furic acid, the effect of sulfur trioxide on some of these acid systems was also investigated. Sulfur trioxide was found to have no effect on the conductivities of solutions of NbF_5 and PF_5 both of which have negligible acidic properties, but it was found to have a considerable effect on the conductivities of AsF_5 solutions. For example, at a concentration of 0.11 *m*, addition of sulfur trioxide to give the mole ratio $SO_3/AsF_5 = 1$ increased the conductivity by more than three times and further addition of sulfur trioxide to give the mole ratio $SO_3/AsF_5 = 3$ increased the conductivity by more than seven times (Figure 2). The conductivity was not much affected by larger amounts of sulfur trioxide, and we presume that, as for SbF_5, arsenic pentafluoride combines with a maximum of 3 mol of sulfur trioxide to give $AsF_2(SO_3F)_3$. Thus $AsF_5 \cdot SO_3$ which we presume to be $AsF_4 \cdot SO_3F$ is a somewhat weaker acid than SbF_5 but $AsF_5 \cdot 3SO_3$ which we presume to be $AsF_2(SO_3F)_3$ is a rather stronger acid than SbF_5 although not as strong as the acid $H[SbF_2(SO_3F)_4]$. The rather high acidity of $AsF_4(SO_3F)$ was confirmed by a conductometric titration with KSO_3F which gave a minimum conductivity at $KSO_3F/AsF_4(SO_3F) = 0.31$ compared with the minimum of $KSO_3F/SbF_5 = 0.41$ observed in the titration of SbF_5 (Figure 2). Solutions of SO_3 in $HSO_3F–BiF_5$ are unstable and deposit a white precipitate on standing.

We conclude therefore that the order of increasing acid strength of the fluorides in fluorosulfuric acid is: $PF_5 \sim NbF_5 < TiF_4 \sim AsF_5 < BiF_5 < AsF_4(SO_3F) < SbF_5 < AsF_2(SO_3F)_3 < SbF_2(SO_3F)_3$. It is interesting to note that, in the series of pentafluorides PF_5, AsF_5, SbF_5, and BiF_5, antimony pentafluoride is the strongest acceptor for fluorosulfate and presumably the strongest Lewis acid in general. Replacement of fluorine by the fluorosulfate group appears generally to cause an increase in the acceptor strength, but unfortunately the maximum acidity that is, in principle, possible cannot be obtained as the pentafluorosulfates do not appear to be stable. At the present time therefore it appears that $SbF_2(SO_3F)_3$ is the strongest known acceptor for fluorosulfate ion and that $HSO_3F–SbF_5–nSO_3$, where $n \geqslant 3$, is the strongest proton-donating medium, *i.e.*, the strongest acid in the Brønsted sense. The increase in acidity on replacing fluoride by fluorosulfate may be reasonably attributed to the greater dispersal of negative charge that is made possible by the introduction of fluorosulfate groups.

It should be emphasized that the above conclusions concerning the acidity of the $HSO_3F–SbF_5–nSO_3$ and $HSO_3F–AsF_5–nSO_3$ systems refer only to rather dilute solutions of SbF_5. The effect of sulfur trioxide on the acidity of the very concentrated solutions of SbF_5 in HSO_3F that have been referred to as "magic acid" by Olah, *et al.*,[3] has not yet been determined. In such concentrated solutions conductometric measurements cannot be interpreted with any certainty and other methods must be used to determine relative acidities, *e.g.*, the measurement of the Hammett acidity function. Such an investigation is in progress in our laboratories. There seems to be no reason to think that the system $HSO_3F–SbF_5$ has any unique acid properties that would justify the use of the term "magic acid." It would seem more satisfactory to use the term superacid[2] to describe all those systems that have higher acidities than anhydrous sulfuric or fluorosulfuric acid.

