

Chemistry in nitric acid solutions

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Abstract - High field multinuclear n.m.r. spectroscopy can be applied with advantage to the study of inorganic solutes in 100% nitric acid and mixtures with dinitrogen tetraoxide or pentaoxide. The behaviour of phosphorus halo- and oxo-compounds in high density acid, HDA (44 wt.% dinitrogen tetraoxide in pure nitric acid) reveals the hydrolytic character of this type of medium and in 100% nitric acid, indicates the latter to be more highly protonating than its Hammett acidity function would suggest. In the present lecture, attention is focussed on solutions of vanadium and aluminium compounds, especially in relation to ^{51}V and ^{27}Al n.m.r. studies, and the results emphasise that metal chemistry occurring in nitric acid solutions can be much richer than might be inferred solely from a knowledge of isolable solid products.

INTRODUCTION

Pure (100%) nitric acid is in some respects a unique solvent system (ref. 1,2). The extensive and unusual self-dissociation (1)



(concentration of each dissociation product $\sim 0.25 \text{ mol kg}^{-1}$) accounts for its exceptionally high electrical conductivity ($\kappa = 3.72 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C) and also for the presence of unprotonated but solvated water molecules which have a profound effect on chemistry in nitric acid solutions.

Physical properties of 100% nitric acid and its solutions with dinitrogen tetraoxide (red fuming nitric acids, which are important oxidiser components of liquid rocket propellants) and dinitrogen pentaoxide (nitric oleums) have been extensively studied (ref. 1,2) but little information was available hitherto on chemistry in these liquids.

Our long-standing interest in these solvent media has been further stimulated by involvement with technological problems arising from the corrosion of metals by red fuming nitric acids when used as liquid rocket propellant oxidisers. In rocket engines, these liquids are in contact with stainless steels or aluminium alloys and contain a small amount (ca. 0.7 wt.%) of hydrogen fluoride, added to inhibit metal corrosion. Many other compounds have been tested as inhibitors, one of the most successful alternatives to hydrogen fluoride being phosphorus pentafluoride, and this has led to an interest in both metallic and non-metallic solutes in nitric acid and its dinitrogen tetraoxide and pentaoxide solutions.

We are using high field multinuclear n.m.r. spectroscopy to characterise (sometimes novel) chemical species generated and stabilised in these solvent media and these species, in turn, help to elucidate the nature of the media themselves; both solvent and solute magnetic nuclei may be exploitable.

NON-METAL COMPOUNDS AS SOLUTES

The behaviour of phosphorus pentafluoride, difluorophosphoric acid and phosphoric oxide in a mixture of dinitrogen tetraoxide (44 wt.%) and nitric acid ('high density acid', HDA), studied by ^{19}F and ^{31}P n.m.r. spectroscopy, reveals the hydrolytic nature of this medium (ref. 3). The hydrolysis of all three solutes is, however, time-dependent and incomplete (except at low concentrations), equilibrium mixtures of fluorophosphate species (from phosphorus pentafluoride or difluorophosphoric acid) or phosphoric acids (from phosphoric oxide) being ultimately obtained. Preliminary results indicate that the reaction of phosphorus pentafluoride with 100% nitric acid is similar to that with HDA. The hydrolysis of phosphoric oxide in 100% nitric acid is more extensive and rapid than in HDA, although similar species are observed in both media. These hydrolytic reactions of phosphorus compounds suggest that solvation of the water molecules in 100% nitric acid or HDA limits their usual chemical reactivity (ref. 2). ^{17}O , ^{19}F and ^{31}P n.m.r. spectroscopy has been used (ref. 4) to investigate the protonating ability of 100% HNO_3 towards POCl_3 , POBr_3 , HPO_2F_2 and PO_3F_2 ; the results show the acid to be more strongly protonating than indicated by its

Hammett acidity-function (ref. 5), $-H_0 = 6.3$. This value is, however, known to be unreliable owing to the difficulties encountered with many indicators at nitric acid concentrations above 65%. The n.m.r. results suggest that the true value is similar to those of H_2SO_4 ($-H_0 = 11.12$, ref. 6) and HSO_3Cl ($-H_0 = 12.78$, ref. 7).

