lated to the solvating properties of these nonassociated solvents compared to those of water and methanol.

It should be noted that the simple factors which seem to explain the activation enthalpies for exchange on vanadyl ion do not work for nickel(II). For instance the activation energy for water exchange is 5 kcal mol^{-1} less than that for methanol exchange on nickel(II). This difference is in the opposite direction to that predicted from basicity, steric, or crystal field effects. This fact seems to point to some as yet unconsidered factor, such as transition-state solvation, as being an important kinetic factor. It can only be hoped that study of a wider range of solvents and metal ions will lead to a better understanding of the factors controlling ligand exchange.[23]

(23) NOTE ADDED IN PROOF.—Slightly revised kinetic parameters have been obtained by least-square computer analysis of the data in acetonitrile, dimethylformamide, and methanol.

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A Proton Magnetic Resonance Solvation Study of Aluminum Perchlorate in Aqueous Mixtures of Dimethyl Sulfoxide, Dimethyl Sulfone, Dimethyl Sulfate, Tetramethylene Sulfoxide, Tetramethylene Sulfone, Acetone, and Tetrahydrofuran

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A proton magnetic resonance solvation study of Al(III) in aqueous mixtures of dimethyl sulfoxide (DMSO), dimethyl sulfone (DMSO$_2$), dimethyl sulfate (DMSO$_4$), tetramethylene sulfoxide (TMSO), tetramethylene sulfone (TMSO$_2$), acetone, and tetrahydrofuran (THF) has been completed. At low temperatures, proton exchange is slowed to such an extent in these systems that separate resonance signals are observed for bulk water and water molecules in the Al(III) solvation shell. Coordination numbers were measured by direct integration of the two water signals. Of the five sulfur-containing solvents, only DMSO and TMSO can effectively compete with water for Al(III), the remaining three being very inactive in this regard. This conclusion was reached by the observation and integration of separate resonance signals for bulk and complexed molecules of the sulfoxides. These results indicate a correlation of solvating ability with the basicity of the solvents in this series. Although acetone and THF also are inactive when there is enough water to saturate the Al(III) solvation shell, at low water concentration they can solvate this ion. Spectra of aqueous solutions of Al(ClO$_4$)$_3$ in acetone, THF, and acetone–THF revealed separate resonance signals for bulk and complexed molecules of the nonaqueous components. These spectra also revealed evidence for contact ion pairing and possibly a steric hindrance to solvation.

Introduction

Since aqueous solvent mixtures are used extensively as media for a variety of investigations, including electrochemical and kinetic studies, it is important to have information concerning the structure of these systems and the nature of the solvation of ions when present. Cation coordination numbers in water and aqueous solvent mixtures have been determined by isotopic dilution,[1,2] ion-exchange,[3-5] and uv absorption[6] methods, all of which take advantage of a slow solvent-exchange process. Systems studied include Al(III) in water,[1] Co(II) in water–methanol,[2] and Cr(III) in water–methanol,[3,4] water–ethanol,[5] and water–dimethyl sulfoxide.[6] These methods are precise but they are relatively time consuming and they are limited to the study of only a few ions. Recently, numerous coordination number measurements have been made by nuclear magnetic resonance techniques which utilize the fact that separate resonance signals are observed for bulk and complexed solvent molecules when solvent exchange is slow. Systems studied in this way include aqueous solutions of Al(III), Be(II), Ga(III), and Ni(II), all by an ^{17}O method;[7-10] Al(III) in dimethyl sulfoxide (DMSO),[11,12] N,N-dimethylformamide (DMF),[12-16] and liquid ammonia (^{14}N resonance);[17] Mg(II) in methanol;[18,19] Co(II) in methanol[20] and DMF;[21] Ni(II) in methanol[22] and DMSO;[23] and Be(II) in DMF.[24]

We recently demonstrated that by cooling aqueous

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solutions of a variety of diamagnetic ions to temperatures in the range of -20 to $-100°$, proton exchange can be slowed sufficiently to permit the direct observation of resonance signals for bulk and complexed water molecules.[25-30] Using this direct proton magnetic resonance (pmr) method Al(III),[25-28] Be(II),[28] Ga(III),[28] In(III),[28] and Mg(II)[28,29] have been studied in detail in water and aqueous solvent mixtures, while Sc(III), Y(III), and Th(IV) have been investigated in aqueous acetone mixtures.[30] Al(III) in aqueous acetonitrile[31] and Mg(II) in several solvents[32] also have been studied by this method.

