

Study of Ionic Solvation and Determination of Solvation Numbers of Alkaline Earth Cations with HMPA in Nitromethane Using ^1H NMR Technique

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ABSTRACT: A proton NMR method for the determination of solvation numbers of alkaline earth cations with hexamethyl phosphoramide (HMPA) in nitromethane (NM) as diluent is described. The method is based on monitoring the resonance frequency of HMPA protons as a function of HMPA/metal ion molar ratio at constant metal ion concentration. The average solvation number of cations, \bar{n} , at any HMPA/metal ion ratio obtained from the NMR chemical shift-molar ratio data was plotted against the molar ratios values. The solvation numbers of each alkaline earth cation was determined from the limiting value of the corresponding \bar{n} , vs. molar ratio plot.

KEY WORDS: Ionic solvation, Solvation number, Alkaline earth cations, Nitromethane, Nuclear Magnetic Resonance

INTRODUCTION

Since most chemical reactions carrying out in laboratories, industry, or occurring in biological systems, involve interactions of dissolved chemical species in some solvent, the influence of solvent nature on thermodynamic, 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 interactions (ionic solvation) [1,2].

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

and in nonaqueous solvents [3-5]. 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 the solvation shell are separated under some assumptions.

The use of nuclear magnetic resonance spectroscopy in the study of solute-solvent interactions and determination of solvation number which began in 1960's [5] has opened a new era in such studies and resulted in a remarkable accumulation of solvation data. Direct observation of the extent to which a cation is solvated has been achieved by examining the

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spectral properties of either the solvating agent [15–17] or in favourable cases, the cation itself [18,19]. Indirect influence of the extent of cation solvation on the spectral properties of anions has also been used to study cation–solvent interactions and to obtain solvation numbers [8,20].

There are only a few studies on the solvation of alkaline earth perchlorates in nonaqueous solvents [8,12,21]. In a study for determination of solvation number of Mg^{2+} , Ca^{2+} and Sr^{2+} (perchlorates), a value of 6 has been reported for the solvation numbers of Mg^{2+} , Ca^{2+} and Sr^{2+} in acetonitrile [20]. For Ba^{2+} solvation number of 6 in ethers has been found [13].

The purpose of the work described in this paper is to study the solvation of Mg^{2+} , Ca^{2+} and Sr^{2+} perchlorates with HMPA in the absence and presence of water in nitromethane solutions as the diluent using 1H NMR technique.

EXPERIMENTAL

Materials

Calcium and strontium perchlorates were prepared from their carbonate salts (all from Merck, Darmstadt, Germany) in perchloric acid. Magnesium perchlorate was prepared by dissolving the Mg metal (Merck) in perchloric acid.

The resulting perchlorate salts were recrystallized several times from deionized water and dried in vacuum oven at about $150^\circ C$ for 48 h. The salts were further dried at $200\text{--}250^\circ C$ under a flow of dry nitrogen for 24 h. Hexamethylphosphoramide (HMPA), was purchased from Merck. Nitromethane was distilled using a vigreux column (80 cm) at reduced pressure; the middle 70% fractions of the distillates were used in all of the experiments.

Instruments

Proton NMR measurements were carried out on a Bruker AW–80 spectrometer at a field of 18.79 KG. In all experiments, nitromethane peak was used as an internal standard.

Procedure

In order to prepare the required solutions for NMR measurements, the perchlorate salts were dis-

solved in nitromethane at a concentration of 2.0×10^{-2} M, and appropriate quantities of the solvent and H_2O were added by weight at constant metal ion concentration.

In a series of experiments water was present at a H_2O to cation molar ratio of 6.

RESULTS AND DISCUSSION

Studies on the solvation of Mg^{2+} , Ca^{2+} and Sr^{2+} ions with HMPA was performed in NM as an inert solvent. NM with the Gutmann donor number of 2.6 is well known as a much weaker solvating medium than HMPA with a donor number of 29.8 [6]. Consequently, NM has successfully been used as diluent in the study of ionic solvation of alkali ions with HMPA [17,20].