METALS AND METAL COMPOUNDS AS SOLUTES

The work related to rocket propellants revealed that reactions of most metals with 100 nitric acid had not been previously studied. A qualitative survey of the reactions of a number of metals with pure nitric acid was therefore undertaken (ref. 8). The results are summarised in Table 1. Products of reaction of anhydrous metal salts with pure nitric acid (ref. 9) are shown in Table 2 and highlight the availability of molecular water in the acid.

TABLE 1. Reaction of pure HNO_3 with metals

Solution complete within			Evidence of inhibition by film (d)	No evidence of reaction (e)
1 day (a)	1 week (b)	1 month (c)		
Mg	Cr (powder)	Fe	Ca	Be
Sc		Mn	Cu	Al
V	Ni		Ag	Ti
Co	Cd		Bi	Pt
Zn	U			Sn
Hg				

TABLE 2. Products of reaction of anhydrous metal salts with pure HNO_3

Reactant	Product
$CrCl_3$	$Cr(NO_3)_3 \cdot 2H_2O$
$MnCl_2$	$Mn(NO_3)_2 \cdot 2H_2O$
$FeCl_3$	$Fe(NO_3)_3 \cdot 2H_2O$
$CoCl_2$	$Co(NO_3)_2 \cdot 2H_2O$
$NiCl_2$	$Ni(NO_3)_2 \cdot 2H_2O$
$CuCl_2$	$Cu(NO_3)_2 \cdot 2H_2O$
$Cu(NO_3)_2$	$Cu(NO_3)_2 \cdot 1.67H_2O$

As the main focus of the present lecture, attention is now directed to recent work on solutions of vanadium and aluminium compounds in which advantage has been taken of the ^{51}V and ^{27}Al nuclei as n.m.r. probes.

SOLUTIONS OF VANADIUM COMPOUNDS

Solutions of vanadium(V) in 100% nitric acid can be prepared from a variety of starting materials; vanadium metal, MVO_3 ($M = NH_4^+$, Na^+), $VO(NO_3)_3$, $V_2O_5 \cdot nH_2O$ ($n = 0.5, 1.0$) or V_2O_5 . The latter is virtually insoluble in 100% nitric acid, but a pale yellow solution can be produced by adding an ionic nitrate such as NH_4NO_3 . The ^{51}V n.m.r. spectra of such solutions at vanadium concentrations less than ca. 0.5 mol kg^{-1} all display a single resonance ($\delta(^{51}V) = -753 \pm 1$ ppm, referred to $VOCl_3$ as standard), which is assigned to $VO(NO_3)_3$ on the basis of previous n.m.r. studies (ref. 10).

The ^{14}N spectra of these solutions contain, in addition to the solvent resonance ($\delta(^{14}N) = -34 \pm 3$ ppm, referred to NO_3^- as standard) a peak assignable to covalent nitrate ($\delta(^{14}N) = -16.8 \pm 1$). Measurement of the areas under the ^{14}N resonances indicates the presence of three nitrate groups per vanadium in solution, consistent with the production of $VO(NO_3)_3$. In addition, the ^{17}O n.m.r. spectrum of 3.3% ^{17}O enriched $V_2O_5 \cdot H_2O$ in 100% HNO_3 contains a peak ($\delta(^{17}O) = 1401$ ppm, referred to H_2O as standard) assignable to the vanadyl oxygen of $VO(NO_3)_3$.

A further ^{51}V resonance is observed when the 100% HNO_3 solution exceeds 0.5 mol kg^{-1} in vanadium concentration (Fig. 1), and also when H_2O or NO_3^- or N_2O_4 is added to $VO(NO_3)_3$ in 100% HNO_3 (when dissolved in 100% nitric acid, N_2O_4 is almost completely ionised (2)



up to a concentration of 1.6 mol kg^{-1} , ref. 11). High concentration, or added NO_3^- , even in small amounts, also broadens and shifts the bound nitrate ^{14}N resonance towards the solvent resonance until they merge. Concentration or H_2O addition also deepens the orange colour of the solution.

The second ^{51}V peak moves to higher frequency at higher concentration (Fig. 2; the values of 'apparent vanadium concentration' given in this Figure refer to the proportion of the total concentration of vanadium, added as ammonium metavanadate, represented by the second peak, calculated from the peak areas) or when H_2O is added (Fig. 3), unlike that of $VO(NO_3)_3$. This implies that it arises from more than one species. There are several reasons to believe that some of these species are polymeric.

