AN FT-IR SPECTROSCOPIC INVESTIGATION OF IONIC SOLVATION OF ALKALINE EARTH CATIONS WITH DIMETHYLSULFOXIDE IN ANHYDROUS ACETONITRILE

S. Monshi[1] and M. Shamsipur[2]*

[1]Department of Chemistry, Razi University, Kermanshah, Islamic Republic of Iran
[2]Department of Chemistry, Shiraz University, Shiraz, Islamic Republic of Iran

Abstract

The interaction between DMSO and alkaline earth perchlorates in anhydrous acetonitrile was investigated by FT-IR spectroscopy. A quantitative study was performed to determine the average number of bonded DMSO molecules using v_7 (S-O) and v_{22} (C-S) vibrations. Changes in coordination numbers were observed both with increasing atomic numbers and the solvent composition. None of the investigated systems shows any interaction with either perchlorate ions or acetonitrile molecules. Apparent equilibrium constants were estimated from the average coordination numbers.

Introduction

The solvation of metal ions by protic and aprotic solvents has been the subject of numerous experimental and theoretical studies [1-4]. The main objective of such investigations have been the determination of the solvation number defined as the number of solvent molecules occupying the inner solvation shell of the ions, elucidation of both the nature and extent of ion-solvent interactions and identification of the important species available in solution such as contact ion pair (CIP), solvent separated ion pair (SSIP), and dissociated ions. However, there have been few studies of ion-solvent interactions in solutions of the perchlorates of alkaline earth cations in nonaqueous solvents [5-8].

*To whom all correspondence should be addressed

Application of spectroscopic techniques including infrared, Raman and nuclear magnetic resonance spectrometries for investigation of the solvation phenomena has become quite widespread within the last two decades [3,4,9,10]. Direct observation of the extent to which the cation is solvated has been made by examining the spectral properties of either the solvating or in favorable cases, the cation itself. Indirect influence of the cation solvation has been investigated by considering the degree to which cation-anion interactions are reflected in the spectral properties of the counter anion [11]. We have recently reported an NMR study of ionic solvation of alkaline earth cations with dimethylsulfoxide (DMSO) in nitromethane solution [8]. In this paper we report on a systematic FT-IR spectroscopic investigation of the interaction between DMSO and Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} perchlorates in anhydrous acetonitrile. The average coordination number of the metal ions used is determined and the apparent stability constants for the fixation of the

last DMSO molecules are evaluated from the resulting data.

Experimental Section

The alkaline earth perchlorate salts were prepared according to a known procedure [7], by treating the solid metal carbonates (Aldrich) with aqueous $HClO_4$ (30%, Merck) until effervescence ceased. The pH was then found to be about 7.0. Excess solid carbonate was filtered off and the filtrate was concentrated by the evaporation of water. The solution was cooled down to room temperature and the crystalline salt was obtained as a white precipitate. Filteration followed by recrystalization of the salt with triply distilled deionized water (three times) which afforded the pure crystalline salt. The $Mg(ClO_4)_2$ salt was dried under nitrogen gas in the temperature range of 130°C to 230°C in a stepwise manner [12]. Other alkaline earth perchlorate salts were dried in a vaccum at 150°C to 250°C. Anhydrous acetonitrile (AN, HPLC grade, Aldrich) was stored over 3Å molecular sieves. Dimethylsulfoxide (DMSO, spectroscopic grade, Fluka) was purified and dried by distillation over 3Å molecular sieves and stored over them.

The FT-IR spectra were recorded on a Bruker IFS-88 FT-IR spectrometer. The data acquisition and handling system included a 16-bit converter, a 256-Kbyte 24-bit Aspect 1000 computer and a 170-Mbyte Hitachi hard disk unit. A KBr cell window and the corresponding polishing kit were used for spectral measurements. The mid-IR spectra were measured under the following conditions: N_2 purge, 1 cm^{-1} bandpass, 4 points/spectral element, 300 scans. The recorded data are the average of several measurements performed on at least two independently prepared solutions.

