proton NMR method for the determination of the solvation numbers of alkaline earth cations with dimethylsulfoxide (DMSO) in nitromethane as diluent is described. The method is based on the monitoring of the resonance frequency of DMSO protons as a function of DMSO to metal ion mole ratio while keeping the metal ion concentration constant. The average solvation number of cations $\bar{n}$ at any DMSO/metal ion mole ratio was calculated from the NMR chemical shift mole ratio data and was plotted against the mole ratio values. The solvation numbers of alkaline earth cations were extracted from the limiting values of the corresponding $\bar{n}$-mole ratio plots and were found to be 6 for Ba^{2+}, Sr^{2+} and Ca^{2+} ions and 5 for Mg^{2+} ion. Effect of the presence of water on the solvation numbers of alkaline earth cations with DMSO was studied. In this case, the variation in the resonance frequency of H_2O, brought about upon titration of the cations by DMSO, was also used to estimate the solvation number of cations with DMSO.

Introduction

Since most chemical reactions carried out in laboratories or in industry, or occurring in biological systems, involve interactions of dissolved chemical species in some solvent, the influence of solvent on the thermodynamics, kinetics and mechanism of such reactions is of great importance. One of the fundamental aspects of the solvent effect in electrolyte solutions is the extent of cation-solvent interaction (ionic solvation).

A wide variety of physicochemical methods have been employed for the study of ionic solvation and determination of solvation numbers of ions in water

and in nonaqueous solvents [1, 4]. These methods are based on measuring the static and dynamic properties of ions in solution in which the bulk solvent molecules, and those participating in ionic solvation, are conventionally separated under some assumptions.

The use of nuclear magnetic resonance spectrometry in the determination of solvation numbers in the 1960's [1] opened a new era in such studies and resulted in a remarkable accumulation of solvation data. The solvent [5-15], cation [16-19] and anion [20-23] resonance have been used extensively in such studies.

Despite a considerable amount of research work reporting on the ionic solvation of alkaline earth ions in aqueous solutions [1, 4], there are only a few such studies on nonaqueous solvents [2, 5, 7, 23]. In this paper, we wish to report a study of the ionic solvation

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of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ions with dimethylsulfoxide in nitromethane as diluent using the ^1H NMR technique.

Experimental Section

Magnesium perchlorate was prepared by dissolving the metal Mg (Merck) in perchloric acid. Calcium, strontium and barium perchlorates were prepared from their carbonate salts (all from Merck) and perchloric acid. The resulting perchlorate salts were recrystallized several times from deionized water and dried in a vacuum oven at about 150°C for 48 h. The salts were further dried at 200-250°C under a flow of dry nitrogen for 24 h.

Nitromethane (NM, Fluka) was dried over BaO and distilled at reduced pressure. Dimethylsulfoxide (DMSO, Fluka) was dried over Linde 4Å molecular sieves and distilled at reduced pressure. The middle fraction of the distilled solvents was used in the experiments.

In order to prepare the required solutions for NMR measurements, the perchlorate salts were dissolved in nitromethane at a concentration of 0.02 M and appropriate quantities of DMSO and H_2O were added by weight.

Proton NMR measurements were carried out on a Bruker AW-80 spectrometer at a field of 18.79 kG. In all experiments, TMS was used as an internal standard. All experiments were carried out at 30°C.

Results and Discussion

The study of the solvation of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ions with DMSO was carried out in NM as an inert solvent. NM, with the Gutmann donor number of 2.7, is well known as being a much weaker solvating medium than DMSO with a donor number of 29.8 [24] and, consequently, it has already been used successfully as a diluent in the study of ionic solvation of alkali ions with DMSO [12, 22]. The variation of the resonance frequency of DMSO methyl protons was measured as a function of DMSO-to-metal-ion mole ratio in two different series of solution. The first series of experiments was performed in the absence of water, while in the second series water was present with a H_2O to metal ion mole ratio of 6. The results are shown in Figure 1. It should be noted that, in all NMR spectra obtained, the corresponding signals for NM, DMSO and water protons are well removed from each other, so that the DMSO and H_2O chemical shifts can be measured accurately.