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Line Broadening of the Proton Magnetic Resonance of Nonaqueous Solvents by Vanadyl Ion

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The solvent proton line broadening caused by solvated vanadyl ion has been measured in the solvents acetonitrile, dimethyl sulfoxide, trimethyl phosphate, and trimethyl phosphite. Chemical exchange control of the line broadening was observed only in acetonitrile, from which $k_{ex} = 2.85 \times 10^3$ sec^{-1} (25°, assuming four exchanging solvent molecules in the coordination sphere of the vanadyl ion), $\Delta H^{\ddagger} = 7.05$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -20$ cal mol^{-1} deg^{-1}. Comparison of the calculated and observed dipolar broadening indicates that only a lower limit can be placed on the exchange rates of dimethyl sulfoxide and trimethyl phosphate while an upper limit is obtained for the trimethyl phosphite system.

Introduction

The nmr line-broadening technique has been applied to a number of systems to determine ligand exchange rates on metal ion complexes. This report describes the application of this technique to the solvated vanadyl ion in several nonaqueous solvents. The results are considered in relation to previous work on the water,[1,2] methanol,[3] and N,N-dimethylformamide[4] exchange rates on vanadyl ion and the rates for several nonaqueous solvents on cobalt(II) and nickel(II).[5–7]

In the vanadyl–acetonitrile system the solvent ex-

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change rate is determined from the nmr line broadening. However in the other solvents studied here—dimethyl sulfoxide, trimethyl phosphate and trimethyl phosphite—chemical exchange never becomes a significant relaxation mechanism. In order to decide whether exchange is faster or slower than the observed relaxation, it is necessary to determine if relaxation is occurring in the inner or outer coordination spheres of the vanadyl ion. The criteria for distinguishing between these two alternatives are discussed.

Experimental Section

Hydrated vanadyl tetrafluoroborate was prepared by double decomposition of barium tetrafluoroborate and vanadyl sulfate (Fisher reagent). Barium sulfate was filtered from the aqueous solution and the water was removed under vacuum at 25° to yield blue crystals of hydrated vanadyl tetrafluoroborate.

Acetonitrile (Baker Analyzed reagent), trimethyl phosphate (Aldrich), trimethyl phosphite (Matheson Coleman and Bell), and dimethyl sulfoxide (Fisher reagent) were purified and dried by double vacuum distillation from Linde Molecular Sieves, only the middle fraction being retained in each case. The solvents were stored under vacuum.

The vanadyl complexes with these solvents were prepared by adding 5 g each of hydrated vanadyl tetrafluoroborate and Linde Molecular Sieves to approximately 100 ml of freshly distilled solvent. *Note: the reaction with trimethyl phosphite is very exothermic and reagents must be mixed slowly or the solvent may ignite and explode.* The mixture was stored under vacuum for 5–6 hr and then the Molecular Sieves were removed by filtration and the solvent was removed by vacuum distillation. The oil which remained was redissolved in a minimum amount of solvent and filtered. The solution was then cooled to −10° in an attempt to obtain a crystalline product. All operations were carried out under vacuum.

Crystals were obtained for the acetonitrile and dimethyl sulfoxide complexes. *Anal.* Calcd for $VO(CH_3CN)_5(BF_4)_2$: C, 26.9; H, 3.39; N, 15.7. Found: C, 25.9; H, 3.28; N, 15.7. Calcd for $VO((CH_3)_2SO)_5(BF_4)_2$: C, 19.1; H, 4.81. Found: C, 19.4; H, 4.99.

The trimethyl phosphite and trimethyl phosphate complexes could not be obtained in crystalline form. The former solvent was removed by prolonged vacuum distillation leaving a viscous oil which was analyzed directly. *Anal.* Calcd for $VO(P(OCH_3)_3)_8(BF_4)_2$: C, 23.4; H, 5.88. Found: C, 23.7; H, 5.85. Vanadyl concentrations were subsequently determined on the basis of the 8:1 mole ratio of trimethyl phosphite to VO^{2+} indicated by the analysis.

The concentrations in the vanadyl–trimethyl phosphate system were determined spectrophotometrically using the extinction coefficients given in ref 8.