Results and Discussion

Among 24 vibrational modes of DMSO, four are affected considerably by the complexation with alkaline earth cations. These vibrational modes are listed in Table 1, along with their assignment in C_s symmetry [13]. As it is seen, the largest shifts upon complexation with alkaline earth cations occur for S-O (v_7) and C-S (v_{22}) stretching vibrations. The v_7 shift decreases by increasing the atomic number of the cations, from 40 to 31 cm^{-1} and slightly decreases by increasing the DMSO concentration in each case. The relatively strong bathochromic shift in v_7 emphasizes the coordination of DMSO molecules to the metal ions through the oxygen atom. The other shifts are opposite in sign and in lower extent (6-20 cm^{-1}), but show the same tendencies as the v_7 shift.

From the data given in Table 1, it is clearly seen that the magnitude of shift in different vibrational modes of DMSO, brought about upon complexation with alkaline

earth cations, increased by decreasing the atomic number of the metal ions (i.e. in the order Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}). As it is expected, the Mg^{2+} ion with the largest charge density in the series has the strongest interaction with DMSO molecule, which in turn results in the largest shift in the frequency of the DMSO vibrational modes.

The FT-IR differences spectra of 0.2 M solution of DMSO in acetonitrile in the spectra for the Mg $(ClO_4)_2$-DMSO-AN system are shown in Figure 1. All spectra are corrected for the diluent and perchlorate ion. The spectral subtractions were performed in the region 1130-600 cm^{-1}. It should be noted that no interaction between the alkaline earth cations and perchlorate ion or acetonitrile molecules was detected in the investigated solutions. This was supported by observing no change in both the pattern and wave numbers of the perchlorate spectrum when either various concentrations of the alkaline earth perchlorate solutions (from 0.01 M to 0.4 M) were used or an excess amount of the metal ions was added to the perchlorate solutions. As it is evident from Figure 1, in the above spectral region, that v_7 and v_{22} of DMSO are very sensitive to its interaction with alkaline earth cations. The resulting shifts brought about upon complexation with M^{2+} ion are as follows:

$v_7 (cm^{-1})$

free: 1061

bonded: 1020 (Mg^{2+}); 1025 (Ca^{2+}); 1028 (Sr^{2+}); 1029 (Ba^{2+})

$v_{22} (cm^{-1})$

free: 697

bonded: 717 (Mg^{2+}); 713 (Ca^{2+}); 711 (Sr^{2+}); 710 (Ba^{2+})

Thus, two vibration bands v_7 and v_{22} could be monitored to determine the average number of coordinated DMSO molecules per M^{2+} ion. The v_7 vibration of free DMSO at 1061 cm^{-1} is an asymmetric band comparised of two components v_7^a and v_7^b [14]. It is strong ($\varepsilon = 430 \pm 7$ L mol^{-1} cm^{-1}) but interferes with the low intensity v_{20} $r(CH_3)$ vibtration of DMSO. The v_{22} band is also suitable for quantitative analysis because it is free of interference, although its intensity is small ($\varepsilon = 43 \pm 3$ L mol^{-1} cm^{-1}).

The complexation of an alkaline earth cation, M^{2+}, with DMSO molecules in AN solution can be shown by

$$M^{2+} + xDMSO \rightleftharpoons M(DMSO)_n^{2+} + (x-n) DMSO \quad (1)$$

where n indicates the stoichiometry of the resulting solvato-complex. This stoichiometry is described by the coordination number, defined as the number of solvent molecules in the first coordination shell which are in contact with the central cation. On the other hand, the more distant, but partially ordered solvent molecules, form a secondary solvation shell. Some experimental methods indicate that the solvent molecules are involved in the primary solvation shell, while some other methods

detect both the primary and secondary solvation shell [1].