Figs. 1,2 and 3 show the resulting NMR spectra at various HMPA to metal ion molar ratio for Mg^{2+} , Ca^{2+} and Sr^{2+} perchlorates, respectively. As it is seen, the resonance frequency of HMPA protons shift up-field upon increasing the HMPA to metal ion molar ratio. Since the ionic strength of the solutions are constant (constant salt concentrations) and viscosity changes are negligible, (HMPA being relative to NM), any change in the chemical shift of protons of HMPA can be related to its interaction with metal ion. In fact the spectra of HMPA in NM at several concentrations in the absence of any salt were

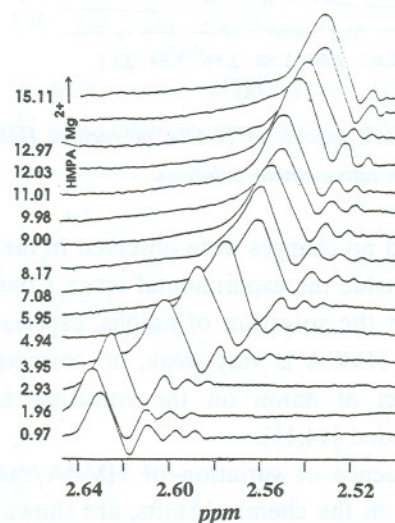


Fig. 1: 1H NMR spectra of HMPA at various $HMPA/Mg^{2+}$ molar ratios in nitromethane solutions.

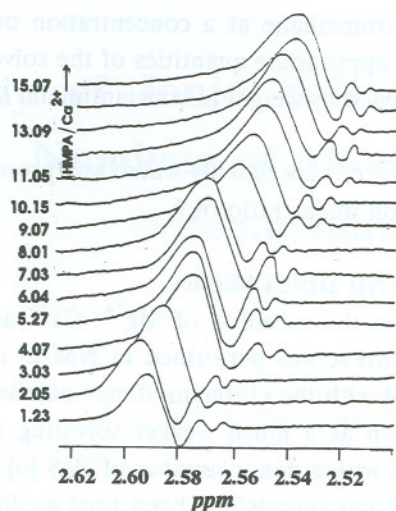


Fig. 2: ^1H NMR spectra of HMPA at various HMPA/ Ca^{2+} molar ratios in nitromethane solutions.

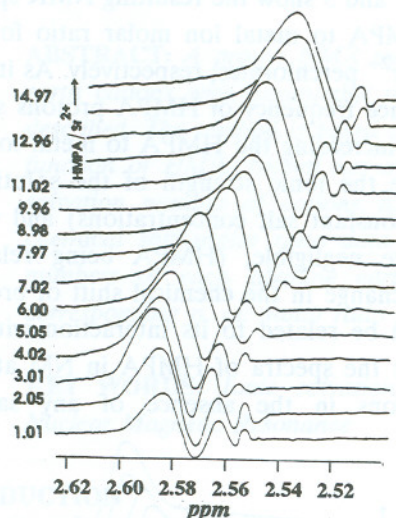


Fig. 3: ^1H NMR spectra of HMPA at various HMPA/ Sr^{2+} molar ratios in nitromethane solutions.

recorded and no changes were observed in the chemical shifts outside the experimental error. Considering the fact that the solvation of anions, especially perchlorate, in HMPA is very weak, no correction due to the effect of anion on the solvation numbers found is needed [14,15].

The influence of variation of HMPA/metal ion molar ratio on the chemical shifts, are shown in Fig. 7. As it is seen, the initial chemical shift of HMPA protons and the range of chemical shift (i.e. the difference between the chemical shifts at very low

and very high HMPA/M molar ratio) is the largest for Mg^{2+} in the series and the least for Sr^{2+} ion.

This behaviour indicates an increase in solvation energy in accordance with the charge/size ratio in the order of $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+}$. The high charge density on the small and "hard" Mg^{2+} ion leads to a stronger ion-dipole bonding than the diffuse charge on the larger "soft" Sr^{2+} ion.

In contrast to the previous studies [16,17], the chemical shift-molar ratio plots given in Fig. 7 show no distinct break to be used as an indication for the determination of the solvation numbers. Thus, the resulting NMR data were used to determine the average solvation number, \bar{n} , at any given HMPA/metal ion molar ratio, as follows. For all of the solutions, even at high HMPA/M molar ratios, only one HMPA signal was observed. This is due to a fast exchange between the free and bound HMPA molecules in the NMR response time scale at room temperature. Therefore, the chemical shift of HMPA protons (δ_{obs}) is a population average of the characteristic chemical shifts in the two different sites. (i.e. HMPA in the bulk and HMPA in the solvation shell). The observed chemical shift can be written as:

$$\delta_{\text{obs}} = X_f \delta_f + X_b \delta_b \quad (1)$$

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 HMPA molecules, respectively.