First, when H_2O is added to solutions $\geq 0.4 \text{ mol kg}^{-1}$ in vanadium, solid is precipitated. Second, the observed colour changes are similar to those reported for vanadate-sulphuric acid and vanadate-perchloric acid systems. Begun et al. (ref. 12) have proposed for the latter systems that these colour changes arise from the formation of the dimeric species $V_2O_3^{4+}$, with further polymerisation occurring at high vanadium concentrations. Third, the presence of polymers in the $VO(NO_3)_3$ - HNO_3 - H_2O system, even at low vanadium concentrations, can be demonstrated by the ^{51}V n.m.r. results when H_2O is added in small amounts. A plot of % vanadium present as $VO(NO_3)_3$ against added H_2O for various vanadium concentrations (Fig. 4)

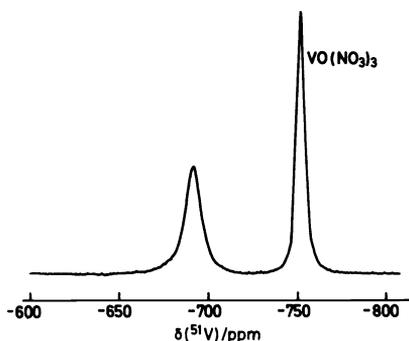


Fig. 1. ^{51}V n.m.r. spectrum of NH_4VO_3 (0.9 mol kg^{-1}) in 100% HNO_3

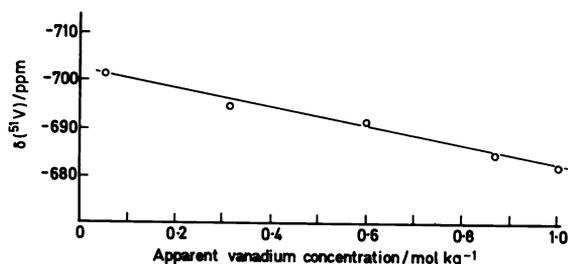


Fig. 2. Variation of $\delta(^{51}\text{V})$ with apparent vanadium concentration (second peak, see text) for NH_4VO_3 in 100% HNO_3 solutions

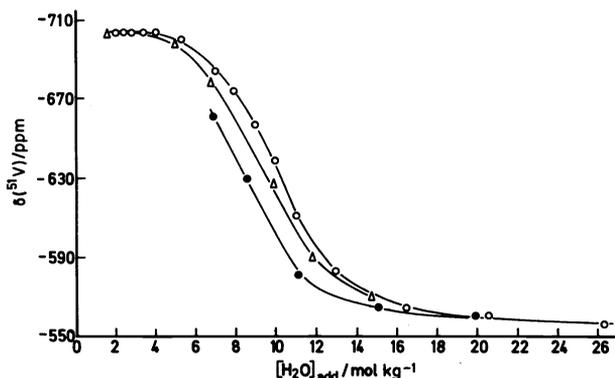


Fig. 3. Variation of $\delta(^{51}\text{V})$ (second peak) for $\text{VO}(\text{NO}_3)_3$ in HNO_3 solutions with concentration of added H_2O ($[\text{H}_2\text{O}]_{\text{add}}$) $[\text{VO}(\text{NO}_3)_3]/\text{mol kg}^{-1}$, \circ 0.070, Δ 0.047, \bullet 0.007

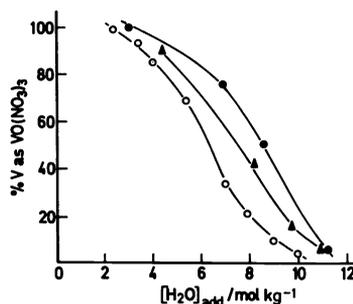


Fig. 4. Variation of % total vanadium as $\text{VO}(\text{NO}_3)_3$ for $\text{VO}(\text{NO}_3)_3$ in HNO_3 solutions with concentration of added H_2O ($[\text{H}_2\text{O}]_{\text{add}}$) $[\text{VO}(\text{NO}_3)_3]/\text{mol kg}^{-1}$, \circ 0.070, Δ 0.026, \bullet 0.007

