INORGANIC COMPLEXES OF ALUMINIUM IN AQUEOUS SOLUTION

THESIS

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CONTENTS

CHAPTER 1.

INTRODUCTION AND LITERATURE REVIEW.

The ability of aluminium to form complex ions in aqueous acidic solutions is well known, the study of hydrolysed species of aluminium, for example, being of considerable current interest. Investigations of the hydrolytic equilibria have been made using numerous techniques including potentiometric and conductivity measurements and such methods have also shown the presence of soluble complexes of aluminium fluoride, phosphate, and fluorophosphate in suitable binary and ternary aqueous systems. The role of such complexes and their equilibria is of importance in many fields. The study of aluminium hydrolysis is of interest to the water chemist for the clarification of industrial and potable water. The agricultural chemist requires knowledge of these species for investigations of plant nutrition and predogenesis. Recently it has been suggested that complexes of aluminium containing phosphate and/or fluoride may be important contaminants in by-product gypsum produced during the manufacture of phosphoric acid from phosphate rock. In order to assess the chemistry of aluminium in such situations it is necessary to first obtain a complete understanding of the nature of the complexes and their equilibria in pure binary and tertiary aqueous systems. Such knowledge is not yet complete and considerable speculation exists as to the equilibria and species formed.

Two spectroscopic techniques are particularly suitable for the study of complexes in aqueous media namely nuclear magnetic resonance (n.m.r.) and Raman spectroscopy. The former can supply considerable information when more than one magnetic nucleus is available for study in the same system. Despite the suitability of the above aluminium complexes for such studies, investigators have limited their attention to the aquated aluminium ion $Al(H_2O)_n^{3+}$ (^1H and ^{17}O) and to the alumino fluorides (^{19}F and ^{27}Al).

This present investigation uses n.m.r. spectroscopy to examine the aqueous aluminium ion, $Al(H_2O)_n^{3+}$ and the soluble complexes formed from its hydrolysis, the study then being extended to other complexes including those in aqueous binary and ternary systems containing fluoride and phosphate ions. The complexes are detected by their ^1H ^{19}F ^{27}Al or ^{31}P resonances where applicable. A limited Raman investigation is also included and in both studies work is confined to soluble complexes in acidic solution.

Before presenting the results of these investigations it is first convenient to review the literature available on these systems. This is followed by a short discussion on those properties of the nucleus which are important in the study of inorganic complexes, chapter 2, and the experimental techniques employed, chapter 3. Following the results of the n.m.r. studies, chapters 4 to 8, a separate chapter is presented on the results of Raman investigations.

LITERATURE REVIEW.

A. Hydrolysis of Aluminium Salts in Acidic Solutions.

Despite extensive investigations of the hydrolysis of aluminium salts, the composition of the hydrolysed species is still not known with any degree of certainty. The dissolution of an aluminium salt in water may be represented in the simplest terms by the equilibria in which the hydrated chloride salt is used.

$$AlCl_3 6H_2O \text{ solid} \overset{H_2O}{\rightleftharpoons} Al(H_2O)_n^{3+} + 3Cl^- \qquad (1 - 1)$$

The formation of the aquated aluminium ion is shown with a co-ordinated or 'bound' water shell, and this ion is thought to represent the total aluminium present in most acidic salt solutions of concentrations between 0.1 and 2.0 M. When such solutions are greatly diluted or the pH is raised, the occurrence of other aluminium species is evident. A number of methods have been employed to study these complexes and include potentiometric titrations,[1-9] pH titrations,[10-20] cryoscopy,[21-23] diffusion,[24-26] reaction kinetics,[27,28] conductivity,[19,29] light scattering,[30] ion exchange,[31] coagulation.[32,33] Solutions are prepared in general by one of two methods. Either alkali is added to an acid salt dissolved in water or else the precipitated hydroxide is redissolved in dilute acid. In most procedures an Al : OH ratio or charge is determined and the composition of the species postulated from this evidence.

As early as the 1890's the first hydrolytic product of aluminium in solution was proposed and this may be represented by the equilibrium

$$\mathrm{Alaq}^{3+} + H_2O \rightleftharpoons \mathrm{AlOHaq}^{2+} + H_3O^{+} \qquad (1 - 2)$$

The hydration sphere of the aquated aluminium ion is simplified to the term aq for convenience, as in many early papers it was not represented in such equilibria. In 1899 Ley[27] calculated a hydrolysis constant for such a reaction and a value of -4.9 was obtained where

$$K_1 = \log_{10}\left([\mathrm{AlOHaq}^{2+}][H^+]/[\mathrm{Alaq}^{3+}]\right)$$

Since the above date, evidence for this simple monomeric hydrolysis has been proposed by many investigators, the concentration of aluminium salts used being in the range 10^{-2} to 10^{-5}M. Table 1 - 1 summarizes the hydrolysis constants calculated by these workers.

Three recent papers by Frink and Peech[19] (1963), Holmes, Cole and Eyring[38] (1968) and Sullivan and Singley[20] (1968) again conclude that hydrolysis proceeds according to the simple monomeric mechanism. The latter authors also state that the aquated aluminium ion is still the predominant species in the pH range 3 to 4.5.

Notwithstanding the concordant values for the first stage hydrolysis constant the general applicability of this mechanism has been repeatedly questioned. Kubota[18] found revidence for the existence of dimers of the type $Al_2(OH)_2aq^{4+}$ formed according to the equilibrium

$$2\,Alaq^{3+} + 2H_2O \rightleftharpoons Al_2(OH)_2aq^{4+} + 2H_3O^{+} \qquad (1 - 3)$$

A concentration dependence was reported by Faucherre[13,14] who found that dimers were formed only in aluminium salt solution more concentrated than 0.01 M whereas the monomeric hydrolysis mechanism was applicable to aluminium ion concentrations of less than 0.005 M.

Table 1-1.

Hydrolysis Constant, K_1, for Monomeric Hydrolysis of Aluminium.

Investigator		Ref.	Temp.	K_1
(1899)	H. Ley	27	77°	-4.12
(1907)	N. Bjerrum	29	25°	-4.85
(1908)	H.G. Denham	1	25°	-4.29
(1928)	J.N. Brönsted, K. Valquartz	28	15°	-4.89
(1948)	J. Faucherre	13	20°	-5.97
(1954)	J. Faucherre	14	20°	-5.74
(1949)	S. Lacroix	15	18°	-4.60
(1953)	T. Ito, N. Yui	16	25°	-5.10
(1954)	R.K. Schofield, A.W. Taylor	17	15°	-5.28
			20°	-5.15
			25°	-4.98
(1955)	J. Kenttämaa	9	25°	-4.96
(1956)	H. Kubota	18	25°	-5.03
(1962)	C.R. Frink, M. Peech	19	25°	-5.02
(1968)	J.H. Sullivan, J.E. Singley	20	25°	-5.07

A recent investigation (1969) by Grunwald and Dodd-Wing Fong[34] again suggests that significant dimerisation occurs. Recorded hydrolysis constants K_2 for this equilibrium are given in Table 2 - 1 where $K_2 = \log_{10} (\{[Al_2(OH)_2aq^{4+}] [H^+]^2\} / [Alaq^{3+}]^2)$

Turner[37] (1969) studied the hydrolysis of aluminium chloride solutions (10^{-2} to 10^{-4}M) using an 8-quinolinolate-chloroform extraction procedure and detected three soluble aluminium complexes. These were $Al(H_2O)_6^{3+}$, $AlOHaq^{2+}$ and a polynuclear species of unknown size.

Further aluminium complexes have been suggested by Brosset[6,7] and Sillen[35]. The former author suggested that the major products of hydrolysis were also polynuclear complexes even at low degrees of hydrolysis. These were either a single complex such as $Al_6(OH)_{15}aq^{3+}$ given by the equilibrium

$$6Alaq^{3+} + 15H_2O \rightleftharpoons Al_6(OH)_{15}aq^{3+} + 15H_3O^+ \qquad (1 - 4)$$

where $K_6 =$

$$\log_{10} (\{[Al_6(OH)_{15}aq^{3+}] [H^+]^{15}\} / [Alaq^{3+}]^6]) = -47$$

or an infinite series of complexes with the formula $Al[(OH)_5Al_2]_naq^{3+n^+}$ the first formed complex having an equilibrium

$$3Alaq^{3+} + 5H_2O \rightleftharpoons Al_3(OH)_5aq^{4+} + 5H_3O^+ \qquad (1 - 5)$$

$$K_S = \log_{10} (\{[Al_3(OH)_5\,aq^{4+}] [H^+]^5\} / [Alaq^{3+}]^3) = -15$$

Table 1 - 2.

Hydrolysis Constant, K_2, for Dimeric Hydrolysis of Aluminium.

Investigator	Ref.	K_2
J. Faucherre	13	-8.24
J. Faucherre	14	-8.06
J. Kenttämaa	9	-7.55
H. Kubota	18	-6.27

Sillen in a review of Brosset's work suggested a further species $Al_{13}(OH)_{32}aq^{7+}$.

Matijevic et al.[32,33] from studies of the coagulation effects of aluminium salts on aqueous sols of silver halides deduced the charge of the hydrolysed aluminium species. At pH's less than 4 in the concentration range 10^{-2} to 10^{-4} M the trivalent aquated aluminium ion was the predominant species while in the pH range 4 to 7 a tetravalent hydrolysis product existed and a suggested equilibrium was

$$8Alaq^{3+} + 20OH \rightleftharpoons Al_8(OH)_{20}aq^{4+} \qquad (1 - 6)$$

Other reported hydrolysed species of aluminium include $Al(OH)_2aq^{+}$(3), $Al_2(OH)_5aq^{+}$(3),(36), $Al(OH)_3aq$(20) and $Al_3(OH)_8aq^{+}$.(36)

Conflicting evidence is found by many authors on the effect of aging on the rate of attaining equilibrium. Frink and Peech noted over an eight month period that $AlCl_3$ solutions more dilute than 0.0005M tended to become more acid on standing while at concentrations greater than this, the equilibrium was attained immediately. Brosset stated that the formation of $Al^{3+} - OH^{-}$ complexes takes of the order of 10 - 30 hours at 20°C and an intermediate precipitate was often observed in solutions prepared by adding alkali to an acid salt, the precipitate gradually redissolving. Matijevic [32] 'artificially aged' solutions by warming at 90° and found that the pH of such solutions decreased during 'aging'.

In conclusion it can be seen that numerous species have been postulated as the result of hydrolysis of aluminium. Many investigators, however, favour a monomeric or dimeric equilibria and concordant values for the respective hydrolysis constants have been obtained.

B. The Aquated Aluminium Ion.

The hydration of the aquated aluminium ion, $Al(H_2O)_n^{3+}$, in acid solution, has been the subject of considerable interest during the last few years and has been investigated as a separate field distinct from hydrolysis. Studies have been made of the hydration number, structural characteristics, and kinetic and thermodynamic parameters governing the exchange of water and hydrogen between the hydration sphere and non-co-ordinate water.

Jackson, Lemons, and Taube,[39] using ^{17}O enriched solutions first observed separate ^{17}O n.m.r. signals which could be attributed to bound and non-co-ordinated (bulk) water. A small concentration of a paramagnetic ion was added to separate the two resonances but the signal-to-noise ratio was too poor to enable a determination of n, the hydration number of aluminium. Later Connick and Fiat[40] repeated this work and were able to obtain values of 6.07, 5.95, 5.86 and 5.82 from four separate measurements of the two resonances.

Initial studies of the rate of exchange with the bound water were made by isotopic dilution technique[41] with ^{18}O. Results indicated that the half life of the oxygen on the ion was greater than 0.02 sec. but considerably less than 3 minutes. This technique also confirmed the number of water molecules in the primary hydration sphere to be 6. Recently Fiat and Connick[42] re-examined ^{17}O enriched aluminium solutions by n.m.r. and calculated that the lifetime of oxygen in the hydration sphere was 7.5 sec. at 25° and that the enthalpy and entropy of oxygen exchange were 27 kcal/mole and 28 kcal deg^{-1} mole^{-1}.

Proton exchange rates have been obtained from measurements of proton relaxation times in a study by Lohmann.[43] The lifetime of the protons on the aquated aluminium species was found to be pH dependent and of the order 10^{-5} sec. Owing to this rapid exchange the proton n.m.r. signal of aluminium salt solutions at room temperature is a singlet but it has been shown by Schuster and Fratiello[44,45] that if a highly concentrated solution of $AlCl_3$ is cooled to -50° then the exchange rates are sufficiently slow to enable the resolution of separate ^1H resonances for bulk and bound water. Direct integration of these signals gave n = 6.0 - 6.1 and a rate constant of 10^5 per sec. was calculated for proton exchange at 25°. An activation enthalpy ΔH for solvent exchange was determined as 24 kcal/mole but it was stated that this value was thought to be high and reservations were made over the figures used for the calculation. Similar proton studies have been emulated by Matwiyoff[46] on aluminium nitrate solutions.

Supran and Sheppard,[47] by a double resonance experiment, were able to demonstrate the covalent nature of the oxygen aluminium bond of the aquo-species in a study of aqueous mixtures of acetonitrile and aluminium perchlorate. Perturbation of a proton resonance attributed to a hydrated aluminium ion was observed when aluminium was irradiated at the resonance frequency of the aquated ion.

Recently Stephens and Schweitzer[48] have noted that the coalescence temperature of the proton signals of bound and bulk water increased on addition of an inert salt such as calcium nitrate.

Grunwald[49] (1969) studied the kinetics of proton exchange between the $Al(H_2O)_6^{3+}$ ion and water in dilute acid. Using proton n.m.r. techniques at room temperature he determined a rate constant of 1.1×10^5 sec.$^{-1}$ for acid dissociated of the aquated aluminium ion. A second kinetic process was found, this being a reaction between $Al(OH_2)_6^{3+}$, $Al(OH_2)_5OH^{2+}$ and two or more water molecules. A rate constant as high as 9×10^8 sec.$^{-1}$ M^{-1} was determined for this reaction. Between pH 3 and 4, and at aluminium concentrations above 0.01 M, the formation of a hydrous $Al\text{-}O\text{-}Alaq^{4+}$ species was suggested.

From these investigations it may be concluded that the bound water to aluminium shows considerable covalent character, the oxygen exchanges slowly while the hydrogen exchange is relatively rapid.

Several investigators[50-52] have detected the aquated aluminium ion in general ^{27}Al n.m.r. investigations. A broad signal was obtained 30 to 50 Hz wide and it was detected as the derivative. No attempts have been made to study this resonance with respect to hydrolytic equilibria or exchange reactions.

C. Aluminium Fluoride Complexes.

The existence of a series of fluoroaluminate ions of the type $AlF_n^{(3-n)+}$, where n = 1 to 6, was first postulated by Brosset[53] in 1943. Using potentiometric techniques[54,55] he calculated their stability constants in dilute solution (10^{-3} M) and at constant ionic strength ($\mu = 0.5$). The following values were obtained

$$Al^{3+} + F^- \rightleftharpoons AlF^{2+} \qquad K_1 = 6.13$$

$$AlF^{2+} + F^- \rightleftharpoons AlF_2^+ \qquad K_2 = 5.02$$

$$AlF_2^+ + F^- \rightleftharpoons AlF_3 \qquad K_3 = 3.85$$

$$AlF_3 + F^- \rightleftharpoons AlF_4^- \qquad K_4 = 2.74$$

$$AlF_4^+ + F^- \rightleftharpoons AlF_5^{2-} \qquad K_5 = 1.63$$

$$AlF_6^{2-} + F^- \rightleftharpoons AlF_6^{3-} \qquad K_6 = 0.47$$

where $K_1 = \log_{10} ([AlF^{2+}] \ / \{ [Al^{3+}] [F^-] \})$ etc.

It is clear that such complexes are stable and that the concentration of free fluoride is very small when the total aluminium and fluoride concentrations are similar.

Further potentiometric studies were made by Pozin et al.[56] and Savehenko et al.[57] The former confirmed the presence of AlF^{2+} in the system $Al_2(SO_4)_3$ - HF while the latter demonstrated the existence of AlF_2^+ in the system $Al(NO_3)_3$ - HF. Neither found any indication of the presence of AlF_3 or more highly co-ordinated ions, nor did they attempt the calculation of any stability constants.

Connick and Poulson[50] detected both AlF^{2+} and AlF_2^{+} in the system $Al(NO_3)_3$- NaF at approximately molar concentrations using ^{19}F n.m.r. techniques. At 40 M Hz two overlapping resonances were obtained from which the concentrations of fluorine were calculated and found to agree with the concentrations for AlF^{2+} and AlF_2^{+} postulated by Brosset for such an Al/F ratio. Only a single resonance was observed for solutions which contained higher alumino fluoride complexes. The ^{27}Al resonance at 10.4 M Hz was undetected when aluminium was complexed, but the signal of $Al(H_2O)_6^{3+}$ was easily observed and its intensity was in accordance with that calculated from Brosset's constants.

D.E. O'Reilly[51] as part of a general study of ^{27}Al resonances attributed a broad signal 15 ppm downfield of $Al(H_2O)_6^{3+}$ to AlF_2^{+}. The system was an acid solution of $AlCl_3 6H_2O$ to which KF had been added: no further details were given.

Yamazaki and Takeuchi[58] re-examined the work of Connick and Poulson using ^{19}F n.m.r. at 56.4 M Hz. The presence of AlF^{2+} and

AlF_2^+ was confirmed in solutions of molar ratio $NaF/Al(NO_3)_3 = 1.0$, and also the coalescence of these two resonances to give a single resonance at molar ratios of 2.0 or greater. However on cooling such solutions to - 3 ° they were able to demonstrate that fast exchange caused coalescence at room temperature and a third resonance was detected at molar ratios 1.5 to 3. This they attributed to higher alumino fluoride complexes of the type $AlF_n^{(3-n)+}$ where $n = 3$ to 6. At a molar ratio of 6.0, two resonances were observed at - 3 °, one of which was attributed to free fluoride ion and the other to the higher alumino fluorides.

Latimer and Jolly[59] determined calorimetrically the heats and entropies for the reactions cited by Brosset. From these results it was concluded that variations in temperature were probably not an important factor in these quilibria since the heats of complexing are small.

D. Aluminium Phosphate and Fluoro-Phosphate Complexes.

Little attention has been paid to these complexes in comparison to the studies on the previously mentioned species. Bjerrum[60] in 1932 found evidence for the formation of various phosphatoaluminium complexes which he assumed to be of the types $[Al(H_2PO_4)]^{2+}$,

$[Al(HPO_4)]^+$, $[Al(H_2PO_4)_2]^+$, $[Al(HPO_4)_2]^-$ and $[Al(HPO_4)_3]^{3-}$. His evidence was based on conductivity and pH measurements on solutions of aluminium chloride and sodium dihydrogen phosphate.

In a series of investigations Salmon[61-64] and his co-workers studied aluminium chloride solutions containing phosphoric acid and sodium dihydrogen phosphate, by ion exchange techniques and pH measurements. No complex ions were sorbed by cation or anion exchangers from aluminium chloride-phosphoric acid solutions of molar ratios $H_3PO_4/AlCl_3$, 0.21 to 4.90. With aluminium chloride-sodium dihydrogen phosphate systems in the range $NaH_2PO_4/AlCl_3$, 0.6 to 2.73, sorbtion of ions by cation exchangers gave evidence for $[Al_2(PO_4)]^{3+}$, $[Al_2(PO)_4\ (OH)]^{2+}$, $[Al_2(PO_4)(OH)_2]^+$, $[AlHPO_4]^+$ and $[AlH_2PO_4]^{2+}$ complexes. No sorbable anionic complexes appeared to form. The complexes $[AlH_2PO_4]^{2+}$ and $[Al(H_2PO_4)_2]^+$ were postulated in systems containing phosphoric and sodium dihydrogen phosphate.

A single study of the aluminium phosphato-fluorides has been made. Pozin <u>et al.</u>[56] studied the system HF - $AlPO_4$ and suggested the formation of an $AlF_2H_2PO_4$ complex.

E. Other Soluble Complexes of Aluminium.

Considerable speculation has existed for a number of years on the possible occurrence of complexes of aluminium with other anions, particularly those containing chloride, nitrate or sulphate.

Chloride complexes have been postulated as species the equilibria of which might interfere in the study of the hydrolysis of aluminium chloride solutions.[19, 38] Guiter[12] explained such hydrolysis by complexes of the type $AlCl_x(OH)_{3-x}^{3-x^+}$. However more recent investigations[65] show that while chloride complexes do exist in solvents other than water, their occurrence in aqueous solution must be negligible and Kraus and his co-workers[66,67] found that even in 12 M HCl there was no evidence of complexing of $Alaq^{3+}$.

Evidence for nitrate complexes has come mainly from Raman studies.[68] An additional band is seen in aluminium nitrate solutions which is not present in other salt solutions such as sodium nitrate. The previously mentioned proton n.m.r. studies of cooled aluminium nitrate solutions[46] present strong evidence that aluminium exists in such solutions as the aquated aluminium ion $Al(H_2O)_6^{3+}$ and it has been suggested[69] that any nitrate complexes formed probably involve a secondary hydration sphere.

The existence of both aluminium sulphate and bisulphate complexes has been reported. Behr and Wendt[70] studied the following equilibria in dilute solution

$$Alaq^{3+} + SO_4^{2-} \rightleftharpoons AlSO_4aq^+$$

$$AlSO_4aq^+ + SO_4^{2-} \rightleftharpoons Al(SO_4)_2aq^-$$

He obtained equilibrium constants for the two reactions of $10^{3.2}$ and $10^{1.9}$ respectively. Nishide and Tsuchiya[71] studied solutions of potassium aluminium sulphate using conductivity methods and interpreted their results as evidence for the formation of an ion pair $[Al(H_2O)_6]SO_4^+$. Raman[68] studies also suggest that aluminium sulphate complexes are solvent separated at least one water molecule being trapped between the metal and sulphate ion. This interpretation is consistent with Eigen's[72] findings from chemical relaxation spectra.

Salmon[64] during his ion exchange and pH studies of aluminium phosphate complexes noted a competing equilibrium when sulphate was present and suggested that sulphato-complexes present in the solutions could exert a buffering effect

$$AlSO_4^+ + H^+ \rightleftharpoons AlHSO_4^{2+}.$$

SUMMARY.

The preceding review has indicated some of the possible complexes and equilibria likely to be encountered in studies of aqueous aluminium chemistry. The following questions remain unanswered by the previous investigators and they act as a starting point for this present study:

a) Does aluminium hydrolysis proceed via a monomeric or a dimeric species, or are polynuclear complexes involved even at low degrees of hydrolysis ?

b) Can alumino fluoride complexes higher than AlF_2^+ be identified and their stability confirmed by n.m.r. ?

c) Do all the proposed aluminium phosphate species exist ?

d) Can a family of aluminium fluorophosphates be detected ?

CHAPTER 2.

APPLICATION OF N.M.R. TO THE STUDY OF INORGANIC COMPLEXES AND THEIR EQUILIBRIA IN AQUEOUS SOLUTION.

Much of the structural information obtained from typical spin coupling associated with proton and fluorine spectra of organic or organo complexes is often absent in the n.m.r. spectra of inorganic complexes. It is necessary in such cases for the spectroscopist to obtain chemical information from consideration of other properties of the nucleus evident in the spectra. Many excellent text books[73-76] are now available which give a comprehensive coverage of the basic theory but its application is biased in most cases towards the understanding of ^{1}H or ^{19}F spectra.

Since the major section of this Thesis is concerned with n.m.r. investigations, those properties of the nucleus which are important in the study of totally inorganic complexes are discussed in this chapter, a basic knowledge of the principles of n.m.r. being assumed.

A. Factors Effecting Signal Strength and Relative Sensitivities of Nuclei.

The frequency ν required to induce transitions between neighbouring energy levels in a nucleus of spin quantum number I in a steady magnetic field Ho can be found from the Bohr frequency condition

$$h\nu = \frac{\mu Ho}{I} \qquad (2 - 1)$$

or

$$\nu = \frac{\gamma Ho}{2\pi} \qquad (2 - 2)$$

where h is the Planck constant, μ is the maximum observable component of the nuclear magnetic moment, and γ is the magnetogyric ratio which equals $\frac{\mu}{I\hbar}$ where $\hbar$ is the modified Planck constant $(\frac{h}{2\pi})$.

The observed frequency is thus proportional to the applied magnetic field and the energy difference μ Ho increases with increasing field strength. Since the signal strength depends on μ Ho it is advantageous when studying any magnetically active nucleus $(I \neq o)$ to work at the highest field possible for the instrument. This may be of paramount importance when studying nuclei of low sensitivity or where the concentration of a complex is less than 1.0 M and the resonance is broadened by exchange reactions or quadrupole relaxation. In such circumstances the signal may lie undetected in the natural noise of the spectrum if a low field is used. However, much information can be lost through the use of a high field which has a poor homogeneity. Many quadrupole nuclei have a surprisingly narrow linewidth in favourable environments and if this is broadened due to inhomogeneity of the field then exchange reactions indicated by line-broadening may pass unnoticed.

The relative signal strength of nuclei is related to their spin quantum number I and to the magnetic moment μ. With constant field strength and number of nuclei in the sample coil it may be shown[73(a)] that the signal strength is proportional to

$$\frac{I+1\mu^{3}}{I^{2}}$$

The value $\frac{I+1}{I^2}$ falls rapidly with increasing I and for ^{1}H, ^{19}F, ^{31}P $I = \frac{1}{2}$ and thus $\frac{I+1}{I^2} = 6$, while for ^{27}Al $I = \frac{5}{2}$ and $\frac{I+1}{I^2} = 0.56$. The intensity of the aluminium resonance would be expected to be significantly smaller than the spin half nuclei used in this investigation but in this case a large μ^{3} term gives a signal greater than ^{31}P which has a small magnetic moment as shown in Table 2 - 1.

B. Nuclear Magnetic and Electric Quadrupole Relaxation.

Two relaxation times may be distinguished after a system of nuclear magnets in equilibrium with a magnetic field Ho is perturbed by a rotating magnetic field, the frequency of which is described in equation 2 - 1. These are the Spin-Lattice or Longitudinal relaxation time T_1 concerned with changes in the longitudinal magnetisation of the nuclei in the same direction as the main field and the Spin-Spin or Transverse relaxation time T_2 concerned with changes in transverse magnetisation. It can be shown by the Bloch equations[73(b)] that the linewidth of the resonance line at half amplitude for a system of nuclear magnets equals $\frac{1}{\pi T_2}$ Hz. Much fine structure is lost in the spectra of many inorganic complexes due to rapid relaxation mechanisms producing line broadening. However additional information can be obtained from a study of linewidths and this section indicates the various sources of line broadening.

Table 2 - 1.

Relative Intensities of Nuclei.

Nuclei	Spin I	Magnetic Moment in Units of the Nuclear Magneton	Relative Intensity at Constant Field	Relative Intensity at Constant Frequency
^{1}H	$\frac{1}{2}$	2.79268	1.0	1.0
^{19}F	$\frac{1}{2}$	2.6273	0.833	0.941
^{31}P	$\frac{1}{2}$	1.1305	0.0663	0.405
^{27}Al	$\frac{5}{2}$	3.6385	0.206	3.04

Magnetic Relaxation of Nuclei $I = \frac{1}{2}$.

During the process of relaxation some nuclei must yield the energy absorbed during perturbation of the equilibria by the rotating magnetic field. The nucleus is quite isolated mechanically from its surroundings and spontaneous emission is virtually impossible. Energy-state changes can only be made by interaction with a magnetic field fluctuating at the Larmor frequency ($\omega = 2\pi\nu$ where ν is the frequency for transitions equation 2 -2). Random high frequency fluctuations in liquids are produced by magnetically active nuclei undergoing Brownian motion producing fluctuating fields at the neighbouring nuclei. Such frequency fluctuations can be shown[82] to contain all frequencies below that appropriate to the correlation time τc of the Brownian motion and in inviscid liquids this includes the nuclear resonance frequency, figure 2 - 1(a). Brownian motion provides the internal relaxing field for both longitudinal and transverse relaxation and for interactions between like spins ($I = \frac{1}{2}$) both T_1 and T_2 are normally equal. Since the intensity of the field is proportional to τc the relaxing field is sensitive to viscosity changes,[83, 84,] figure 2 - 1 (b). As viscosity increases both T_1 and T_2 will become shorter resulting in a broader line which is less easily saturated. In proton spectra

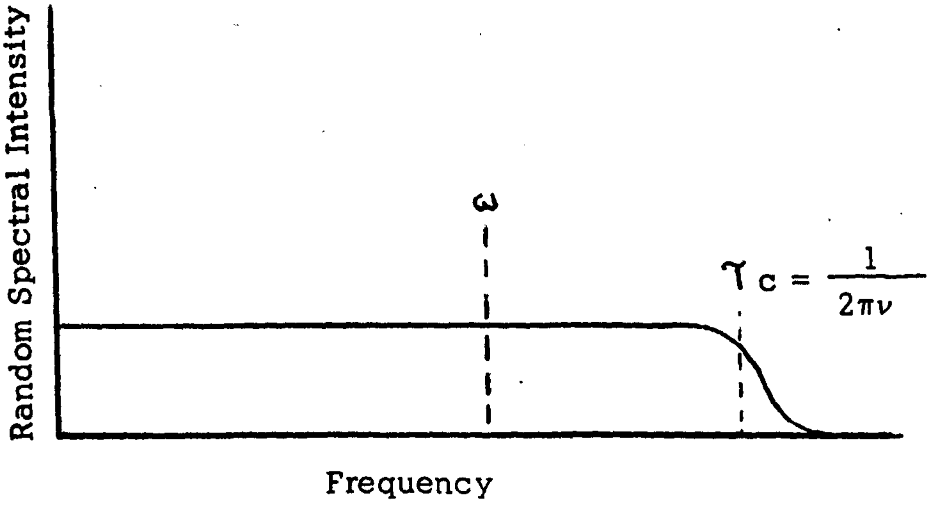


Figure 2 - 1 (a) Frequency Spectrum due to random motion

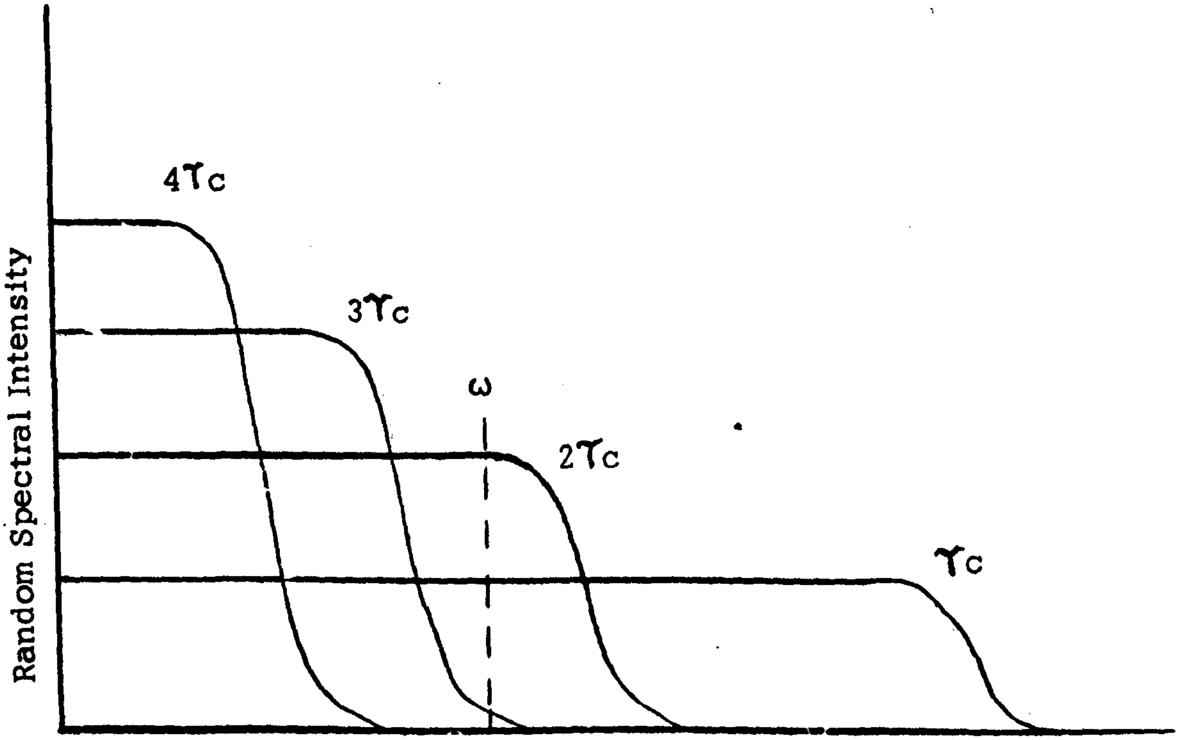


Figure 2 - 1 (b) Effect of τ c on random spectral intensities

of organic complexes small differences in the viscosities of relative solutions may pass unnoticed since the natural linewidths can be much less than the homogeneity of the magnet. However when linewidths are greater than the homogeneity and this is more likely in the study of inorganic complexes, viscosity broadening can become very noticeable and must not be confused with exchange broadening which is discussed later. In highly viscous media where motion is considerably restricted T_1 need no longer equal T_2, the former becoming longer due to the small relaxing field while the latter is shorter due to direct through-space spin-spin interaction.

When the interaction is between unlike spins, T_2 can have a smaller value than T_1.[76(a)] A spin-coupled nucleus which is relaxing very rapidly can also reduce T_2 and not T_1.[76(b)] Thus for inorganic nuclei with $I = \frac{1}{2}$ there can exist the situation of easy saturation due to a long T_1 but a broadened line due to a short T_2.

Electric Quadrupole Relaxation.

Nuclei of spin angular momentum quantum number $I = \frac{1}{2}$ possess a spherical charge distribution. For nuclei with $I > \frac{1}{2}$ relaxation times are usually much shorter than is predicted by the magnetic relaxation mechanisms discussed above. Such nuclei possess a non-spherical charge distribution resulting in the nucleus experiencing a torque if placed in an electric field gradient. These field gradients can originate in the electron cloud which surrounds the nucleus and which is distorted by bond formation. Fluctuations occur in field gradient direction as the nucleus undergoes Brownian motion and such fluctuations can contain the Larmor frequency which causes quadrupole relaxation in the same manner as for magnetic relaxation.

Theoretically and experimentally it has been shown[76(c)] that

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{3}{40\pi}\left(\frac{2I+3}{I^2(2I-1)}\right)\left(1+\frac{A^2}{3}\right)\left[\frac{eQ}{\hbar}\,\frac{d^2V}{dz^2}\right]^2 \tau_c \qquad (2-3)$$

where Q is the quadrupole moment of the nucleus of spin I, A is an asymmetry factor which is zero for an axially symmetrical system, $\frac{d^2V}{dz^2}$ is the maximum component of the electrical field gradient tensor at the nucleus and τ_c is the correlation time of the motion which produces changes in the field gradient direction. The derivation of the equation assumes τ_c is such that the condition of extreme narrowing holds i.e. $\omega\tau_c \ll 1$ where ω is the Larmor frequency of the nucleus at the chosen magnetic field.

The value of Q is constant for a given nucleus but conversely the value of the field gradient $\frac{d^2V}{dz^2}$ depends entirely on the environment and thus the linewidth of a quadrupole nucleus can vary considerably depending on its surrounding configuration.

Gordy[77] has discussed the source of field gradients in diamagnetic molecules and stated that virtually the whole of the gradient originates from distortion in the bonding electrons near the nucleus.

Limited knowledge of the detailed distribution of electrons in the molecule restricts the calculation of values for the field gradients. It is possible however to recognise extremes. An isolated monatomic ion has its electron spherically distributed around the nucleus producing a zero field gradient. Hence any nucleus in a molecule whose substituents approach spherical symmetry would be expected to lie in a region of small field gradients. Using observed relaxation rates from n.m.r. linewidths small field gradients have been found for octahedral, tetrahedral, and, surprisingly, planar and x - y - x linear molecules. Such conformations are also axially symmetrical.

At the other extreme there are environments where the whole of the bonding electronic shape is located at one side of the nucleus producing a highfield gradient. If the charge distribution is not axially symmetrical the symmetry term of equation 2 - 3 also becomes greater than unity. Relaxation times will be small and hence the linewidth large.

The equation for quadrupole relaxation also contains the term τc the correlation time. From Debye's formula τ c is proportional to the viscosity of the solution η

$$\tau c = 4\pi \eta a^3 / 3KT \qquad (2 - 4)$$

where a is the effective molecular radius, K, is the Boltzmann constant and T is the absolute temperature. Therefore the linewidth of a particular species will be proportional to viscosity. The term $\frac{4\pi a^3}{3}$ indicates that τ c is also a function of molecular volume, this having its corresponding effect on linewidths, and so it can be seen that molecular configuration can make two quite different contributions to quadrupole relaxation one via τ c and the other via the field gradient.

C. The Effect of Chemical Equilibria and Molecular Motion on N.M.R. Spectra.

The longitudinal relaxation time T_1 must be longer than 0.1 sec. if high resolution spectra are to be obtained. The long time scale inherent in n.m.r. spectroscopy allows many phenomena occurring in a shorter time to affect the resonance signal; this includes chemical exchange.

Exchange between Two Different Chemical Environments.

a) Slow Exchange.

If the two observed nuclei are present in chemically different environments, then separate signals are generally recorded for each environment. Each nucleus is partly shielded from the full strength of the applied magnetic field by the action of the rapidly moving electrons and the degree of shielding is a characteristic of a particular chemical environment. The resonance positions are thus chemically shifted.

When no exchange occurs two separate signals will be observed. Providing the chemical shift difference between the two sites A and B is sufficiently large two distinct signals will also be seen when the rate of exchange is slow. However line broadening of both resonances will be observed in excess of that from the normal spin-spin relaxation mechanism. If no overlap of the resonances occurs then it may be shown[74(a)] that for resonance A the linewidth is given by the equation

$$T_2^{-1} = T_{2A}^{-1} + \tau_A^{-1} \qquad (2 - 5)$$

where τ_A is the first order lifetime of the nucleus in site A, and T_{2A} and T_2 are the transverse relaxation times in the presence and absence of exchange.

The resonance of B has similar properties and thus an estimate of τ_A and τ_B can be made from linewidth measurements.

b) Very Fast Exchange.

For conditions of fast exchange only a single line is observed,[74(b)] resonance absorption occurring when the radio-frequency ω has the value

$$\omega = p_A \, \omega_A + p_B \, \omega_B$$

where p_A and p_B and ω_A and ω_B are the respective fractional populations and resonance positions of signal A and B.

When exchange is sufficiently fast the linewidth of the single resonance is independent of the exchange process and is determined by the spin-spin relaxation mechanism only. For this condition the linewidth is given by

$$T_2^{-1} = p_A \, T_{2A}^{-1} + p_B T_{2B}^{-1} \qquad (2 - 6)$$

where T_{2A} and T_{2B} are the relaxation times of the two species. If exchange rates do contribute to the linewidth then the above equation becomes modified to

$$T_2^{-1} = p_A T_{2A}^{-1} + p_B \, T_{2B}^{-1} + p_A^{2} p_B^{2} \, (\Delta \omega_A - \Delta \omega_B)(\tau_A + \tau_B)$$

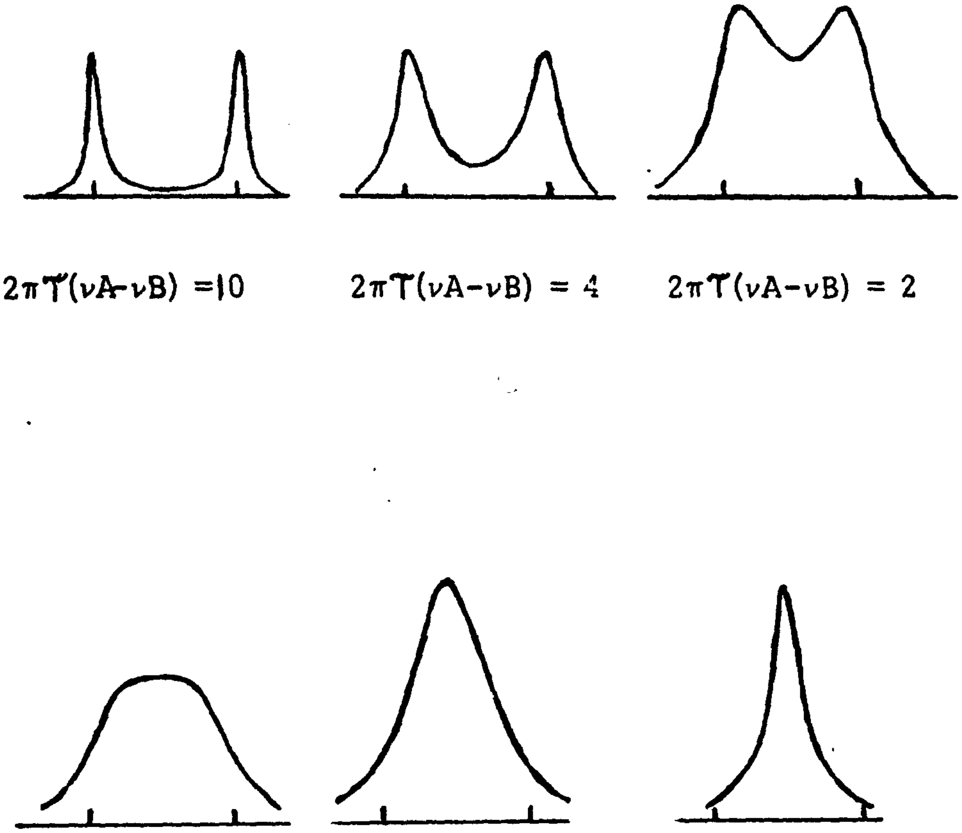
The linewidth in any high resolution experiment is limited by inhomogeneity of the main magnetic field and so clearly there is a limit to the contribution from exchange which can be measured without resorting to transient methods such as spin echoes techniques.

c) Intermediate Rates of Exchange.