Since,

$$X_b + X_f = 1 \quad (2)$$

Eq. (1) can be written as :

$$\delta_{\text{obs}} = \delta_b X_b + \delta_f(1 - X_b) \quad (3)$$

and by rearrangement:

$$X_b = \frac{\delta_{\text{obs}} - \delta_f}{\delta_b - \delta_f} \quad (4)$$

Now, the average solvation number (\bar{n}) of the metal ions with respect to HMPA at any HMPA/ M^{2+} molar ratio can be calculated from :

$$\bar{n} = \frac{[\text{HMPA}]_t - [\text{HMPA}]_f}{[\text{M}]_t} \quad (5)$$

or

$$\bar{n} = \frac{[\text{HMPA}]_b}{[\text{M}]_t} \quad (6)$$

or

$$\bar{n} = \frac{[\text{HMPA}]_b \cdot X_b}{[\text{M}]_t} \quad (7)$$

Where $[\text{HMPA}]_b$, $[\text{HMPA}]_f$, $[\text{HMPA}]_t$ and $[\text{M}]_t$ refer to the concentrations of bound HMPA, free HMPA, total HMPA and total concentration of the metal ion, respectively. Substitution of Eq. (4) in Eq. (7) results in,

$$\bar{n} = \frac{(\delta_{\text{obs}} - \delta_f)[\text{HMPA}]_t}{(\delta_b - \delta_f)[\text{M}]_t} \quad (8)$$

The average solvation number at each HMPA/M ion molar ratio was calculated with the aid of Eq. 8. δ_f was obtained from the NMR spectrum of HMPA in NM solution. This was 200.2 HZ regardless of the concentration of HMPA. δ_b in the case of each metal ion was determined from the max. point in chemical shift-molar ratio plots.

The calculated values of \bar{n} against molar ratio for Mg^{2+} , Ca^{2+} and Sr^{2+} ions are shown in Figs. 9,10 and 11 respectively. It is observed from these plots that the value of \bar{n} increases by an increase in HMPA/M until a limiting molar ratio is reached, beyond of which no appreciable change in \bar{n} is observed. The limiting \bar{n} value, or the solvation number of the metal ion is 4 for Mg^{2+} ion and 5 for Ca^{2+} and Sr^{2+} ions.

To compare the ability of H_2O with HMPA in solvation of alkaline earth ions, ^1H NMR spectra of a series of solutions of alkaline earth perchlorates in NM at a constant concentration of water ($\text{H}_2\text{O}/\text{M}=6$) and varying concentrations of HMPA were recorded. The resulting spectra are shown in Figs. 4,5

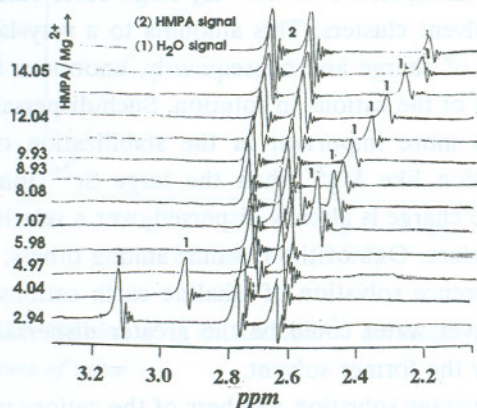


Fig. 4: ^1H NMR spectra of HMPA and H_2O at various $\text{HMPA}/\text{Mg}^{2+}$ molar ratios in nitromethane solutions.

and 6. The measured chemical shifts of HMPA and H_2O protons at different molar ratios are shown in Fig.8.

It is observed, analogous to Fig. 7 that for all of the ions the resonance frequency of HMPA protons

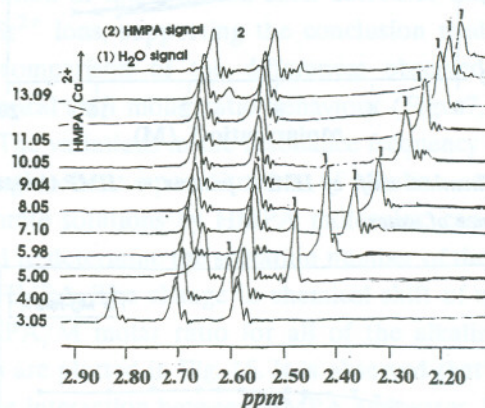


Fig. 5: ^1H NMR spectra of HMPA and H_2O at various $\text{HMPA}/\text{Ca}^{2+}$ molar ratios in nitromethane solutions.

