High Resolution ^{45}Sc Nuclear Magnetic Resonance: A New Tool for Studies of Scandium Compounds in Solution

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Summary Preliminary experiments with high resolution ^{45}Sc n.m.r. spectroscopy demonstrate the sensitivity of the chemical shift to variations of the co-ordination environment of the scandium(III) ion and suggest that this technique may be useful for studies of scandium compounds in solution.

INTEREST in the chemistry of scandium has increased considerably recently, with the syntheses of many new scandium compounds being described.[1] However, the techniques available for providing information concerning the nature of the chemical environment about the scandium in these compounds are limited due to the $3d^0$ configuration of the scandium(III) ion, which is the usual oxidation state displayed by this element. ^{45}Sc n.m.r. spectroscopy may be a powerful tool for chemical studies of scandium compounds, since the ^{45}Sc nuclide has 100% natural abundance and a high sensitivity compared to protons at constant field, (0·3). We report here ^{45}Sc n.m.r. spectra for several scandium salts in aqueous solution.

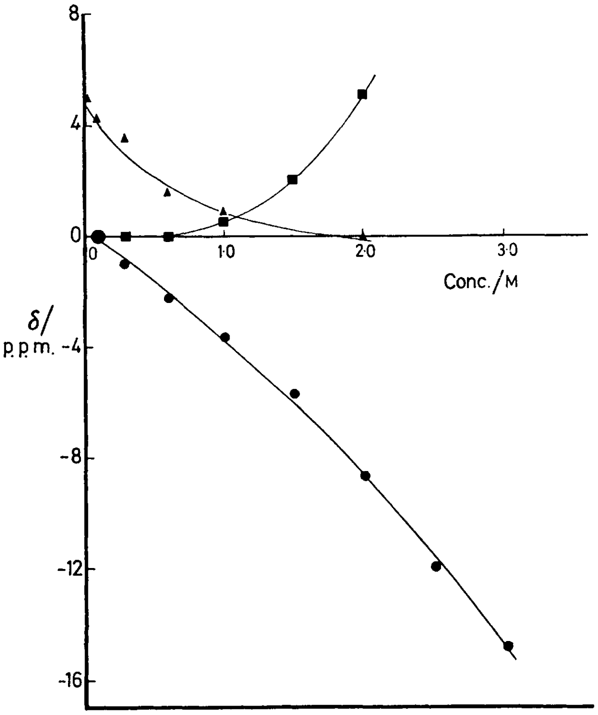

Figure. Concentration dependence of chemical shift (δ). ■ Cl$^-$, ● ClO$_4^-$, ▲ NO$_3^-$.

Spectra were obtained at a field of 5·33 T and a frequency of 55·1 MHz with a spectrometer constructed in this department.[2] Data were collected by a few time-averaged continuous wave scans using 5 mm n.m.r. tubes. The reference solution was contained in a capillary centred in the 5 mm tube.

The Figure shows the concentration dependence of the chemical shift (δ) for solutions of scandium chloride, perchlorate, and nitrate. The Table presents chemical-shift data and line widths obtained for the series of scandium salts studied. Quoted chemical shifts are referred to an aqueous 0·1M Sc(ClO$_4$)$_3$ solution, with increasing values corresponding to decreasing shielding. It can be seen that a wide range of concentration dependent chemical shifts, both upfield and downfield from the reference solution, is observed. For chloride, perchlorate, and bromide solutions, the chemical shifts all approach the same value at low concentrations. Thus at these concentrations, the species† obtained is anion independent and may be the [Sc(OH)]$^{2+}$ ion which has been suggested to predominate at low concentration.[3,4] As the concentration of the salts is increased, the observed chemical shift is dependent on both the concentration and the anion, the magnitude of δ and the line width both increasing with increasing concentration. For the chloride and bromide, the changes may be assigned to the formation of species which include chloride and bromide, both of which form complex ions with scandium(III) in aqueous solution.[5] However, for the perchlorate solutions, the change in chemical shift is probably due to the formation of polymeric hydroxy-species. Such species have been identified in scandium perchlorate solutions by several authors.[3,6]

Table. ^{45}Sc n.m.r. data for some scandium salts in aqueous solution[a]

Scandium salt,	conc. (M)	Chemical shift[b] δ, p.p.m.	Line width[c] (Hz)
ScCl$_3$	2·0	+ 5·1	188
	1·0	+ 0·5	46
	0·1	− 0·1	53
ScBr$_3$	2·0	− 5·4	183
	1·0	− 2·5	175
	0·1	0·0	93
Sc(ClO$_4$)$_3$	3·0	−14·8	105
	0·6	− 2·2	81
	0·1	0	86
Sc(NO$_3$)$_3$	2·0	− 0·1	1655
	1·0	+ 0·9	1004
	0·1	+ 4·3	456
Sc$_2$(SO$_4$)$_3$	1·0	+ 6·7	454
	0·6	+ 7·3	272
	0·1	+ 9·1	197

[a] Results obtained at ambient temperature. [b] Relative to 0·1M aqueous Sc(ClO$_4$)$_3$ solution. Increasing values correspond to decreasing shielding. Error limits ± 1 p.p.m. Not corrected for instrumental broadening.

Scandium nitrate and sulphate behave in a different manner to those salts described above. At low concentrations, the chemical shifts are different and do not approach the limiting value observed for the chloride, perchlorate, and bromide salts. Thus, species which involve the anions must be present in significant concentrations in the nitrate and sulphate systems. As the concentration of the salt increases, both δ and the line widths change in a manner which may be correlated with the formation of complex ions containing nitrate and sulphate ions.[7]

Thus, it is apparent that quite small changes in the chemical environment of scandium may be detected by ^{45}Sc n.m.r. spectroscopy. Large changes in chemical environment lead to considerable chemical shifts, for example for Sc(acac)$_3$, in benzene, δ is +85 p.p.m.

Further development and refinement of ^{45}Sc n.m.r. spectroscopy is anticipated. It should be possible to correlate chemical shifts with the nature of ligands coordinated to the scandium ion in solution, and by analysis of the line shapes calculate stability constants for individual species. The technique should prove to be extremely useful for future chemical studies of scandium compounds in solution.

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† It is assumed that all species are hydrated in solution.

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