Gutowsky and Holm[78] have indicated the changes in line shape function for increasing exchange rates between two positions from very slow to very fast as shown in figure 2 - 2. The population of the two sites is assumed equal and τ is equal to half of the lifetime on either site. Increase in the rate of exchange is seen to lead to a gradual coalescence of the two resonances.

d) Several Chemical Species.

If exchange is sufficiently fast then only a single resonance will be observed. Multiple lines will occur if the exchange is slow, and the intensities of the lines will be governed by the population densities of the sites. Intermediate rates of exchange will lead to the gradual coalescence of the separate lines in a similar manner to that outlined for exchange between two sites.



$2\pi\tau(\nu A-\nu B) = 10$ $2\pi\tau(\nu A-\nu B) = 4$ $2\pi\tau(\nu A-\nu B) = 2$

$2\pi\tau(\nu A-\nu B) = \nu 2$ $2\pi\tau(\nu A-\nu B) = 1$ $2\pi\tau(\nu A - \nu B) = 0.5$

Figure 2 - 2 Change of line shape for increasing exchange rate between two positions with equal populations. The intensities are not on comparable scales

The Effect of Exchange on Spin Multiplets.

Exchange of atoms or groups can broaden and collapse spin multiplets in much the same way as discussed for chemically shifted lines. Under conditions of slow exchange the components of spin multiplets are sharply defined. As the rate is accelerated they are broadened and then caused to overlap until finally a single line results. The critical factor which determines when collapse occurs in the separation of adjacent lines. When the relation $2\pi J \Upsilon = \sqrt{2}$ is satisfied, where J equals the coupling constant, the lines of a spin multiplet are broadened sufficiently for the individual lines to be no longer discernible.

Quadrupole Relaxation and Chemical Exchange.

Chemical exchange can also be a source of quadrupole relaxation. As was previously described such relaxation is brought about by changes in field gradient direction as the molecule undergoes Brownian motion and similar changes will occur if the groups attached to a quadrupole nuclei rearrange themselves. A molecule with a high field gradient when exchanging via a short-lived transient state to a conformation with the same high gradient, but in an opposite direction, is one such example. A molecule with a lowfield gradient exchanging via a short-lived transient state with a higher field gradient, to another lowfield gradient conformation will also produce a series of torque impulses at the nucleus.

If τ is the average lifetime of a molecule between exchanges and ω the Larmor frequency, then for fast exchange such that $\tau \ll \frac{1}{2\pi\omega}$ exchange relaxation is small but becomes more important as τ lengthens and is at a maximum when $\tau = \frac{1}{2\pi\omega}$. For a long τ, the exchange relaxation becomes once again small.

Thus a quadrupole nucleus with attached ligands producing a high field gradient may nevertheless have a narrow linewidth if ligand exchange is sufficiently fast, since this can produce changes in field gradient direction several times during one Larmor period, and these have little opportunity to cause interaction.

D. The Use of N.M.R. as a Quantitative Analytical Tool.

Several approaches are open to the chemist who requires quantitative analytical data from his spectra. The choice in most cases will be governed by factors such as exchange reactions, number of chemically different species in solution and relative intensities and linewidths of the resonances. The Bloch equations give the shape function of the absorption curve at frequency ν as

$$\alpha(\nu) = \frac{2T_2k}{1 + 4\pi^2(\nu o-\nu)^2T_2^{\,2}} \qquad (2 - 7)$$

where K is a number which includes the spectrometer constants and number of nuclei in the detector coil, T_2 is the transverse relaxation time and νo the position of maximum peak height. Therefore, provided no saturation occurs, the relative intensities of two or more absorption bands recorded in the same spectra are proportional to the number of nuclei in the chemical groupings. Spectrometer conditions are assumed to be constant throughout the recording and $T_1 \approx T_2$.

Saturation occurs when the population of nuclei in the lower energy level becomes very small (i.e. the energy states are equalised) which is caused by the application of too intense a radiofrequency field. Saturation is greatest for the radiofrequency which gives the shape function $g(\nu)$ its maximum value and it may be shown that.[74(c)]

$$Zo = [\, 1 + \gamma^2 H_1{}^2 T_1 T_2]^{-1} \qquad (2 - 8)$$

where Zo is the saturation factor for the maximum value of $g(\nu)$, γ is the magnetogyric ratio and H_1 is the strength of the oscillating radiofrequency. Under conditions of no saturation the signal intensity is proportional to the strength of the applied radiofrequency. When saturation occurs the signal not only decreases in size, but the line broadens because the diminution of $g(\nu)$ is most effective at the frequency corresponding to the line centre.

Absolute intensity measurements are very difficult to make due to the dependence of the signal strength on many instrumental factors such as the filling factor of the receiver coil, the effective bandwidth of the amplifier and its noise factor. However if absorption band intensities are referred to a calibration curve obtained from standard samples, then the relative concentrations of a nuclei in different samples can be compared. For this purpose the entire spectrometer must have adequate stability linearity and reproducibility; measurements should also be made at the same radiofrequency.

The measurement of the intensity or even linewidths of broad resonances present several difficulties, especially when base line instabilities or high signal-to-noise ratio of an instrument complicate their detection. On certain spectrometers this task is facilitated by observing the signal in the derivative instead of the absorption mode. Quantitative information may still be obtained from such spectra, the product of peak-to-peak height and peak-to-peak separation being proportional to the concentration of nucleus detected provided the field modulation amplitude is proportional to the linewidth of the resonance. It is often difficult to know exactly when the modulation amplitude is correct for the linewidth concerned. Too high an amplitude produces broadening of the line, while too low an amplitude reduces the intensity of the signal and it has been suggested[79] that intensity or linewidth measurements using this technique are subject to modulation broadening even though the spectra were recorded using the correct modulation amplitude. If a narrow resonance overlaps a broad signal then further difficulties are encountered. The modulation frequency used must be smaller than the width of the narrow line to avoid producing side bands of the latter and if any direct comparison of the two is required then the amplitude must also be proportional to the narrow signal. This will of course reduce the intensity of the broad signal and separate spectra may have to be run using conditions ideal for each signal in question. It can be seen therefore that it is always advantageous to obtain absorption mode spectra if the conditions allow.

Several methods are available for the measurement of spectral band areas. If exchange reactions are slow then the absorption mode resonances will be Lorentzian provided no overlap of signals occurs and it is feasible to obtain areas from the product of the peak height and width at half amplitude. Alternatively the areas may be measured using a planimeter, by tracing or weighing. These latter procedures are preferred when the line shape is non-Lorentzian. Some spectrometers provide electronic integrating circuits applied to the output stage, but these are usually only of use when no overlap of the resonances occur. Commercial instruments are available for resolving overlapping signals although, with practice, a surprising degree of accuracy can be obtained in simple cases when the curves are resolved by eye.

Quantitative information can also be obtained in certain cases from chemical shift measurements. If fast exchange reduces multiple signals to a single resonance then the position of this resonance will be a weighted average of the individual chemical shifts and concentrations. This procedure however depends on knowledge of the chemical shifts when no exchange occurs and the lifetime of the nucleus should be the same at each site.

CHAPTER 3.

EXPERIMENTAL.

A. Preparation of Solutions.

General information on solution preparation is given below, detailed discussions being included with the relevant investigations for the sake of continuity.

Wherever possible solutions were prepared from 'AnalaR' reagents. Aluminium nitrate was not available as the 'AnalaR' salt and Grade A Hopkin and Williams $Al(NO_3)_3\ 9H_2O$ (maximum Fe content 0.01%) was therefore used. Tests showed that even twice this concentration of iron did not cause any noticeable paramagnetic broadening of linewidths in the n.m.r. investigations. Aluminium chloride solutions were prepared by refluxing 'AnalaR' aluminium wire in the requisite concentration of 'AnalaR' hydrochloric acid (approximately 10 ml conc. HCl s.g. 1.18/g. Al.). Solution concentrations ranged from 0.1 to 10 M for both n.m.r. and Raman investigations. Binary and ternary aqueous systems were prepared by mixing weighed aliquots of the relevant pure salt or acid solution in 10, 25, 50 or 100 ml volumetric flasks and making up to volume with distilled water.

B. Analysis.

All analyses were made in duplicate on pure salt or acid solutions rather than on the binary or ternary systems thus avoiding possible interference due to complexing. Aluminium analyses were made using a standard e.d.t.a.-zinc sulphate titration procedure with Eriochrome Black T indicator.[85(a)] Fluoride and chloride concentrations were determined by gravimetric analysis as calcium fluoride [85(b)] and silver chloride[85(c)] respectively. Phosphate concentrations were determined on diluted solutions by titrimetry.[85(d)]

C. Instrumental Techniques.

1. Nuclear Magnetic Resonance.

Two spectrometers were used, an A.E.I. RS2 and a Bruker Spectrospin H-F-X_5. The former was employed for the first two years of the investigation until replaced by the Bruker. It was possible to record over twice the number of spectra in one third of the time with the latter instrument owing to its higher sensitivity and stability.

A.E.I. RS2.

The following nuclei were observed at the frequencies indicated

^{19}F, ^{1}H	60 MHz
^{27}Al	15 MHz
^{31}P	20 MHz

Sample tubes of 5 mm external diameter were used for the ^{19}F investigations and 9 mm external diameter for the ^{27}Al and ^{31}P experiments. Samples were not spun since only relatively broad signals were observed in the ^{19}F studies ($>$ 15 Hz) and the spinning noise made this undesirable in the ^{27}Al and ^{31}P investigations. Wherever possible signals were observed in the absorption mode but when broad resonances were encountered these were recorded as their derivative signal using a field modulation frequency of 23 or 10 Hz. The latter frequency was used when broad and narrow resonances ($<$ 23 Hz but $>$ 10 Hz) were observed during the same sweep, thus avoiding production of side bands on the narrow resonance. Great care was still required to avoid distortion of such resonances due to the use of too large a filter constant. For this reason derivative spectra were recorded at a sweep speed sufficiently slow for sharp line delay to be negligible.

Variable-temperature investigations were undertaken using the standard RS2 equipment. Sample size was restricted to 5 mm diameter tubes and spinning was not feasible owing to the increase in noise at high or low temperatures. The temperature of a sample was obtained by replacing the sample tube with a similar size tube containing a precalibrated thermocouple immersed in oil. Temperature control was ± 1.5°. The calibration of spectra and measurement of chemical shifts were made with sidebands produced by normal field modulation techniques.

Bruker Spectrospin H-F-X_5.

^{1}H, ^{19}F, ^{27}Al and ^{31}P resonances were detected at the following frequencies

^{1}H	90M Hz
^{19}F	84.66 M Hz
^{27}Al	23.45 M Hz
^{31}P	36.43 M Hz

Spinning sample tubes of 5 mm external diameter were used for both ^{1}H and ^{19}F investigations and 10 mm tubes for the ^{27}Al and ^{31}P experiments. The latter were also spun, no detrimental effect being produced on the signal-to-noise ratio even when high transmitter powers were employed. The resonances were observed in the absorption mode. The magnetic field was continuously modulated at a frequency of 3.8 k Hz. A modulation index* of 1.8 gave the optimum signal-to-noise ratio for ^{1}H and ^{19}F resonances and resulted in the main absorption band being recorded, the first side bands being phased to zero. For the ^{27}Al and ^{31}P signals the maximum signal-to-noise ratio was obtained using a modulation index of 0.5 and this resulted in the recording of the first left- or right-hand side band of these resonances, the main absorption signal being reduced to zero. The first sidebands were adjusted by phase controls to give a positive signal. Every sweep amplitude of the instrument was calibrated by the manufacturers in Hz per cm. in relation to the spectra drawn by the pen recorder and this

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* Modulation index = $\gamma \times \frac{\text{Modulation frequency}}{\text{Modulation amplitude}}$ where γ is the magneto-gyric ratio.

was further confirmed by a counter which gave a continuous calibration of the recorder for any sweep amplitude used.

Owing to the base line stability and good signal-to-noise ratio, all resonances could be observed in the absorption mode and it was not necessary to resort to derivative investigations even for broad signals.

Variable-temperature studies were made using the standard Bruker equipment. Temperature control was ± 0.75°, the temperature being monitored continuously by a thermocouple placed to within 2 mm of the base of the sample, the temperature-controlled gas flow passing over the sample tube down on to the thermocouple. Sample tube size varied from 5 mm for ^{1}H, ^{19}F and ^{31}P investigations to 10 mm for the ^{27}Al studies and all samples were spun.

Chemical Shift Measurements.

Chemical shifts were reported as x ppm upfield or downfield of a standard signal. When internal standards were not compatible with a system, an external standard was included in a fine capillary tube, the sample being spun. Since this was not feasible for 9 mm tubes on the RS2 instrument the standard procedure of substitution had to be employed with the position of the resonances being noted on a precalibrated recorder paper or oscilloscope graticule in the order standard, sample, standard. This procedure minimised inaccuracies due to drifting.

When no internal standard was present the method of substitution was also employed on the Bruker and it was possible to reduce drift to 4 Hz hour.

Quantitative Studies.

A discussion of the precautions necessary for quantitative n.m.r. investigations has already been given in the previous chapter. The following techniques were employed during this investigation. The area under a resonance is often referred to as its 'intensity' and this term, therefore, is never used to describe the height of a peak.

Transmitter Power Calibration.

During studies with the Bruker it became necessary to compare the peak areas of resonances of widely different linewidths necessitating the use of different transmitter powers. A calibration curve of signal intensity against transmitter power was therefore prepared in order to check the various power settings.

The ^{27}Al resonance of the aquated aluminium ion at various concentrations was used. High salt concentrations (2.0 M or above) gave a viscosity-broadened signal which enabled high transmitter powers to be calibrated without saturation, while dilute solutions (1.0 M or less) gave a sufficiently narrow signal for a good signal-to-noise ratio to be obtained at low powers. Sufficient overlap between the concentrated and dilute solutions allowed a calibration from 0 to 50 dbs transmitter power to be obtained.

General Techniques.

The linewidths and peak heights of all resonances were compared at different transmitter powers in order that the maximum power could be chosen which caused no saturation of the signal. The same sample tube was used to record all spectra for a given series of quantitative estimations. This eliminated any inaccuracies due to variations in the internal diameter of different tubes. Care was also taken to avoid distortion of a signal due to the use of too high a filter constant. This precaution was particularly necessary when comparing narrow and wide resonances.

Peak Intensity Measurements.

Several techniques were employed to measure peak intensities. If no overlap of resonances occurred and exchange rates were slow (line shapes approximately Lorentzian) then the product of peak height and peak width at half amplitude was taken. No significant difference was found between this procedure and weighing cut-out tracings from good quality tracing paper. A precision of at least ± 5% was estimated for both procedures. The latter method was preferred when line shapes were modified by exchange reactions.

Multiple overlapping resonances were resolved using a Dupont Model 310 Curve Resolver the signal shape being standardized to a Lorentzian Peak. The relative intensities were obtained for the resolved resonances by using an integrating circuit provided on the instrument. Up to five overlapping resonances could be resolved on this instrument.

Viscosity Measurements.

Viscosity measurements of solutions were made using a Well's Brookfield Micro Viscometer. The calibration of this instrument was checked using 20 and 50 wt. % aqueous sucrose solutions prepared from 'AnalaR' sucrose. These two solutions gave viscosities of 1.695 and 12.40

cP respectively at 25°.

Whenever it was necessary to measure viscosities at different temperatures the temperature of the viscometer could be varied by pumping water from a thermostatic bath through the viscometer jacket. By using this procedure temperatures could be held to within ± 0.5°.

2. Raman Spectrometer.

Raman spectra were obtained using a Cary Model 81 Raman Spectrometer. Samples were irradiated with the 435·835 nm mercury line. Initial work was carried out using a filter solution consisting of ethyl violet, iso-propyl alcohol and o-nitrotoluene (1.09 g : 3 litre : 125 ml) to filter extraneous mercury lines. Due to the poor response of the instrument at the time of this work and to the rapid deterioration of the filter solution (half-life less than one day) this was discarded and replaced by pure iso-propyl alcohol which resulted in a ten-fold increase in sensitivity. As a result of this action special care was taken to note all mercury lines which appeared in the regions of the spectrum under examination.

Standard 7 mm diameter sample tubes were used throughout this work, the sample temperature being approximately 35°.

Intensity calculations and resolution of overlapping bands were made using the Dupont Model 310 Curve Resolver, the shape of the bands being standardized to a Guassian curve.

D. pH Measurements.

pH measurements were made using either an E.I.L. Model 23A or a Radiometer Model 111 TC pH meter. Both instruments were standardized with pH 4.0 buffer prior to use.

CHAPTER 4.

HYDROLYSIS OF ALUMINIUM SALTS.

In order to facilitate a comprehensive discussion the results of aluminium hydrolysis investigations are divided into two sections; Part I Room Temperature Studies; Part II Variable Temperature Studies. A general discussion reviewing the results of both sections is then given in Part III.

PART I.

ROOM TEMPERATURE STUDIES.

Three nuclei are available for studying hydrolysed aluminium species, these being ^{1}H, ^{17}O and ^{27}Al. Proton investigations would be expected to be hindered by rapid exchange mechanisms at room temperature[44-46, 49] resulting in a single resonance representing all species, the linewidth or chemical shift of which would be difficult to interpret. Equipment was not available for detecting ^{17}O on either the RS2 or the Bruker and so the choice of nucleus for the major section of this study fell to ^{27}Al.

The ^{27}Al resonance of the aquated aluminium ion has been detected by several workers[50-52] and a linewidth of between 30 to 50 Hz noted, the resonance usually having been recorded as the derivative.

The ^{27}Al nucleus has a quadrupole moment ($Q = 0.149 \times e \times 10^{-24} cm^2$) and so its linewidth will be governed by all factors given in equation 2 - 3 including quadrupole relaxation mechanisms and viscosity. Quadrupole relaxation will be related to all processes causing a field gradient at the aluminium nucleus. Motion of the ion $Al(H_2O)_6^{3+}$ itself can be disregarded since this has octahedral symmetry and zero field gradient. In contrast, free water molecules in motion near the ion should cause relaxation since the ionic charge induces dipoles in the water molecules and these will produce fluctuating field gradients at the nucleus. However the fixed hydration sphere will keep the mobile water molecules at a distance so that the effect will be small.

Relaxation will also be caused by rapid exchange reactions wherein molecules having field gradients are formed. Hydrolysis might be expected to contribute in this way. The oxygen and hydrogen exchange around the aluminium ion might also be expected to cause relaxation since each exchange is accompanied by a pulse of field gradient at the central nucleus. However both exchange rates are considerably lower than the Larmor frequency at the aluminium nucleus so that the condition of extreme narrowing does not apply.

Since τ_c, the correlation time, is related to viscosity the linewidth will also be proportional to solution viscosity and the magnitude of this relationship should be assessed before conclusions can be drawn on equilibria effecting relaxation mechanisms. Accordingly the effect of viscosity was first investigated.

A. Effect of Viscosity on ^{27}Al Linewidths.

Aqueous solutions of aluminium sulphate, nitrate, and perchlorate were prepared, the solution concentration of which ranged from 2.25 M to 0.2 M. Viscosity and linewidth measurements were made on the same solutions and the results are given in table 4 - 1 and figure 4 - 1, measurements being made on the RS2 at 15 M Hz.

Several important factors are immediately obvious from this study. The linewidth for the hexa aquo ion is considerably less than those previously reported (30 - 50 Hz) and the signal was therefore easily recorded in the absorption mode. There could be several reasons for this discrepancy; the homogeneity of the RS2 magnet was considerably better than those used by previous investigators; detection of the aquo ion as a derivative signal had resulted in modulation broadening or the modulation frequency was too large for the linewidth; only highly viscous solutions had been investigated.

Table 4 - 1.

^{27}Al Linewidths at Various Concentrations of Aluminium Sulphate, Nitrate and Perchlorate.

Aluminium Sulphate			Aluminium Nitrate			Aluminium Perchlorate		
Molarity	Viscosity cP	Linewidth Hz	Molarity	Viscosity cP	Linewidth Hz	Molarity	Viscosity cP	Linewidth Hz
1.1	12.8	38	2.2	8.1	13	2.45	7.7	17.0
0.9	8.9	30	2.0	6.5	11	2.20	5.4	12.2
0.8	7.0	25	1.8	4.4	9.2	1.90	4.1	10.0
0.7	5.3	22.5	1.6	3.5	7	1.50	2.6	8.4
0.55	3.9	17.5	1.4	2.8	6.5	0.25	1.4	5.9
0.25	2.1	12.5	1.2	2.2	6.5	0.37	1.05	5.9
0.125	1.25	10.0	0.5	1.3	6			

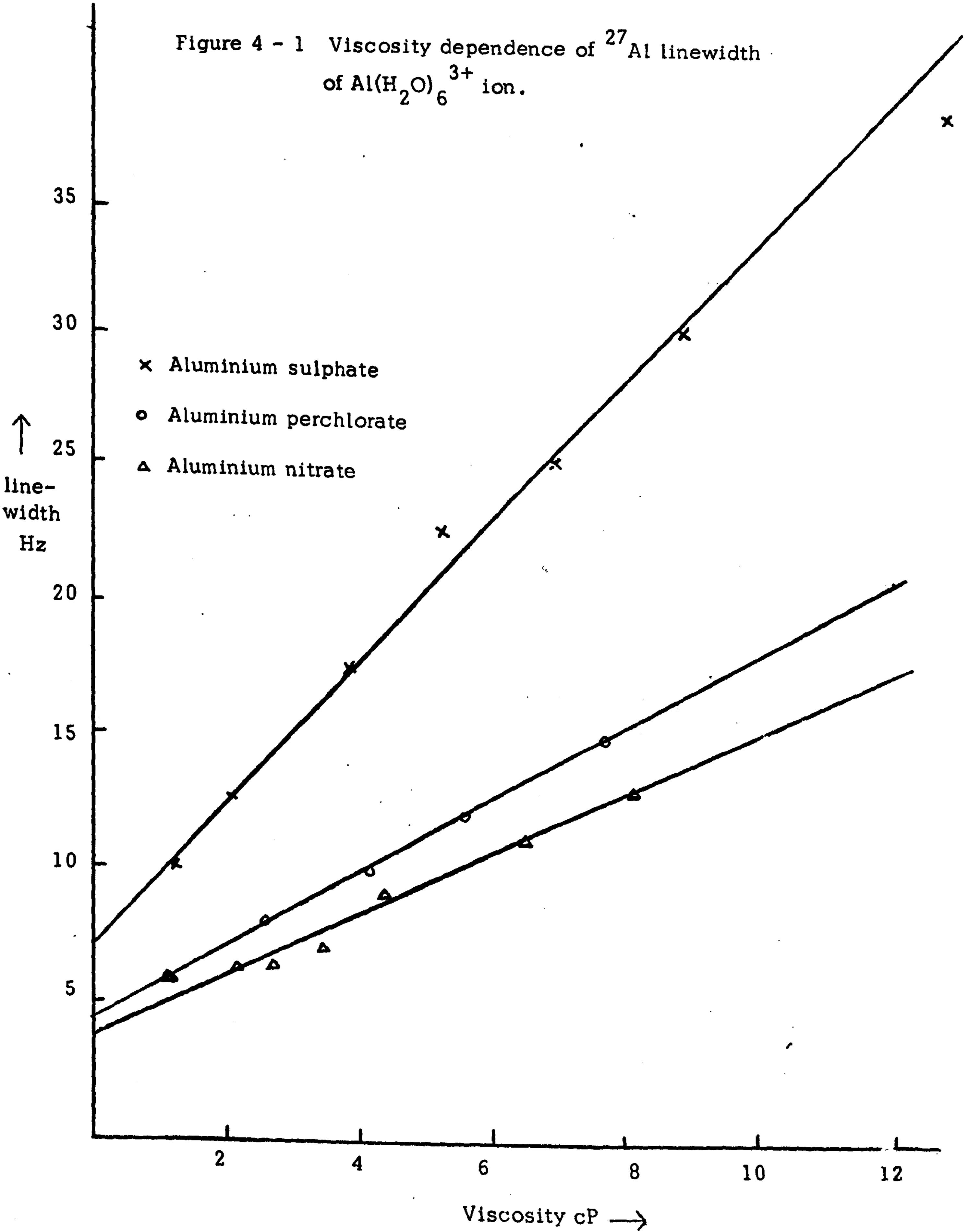


Figure 4 - 1 Viscosity dependence of ^{27}Al linewidth of $Al(H_2O)_6{}^{3+}$ ion.

A straight-line relationship is obtained between viscosity and linewidths for all the salts investigated and the magnitude of this dependence is seen to be quite substantial. However even allowing for an inhomogeneity of 1.5 Hz (the samples were not spun), all plots are seen to have a positive intercept. Such straight line plots with positive intercepts have been found by investigators using nuclei other than ^{27}Al ^{86} so strictly linewidth is not proportional to viscosity but follows a linear equation of the form

$$\Delta\frac{1}{2} = a + b\,(\eta - \eta\omega\ )$$

where $\Delta\frac{1}{2}$ is the linewidth at half amplitude, η is the viscosity of the solution, $\eta\,\omega$ the viscosity of pure water and a and b are constants. Thus one cannot assume direct proportionality between linewidth and viscosity, but where the former has to be corrected for the latter the assumption of such a relation provides a more accurate answer than the uncorrected width.

A closer examination of the viscosity-linewidth graphs reveals a third important factor. The slope of the aluminium sulphate plot is considerably greater than those for either the nitrate or perchlorate. a larger positive intercept is also obtained. Examination of the relative pH's of the solutions showed that while a 1 M aluminium nitrate or perchlorate solution had a pH less than 1, a value of 2.3 was recorded for 0.5 M aluminium sulphate, $Al_2(SO_4)_3$. The addition of nitric acid to reduce the pH of such a solution to less than 1 resulted in a narrowing of the resonance and a series of aluminium sulphate solutions were therefore prepared with added acid to give a pH of approximately 0. The linewidths and viscosities are given in table 4 - 2 and figure 4 - 2.

The graph for acidified aluminium nitrate is also shown in figure 4 - 2 and it can now be seen that both nitrate and sulphate plots show similar relationships. Clearly pH has a marked effect on the linewidth of the aquated aluminium ion. For the reasons discussed previously this could indicate exchange reactions, possibly with a hydrolysed species and this was therefore investigated.

B. Effect of pH on Linewidth.

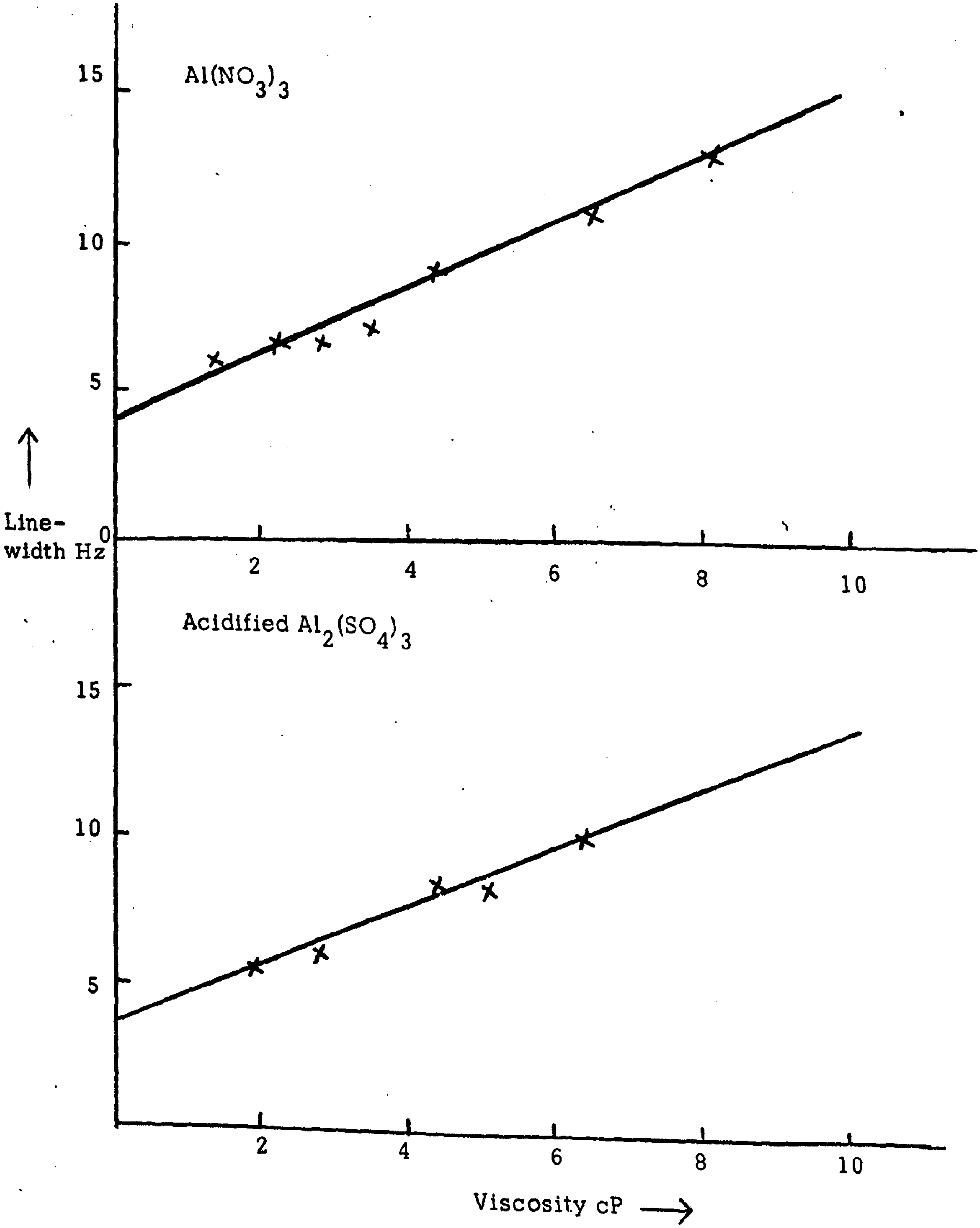
The low acidity of aluminium sulphate solutions would appear to make this salt a suitable subject of linewidth versus pH studies. However such solutions, as discussed later in chapter 5, contain interferring equilibria which would make the results of any investigations inaccurate. Aluminium nitrate was therefore chosen but owing to the high initial pH of any solution, it was first necessary to prepare a stock

Table 4 - 2.

^{27}Al Linewidths at Various Concentrations of Acidified Aluminium Sulphate in 1.6 M HNO_3 at 15 M Hz.

Molarity	Viscosity cP	Linewidth Hz
0.8	6.4	10
0.75	5.1	8.3
0.70	4.4	8.5
0.65	2.8	6.0
0.23	1.9	5.5
0.2	1.65	4.7
0.125	1.5	4.5

Figure 4 - 2 Viscosity dependence of ^{27}Al linewidths of $Al(H_2O)_6^{3+}$ in solutions of aluminium nitrate and acidified aluminium sulphate



solution of lower acidity. This was obtained by adding 1 M sodium aluminate dropwise to a 2 M aluminium nitrate solution until a pH of 3.25 was obtained. Slight temporary precipitation occurred as the pH was approached but this was easily dissolved by shaking the solution. Above the pH the gelatinous hydroxide was difficult to redissolve. Aliquots of this solution were adjusted to different pH's by addition of 7 N HNO_3 and then made up to a constant volume to give a final aluminium concentration of 1.4 M. This procedure limited the concentration of foreign ions in the system and minimised the viscosity differences between different aliquots. The results of viscosity linewidth and pH measurements are given in table 4 - 3 using the RS2 at 15 M Hz.

The observed linewidths are seen to decrease with pH even though the viscosity of the corresponding solutions increases. As has been previously discussed, such changes are unlikely to be caused by the changes in rate of proton or oxygen exchange of the aquated aluminium ion since both these are slower than the Larmor frequency of the ^{27}Al nucleus at the field used. The results would appear to indicate a mechanism where the linewidth is a result of exchange between $Al(H_2O)_6^{3+}$ with a long relaxation time and small field gradient and a

Table 4 - 3.

^{27}Al Linewidths of 1.4 M Aluminium Nitrate at Varying pH.

Sample	pH	Viscosity cP	Observed Linewidth Hz	Linewidth in Hz corrected for Magnetic Inhomogeneity^{+} and Viscosity*
1	3.25	1.78	19.2	17.7
2	3.15	1.84	16.0	14.0
3	3.05	1.93	15.4	12.8
4	2.96	1.96	14.6	11.9
5	2.84	2.10	13.6	10.3
6	2.62	2.35	11.7	7.7
7	2.31	2.76	10.4	5.7
8	1.8	2.78	8.8	4.7
9	0.5	2.80	6.4	3.1

+ 1.5 Hz magnetic inhomogeneity subtracted since samples not spun.

* Viscosities of all solutions corrected to viscosity of sample 1.

second species with a shorter relaxation time, the concentration of which is pH dependent. Such a mechanism could result from monomeric or dimeric hydrolysis of the aquo aluminium ion, the hydrolysed species being the asymmetrical ion with a shorter relaxation time.

The chemical shift of the least and most acid solutions was the same within experimental error (± 0.1 ppm). Therefore exchange between the species could either be very fast, a single line representing all complexes, or slow, the resonances as yet not detected. The two cases will be discussed separately.

1) Fast Exchange

The linewidth of a single line resulting from fast exchange between two lines of width $\frac{1}{\pi T_{2A}}$ and $\frac{1}{\pi T_{2B}}$ may be derived from equation 2 - 6.

$$\text{Linewidth} = \frac{1}{\pi T_2} = \frac{PA}{\pi T_{2A}} + \frac{PB}{\pi T_{2B}}$$

From the monomeric equilibrium (1 - 2) and adding the water of hydration we have

$$\frac{[Al(H_2O)_5OH^{2+}]}{[Al(H_2O)_6{}^{3+}]} = \frac{K_1}{[H^+]}$$

If environment A is due to $Al(H_2O)_6^{3+}$ and B to $Al(H_2O)_5OH^{2+}$ then

$$PB = \frac{[Al(H_2O)_5OH^{2+}]}{[Al(H_2O)_6^{3+}] + [Al(H_2O)_5OH^{2+}]}$$

and since K_1 is small and $[H^+]$ relatively large then $[Al(H_2O)_5OH^{2+}]$ will be small and PA $\approx$ 1. Thus

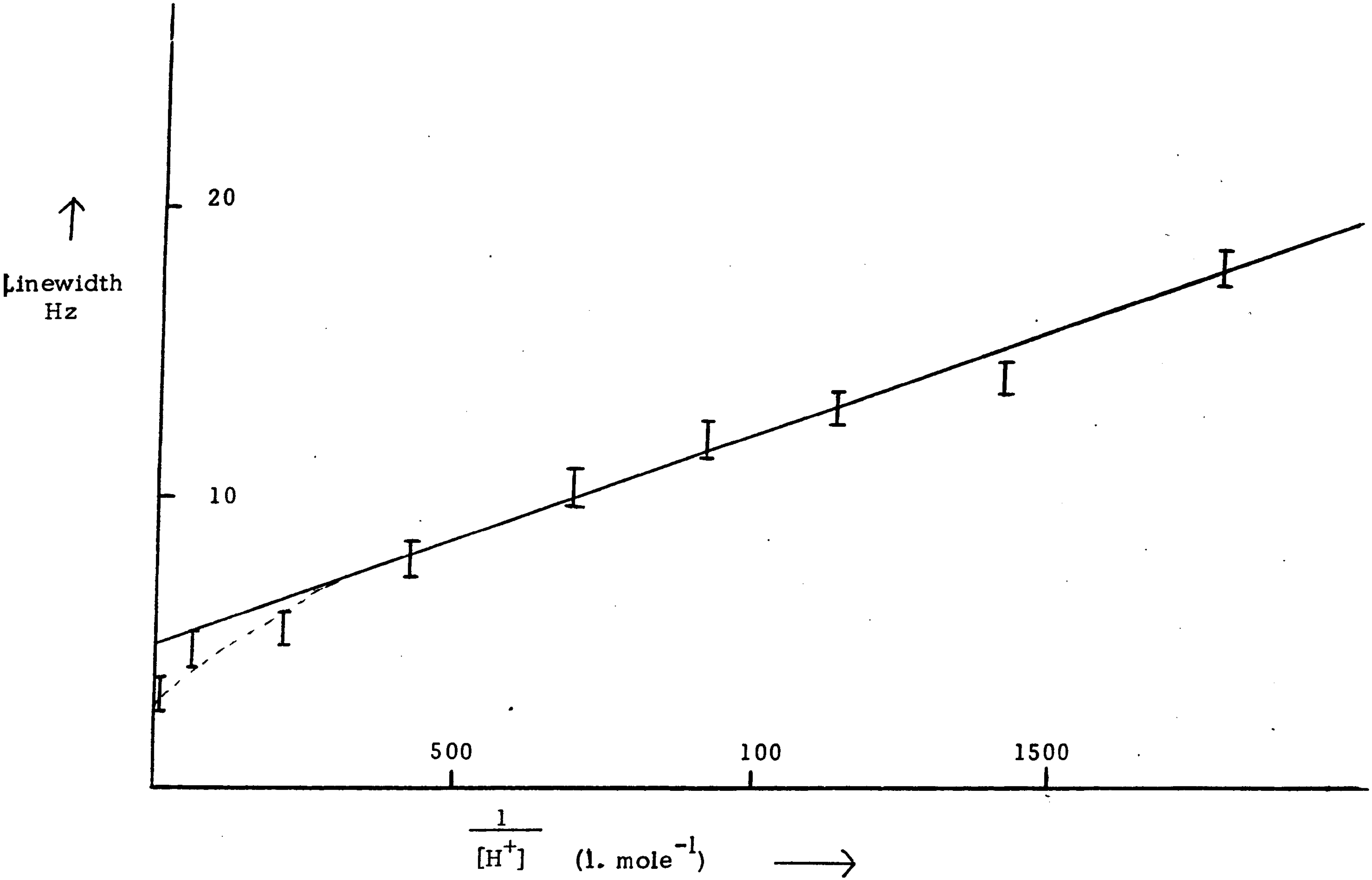
$$PB = \frac{[Al(H_2O)_5OH^{2+}]}{[Al(H_2O)_6^{3+}]} = \frac{K_1}{[H^+]}$$

whence

$$\Delta\frac{1}{2} = \frac{1}{\pi T_{2A}} + \frac{K_1}{[H^+]} \times \frac{1}{\pi T_{2B}}$$

Thus the linewidth if plotted against $\frac{1}{[H^+]}$ should follow a straight line of slope $\frac{K_1}{\pi T_{2B}}$ provided T_{2A} and T_{2B} are independent of pH. The results in figure 4 - 3 where linewidths after corrections for viscosity and 1.5 cps magnetic homogeneity are plotted against $\frac{1}{[H^+]}$, show that a straight line is obtained. This would appear to offer strong support to a monomeric reaction of type (1 - 2) since polymerisation reactions would give rise to a power dependence of $\frac{1}{[H^+]}$, and even

Figure 4 - 3 ^{27}Al linewidths (corrected for viscosity and magnetic inhomogeneity) in 1.4 M $Al(NO_3)_3$ as a function of the reciprocal of hydrogen-ion concentration.



$\frac{1}{[H^+]^2}$ for dimer formation does not give such a satisfactory fit.

However the slope of the line gives the value of $\frac{1}{\pi T_{2B}}$ as approximately 1000 Hz and this would appear a large width for the ion $Al(H_2O)_5OH^{2+}$ where the aluminium remains octahedrally surrounded by oxygen. The magnitude of this linewidth is comparable to those obtained from trimethyl and triethyl aluminium dimers[80] and it could therefore be suggested that a monomeric equilibrium is followed by polymerisation perhaps involving a non-protolysed molecule giving a species with a broad ^{27}Al linewidth.

The continued fall in linewidth at high acidity is very noticeable and could possibly be due to the onset of direct proton exchange of the type thought to occur for nickel and cobalt.[81] In such exchange mechanisms one molecule of the bound water shell is protonated to form a bound H_3O^+ and this then deprotonates with a bulk water molecule.

2) Slow Exchange.

Slow exchange mechanisms could also affect the linewidth of the aquated aluminium ion. From equation 2 - 5 it is seen that the widths of two resonances undergoing exchange are dependent on Υ the lifetime of the nucleus at each site. Large variations in the relative concentrations of two species would alter the lifetime of a nucleus at each site. Changes of Υ at the $Al(H_2O)_6^{3+}$ site would be small if only the monomeric equilibrium was involved ($K_1 \approx -5.0$). The existence of a second equilibrium capable of influencing Υ only became apparent when using the more sensitive Bruker and the results of these investigations are therefore first discussed in the following sections.

C. The Effect of pH on the Intensity of the ^{27}Al Resonance of the $Al(H_2O)_6^{3+}$ Ion.

Variable intensities of the aquated aluminium ion resonance were first observed when comparing a calibration series of aluminium chloride and nitrate solutions. The areas were considerably less in the former. Preparation of the chloride solution involved refluxing aluminium wire in a slight excess of concentrated hydrochloric acid. During the initial reaction, copious amounts of hydrochloric acid fumes were liberated and consequently it was not surprising to find that the pH of the chloride solutions were higher than those of the nitrate solutions. Acidification of the chloride solution to a pH less than 1.0 resulted in an increase in the intensity (area) of the $Al(H_2O)_6^{3+}$ resonance and a decrease in the linewidth. The intensity of this aquo ion resonance was now compatible with that obtained in a similar concentration of aluminium nitrate. Further acidification of the chloride or nitrate solution resulted in no further increase of the resonance areas. The intensities of a standard calibration series of aluminium chloride solutions before and after acidification are given in table 4 - 4 and figure 4 - 4. They are compared to an aluminium nitrate calibration series containing no added acid. Intensity measurements were made using the Bruker spectrometer at 23.45 M Hz.