indicates that the proportion of $\text{VO}(\text{NO}_3)_3$ increases with decreasing vanadium concentration for the same amount of added H_2O to an extent greater than can be explained simply from dimerisation. It is also significant to note that $\text{VO}(\text{NO}_3)_3$ is unexpectedly resistant to hydrolysis in nitric acid solution, being easily detectable at H_2O concentrations of 12 mol kg^{-1} (ca. 78% HNO_3). Here the behaviour in HNO_3 is in marked contrast to that in organic media where $\text{VO}(\text{NO}_3)_3$ reacts quantitatively with H_2O (ref. 10). The generation and stability of $\text{VO}(\text{NO}_3)_3$ in nitric acid solutions, and its persistence even in the presence of water, is quite remarkable when it is recalled that prior to this work, $\text{VO}(\text{NO}_3)_3$ had only been obtained from the reactions of divanadium pentoxide (3) or vanadium oxide trichloride (4) with dinitrogen pentoxide under strictly anhydrous conditions (ref. 13)



The shift variation of the second ^{51}V resonance in the $\text{VO}(\text{NO}_3)_3$ - HNO_3 - H_2O system (Fig. 3), at low vanadium concentrations, consists of three distinct regions. In the initial region $\delta(^{51}\text{V})$ is constant at -704 ± 1 ppm. In the intermediate region $\delta(^{51}\text{V})$ changes fairly rapidly with added H_2O from -704 to -560 ppm. In the final region $\delta(^{51}\text{V})$ changes slowly from -555 to ca. -545 ppm. The ^{51}V shift in the initial region is very similar to those observed (ref. 10) for the newly reported nitrate-dimer, $\text{V}_2\text{O}_3(\text{NO}_3)_4$, in acetonitrile or nitromethane solution (-724 and -710 ppm, respectively). This dimer is the initial product formed in these organic media by the controlled hydrolysis of $\text{VO}(\text{NO}_3)_3$ (5)



so this seems likely to be the case also in very concentrated nitric acid. This dimeric molecule is novel for nitrate-complexes, since these are normally monomeric (e.g. $\text{Ti}(\text{NO}_3)_4$, ref. 14, and $\text{VO}(\text{NO}_3)_3$, ref. 15) or extensively polymerised (e.g. $\text{Cu}(\text{NO}_3)_2$, ref. 16). The only nitrate-oligomer of known structure is tetrameric $\text{Be}_4\text{O}(\text{NO}_3)_6$ (ref. 17) although compounds of composition $\text{Ir}_3\text{O}(\text{NO}_3)_{10}$ (considered, on the basis of infrared spectroscopic evidence, to be $\text{Ir}_3\text{O}(\text{NO}_3)_9 + \text{NO}_3^-$, ref. 18) and $\text{Al}_3\text{O}(\text{NO}_3)_{10} \cdot 8\text{H}_2\text{O}$ (ref. 19) have been reported. Interestingly, in comparison to the vanadium-100% nitric acid system, the hexanitrate-complex $\text{Ir}(\text{NO}_3)_6^{2-}$ transforms to the oxo-species $\text{Ir}_3\text{O}(\text{NO}_3)_{10}$ in 100% nitric acid solution (ref. 20).

In the intermediate region the solutions become intensely yellow (the absorbance at 400 nm is a maximum at ca. 9.5 mol kg⁻¹ H₂O) and then fade in colour. This fading can be attributed to the breakdown of polymerised species to give primarily [VO₂(H₂O)₄]⁺ ($\delta(^{51}\text{V}) = -546$ ppm) the existence of which in aqueous acid is well established.

In the final region, where VO(NO₃)₃ is absent, the changes in ⁵¹V chemical shift are probably due to changes in solvation and/or the degree of protonation of [VO₂(H₂O)₄]⁺. It is interesting to note that, notwithstanding the wealth of vanadium species revealed by n.m.r. spectroscopy of nitric acid solutions, the only solid products which have been isolated from solutions of vanadium in HDA, 100% nitric acid and 70% nitric acid are V₂O₅·1.0H₂O, V₂O₅·0.5H₂O and V₂O₅·2H₂O, respectively (ref. 21). This is, no doubt, the consequence of inevitable changes in complex equilibria during crystallisation attempts by evaporation of nitric acid solutions.

SOLUTIONS OF NO₂⁺[Al(NO₃)₄]⁻

Nitronium tetranitratealuminum(III), prepared by a previously published method (ref. 22), was selected as the aluminium-containing solute, since this anhydrous compound adds no new species, other than the [Al(NO₃)₄]⁻ anion, to the solvent medium.