As is seen, the resonance frequency of DMSO protons shifts upfield upon increasing the DMSO to metal ion mole ratio. In all cases studied, the DMSO reso-

nance frequency in the presence of water is lower than that in the absence of water, at low DMSO to metal ion mole ratios. This difference in DMSO resonance frequency can be related to the extent of the contribution of H_2O molecules in the metal ion solvation shell which is, of course, dependent on the nature of the cation; it varies in the order $Mg^{2+} >> Ca^{2+} > Sr^{2+} > Ba^{2+}$. This trend supports the reported decrease in the hydration energy of alkaline earth cations by increasing the ionic size [1, 25]. However, by increasing the concentration of DMSO (or DMSO to metal ion mole ratio), the water molecules participating in the solvation shell would be replaced by DMSO and, consequently, the DMSO resonance frequency in both series of experiments approach more or less the same values (Fig. 1).

In contrast to the previous studies [11, 12], the chemical shift-mole ratio plots given in Figure 1 possess no distinct break to be used as an indication for the estimation of alkaline earth solvation numbers. Thus, the resulting NMR data were used to determine the average solvation number, $\bar{n}$, at any given DMSO to metal ion mole ratios, as follows. In all cases, the chemical shift of the population averaged signal observed for DMSO in the two different environments (i.e. free and bound) can be written as:

$$\delta_{obs} = x_i\delta_i = x_f\delta_f + x_b\delta_b \qquad (1)$$

where x_f and x_b are the mole fractions and δ_f and δ_b are the chemical shifts of the free and bound DMSO molecules, respectively. It should be noticed, however, that δ_b is assumed to be independent of the composition of the solvation shell of the ions [11, 12]. Since,

$$x_f + x_b = 1 \qquad (2)$$

the equation (1) can be written as:

$$\delta_{obs} = (1-x_b)\delta_f + x_b\delta_b \qquad (3)$$

and, by rearrangement:

$$x_b = \frac{\delta_{obs} - \delta_f}{\delta_b - \delta_f} \qquad (4)$$

Now, the average solvation number at any DMSO/metal ion mole ratio can be calculated from:

$$\bar{n} = \frac{[DMSO]_b}{[M]_t} \qquad (5)$$

or

$$\bar{n} = \frac{x_b [DMSO]_t}{[M]_t} \qquad (6)$$

where $[DMSO]_b$, $[DMSO]_t$ and $[M]_t$ refer to the concentration of bound DMSO, total concentration of DMSO and total concentration of metal ion, respectively. By substitution of the equation (4) in (6), we

have:

$$\bar{n} = \frac{(\delta_{obs} - \delta_f)\,[DMSO]_t}{(\delta_b - \delta_f)\,[M]_t} \qquad (7)$$

the δ_f was obtained from the NMR spectrum of DMSO in NM solution and δ_b for the case of each metal ion was evaluated by extrapolation of the corresponding chemical shift-mole ratio plots to the mole ratio of zero.