As it is obvious from Figure 1, the absorbance measurements of the 1061 cm^{-1} (free DMSO) and 1020 cm^{-1} (bound DMSO) vibrations could be used to evaluate the average number of the bonded DMSO molecules to Mg^{2+} ion. Plots of the absorbance of the two selected vibrations against the alkaline earth cation to the DMSO mole ratio in the case of Mg^{2+} and Ca^{2+} ions are shown in Figure 2. The corresponding plots for Sr^{2+} and Ba^{2+} ions are very similar to that of the Ca^{2+} ion. The curves for the bonded DMSO increase linearly up to a mole ratio of 0.20 (for Mg^{2+} ion) or 0.167 (for other cations) and level off at higher mole ratios. Such an absorbance mole ratio behavior indicates the stoichiometry of 5 (in the case of Mg^{2+} ion) or 6 (in the cases of other cations) of the

resulting M^{2+} - DMSO solvato-complexes. It is interesting to note that extrapolating to zero the lines depicting the variation in abosrbance of free DMSO (1061 cm^{-1} vibration) usually yields intercepts at larger M^{2+}/DMSO mole ratios. This points to the presence of equilibria:

$$M(DMSO)_{x-1}^{2+} + DMSO \underset{}{\overset{K_x}{===}} M(DMSO)_x^{2+} \qquad (2)$$
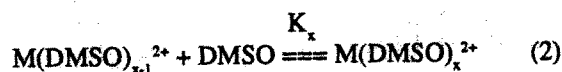
The coordination number of alkaline earth cations with DMSO in AN solution was further investigated by keeping the concentration of metal ions constant and varying the concentration of DMSO in AN Solution. The FT-IR difference spectra of 0.1 M solutions of Ca(ClO$_4$)$_2$ in AN containing various amounts of DMSO are shown in

Table 1. Observed shifts, v(coordinated)- v(free), for vibrations assigned to coordinated DMSO molecules in 0.2 M DMSO solutions in AN containing various amounts of alkaline earth perchlorates

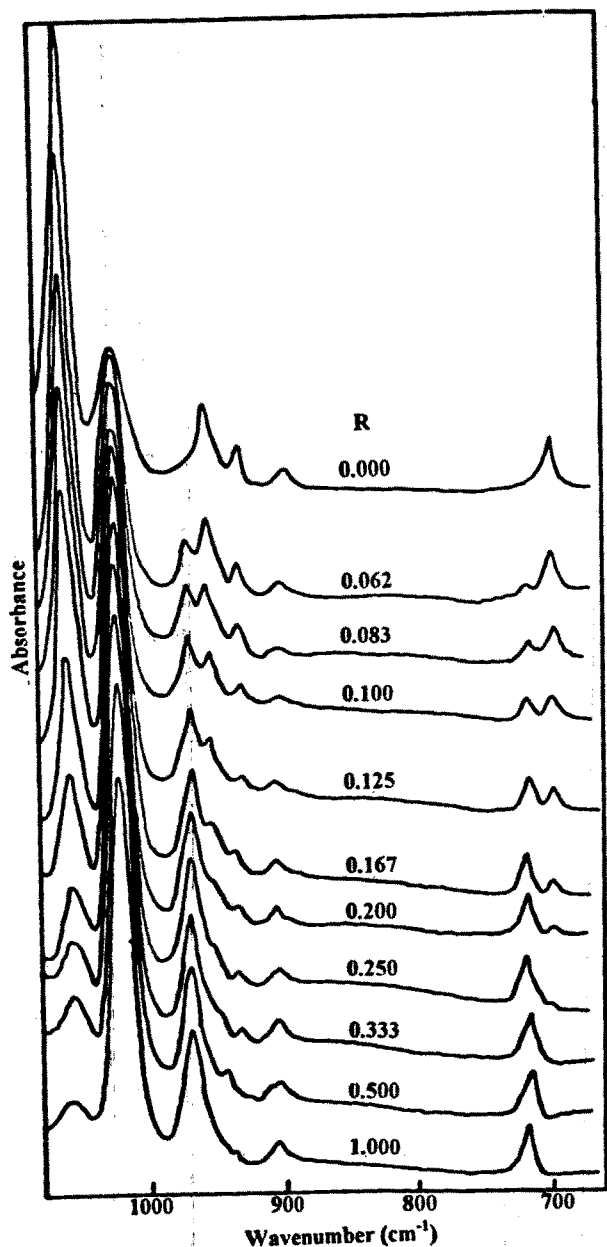| M^{2+}	R^a	v_{22} (C-S) A" 697 cm^{-1}	v_9 (CH3)A" 927 cm^{-1}	v_{21} (CH3)A' 950 cm^{-1}	v_7 n(SO)A' 1061 cm^{-1}
Mg^{2+}	1	20	17	18	- 40
	5	18	16	16	- 40
	10	17	15	15	- 40
	20	17	15	15	- 40
Ca^{2+}	1	16	13	13	-35
	5	15	12	12	-35
	10	14	11	11	-34
	20	14	11	11	-34
Sr^{2+}	1	14	10	11	-33
	5	13	9	10	-32
	10	13	9	9	-32
	20	12	9	9	-31
Ba^{2+}	1	13	9	9	-32
	5	11	8	7	-31
	10	11	7	7	-31
	20	11	7	6	-30