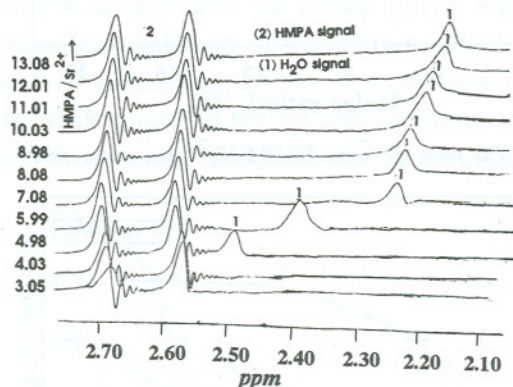


Fig. 6: ^1H NMR spectra of HMPA and H_2O at various $\text{HMPA}/\text{Sr}^{2+}$ molar ratios in nitromethane solutions.

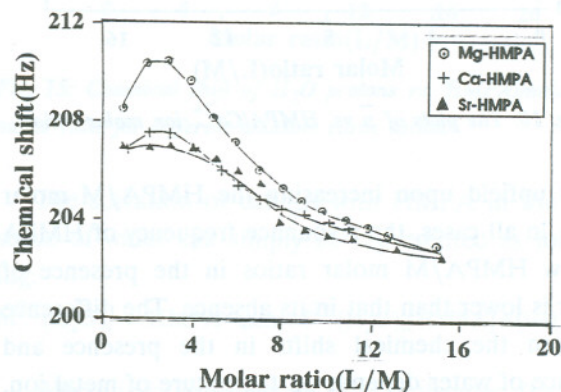


Fig. 7: Chemical shift of HMPA protons vs. HMPA/metal in the absence of water.

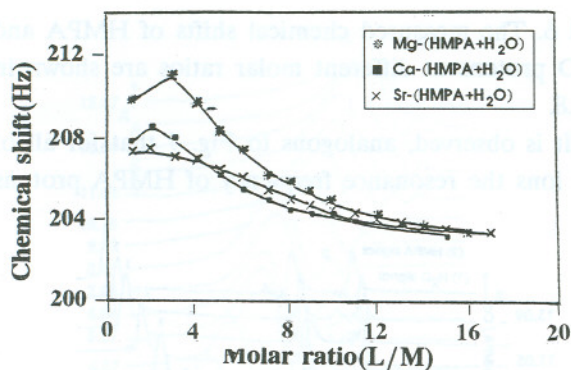


Fig. 8: Chemical shift of HMPA protons vs. HMPA/metal in the presence of water.

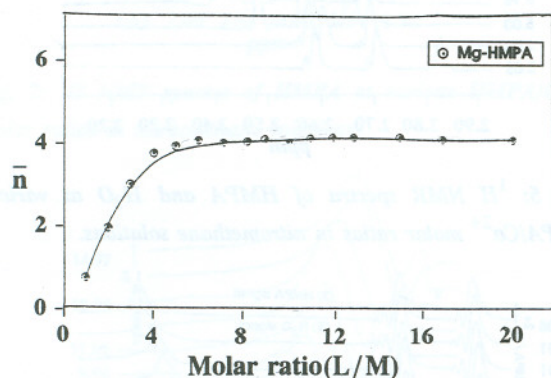


Fig. 9: The plots of \bar{n} vs. HMPA/Mg²⁺ ion molar ratio

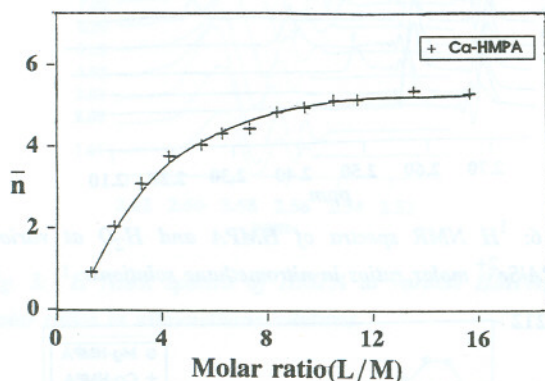


Fig. 10: The plots of \bar{n} vs. HMPA/Ca²⁺ ion molar ratio

shifts upfield upon increasing the HMPA/M molar ratio. In all cases, the resonance frequency of HMPA at low HMPA/M molar ratios in the presence of water is lower than that in its absence. The difference between the chemical shifts in the presence and absence of water depends on the nature of metal ion, and varies in the order of Mg²⁺ > Ca²⁺ > Sr²⁺. This difference can be attributed to the participation of