The resulting plots of $\bar{n}$ vs. DMSO to metal ion mole ratio in the presence and absence of water for Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ions are shown in Figure 2. As is seen, $\bar{n}$ value increases by an increase in $[DMSO]/[M^{2+}]$ until a given mole ratio is reached, beyond which no change in $\bar{n}$ is observed. The limiting value of $\bar{n}$ (the solvation number of metal ion) in the absence of water is 6 for Ca^{2+}, Sr^{2+} and Ba^{2+} ions,
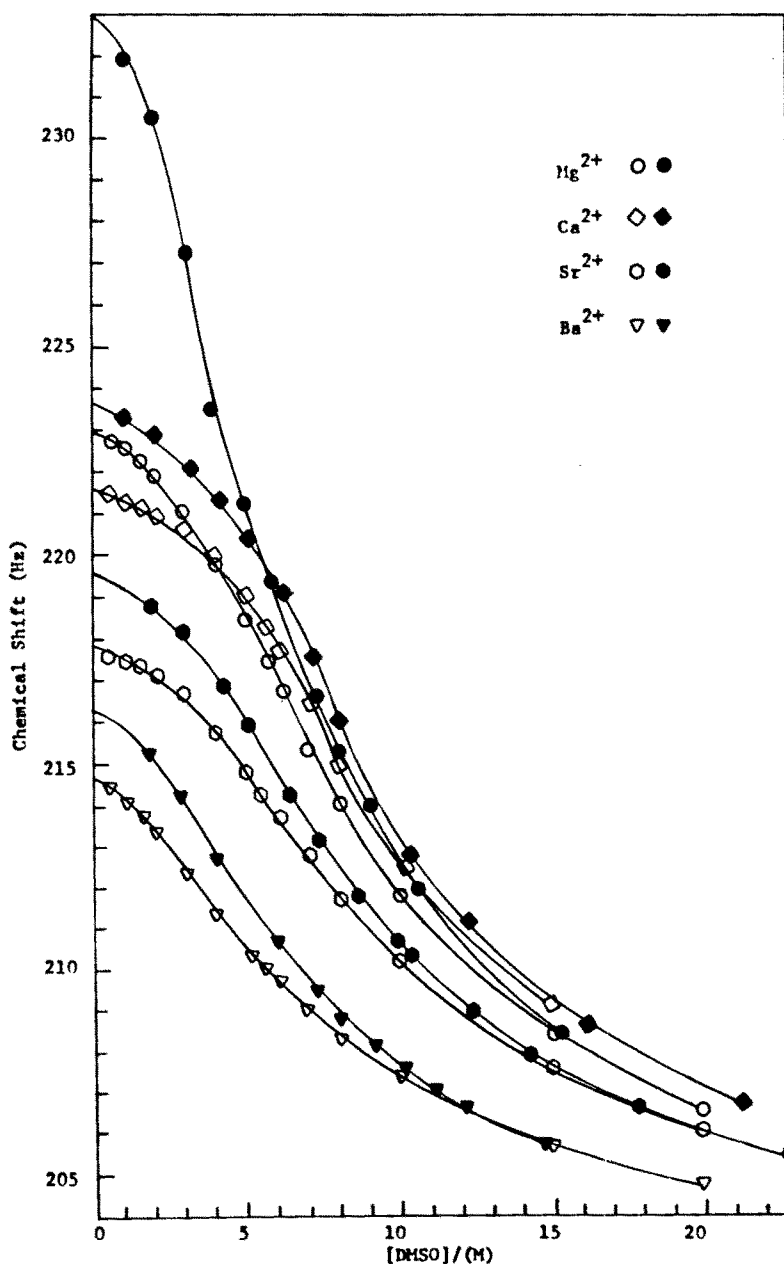