The sensitivity of this technique has made it amenable for solvation studies in mixed solvents even at low water and salt concentrations. In a previous study of Al(III) in aqueous mixtures, it was observed that only DMF and DMSO were able to replace water molecules in the cation solvation shell, acetone, dioxane, tetrahydrofuran (THF), and tetramethylurea (TMU) being totally inactive in this regard.[27] Since these results appeared to reflect a correlation of solvating ability with the ligand basicity, the present study was undertaken to substantiate this postulate. Toward this end, the solvents dimethyl sulfoxide (DMSO), dimethyl sulfone (DMSO$_2$), dimethyl sulfate (DMSO$_4$), tetramethylene sulfoxide (TMSO), and tetramethylene sulfone (TMSO$_2$) were chosen, since they are all highly polar but differ widely in basicity. We also hoped to discover under what conditions even slightly basic solvents, such as acetone and THF, could solvate an ion in aqueous solution. These systems were studied at very low concentrations of water.

Experimental Methods

All spectra and peak area integrations were recorded on a Varian A-60 nmr spectrometer equipped with a variable-temperature system permitting operation from -100 to $+200°$. This pmr coordination number method has been described in previous reports.[25-30] Salts and solvents were all reagent grade and they were used as received. Solutions were prepared by the addition of the nonaqueous solvent component to a stock solution of Al(ClO$_4$)$_3$, the concentration of which was determined by passage through a Dowex 50W-X8 cation-exchange column and titration of the resulting solution. The solutions of low water content, that is, those in which the water to Al(III) mole ratio was less than 6, were prepared by mixing acetone or THF solutions of AlCl$_3$ and AgClO$_4$·xH$_2$O and evaluating the water content by integration of the signal areas.

Results

The coordination number results for a series of aqueous solvent mixtures are summarized in Table I. Listed in the first two columns are the mole ratios of water to the nonaqueous component of study and the

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TABLE I

Al(III) COORDINATION NUMBERS IN AQUEOUS ACETONE MIXTURES OF DIMETHYL SULFOXIDE (DMSO), DIMETHYL SULFONE (DMSO$_2$), DIMETHYL SULFATE (DMSO$_4$), TETRAMETHYLENE SULFOXIDE (TMSO), AND TETRAMETHYLENE SULFONE (TMSO$_2$)

Solvent mole ratios		Temp, °C	[Al(ClO$_4$)$_3$], M	Al(III) coordn no.	
H$_2$O: DMSO	H$_2$O:acetone			H$_2$O	Solvent
14:1	1:1	-50	0.22	5.2	0.9
7:1	1:1	-50	0.21	4.1	1.7
2:1	1:1	-50	0.20	3.2	2.7
1:1	1:1	-50	0.16	3.1	3.1
H$_2$O: DMSO$_2$					
10:1	No acetone	-35	1.0	6.1	
10:1	No acetone	-52	1.5	6.2	
H$_2$O: DMSO$_4$					
1.5:1	2:1	-40	0.21	5.8	
1:1	1:3	-44	0.12	5.6	
H$_2$O: TMSO					
8:1	1:1	-50	0.21	3.9	(2.1)
3:1	1:2	-50	0.26	2.7	(3.3)
1.5:1	1:2	-50	0.17	3.1	(2.9)
H$_2$O: TMSO$_2$					
1:1	1:3	-46	0.12	6.2	
1:2	1:6	-42	0.11	5.9	
1:3	1:6	-40	0.11	5.8	

ratios of water to acetone, respectively. The temperatures at which the measurements were made are listed next, followed by the Al(ClO$_4$)$_3$ concentration. In columns 5 and 6, respectively, the contributions of water and the nonaqueous component to the Al(III) solvation shell are given. The use of acetone as a diluent is allowed by the conclusive demonstration of the inert nature of this solvent in previous works.[27-30,32] Dilution with acetone was necessary to decrease the solution viscosity and, consequently, signal broadening, thereby resulting in more accurate coordination number measurements. Solubility problems prevented the addition of acetone to the DMSO$_2$ system and limited measurements to only one solvent concentration of high water content.