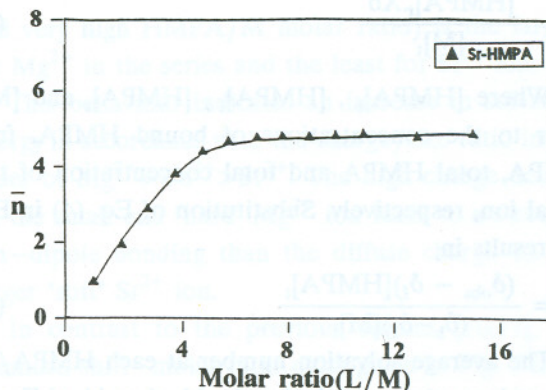


Fig. 11: The plots of \bar{n} vs. HMPA/Sr²⁺ ion molar ratio

H₂O in the metal ion solvation shell, which of course depends on the nature of the cation. The above observations support the fact that the hydration energy of alkaline earth cations decreases with the increase in the ionic size [5,7,21]. However, by increasing the concentration of HMPA, the water molecules in the solvation shell are replaced by HMPA and consequently, the HMPA resonance frequencies in both series of experiments approach more or less the same values. It is interesting to note that the limiting molar ratios increase in the order Mg²⁺ < Ca²⁺ < Sr²⁺ indicating an increase in solvation energy with charge density from Mg²⁺ to Sr²⁺.

An alternative way to view the stability order of the solvated species, i.e. Mg²⁺ > Ca²⁺ > Sr²⁺, is to consider the dispersal of charge, brought about upon the solvation of cations. In the solvated species, the large charge densities originally concentrated on M²⁺ ions are now distributed over the very large outer surface of the solvent clusters. This amounts to a very large dispersal of charge and consequently, enormous stabilization of the cations in solution. Such dispersal of charge is more important in the stabilization of a small cation like Mg²⁺ than the large Sr²⁺ ion in which the charge is already dispersed over a relatively larger surface. One of the reasons, among others, for the preference solvation of alkaline earth cations by HMPA over water could be the greater dispersal of charge by the former solvent.

The average solvation numbers of the cations with HMPA in the presence of water were calculated and the results are shown in Figs. 12,13 and 14. The δ_f

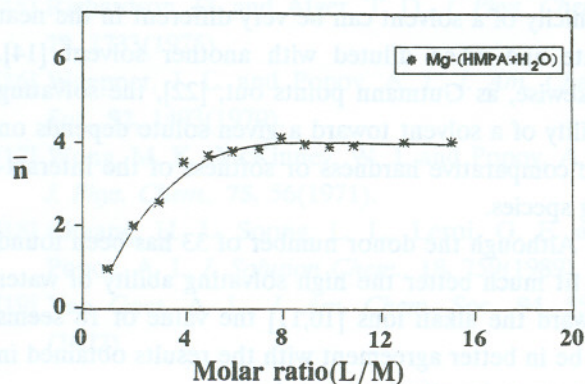


Fig. 12: The plots of \bar{n} vs. HMPA/Mg²⁺ ion molar ratio in the presence of water

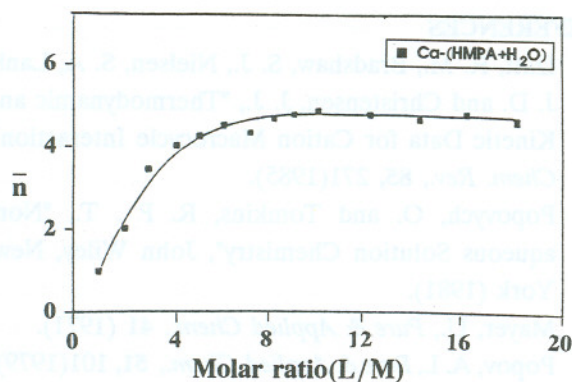


Fig. 13: The plots of \bar{n} vs. HMPA/Ca²⁺ ion molar ratio in the presence of water

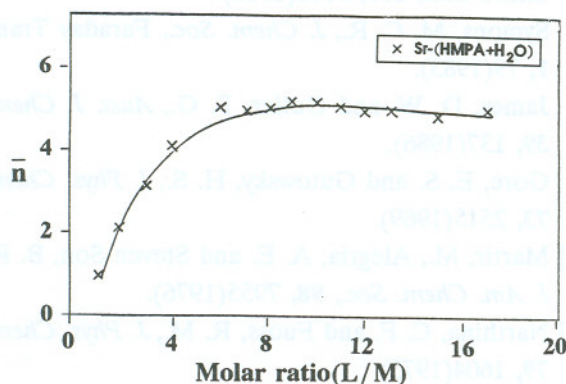


Fig. 14: The plots of \bar{n} vs. HMPA/Sr²⁺ ion molar ratio in the presence of water

value in this case was 200.2 HZ and δ_b values were obtained as in the previous case.

