

A PROTON MAGNETIC RESONANCE SOLVATION STUDY OF  
ALUMINUM CHLORIDE IN DIMETHYLSULFOXIDE-WATER MIXTURES

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We wish to report the determination of Al(III) coordination numbers in dimethylsulfoxide (DMSO)-water mixtures over a range of solvent concentration by a proton magnetic resonance technique. In  $\text{AlCl}_3$  solutions of these solvent mixtures separate proton resonance signals are observed for water and DMSO molecules in the Al(III) solvation shell and in bulk medium. Previous authors<sup>(1,2)</sup> have reported the observation of proton resonance signals for complexed water in diamagnetic electrolyte solutions, but in one case (1) the bulk water signal was not distinguishable and in the other (2), the experiments were possible only with trace amounts of water present. Our measurements were made in solvent mixtures ranging in concentration from 10:1 to 2:1 mole ratios of water to DMSO, using a Varian A60 NMR Spectrometer equipped with a Varian-6057 variable temperature device.

A typical spectrum exhibited by one of these solutions, a 2 M  $\text{AlCl}_3$  solution in a 10:1  $\text{H}_2\text{O}$  to DMSO mixture, is shown in Fig. 1, with the electronic integration lines superimposed on the resonance peaks. The integration lines are shown to illustrate the relative ease with which coordination numbers can be measured. At temperatures in the region of  $-20^\circ\text{C}$ , the proton exchange in these mixtures, and, in fact, in pure water solutions of  $\text{AlCl}_3$ (3), is slowed to an extent which permits the observation of bulk and complexed water proton signals. The separate DMSO signals are clearly distinguishable even at room temperature.

The coordination number results for all solutions studied are listed in Table I.

Table I. Al(III) Coordination Numbers in Dimethylsulfoxide-Water Mixtures.

Solvent Mole Ratios H <sub>2</sub> O/DMSO	AlCl <sub>3</sub> Concentration (moles/liter)	Al(III) Coordination Numbers		
		H <sub>2</sub> O	DMSO	Total
10:1	2.0	5.01 <sup>±</sup> 0.10	0.92 <sup>±</sup> 0.01	5.93
10:1	1.0	5.63 <sup>±</sup> 0.26	0.53 <sup>±</sup> 0.04	6.16
5:1	1.8	4.12 <sup>±</sup> 0.17	1.69 <sup>±</sup> 0.02	5.71
5:1	1.0	4.97 <sup>±</sup> 0.13	1.28 <sup>±</sup> 0.06	6.25
3.5:1	1.5	3.56 <sup>±</sup> 0.10	2.02 <sup>±</sup> 0.03	5.58
3.5:1	1.0	4.06 <sup>±</sup> 0.12	1.92 <sup>±</sup> 0.04	5.98
2:1	1.0	3.08 <sup>±</sup> 0.04	2.61 <sup>±</sup> 0.01	5.69

As indicated in Fig. 1, the water resonance signals were integrated at -20°C, the temperature at which the water signals were sharpest, while the DMSO measurements were made at +35°C. Integration of the DMSO signals at -20°C was carried out in the 10:1 mixtures and agreement of the results with those obtained at +35°C was observed. However, since the DMSO integrations were facilitated at +35°C by the increased sharpness of the signals, this temperature was used throughout the study. Listed in Table I in columns 3 and 4, respectively, are the water and DMSO contributions to the Al(III) coordination shell, while in the last column the sums of these contributions are listed.

Several trends in the data are readily apparent. For example, DMSO, as indicated by its contribution to the Al(III) solvation shell even in the 10:1 mole ratio system, competes effectively with water for ions in solution. Further, the DMSO portion of the total coordination number increases with concentration, until in the 2:1 solvent mixture, the number of water and DMSO molecules in the solvation shell are almost equal. This trend can be explained, in part, by changes in the relative amounts of the two solvents present, but it also may indicate that to some extent, solvation occurs preferentially by DMSO.