The ²⁷Al n.m.r. spectra of solutions of NO₂⁺[Al(NO₃)₄]⁻ in 100% nitric acid are concentration dependent (Fig. 5). They are also complicated by the overlap of a number of resonances in a very narrow chemical shift range. However, at modest concentrations, and the highest available field, up to 6 separate resonances can be resolved (Fig. 5(c)), all in the chemical shift range expected for octahedral species (referred to [Al(H₂O)₆]³⁺ as standard). The ¹⁴N n.m.r. spectra of all aluminium solutions in 100% nitric acid and related media give rise to a single resonance, indicative of rapid exchange between bound and solvent nitrate. The different ²⁷Al resonances are attributed to species differing in the number of water and nitrate ligands and likely to be monomers at the aluminium concentration giving rise to spectrum (c) of Fig. 5. The range of possible monomeric octahedral complexes (assuming nitrate to be a unidentate ligand) is shown in Table 3.

How can the individual species responsible for the spectrum of Fig. 5(c) be identified? Addition or removal of H₂O should indicate which resonances correspond to H₂O coordination. The H₂O content of 100% nitric acid can be reduced by the addition of its anhydride, dinitrogen pentoxide, which is completely ionised (6) in solution in the acid,



the resulting solution being termed a nitric oleum. Addition of N₂O₅ will thus drive equilibrium (1) to the left. However, progressive additions of N₂O₅ to HNO₃ are more difficult, experimentally, than additions of H₂O to a nitric oleum and the latter approach was chosen.

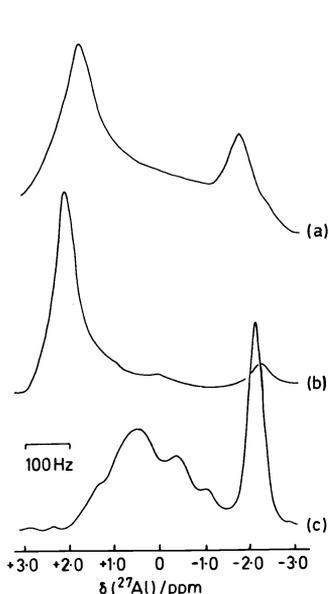


Fig. 5. 104.3 MHz ²⁷Al n.m.r. spectra of NO₂⁺[Al(NO₃)₄]⁻ in 100% HNO₃. [Al]/mol dm⁻³ (a) 1.33, (b) 0.370, (c) 0.016

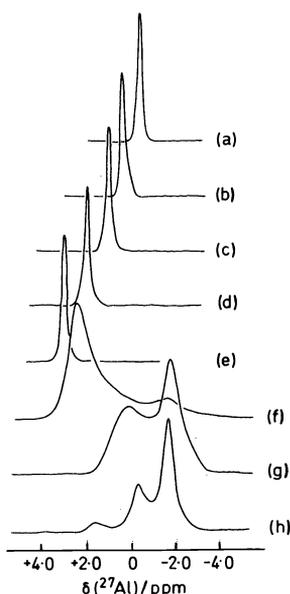


Fig. 6. 65.2 MHz ²⁷Al n.m.r. spectra showing the effect of H₂O addition to NO₂⁺[Al(NO₃)₄]⁻ (0.54 mol dm⁻³) in nitric oleum. See Table 4 for experimental conditions.

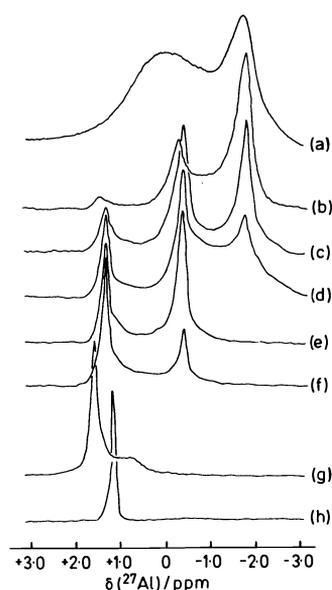


Fig. 7. 65.2 MHz ²⁷Al n.m.r. spectra showing the effect of H₂O addition to NO₂⁺[Al(NO₃)₄]⁻ (0.016 mol dm⁻³). See Table 5 for experimental conditions.