It is apparent from these results that the pH of the solution has a profound effect on the intensity of the resonance of the $Al(H_2O)_6^{3+}$ ion. Moreover it would be reasonable to assume that in a series of solutions such as those used in the preceding linewidth studies, the intensity of the resonance should also decrease with increasing pH. Re-examination of these spectra showed this to be so. The reason for not immediately noting this in the linewidth studies using the RS2 was simple. As the linewidths broadened two increases in transmitter power were required to give a satisfactory signal-to-noise ratio. These increases, together with adjustments in gain, gave the impression of constant intensity. With the Bruker, all samples, irrespective of linewidth, could be examined at one transmitter power and gain.

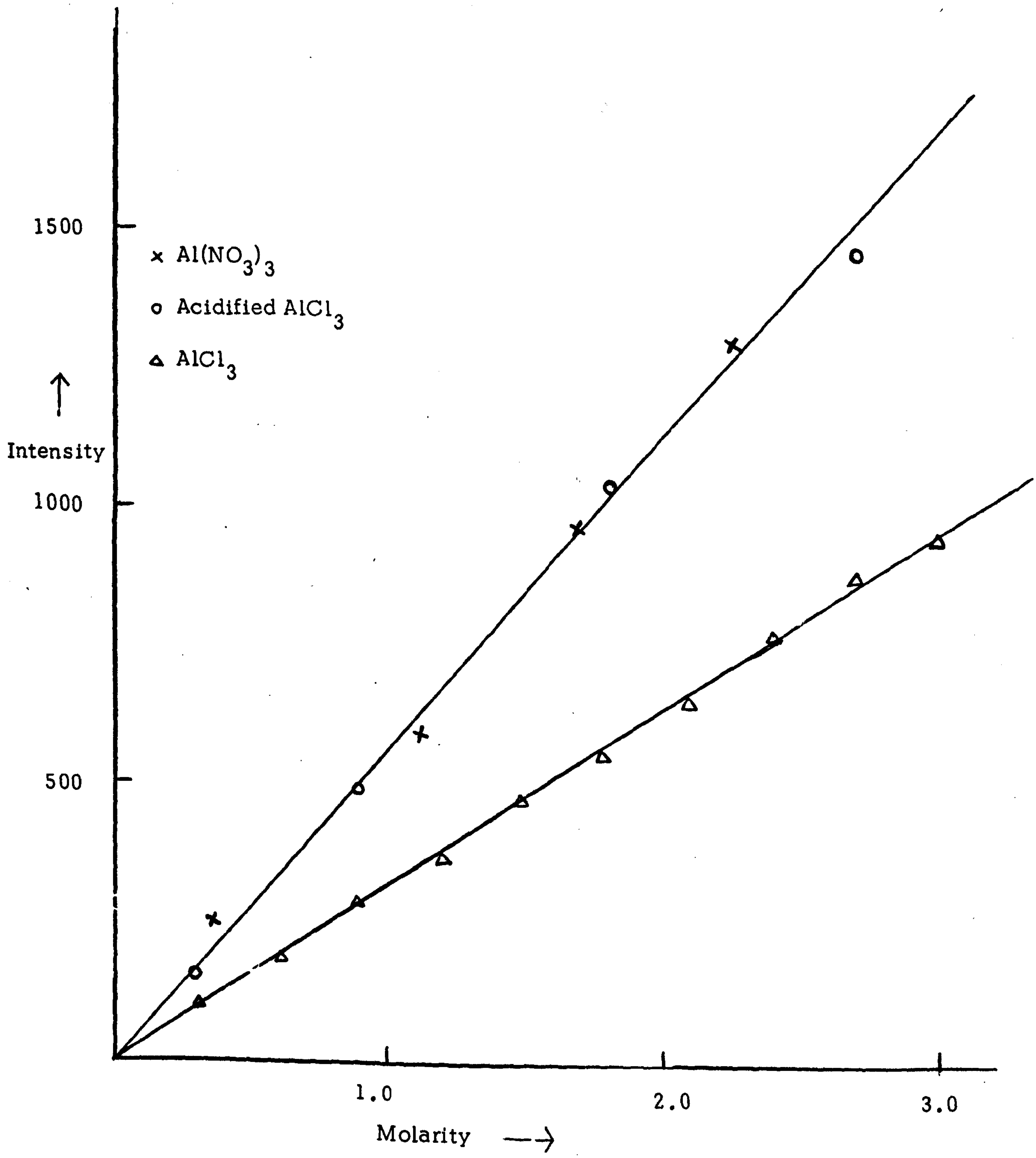
Table 4 - 4.

Intensities* of the ^{27}Al Resonance of $Al(H_2O)_6^{3+}$ in Aluminium Chloride and Nitrate Solutions.

Aluminium Chloride No added Acid			Aluminium Chloride Acid Added			Aluminium Nitrate		
Molarity	pH	Intensity	Molarity	pH	Intensity	Molarity	pH	Intensity
3.0	1.32	957						
2.7	1.40	899	2.7	< 1	1470	2.25	< 1	1300
2.4	1.55	771						
2.1	2.05	650				1.70	< 1	967
1.8	1.95	554	1.8	< 1	1040			
1.5	1.43	472						
1.2	2.78	371				1.12	< 1	590
0.9	2.95	290	0.9	< 1	500			
0.6	3.28	196						
0.3	3.38	111	0.3	< 1	156	0.56	< 1	260

* Expressed in arbitrary units.

Figure 4 - 4 Intensities of the ^{27}Al resonance of $Al(H_2O)_6^{3+}$ in aluminium chloride and nitrate solutions



Evidently a considerable quantity of aluminium was present as the hydrolysed species in the most concentrated sample of aluminium chloride investigated. The detection of this as a separate ^{27}Al resonance was therefore a feasible proposition and a search for this resonance was undertaken.

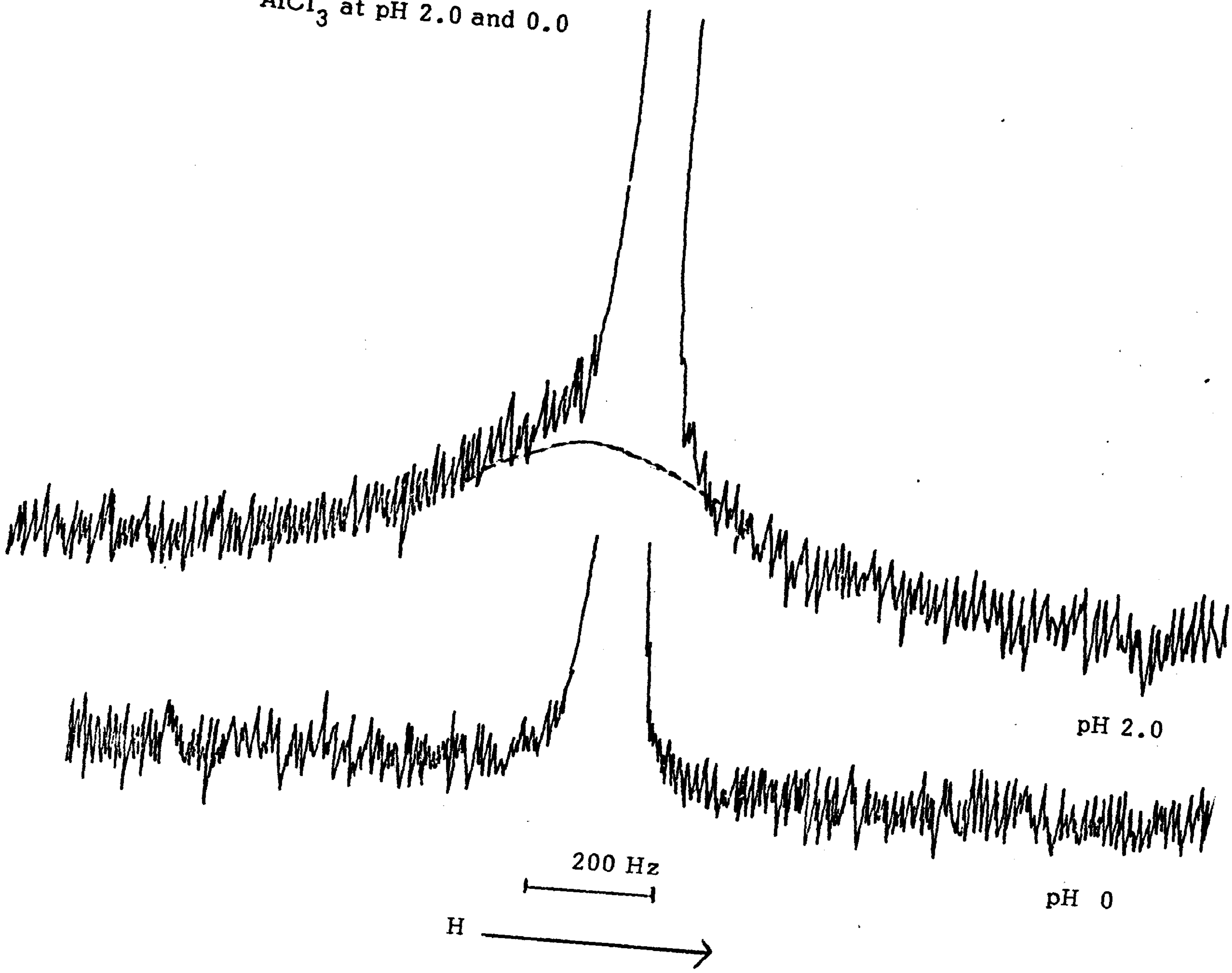
D. ^{27}Al Resonance of Hydrolysed Aluminium.

A 3 M aluminium chloride solution of pH 1.4 was initially used for this investigation. A search, 5 K Hz either side of the aquated aluminium ion revealed no other resonance, the transmitter power used being such that it caused no saturation of the aquo ion resonance. Power was therefore increased to a maximum and the search repeated. Under these conditions a broad signal was just detectable between 3 and 4 ppm downfield of the $Al(H_2O)_6^{3+}$ resonance. The latter was clearly saturated at this R F level and the spectrum appeared similar to those sometimes obtained when the signal phase is maladjusted. Obviously the viscosity of the highly concentrated solution would also hamper detection by broadening any signal present. Two 6 ml. aliquots of the 3 M solution were therefore taken. To one aliquot, 2 ml. of conc. HNO_3 and 2 ml. distilled water were added, the second aliquot being diluted with 4 ml. of distilled water. The spectrum of the acidified sample was then obtained at maximum transmitter power with the phasing adjusted to give a perfectly symmetrical although saturated signal. No hydrolysed aluminium was assumed to be present in this sample the pH being less than 0.1. The spectrum of the unacidified sample was recorded immediately and superimposed above that of the acid sample. Identical instrument settings were used for each spectrum. Figure 4 -5 shows that a second resonance is clearly visible downfield of the aquated aluminium ion. Resolution of the two signals gives a linewidth of 400 to 500 Hz for the hydrolysed species with a chemical shift of 3.4 ppm (79.7 Hz) downfield of the $Al(H_2O)_6^{3+}$ resonance.

The linewidth of the aquated aluminium ion in the presence of the hydrolysed species was obtained by recording the spectra at a reduced transmitter power. A value of 40 Hz was obtained. Equation 2 - 4 shows that the linewidth of a quadrupole nucleus can be related to $\frac{4\pi a^3}{3}$ where a is the molecular radius. Thus

$$\frac{\text{radius of } Al(H_2O)_6^{3+}}{\text{radius of unknown Al ion}} = \sqrt[3]{\frac{40}{450}} = 0.45$$

Figure 4 - 5 ^{27}Al spectrum of 1.8 M $AlCl_3$ at pH 2.0 and 0.0



A value of 0.5 would be obtained for a dimer of radius twice that of the $Al(H_2O)_6^{3+}$ ion, while a trimer or higher polynuclear species would give a value of 0.33 or less. The magnitude of the observed value would appear to offer considerable evidence for significant quantities of dimer in solution. This resonance could still be detected when the concentration of the above solution was halved.

An estimate of the quantity of hydrolysed species present was made in the following manner. The intensity of $Al(H_2O)_6^{3+}$ in the acidified solution above was recorded under conditions of no saturation and compared to the intensity of the $Al(H_2O)_6^{3+}$ resonance in the solution of high pH. The latter solution was then recorded at maximum transmitter power and an estimate of the intensity of the broad resonance made. This was converted to an intensity compatible with the transmitter power used for recording the $Al(H_2O)_6^{3+}$ signals. At these levels the intensity of the hydrolysed species and aquated aluminium ion of the unacidified sample equalled the intensity of aquated aluminium in the acidified sample within an experimental error of ± 7.5 %. Thus the majority of aluminium lost from the $Al(H_2O)_6^{3+}$ resonance on raising the pH of a solution would appear to be present in the broad resonance attributable to dimer.

An estimate of the minimum lifetime τ of the proposed dimer can be made using the equation for the coalescence of two resonances, figure 2 - 2.

$$\tau = \frac{1.4}{2\pi\Delta\sigma}$$

where $\Delta\sigma$ is the difference in chemical shifts of the dimer and $Al(H_2O)_6^{3+}$ in Hz. A value of τ in excess of 3 m sec. is obtained.

The intensity of the resonance of the hydrolysed species is subject to greater errors of estimation than that of the aquated aluminium ion $Al(H_2O)_6^{3+}$ due to the breadth of the former. It would appear from this and the preceding section that if solutions are sufficiently acidic then all the aluminium is present as the aquated ion. Any loss in the intensity can be attributed to the hydrolysed species which appears as a broad resonance. Thus a simple procedure is apparent for measuring the quantities of aquated aluminium ion and hydrolysed species in solutions of varying pH's by comparative intensity measurements of the aquated ion. Further quantitative studies of aluminium chloride solutions were therefore undertaken using this procedurc for studying hydrolytic reactions.

E. Detailed Hydrolysis Studies.

Two 100 ml. stock solutions of approximately 3 M aluminium chloride were prepared by dissolving 8.1 g. of aluminium wire in 80 ml. of concentrated hydrochloric acid. After dissolution of the metal it was noted that further hydrochloric acid could be removed by evaporating the solutions to half their original volume and then re-making to volume with distilled water. This procedure was repeated three times for each stock solution. Increasing increments of 7.7 N HNO_3 were then added to 5.5 ml. aliquots of one stock solution, hereafter referred to as Series A, until the pH of the most acidic sample was less than 0.5. The volume of all solutions was adjusted to 10 ml. with distilled water and analysis gave a concentration of aluminium for each solution as 1.65 ± 0.02 g. atom / litre. A similar procedure was used for the second stock solution, Series B I with the exception that 8 ml. aliquots were used to give a final concentration of aluminium as 2.44 ± 0.02 g. atom / litre and 10.0 N HCl replaced nitric acid for pH adjustments. This latter series, after pH and intensity measurements, was diluted twice to give concentrations of 1.22 and 0.62 g. atom/litre aluminium, Series B II and B III respectively, and pH - intensity measurements were repeated after each dilution. The results of all the measurements together with the volumes of added acid are given in tables 4 - 5 to 4 - 8. Spectra were recorded on the Bruker at 23.45 M Hz. The concentration of aluminium is reported as g. atom/litre to avoid any confusion which might arise if the ion $Al(H_2O)_6^{3+}$ and the hydrolysed species were compared as molar quantities in a mass balance.

The important features of the intensity - pH measurements given in these tables may be summarised as follows:

(1) As the acidity of all solutions increases, so does the intensity of the aquo aluminium resonance.

(2) In Series A and B I, a concentration of acid is attained above which no further increase in the intensity of the aquo ion $Al(H_2O)_6^{3+}$ is observed for further increments of acid.

(3) If the total aluminium is assumed 'visible' as the aquated aluminium ion at these pH's then the concentrations of the aquated and hydrolysed aluminium may be calculated for the less acid solutions. These are given in the relevant tables.

(4) The intensities of the most acid solution in Series B II and III were exactly one half and one quarter of that for sample 10, Series B I.

Table 4 - 5.

Relative Intensities of the Aquated Aluminium Ion at Various pH's.

Series A

Al concentration = 1.65 g. atom/litre.

Sample	ml.7.7N HNO_3	pH	Relative Intensity of $Al(H_2O)_6^{3+}$	g. atom/litre $Al(H_2O)_6^{3+}$	g. atom/litre Al Hydrolysed.
1	0	2.60	98	0.65	1.00
2	0.2	2.41	118	0.78	0.87
3	0.4	2.35	127	0.84	0.81
4	0.6	2.28	133	0.88	0.77
5	0.8	2.22	138	0.92	0.73
6	1.0	2.20	163	1.08	0.57
7	1.2	2.10	170	1.13	0.52
8	1.4	1.98	198	1.32	0.33
9	1.6	1.87	215	1.43	0.22
10	1.8	1.61	225	1.50	0.15
11	2.0	0.30	249	1.65	0.0
12	4.5	0.0	248	1.65	0.0

Table 4 - 6.

Relative Intensities of the Aquated Aluminium Ion at Various pH's.

Series B I

Al Concentration = 2. 44 g. atom/litre

Sample	ml. 10.0 N HCl	pH	Relative Intensity of $Al(H_2O)_6^{3+}$	g. atom/litre $Al(H_2O)_6^{3+}$	g. atom/litre Al Hydrolysed
1	0	1.95	188	0.98	1.46
2	0.2	1.75	208	1.09	1.35
3	0.4	1.62	227	1.19	1.25
4	0.6	1.53	245	1.28	1.16
5	0.8	1.40	285	1.49	0.95
6	1.0	1.27	287	1.50	0.94
7	1.2	1.10	346	1.81	0.63
8	1.4	0.98	359	1.88	0.56
9	1.6	0.83	388	2.03	0.41
10	2.0	0.30	465	2.44	0.00
11*	2.5	0.1	440	2.44	0.00

* Total volume of sample 10.5 ml.

Table 4 - 7.

Relative Intensities of the Aquated Aluminium Ion at Various pH's.

Series B II

Al Concentration = 1.22 g.atom/litre

Sample	ml.10.0 N HCl	pH	Relative Intensity of $Al(H_2O)_6^{3+}$	g. atom/litre $Al(H_2O)_6^{3+}$	g. atom/litre Al Hydrolysed
1	0	2.81	92	0.49	0.73
2	0.1	2.78	106	0.56	0.66
3	0.2	2.72	121	0.64	0.58
4	0.3	2.67	130	0.69	0.53
5	0.4	2.59	142	0.75	0.47
6	0.5	2.50	157	0.83	0.39
7	0.6	2.30	180	0.95	0.27
8	0.7	2.20	203	1.07	0.15
9	0.8	2.13	212	1.12	0.10
10	1.0	1.75	230	2.22	0.00

Table 4 - 8.

Relative Intensities of the Aquated Aluminium Ion at Various pH's.

Series B III

Al Concentration = 0.61 g. atom/litre.

Sample	ml. 10.0 N HCl	pH	Relative Intensity of $Al(H_2O)_6^{3+}$	g. atom/litre $Al(H_2O)_6^{3+}$	g. atom/litre Al Hydrolysed
1	0	3.6	52	0.28	0.33
2	0.05	3.55	56	0.30	0.31
3	0.10	3.50	59	0.32	0.30
4	0.20	3.42	71	0.38	0.23
5	0.25	3.38	75	0.40	0.21
6	0.30	3.31	82	0.44	0.17
7	0.35	3.15	90	0.48	0.13
8	0.40	3.00	102	0.55	0.06
9	0.50	2.8	114	0.61	0.00

Since this latter solution contained all the aluminium as the aquated ion then similar calculations for the concentration of hydrolysed aluminium can be made for Series B II and III.

The simple monomeric and dimeric equilibria discussed in the previous sections may be expressed in the form

$$n\,\mathrm{Alaq}^{3+} \rightleftharpoons \mathrm{Al}_n(\mathrm{OH})_n^{n(3-n)^+} + n\,\mathrm{H}^+$$

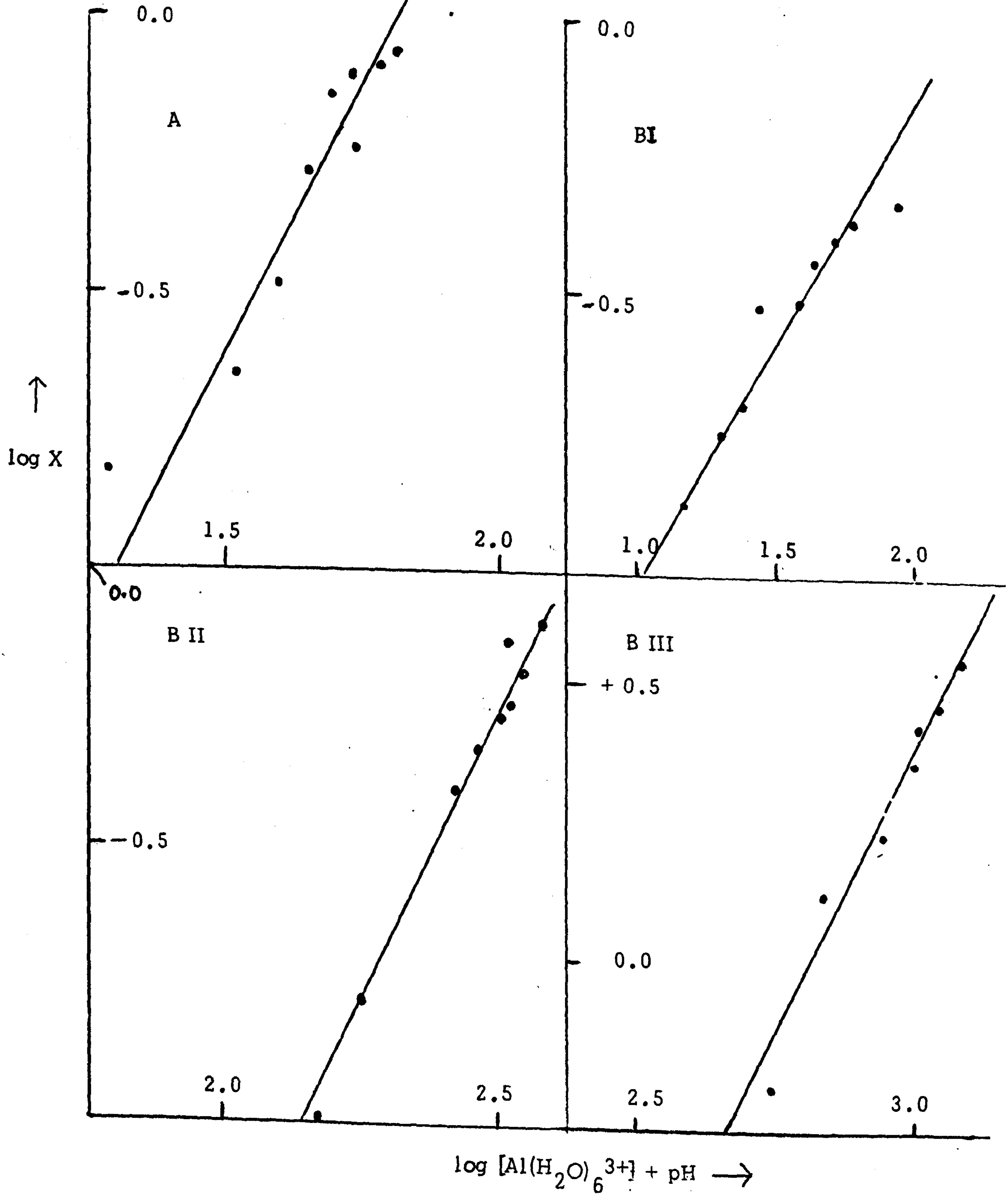
with a hydrolysis constant $K = \dfrac{[\mathrm{Al}_n(\mathrm{OH})_n^{n(3-n)^+}]\,[\mathrm{H}^+]^n}{[\mathrm{Alaq}^{3+}]^n}$

then

$$\log K = \log [\mathrm{Al}_n(\mathrm{OH})_n^{n(3-n)\,+}] + n \log [\mathrm{H}^+] - n \log (\mathrm{Alaq}^{3+}]$$

A plot of $\log [\mathrm{Al}_n(\mathrm{OH})_n^{n(3-n)\,+}]$ against $\log [\mathrm{Alaq}^{3+}]$ + pH should be a straight line of slope n. Such plots are shown in figure 4 - 6 for the results obtained in table 4 - 5 to 4 - 8. A slope of 1.8, 2.0 and 1.9 ± 0.2 is obtained for the 1.65, 1.22 and 0.61 g. atom/litre aluminium solutions. This value again suggests a significant dimeric equilibrium with

Figure 4 - 6 Plot of log X vs. log $[Al(H_2O)_6^{3+}]$ + pH where X is the concentration of hydrolysed aluminium



$$K_2 = \frac{[Al_2(OH)_2aq^{4+}]\,[H^+]^2}{[Alaq^{3+}]^2}$$

A plot of $\frac{[Al_2(OH)_2aq^{4+}]^{\frac{1}{2}}}{[Alaq^{3+}]}$ against $\frac{1}{[H^+]}$

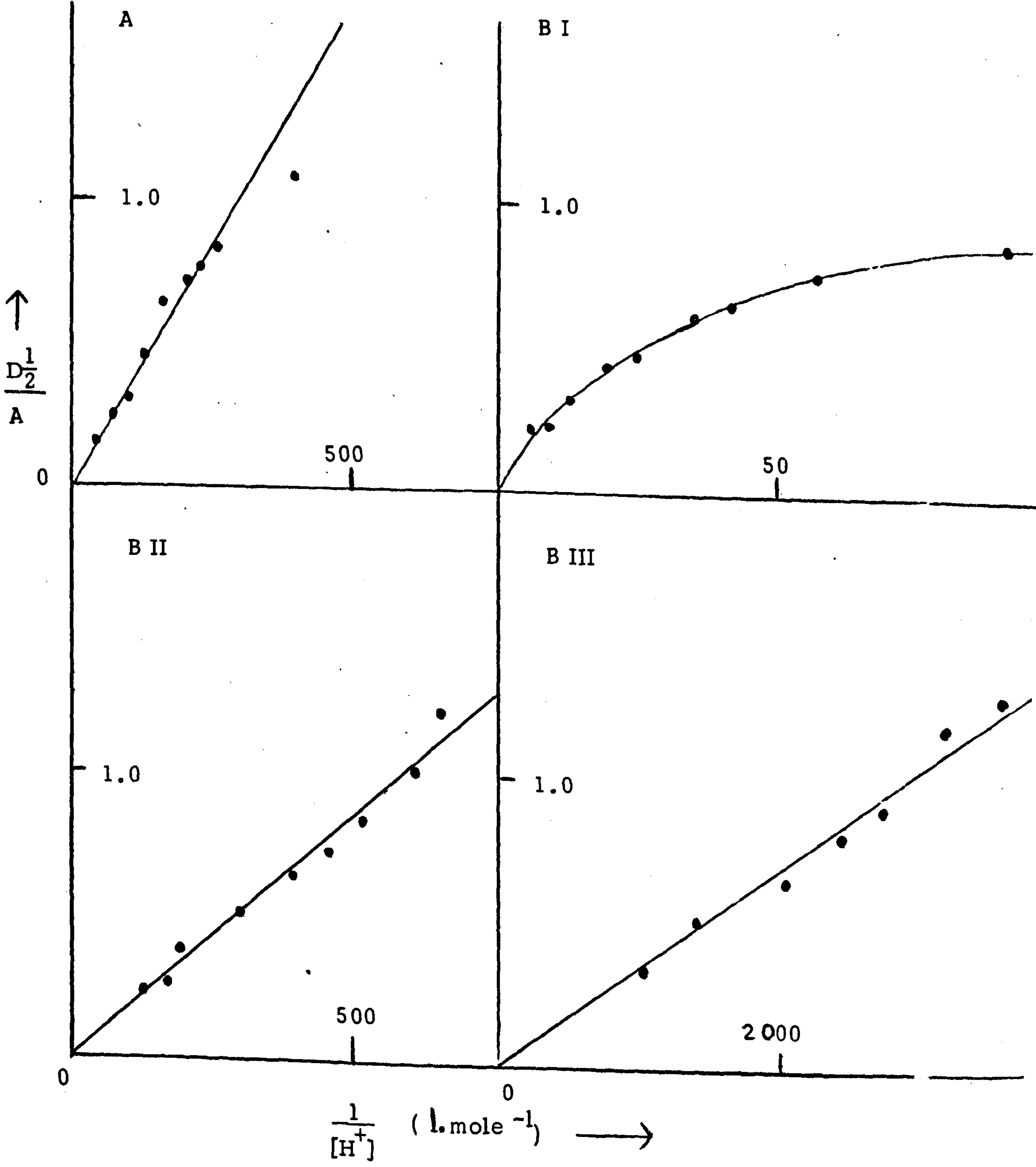
should be a straight line with an intercept through the origin. The square root is taken in order to condense the spread of results on the $\frac{1}{[H^+]}$ axis. Such representations are shown in figure 4 - 7 and satisfactory plots are obtained for these solutions with a slope of 2 in figure 4 - 6. Hydrolysis constants, expressed as $\log_{10}$, may be calculated and values of -5.00, -5.46 and -6.90 are obtained for Series A, B II and B III. These results are in reasonable agreement with those found by previous workers (-6.27 to -8.24) using potentiometric techniques.

Consideration of the quantities of acid added in each series enables the relationship to be obtained between the concentration of aluminium converted from the hydrolysed species to the aquo ion per g. atom of hydrogen. Thus for example, in Series A, 2.0 ml. of 7.7 N HNO_3 converts 1.0 g. atom/litre Al to the aquo ion.

Figure 4 - 7 Plot of $[Al_2(OH)_2aq^{4+}]^{\frac{1}{2}}/[Al(H_2O)_6^{3+}]$ vs. $1/[H^+]$

$D = [Al_2(OH)_2aq^{4+}]^{\frac{1}{2}}$

$A = [Al(H_2O)_6^{3+}]$



After allowing for the hydrogen ion concentration in solution the Al : H ratio is given as 1 : 1.1. An error of ± 10% must be given for this and other values obtained for Series B shown in table 4 - 9, this error arising from original calculation of added hydrogen ion concentration from a small volume of concentrated acid.

Table 4 - 9.

Concentration of Aluminium Liberated per g. atom Hydrogen.

Series	A	B I	B II	B III
Al : H ratio	1 : 1.1	1 : 1.0	1 : 1.3	1 : 1.3

An Al : H ratio of 1 : 1 would be obtained for the dimeric equilibrium. These values fall close to this figure.

PART II.

VARIABLE TEMPERATURE STUDIES.

The purpose of this study was two-fold

a) to determine the mechanisms governing the linewidth of the ^{27}Al resonance of the $Al(H_2O)_6^{3+}$ at varying temperature

b) to explore the possibility of detecting the hydrolysed species of aluminium using low-temperature proton studies.

A. ^{27}Al Resonance Studies of the Aquated Aluminium Ion $Al(H_2O)_6^{3+}$.

Initial investigations were made using the RS2 spectrometer and a full study was attempted on those samples used for the pH studies of linewidths, Part I, Section B. However the reduction in sample size required for the variable temperature probe (from 9 mm OD tubes to 5 mm), and the increase in the signal-to-noise ratio at elevated temperature made the accurate determination of broader linewidths impossible for the samples of higher pH. As a consequence full data was only obtained on the most acidic samples together with an extra solution of 1.5 M $AlCl_3$. The results are shown in table 4 - 10, a temperature range of -13° to + 108° being studied. Viscosity measurements are included for each sample. These were experimentally determined

Table 4 - 10.

Temperature Dependence of ^{27}Al Linewidths.

1.4 M Aluminium Nitrate pH 0.5

Temperature °C	Viscosity cP	Linewidth Hz	Corrected Linewidth for Magnetic Inhomogeneity and Viscosity Hz
-13	8.24	46.0	44.5
- 2	6.16	25.0	31.4
0	5.82	19.8	27.3
+25	3.2	6.4	12.6
+31	2.8	4.6	9.1
+41	2.3	4.0	8.9
+52	1.89	3.4	8.2
+63	1.54	4.2	14.4
+73	1.31	3.6	13.2
+88	1.04	3.5	15.8
+104	0.85	3.0	14.5

1.4 M Aluminium Nitrate pH 1.8

Temperature °C	Viscosity cP	Linewidth Hz	Corrected Linewidth for Magnetic Inhomogeneity and Viscosity Hz
-13	8.05	66	64.5
+ 2	5.25	21.8	31.1
+ 9	4.47	19.8	32.9
+25	2.76	8.4	20.1
+31	2.69	6.8	15.8
+52	1.81	5.0	15.5
+63	1.48	5.0	19.0
+73	1.25	5.0	22.5
+88	1.00	5.5	32.2
+104	0.81	6.8	52.5

... continued ...

... continued ...

Table 4 - 10.

Temperature Dependence of ^{27}Al Linewidths.

1.4 M Aluminium Nitrate pH 2.32

Temperature °C	Viscosity cP	Linewidth Hz	Corrected Linewidth for Magnetic Inhomogeneity and Viscosity Hz
-10	6.68	66.0	70.9
0	5.07	35.5	49.2
+ 2	4.79	32.6	47.5
+ 5	4.47	25.3	39.2
+25	2.72	10.8	25.0
+31	2.45	9.1	22.7
+41	1.99	8.0	23.9
+52	1.65	8.2	29.8
+63	1.34	9.0	41.11
+73	1.14	9.0	48.7
+88	0.91	10.0	66.5
+104	0.64	13.0	131

1.5 M Aluminium Chloride pH 2.4

Temperature °C	Viscosity cP	Linewidth Hz	Corrected Linewidth for Magnetic Inhomogeneity and Viscosity Hz
+25	3.02	14.0	32.1
+32	2.63	11.5	29.3
+43	2.14	10.2	31.0
+52	1.74	10.2	38.8
+63	1.44	12.5	59.2
+73	1.23	13.6	76.5
+88	0.97	17.0	124
+104	0.79	21.5	200

for the range 5 to 85°. Below 5°, condensation in the sample cell made accurate viscosity determinations impossible and results for lower temperatures were extrapolated from viscosity temperature plots. Evaporation above 85° also induced large errors in the determination, so results for higher temperatures were also extrapolated. Two procedures were used. Either viscosities were plotted against temperature expressed as °C or else $\log_{10}$ of the viscosity was plotted against $^1/_T$ where T is expressed in °K. The latter procedure is based on an Arrhenius type equation

$$\eta = A \exp E_{vis}/RT$$

and straight line is obtained for many solutions. Figure 4 - 8 shows such a plot for both aluminium nitrate and chloride solutions and an activation energy of viscosity E_{vis} of 3.8 kcal/mole for both salts is obtained.

It is obvious that there is a large (ten-fold) variation in the viscosity of the samples examined. Even without viscosity corrections there is a marked increase in the linewidth of the least acid solution as the temperature is increased. Magnetic inhomogeneity and viscosity corrected linewidths are shown in figure 4 - 9. The viscosity of each solution at -13° was used as a standard. The increase in the linewidth of the least acidic solution is even more marked. The linewidths

Figure 4 - 8 Plot of log η vs. the reciprocal of temperature for aluminium nitrate and chloride solutions

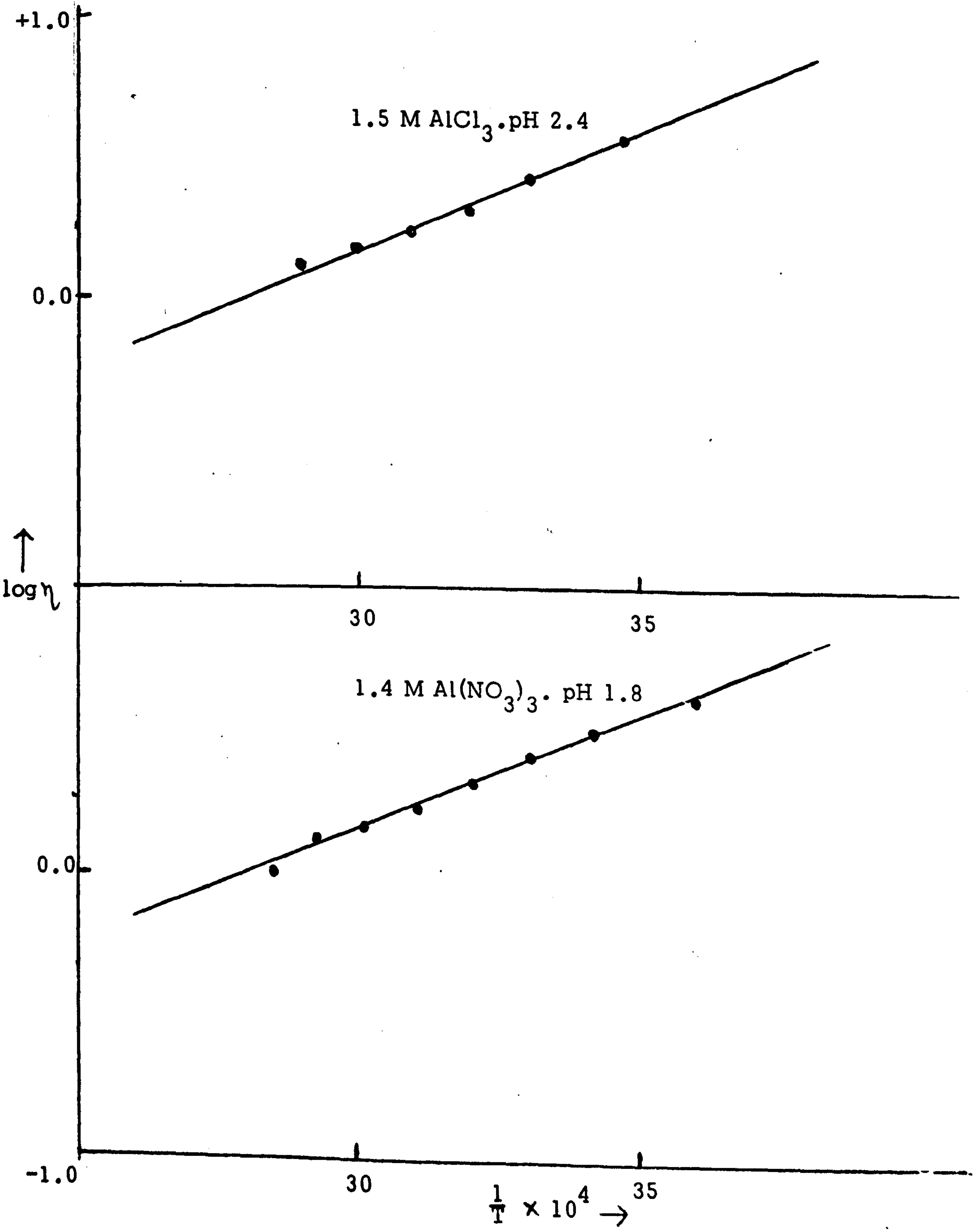
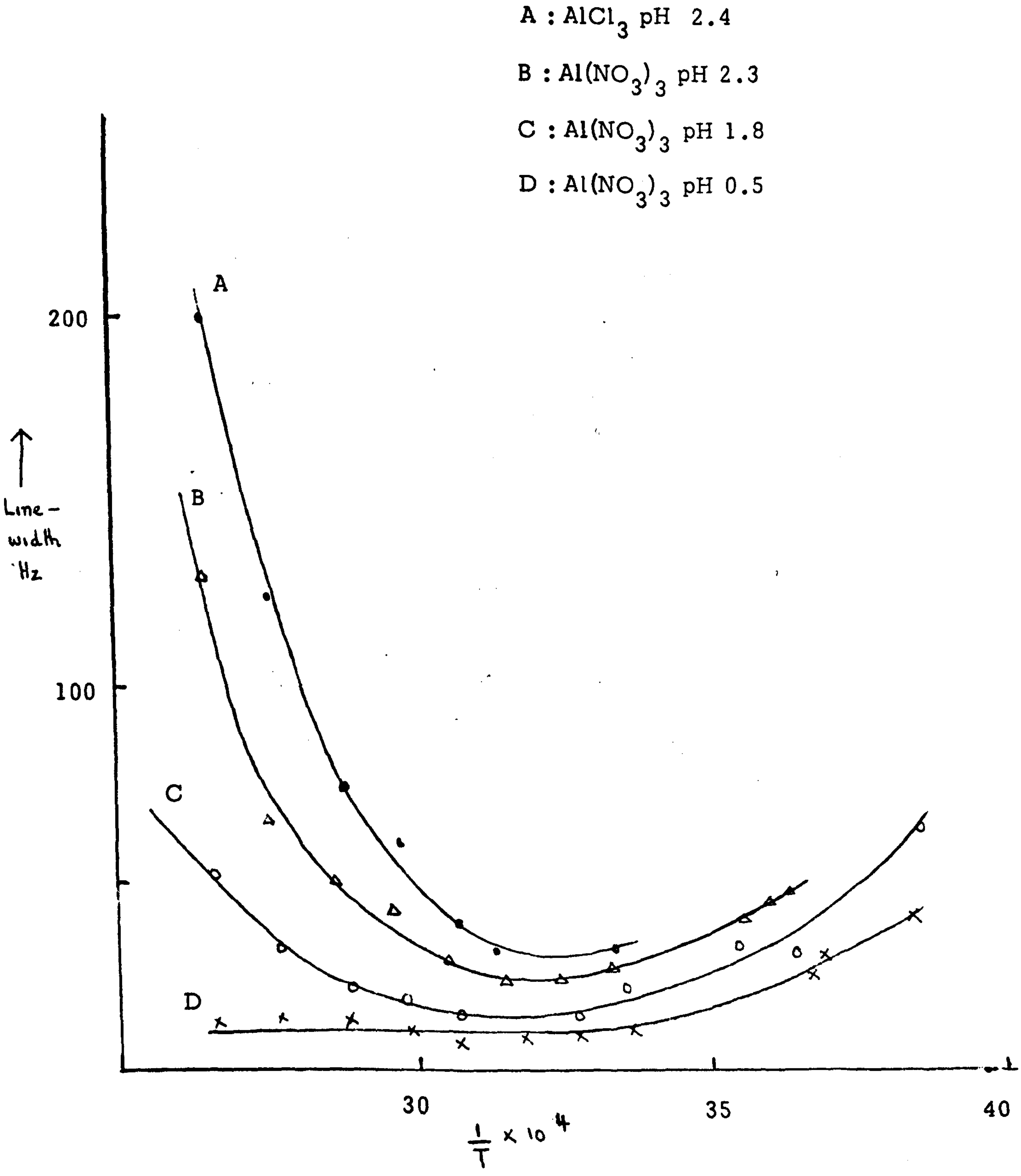


Figure 4 - 9 ^{27}Al linewidths (corrected for viscosity and magnetic field inhomogeneity) as a function of inverse temperature



also appear to be pH dependent at all temperatures. Because of this it is not possible to ascribe any of the changes observed to the onset of whole-water exchange since to be pH dependent this would have to occur mainly via the protolysed species.