The complexes were all stored under vacuum and all transfers were made in a dry nitrogen atmosphere or under vacuum. Nmr and visible spectrum samples were prepared, transferred to 5-mm o.d. and 1-cm i.d. tubes, respectively, and sealed off, under vacuum.

The absorption spectra of the complexes were recorded on a Cary Model 14 spectrophotometer. Varian Associates HA-60 and HA-100 nmr spectrometers equipped with Model 4343 temperature controllers and the standard variable-temperature probes were used for the nmr spectra. Spectra were run in the HA mode using a Hewlett-Packard Model 200 AB audio oscillator for the lock-on signal. Line widths were reproducible to ±2 Hz on both nmr spectrometers and were a linear function of vanadyl ion concentration in all systems studied.

Results

The absorption spectra of the vanadyl complexes prepared here show the typical long-wavelength absorption and the accompanying shoulder; however, only the trimethyl phosphite and trimethyl phosphate complexes show the short-wavelength absorption. The spectra for the dimethyl sulfoxide, trimethyl phosphate, and acetonitrile complexes agree with those previously reported by Gutmann and Laussegger.[8] (See Table I.)

TABLE I

SPECTRAL PROPERTIES OF VANADYL ION IN VARIOUS SOLVENTS

Compound	Solvent[d]	Spectral band max, cm^{-1}			Dq, cm^{-1}
$VO(BF_4)_2$	DMSO	12,100	14,300	...	1430
$VO(BF_4)_2$	TMPA	12,200	13,900	26,300	1390
$VO(BF_4)_2$	TMPI	12,500	14,500	24,100	1450
$VO(BF_4)_2$	CH_3CN	12,750	14,800	...	1480
$VO(ClO_4)_2$	DMF[a]	12,680	15,400	...	1540
$VO(ClO_4)_2$	CH_3OH[b]	13,300	15,500	27,400	1550
$VO(SO_4)_2$	H_2O[c]	13,000	16,000	...	1600

[a] See ref 4. [b] See ref 3. [c] See ref 9. [d] The solvent name abbreviations are: DMSO, dimethyl sulfoxide; TMPA, trimethyl phosphate; TMPI, trimethyl phosphite; DMF, dimethylformamide.

The values of Dq are calculated from the crystal field theory spectral assignments made by Ballhausen and Gray.[9] The molecular orbital theory developed by these authors could be used to interpret the spectra but Dq values seem to provide a simple parameter for comparison to other systems. The order of Dq values for water, methanol, dimethylformamide, and dimethyl sulfoxide is typical of that found in nickel(II) complexes.[10] From previous work, the Dq values of acetonitrile[10] and trimethyl phosphite[11] are expected to be higher than that of water whereas they are definitely lower than that of water in the vanadyl system. However the former results are based on nickel(II) and cobalt(III) complexes, respectively, and the Dq values may be high owing to metal to ligand π bonding, which apparently is not so important in the vanadyl complexes. The high Dq value for the acetonitrile complexes of cobalt(II) and nickel(II) has been noted previously and explained in a similar manner by Matwiyoff and Hooker.[6]

The molal nmr relaxation time T'_{2p} was determined from the nmr line broadening using the expression

$$(T'_{2p})^{-1} = \frac{\pi(\Delta\nu_{obsd} - \Delta\nu_{sol})}{m} \quad (1)$$

where $\Delta\nu_{obsd}$ is the full line width at half-height of the bulk solvent resonance in an m molal VO^{2+} solution, and $\Delta\nu_{sol}$ is the line width in the pure solvent. Plots of log $(T'_{2p})^{-1}$ *vs.* the reciprocal of the absolute temperature are shown for acetonitrile in Figure 1 and for dimethyl sulfoxide, trimethyl phosphate, and trimethyl phosphite in Figure 2.