Figure 1. Chemical shift of DMSO protons vs. DMSO/ metal ion mole ratio for different alkaline earth cations in the absence (full dots) and presence (empty dots) of water
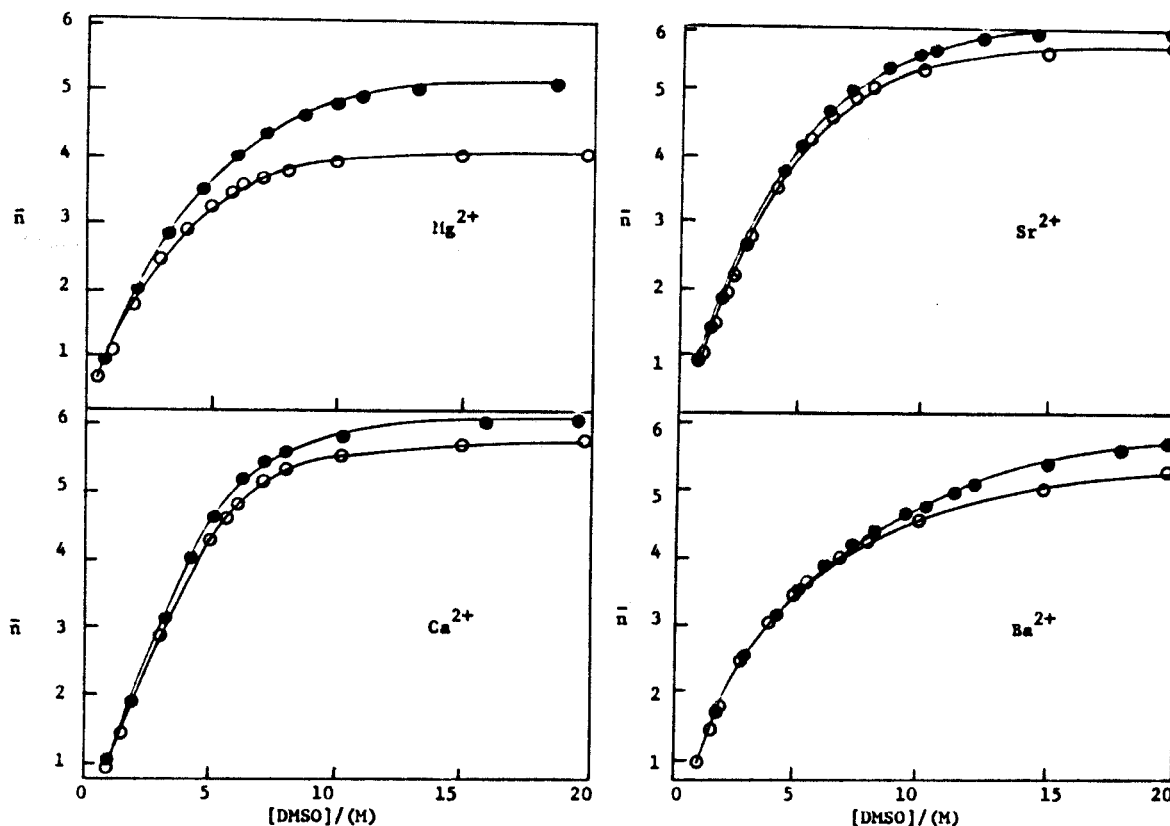
Figure 2. The plots of $\bar{n}$ vs. DMSO/metal ion mole ratio for different alkaline earth cations in the absence (full dots) and presence (empty dots) of water

which is consistent with the coordination number of 6 reported for these cations [1, 3, 23]. On the other hand, a solvation number of 5 is obtained for the Mg^{2+} ion. It should be noted, however, that there is ambiguity about the coordination number of magnesium ion in the literature. Different coordination numbers ranging from 4 to 8 have been reported for the Mg^{2+} ion in aqueous [6, 8, 9, 10] and nonaqueous solutions [5, 7, 23], using NMR and Raman spectroscopy. Based on the space requirements and steric properties of the bulky DMSO molecules (in comparison with H_2O) and the relatively small size of the Mg^{2+} ion, a solvation number of 5 for the Mg^{2+} ion seems to be reasonable. It is interesting to note that the limiting DMSO to metal ion mole ratio, at which the cation is completely solvated by DMSO molecules, for different alkaline earth cations increase in the order $Mg^{2+}>Ca^{2+}>Sr^{2+}>Ba^{2+}$, reflecting the fact that the solvation energy becomes less negative by an increase in the charge to size ratio from magnesium to barium ions.

However, as is clear from Figure 2, the solvation number of alkaline earth cations with DMSO in the presence of water is less than that observed in DMSO

solution alone, indicating some contribution of H_2O molecules to the corresponding solvation shells. The extent of water contribution to the solvation shell decreases from Mg^{2+} to Ba^{2+} ions, supporting the reported trend in the hydration energy of alkaline earth cations [1, 25].

The variations in resonance frequency of water protons, brought about upon titration of the alkaline earth perchlorates by DMSO molecules in NM solutions, can also be used to estimate the solvation numbers of the cations with DMSO. The change in the chemical shift of water (with a constant concentration in NM) was monitored as a function of DMSO to metal ion mole ratio for different alkaline earth perchlorates and the resulting plots are shown in Figure 3.