The most acidic solution examined had a pH of 0.5 and would therefore be expected to contain negligible concentrations of hydrolysed aluminium. The linewidths of this solution at high temperatures appear to be independent of temperature and thus the broadening observed for the less acidic solutions could be explained by the onset of exchange between the dimer and the aquated aluminium ion.

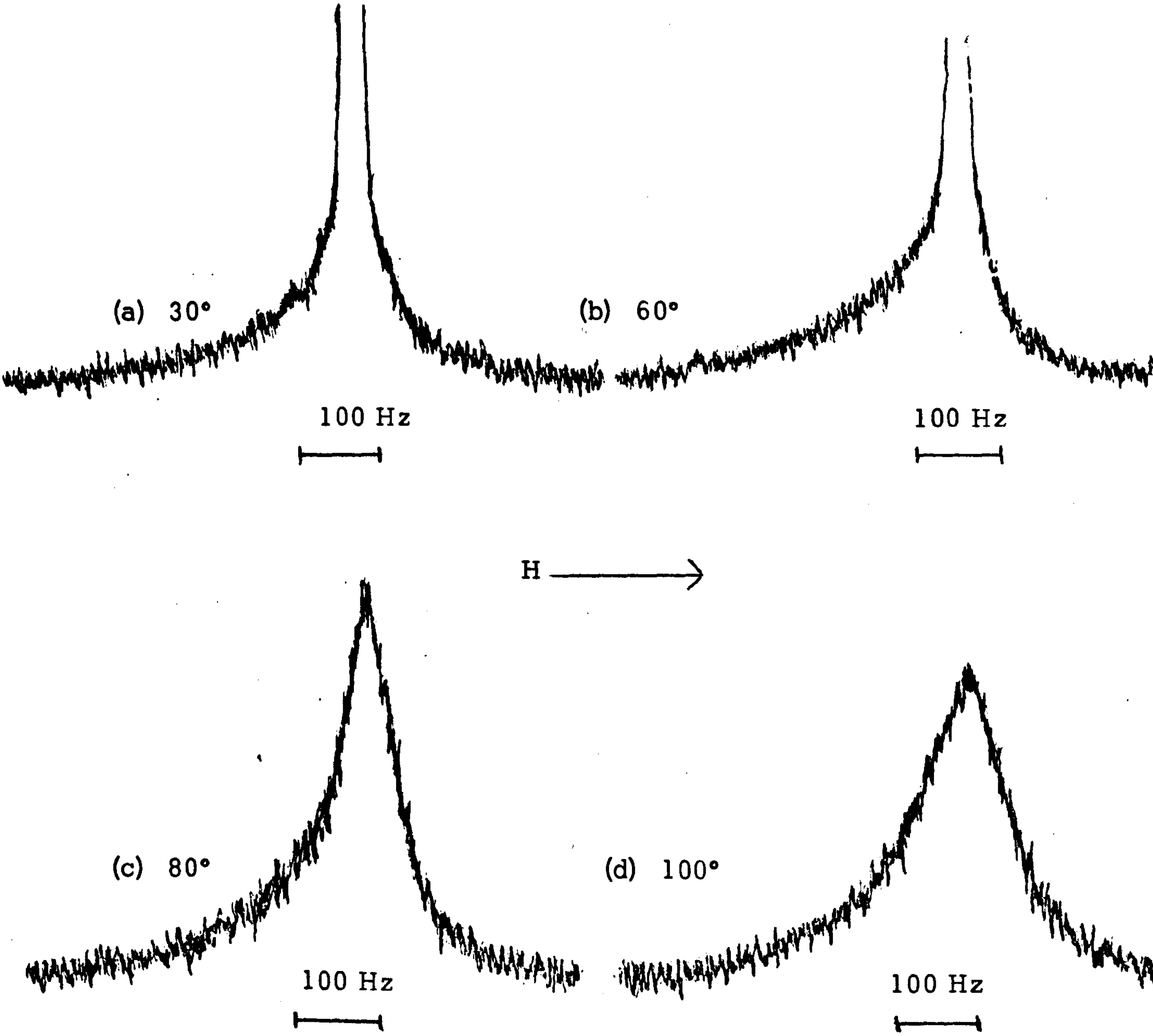
The increase in linewidths at temperatures lower than 35° is harder to explain. If an exchange mechanism is involved between the $Al(H_2O)_6^{3+}$ ion and a hydrolysed species then the linewidth of the most acidic solution should again be independent of temperature. This, it appears, is not so. It has been shown in the previous chapter that a linewidth is not strictly proportional to viscosity, but is linearly related to it, and this could offer a possible explanation, insufficient corrections for viscosity changes becoming apparent at the lower temperature where such changes are very large.

The increase in linewidth of the least acidic solution with temperature is obvious even without viscosity corrections and it was therefore decided to investigate the high temperature region further using the Bruker. A 2.0 M $AlCl_3$ solution was chosen for this purpose, the pH being 2.0. Spectra were recorded at a sweep amplitude of 40 Hz/cm and at a transmitter power sufficient to detect the dimer. At 30° the dimer could clearly be seen downfield of the $Al(H_2O)_6^{3+}$ resonance which was saturated , figure 4 - 10(a). At 60° the dimer was observed more clearly, the lower solution viscosity showing its effect in the apparent decrease in linewidth, figure 4 - 10(b). An estimated value of 350 Hz was obtained for this temperature compared to 450 Hz at 20°.

The $Al(H_2O)_6^{3+}$ resonance was no longer saturated at 80°, figure 4 - 10(c). At 100° the $Al(H_2O)_6^{3+}$ signal was greatly broadened but the dimer could still be detected on the left shoulder of the resonance, figure 4 - 10 (d).

Exchange between the dimer and $All(H_2O)_6^{3+}$ species can explain the linewidth broadening observed with the latter resonance during high temperature studies on the RS2. The difference in chemical shift between the two resonances was difficult to estimate accurately

Figure 4 - 10 High-temperature ^{27}Al spectra of 2 M $AlCl_3$ of pH 2.0



by eye, but it would appear similar at 100° and 20° within an error of 1 ppm. Since two resonances can still be detected at 100°, slow or intermediate rates of exchange still prevail. Moreover the initial calculation of 3 m.sec. for the lifetime of the dimer obtained in the previous studies would now appear to be a greatly underestimated value.

In numerous studies of reaction rates it has been found that the rate at room temperature increases by a factor of two to three with a 10° rise in temperature. If the lifetime of the dimer at 100° is given a value of 3 m.sec., assuming the chemical shift difference is still 3.4 ppm, then the lifetime at 20° can be calculated to be approximately 0.75 sec.

The equation for slow exchange (2 - 5) shows that the linewidth of the observed resonance is dependent on a contribution from $\frac{1}{\tau}$ where τ is the lifetime of the nucleus at the specific site. On inserting the revised figure for the lifetime of the dimer at room temperature into equation 2 - 5 an estimate of the contribution of exchange to linewidth at this temperature can be made. This is found to be approximately 0.5 Hz.

In the previous pH linewidth studies at room temperature, Part I, Section 2, the observed increase in linewidths with decreasing acidity were explained in terms of a fast exchange mechanism between the aquated aluminium ion and monomer. Slow exchange with dimer could also contribute to linewidth increases and the above investigation shows that this is so. However the calculated contribution at 20° for dimer $Al(H_2O)_6^{3+}$ exchange is small in comparison to the observed linewidth increases and this gives weight to the interpretation of pH linewidth results at room temperature by a monomeric exchange mechanism.

B. Low-Temperature Proton Studies.

Previous investigators[44-46] have shown that if highly concentrated solutions of aluminium chloride are cooled to -50° then separate proton signals can be obtained for bound (co-ordinated) and free (non-co-ordinated) water. Obviously the presence of significant quantities of dimer should perturb such a system and investigations were therefore undertaken to determine its effect.

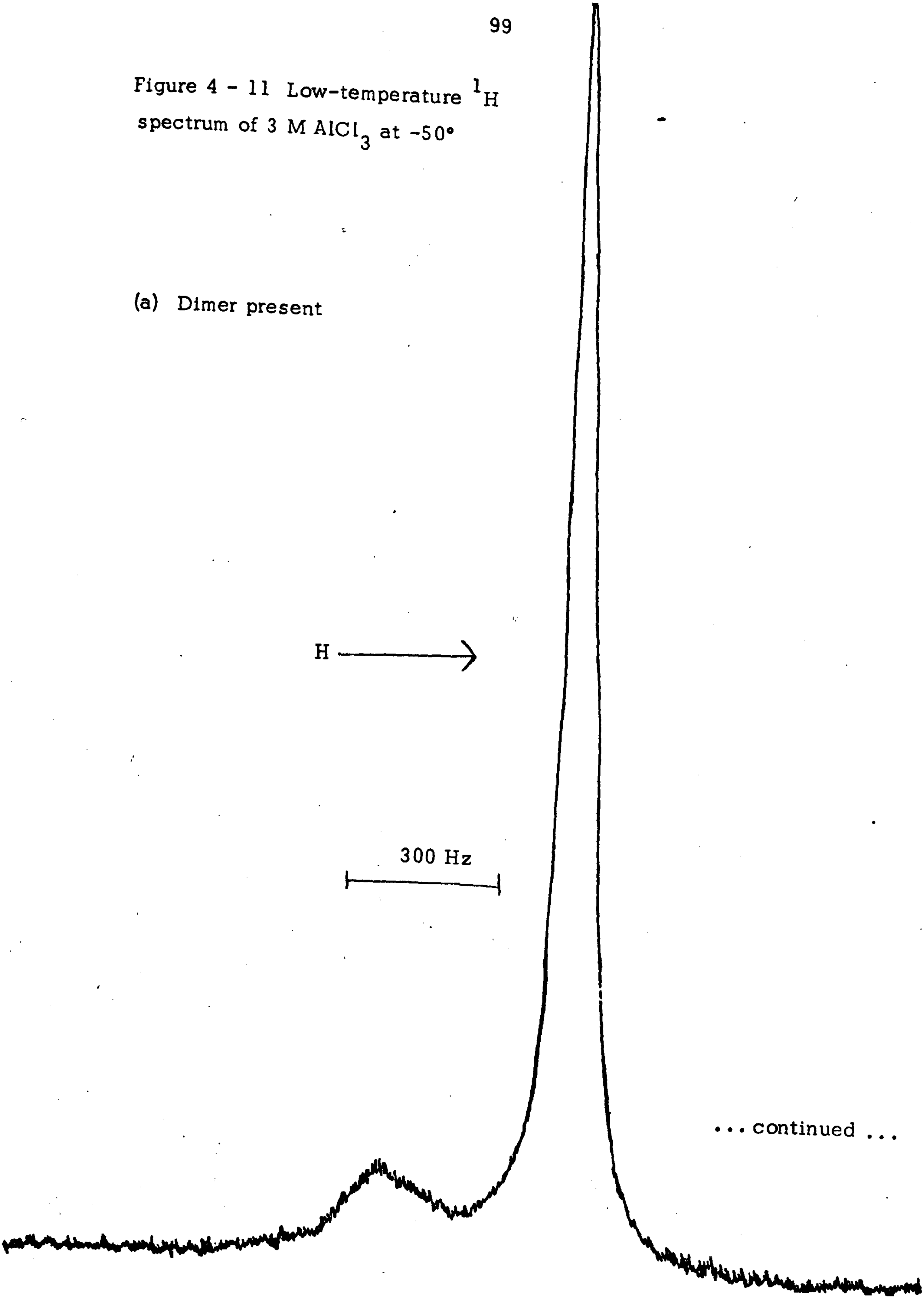
A 3.0 M solution of $AlCl_3$ was prepared and ^{27}Al studies showed it to contain approximately 0.75 M dimer. Spectra were recorded for this solution at a temperature of -50° and compared to a similar solution in which all the dimer had been converted to the $Al(H_2O)_6^{3+}$ ion by addition of acid. In figure 4 - 11 the two spectra are compared. The signal of bound water was observed 4 ppm downfield of the bulk water resonance. No new resonance was observed for the solution containing significant quantities of dimer. However the intensity of the bound water resonance in this sample may be seen to be less than that in the acidified sample (both spectra were recorded at the same spectrometer settings). A reduction in the intensity of the proton signal for the bound water in the presence of dimer could occur in two ways

1) the bound water signal represents both the dimer and $Al(H_2O)^{3+}$ ions and the reduction is proportional to the lower number of protons in the dimer

2) the bound water signal represents only the ion $Al(H_2O)_6^{3+}$ and fast proton exchange gives only a single resonance for the dimer and free water.

Figure 4 - 11 Low-temperature ^1H spectrum of 3 M $AlCl_3$ at -50°

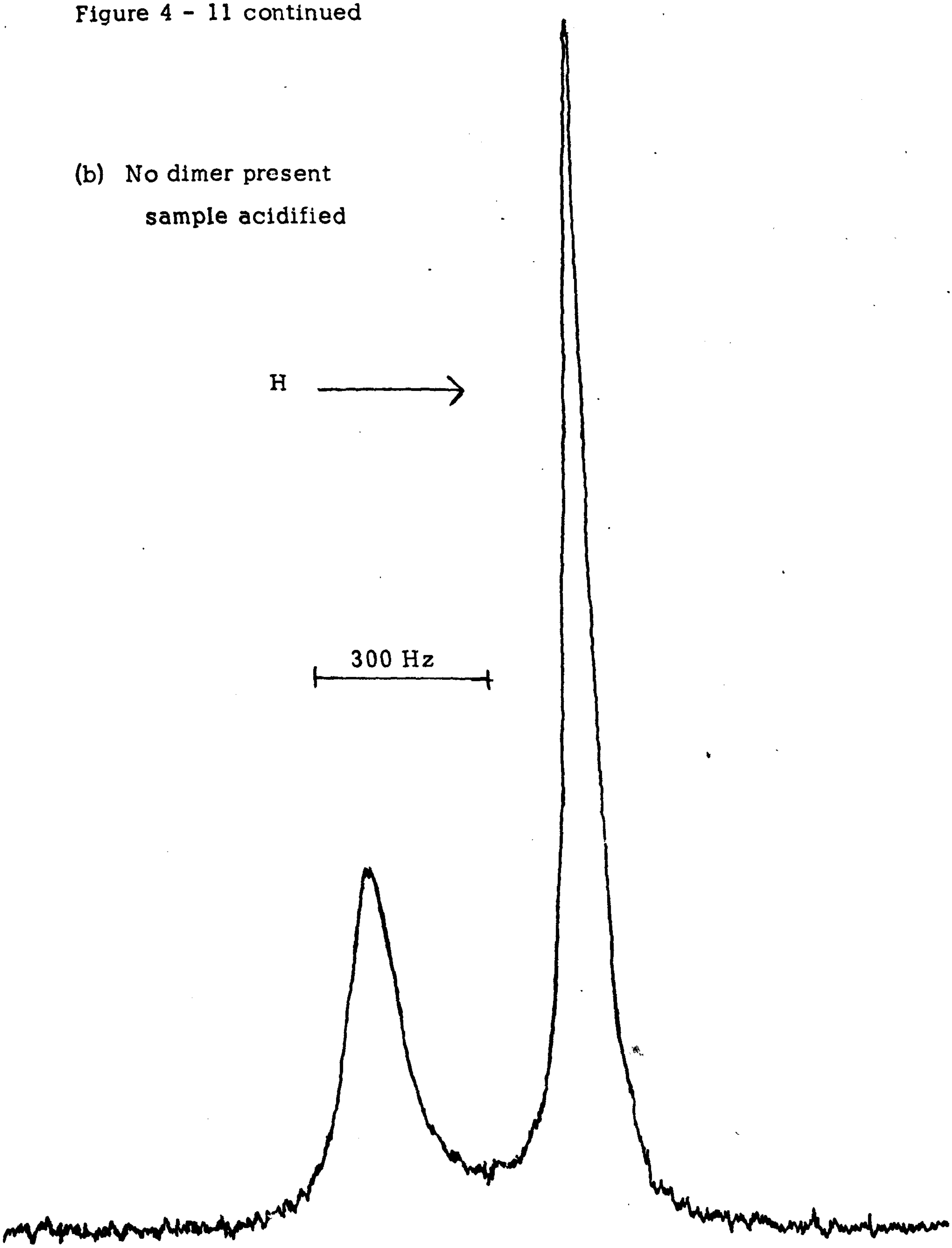
(a) Dimer present



... continued ...

Figure 4 - 11 continued

(b) No dimer present
sample acidified



Further investigations were obviously required in order to elucidate this problem A 3.75 M aluminium chloride solution was therefore prepared in the normal manner and 6 x 8 ml. aliquots taken. To these increasing increments of nitric acid (s.g. 1.42) were added until the most acidic solution had a pH of less than 0.1. The volumes of all solutions were made up to 10 ml. with distilled water. ^{27}Al resonance measurements were first made in order to obtain the comparative concentrations of $Al(H_2O)_6^{3+}$ and dimer. Low temperature proton spectra were then recorded and the relative intensities of the bound and free water calculated. The chloride concentration of the 3.75 M stock solution was determined using standard gravimetric procedures and a value of 7.8 g. atom/litre was obtained. From a determination of the specific gravity of this solution (1.303) the relative intensities of the bound and free water were converted to mole H_2O, bound or free, after due corrections were made for the added water or acid. Table 4 - 11 gives these results together with the concentration of dimer and $Al(H_2O)_6^{3+}$ in the corresponding solutions.

The bound water is seen to be directly proportional to the concentration of $Al(H_2O)_6^{3+}$. This is confirmed by calculating hydration

Table 4 - 11.

Comparative Intensities of Bulk and Bound Water in the Presence of Differing Concentration of $Al(H_2O)_6^{3+}$ and $Al_2(OH)_2aq^{4+}$.

Mole $Al(H_2O)_6^{3+}$	Mole $Al_2(OH)_2aq^{4+}$	Mole Added $H NO_3$	Mole H_2O			Temp. of Sample °C	Calculated Hydration Number
			Total	Bound	Bulk		
1.12	0.94	0	52.1	6.8	45.3	-64	6.1
1.46	0.78	0.64	51.1	8.7	42.4	-59	6.0
1.90	0.55	1.28	50.8	11.0	39.8	-59	5.8
2.02	0.49	1.92	49.1	12.1	37.0	-50	6.0
2.51	0.245	2.56	48.0	14.9	33.1	-47	5.9
3.00	0	3.20	47.0	18.1	28.9	-47	6.0

numbers for this species from the observed concentration of bound water and a value of 6.0 ± 0.1 is obtained. The low field resonance, therefore, represents only the water bound to the $Al(H_2O)_6^{3+}$ ion and the signal assigned to bulk water must represent the dimer and non-co-ordinate water.

It was noted during the recording of these spectra that the coalescence temperature of the two water resonances rose as the acidity of the solutions increased. Coalescence commenced at approximately -39° with the samples containing the most dimer, while a temperature of -8° was noted for the sample with no dimer present. Stephens and Schweitzer[48] were able to reduce the coalescence temperature of aluminium chloride solutions by the addition of an inert salt, such as calcium nitrate, which reduced the bulk water concentration. The bulk water concentration in table 4 - 11 represents both non-co-ordinate water and water associated with the dimer hydration sphere. If exchange of protons is fast on the latter, and this is a reasonable assumption since no separate resonance for this species is obtained, then the ratio of bound water of the $Al(H_2O)_6^{3+}$ to non-co-ordinate and dimer water should effect the coalescence temperature. The ratio difference between the least and most acid sample is large (1.6 and 6.8 respectively) and the increase of the coalescence temperature of the samples could thus be explained by the differing concentrations of bound and non-co-ordinate plus dimer water.

Attempts were made to separate the resonances of non-co-ordinate water and dimer by the use of a paramagnetic salt. Cobaltous chloride was added at varying concentrations between 0.05 and 0.2 M. As the concentration of this salt increased, the linewidth of the bound and bulk water resonances broadened until only a single broad peak could be detected. The chemical shift difference between the two signals remained approximately the same during the initial stages of broadening and no new resonance was observed.

PART III.

DISCUSSION AND CONCLUSIONS.

Considerable evidence has been obtained for the formation of dimer of the type $Al_2(OH)_2aq^{4+}$ on hydrolysis of the aquated aluminium ion. The equilibrium

$$2Alaq^{3+} \rightleftharpoons Al_2(OH)_2aq^{4+} + 2H_3O^+$$

has provided a satisfactory interpretation of the experimental results for solutions of aluminium chloride in the concentration range 0.6 to 1.65 M. That dimer formation involves only the species $Alaq^{3+}$ cannot be assumed and a stepwise equilibrium can be suggested involving the monomer $AlOHaq^{2+}$

$$Alaq^{3+} + H_2O \rightleftharpoons AlOHaq^{2+} + H_3O^+ \qquad \text{then}$$

either

$$2\ AlOHaq^{2+} \rightleftharpoons Al_2(OH)_2aq^{4+}$$

or

$$H_2O + AlOHaq^{2+} + Alaq^{3+} \rightleftharpoons Al_2(OH)_2aq^{4+} + H_3O^+$$

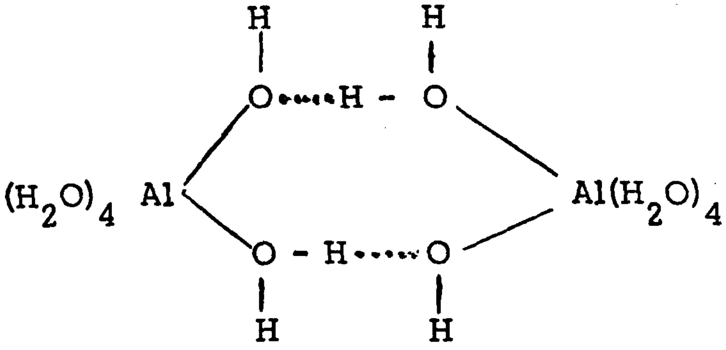
The monomeric equilibrium could exist in all solutions studied. Some evidence of this is obtained from the fast exchange interpretation of linewidth variations with pH at room temperature. A dimeric equilibrium could also contribute to such variations by a slow exchange mechanism and high temperature studies show that slow exchange does occur between dimer and the aquated aluminium ion. However the contribution at room temperature would appear small compared to the observed linewidth changes offering support for a monomeric equilibrium interpretation. Quantitative studies of the proportion of the dimer and the $Al(H_2O)_6^{3+}$ species in solution show that the concentration of a monomer is small in comparison to the dimer which is in keeping with the hydrolysis constant K_1 for the monomeric equilibrium.

The existence of more than one hydrolysis equilibrium has been suggested from the results of recent papers by Sullivan,[20] Turner,[37] and Grunwald.[34, 39] The polynuclear species found by Turner and the hydrous complex $Al{-}O{-}Alaq^{4+}$ suggested by Grunwald could well be the dimer. It is of interest to note that Grunwald reported faster rates of proton exchange for the hydrous complex (of the order 10^{9} $sec.^{-1}$) than the $Al(H_2O)_6^{3+}$ species (10^{5} $sec.^{-1}$) and this is in keeping with the identification of the former as the dimer. Faster proton exchange was suggested by low temperature ^1H studies in this present investigation.

All authors reported the monomeric equilibrium.

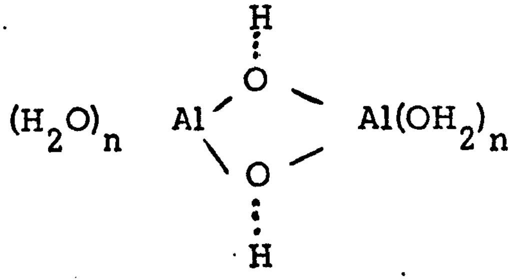
The structure of the dimer may be represented in several ways including

(1)



(2) $(H_2O)_m - Al - O - Al\,(OH_2)_m$

(3)



A lifetime of at least 3 m. sec. has been calculated for the dimer from room temperature studies but high temperature investigations suggest the value is considerably larger and is closer to 0.75 sec. Both times imply a stable structure more in keeping with (2) or (3) than (1).

The lifetime of the latter would be expected to be much less than 3 m. sec. since it would be controlled essentially by diffusion and would be nearer 10^{-9} sec. ^{17}O n.m.r. investigations might resolve this problem.

The observed hydrolysis constants K_2 for dimer formation are in reasonable agreement with those obtained by previous investigators using classical techniques in dilute solutions. The latter determined values ranging from -6.27 to -8.24; the present studies gave values of -5.00 -5.46 and -6.90. The agreement is more satisfactory when it is considered that the present K_2 constants were determined in concentrated solution and variables such as activities of the ions and water concentration have been neglected. Such variations as do exist for the determined K_2 values (increase with concentration) and the divergence from the simple dimer equilibrium for the most concentrated solution studied (2.44 M $AlCl_3$) could be explained by neglect of these parameters in the calculations.

The contribution of these variables is difficult to assess accurately. The extended Debye-Hückel equation [87] does not apply to the calculation of activities of ions, the concentration of which is greater than 0.1 mole, and very large errors can be obtained even with modified formula.[87(a)] If dimer formation is to be expressed by an expanded equilibrium which includes water concentration and hydration sphere numbers, then knowledge is required of the hydration sphere of the dimer itself. The results from the present low-temperature proton studies imply fast proton exchange on the dimer, but oxygen exchange may be slow and ^{17}O investigations could then possibly provide information on this subject and allow calculations of the hydration number. Divergence from the simple dimeric equilibrium is most noticeable where variations in water concentration and activities would be expected to be greatest and further investigations will be required before their full contribution can be assessed.

No investigations have been made of the effect of aging. Solutions were normally prepared 24 hours prior to pH and intensity measurements and from that factor they are compatible. Since it was found that hydrochloric acid could be removed by evaporating the aluminium chloride solutions, it is obvious that 'artificial' aging by heating similar concentrated solutions will have a marked effect on the pH of solution.

The ease with which dimer is formed in concentrated aluminium is obvious from the results of this investigation. It is equally obvious that without corrections, the presence of dimer can invalidate the results of low temperature proton studies of the hydration and kinetics of the $Al(H_2O)_6^{3+}$ ion. Similar remarks apply to ^{17}O investigations.

^{27}Al n.m.r. has proved a satisfactory technique for the study of aluminium hydrolysis. It should be feasible to extend such investigations to solutions containing a stable phase of precipitated hydroxide, to obtain information on possible large polynuclear species, and then to continue the studies on highly alkaline solutions.

CHAPTER 5.

COMPLEXES OF ALUMINIUM WITH ANIONS OTHER THAN HYDROXIDE, FLUORIDE, AND PHOSPHATE.

A. Chloride, Nitrate and Perchlorate Complexes of Aluminium.

Throughout the preceding investigation, the possibility of aluminium forming complexes with anions other than the hydroxide ion was borne in mind. No evidence was obtained for any such complexes even in the most concentrated solutions studied. Aluminium chloride, nitrate and perchlorate solutions at similar concentrations, gave identical intensities for the $Al(H_2O)_6^{3+}$ resonance, provided no dimer was present. The only exception was found for aluminium sulphate solutions, the results of which are described below.

B. Bisulphate Complexes of Aluminium.

^{27}Al n.m.r. studies using the RS2 spectrometer commenced early in 1967. It was immediately obvious that, in solutions of aluminium sulphate, there was a new and previously undetected resonance 3.3 ppm to highfield of the $Al(H_2O)_6^{3+}$ signal. This resonance was in fact found by J.W. Akitt who was tuning the spectrometer for the first time on the ^{27}Al nucleus.

Since similar resonances could not be detected in chloride, nitrate or perchlorate solutions, this implied a complex involving the sulphate ion. In the present work it was found that the highfield resonance could be intensified by the addition of sulphuric acid and a series of samples were therefore prepared containing a constant concentration of aluminium sulphate (0.45 M) and varying increments of sulphuric acid. In table 5 - 1 the relative intensities of the $Al(H_2O_6)^{3+}$ ion and the upfield resonance are compared to the concentration of sulphuric acid present. The concentration of the ions SO_4^{2-}, HSO_4^- and H_2SO_4 in aqueous sulphuric acid solutions have been studied by Young[88] using Raman spectroscopic techniques. The results of this work are shown in figure 5 - 1. The intensity of the Al-complex is observed from table 5 - 1 to increase with the concentration of bisulphate ion present and such concentrations are therefore included in this table together with the calculated concentration of water in each sample.

Since only one peak is seen, the simplest model postulates the formation of a single complex according to the equilibrium

$$Al(H_2O)_6^{3+} + nHSO_4^- \rightleftharpoons Al(HSO_4)_n(H_2O)_{6-n}^{(3-n)+} + nH_2O$$

The formation constant is given by

$$K_1 = \frac{[Al(HSO_4)_n(H_2O)_{6-n}^{(3-n)+}]\,[H_2O]^n}{[Al(H_2O)_6^{3+}][HSO_4^-]^n}$$

Table 5 - 1.

Relative Intensities of ^{27}Al Resonances of $Al(H_2O)_6^{3+}$ and Al-Complex as a Function of Sulphuric Acid Content.

Molarity Aluminium Sulphate	Molarity Sulphuric Acid	Molarity HSO_4^-	Mole H_2O	Intensity $\frac{\text{Al-Complex}}{Al(H_2O)_6^{3+}}$
0.45	1.8	1.3	44.1	0.07
0.45	2.4	1.8	40.3	0.10
0.45	3.6	2.4	38.5	0.15
0.45	4.4	3.1	35.8	0.25
0.45	5.4	3.8	33.1	0.33
0.45	10.8	9.6	16.3	1.32

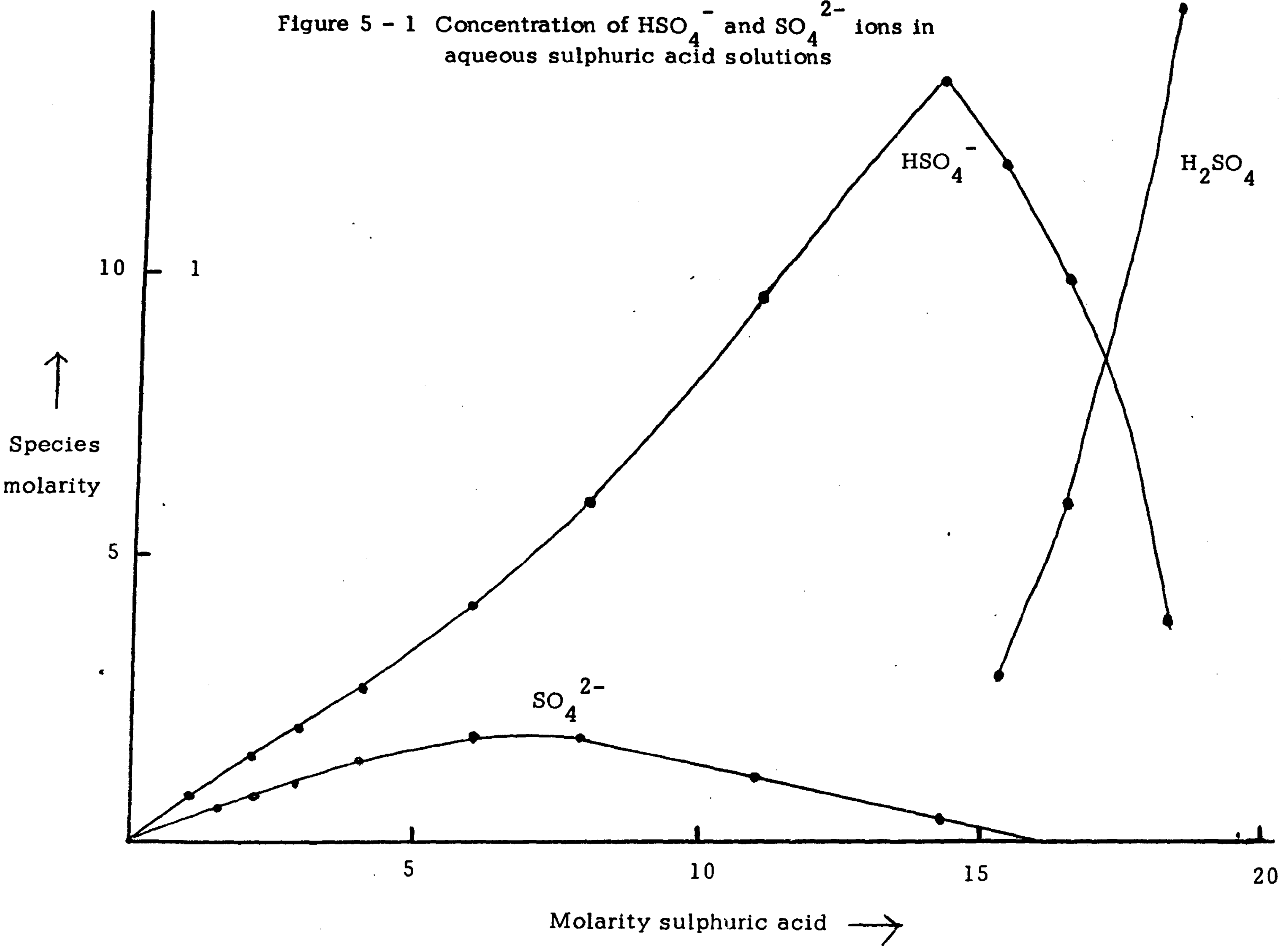


Figure 5 - 1 Concentration of HSO_4^- and SO_4^{2-} ions in aqueous sulphuric acid solutions

If it is assumed that the aluminium bisulphate complex formation results in adjustment of the $H_2SO_4^- HSO_4^- - SO_4^{2-}$ equilibrium to give the original concentration of HSO_4^- shown in figure 5 - 1, then

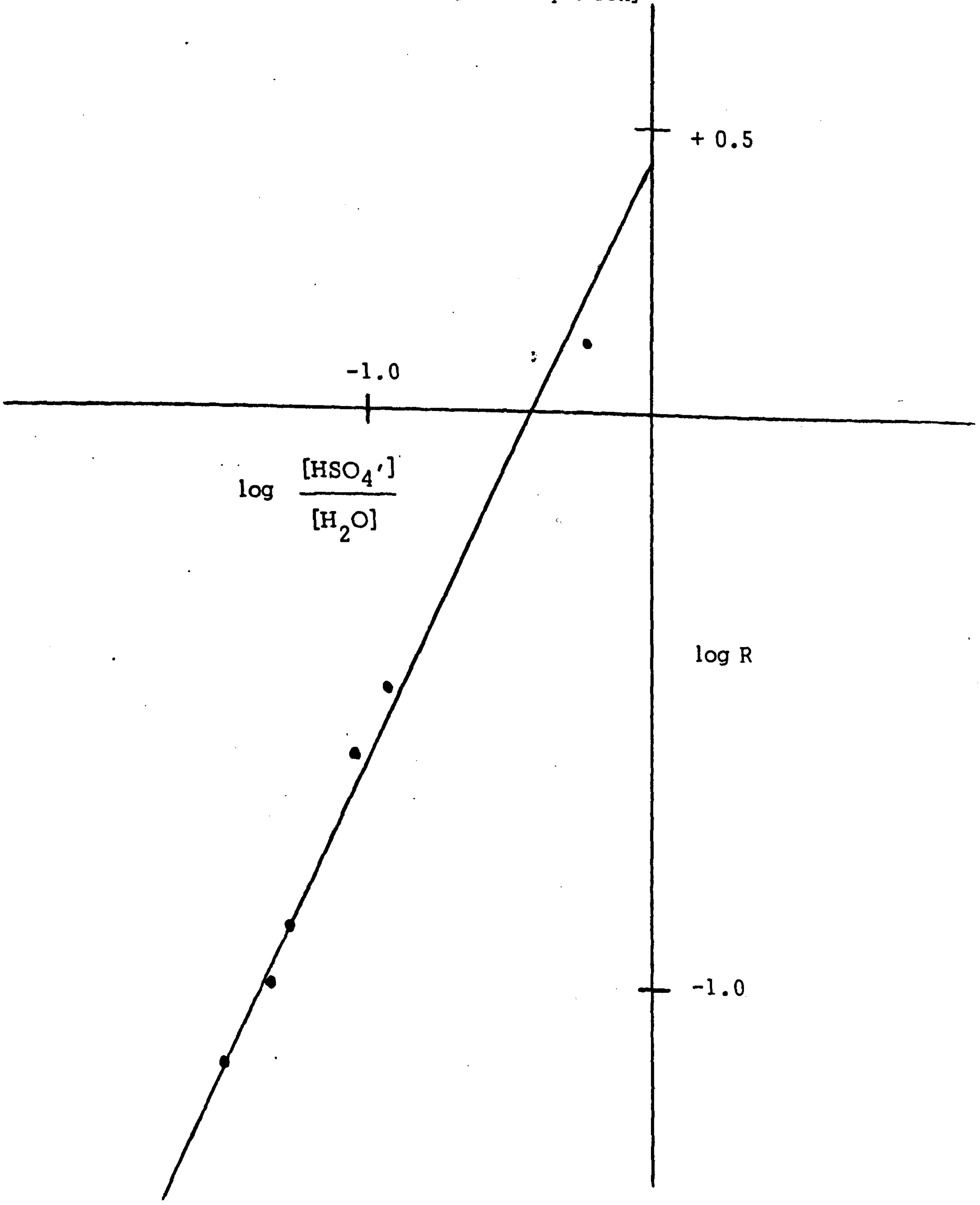
$$\log R = \log K_1 + n \log \frac{[HSO_4^-]}{[H_2O]}$$

where $R = \dfrac{[\text{Bisulphate Complex}]}{[Al(H_2O)_6^{3+}]}$

A plot of log R against log $\left([HSO_4^-] / (H_2O] \right)$ is shown in figure 5 - 2. The line has a slope of 1.05 indicating that n = 1 and that the complex is $Al(HSO_4)(H_2O)_5^{2+}$ with a formation constant of log $K_1 = 0.45$.

The width of the bisulphate resonance was approximately 30% greater than the $Al(H_2O)_6^{3+}$ signal in all solutions studied, both being dependent on viscosity. The replacement of H_2O by charged HSO_4' might be expected to set up a field gradient at the aluminium nucleus. The linewidth suggests however that the bonding to the HSO_4^- and H_2O oxygen is similar and this supported by the similar stabilities of the two complexes. The small highfield shift observed is consistent with electron density from the HSO_4^- ion being transferred to the aluminium.

Figure 5 - 2 Plot of log R vs. log $[HSO_4^-]/[H_2O]$, where R = [bisulphate complex] / [hexa-aquo ion]



The existence of this complex provides further evidence that the rate of exchange of oxygen around the aluminium is slow, while the narrow ^{27}Al linewidth supports the hypothesis that the protolysed ion $AlOHaq^{2+}$ should also have a narrow line.

Shortly after the completion of this work a short communication was published by Lutz[89] in which he noted the existence of a resonance other than $Al(H_2O)_6^{3+}$ in solutions of aluminium sulphate. The resonance was not identified but its chemical shift was similar to the bisulphate complex found above.

