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A DIRECT ^{13}C and ^{1}H NMR STUDY ON THE CATION SOLVATION OF ALUMINUM PERCHLORATE SOLUTIONS IN AQUEOUS MIXTURE OF 3-METHYLSYDNONE

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The solvation of 3-methylsydnone molecule to aluminum ion in water - 3-methylsydnone mixture was studied by ^{13}C and ^{1}H NMR signal area measurements on the aluminum perchlorate solutions. 3-Methylsydnone solvation number was found to be 0.5 to 2.5 for the solution at mole ratios of Al to water greater than 1 : 20.

3-Methylsydnone (MS) is an interesting non-aqueous solvent with its good dissolving power of electrolytes, the miscibility with water at all composition and high relative permittivity of 144 due to the large dipole moment, 7.3 D, of the molecule.[1,2] The solvation of ions with high charge (Al^{3+}, Ga^{3+}, etc.) in the aqueous mixtures of organic solvents has been studied extensively by ^{1}H NMR technique based on the feasibility in measuring the area of the separate resonance signals arising from bound and bulk solvent molecules.[3-5] In $Al(ClO_4)_3$ - MS - H_2O system, it was found that the separate signals of ^{13}C and ^{1}H of MS appear at room temperature if the concentration of $Al(ClO_4)_3$ is high. An example of the spectra is shown in Fig.1. Thus we attempted to determine the solvation number of MS for Al^{3+} in the system from the signal area measurement of the NMR spectra.

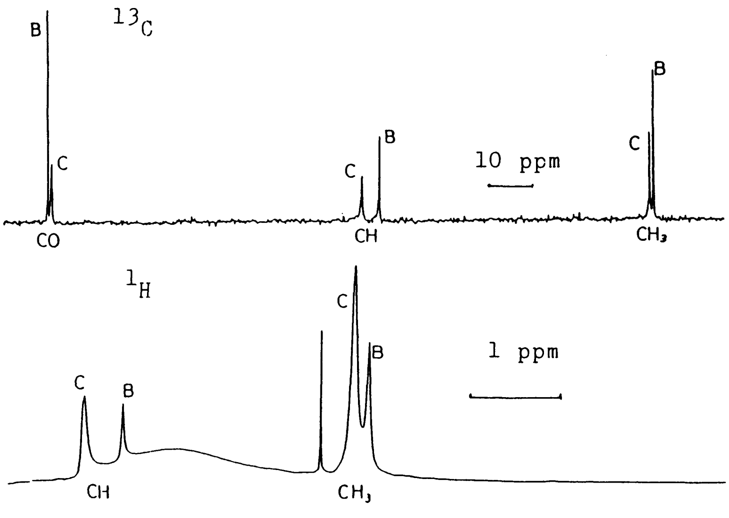

Fig.1. MS ^{13}C and ^{1}H NMR spectra of an $Al(ClO_4)_3$ solution in MS - H_2O mixture at 30 °C. Mole ratio of Al : MS : H_2O is 1 : 2.3 : 9.2. The signal arising from bulk and coordinated MS (B and C) molecule are labeled. The narrow line in ^{1}H spectrum is due to HDO of a capillary tube containing D_2O used in the NMR tube for a ^{2}D internal lock device.

Aluminum perchlorate hexahydrate was prepared by neutralizing aluminum hydroxide with perchloric acid and the recrystallized salt was dried in a vacuum desiccator containing P_2O_5. The water content was confirmed by a total cation analysis using a cation exchange column. MS was synthesized and purified as previously described.6) Spectral grade acetone was used without furthur purification. NMR spectra were recorded on a JEOL FT-90Q NMR spectrometer at 30 ± 1 °C. ^{13}C spectra were obtained at the gated decoupling by using a pulse modulated wide band decoupler, where the decoupler is gated on only during the data aquisition period to prevent appreciable NOE effect.

As can be seen in Fig.1, the coordinated MS molecule gives ^{13}C and ^{1}H signals at lower fields from the signals of bulk MS except the ^{13}C signal of carbonyl carbon, which is located at higher field from the bulk signal and the separation varies most appreciably with the composition of the solution. The proton exchange rate of water is so rapid that only a broad signal of water proton was observed at the temperature. Since the respective ^{13}C signal due to a coordinated MS molecule consists of a single peak as well as the ^{1}H signal, it is not possible to estimate the population distribution of the species like $Al(MS)_m(H_2O)_{n-m}$ and only an averaged solvation number is obtainable from the measurement of signal area ratios of coordinated and bulk MS. The ratios obtained from each of the pair of separated signal in the ^{13}C and ^{1}H spectra agreed within an error of 10 %. Table 1 summarizes the results.