The pmr spectra of solutions of Al(ClO$_4$)$_3$ in aqueous DMSO and TMSO mixtures clearly reveal separate resonance signals for bulk and complexed molecules of water and the nonaqueous component. As shown previously,[26,27] the contributions of water and DMSO to the Al(III) solvation shell could be determined independently by integrating the peak areas in the spectrum. However, this was not possible in the water–TMSO system owing to the more complex spectral patterns of this solvent and overlapping peaks. Only the water signals could be integrated, thereby providing the coordination number entries for this system in Table I. The TMSO contributions were obtained by assuming a total coordination number of 6 and subtracting the water result. The spectra of the remaining systems revealed separate water resonance peaks but only one set of signals for DMSO$_2$, DMSO$_4$, and TMSO$_2$. The

coordination numbers of Table I are the results of three separate measurements made with a precision of about 5%. The coordination number measurements of Al(III) in aqueous mixtures of acetone and tetrahydrofuran (THF) will be discussed with reference to the spectra obtained with these solutions, shown in Figures 1–3, respectively.
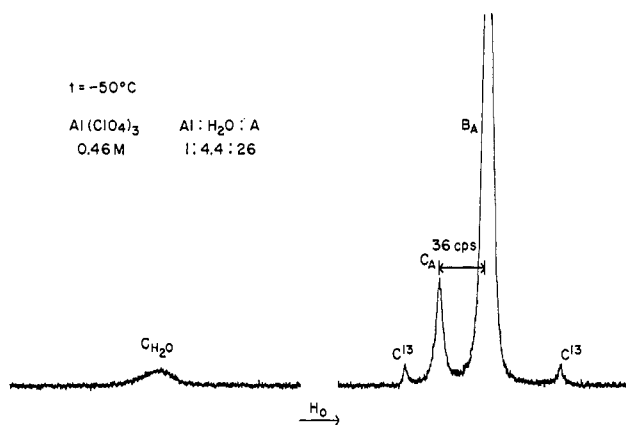

Figure 1.—The proton magnetic resonance spectrum of a 0.46 M Al(ClO₄)₃ solution in a 1:6 mole ratio mixture of water–acetone. The signals arising from complexed water (C$_{H_2O}$) and bulk (B$_A$) and complexed (C$_A$) acetone are labeled in the diagram.
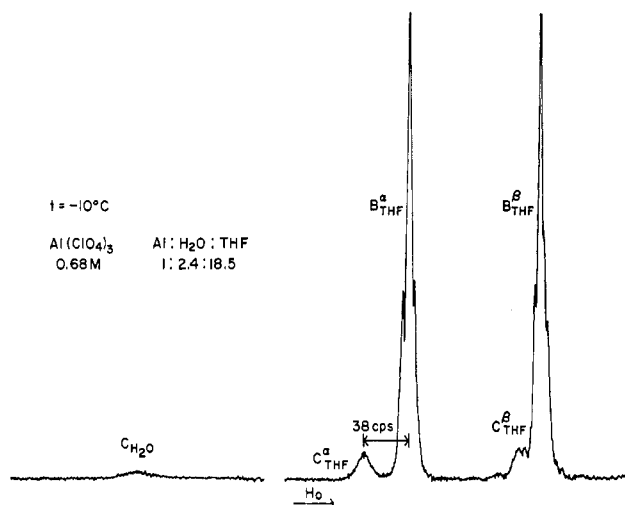

Figure 2.—The proton magnetic resonance spectrum of a 0.68 M Al(ClO₄)₃ solution in a 1:8 mole ratio mixture of water–THF. The signals arising from complexed water (C$_{H_2O}$) and bulk (B$_\alpha$ and B$_\beta$) and complexed (C$_\alpha$ and C$_\beta$) THF are labeled in the diagram.