The temperature dependence of the line broadening

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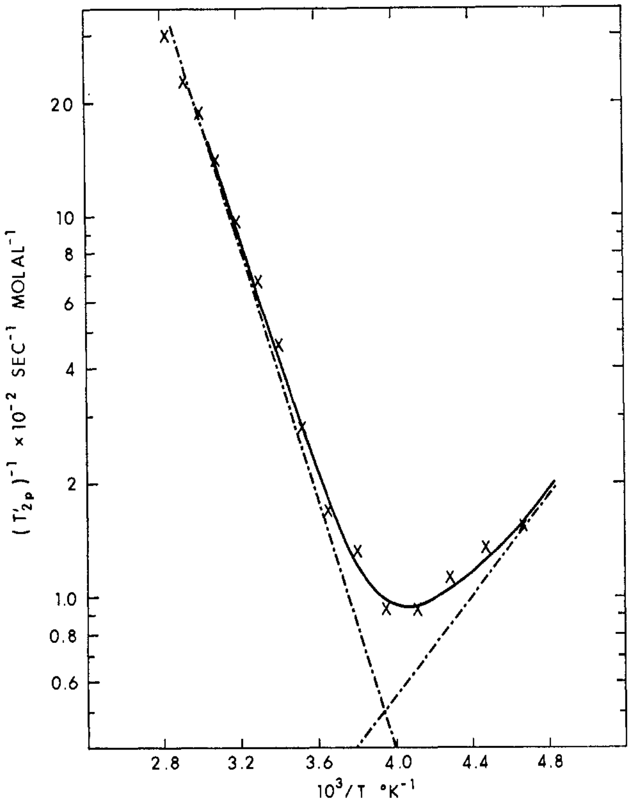

Figure 1.—Temperature dependence of $(T'_{2p})^{-1}$ for methyl protons in acetonitrile solutions of $VO(CH_3CN)_5(BF_4)_2$.

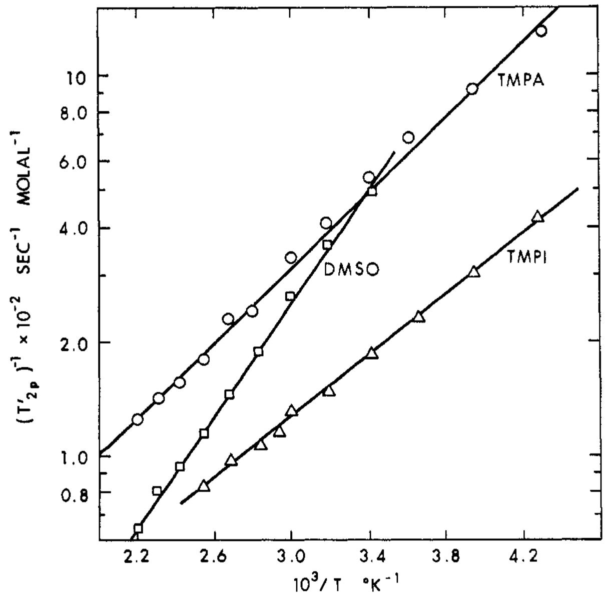

Figure 2.—Temperature dependence of $(T'_{2p})^{-1}$ for the solvated vanadyl ion in the respective solvents—trimethyl phosphate (TMPA), dimethyl sulfoxide (DMSO), and trimethyl phosphite (TMPI).

in the acetonitrile system is typical of that observed in a number of systems previously. In the temperature range above about −20° the solvent proton relaxation is controlled by the rate of solvent exchange into the first coordination sphere of the vanadyl ion. Under these conditions

$$(T'_{2p})^{-1} = P_m(\tau_m)^{-1} = (n/S)(\tau_m)^{-1} \qquad (2)$$

where n is the number of exchanging solvent molecules, S is the molal solvent concentration, and τ_m is the lifetime of a solvent molecule in the first coordination sphere of the metal ion. The theory has been presented by Swift and Connick[12] and discussed in several recent references.[1,2,5,6]