Table 1. Solvation number of MS for Al^{3+} and ^{13}C and ^{1}H chemical shift differences between coordinated and bulk MS molecules

Mole ratio			Solvation number	^{13}C Δδ/ppm a)			^{1}H Δδ/ppm	
Al	MS	H_2O		C-O	C-H	$N-CH_3$	C-H	$N-CH_3$
1	7.1	19.9	0.5	-	-	1.14	0.63	0.23
1	7.1	15.5	0.8	-	4.23	1.03	0.61	0.22
1	6.6	9.6	1.6	-	4.31	1.00	0.60	0.22
1	6.0	9.1	1.8	-	4.23	1.03	0.58	0.20
1	7.2	8.8	1.8	-	4.39	1.03	0.62	0.22
1	7.1	6.9	2.3	-	4.55	1.03	0.62	0.21
1	7.0	5.9	2.5	-	4.68	1.03	0.61	0.21
1	3.4	9.5	1.5	- 1.08	3.60	0.92	0.49	0.18
1	2.3	9.2	1.5	- 1.46	3.25	0.82	0.45	0.16
1	2.0	9.0	1.5	- 1.57	3.25	0.81	0.44	0.16
1	1.8	8.1	1.4	- 1.82	2.95	0.76	0.39	0.14
1	10.0	10.0	1.4	-	4.66	1.08	0.69	0.24

a) A minus sign indicates an upfield shift by coordination.

The carbonyl carbon ^{13}C signal of coordinated MS was somewhat broader than the other peaks and overlapped with the bulk signal when the separation is not large enough. The shift differences (Δδ) of ^{13}C and ^{1}H of coordinated and bulk MS are also listed in Table 1. In a solution containing a 1 : 7 : 30 mole ratio of Al : MS : H_2O, any signal of coordinated MS was not detected. In Fig.2, the solvation number data of the solutions which contain Al and MS at a mole ratio close to 1 : 7 are plotted as a function of the Al to H_2O mole ratio.

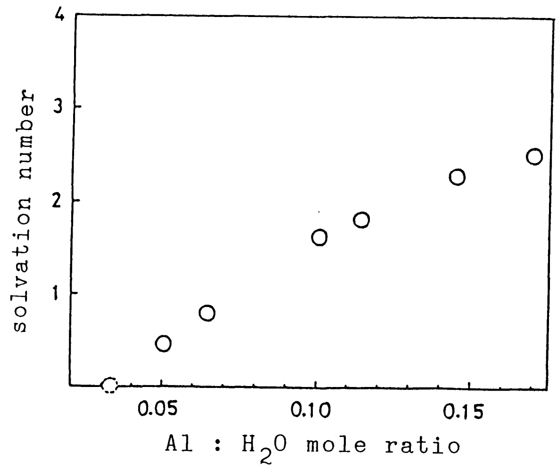

Fig.2. Solvation number of MS in $Al(ClO_4)_3$ - MS - H_2O system containing Al and MS at approximately 1 : 7 mole ratio plotted vs. Al to H_2O mole ratio.

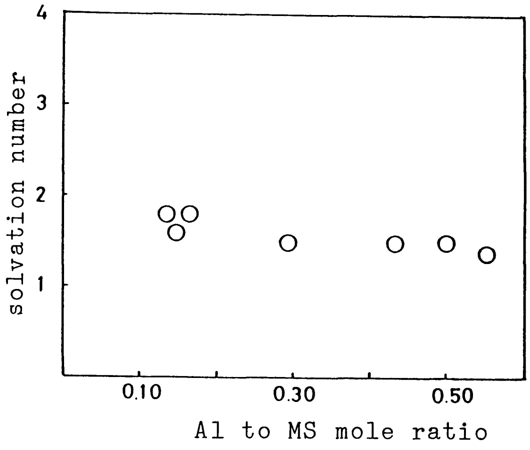

Fig.3. Solvation number of MS in $Al(ClO_4)_3$ - MS - H_2O system containing Al and H_2O at approximately 1 : 9 mole ratio plotted vs. Al to MS mole ratio.