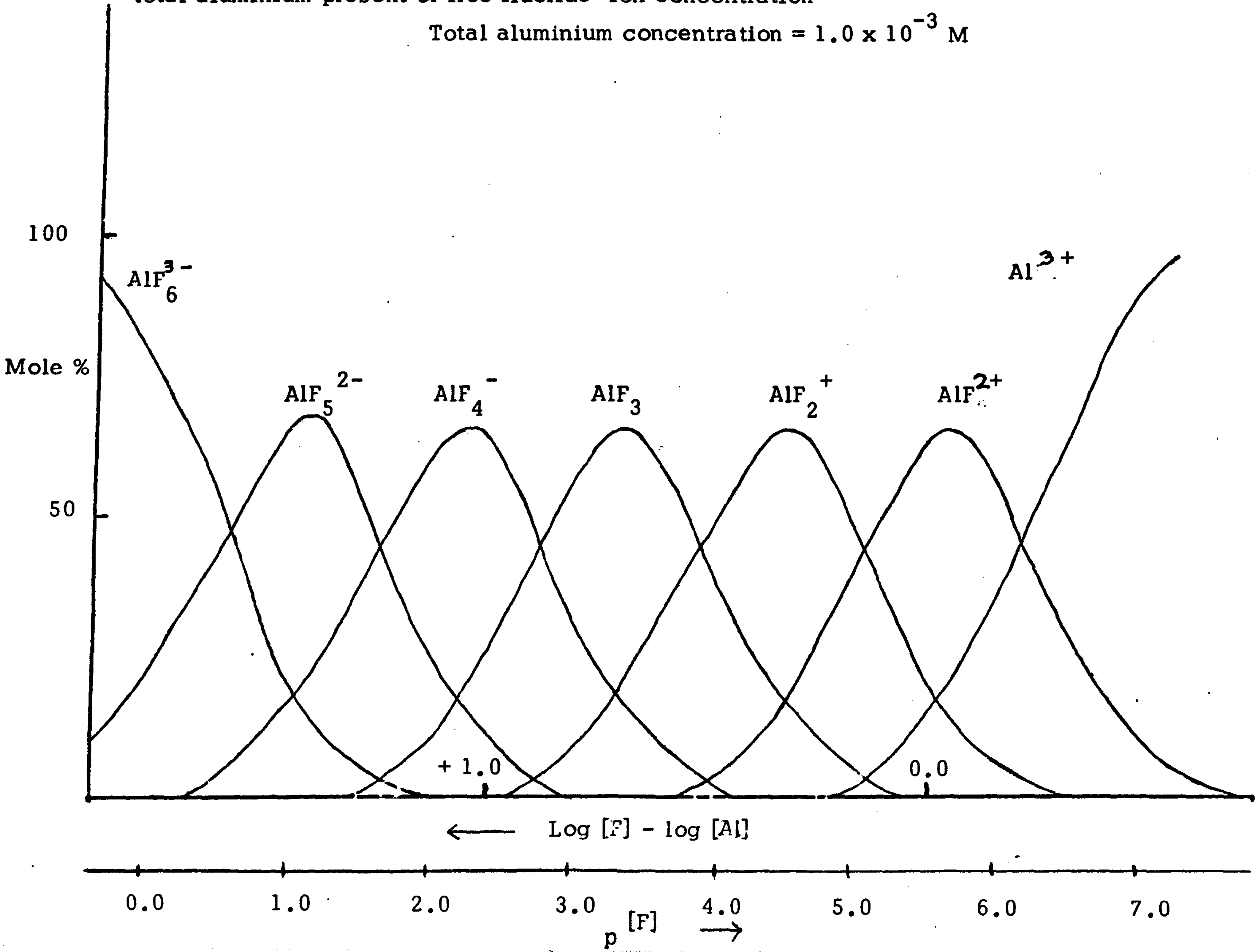
CHAPTER 6.

ALUMINIUM FLUORIDE COMPLEXES.

Previous ^{19}F n.m.r. investigations by Connick and Poulson,[50] and Yamazaki and Takeuchi,[58] have detected resonances for the species AlF^{2+} and AlF_2^+ in aqueous solutions containing aluminium and fluoride ions. The species were identified by comparing the relative intensities of the two resonances to calculated intensities derived from Brosset's[53] stability constants for these species. Such constants, determined in the presence of excess nitric acid, show that as the ratio of free fluoride ion increases in solution, so does the concentration of the higher aluminium fluoride complexes. This may be represented in a graphical manner, figure 6 - 1, where the distribution of the six aluminium fluoride species are related to the free fluoride ion (F^-) concentration and also to the total aluminium and fluorine present. When the concentrations of aluminium and fluorine are similar, the concentration of free fluoride ion is very low. As the ration F/Al is increased, the increase in free fluoride ion is evident in n.m.r. spectra from the coalescence of the AlF^{2+} and AlF_2^+ resonances due to the onset of fast exchange. Low-temperature studies by Yamazaki and Takeuchi on such solutions at -3° revealed the presence of two other resonances, one of which they attributed to higher aluminium fluorides of the type $AlF_n^{(3-n)+}$ where n = 3 to 6, and the other to uncomplexed fluoride itself.

Figure 6 - 1 Concentration of aluminium fluoride species relative to the ratio total fluoride/ total aluminium present or free fluoride ion concentration

Total aluminium concentration = 1.0×10^{-3} M



None of the above investigators had observed the ^{27}Al resonance of these complexes but O'Reilly[51] in a general study of aluminium complexes attributed a ^{27}Al resonance to AlF^{2+} in a fluoride-containing system. This present investigation is divided into two sections a) ^{19}F n.m.r. studies of the aluminium fluoride complexes, b) ^{27}Al n.m.r. studies.

A. ^{19}F N.M.R. Studies.

The objectives of this study may be summarized as follows:

a) to identify and confirm the stability of the AlF^{2+} and AlF_2^+ ions detected in previous studies of aqueous $Al(NO_3)_3$ - NaF systems;

b) to extend such studies to aluminium-ammonium fluoride systems, no previous investigations having been made on these

c) to determine more precisely the higher aluminium fluorides detected in previous low-temperature investigations.

1. Room Temperature Studies.

Systems $Al(NO_3)_3$ - NaF and $Al_2(SO_4)_3$ - NaF.

Initial experiments quickly established the presence of two overlapping resonances in solutions containing equimolar concentrations of aluminium and fluorine. The resonances, visible in the absorption mode, were identified as AlF^{2+} and AlF_2^+, 80.7 and 80.3 ppm respectively upfield of an external trifluoroacetic acid standard. A linewidth of 17 ± 2 Hz was calculated for each resonance, after correcting for overlap. The procedure for identification was similar to that used by Connick. The relative peak intensities were assumed proportional to the concentration of fluorine present. The intensity of the resonance at 80.3 ppm divided by the intensity of the resonance at 80.7 ppm equalled 1.8 agreeing with the theoretical intensities of $\frac{AlF^{2+}}{AlF_2^{+}}$ calculated from Brosset's stability constants.

Increase in the fluoride content of the above solution resulted in a decrease of the AlF^{2+} resonance and an increase of the AlF_2^{+} signal until at a sodium fluoride concentration of 2.0 M only one single resonance was obtained at a chemical shift equal to that of AlF_2^{+}. Further increases in the fluoride content of the solution resulted in a precipitate being formed which was identified as AlF_3 from X-ray analysis.

A decrease in the fluoride concentration to give an F/Al ratio of less than 1 resulted in an increase in the $\frac{AlF^{2+}}{AlF_2^{+}}$ ratio.

A comparison of the relative intensities of the two species is given in Table 6 - 1 and the results are compared to theoretical values derived from Brosset's constants. Spectra were recorded at 60 M Hz on the RS2 spectrometer and typical examples are shown in figure 6 - 2.

The results are commensurate to those obtained from the two previous ^{19}F n.m.r. investigations in which aqueous $Al(NO_3)_3$ - NaF or HF systems were studied. The observed and calculated ratios agree favourably. The most accurate results are obtained where peak intensities are comparable, since at either extreme, the signal-to-noise ratio increases the error of determination of the weaker signal. However the results of the aluminium sulphate system are of special interest. This section of the investigation was undertaken before the dimeric and bisulphate equilibria were fully investigated and their significance in solutions of aluminium sulphate appreciated. Aqueous solutions of aluminium sulphate will contain both equilibria (a pH of 2.3 for a 0.5 M $Al_2(SO_4)_3$ has previously been mentioned). The aluminium fluoride complexes in the $Al_2(SO_4)_3$ - NaF system will therefore be present in two competing equilibria. However the relative intensities of $\frac{AlF^{2+}}{AlF_2^{+}}$ for such solutions are in agreement to those obtained

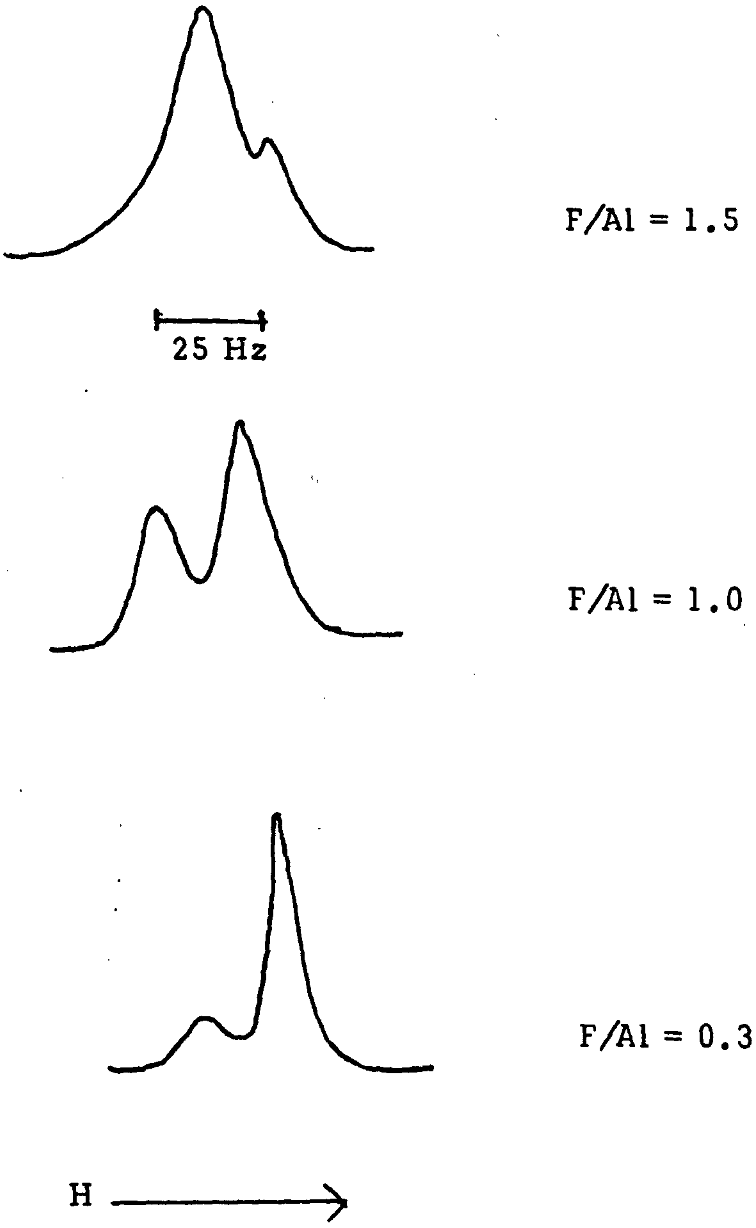
Table 6 - 1.

Comparison of Relative Intensities of ^{19}F Resonances of AlF^{2+} and AlF_2^+ at different F/Al Ratios.

Solution Composition g./atom/litre		Ratio F/Al	Relative Intensities $\frac{AlF^{2+}}{AlF_2^+}$	
F	Al		Observed	Calculated
0.5	0.5^{+}	1	1.7	1.8
1.0	1.0*	1	1.8	1.8
1.5	1.5^{+}	1	1.7	1.8
1.0	1.5*	0.66	4.0	4.7
1.0	0.66*	1.5	0.45	0.49
1.0	1.33*	0.75	2.6	2.3

$^{+}$ $Al(NO_3)_3$ * $Al_2(SO_4)_3$

Figure 6 - 2 ^{19}F spectra of AlF^{2+} and AlF$_2^+$ at 60 M Hz



with the nitrate salt, within experimental error (± 7.5%). This is in keeping with the high stability of the first formed aluminium fluorides in comparison to the dimer and aluminium bisulphate complexes, especially when the latter two species are present in low concentration.

A single resonance is obtained at room temperature with solutions of F/Al ratio 2. Yamazaki and Takeuchi were able to demonstrate that fast fluorine exchange caused coalescence of AlF^{2+} and AlF_2^+ since on cooling such a sample to -3°, exchange rates were lowered and AlF^{2+}, AlF_2^+ and third resonance could be detected, the latter signal was attributed to higher aluminium fluoride complexes.

System $Al(NO_3)_3$ - NH_4F and $A_2(SO_4)_3$ - NH_4F

The high solubility of ammonium fluoride in water makes it a convenient source of fluoride ions. Moreover this salt was used by Brosset in his original potentiometric studies of the aluminium fluoride complexes and it was immediately apparent that it suppressed the formation of insoluble AlF_3, which had previously been encountered with NaF when used at molar F/Al ratios greater than 2.0. A molar ratio of 3.5 could be obtained with NH_4F before precipitation occurred and this precipitate was identified by X-ray analysis as $(NH_4)_3AlF_6$.

At F/Al ratios between 1.0 and 1.5, two resonances were observed which were identified as AlF^{2+} and AlF_2^+ using the procedure described previously. At ratios between 1.5 and 2.5 a third overlapping resonance appeared 1.0 ppm downfield of the AlF_2^+ signal. At a ratio of 3.0 the AlF^{2+} resonance was no longer visible and the AlF_2^+ and unidentified resonance broadened from 24 Hz to 30 ± 2 Hz. This was accompanied by a decrease in the chemical shift between the resonances. At an F/Al ratio of 3.5 only a single resonance was observed with a linewidth of 32 ± 2 Hz.

In table 6 - 2 the observed and calculated intensities are shown for the three resonances at varying F/Al ratios. The relative intensities of AlF_2^+ and AlF^{2+} are expressed as the ratio $\frac{AlF^{2+}}{AlF_2^+}$ and the intensities of AlF_2^+ and the new resonance X as $\frac{X}{AlF_2^+}$. The latter ratio is compared to the calculated value of $\frac{AlF_3}{AlF_2^+}$ obtained from Brosset's constants.

Table 6 - 2.

Relative Intensities and Chemical Shifts of the Fluoride Resonances.

Solution Composition g.atom/litre		Ratio F/Al	No. of Peaks	Chemical Shift ppm †			Intensity AlF^{2+}/AlF_2^+		Intensity X/AlF_2^+	
F	Al			AlF^{2+},	AlF_2^+,	X	Obs.	Calc.	Obs.	Calc.
1	1^*	1.0	2	79.4	78.7	-	1.6	1.8	-	-
1.5	1^*	1.5	3	79.1	78.3	77.3	0.49	0.49	0.13	0.12
2	1^*	2.0	3	78.8	78.1	77.1	0.20	0.15	0.33	0.30
2.5	1^*	2.5	3	78.5	77.7	76.9	0.15	0.1	1.2	0.7
3	1^*	3.0	2	-	77.0	76.3	-	-	2.2	1.5
3.5	1^*	3.5	1	-	-	75.9	-	-	-	-
2.5	1^+	2.5	3	78.5	77.7	76.9	1.7	1.8	1.1	0.7
2	1^+	2.0	3	78.8	78.1	77.1	0.19	0.15	0.31	0.30
1	1^+	1.0	1	79.4	78.7	-			1.7	1.8
3.0	1.5^*	2.0	3	78.8	78.0	77.1	0.18	0.15	0.32	0.30

* $Al_2(SO_4)_3$　　+ $Al(NO_3)_3$　　† Upfield of trifluoroacetic acid

The observed intensities of $\frac{AlF^{2+}}{AlF_2^{+}}$ again agree well with calculated values. Moreover the intensity of the new resonance would appear compatible to the species AlF_3 postulated by Brosset for the F/Al range 1.5 to 2.0. From consideration of his results it may be inferred that significant concentrations of AlF_4^- are present at F/Al ratios of 2.5, 3.0 and 3.5 (calculated values are 1.20, 3.5 and 10.6 mole % respectively). Since no new resonance was observed for the AlF_4^- species at these concentrations, it is assumed that the low-field signal attributed to AlF_3 at F/Al ratio between 1.5 and 2.0, represents AlF_3 and AlF_4^- at ratios between 2.0 and 3.5. At these latter ratios significant quantities of unreacted fluoride will also be present as the species F^-, HF and HF_2^-. A value of some 15 mole % may be calculated from Brosset's data at a F/Al ratio of 3. Since the free fluoride could not be detected as separate resonances the intensity of the lowfield resonance will also contain a contribution from the above.

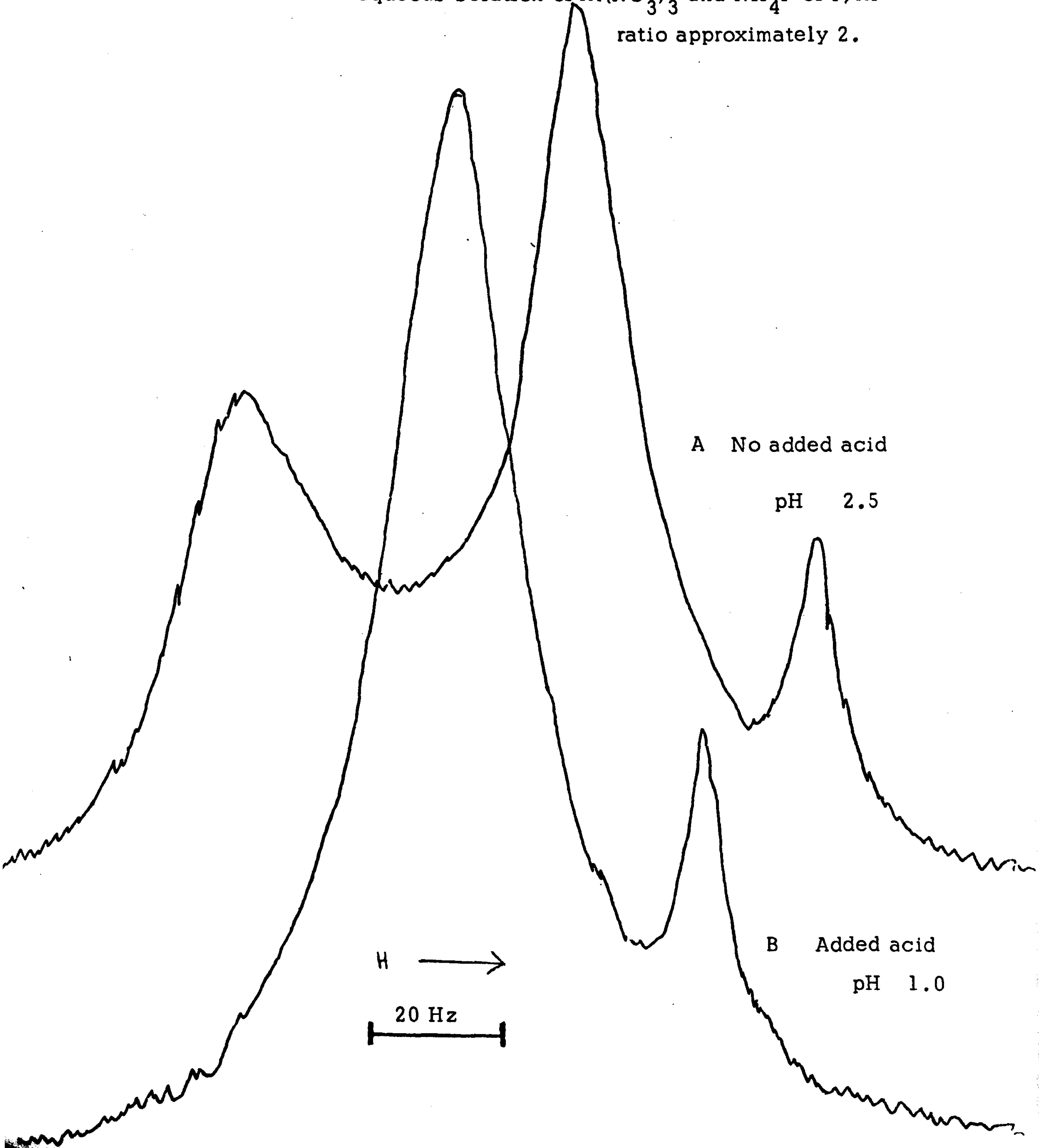
The intensity and chemical shift of the lowfield resonance are similar to those obtained by Yamazaki and Takeuchi in their low temperature studies of the $Al(NO_3)_3$ - HF systems. For F/Al ratios of 1.5 and 2.0 they quote relative intensities of 1.0 : 2.0 : 0.23

and 1.0 : 7.1 : 2.4 for the AlF^{2+}, AlF_2^{+} and Al - F complex signals. Comparative relative intensities found in this investigation are 1.0 : 2.0 : 0.18 and 1 : 6.4 : 1.5. The agreement is fair considering the differing conditions for obtaining the spectra.

The difference between the NH_4F and NaF systems studied at room temperature are obvious. Exchange rates in the former appear to be slower than in the NaF system and this allows the detection of higher aluminium fluorides without resorting to low-temperature studies.

The reason why exchange should be slower with NH_4F is less obvious. During the preparation of solutions containing NH_4F, to give F/Al ratios greater than 2.0, it was noted that a small amount of a gelatenous precipitate formed on addition of the fluoride salt to the aluminium solution. The precipitate dissolved quickly on shaking. The pH of a 1 M $Al(NO_3)_3$ solution containing 2.0 M NH_4F was found to be 2.5. The pH of 1 M solution with no added fluoride ion is less than 1.0 and thus the precipitate formed could be aluminium hydroxide and this infers the presence of a small concentration of dimer in solution (approx. 0.1 M). If exchange rates are lowered by the presence of small concentrations of dimer or dimeric fluorides then some indication of this should be obtained from the study of the NaF systems. Both NaF and NH_4F are slightly basic in solution. When fluoride is not complexed to aluminium it will be present in solution as F^-, HF, and HF_2^-, the formation of the latter two species favouring dimer formation. In this respect both salts should behave in an identical manner but no indication could be found of AlF_3 in the NaF systems at F/Al ratios between 1.5 and 2.0 at room temperature. However, an addition of acid to a NH_4F sample of F/Al ratio of approximately 2.0, a pH of less than 1.0 being obtained, the signals attributed to the higher aluminium fluorides and AlF_2^+ coalesced to a singlet. A small resonance due to AlF^{2+} was still visible and was of the same intensity as in the unacidified sample. The intensity of the singlet equalled that of the separate resonances attributed to AlF_2^+ and the higher aluminium fluorides. The spectra recorded before and after acid addition are shown in figure 6 - 3. The behaviour observed is consistent with a difference in fluoride exchange rates of the two samples. The addition of acid results in an increased rate. If acid addition resulted in major changes of equilibria present then the intensity of AlF^{2+} would increase or decrease on acid addition. This it did not. It would appear therefore from these results that fluorine exchange is apparently slower in the NH_4F systems due to the presence of small concentrations of an acid-sensitive species the equilibria of which does not interfere too greatly with aluminium fluoride formation as postulated

Figure 6 - 3 The effect of acid on the ^{19}F spectrum of an aqueous solution of Al(NO$_3$)$_3$ and NH$_4$F of F/Al ratio approximately 2.



by Brosset. Evidently further investigations are required to elucidate this problem.

The differences observed between the ammonium and sodium systems were not only confined to the number of detected resonances. A cation effect can be observed from a study of the chemical shifts of the three resonances (table 6 - 2) in relationship to the total NH_4^+ ion concentration. As the ammonium ion concentration increases, the chemical shift of the three resonances shows a downfield drift equivalent to 0.6 ppm/mole NH_4^+, figure 6 - 4. The chemical shifts were obtained relative to an external trifluoroacetic acid standard and thus no magnetic susceptibility corrections were made. Inclusion of this standard as an internal reference at a concentration of 0.5% $^v/_v$ resulted in no discernible difference in the spectra and the downfield drift was confirmed as real. Connick in his studies of the aluminium fluorides noticed a similar dependence of the chemical shift of AlF^{2+} and AlF_2^+ on sodium. In this case, an upfield chemical shift of 1.2 ppm/mole Na^+ ion was induced by addition of sodium nitrate or perchlorate. No internal standard was used but again these shifts were found to be correct in this present investigation when trifluoroacetic acid was used as an internal reference, figure 6 - 5.

Figure 6 - 4 Dependence of chemical shift of AlF^{2+}, AlF_2^+ and $AlF_n^{(3-n)+}$ on NH_4^+ concentration

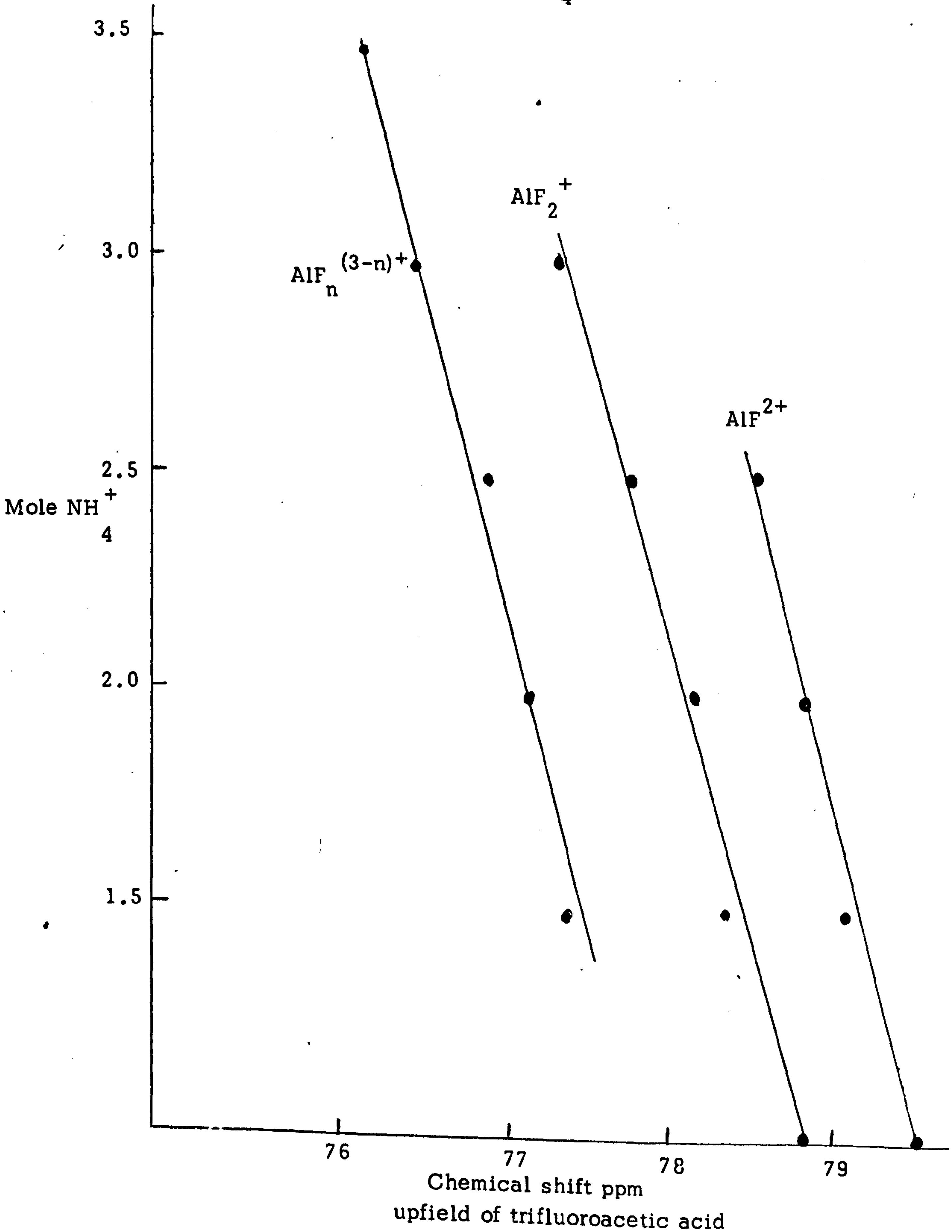
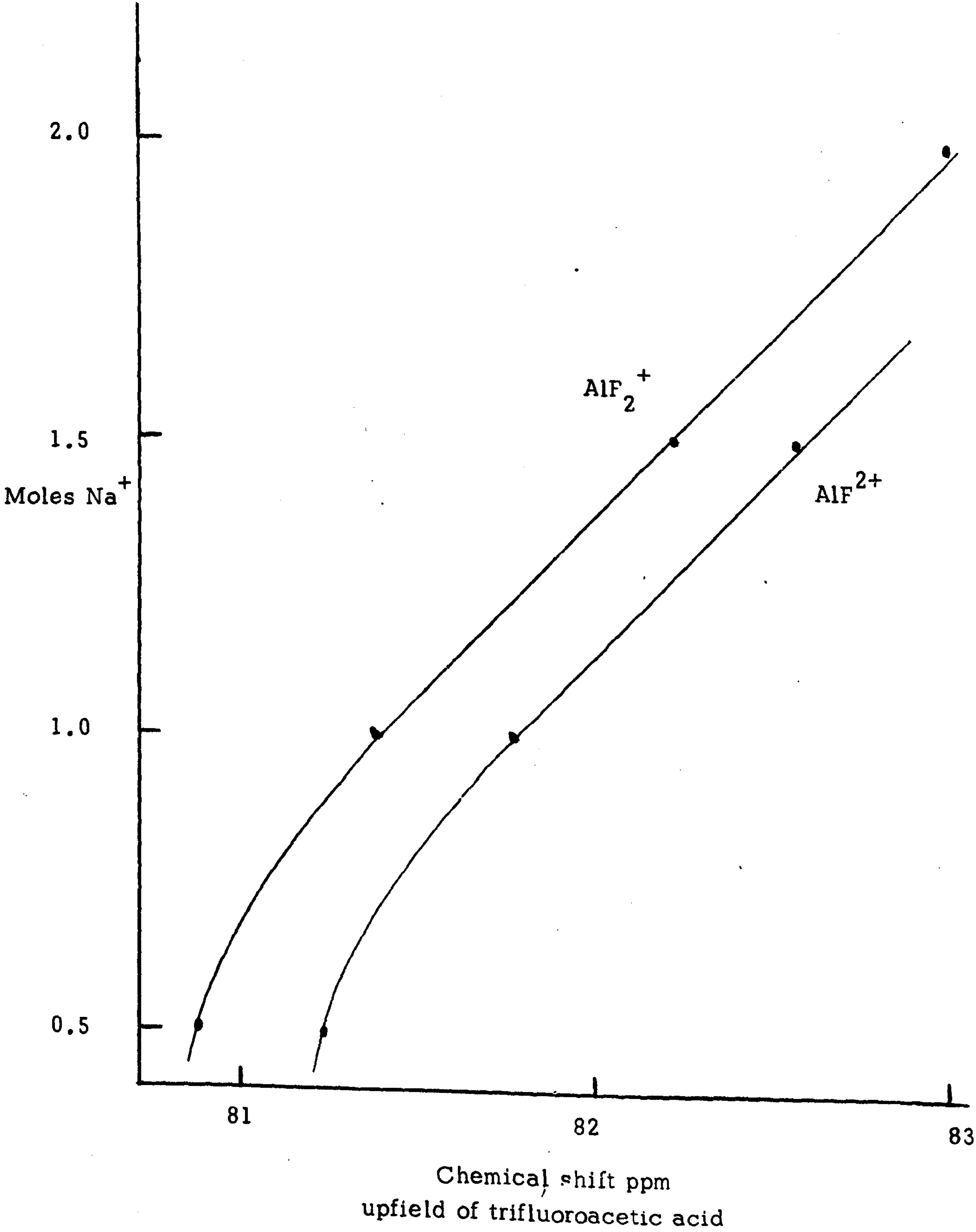


Figure 6 - 5 Dependence of chemical shift of AlF^{2+} and AlF_2^+ on Na^+ concentration



The exact cause of these specific interactions is not known although it has been suggested[50] that the cation interferes with the outer hydration spheres of either the fluoride ions or aluminium fluoride complexes. There could possibly be a link between the different signs of the chemical shifts of NaF and NH_4F with the anomalies observed with spectra of the latter system at room temperature

2. Low-Temperature Studies.

The low-temperature studies of the system $Al(NO_3)_3$ - NaF or HF by Yamazaki and Takeuchi have already been mentioned. Spectra were recorded for F/Al ratios 1, 1.5 , 2.0 and 3.0 and their results would appear compatible to those obtained in this present investigation using NH_4F as a fluoride ion source at room temperature. No attempt was made by these authors to compare the intensities of the resonance of the aluminium fluorides to theoretical intensities calculated from Brosset's stability constants. The new resonance observed at low-temperature was attributed to complexes of the type $AlF_n^{(3-n)+}$ where n = 3 to 6. From the previous discussion it would appear from their calculated intensities, that such a resonance can be assigned to the aluminium fluorides AlF_3, AlF_4^- and to the fluoride ions F^-, HF and HF_2^-.

They also studied a solution of F/Al ratio 6.0 and at a temperature of -3° only two resonances were visible, the chemical shift difference being 7.1 ppm. The lowfield resonance was designated free fluoride ion while the highfield resonance was attributed to aluminium fluoride complexes. Thus even at low temperature fast exchange appears to collapse the individual resonances of the aluminium fluoride complexes. Consideration of Brosset's constants suggests the presence of AlF_3, AlF_4^{1-} and AlF_5^{2-} at an F/Al ratio of 6.

In view of these results it was decided to investigate the aluminium - ammonium fluoride system at low temperature with the possibility in mind of the apparent slow exchange in this system allowing the detection of further individual resonances.

System $Al(NO_3)_3$ - NH_4F

The results of low-temperature studies are shown in table 6 - 3 the spectra being recorded at 84.66 M Hz. Typical spectra are given in figure 6 - 6.

The concentration of ammonium fluoride was kept constant at 1 mole throughout the series and varying F/Al ratios were obtained

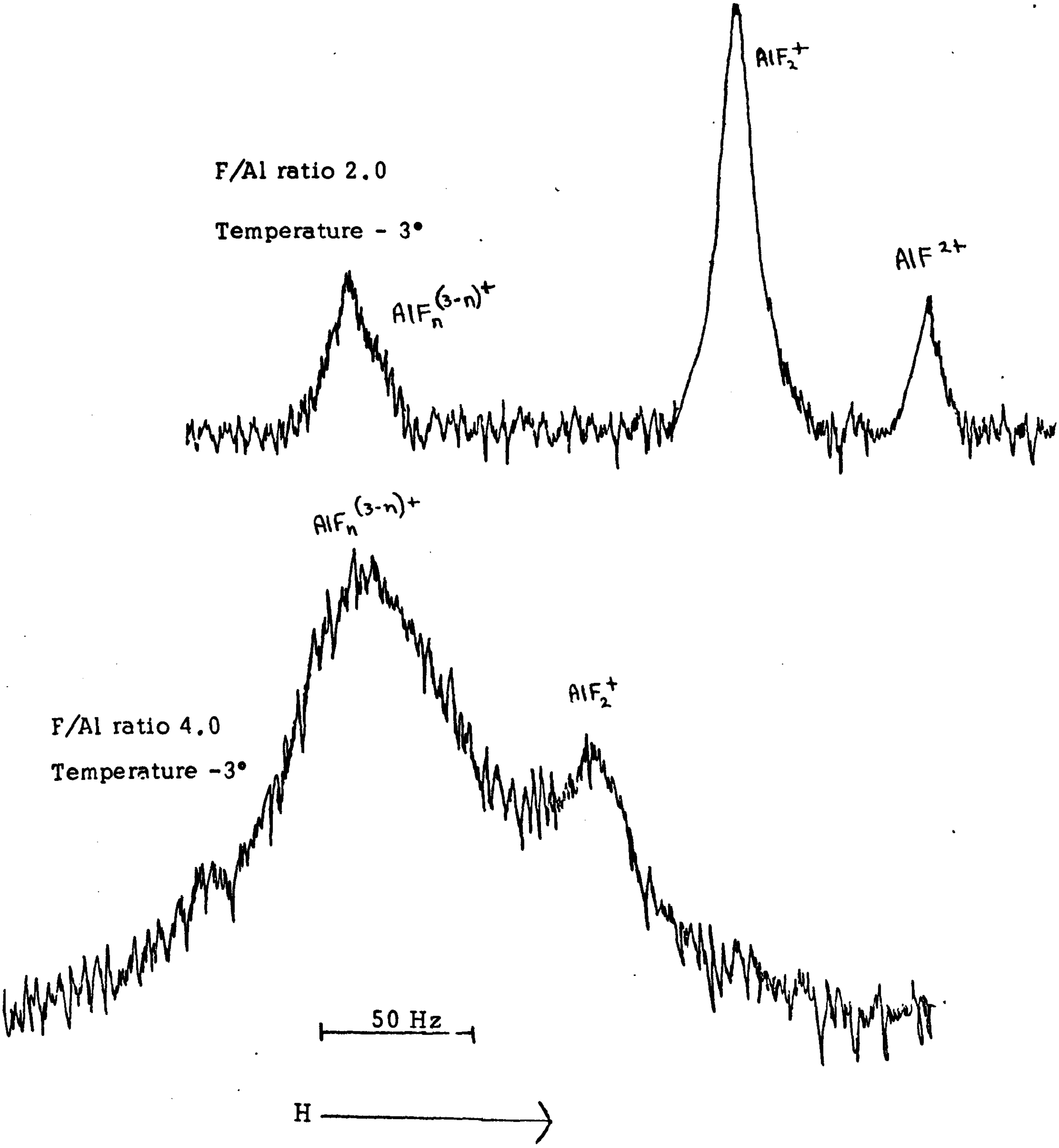
Table 6 - 3.

Low Temperature ^{19}F Studies of Aluminium Fluorides: System $Al(NO_3)_3 - NH_4F$ at -3°.

Solution Composition g. atom/litre F	Al	Ratio F/Al	No. of Peaks	Chemical Shift ppm* AlF^{2+},	AlF_2^+,	$AlF_n^{(3-n)+}$	Intensity $\frac{AlF^{2+}}{AlF_2^+}$ Obs.	Calc.	Intensity $\frac{AlF_n^{(3-n)+}}{AlF_2^+}$ Obs.	Calc.
1	1	1	2	79.6	78.9		1.7	1.8	-	-
1	0.5	2	3	79.6	78.9	77.4	0.14	0.15	0.36	0.30
1	0.33	3	3	-	78.9	77.4	-	-	2.1	2.1
1	0.25	4	2	-	77.9	77.3	-	-	4.2	4.5
1	0.16	6	1	-	-	76.9	-	-	-	-

* Upfield of trifluoroacetic acid

Figure 6 - 6 Low temperature ^{19}F spectra of aluminium nitrate-ammonium fluoride solutions



by adjusting the aluminium concentration. It was possible using this procedure to obtain F/Al ratios as high as 6 without precipitation of $(NH_4)_3AlF_6$. However, at and above a ratio of 4 the hydroxide precipitate was very difficult to redissolve, even with constant shaking or warming, and consequently small increments of acid were added until a clear solution was obtained. The resultant solutions then contained approximately 0.2 M of added HNO_3. Spectra were recorded at a temperature of -3°, lower temperatures than this resulting in the freezing of the solutions.

At an F/Al ratio of 1, AlF^{2+} and AlF_2^+ were clearly visible the linewidth of both being 11 ± 1 Hz. Increasing the ratio to 2.0 resulted in the appearance of the resonance attributed to higher aluminium fluorides, downfield of AlF_2^+. All three signals were clearly separated with no overlap. At an F/Al ratio of 3, AlF^{2+} was no longer visible and the remaining two resonances broadened to give values of 50 Hz for the higher aluminium fluorides and 30 Hz for AlF_2^+. Two peaks could still be distinguished at a ratio of 4, these being the signal due to the higher aluminium fluorides and AlF_2^+. The intensity of the latter was now much smaller in comparison to the former. Only one resonance 100 Hz was obtained at an F/Al ratio of 6. No resonance could be detected compatible with that for the free fluoride ion detected by

Yamazaki and Takeuchi in their study of the $Al(NO_3)_3$ - HF systems at -3°.

The observed intensities for $\frac{AlF^{2+}}{AlF_2^+}$ and $\frac{AlF_n^{(3-n)+}}{AlF_2^+}$ agree well with calculated values obtained from Brosset's constants. The theoretical intensity of $AlF_n^{(3-n)+}$ was calculated assuming that this resonance represented the species AlF_3, AlF_4^-, F^- HF and HF_2^-, as discussed in the previous section.

Addition of acid to samples of F/Al ratio 2.0 and 3.0 resulted in no observable difference in the relative intensities of all resonances, the pH of the solutions being less than 0.5.

It is obvious that these results are only slightly different from those obtained for ammonium fluoride at room temperature. The decrease in temperature only slightly lowers the rate of fluorine exchange which results in comparatively narrow lines for the observed resonances and the separation of AlF_2^+ and $AlF_n^{(3-n)}$ at a F/Al ratio of 4. At room temperature only a singlet was obtained for this ratio. Fast rates of exchange however still prevail at F/Al ratios of 6 resulting in only a single resonance being observed. These rates would appear to be faster than in the HF system at an F/Al of 6.0 since no separate resonance was observed for free fluoride ion observed by Yamazaki. The good agreement between the observed and calculated values of $\frac{AlF_n^{(3-n)+}}{AlF_2^{+}}$ is further evidence for the assignment of the low-field resonance to the species AlF_3, AlF_4^-, F^-, HF and HF_2^- for F/Al ratios 1.5 to 4.0.

B. ^{27}Al N.M.R. Studies.

At F/Al ratios of 1.5 or less, significant quantities of unreacted aluminium will be present in solution as the $Al(H_2O)_6^{3+}$ ion, assuming no dimer present. The concentration of the aquated ion will increase as the F/Al ratio decreases. Connick in his studies of the aluminium fluorides was able to detect this unreacted aluminium and the concentrations found were in agreement once more with theoretical concentrations calculated from Brosset's constants. He was unable however to observe any resonances which could be attributed to the aluminium fluoride complexes. O'Reilly, in a general investigation of aluminium salts detected a broad resonance in an acidic solution of KF and $Al(NO_3)_3$ which he attributed to AlF^{2+}. The resonance was 330 Hz wide and 15 ppm downfield of $Al(H_2O)_6^{3+}$. No details of solution composition were given.