In the region below −20° in Figure 1, inner-sphere exchange is slow and the relaxation is controlled by the dipolar interaction of the unpaired electron with solvent molecules in the outer coordination spheres of the vanadyl complex. Luz and Meiboom[7] have obtained an expression for estimating this contribution to the line broadening (eq 4) by integrating the dipole relaxation[13,14] (eq 3) from the outer-sphere interaction distance (d_o) to infinity. Inner-sphere dipolar broadening is given by[15]

$$(T'_{2p})^{-1}_{\text{inner}} = \frac{7}{15}\left(\frac{\gamma_I^2\beta^2g^2S(S+1)}{r_i^6}\right)P_m\tau_c = \frac{11.5 \times 10^{16}}{r_i^6}S(S+1)P_m\tau_c \qquad (3)$$

Outer-sphere dipolar broadening is given by[15]

$$(T'_{2p})^{-1}_{\text{outer}} = \frac{7}{15}\gamma_I^2\beta^2g^2S(S+1)n\tau_c\int_{d_o}^{\infty}\frac{4\pi r^2}{r^6}dr = \frac{2.90 \times 10^{14}}{d_o^3}\rho S(S+1)\tau_c \qquad (4)$$

where n is the number of paramagnetic ions per cubic centimeter and ρ is the density of the solvent. All concentrations are in molal units and interaction distances are in ångströms. The other symbols have their usual meaning.

In the acetonitrile system there is no doubt that the low-temperature region is due to outer-sphere relaxation, since the nmr line broadening shows that inner-sphere exchange is slow at low temperature. However, for all of the other solvents investigated, no chemical-exchange-controlled line broadening is observed and it is not known whether exchange is fast and T_{2p} is controlled by the inner-sphere dipole–dipole relaxation or if exchange is slow and the observed broadening is due to outer-sphere dipole–dipole relaxation. In principle, using eq 3 and 4, the inner- and outer-sphere broadening can be calculated and the results are compared to the observed values to decide whether one is observing inner- or outer-sphere relaxation. The obvious difficulty with this approach is that the correlation time (τ_c) is not known and the interaction distances can only be estimated to about ±0.2 Å or worse for the outer-sphere case.

It has been found previously for the VO^{2+}, dimethylformamide, and methanol systems[3,4] that the correlation time (τ_c) can be calculated from the epr line widths of the vanadium hyperfine lines of the solvated vanadyl

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ion. This procedure makes use of the theory developed by Kivelson, *et al.*,[16,17] to calculate the epr line widths and to explain the variations in width with the nuclear spin quantum number of vanadium. In the VO^{2+}–dimethylformamide system the correlation time derived from the epr theory gave reasonable inner- and outer-sphere interaction distances. Similar results have been found for outer-sphere relaxation in the VO^{2+}–methanol system.[3]

In the other three solvents studied, in which exchange rates could not be measured, the correlation times have been determined from the epr line widths of the solvated vanadyl ion. These correlation times were then used in eq 3 and 4 to calculate interaction distances. The results are shown in Table II. It should be noted that in the calculation of d_o the observed $(T'_{2p})^{-1}$ values have been corrected for the dipolar broadening resulting from one rapidly exchanging solvent molecule undergoing inner-sphere dipolar broadening. This is presumed to be the solvent molecule *trans* to the vanadyl oxygen. This correction was made using the estimated r_i given in Table III and eq 3. Such a correction was found necessary in the methanol system[3] to explain the relative dipolar broadenings of the methyl and hydroxy protons at low temperatures. This factor also gives a more reasonable outer-sphere distance of 9.4 Å in the acetonitrile system, compared to a value of 7.9 Å from the uncorrected $(T'_{2p})^{-1}$.