The figure shows that direct MS solvation decreases rapidly with the dilution of the solution with water. On the other hand, if the Al to H_2O mole ratio is kept at around 1 : 9, the solvation number of MS increases quite slowly with the increase of MS to Al mole ratio, as shown in Fig.3. It can be seen from Table 1 that ^{13}C $\Delta\delta$ of the carbonyl carbon atom increases, while those of the methine and methyl carbon atoms decrease with an increase in Al to MS ratio. In MS - H_2O mixtures, it has been shown that the ^{13}C signals of carbonyl, methine and methyl carbon atoms of MS shift to downfield with an increase in the water mole fraction, and the magnitude of the shift variation decreases in that order.[6)] The variation of the ^{13}C $\Delta\delta$ with the Al to MS mole ratio may be considered as mainly due to the downfield shifts of the bulk MS signals arising from a decrease in bulk MS fraction as a result of the coordination.

The effect of dilution of the solution by acetone on the MS solvation number was examined by recording ^{13}C and ^{1}H NMR spectra of the solution containing $Al(ClO_4)_3$, MS and H_2O at approximately 1 : 2 : 9 mole ratio and varying amount of acetone. The result is presented in Table 2. No signal of coordinated acetone was observed in both ^{13}C and ^{1}H spectra. The solvation number decreases from 1.5 to 0.7 by adding acetone up to the acetone to Al mole ratio of 12 : 1. Fratiello et al. reported the solvation number of dimethyl sulfoxide (DMSO)[4)] and hexamethylphosphotriamide (HMPT)[5)] in $Al(ClO_4)_3$ solutions of the solvent - H_2O - acetone mixtures. In 0.16 M $Al(ClO_4)_3$ solution of the solvent composition, 1 : 1 : 1 mole ratio of DMSO : H_2O : acetone, the reported cation solvation number is 3.1 at - 50 °C, and that of HMPT is 1.7 even in the solution of high content of acetone (Al : HMPT : H_2O : acetone mole ratio ; 1 : 2 : 17 : 170). The solvating ability of MS to Al^{3+} ion seems to be not so high as but far below from those of DMSO or HMPT judging from the comparison of MS solvation numbers listed in Tables 1 and 2 with the above quoted data.

Table 2. Solvation number of MS for Al^{3+} and ^{13}C and ^{1}H chemical shift differences between coordinated and bulk MS molecules in $Al(ClO_4)_3$ - MS - H_2O - acetone system

Mole ratio Al : MS : H_2O : acetone	Solvation number	^{13}C $\Delta\delta$/ppm[a)] C-O	C-H	N-CH_3	^{1}H $\Delta\delta$/ppm C-H	N-CH_3
1 : 2.5 : 9.2 : 0.8	1.4	- 1.46	3.25	0.81	0.45	0.16
1 : 2.3 : 9.3 : 1.8	1.3	- 0.98	3.79	0.92	0.51	0.18
1 : 2.5 : 9.2 : 3.2	1.2	- 0.76	4.01	0.92	0.55	0.22
1 : 2.3 : 9.2 : 4.6	1.0	- 0.65	4.06	1.03	0.55	0.19
1 : 2.3 : 9.3 : 9.0	0.8	-	4.77	1.03	0.64	0.21
1 : 2.3 : 9.2 : 11.9	0.7	-	4.94	1.03	-	0.31

a) A minus sign indicates an upfield shift by coordination.

The factors affecting the solvating ability are supposed to be the donating power of the functional group and some steric factor rather than the overall dipole moment of the molecule, as Fratiello et al. pointed out in their early work.[3)]

The ^{27}Al spectra were recorded at 23.3 MHz for some of the solutions listed in Table 1. An example of the spectra is shown in Fig.4. As illustrated in the figure, the ^{27}Al spectra obtained were all broad and seemed to be composed of more than one peak overlapping with different line widths. Although it is not possible to know the shift and line widths of the overlapping peaks, the spectra suggest that there may exist certain Al species different in the composition of their direct solvation sheath.

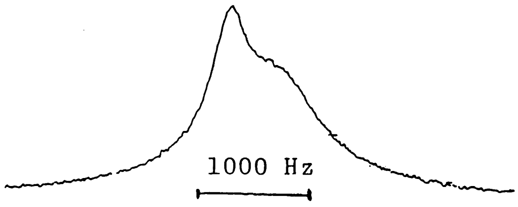

Fig.4. 23.3 MHz ^{27}Al NMR spectrum of a solution of $Al(ClO_4)_3$ in MS - H_2O where Al : MS : H_2O mole ratio is 1 : 6.6 : 9.6.

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