The data of Table I appear to indicate that ion-pair formation, of the type involving chloride ion in the first coordination shell of Al(III), does not occur even at 1 M AlCl<sub>3</sub>,

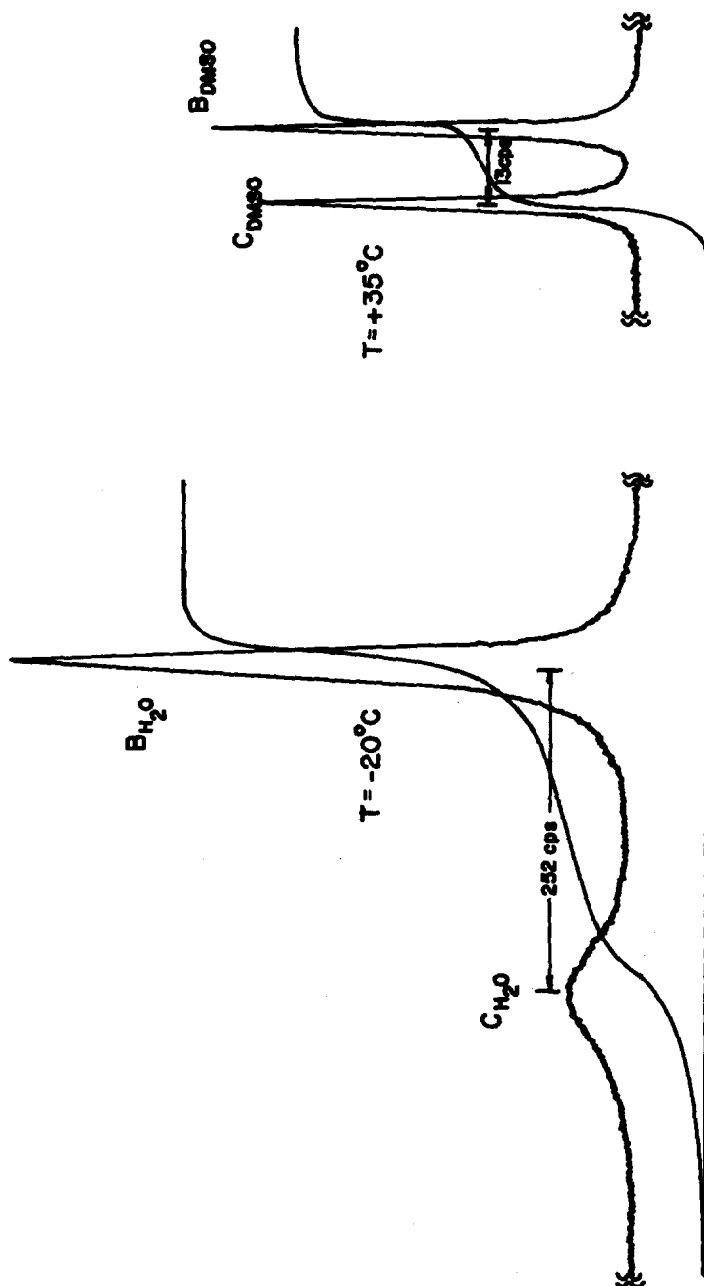


FIG. 1

The proton magnetic resonance spectrum of a 2 M  $\text{AlCl}_3$  solution in a 10:1 mole ratio mixture of water to DMSO, illustrating the signals due to bulk solvent ( $\text{B}_{\text{H}_2\text{O}}$  and  $\text{B}_{\text{DMSO}}$ ) and solvent in the  $\text{Al(III)}$  coordination shell ( $\text{C}_{\text{H}_2\text{O}}$  and  $\text{C}_{\text{DMSO}}$ ). The water and DMSO signals were recorded on a Varian A60 Spectrometer at different spectral amplitudes.

except in the 2:1 solvent mixture. At higher salt concentrations, ion-pairing may be present in the 5:1 and more likely in the 3:5:1 systems. These conclusions are based on the fact that the total coordination number of Al(III) is six for its first solvation shell, as expected (3-7), in all but those solutions mentioned, whereas it would be less if chloride ion were replacing a solvent molecule. In view of the high dielectric constants of water (80) and DMSO (49), extensive ion pairing should not be expected.

The data of Table I, for the 10:1, 5:1, and 3.5:1 mixtures, show that the amount of water in the Al(III) solvation shell increased while that of DMSO decreases, with decreasing  $\text{AlCl}_3$  concentration. Presently, no explanation can be offered for this feature of the results.

To elucidate the observations based on these preliminary measurements, further studies in aqueous DMSO and a variety of organic solvents differing in dielectric constant and solvating ability are in progress. Also in progress are temperature studies which will yield rate constants and activation energies for solvent exchange, for both water and the organic component, in the same solution.

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