Initial ^{27}Al studies in this present investigation were undertaken using the RS2 spectrometer. The $Al(H_2O)_6^{3+}$ resonance was quickly observed at F/Al ratios of 1.5 or less. Table 6 - 4 shows the calculated and theoretical concentrations of aluminium present. The system studied was $Al(NO_3)_3$ - NaF and agreement is seen to be good between calculated and observed values.

No other resonances were observed as either derivative or absorption mode signals for solutions up to a F/Al ratio of 1.0. At a ratio of 1.5 however indications were obtained of a broad resonance underlying the $Al(H_2O)_6^{3+}$ signal. Spectra were recorded as the derivative and owing to the very high modulation amplitude required to observe this broad signal, severe over-modulation of the $Al(H_2O)_6^{3+}$ signal was obtained making an accurate assessment of the area or linewidth of the former impossible.

Investigations were continued on the Bruker detecting the signals in the absorption mode. Solutions were prepared from NH_4F and $Al(NO_3)_3$ in the manner previously described to give a F/Al range from 5.0 to 1.0. Spectra were recorded at maximum transmitter power. The number of resonances observed and their relative intensities are shown in table 6 - 5.

Table 6 - 4.

Concentration of Aquo-Aluminium Ion at Varying F/Al Ratios at Room Temperature.

Solution Composition g.atom/litre		F/Al	Concentration of $Al(H_2O)_6^{3+}$ Mole		Linewidth Hz
F	Al	Ratio	Observed	Calculated	
0	1.0	0.0	1.0	1.0	20
0.3	1.0	0.3	0.61	0.64	20
0.5	1.0	0.5	0.49	0.53	22
1.0	1.0	1.0	0.16	0.15	25
1.5	1.0	1.5	0.04	0.035	30

Table 6 - 5.

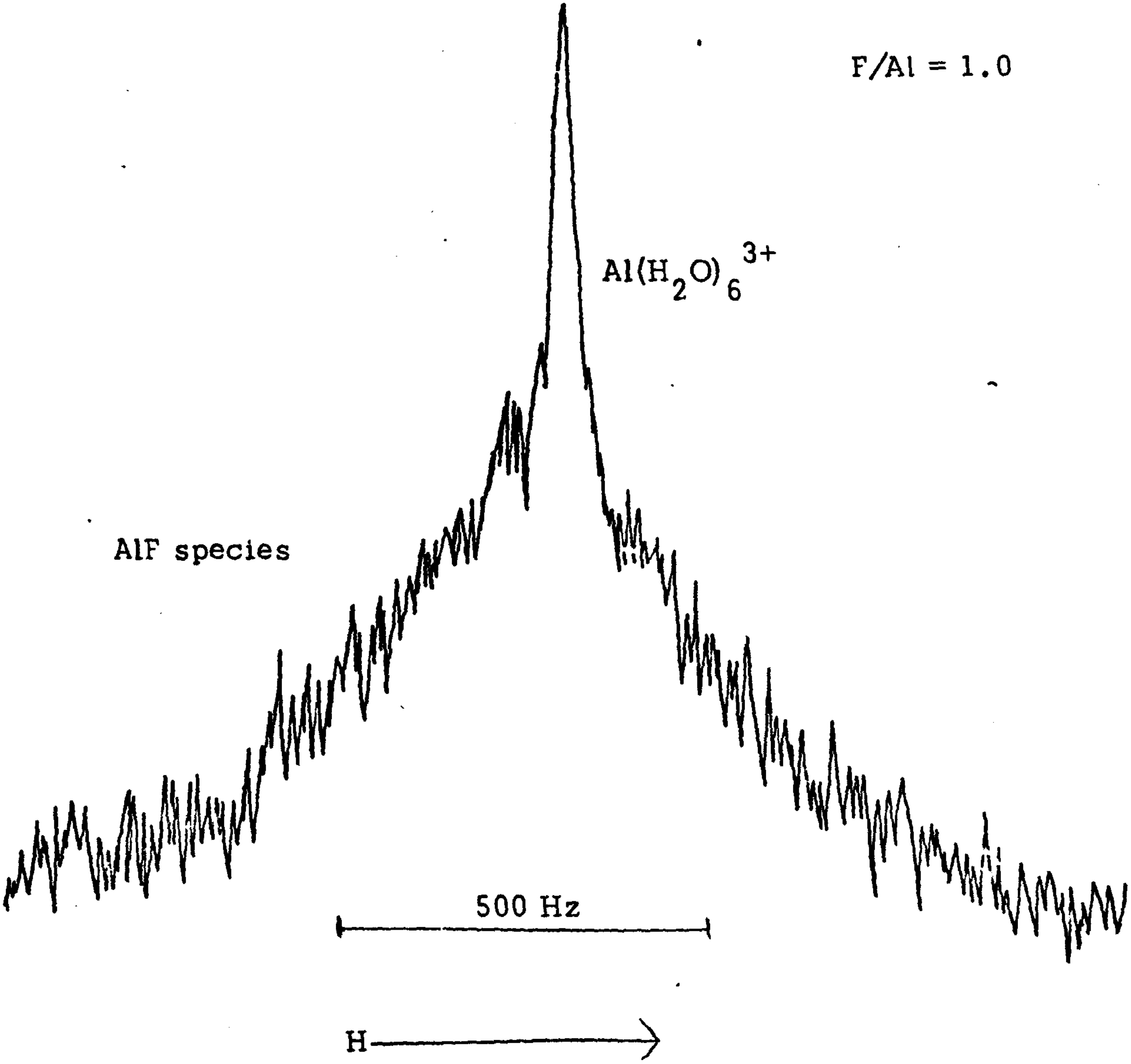
Variation of ^{27}Al Resonance with Solution Composition.

Solution Composition g.atom/litre		Ratio F/Al	No. of Resonances Observed	Intensity of Resonances		Linewidth Hz AlF Complexes
F	Al			AlF Complexes	$Al(H_2O_6^{3+}$	
1.0	0.2	5	1	18	-	550 ± 50 Hz
1.0	0.4	2.5	1	36	-	550 ± 50 Hz
1.0	0.6	1.66	1	52	-	550 ± 50 Hz
1.0	0.8	1.25	2	72	1.5	550 ± 50 Hz
1.0	1.0	1.0	2	78	8	550 ± 50 Hz
0.5	1.0	0.5	2	44	40	550 ± 50 Hz

A single broad resonance, 550 Hz wide, was obtained for a solution of F/Al composition 5. As the ratio was decreased to 2.5 and then to 1.66 the intensity of the signal remained proportional to the total aluminium concentration present. No significant quantities of $Al(H_2O)_6^{3+}$ should be present in any of these high ratios, the aluminium complexes formed at ratios of 5.0 being AlF_3, AlF_4^- and AlF_5^{2-}; at 2.5, AlF^{2+}, AlF_2^+, AlF_3 and AlF_4^-; and at 1.66, AlF^{2+}, AlF_2^+ and AlF_3. Since the intensity of the resonance is proportional the aluminium concentration over a wide spectrum of complexes, the single resonance observed must represent all species, the chemical shift and linewidths of the individual resonances being so similar that they cannot be resolved.

At a F/Al ratio of 1.22 small quantities of unreacted $Al(H_2O)_6^{3+}$ should be present. This was detected as a small peak on the apex of the broad resonance. Decreasing the F/Al ratio to 1.0 and then to 0.5 resulted in an increase for the $Al(H_2O)_6^{3+}$ signal and a decrease in the intensity of the resonance attributed to the AlF complexes. The relative intensities of these two signals are seen to be in keeping with the assignment made above (cF also table 6 - 4).

Figure 6 - 7 ^{27}Al spectrum of a solution of $Al(NO_3)_3$ and NH_4F



The chemical shift of the resonance attributed to the AlF species was only slightly different to that of $Al(H_2O)_6^{3+}$, a value of 2.0 ± 0.5 ppm downfield of the latter resonance being calculated. A typical spectrum of a solution of F/Al ratio 1.22 is shown in figure 6 - 7. The linewidth of the aluminium fluoride resonance is presumably a reflection of an increased field gradient at the nucleus as a result of fluorine replacing water molecules of the hydration shell of $Al(H_2O)_6^{3+}$.

Discussion.

Results of ^{19}F n.m.r. investigations of the aluminium fluoride complexes have been interpreted as evidence for the formation of the species AlF^{2+}, AlF_2^+, AlF_3 and AlF_4^-. The stabilities of these species agree with constants determined by Brosset who calculated values of

AlF^{2+}	$\log K_1 = 6.13$
AlF_2^+	$\log K_2 = 5.02$
AlF_3	$\log K_3 = 3.85$
AlF_4^-	$\log K_4 = 2.74$

The majority of this investigation was undertaken before the full significance of aluminium hydrolysis was realised with respect to dimer formation and pH variations. Consequently experiments were not designed to eliminate or investigate the possible formation of dimeric fluorides. Results do suggest that if the hydrolysis products of $Al(H_2O)_6^{3+}$ are present in small quantities then the formation of the above aluminium of fluorides is not inhibited. The influence of pH-dependent species would appear to be more important with respect to rates of fluorine exchange. There is considerable room for further studies on this subject.

^{27}Al n.m.r. investigations have shown that only one resonance is observed for all fluoride species. The chemical shift and linewidth of the individual resonances are assumed to be too similar to allow resolution of the signal into individual peaks.

CHAPTER 7.

ALUMINIUM PHOSPHATE COMPLEXES.

Previous studies of aqueous aluminium chloride-sodium dihydrogen phosphate and aluminium phosphate-phosphoric acid systems by pH, conductivity and ion exchange techniques[60-64] have furnished evidence for the existence of both cationic and anionic phosphatoaluminium complexes. The majority of these investigations were made using phosphate concentrations of less than 1 mole and the assigned structures of the aluminium complexes were based on the assumption that the simple phosphate ions $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} were present in solution and reacted with the aluminium. Thus complexes of the type $Al(H_2PO_4)_2^+$ or $Al(H_2PO_4)^{2+}$ were postulated.

No references have been found to any n.m.r. studies of these complexes and it was therefore decided initially to investigate aqueous aluminium nitrate-phosphoric acid acid systems. Such should provide highly acidic solutions in which the aluminium would be present as the $Al(H_2O)_6^{3+}$ ion with competing dimeric equilibria absent. After knowledge had been obtained of the complexes present in the former, investigations could then be extended to solutions where a high proportion of aluminium was present as the dimer. The nuclei chosen for the major section of these studies were obviously ^{27}Al and ^{31}P. All spectra were obtained on the Bruker spectrometer unless otherwise stated.

A. Phosphate Complexes of Aluminium Formed in the Presence of $Al(H_2O)_6^{3+}$.

1. ^{31}P Studies at Room Temperature.

The ^{31}P spectra of aqueous solutions of orthophosphoric acid is well documented,[90] A concentrated solution s.g. 1.75 gives a single resonance 10 to 11 Hz wide, the individual species present being undetected as separate signals due to rapid exchange mechanisms. As the acid is diluted, the linewidth of the resonance becomes narrower due to the decrease in viscosity. No change in the chemical shift of the resonance is apparent until the concentration of the acid is much less than 1.0 M or the pH is raised above 1.0. A downfield shift then commences which amounts to a value of 1 ppm at a pH of 4.0. This is a reflection of the average number of protons bound to each phosphate ion, a solution containing only PO_4^{3-} having a chemical shift of some 13 ppm downfield of an orthophosphoric acid standard.

The present studies on aluminium phosphate complexes began with a solution containing 1M $Al(NO_3)_3$ and 0.8 M H_3PO_4. Four broad resonances of equal intensity were visible, the chemical shifts being A 0.0, B 8.6, C 13.2, and D 15.6 ppm upfield of an 85% orthophosphoric acid standard (external). The widths of the resonances at half amplitude were A 75 Hz and B, C and D 100 Hz, the last three signals overlapping. On increasing the phosphoric acid content to 3.2 M, the $Al(NO_3)_3$ concentration remaining constant at 1 M, the resonances C and D coalesced to give a single peak of chemical shift 12.4 ppm. The intensity of peak A was noticeably greater than the two other resonances and its chemical shift was now different to that of the standard, being 1 ppm to highfield of 85% H_3PO_4. All resonances were observed to be coalescing in a solution containing 5.6 M H_3PO_4 and 1 M $Al(NO_3)_3$ and at a concentration of 8.0 M H_3PO_4, only a single signal was obtained, 100 Hz wide, and 1.8 ppm upfield of H_3PO_4. Typical spectra are shown in figure 7 - 1, the spectrometer used being the Bruker at 36.43 M Hz. In table 7 - 1 information is given on the chemical shifts and linewidths of the resonances at varying H_3PO_4/Al ratios.

The relative changes in chemical shifts and linewidths of the resonances can be explained simply in terms of exchange mechanisms. At high phosphoric acid concentrations fast rates of exchange result in only a single resonance being observed for all species present. As the concentration of acid is decreased so does the exchange rate, resulting in the observation of separate signals.

Figure 7 - 1 ^{31}P Spectra of aluminium nitrate-phosphoric acid solutions at room temperature

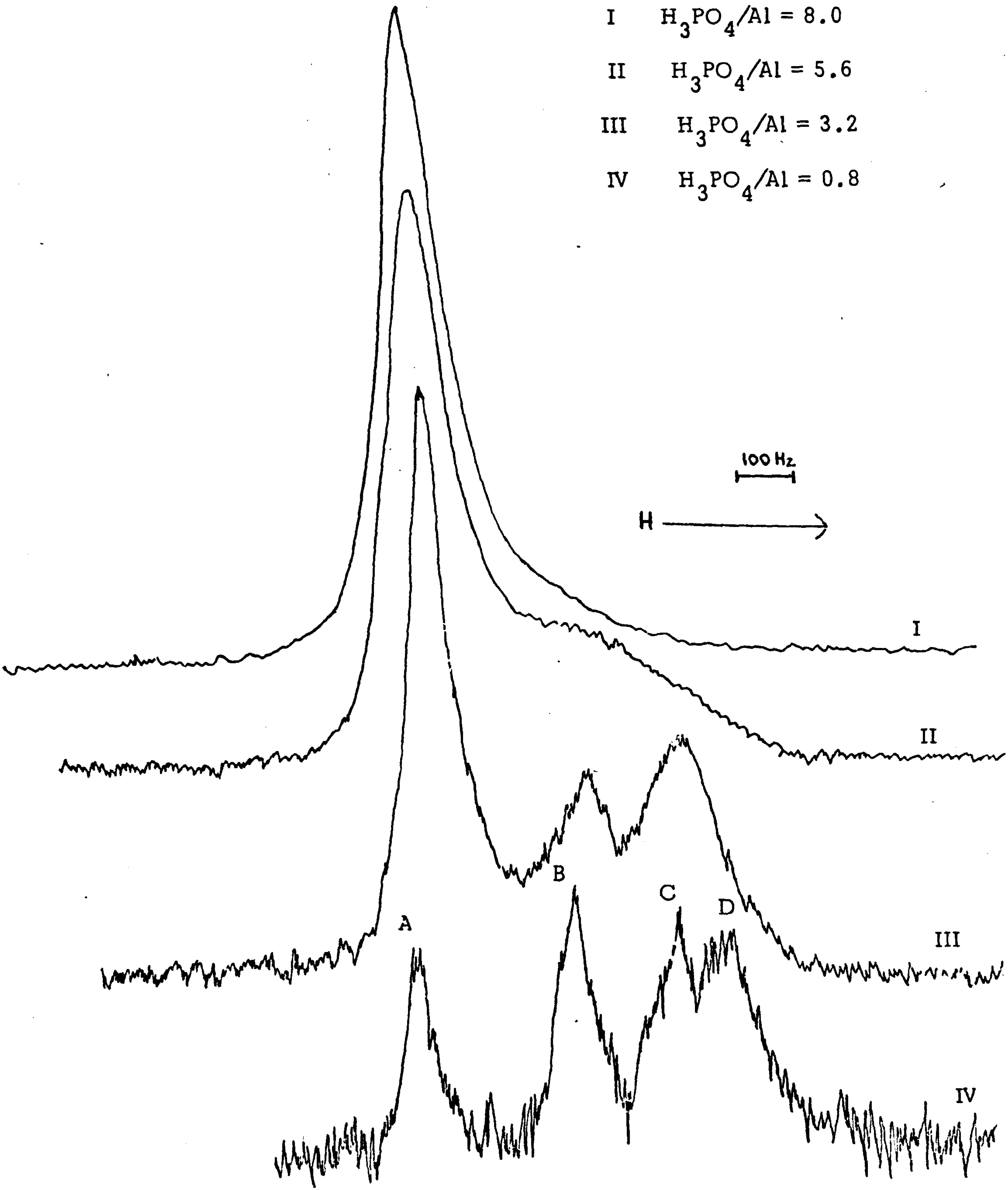


Table 7 - 1.

Comparison of Linewidths and Chemical Shifts of ^{31}P Resonances at Room Temperature.

Solution Composition											
Mole		Ratio	Number of	Linewidth				Chemical Shift+			
$Al(NO_3)_3$	H_3PO_4	H_3PO_4/Al	Resonances	Hz				ppm			
				A	B	C	D	A	B	C	D
1.0	8.8	8.8	1	100				1.84			
1.0	7.2	7.2	1	120				1.80			
1.0	5.6	5.6	2	110	350			1.38	3.8		
1.0	4.8	4.8	3	110	150	175		1.10	8.85	12.5	
1.0	3.2	3.2	4	90	150	150	140	0.60	8.80	13.7	15.3
1.0	1.6	1.6	4	80	100	150	130	0.0	8.6	13.2	15.6
1.0	0.8	0.8	4	75	100	110	100	0.0	8.6	13.2	15.6
0	16.0	-	1	10	-	-	-	0.0	-	-	-

+ Upfield of H_3PO_4

It was just feasible to detect the above resonances using the RS2, the signals being recorded as their derivatives. The chemical shift of all peaks at 20 M Hz were within ± 1.5 ppm of those obtained on the Bruker confirming the presence of phosphorus in four distinct chemical environments.

The chemical shift of the lowfield resonance (A) cannot be distinguished from that of phosphoric acid when exchange is slow. This signal could therefore represent free unreacted phosphoric acid, the remaining three resonances being phosphate complexes of aluminium.

It can be seen in table 7 - 1 that even at the lowest concentrations of phosphoric acid studied (0.8 M), the linewidths of all resonances are still broad in comparison to a pure H_3PO_4 standard. If this was still the result of exchange reactions then obviously low-temperature studies might provide further information. Such investigations were therefore undertaken.

2. Low-Temperature ^{31}P Investigations.

The results of the low-temperature investigations are summarized in table 7 - 2. The high solute concentration in some of the samples enabled temperatures as low as -50° to be obtained before the solutions froze. The first solution examined contained 8.0 M H_3PO_4 and 1 M

Table 7 - 2.

Comparison of Linewidths and Chemical Shifts of ^{31}P Resonances obtained from Low-Temperature Studies at -15°.

Solution Composition Mole		Ratio	Number of	Linewidth Hz				Chemical Shift ppm +			
$Al(NO_3)_3$	H_3PO_4	H_3PO_4/Al	Resonances	A	B	C	D	A	B	C	D
0.5	12.4	24.8	2	30	50			0.0	7.6		
1	8.0	8.0	3	20	50	80		0.0	7.6	12.3	
1	6.4	6.4	4	20	50	70	50	0.0	7.6	12.3	15.7
1	4.8	4.8	4	15	50	65	50	0.0	7.6	12.3	15.7
1	3.2	3.2	4	10	50	60	50	0.0	7.6	12.3	15.7

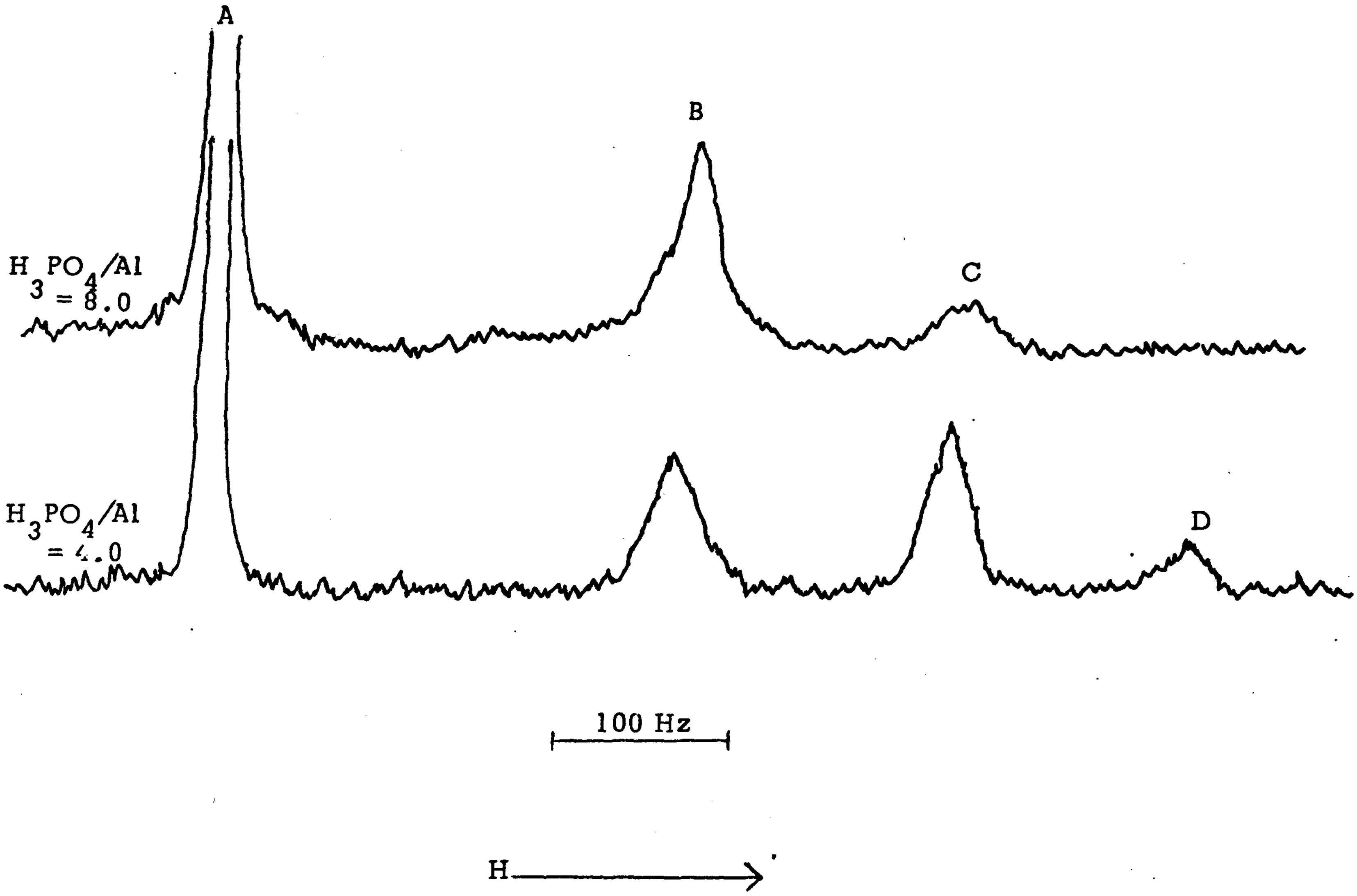
+ Upfield of H_3PO_4

$Al(NO_3)_3$. At room temperature a single peak was obtained. However on cooling to -15°, three resonances could clearly be distinguished, no overlap of the signals occurring. The resonances were identified by their chemical shifts as unreacted phosphoric acid A and the two aluminium phosphate complexes B and C. The intensity of the free-acid peak was far greater than that of B and C, the latter being the least intense. Recorded linewidths were A 10 Hz, B 30Hz, and C 30 Hz. An increase in the H_3PO_4/Al ratio above 8 resulted in a decrease in the intensity of C and a marked increase in A. At a ratio greater than 20 only the unreacted acid and aluminium complex (B) could be detected.

Decreasing the H_3PO_4/Al ratio below 8.0 resulted in an intensification of peak C and the appearance of resonance D of linewidth 50 Hz, and at a ratio of 3.2 the spectrum obtained was similar to that recorded at room temperature with the exception of reduced linewidths due to slower exchange rates. Typical spectra are shown in figure 7 - 2.

Further investigations at temperatures as low as -50° detected no other broad resonances besides those already discussed. However in the temperature range -40° to -50°, fine structure was observed for resonance B, the aluminium phosphate complex signal adjacent to unreacted

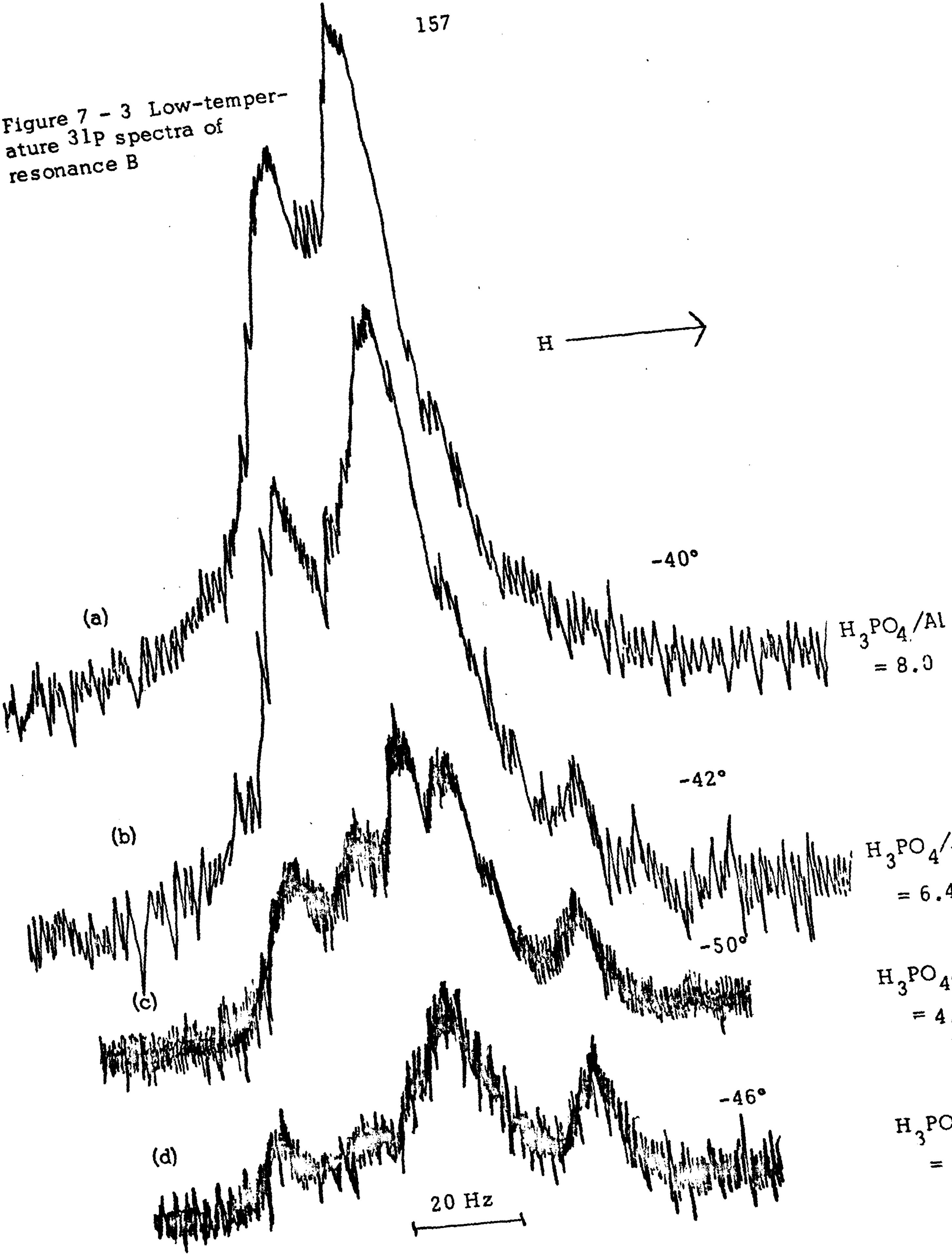
Figure 7 - 2 Low-temperature ^{31}P spectra of aqueous aluminium nitrate phosphoric acid solutions



phosphoric acid. This structure was observed for solutions of H_3PO_4/Al ratios between 8.0 and 3.2, the other complex resonances at these ratios showing no such splitting, being 50 -70 Hz wide. Typical spectra of resonance B are shown in figure 7 - 3.

The temperature at which the maximum fine structure was observed was dependent of the solution composition. At an H_3PO_4/Al ratio of 8.0 the maximum resolution was obtained at -40 ± 2°, figure 7 - 3(a). Lower temperature than this resulted in viscosity broadening and a single flat-topped resonance resulted. At higher temperatures, increased exchange rates resulted in a singlet. A temperature of -42 ± 2 was most suitable for a ratio of 6.4 while the decreased viscosity of a ratio of 4.8 allowed the maximum resolution to be observed at -50 ± 2°. The latter spectra, figure 7 - 3(c) provides the most structural information. At a H_3PO_4/Al ratio of 3.2 the spectrum was recorded at a temperature of -46 ± 2°, figure 7 - 3(d), a lower temperature than this resulting in the solution freezing. As a consequence of this temperature, some of the fine structure observed in the previous spectra at a lower temperature is not apparent in the sample of ratio 3.2.

Figure 7 - 3 Low-temperature 31P spectra of resonance B



The structure of resonance B could arise in several ways. Each peak, or group of peaks could represent different complexes or different steric arrangements of one complex. Coupling of one phosphorus or several phosphorus nuclei to protons, phosphorus or aluminium could also be responsible. It would appear however from figure 7 - 3 that all spectra contain the same basic elements irrespective of the H_3PO_4/Al ratio, any differences which do occur being explained by increasing viscosity as the ratio increases and different temperatures for recording the spectra. The latter would effect exchange rates and coalescence of the resonances. If a similar spectrum is observed over a range of phosphoric acid-aluminium ratios, then this would not favour the assignment of each resonance to a separate complex.

It was obvious that further information would be required before the nature of the complexes present could be discussed and ^{27}Al investigations were therefore undertaken.

3. ^{27}Al Investigations of Aluminium Phosphate Complexes at Room Temperature.

The intensity of the aquo aluminium resonance was noted for a number of solutions containing 1 M $Al(NO_3)_3$ and increasing increments of phosphoric acid. A progressive decrease of the $Al(H_2O)_6^{3+}$ signal area was observed with increasing H_3PO_4 content of the sample. At an H_3PO_4/Al ratio of 0.8 a second peak was detected, 100 Hz wide, and 7.7 ppm upfield of the $Al(H_2O)_6^{3+}$ resonance. The intensity of this highfield resonance increased as the result of further increments of phosphoric acid to the sample. This was accompanied by a broadening of the linewidth, a value of 280 Hz being recorded at an H_3PO_4/Al ratio of 4.0. At ratios higher than this the $Al(H_2O)_6^{3+}$ resonance was no longer visible. Quantitative estimations of the intensity of the signal at these ratios were within ± 7% of the intensity of the aquated aluminium ion in a 1 M $Al(NO_3)_3$ solution containing no phosphoric acid. All aluminium would therefore appear to be complexed as phosphate species at these ratios.

Spectra obtained at 23.45 M Hz are shown in figure 7 - 4. The increases in linewidths observed at high H_3PO_4/Al ratios could be accounted for by the greater viscosity of the solutions. It would also appear that only a single ^{27}Al resonance represents all three complexes observed in the ^{31}P studies. However, a closer inspection of figure 7 -4 (a) and (b) reveals a broad shoulder on the lowfield side of the aluminium phosphate signal. Figure 7 - 5 shows the resolved spectra of the sample of ratio 1.6, a value of 150 Hz being estimated for the linewidth of the second aluminium phosphate resonance. The chemical shift of this resonance can just be distinguished from that of $Al(H_2O)_6^{3+}$,

Figure 7 - 4

^{27}Al spectra of aqueous $Al(NO_3)_3$ - H_3PO_4 solutions at room temperature

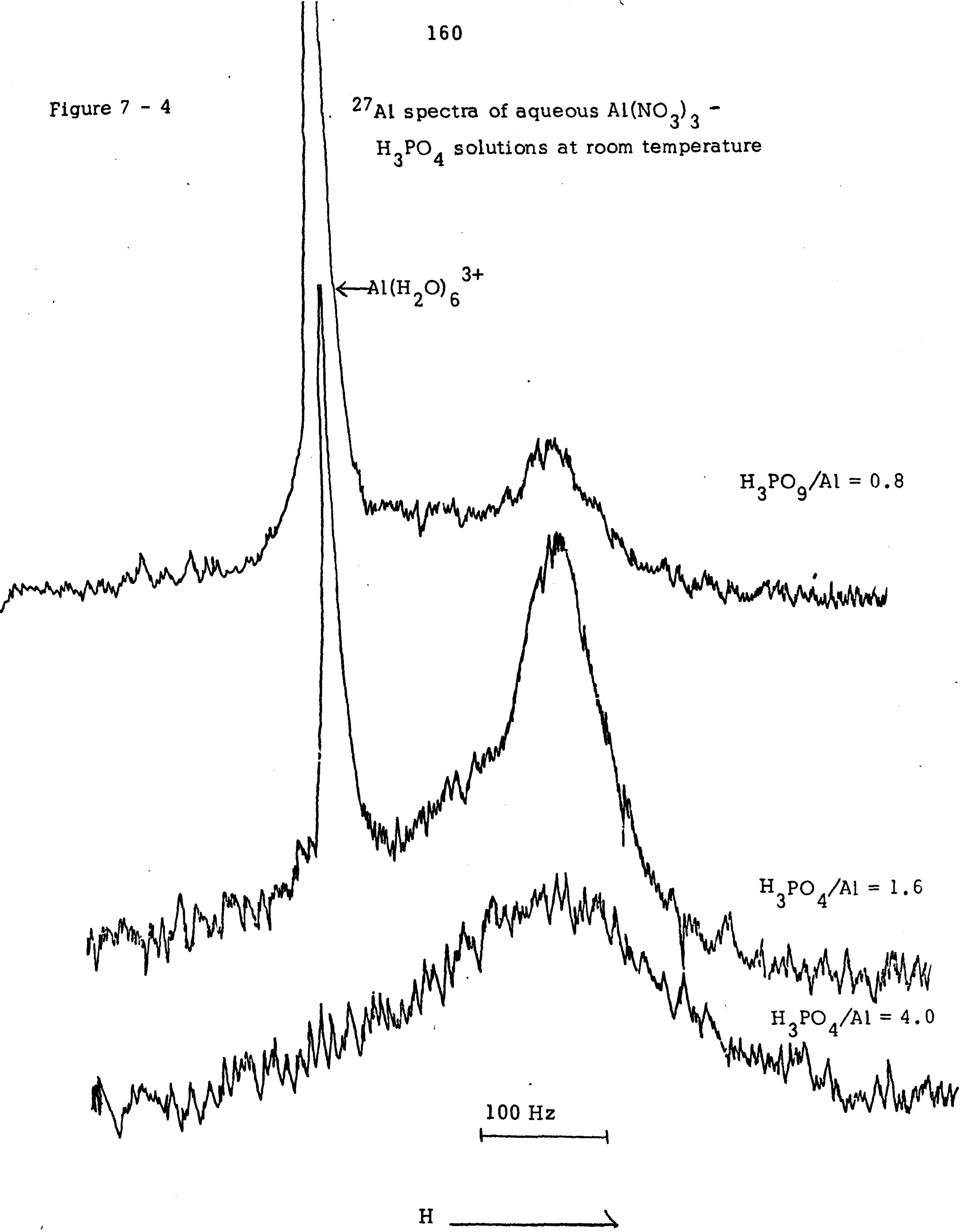
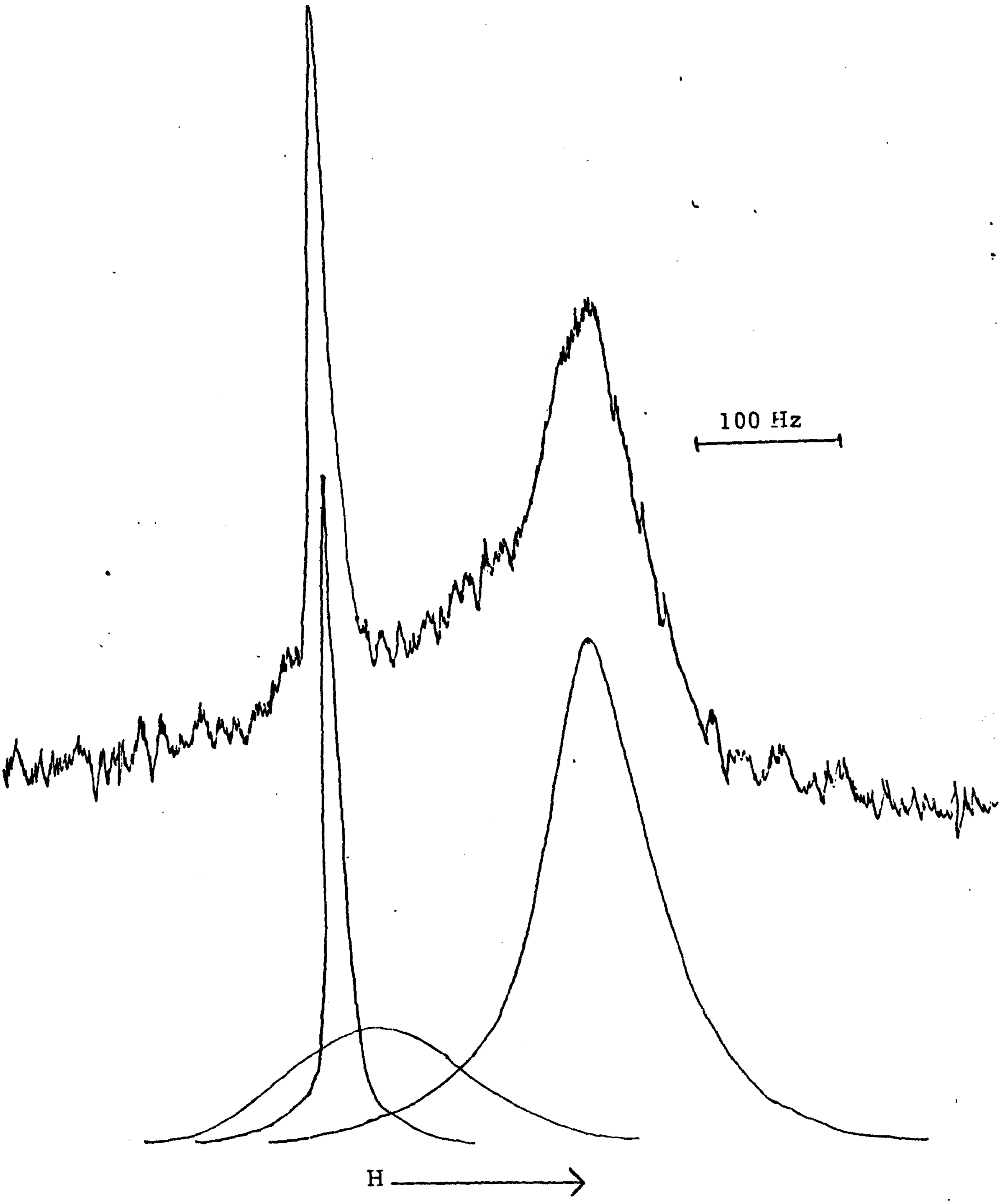


Figure 7 - 5 Resolved ^{27}Al Spectrum of solution containing 1M $Al(NO_3)_3$ and 1.6 M H_3PO_4.



a value of 1.0 ppm upfield of the aquated aluminium signal being calculated. The intensity of the lowfield ^{27}Al resonance of the phosphate complexes is approximately one-third to half that of the resonance at 7.7 ppm. In ^{31}P studies of similar solutions at room-temperature, three aluminium phosphate signals can be detected. Since only two comparative ^{27}Al signals can be found this would suggest that two of the aluminium phosphate complexes have similar bonding, chemical environments or size, these being different from the third complex. At H_3PO_4/Al ratios higher than 1.6 the resolution of the two ^{27}Al resonances of the Al - P complexes became progressively harder due to viscosity broadening of each signal.

The width of the resonances for such complexes imply short ^{27}Al relaxation times at room temperature. These times would be even less at -50° due to the increased viscosity of solution. Aluminium phosphorus coupling would not therefore appear to be the cause of the fine structure observed in the low-temperature ^{31}P studies.

The ^{27}Al resonances of the aluminium phosphate complexes would not appear to be so informative as comparative ^{31}P spectra. However quantitative analysis of the concentration of residual $Al(H_2O)_6^{3+}$ in such systems in conjunction with ^{31}P determination of the concentration of phosphorus in each complex should provide information on the stoichiometry of the systems. Such investigations were therefore undertaken.

4. Quantitative Analysis of Aluminium Phosphate Complexes.

The determination of the concentration of phosphorus complexed as aluminium phosphates at varying H_3PO_4/Al ratios necessitated low-temperature ^{31}P investigations. This enabled information to be obtained at high ratios where exchange rates gave a single resonance for all species present at room temperature. However, the reduction of sample tube size, from 10 mm at room temperature, to 5 mm for low-temperature studies, made it imperative that the most concentrated solutions were used in order to obtain a good signal-to-noise ratio at low H_3PO_4/Al ratios.