Figure 3.—The proton magnetic resonance spectrum of a 0.4 M Al(ClO₄)₃ solution in a roughly 1:1:1 mole ratio mixture of water–acetone–THF. The signals arising from complexed water (C$_{H_2O}$), THF (α_{THF} and β_{THF}), bulk (B$_A$), and complexed (C$_A$) acetone are labeled in the diagram.

Discussion

In a previous coordination number study[27] it was conclusively demonstrated that, of the solvents N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetone, dioxane, tetrahydrofuran (THF), and tetramethylurea (TMU), only the first two could compete with water for sites at the Al(III) solvation shell in aqueous solutions of this ion. On the basis of the physical properties of these compounds it was felt that a correlation of solvating ability with basicity was evident. For example, DMF and DMSO are
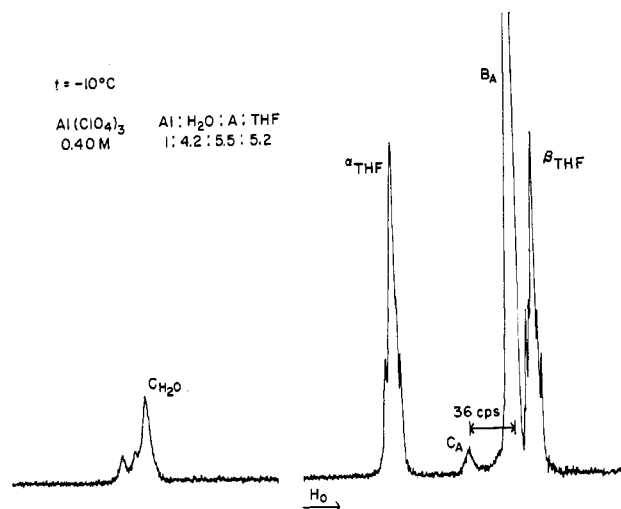
the two most basic solvents of the six, by many orders of magnitude.[33] Furthermore, the solvating ability does not seem to depend on the dipole moment of the molecules. Acetone (μ = 2.7 D), TMU (μ = 3.3 D), DMF (μ = 3.9 D), and DMSO (μ = 3.9 D) are all highly polar, yet only the latter two can solvate a cation in aqueous solution.

All of the compounds chosen for study here are highly polar and in two cases (DMSO, DMSO₂; TMSO, TMSO₂) similar in structure. This latter feature should minimize any steric effects. There is much evidence to support the contention that of the five sulfur-containing compounds, the sulfoxides are much more basic than the sulfate and the two sulfones.[33–36] The basicity of DMSO has been determined by potentiometric[35] and pmr[36] methods, and although the pK_a values determined by the two methods differ by three or four orders of magnitude, there is no doubt that it is a much more basic compound than its sulfone analog. This substantiates the work of Arnett and Douty,[34] who demonstrated the weak, basic nature of TMSO₂.

In view of these facts, the coordination number results of Table I again indicate that solvent basicity is the dominant factor influencing solvating ability in aqueous solution. The pmr spectra and the results in Table I indicate that only DMSO and TMSO can compete effectively with water for Al(III). The less basic DMSO₂, DMSO₄, and TMSO₂ are not at all effective in this regard. Since the relative basicities of these molecules have been determined in aqueous acid solutions,[33–36] Arnett indicated in his thorough review of basicity results[33] that care must be taken

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when these data are applied to Lewis acids other than the proton. In the systems under investigation here, the Lewis acid is actually $Al(H_2O)_6^{3+}$, the structure and size of which could introduce a steric factor. However, the similar structures of some of these compounds reduce the steric role of the base. Also, studies of BF_3 complexes show the same trend in complexing ability, that is, sulfoxide > sulfone.[37-39] Presumably, a similar type of steric effect would be operative in the $Al(H_2O)_6^{3+}$ and BF_3 systems. It would appear that the differences in solvating ability arise from the more fundamental property of basicity.