The solvation of cations with DMSO in the presence of water can simply be represented as:

$$M^{2+} (H_2O)_i + DMSO \rightleftarrows M^{2+} (H_2O)_j DMSO + (i-j) H_2O \quad (8)$$
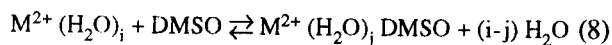
where $i>j$. Two types of H_2O molecules (i. e. unsolvated and solvated) are present during the course of titration. Because of the existence of a fast exchange of water molecules between the two different

sites, only one population averaged NMR signal was observed in all cases studied. The population of unsolvated molecules increases with DMSO concentration. The characteristic upfield shift of water molecules prior to the equivalence point can be explained by taking into account the fact that the unsolvated H_2O resonates at a higher field than the solvated H_2O. Beyond the equivalence point, the chemical shift of H_2O will remain more or less constant. It is interesting to note that the difference between the chemical shifts of the unsolvated and solvated water molecules decreases with different cations in the order $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$, which is probably a result of a decrease in the cation-H_2O interaction from magnesium to barium ions.

Extrapolation of the linear parts of the titration curves gives rise to an intersection at DMSO/M^{2+} mole ratio of about 5 for Mg^{2+} ion and about 6 for other cations used. It is obvious that the sharpness of the equivalence point in such titration curves is dependent upon the relative solvating abilities of the two different solvents replaced; the greater the difference between the solvating ability of the two different solvent molecules, the sharper the equivalence point. Thus, the lack of a sharp equivalence point in the resulting titration curves shown in Figure 3 could be a result of the relatively small difference between the solvating power of H_2O and DMSO for alkaline earth cations, not enough to completely replace the water molecules in the solvation shell by DMSO at equivalence point.

In the original study of the donor number of different solvents, as a reliable scale for their relative solvating abilities, Gutmann and Wychera [24] reported a donor number of 18 for water, which indicates a rather moderate solvating ability in comparison with DMSO, with a donor number of 29.8. It should be noted that there is ambiguity about the donor number of water. As mentioned above, Gutmann cites its value as being 18 [24], determined from calorimetric data, while on the basis of ^{23}Na NMR measurements a value of 33 is reported by Popov and coworkers [26]. It should be emphasized, however, that while the donor numbers are very useful qualitative guides to the solvating abilities of solvents, they are not infallible. For example, the donicity of a solvent can be very different in the neat state from when it is diluted with another solvent [27]. Moreover, as Gutmann points out [28], the solvating ability of a solvent toward a given solute depends on the comparative hardness or softness of the interacting species.

Although the donor number of 33 has been found to fit much better the high solvating ability of water
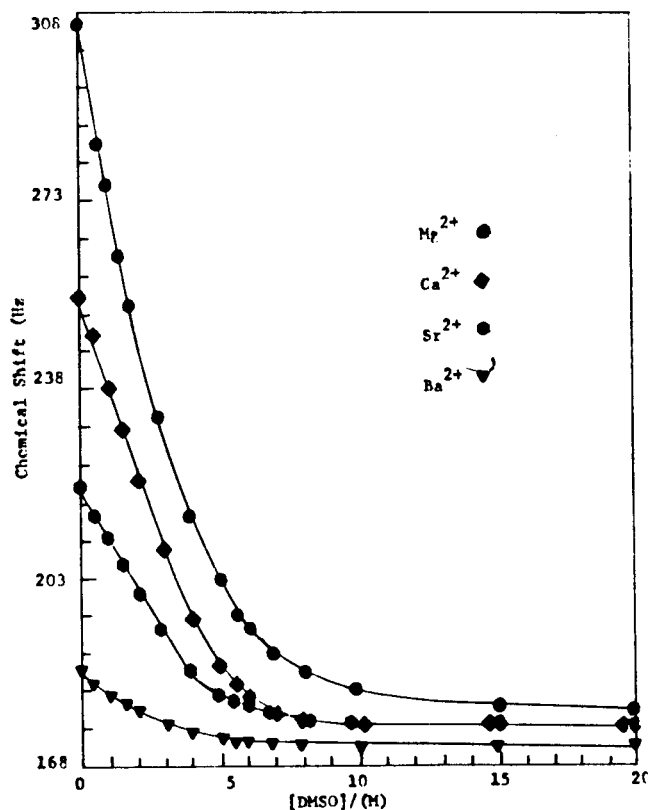

Figure 3. Chemical shift of H_2O protons vs. DMSO/metal ion mole ratio for different alkaline earth cations

toward the alkali ions [29, 30], the value of 18 seems to be in better agreement with the results obtained in this study for alkaline earth ions.

Acknowledgements

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