TABLE 3. Possible octahedral aquo-nitrato-complexes (unidentate nitrate)

$[\text{Al}(\text{H}_2\text{O})_6]^{3+}$
$[\text{Al}(\text{H}_2\text{O})_5(\text{NO}_3)]^{2+}$
$[\text{Al}(\text{H}_2\text{O})_4(\text{NO}_3)_2]^+$ <u>cis</u> and <u>trans</u>
$[\text{Al}(\text{NO}_3)_3(\text{H}_2\text{O})_3]$ <u>fac</u> and <u>mer</u>
$[\text{Al}(\text{NO}_3)_4(\text{H}_2\text{O})_2]^-$ <u>cis</u> and <u>trans</u>
$[\text{Al}(\text{NO}_3)_5(\text{H}_2\text{O})]^{2-}$
$[\text{Al}(\text{NO}_3)_6]^{3-}$

TABLE 4. Addition of H_2O to $\text{NO}_2^+[\text{Al}(\text{NO}_3)_4]^-$ (0.54 mol dm⁻³) in N_2O_5 (30wt%)/ HNO_3

Spectrum (Fig. 6)	Mole ratio H_2O added: Al	Mole ratio N_2O_5 excess: Al
(a)	0.00	10.95
(b)	1.81	9.14
(c)	2.64	8.31
(d)	5.11	5.85
(e)	5.27	5.69
(f)	8.36	2.59
(g)	10.39	0.57
(h)	14.47	

TABLE 5. Addition of H_2O to $\text{NO}_2^+[\text{Al}(\text{NO}_3)_4]^-$ (0.016 mol dm⁻³) in 100% HNO_3

Spectrum (Fig. 7)	Mole ratio H_2O added: Al	Mole ratio $\text{HNO}_3:\text{H}_2\text{O}$
(a)	0	61.5
(b)	82	19.6
(c)	168	9.1
(d)	240	6.4
(e)	372	4.1
(f)	680	2.2
(g)	1080	1.4
(h)	1680	0.9

N_2O_5 can be dissolved in 100% nitric acid up to 30 wt.% at saturation point (ref. 1). Addition of H_2O converts the excess N_2O_5 to HNO_3 . Until a mole equivalent of H_2O has been added, there will be no H_2O present in solution. After this point the acid will behave as pure 100% nitric acid. In 100% nitric acid saturated with dinitrogen pentoxide, containing $\text{NO}_2^+[\text{Al}(\text{NO}_3)_4]^-$, a single Al resonance at -0.6 ppm was observed (Fig. 6(a); Table 4). Addition of water to this solution causes the resonance to move to higher frequency and become sharper. After the addition of ca. 5 mole equivalents of water per mole of aluminium (Fig. 6(e); Table 4) the signal has a shift of +2.8 ppm. Addition of 8.36 mole equivalents H_2O yields a broader resonance at +2.2 ppm with a shoulder at -1.7 ppm (Fig. 6(f)). At 10.39 mole equivalents a spectrum identical to that of Fig. 5(c) (100% HNO_3) was obtained, but the lower field spectrometer employed was unable to resolve the higher frequency peak. Addition of still more water to a composition in the aqueous nitric acid range (Fig. 6(h)) resulted in three signals as found for the addition of H_2O to $\text{NO}_2^+[\text{Al}(\text{NO}_3)_4]^-$ in 100% HNO_3 (see below, Fig. 7 and Table 5).