It was therefore decided to employ aluminium chloride solutions as the source of $Al(H_2O)_6^{3+}$ owing to the high solubility of this salt. A 3 M solution was prepared in the normal manner and then acidified with hydrochloric acid to convert any dimer to the $Al(H_2O)_6^{3+}$ ion. As a result of this action a 1 M solution had a pH of less than 1.0 and was comparative in pH to an aluminium nitrate solution. Aliquots of this acidified solution were added to increments of phosphoric acid to give H_3PO_4/Al ratios ranging from 25 to 0.40. ^{31}P spectra were obtained at a temperature of -10°. At lower temperatures than this the linewidth of unreacted phosphoric acid was narrow in comparison to the Al-P complexes, a width of 2 Hz being obtained at -50° for a ratio of 3.2.

This resulted in saturation of the H_3PO_4 resonance when a transmitter power was used which was suitable for the broader aluminium phosphate complexes. By increasing the temperature to -10° all resonances could be recorded at one transmitter power, the H_3PO_4 signal now being slightly exchange broadened (10 -15 Hz). ^{27}Al spectra were obtained at room temperature on the same samples used for the ^{31}P investigations.

The results of the above studies are shown in tables 7-3(a) and (b). Column 3 of these tables records the concentration of the unreacted aluminium in solution, and when this value is subtracted from the total aluminium present, column 2, the concentration of aluminium complexed as phosphate is easily calculated, column 4. Columns 5 to 8 give the concentrations of phosphorus for the ^{31}P resonances B to D.

At H_3PO_4 ratios of 20 or greater the ^{31}P spectrum shows only two resonances, unreacted phosphoric acid, signal A, and one aluminium phosphate signal, B, 7.6 ppm upfield of the latter. No unreacted aluminium can be detected at these ratios and thus for practical purposes the concentration of aluminium added to the system is equivalent to the concentration of aluminium complexed as phosphate species.

Table 7 - 3(a)

Mass Balance of Aluminium and Phosphorus in $AlCl_3$ - H_3PO_4 System.

Solution Composition			^{27}Al Studies Room Temp		^{31}P Studies Low Temp.			
	Molarity							
Sample	H_3PO_4	$AlCl_3$	Mole $Al(H_2O)_6^{3+}$ unreacted	g. atom/litre Al as Al - P Complexes	Mole H_3PO_4 unreacted	g. atom/litre P as Al - P Complexes		
	1	2	3	4	5 A	6 B	7 C	8 D
1	13.46	0.56	ND	0.56	11.69	1.77	ND	ND
2	10.74	1.01	ND	1.01	7.82	2.90	0.02	ND
3	7.97	0.98	ND	0.98	5.63	1.90	0.44	ND
4	4.79	1.95	ND	1.95	1.38	1.65	1.12	0.64
5	3.99	1.98	ND	1.98	0.91	1.27	1.14	0.67
6	3.16	1.97	ND	1.97	0.52	0.87	0.93	0.84
7	2.39	1.95	0.20	1.75	0.30	0.62	0.65	0.82
8	1.93	1.99	0.36	1.63	0.19	0.43	0.51	0.85
9	1.61	1.90	0.60	1.30	0.08	0.41	0.34	0.78
10	0.99	1.97	1.03	0.96	0.03	0.20	0.16	0.60

ND : Not Detected

Table 7 - 3(b)

Mass Balance of Aluminium and Phosphorus in $AlCl_3$ - H_3PO_4 System.

Solution Composition Molarity			^{27}Al Studies. Room Temp.		^{31}P Studies. Low-Temp.			
Sample	H_3PO_4	$AlCl_3$	Mole $Al(H_2O)_6^{3+}$ unreacted	g. atom/litre Al as Al - P Complexes	Mole H_3PO_4 unreacted	g. atom/litre P as Al - P Complexes		
	1	2	3	4	5 A	6 B	7 C	8 D
11	12.78	0.54	ND	0.54	11.04	1.74	ND	ND
12	8.00	1.02	ND	1.02	5.65	1.95	0.40	N D
13	6.39	0.96	ND	0.96	4.64	1.11	0.48	0.16
14	4.86	1.08	ND	1.08	2.86	1.20	0.67	0.13
15	4.00	2.01	ND	2.01	0.85	1.16	1.28	0.71
16	3.16	1.99	0.13	1.86	0.46	0.93	0.94	0.83
17	2.77	2.02	0.18	1.84	0.35	0.63	0.83	0.96
18	2.55	1.97	0.20	1.77	0.33	0.74	0.71	0.77
19	1.78	2.01	0.49	1.52	0.14	0.43	0.35	0.86
20	1.67	1.99	0.52	1.47	0.15	0.32	0.29	0.91
21	1.26	1.98	0.85	1.13	0.03	0.30	0.29	0.64

ND : Not Detected

Thus if the concentration of phosphorus in resonance B is divided by the total aluminium present then the ratio of phosphorus to aluminium can be obtained for this species. A value of 3.15 and 3.2 is obtained from samples 1 and 11 in tables 7 - 3(a) and (b). This value is obviously close to an integral P/Al ratio for this complex of 3.0.

^{27}Al studies of solutions of low H_3PO_4/Al ratio samples 10 and 21, show that a considerable quantity of aluminium is unreacted and present as the $Al(H_2O)_6^{3+}$ ion. Three ^{31}P resonances of the complex phosphates are visible, resonance D, chemical shift 15.7 ppm upfield of H_3PO_4, being by far the most intense. If resonance A is assigned a 3 : 1 P : Al complex then a value of 1 : 1 is most likely for resonance D in order that the concentration aluminium complexed as phosphate calculated from ^{31}P studies should agree with the value determined from the ^{27}Al investigation. Resonance C would then be either a 2 : 1 P : Al complex or a 1 : 1 complex.

The observed aluminium concentration as phosphate complexes determined in the ^{27}Al studies is compared to calculated values obtained from ^{31}P studies in Table 7 - 4, the assignments above of B = 3, C = 2 or 1, D = 1, P/Al ratio being shown with other possible P/Al ratios.

Table 7 - 4

Comparison of Aluminium Complexed Calculated from ^{27}Al and ^{31}P Studies.

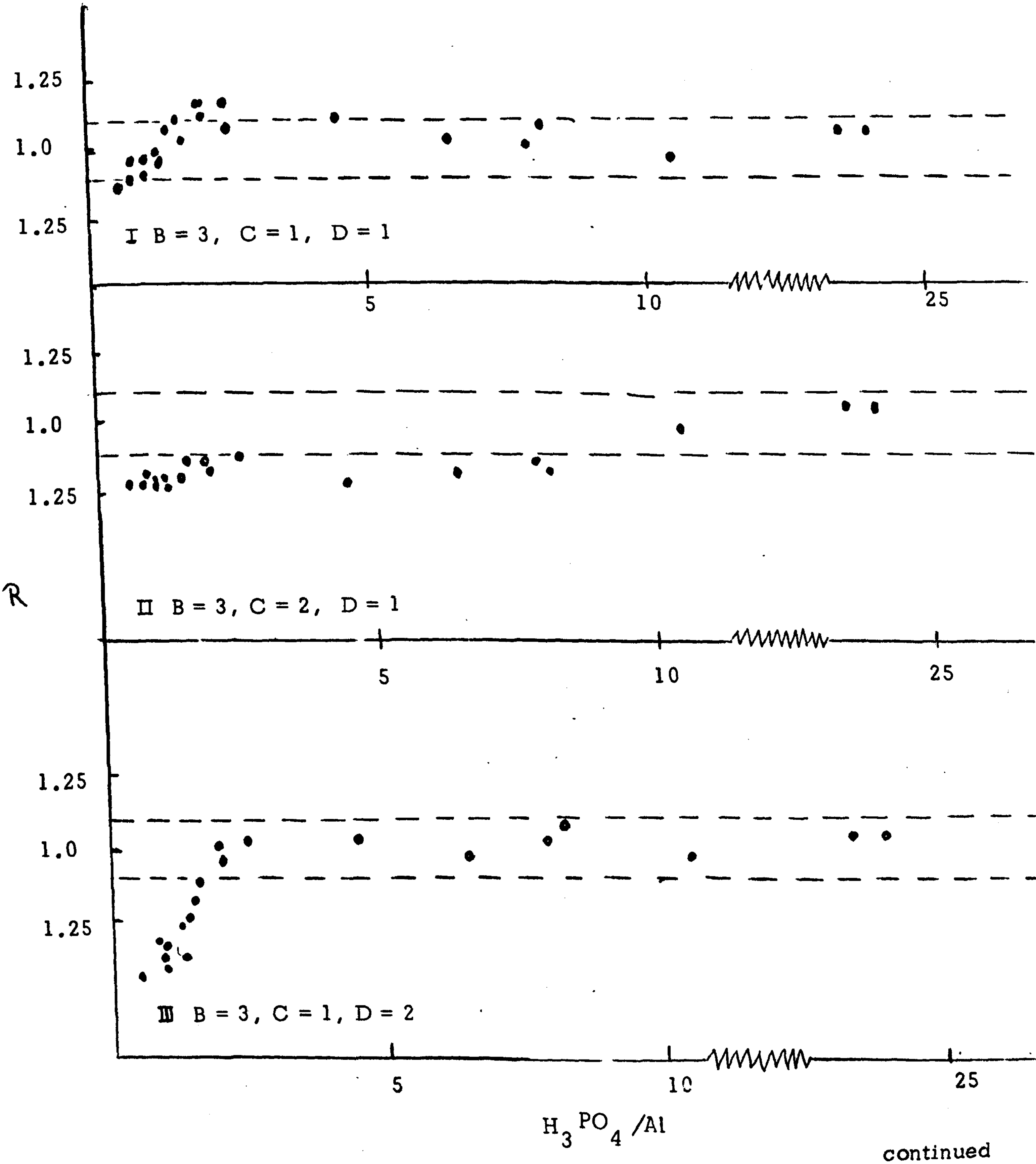
Solution Composition			g. atom/litre Al Complexed from ^{27}Al Studies	Calculated g. atom/litre Al Complexed from ^{31}P studies					
Molarity		$\frac{H_3PO_4}{Al}$ Ratio		B	3	3	3	2	2
H_3PO_4	$AlCl_3$			C	1	2	1	1	2
				D	1	1	2	1	1
13.46	0.56	24.03	0.56		0.59	0.59	0.59	0.88	0.88
10.74	1.01	10.6	1.01		0.99	0.98	0.98	1.47	1.46
7.97	0.98	8.13	0.98		1.07	0.85	1.07	1.39	1.17
4.79	1.95	2.46	1.95		2.31	1.75	1.99	2.58	2.02
3.99	1.98	2.01	1.98		2.23	1.67	1.92	2.44	1.87
3.16	1.97	1.60	1.97		2.06	1.59	1.64	2.20	1.74
2.39	1.95	1.22	1.75		1.67	1.35	1.28	1.78	1.45
1.98	1.99	0.99	1.63		1.50	1.25	1.08	1.57	1.32
1.61	1.90	0.85	1.30		1.26	1.09	0.87	1.32	1.15
0.99	1.97	0.50	0.96		0.83	0.75	0.53	0.86	0.78
12.78	0.54	23.66	0.54		0.58	0.58	0.58	0.87	0.87
8.0	1.02	7.84	1.02		1.05	0.85	1.05	1.37	1.17
6.39	0.96	6.65	0.96		1.01	0.77	0.93	1.20	0.95
4.86	1.08	4.50	1.08		1.20	0.86	1.13	1.40	1.06
4.00	2.01	1.99	2.01		2.37	1.73	2.01	2.57	1.93
3.16	1.99	1.59	1.86		2.08	1.61	1.66	2.24	1.75
2.77	2.02	1.37	1.84		2.00	1.59	1.52	2.10	1.69
2.55	1.97	1.29	1.77		1.73	1.37	1.34	1.85	1.50
1.78	2.01	0.89	1.52		1.35	1.18	0.92	1.42	1.25
1.67	1.99	0.84	1.47		1.31	1.16	0.85	1.36	1.21
1.26	1.98	0.64	1.13		1.03	0.88	0.71	1.08	0.93

The comparisons are made for all solutions studied in tables 7 - 3(a) and (b).

The concentration of aluminium determined in the ^{31}P studies divided by the value found complexed in the ^{27}Al investigations should equal 1.0 at all H_3PO_4/Al ratios for a correct assignment. In figures 7 - 6(a) and (b) this value is shown graphically for the sets of P/Al ratios given in tables 7 - 3(a) and (b). The dotted lines represent the limits of experimental error ($\pm$ 10%).

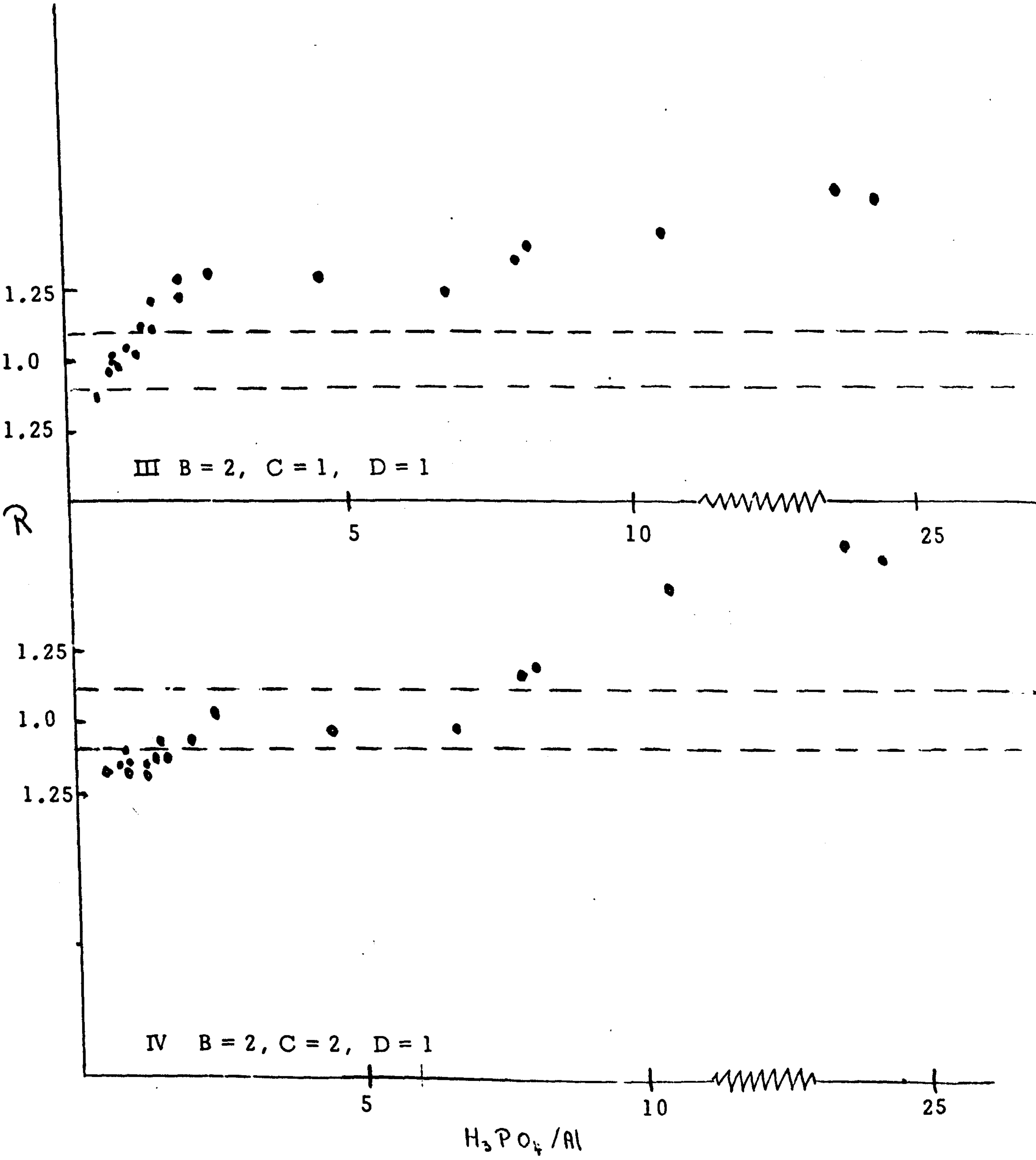
The first assignment gives the most reasonable fit at all H_3PO_4/Al ratios. Even this does not have all values within the limits of experimental error. This could be due to several reasons. It has been assumed that the P/Al ratios for each resonance is an integral and this may not be so. One resonance could also represent more than one phosphate complex. However the deviation of the experimental results from assignment I is not large. For this reason resonance B is ascribed to a complex containing three phosphorus atoms to every aluminium, and resonances C and D, one phosphorus to each aluminium atom. Further quantitative evidence would be required before resonances could be assigned to more than one complex.

Figure 7 - 6 (a) Comparison of P/Al assignments of aluminium phosphate complexes where R equals the aluminium ratio calculated from ^{27}Al and ^{31}P studies



continued

Figure 7 - 6 (b) continued



B. The Nature of Phosphate Ligands in Aluminium Phosphate Complexes.

Discussion of the nature of the aluminium phosphate complexes has so far been limited to a simple model in which only the ratio, P/Al, was considered. In dilute solution ($< 0.1M$) it is a relatively easy task to calculate the concentration of the ions most likely to be reacting with aluminium using the known dissociation constants for H_3PO_4. These are

$$pKa_1 = 2.23$$
$$pKa_2 = 7.21$$
$$pKa_3 = 12.32$$

Information on the ionisation of this acid in concentrated solutions (1 to 10 M) is very sparse and by no means conclusive. Conductivity and potentiometric measurements together with vapour pressure studies[91-93] have all shown that the acid cannot be considered in terms of simple ions obtained in dilute solution. A recent paper by Elmore[93] has attempted to summarise the present knowledge on this subject and to correlate this to measurements of the degree of dissociation of the acid. His results indicate that concentrated acid will contain significant quantities of the unionised species H_3PO_4 and $H_6P_2O_8$, the major ionised complexes being $H_5P_2O_8^-$ and $H_2PO_4^-$.

The reaction of aluminium with more than one type of phosphate ion is therefore feasible for the H_3PO_4/Al ratios studied in the previous section. Further investigations were therefore undertaken in order to attempt to determine more accurately the type of phosphate ligand associated with the aluminium complexes.

1. Low-Temperature Proton Studies.

The high solute content of the samples used in the previous section made them ideal for low-temperature investigations. At H_3PO_4/Al ratios greater than 4.0 only a single resonance was observed for all species present, even at temperatures as low as -75°. The width of the resonance was comparative to the bulk water signal obtained in the study of aluminium chloride solutions.

At H_3PO_4/Al ratios less than 4.0 a second small resonance appeared 4.0 ppm downfield of the signal observed above. As the ratio decreased, the intensity of the second resonance increased. Quantitative determinations of the concentration of water and unreacted aluminium $Al(H_2O)_6^{3+}$ present identified this lowfield resonance as the bound water of the unreacted $Al(H_2O)_6^{3+}$ ion, spectra being recorded at a temperature of -35°.

The protons on any bound water, and phosphate ligand of the aluminium phosphate complexes would appear to be still undergoing fast exchange with bulk water, as was the case for the aluminium chloride dimer system at low temperature. As a consequence, information cannot be obtained on the hydration of the phosphate complexes or the protons bound to the phosphate ligand.

2. The Effect of Hydrochloric Acid on the Distribution of Aluminium Phosphate Complexes.

If all the aluminium phosphate complexes are formed from the one simple phosphate ion (e.g. $H_2PO_4^-$), the number of phosphate units varying between species, then addition of an acid other than H_3PO_4 should suppress the formation of this ion. This would result in a redistribution of the concentration of the aluminium complexes and an increase in the concentration of unreacted phosphoric acid. If, however, more than one type of phosphate ion is involved in the formation of the three aluminium complexes, then acid addition again should suppress the formation of one but not necessarily all phosphate ions since there could be a straight conversion from one phosphate ion to the other. This again would result in a redistribution of the aluminium complexes but in this case the concentration of unreacted acid need not increase.

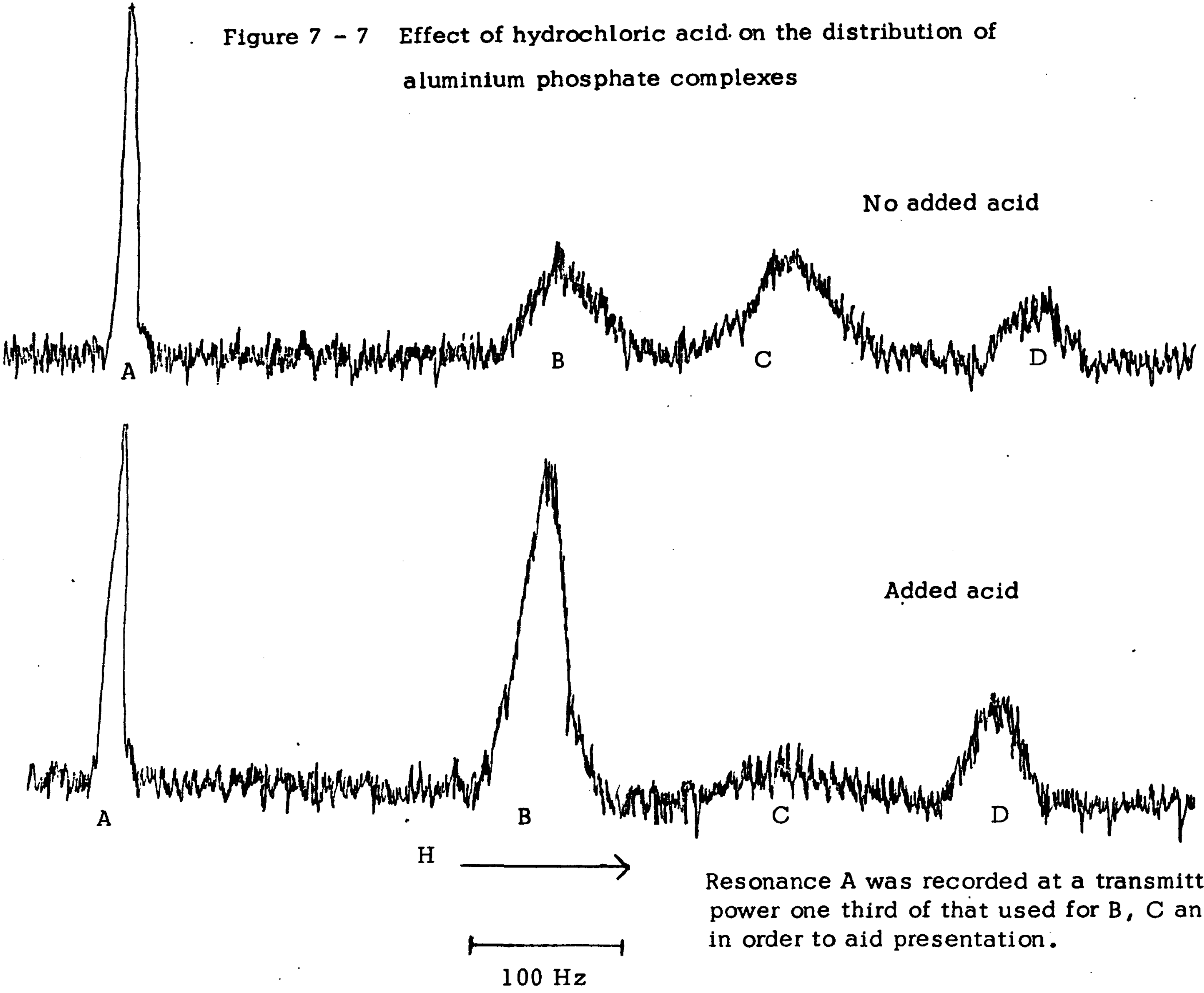
For the purpose of this investigation two solutions were chosen, one containing 1 M $AlCl_3$ and 3.2 M H_3PO_4, and the other 1 M $AlCl_3$ 3.2 M H_3PO_4 and 4 N HCl. Spectra recorded at -20° are shown in figure 7 - 7. The decrease in linewidth of complex resonance B on acid addition is obvious. Calculations of the relative areas of all resonances before and after acid addition show the concentration of unreacted phosphoric acid, A, and also complex D to remain unchanged. However the concentration of species B increases by approximately 50% on acid addition while C decreases by a similar amount.

Such results suggest that all three aluminium phosphate complexes are not formed from the same phosphate ion and that complex C is different in this respect to the other two complexes.

3. Aluminium Chloride - Sodium Dihydrogen Phosphate System.

The replacement of phosphoric acid by sodium dihydrogen phosphate should result in a major change in the concentration of reacting phosphate ions relevant to aluminium complex formation. Moreover it would be reasonable to assume that a large concentration of the $H_2PO_4^-$ ion should be present at high NaH_2PO_4/Al ratios. At low

Figure 7 - 7 Effect of hydrochloric acid on the distribution of aluminium phosphate complexes



Resonance A was recorded at a transmitter power one third of that used for B, C and D in order to aid presentation.

ratios the natural acidity of the aluminium salt could lead to the possible formation of H_3PO_4 and its associate ions found in the H_3PO_4 systems. The results of low-temperature ^{31}P investigations of solutions of varying NaH_2PO_4/Al ratios are shown in table 7 - 5.

At NaH_2PO_4/Al ratios greater than 1.0 the most prominent aluminium phosphate species found was that associated with resonance C, 12.3 ppm upfield of unreacted phosphate. This complex accounted for well over 50% of the phosphate bound to aluminium at a ratio of 3.36 In the H_3PO_4 - $AlCl_3$ system, at a similar ratio, all three complexes contained approximately the same concentration of phosphorus. In the previous section it had been found that the concentration of phosphorus in resonance C was reduced by the addition of acid other than H_3PO_4. The prominence of this resonance in this NaH_2PO_4 system is therefore in keeping with the theory of at least two forms of phosphates reacting with aluminium, one of which would now appear to be the $H_2PO_4^-$ ion.

Although the $H_2PO_4^-$ ion could dissociate into HPO_4^{2-} the concentration of the latter should be negligible considering the acidity of the aluminium chloride solution, a 1.0 M solution without any added phosphate having a pH of approximately 0.5. The pH of the solution

Table 7 - 5.

Comparison of ^{31}P Resonances obtained in Low-Temperature Studies of $AlCl_3$ - NaH_2PO_4 Systems.

Solution Composition		0.5 M $AlCl_3$ 1.68 M $Na_2H_3PO_4$	1.0 M $AlCl_3$ 1.2 M NaH_2PO_4	2.0 M $AlCl_3$ 0.66 M NaH_2PO_4
NaH_2PO_4/Al Ratio		3.36	1.2	0.33
pH		1.6	0.5	0.2
Chemical Shift	A	0.0	-0.5	-
	B	7.6	7.6	7.6
	C	12.3	12.3	12.3
	D	-	15.7	15.7
Concentration of Phosphorus g. atom/litre	A	1.03	0.13	ND
	B	0.15	0.17	0.15
	C	0.5	0.70	0.15
	D	-	0.05	0.30
Temperature of Sample		-4°	-16°	-16°

of 1.0 M $AlCl_3$ and 1.2 M NaH_2PO_4 was also this value which is evidence that the formation of the major aluminium phosphate complex present, resonance C, involves no loss of protons from the phosphate ion in this solution.

At NaH_2PO_4/Al ratios less than 1.0 the acidity of the aluminium chloride used would appear to lead to the formation of H_3PO_4 and its associate ions. The major species present, resonance D, is also found as the dominant species in H_3PO_4/Al systems at this ratio.

The chemical shift of the unreacted phosphate was identical to that of H_3PO_4 at a NaH_2PO_4/Al ratio of 3.36. The spectra for this solution was recorded at -4°, temperatures lower than this resulting in freezing. As a consequence of this high temperature in comparison with those normally used, the resonances were broader due to exchange, a value of 50 Hz being recorded for the unreacted phosphate. Exchange could also account for the identical chemical shift of this free phosphate and an external H_3PO_4 standard, the free $H_2PO_4^-$ ion having a resonance downfield of H_3PO_4. However it was possible to record spectra at lower temperatures (-16°) with the solution containing 1.0 M $AlCl_3$ and 1.2 M NaH_2PO_4 and here the resonance for unreacted phosphate was found slightly downfield of H_3PO_4.

3. ^{31}P Low-Temperature Investigations of D_3PO_4 - $Al(NO_3)_3$ System in D_2O.

This study was undertaken to determine the effect of replacing the majority of protons in the system by dueterium. A solution of D_3PO_4/Al ratio 4.8 was prepared by adding D_3PO_4 and D_2O to solid $Al(NO_3)_3.9H_2O$. This procedure reduced the concentration of protons present in a conventional sample from approximately 100 g. atom/litre to 18, the latter arising from the water of hydration of $Al(NO_3)_3$. Spectra were recorded at a temperature of -45°, similar to those used in the study of the H_3PO_4/Al system.

The spectrum obtained was identical to that obtained for the H_3PO_4 system at a ratio of 4.8. Moreover the fine structure observed for resonance B, figure 7 - 3 was still clearly visible with no alteration in the intensities or number of resonances. Proton coupling would not therefore appear to be the cause of the fine structure, further evidence of this having been obtained in the low-temperature proton studies where no separate signal was observed for protons associated with phosphate species.

Since aluminium coupling has also been discounted due to the short ^{27}Al relaxation times for these species, then it would appear that the structure could arise from phosphorus phosphorus coupling and/or isomers of one aluminium complex. Quantitative analyses favour an assignment of three phosphorus nuclei to every aluminium for this complex and thus both possibilities are feasible.

A homonuclear double irradiation experiment was attempted on this resonance. However, results were inconclusive due primarily to the poor signal-to-noise ratio.

C. Phosphate Complexes of Aluminium Formed in the Presence of Dimeric Aluminium.

1. Room-temperature Studies. $AlCl_3$ - H_3PO_4 System.

For the purpose of this investigation a 3 M $AlCl_3$ solution was prepared in a similar manner to that for the initial study of the aluminium dimer equilibrium. ^{27}Al spectra showed this solution to contain only 40% of the aluminium present as the $Al(H_2O)_6^{3+}$ ion. Aliquots of the above were taken and added to increments of phosphoric acid to give H_3PO_4/Al ratios ranging from 0.2 to 1.6. Results of analyses on ^{31}P spectra are shown in table 7 - 6.

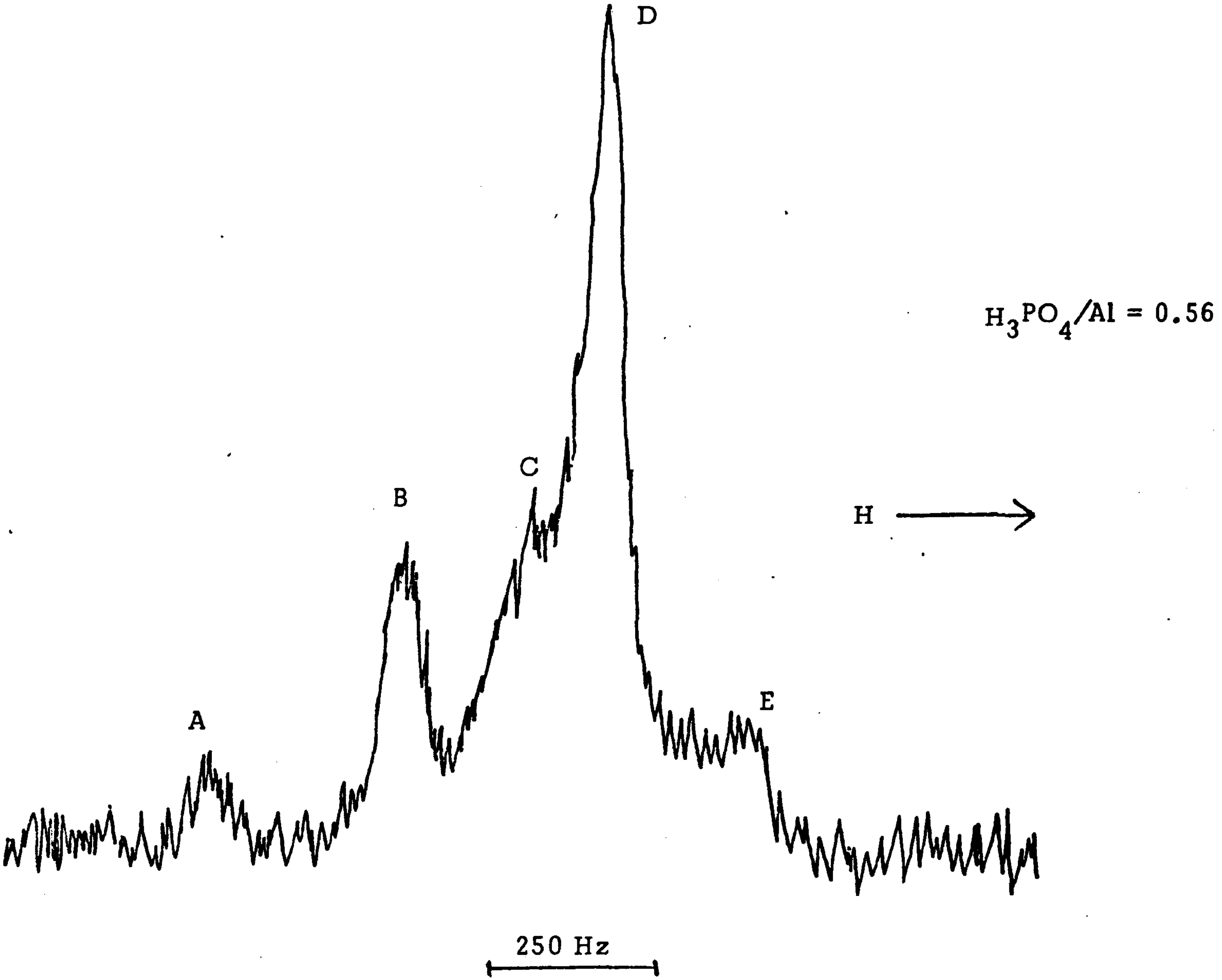
All three resonances observed for aluminium phosphate complexes in the previous studies were visible at ratios greater than 0.75. At smaller ratios a new resonance was visible, 175 Hz wide and 1.70 ppm upfield of unreacted H_3PO_4. As the H_3PO_4/Al ratio decreased the intensity of this highfield signal increased. A typical spectrum is shown in figure 7 - 8.

Table 7 - 6.

Relative Concentrations of Aluminium Phosphate Complexes .

Solution Composition		Moles	g. atom/litre P as Al - P Complexes			
Molarity		H_3PO_4 Unreacted				
H_3PO_4	$AlCl_3$	A	B	C	D	E
3.22	1.99	0.79	0.84	1.24	0.35	-
2.84	1.98	0.49	0.57	1.25	0.59	-
2.42	1.99	0.29	0.51	0.92	0.70	-
2.07	1.97	0.23	0.31	0.78	0.69	0.06
1.63	2.00	0.08	0.25	0.61	0.58	0.11
0.79	1.98	ND	0.08	0.09	0.30	0.32
0.39	1.97	ND	ND	0.06	0.10	0.23

Figure 7 - 8 Room temperature ^{31}P spectrum of aluminium phosphate complexes formed in the presence of aluminium dimer



2. ^{31}P Low-Temperature Studies $AlCl_3 - H_3PO_4$ System.

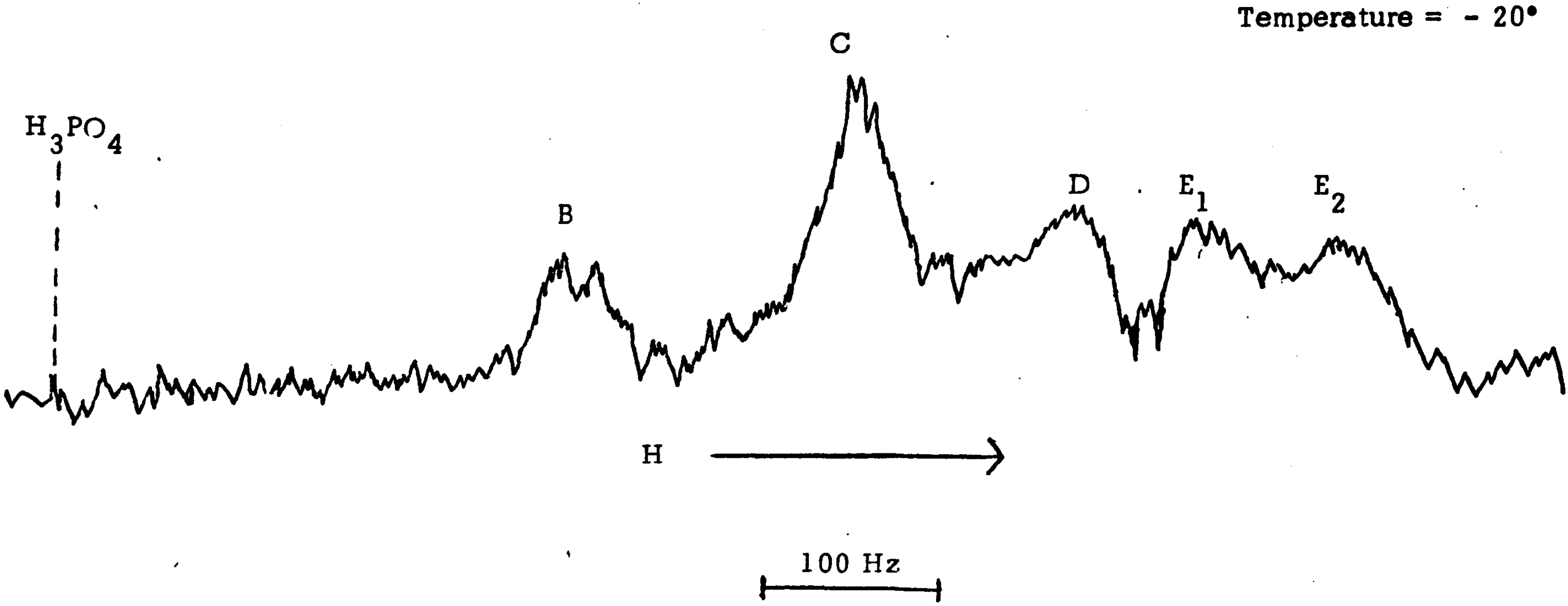
Low-temperature investigations were undertaken on a solution containing 2 M $AlCl_3$ and 1.2 M H_3PO_4. Spectra were recorded at a temperature of -20°. The three aluminium phosphate signals B, C, and D, were clearly visible. However the new highfield signal was now resolved as two separate resonances, E_1 and E_2, each 50 Hz wide and 16.2 and 17.3 ppm upfield of an external standard of H_3PO_4. The spectrum of this sample, figure 7 - 9, shows the five ^{31}P resonances associated with aluminium phosphate complexes. No free H_3PO_4 is visible.

Further investigations were attempted at lower H_3PO_4/Al ratios than the solution above, but the signal-to-noise ratio made the detection and resolution of peaks impossible.

D. Discussion.

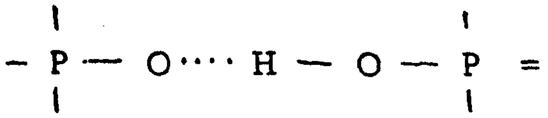
The complicated equilibria existing in aqueous aluminium salt-phosphoric acid systems have been demonstrated. When aluminium is initially present only as the aquated ion $Al(H_2O)_6^{3+}$ then at least three aluminium complexes are formed. The linewidths of the resonances of these complexes in ^{27}Al studies suggest that all species are mononuclear with respect of aluminium. In concentrated phosphoric acid solutions

Figure 7 - 9 Low-temperature ^{31}P spectrum of phosphate complexes of aluminium formed in the presence of dimeric aluminium



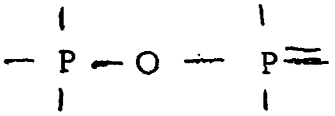
two distinct types of phosphate species would appear to be reacting with the aluminium, one of which could be the ion $H_2PO_4^-$. An aluminium phosphate complex can be ascribed to this ion with a possible formula of $Al(H_2PO_4)_n^{(3-n)+}$ where n = 1.

The identity of the other reacting phosphate ion is by no means certain. Previous investigators using conductivity and potentiometric techniques have suggested significant quantities of the species $H_5P_2O_8^-$ to be present in concentrated H_3PO_4 solutions. Such a complex was depicted as having a



$$-\overset{|}{\underset{|}{P}}-O\cdots H-O-\overset{|}{\underset{|}{P}}=$$

linkage between phosphate groups. Fine structure is observed for the low-temperature ^{31}P spectrum of a complex containing three phosphorus atoms to every aluminium and this could be interpretted in terms of phosphorus-phosphorus coupling from such an ion in conjunction with a third phosphorus species. A direct



$$-\overset{|}{\underset{|}{P}}-O-\overset{|}{\underset{|}{P}}=$$

link in this double phosphate ion would be more in keeping with the observed splitting which does show some similarity to an A B_2 spectrum

Further investigations will be required before definite structures can be assigned. Homonuclear double irradiation at improved signal-to-noise ratios may prove particularly useful in this respect. ^{17}O n.m.r. investigations might also prove informative.

A poor signal-to-noise ratio also limited extensive investigations of the dimeric aluminium-phosphoric acid systems. Two further resonances were observed other than those found in the $Al(H_2O)_6^{3+}$ - H_3PO_4 studies. Salmon in pH and ion exchange studies of aluminium phosphate complexes found evidence for phosphate complexes containing more than one aluminium nucleus. Both resonances could be dimeric phosphates containing for example an $H_2PO_4^-$ ligand. Future n.m.r. investigations might prove informative if they were made in conjunction with pH measurements, which should be a feasible proposition in dimeric systems.

CHAPTER 8.