Another interesting feature of the results of Table I is the increase with concentration of the DMSO contribution to the Al(III) solvation shell. In fact it it has been shown that in pure solvent, Al(III) is solvated by six DMSO molecules.[11] This is in contrast to the TMSO–water system, wherein Al(III) is solvated by a maximum of about three TMSO molecules (and three water molecules), even at the higher concentrations of the nonaqueous component. The solvating ability of TMSO is emphasized by its contribution of two molecules to the Al(III) solvation shell, when water is in excess by an 8:1 mole ratio. Thus, the number of TMSO molecules which can solvate Al(III) may be restricted by a steric effect. This result is similar to that reported for the ethanol–water system wherein Cr(III) was solvated by three ethanol molecules even at high alcohol concentrations.[5] The steric effect proposed to explain the Cr(III) result may be operative in the TMSO–water mixture. In fact, models show that steric hindrance would be severe in these two systems and would appear to limit the number of molecules of the nonaqueous component in the cation solvation shell to a maximum of four. However, six molecules of DMSO can be accommodated around an Al(III) ion, as verified experimentally.[11]

As demonstrated previously[27-30] and as reaffirmed by the data in Table I, weakly basic solvents such as $DMSO_2$, $DMSO_4$, $TMSO_2$, acetone, and tetrahydrofuran (THF) cannot solvate a cation in the presence of water as long as there are enough water molecules to saturate the first solvation shell of Al(III). It was felt that it would be of interest to demonstrate that at suitable concentrations these solvents could solvate Al(III), in spite of their very low basic strengths. In Figure 1, the pmr spectrum of a solution of $Al(ClO_4)_3$ in an acetone–water mixture is shown. The mole ratio of water to Al(III) is only about 4:1 in this system, and since only one low-field signal is observed for water, it was assumed that all molecules of this component are in the Al(III) solvation shell. At higher field, signals arising from bulk and complexed acetone molecules are observed. Integration of the acetone signals provided a contribution of 1.9 for this component to the Al(III)

coordination number. Thus, the principal cationic species in solution can be represented by $Al(H_2O)_4$-(acetone)$_2^{3+}$. This obviously demonstrates that acetone can solvate Al(III), but more importantly it illustrates that this solvent is completely unable to replace water in the Al(III) coordination shell at least at the concentration studied here. Rather, it merely fills sites at the ion which are left vacant as a result of low water concentration. At extremely low water and salt concentrations, however, acetone would probably be able to displace water from the ion solvation shell.

Similar results were obtained with $Al(ClO_4)_3$ in aqueous THF solutions of low water content, as seen in Figure 2. Two sets of THF resonance signals indicate that in the absence of six water molecules per Al-(III), this solvent component can complex the cation. Moreover, peak integrations reveal that the water and THF contributions to the Al(III) solvation shell are 2.4 and 2.1, respectively, this low total reflecting most likely contact ion pairing in this mixture. In view of the low dielectric constant of this mixture, roughly 10, such an occurrence is reasonable. The observation of the multiple water resonance peaks expected if ion pairing is taking place was precluded by the broadness of the signal in Figure 2. The situation was notably improved by the addition of acetone to this solution, as shown in Figure 3. Several resonance signals, arising from differently hydrated Al(III) ions, are visible in the complexed water region. The solution represented in Figure 3 is obviously too complex for a thorough analysis. However, it is noticeable that bulk and complexed resonance signals are observed for acetone but not for THF, even though the latter is much more basic than acetone as indicated by protonation studies[38] and by a study of boron trihalide complexes.[39] It would appear that THF is prevented from solvating $Al(H_2O)_4^{3+}$ by steric hindrance, whereas acetone is not.

In general, the data of Table I and Figures 1–3, providing information concerning the composition of the ionic species in solution, demonstrate the utility of this pmr method. Applications to organic reaction media, kinetic studies, and electrochemical investigations are possible. For example, by analogy to the Al(III) results, one can attempt to disprove or substantiate claims of competitive or selective solvation made on the basis of conductance measurements in aqueous solvent mixtures. The results indicating ion-pairing and steric effects are still preliminary in nature but these measurements are being extended to other systems in a more detailed manner.

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