^{a}R= [DMSO]$_t$/[M^{2+}]$_t$

Figure 1. FT-IR differences spectra of 0.2 M DMSO solutions in AN containing various amounts of $Mg(ClO_4)_2$; $R= [Mg^{2+}]_t/$ $[DMSO]_t$

Figure 3. As mentioned before, no interaction between M^{2+} ions used and perchlorate ion or acetonitrile molecules was detected in this study. Henceforth, the average coordination number of the alkaline earth ions is equal to the average number of bonded DMSO molecules, i.e. n= $[DMSO]_b/[M^{2+}]_{tot}$. In this case the average number of bonded DMSO molecules was calculated from the total DMSO concentration and the free DMSO concentration. The latter was assessed by means of a calibration curve

using the v_{22} vibration of a DMSO molecule with $\epsilon= 43\pm3$ L mol^{-1} cm^{-1}. The resulting n values at three different DMSO to M^{2+} mole ratios of 12,14 and 16 are given in Table 2.

As it was pointed out, the formation of inner-sphere complex between alkaline earth cations could be described in terms of equilibria (2). The apparent equilibrium constant K_x in the case of Ca^{2+}, Sr^{2+} and Ba^{2+} ions was calculated according to the Bjerrum's method [15] and the resulting values are also summarized in Table 2.

As it is expected, the data given in Table 2 clearly show that, first, the average coordination number for each cation slightly increases by increasing the $DMSO/M^{2+}$ ratio in solution and second, the K_x value for each cation decreases by increasing the average coordination number of the cation.
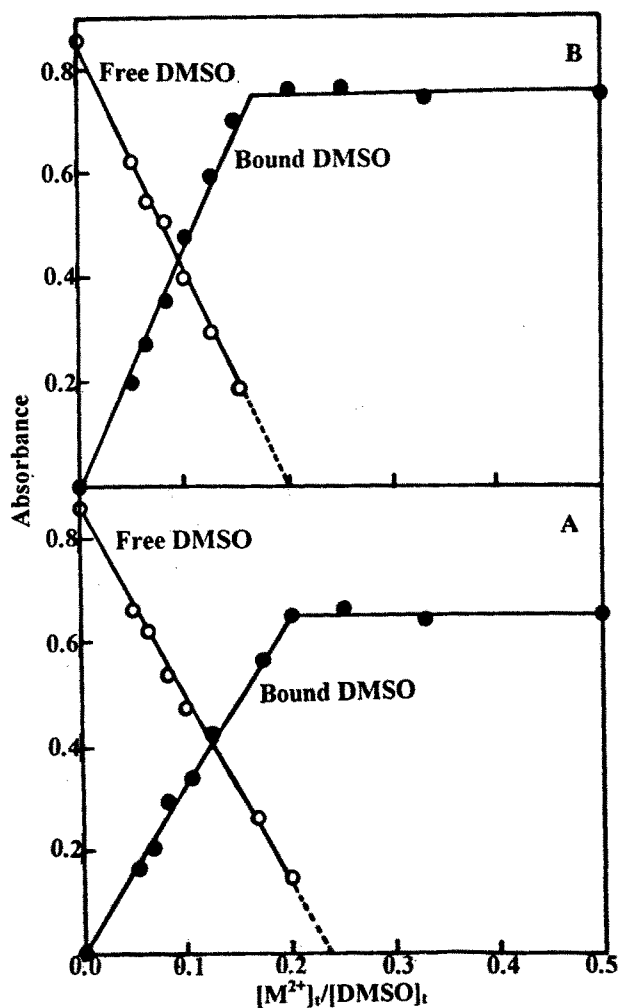