It is interesting to note that, in the presence of water, because of the contribution of H₂O molecules in the solvation shell, the solvation numbers for different cations by HMPA is less than that observed in the absence of water. The extent of water contribution in the solvation shell decreases from Mg²⁺ to Sr²⁺ ions, supporting the conclusion made above by comparison of the differences observed in the chemical shift molar ratio behaviour (Figs. 7,8).

The variations in the resonance frequency of H₂O, brought about upon titration of alkaline earth perchlorate solutions by HMPA molecules, can also be used to determine the solvation number of the cations by HMPA. The change in chemical shift of water vs. HMPA/M molar ratio for all of the alkaline earth ions are plotted in Fig. 15. It is observed that there is some interaction between HMPA and water. In order to make an accurate correction for this interaction, the dissociation constant of alkaline earth ions-HMPA solvate must be known [9,16]. Since these values were unknown, the corrections in Fig. 15 were made by subtracting the base line (obtained by taking the NMR spectra at several concentrations of HMPA in NM containing H₂O) from the corresponding plots.

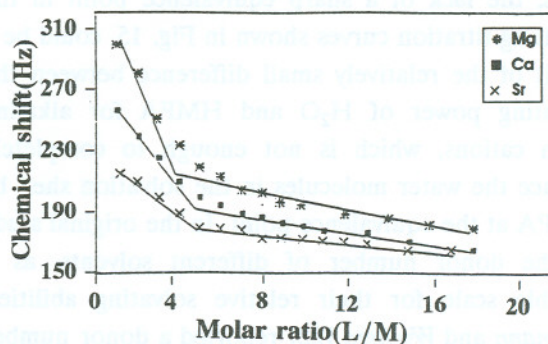
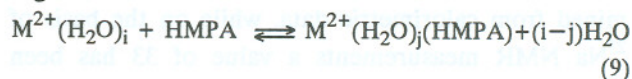


Fig. 15: Chemical shift of H₂O protons vs. HMPA/metal ion molar ratio for different alkaline earth cations

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



Where $i > j$. Two types of H₂O molecules. (i.e. free and bound) are present during the course of titration. Because of the existence of a fast exchange

between the free and bound water molecules, only one population averaged NMR signal was observed in all cases studied. The population of the free molecules increases with increasing the HMPA concentration. The characteristic upfield shift of water molecules prior to the equivalence point can be explained by taking into account the fact that the free H₂O resonates at a higher field than the bound H₂O. Beyond the equivalence point, the chemical shift of H₂O will remain more or less constant. As it is observed in Fig. 15, the differences between the chemical shifts of bound and free water molecules decrease in the order Mg²⁺ > Ca²⁺ > Sr²⁺, which reflects the trend of a decrease in the cation-H₂O interaction from magnesium to strantium ions.

Extrapolation of the linear parts of the titration curves gives rise to an intersection at HMPA/M²⁺ molar ratio of about 4 for Mg²⁺ ion and about 5 for other cations used. It is obvious that, the sharpness of the equivalence point in such titration curves depends on the relative solvating abilities of the two different solvents. The more difference between the solvating ability of the two different solvent molecules, the sharper will be the equivalence point. Thus, the lack of a sharp equivalence point in the resulting titration curves shown in Fig. 15, could be a result of the relatively small difference between the solvating power of H₂O and HMPA for alkaline earth cations, which is not enough to completely replace the water molecules in the solvation shell by HMPA at the equivalence point. In the original study of the donor number of different solvents, as a reliable scale for their relative solvating abilities, Gutmann and Wyckera [22] reported a donor number of 18 for water, which indicates a rather moderate solvating ability in comparison with HMPA, with a donor number of 29.8.

It should be noted that there is an ambiguity about the donor number of water. As it was mentioned above, Gutmann cites this value as 18 [22] determined from calorimetric data, while on the basis of ²³Na NMR measurements a value of 33 has been reported by Popov et al. [23]. It should be emphasized, however, 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 and when diluted with another solvent [14]. Likewise, as Gutmann points out, [22], 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 toward the alkali ions [10,11] the value of 18 seems to be in better agreement with the results obtained in this study for alkaline earth ions.

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