Complete and unambiguous assignment of the resonances is difficult but, again, all occur in the chemical shift region characteristic of octahedral species. The complex present in very concentrated solutions of N_2O_5 in 100% nitric acid is likely to have the maximum number of nitrate ligands per aluminium atom i.e. $[\text{Al}(\text{NO}_3)_6]^{3-}$, which has, indeed, been isolated from such solutions as the potassium salt (ref. 23). The single resonance of Fig. 6(a) is thus assigned to this species, the narrow line being consistent with the expected high symmetry of this complex (the solid state magic angle spinning (MAS) ²⁷Al n.m.r. spectrum of the complex $\text{K}_3[\text{Al}(\text{NO}_3)_6]$ exhibits a single very sharp peak at -5.6 ppm consistent with completely regular octahedral coordination of aluminium). The relatively small movement (ca. 3 ppm) of the peak to high frequency on addition of water (Fig. 6, (a) to (e)) probably involves no change of aluminium species but arises simply from a reduction in the ionic strength of the solution by conversion of ionic N_2O_5 ($\text{NO}_2^+\text{NO}_3^-$) into HNO_3 by H_2O , i.e. by the reverse reaction of the self-dissociation equilibrium (1). The broadening observed in spectrum (f) of Fig. 6 is probably due to some intermolecular exchange and the second peak at -1.7 ppm is assigned to $[\text{Al}(\text{NO}_3)_5]^{2-}$ or $[\text{Al}(\text{NO}_3)_5(\text{H}_2\text{O})]^{2-}$ as the species of second highest $\text{NO}_3^-:\text{Al}$ ratio. This is reasonable since $\text{K}_2[\text{Al}(\text{NO}_3)_5]$ can also be crystallised from nitric oleum (ref. 23). Furthermore, the chemical shift (-6.5 ppm) of the MAS ²⁷Al n.m.r. signal of solid $\text{K}_2[\text{Al}(\text{NO}_3)_5]$ is of low frequency of that for $\text{K}_3[\text{Al}(\text{NO}_3)_6]$ which shows the same trend as the corresponding solution resonances i.e. 0.0 ppm, assigned to $\text{K}_3[\text{Al}(\text{NO}_3)_6]$ (nitric oleum) and -1.7 ppm, assigned to $\text{K}_2[\text{Al}(\text{NO}_3)_5]$ (100% nitric acid). On reaching approximately the 100% HNO_3 composition (Fig. 6(g)), $[\text{Al}(\text{NO}_3)_6]^{3-}$ disappears and a third broad resonance, probably assignable to a number of aquo-nitrato-species in slow intermolecular exchange, is present.

Spectra observed on addition of water to a dilute solution of $\text{NO}_2^+[\text{Al}(\text{NO}_3)_4]^-$ in 100% nitric acid are illustrated in Fig. 7 and the experimental conditions are given in Table 5. (the spectra illustrated in Figs. 7(a) and 6(g) are identical). The three signals at ca. +1.5, 0.0 and -1.5 ppm (Fig. 7(b),(c),(d)) are assigned to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, an average signal arising from fast exchange of a number of aquo-nitrato-complexes and $[\text{Al}(\text{NO}_3)_5(\text{H}_2\text{O})]^{2-}$, respectively. With progressive addition of water, the nitrato-complexes disappear, leaving only the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ signal which, as expected, moves towards the reference zero, again presumably as a result of an ionic strength effect.

Aluminium metal dissolves very slowly in HDA and the compound $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{NO}_3)_3$ crystallises from the solution (ref. 19). A solution of this compound in HDA (0.051 mol dm⁻³) exhibits (ref. 24) three resonances with similar chemical shifts and relative intensities to those of Fig. 7(b).

Inspection of Table 5 shows that the concentration of water is in vast excess of that of aluminium so that if all the water added was available for complexation, only the complex $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ would be formed, even after the first addition. Thus, a very substantial

proportion of the added water is unavailable to aluminium owing to strong solvation of water by nitric acid. It is also interesting that exchange between a number of closely related species is slow enough to enable observation of separate ^{27}Al resonances in a medium such as 100% nitric acid. We must conclude that exchange of coordinated water with solvent and/or replacement of nitrate by water is relatively slow on the n.m.r. timescale. This may again be due to the very strong solvation by nitric acid that water is known to experience in this medium.

CONCLUDING REMARKS

This lecture has sought to illustrate the application of multinuclear n.m.r. spectroscopy to the study of metallic and non-metallic solute species in nitric acid solutions. The vanadium and aluminium systems, chosen as examples, prove to be rather complex, spectral features being dependent on composition of solvent medium, ionic strength and metal concentration but, hopefully, these systems have indicated the potential of the approach. A wide variety of solutes, possessing appropriate nuclei, awaits n.m.r. examination in nitric acid solutions; Na_2MoO_4 , $\text{Rh}(\text{NO}_3)_3$ and NbF_5 are attractive examples.

The technique of multinuclear n.m.r. spectroscopy can, of course, be applied to the study of virtually any non-aqueous solution and we have recently extended our work to other strongly acidic media, for example, difluorophosphoric acid. Reactions of boron compounds with this acid have led to the identification and characterisation in solution of the first simple difluorophosphato-anion, $[\text{B}(\text{PO}_2\text{F}_2)_4]^-$, and recognition of a second species believed to be $[\text{BF}(\text{PO}_2\text{F}_2)_3]$ (ref. 25).

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