Figure 2. Absorbance vs $[M^{2+}]_t/[DMSO]_t$ mole ratio plots using v_7 vibrations of the free and bonded DMSO in 0.2 M DMSO solutions in AN containing various amounts of $Mg(ClO_4)_2$ (A) and $Ca(ClO_4)_2$ (B)
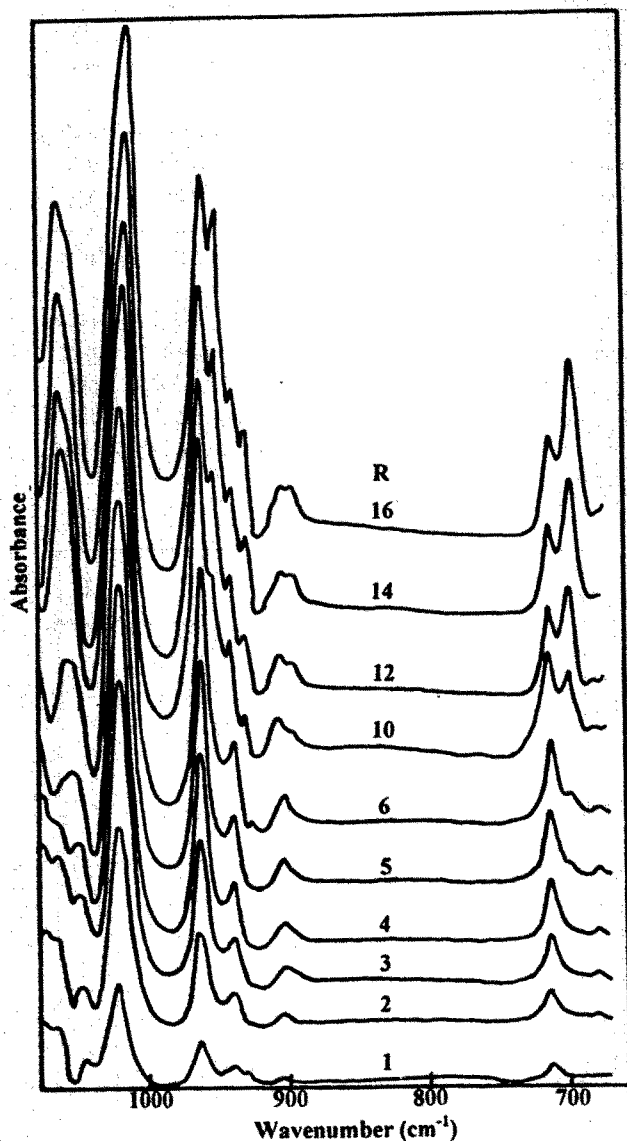
Figure 3. FT-IR difference spectra of 0.1 M Ca(ClO$_4$)$_2$ in AN containing various amounts of DMSO; R= [DMSO]$_t$/[Ca^{2+}]$_t$

Table 2. Average coordination number, n, and apparent equilibrium constants, log K$_x$, for 0.1 M solutions of alkaline earth perchlorates in AN containing various amount of DMSO

Cation	R^a	n	log K$_x$
Ca^{2+}	12	6.0	0.77
	14	6.4	0.62
	16	6.5	0.58
Sr^{2+}	12	5.6	1.50
	14	5.8	1.42
	16	6.0	1.30
Ba^{2+}	12	5.8	2.20
	14	6.0	1.48
	16	6.4	1.31

It is also interesting to note that the K$_x$ values for different alkaline earth cations, at the same mole ratios, decrease in the order Ba^{2+} > Sr^{2+} > Ca^{2+}. Since all the DMSO molecules in the inner coordination sphere appear to be equivalent, such a variation in K$_x$ values may be interpreted as follows. When excess DMSO molecules are added to smaller cations such as Ca^{2+} ion, the inner coordination sphere of the cation expands to accept an additional donor molecule, resulting in a slightly weaker Ca^{2+}-DMSO interaction in solution.

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