Table II

Interaction Distances for Inner- (r_i) and Outer- (d_o) Sphere Dipole–Dipole Broadening

Solvent[c]	$(T'_{2p})^{-1}$, sec^{-1}	r_i, Å (estd[a])	$(T'_{2p})^{-1}_{cor}$,[b] sec^{-1}	$10^{10}\tau_c$, sec	r_i, Å	d_o, Å
CH_3CN	21	5.3	12.5	0.62	6.10	9.4
TMPI	176	4.8	77	1.10	5.70	7.0
TMPA	460	4.9	343	1.32	5.13	4.8
DMSO	455	4.5	357	1.17	4.45	4.3

[a] The r_i values for CH_3CN, TMPI, TMPA, and DMSO are estimated from structures in ref 18–21, respectively. [b] Corrected assuming one rapidly exchanging inner-sphere solvent molecule. $(T_{2p}')^{-1}_{cor}$ is used to calculate d_o. [c] Solvent abbreviations are listed in footnote *d* of Table I.

The estimated interaction distances are based as much as possible on known structures.[18–21] However, because of free rotation about the ligand–metal bond and bonds in the ligand itself, there is actually a range of interaction distances. Those given in Table II are the average of the estimated limits and come rather surprisingly close to the inner-sphere distances calculated from the nmr line broadening.

It is apparent from the results in Table II that in trimethyl phosphate and dimethyl sulfoxide the inner-sphere interaction distance is reasonably close to the estimated interaction distance. In addition, the calculated outer-sphere distances in these solvents are much too short to be reasonable. It seems unlikely, in view of the results in acetonitrile, methanol, and dimethylformamide, that the epr method yields too short a correlation time in dimethyl sulfoxide and trimethyl phosphate. Therefore, it is concluded that solvent exchange is fast in the latter two solvents, and only a lower limit can be established for the exchange rate from the nmr line broadening.

Table III

Kinetic Parameters for Solvent Exchange on the Solvated Vanadyl Ion

Solvent[c]	$10^{-3}k_{ex}$,[a] sec^{-1} (25°)	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$,[a] cal mol^{-1} deg^{-1}
DMSO	>1.52	...	
TMPI	<0.35	...	
TMPA	>0.84	...	
CH_3CN	2.85	7.05	−20
DMF[b]	0.575	7.25	−16
CH_3OH[b]	0.33	12.0	−1.3
H_2O[b]	0.50	13.7	−0.6

[a] Calculated assuming a coordination number of 4. [b] Data for DMF, CH_3OH, and H_2O are taken from ref 4, 3, and 2, respectively. [c] Solvent abbreviations are listed in footnote *d* of Table I.

However the broadening in trimethyl phosphite seems most consistent with outer-sphere relaxation. The calculated outer-sphere interaction distance is reasonable and the inner-sphere distance is 0.9 Å longer than the estimated value whereas in trimethyl phosphate and dimethyl sulfoxide this difference is 0.2 Å or less. This conclusion is indicated also by comparison of the broadening in trimethyl phosphite and trimethyl phosphate since the solvent molalities, densities, and estimated interaction distances are similar, yet the broadening is 2.6 times less in trimethyl phosphite. Therefore, only an upper limit can be placed on the exchange rate of trimethyl phosphite.

The apparent activation energies (kcal mol^{-1}) for the dipole–dipole broadening are: dimethyl sulfoxide, 3.44; trimethyl phosphate, 2.25; trimethyl phosphite, 1.87; acetonitrile, 3.00. These activation energies are parallel to those predicted from the temperature dependence of the viscosity where such data are available.

The ligand exchange rates and activation parameters, from this and previous work on the vanadyl ion, are summarized in Table III. It should be noted that all the exchange rate constants at 25° are within a factor of 6 of each other; however, the activation enthalpy for dimethylformamide and acetonitrile exchange is much lower than that for water and methanol. These differences seem to be most easily rationalized in terms of an SN1-type dissociative mechanism in which ligand basicity[22] and steric effects are the main kinetic factors. The differences in activation parameters, especially $\Delta S^{\ddagger}$, might suggest that acetonitrile and dimethylformamide exchange proceeds by an SN2-type mechanism, but this would not be expected in view of the low basicity of acetonitrile and the steric effects in dimethylformamide. The $\Delta S^{\ddagger}$ differences may be re-

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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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