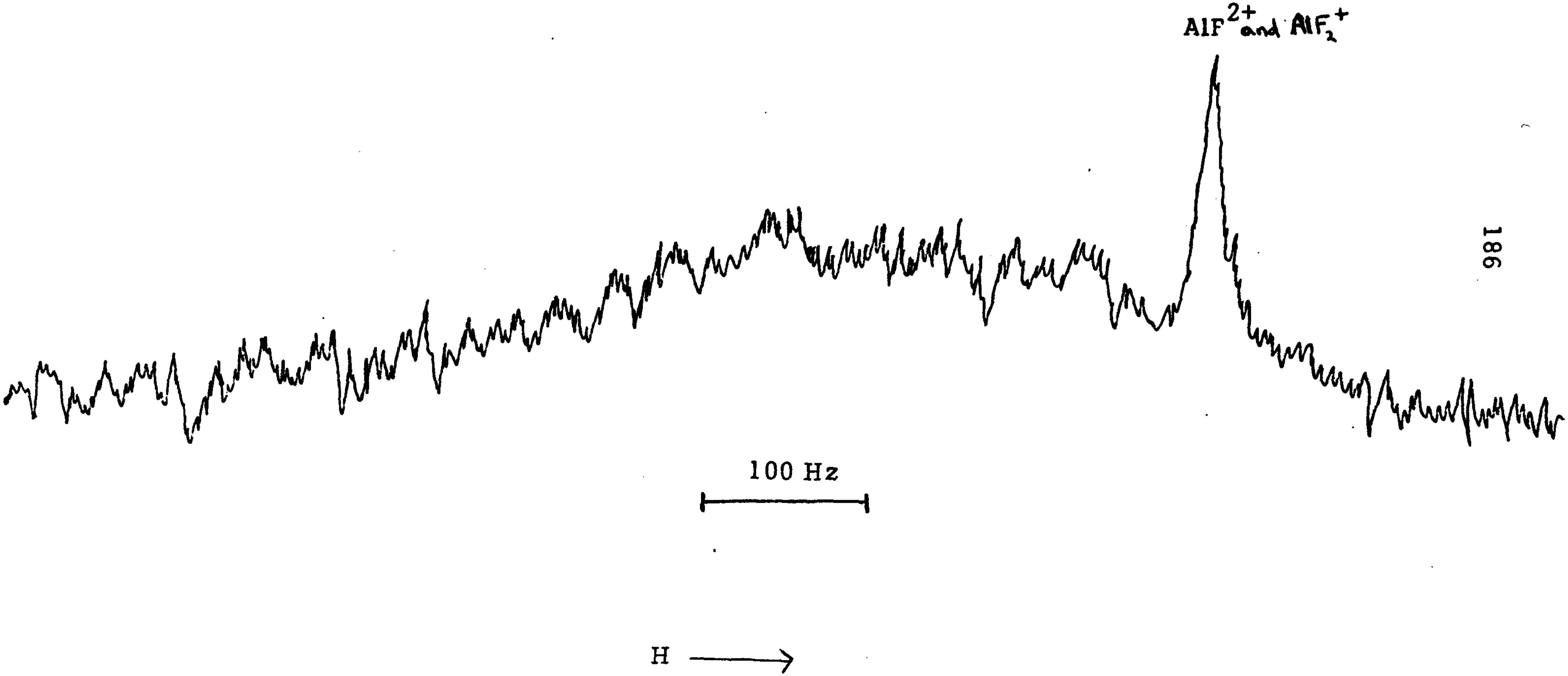
ALUMINIUM FLUOROPHOSPHATE COMPLEXES.

1. Room-Temperature Studies of the $Al(NO_3)_3$ - H_3PO_4 - NaF System.

^{19}F investigations quickly established a reaction between the aluminium fluoro-complexes AlF^{2+} and AlF_2^+ on inclusion of phosphoric acid in solutions containing equimolar concentrations of aluminium nitrate and sodium fluoride. As the concentration of phosphoric acid increased the intensity of both fluoride resonances decreased, this being accompanied by an increase in the linewidths of the two fluoride species. At a concentration of 0.64 M H_3PO_4, two new resonances were observed, 1.2 and 2.4 ppm downfield of AlF_2^+. Both resonances were broad in comparison to the aluminium fluorides, values of 50 to 75 Hz being recorded. In a solution containing 1.28 M H_3PO_4, the linewidth of the lowfield resonances had increased to 500 Hz, AlF_2^+ and AlF^{2+} having coalesced to a single resonance. Further increments of acid resulted in further broadening of all resonances, until only a single asymmetrical peak was observed in a solution containing 2 M H_3PO_4. Typical spectra are shown in figure 8 - 1.

The results obtained in this study could be explained by the formation of aluminium fluorophosphate complexes which are subject to exchange between AlF_2^+ and AlF^{2+} and themselves. Obviously low-temperature ^{19}F investigations were required.

Figure 8 - 1 ^{19}F Spectrum of a solution containing 1 M Al(NO$_3$)$_3$, 1 M NaF and 1.6 M H$_3$PO$_4$ at room temperature



^{31}P investigations at room temperature confirmed the short lifetime of any aluminium fluorophosphate species. Increasing amounts of sodium fluoride were added to a solution containing 1 M $Al(NO_3)_3$ and 1.6 M H_3PO_4. In the absence of fluoride ion all three aluminium phosphate resonances could be detected. However on the addition of F^- all resonances of the Al-P complexes broadened, and at a concentration of 1.5 M NaF they could hardly be resolved. Spectra before and after addition of sodium fluoride are shown in figure 8 - 2.

No new resonances were detected and it is interesting to note from figure 8 - 2 that the concentration of unreacted phosphoric acid would appear to be constant irrespective of the fluoride content of the solution.

2. Low-Temperature Studies of $AlCl_3$ - H_3PO_4 - NaF System.

A 3 M $AlCl_3$ solution was prepared and acidified to remove any dimer present. The first solution examined contained 1 M ACl_3, 1.6 M H_3PO_4 and 0.5 M NaF. The ^{19}F spectrum obtained at -13° is shown in figure 8 - 3, the scale being 100 Hz per cm.

Figure 8 - 2 Room-temperature ^{31}P spectrum of aqueous aluminium chloride-phosphoric acid solutions in the presence and absence of NaF

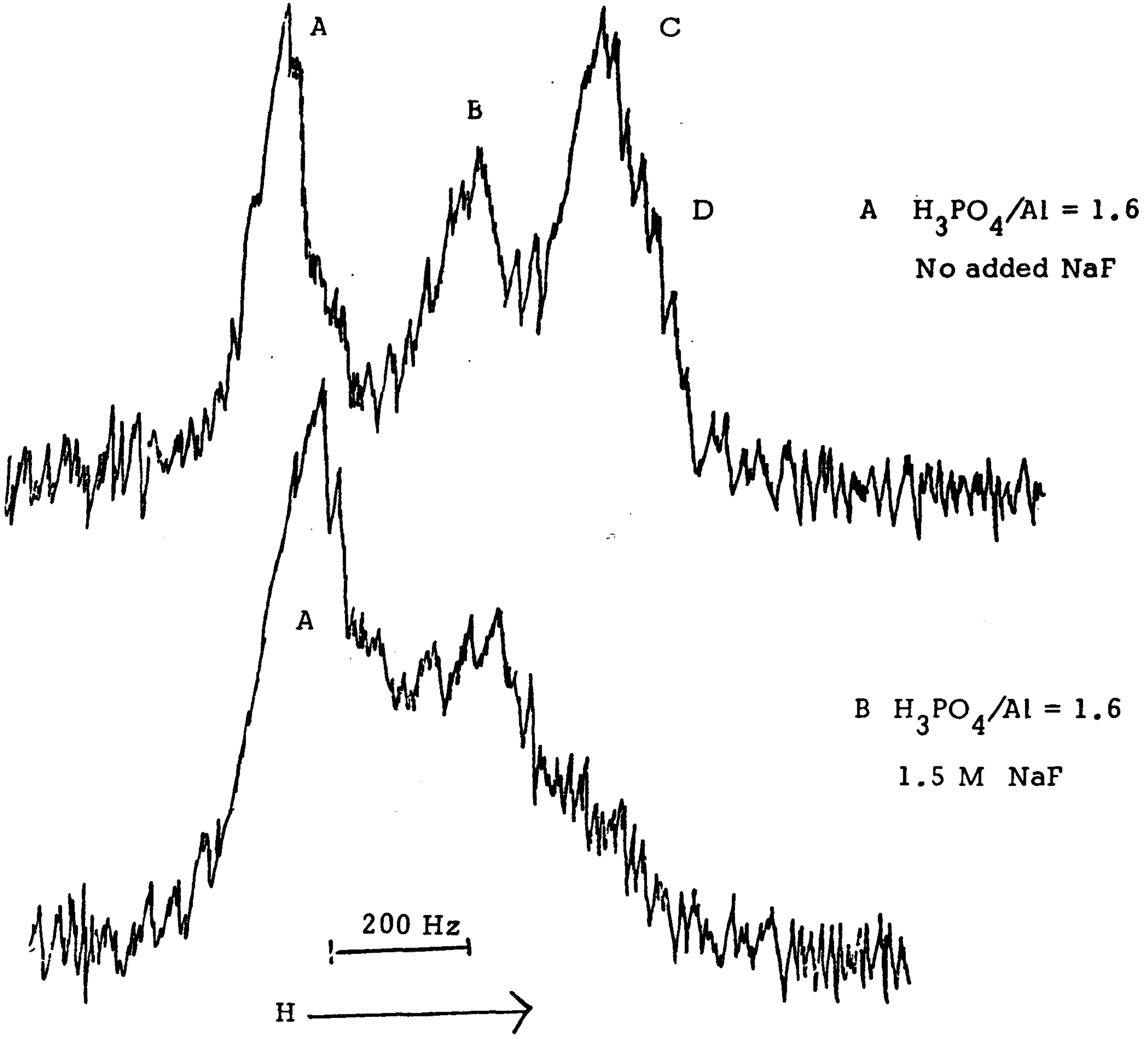
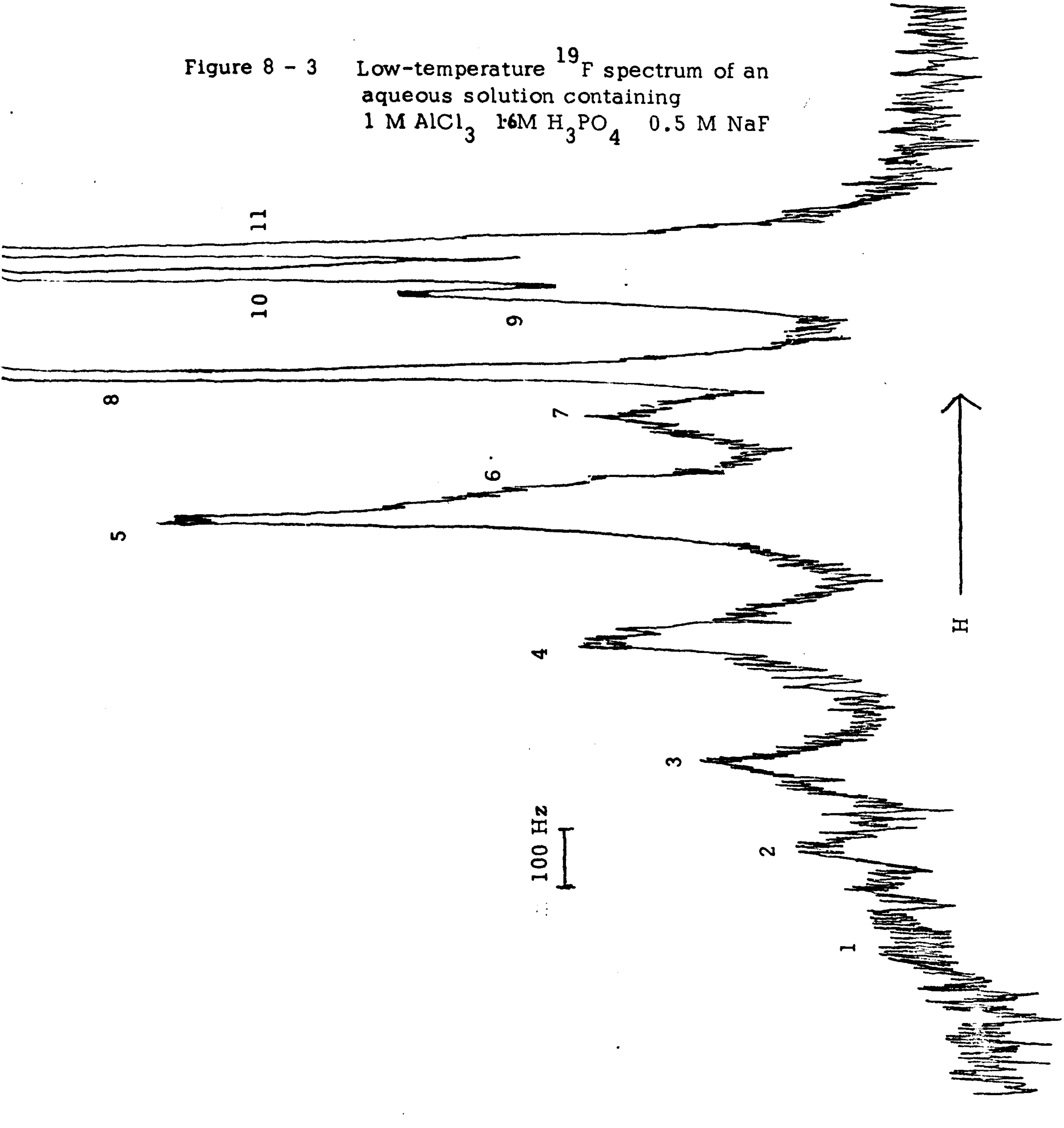


Figure 8 - 3 Low-temperature ^{19}F spectrum of an aqueous solution containing
1 M $AlCl_3$ 1·6M H_3PO_4 0.5 M NaF



All aluminium phosphate complexes will be present at approximately equal concentrations for an H_3PO_4/Al ratio of 1.6. The ^{19}F spectrum would suggest that all these complexes are forming fluoride derivatives. The total number of resonances observed was eleven and their chemical shift from an external standard of $BF_3.Et_2O$ are shown in table 8 - 1. The numbering of the resonances corresponds to that used in figure 8 - 3.

The highfield peaks 9, 10 and 11 were identified as unreacted AlF^{2+}, AlF_2^+ and AlF_3 from their chemical shifts. The eight remaining ^{19}F resonances would therefore appear to be due to the reaction between fluoride ion and aluminium phosphate complexes. No complex formation was observed when a separate solution containing only NaF and H_3PO_4 was studied at this temperature (-13°).

^{31}P low-temperature studies of the above ternary system revealed no new resonances besides those found in the previous studies of the $AlCl_3$ - H_3PO_4 systems. However the resonances for the aluminium complexes were noticeably broader in the solution containing NaF on comparison to a sample containing no fluoride ion. Spectra of two such solutions are shown in figure 8 - 4. The addition of fluoride to the aluminium nucleus of an aluminium phosphate complex would appear to have little effect on the chemical shift of the ^{31}P resonances of such species. No significant difference

Table 8 - 1.

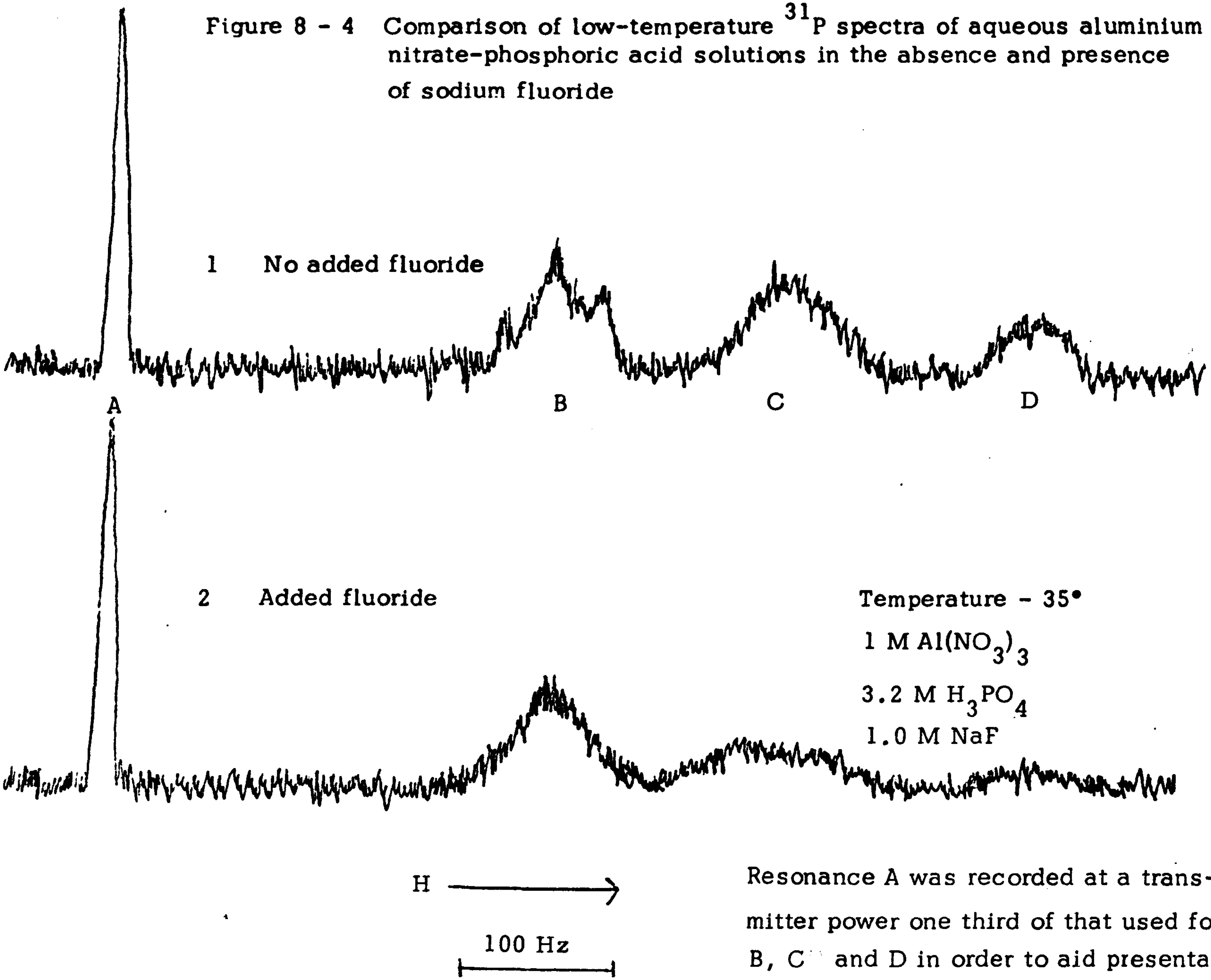
Chemical Shift of ^{19}F Resonances Observed in Low-Temperature Studies of $AlCl_3$ - H_3PO_4 - NaF System.

Resonance Number	Chemical Shift from $BF_3.Et_2O$ ppm.
1	-11.20
2	-10.50
3	- 8.65
4	- 5.80
5	- 3.20
6	- 2.50
7	- 1.05
8	0.0
9	+ 1.60
10	+ 2.20
11	+ 2.65

- : Lowfield of $BF_3.Et_2O$

+ : Highfield of $BF_3.Et_2O$

Figure 8 - 4 Comparison of low-temperature ^{31}P spectra of aqueous aluminium nitrate-phosphoric acid solutions in the absence and presence of sodium fluoride



Resonance A was recorded at a transmitter power one third of that used for B, C and D in order to aid presentation of the spectra could be observed in the concentration of unreacted phosphoric acid in both solutions.

In an attempt to identify the fluoride resonances with their respective aluminophosphate ions, a solution was first prepared containing 12 M H_3PO_4 and 0.5 M $AlCl_3$. Low-temperature ^{31}P spectra confirmed this solution to contain only the 3 : 1, P : Al, aluminium phosphate complex, besides the unreacted acid. On addition of 0.3 M NaF the ^{19}F spectrum at -15° showed the presence of at least three broad resonances, approximately 8 to 9 ppm downfield of $BF_3.Et_2O$. It was difficult to resolve the spectrum accurately, figure 8 - 5, because of the width of the resonances, but the chemical shift of the peaks was similar to those of 1, 2, 3 and possibly 4 in figure 8 - 3.

With a solution containing 2 M $AlCl_3$ and 1.0 M H_3PO_4 the major aluminium phosphate present was species D, found in the ^{31}P studies 15.7 ppm upfield of H_3PO_4. The ^{19}F spectrum, figure 8 - 6, of such a solution containing 0.5 M NaF shows the major aluminium fluorophosphate species to be those associated with resonances 5 and 6. The resonances 7 and 8 and possibly 4 could therefore be ascribed with the fluoride complex of aluminium phosphate complex C. These resonances were in fact found more intense in

Figure 8 - 5 Low-temperature ^{19}F spectrum of an aqueous solution containing 0.5 M $AlCl_3$, 12 M H_3PO_4 and 0.3 M NaF

Temperature -15°

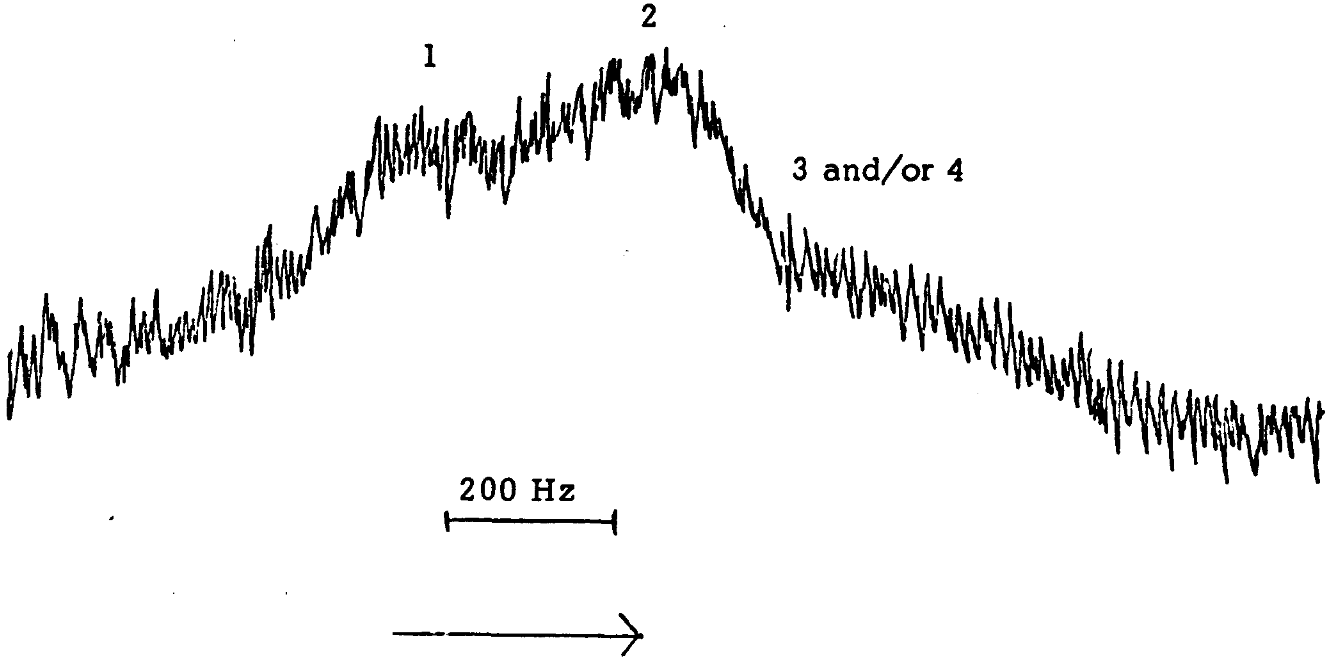


Figure 8 - 6 Low-temperature ^{19}F spectrum of an aqueous solution containing 2 M $AlCl_3$, 1.0 M H_3PO_4 and 0.5 M NaF

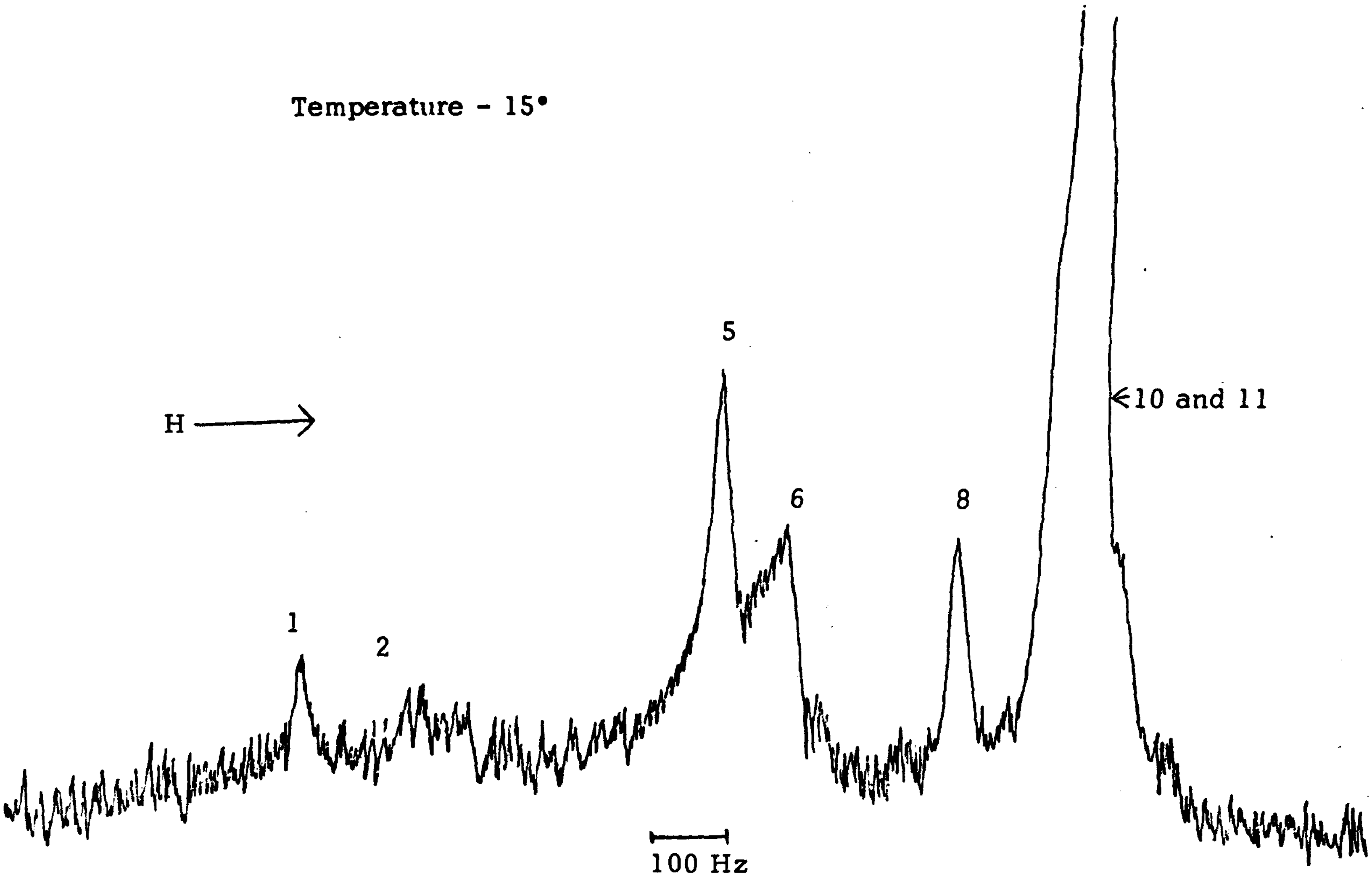

Temperature - 15°

Table 8 - 2.

Assignment of ^{19}F Resonances to Aluminium Fluorophosphate Complexes.

Resonance Number	Chemical shift ppm	Aluminium Phosphate complex with which Fluorine Line is Correlated
1	-11.20	B (= 3 : 1 P : Al)
2	-10.50	B
3	- 8.65	B
4	- 5.80	B or C
5	- 3.20	D (= 1 : 1 P : Al)
6	- 2.50	D
7	- 1.05	C (= 1 : 1 P : Al)
8	0.0	C

the first solution examined, figure 8 - 3 where aluminium phosphate complex C is of initial-equi concentration with the two other Al - P species.

A tentative assignment of the ^{19}F resonances to their corresponding aluminium fluorophosphate complex is given in table 8 - 2.

Discussion.

The number of equilibria present in the solutions examined is obviously large. They can be divided into distinct groups; those associated with the formation of the aluminium fluoride species (at least 3); those associated with aluminium phosphate complexes (3 or more); those associated with aluminium fluorophosphate species (at least 3). All will be inter-related.

An attempt has been made to correlate the ^{19}F resonances of the aluminium fluorophosphate complexes with the aluminium phosphate species from which they are derived. The multiple ^{19}F resonances resulting from the addition of fluoride to each aluminium phosphate species could arise either from isomers of the same complex or complexes containing differing numbers of fluorine atoms. The latter could produce a series of aluminium fluorophosphate ions similar to the simple aluminium fluorides.

The study of these systems obviously warrants further attention.

CHAPTER 9.

RAMAN INVESTIGATIONS.

A limited Raman investigation was undertaken on some of the systems studied previously by n.m.r. techniques including those containing aluminium fluoride and phosphate complexes. The sensitivity of the Cary spectrometer was found to be below specification during this work and, although examinations of the fluoride systems proved negative, weak bands could have been missed. However the Raman technique did supply confirmatory information on the aluminium chloride-phosphoric acid systems and this section is therefore included.

A. Orthophosphates.

The vibrational spectra of orthophosphates including phosphoric acid have mainly been studied by their Raman spectra [94-107] although an increasing interest has been focussed on infrared investigations during the last few years.[106-107] The observed vibrational frequencies for the mono, di and tribasic phosphate ions and phosphoric acid are given in tables 9 - 1 to 9 - 4. Infrared spectra are included in these tables. Trisodium and tripotassium phosphates in aqueous solution show a single strong band in the infrared spectrum at 1004 $cm.^{-1}$. This is the F_2 stretching fundamental seen in the Raman at 1014 - 1025 $cm.^{-1}$. The Raman also shows the A_1 symmetrical stretch, 936 $cm.^{-1}$, and the F_2 and E, O-P-O bending modes at 500 and 380 $cm.^{-1}$ respectively. Reduction from the Td symmetry of the PO_4^{3-} ion leads to a splitting of the F_2 stretching fundamental of PO_4^{3-} to give A and E modes which appear in the infrared spectrum of an aqueous solution of dipotassium phosphate at 988 and 1076 $cm.^{-1}$ respectively. The other A stretching mode appears as a weak band at 862 $cm.^{-1}$ and these assignments are confirmed by the Raman data which show bands at 865, 976 and 1081 $cm.^{-1}$. The symmetry of the $H_2PO_4^-$ ion cannot be higher than C_{2v} and consequently the E mode which occurs at 1080 $cm.^{-1}$ in HPO_4^{2-} is split into two bands at 1072 and 1150 $cm.^{-1}$ as shown in the infrared spectra of the aqueous dihydrogen phosphates.

Table 9 - 1.

Vibrational Frequencies of Tribasic Orthophosphates (cm.$^{-1}$).

Symmetry T_d.

Raman Aq Na_3PO_4 K_3PO_4	Infrared Aq Na_3PO_4 K_3PO_4	Assignment[106]
1014 - 1026 w	1004 s	F_2 stretching mode
936 s		A_1 symmetrical stretching mode
500 w		F_2 O-P-O bending mode
380 w		E O-P-O bending mode

Table 9 - 2.

Vibrational Frequencies of Dibasic Orthophosphates (cm.$^{-1}$).

Symmetry C_{3v}.

Raman[102] Aq KH_2PO_4	Infrared Aq NaH_2PO_4 KH_2PO_4 LiH_2PO_4	Assignment[106]	
	1230 w	P-O-H in-Plane deformation	
1081 dp, w	1076 s	PO_3 "degenerate" stretch E	cf F_2 stretching mode of PO_4^{3-}
976 p, w	988 m	PO_3 symmetrical stretch A	
865 p, s	862 w	P-O-(H) stretch	cf A_1 mode of PO_4^{3-}
537 dp, w		O-P-O bending mode	cf F_2 bending mode of PO_4^{3-}
394 dp, w		O-P-O bending mode	cf F bending mode of PO_4^{3-}

Table 9 - 3.

Vibrational Frequencies of Monobasic Orthophosphates (cm.$^{-1}$) Symmetry C_{2v}.

Raman[97,98,102] Aq KH_2PO_4	Infrared Aq NaH_2PO_4 KH_2PO_4 LiH_2PO_4	Assignment[106]	
	1230 s	P-O-H in-plane deformation	
	1150 vs	PO_2 antisymmetrical stretch	cf F_2 stretching mode of PO_4^{3-}
1069 s, p	1072 vs	PO_2 antisymmetrical stretch (A)	
947 w, dp	947 vs	$P(OH)_2$ antisymmetrical PO stretch	
880 s, p	878 s	$P(OH)_2$ symmetrical PO stretch cf A_1 mode of PO_4^{3-}	
500 w		O-P-O bending modes. cf F_2 bending mode of PO_4^{3-}	
380 w		O-P-O bending mode. cf E bending mode of PO_4^{3-}	

Table 9 - 4.

Vibrational Frequencies of Phosphoric Acid (cm.$^{-1}$)

Raman[97,98,102] Aq H_3PO_4	Infrared Aq H_3PO_4	Assignment[106]
	1250 s	P-O-H in-Plane deformation
1190 w, p	1165 vs	P=O stretching (A)
1052-1079 w, p	1066-1074 w	$P(OH)_3$ "degenerate"
1008 w	1007 vs	PO stretch
890 s, p	885 w	$P(OH_3)_3$ symmetrical PO stretch cf A_1 stretching mode of PO_4^{3-}
500 d, p		O-P-O bending mode cf F_2 bending mode of PO_4^{3-}
390 w 345 w		O-P-O bending modes cf E mode of PO_4^{3-}

The 878, 947 and 1072 cm.$^{-1}$ bands are also observed in the Raman spectrum.

As may be seen, it is difficult to analyse the spectra of phosphoric acid in terms of separate ionic phosphate species. The reported splitting of the E (cf T_d) bending mode in the Raman spectrum is given as evidence for the low symmetry of the H_3PO_4 molecule in aqueous solution, reduced below C_{3v} or C_3 by the effects of hydrogen bonding.[98] Weak Raman bands at 1008 and 1190 cm.$^{-1}$ have been reported,[98] corresponding to the strong infrared bands at 1007 and 1165 cm.$^{-1}$. A weak polarised band at 1078 cm.$^{-1}$ was also observed. In other published Raman spectra [96, 97, 102] only the central weak band in the range 1050 - 1080 cm.$^{-1}$ was reported in this part of the spectrum.

The weak intensities of the above Raman bands were immediately obvious with the first sample of 90% phosphoric acid examined in this present study. The symmetrical PO stretch at 890 cm.$^{-1}$ was by far the most intense band and the F_2 and E, O-P-O bending modes, although less intense, were easily resolved. Dilution of this sample resulted in the symmetrical PO stretch moving slightly to a lower frequency, a value of 868 cm.$^{-1}$ being recorded for 3% phosphoric acid. Owing to the breadth and weakness of the other bands it was difficult to record any movement on dilution.

Quantitative measurements of the intensity of the symmetrical stretching mode showed this to be directly proportional to the concentration of total phosphate present. Figure 9 - 1 shows a calibration graph constructed for the range 0 -4.8 M phosphoric acid. A good linear relationship is seen.

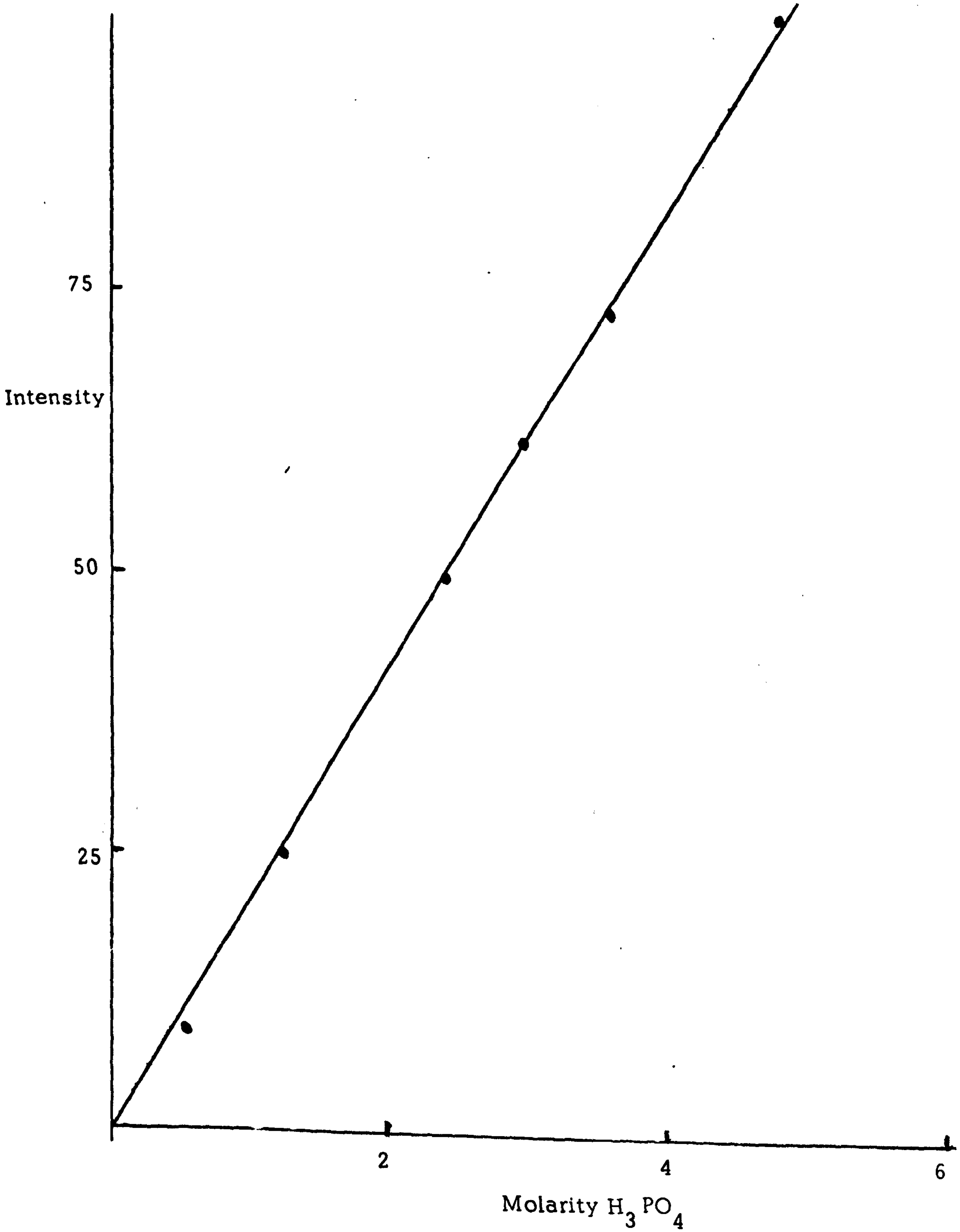
It is concluded therefore that such Raman spectra, while not apparently providing information on the dissociation of the acid, do offer a means of estimating the total phosphate present in solutions which are comparative in concentration to those used in the n.m.r. investigations.

B. Aluminium Phosphates.

An extensive literature search failed to find any previous work relating to the Raman spectra of aluminium phosphates in aqueous solutions. It was therefore decided initially to study the $AlCl_3$ - H_3PO_4 system at -H_3PO_4/Al ratios and concentrations similar to those used in the n.m.r. investigations. Aluminium chloride was chosen so that the spectra would contain no bands arising from the anions of the aluminium salt.

The first solution examined contained 4.8 M H_3PO_4 and 2.0 M $AlCl_3$. The Raman spectrum, Figure 9 - 2 clearly showed the O-P-O, F_2 and E, bending modes and they were of comparable intensity to those in a similar concentration of phosphoric acid with no added aluminium.

Figure 9 - 1 Intensity of P - O stretch at various phosphoric acid concentrations



However, the intensity of the PO symmetrical stretch at 875 $cm.^{-1}$ was reduced and a new overlapping vibration appeared at 902 $cm.^{-1}$. It was difficult to detect bands at a higher frequency than this.;

Decreasing the phosphoric acid content of the solution, the aluminium concentration remaining constant, resulted in a decrease in the intensities of all bands. However, the intensity of the symmetrical stretching mode due to the uncomplexed acid was reduced to a greater extent than the intensity of the new vibration and at a H_3PO_4/Al ratio of 0.3 the latter alone was visible. From n.m.r. investigations it was seen that only aluminium phosphate complexes were detected at this low ratio (no unreacted acid found) and thus the new vibration must represent phosphate complexes of aluminium and could be assigned to their symmetrical PO stretch. This band would also appear to represent all aluminium phosphate complexes.

It has been shown that a linear relationship holds between the total phosphate present and the intensity of the symmetrical stretch in uncomplexed H_3PO_4. A series of solutions were therefore prepared containing H_3PO_4 and aluminium chloride at H_3PO_4/Al ratios comparative to those used in the n.m.r. investigations. The intensities of the symmetrical

Figure 9 - 2 Raman spectrum of H_3PO_4 - $AlCl_3$ system

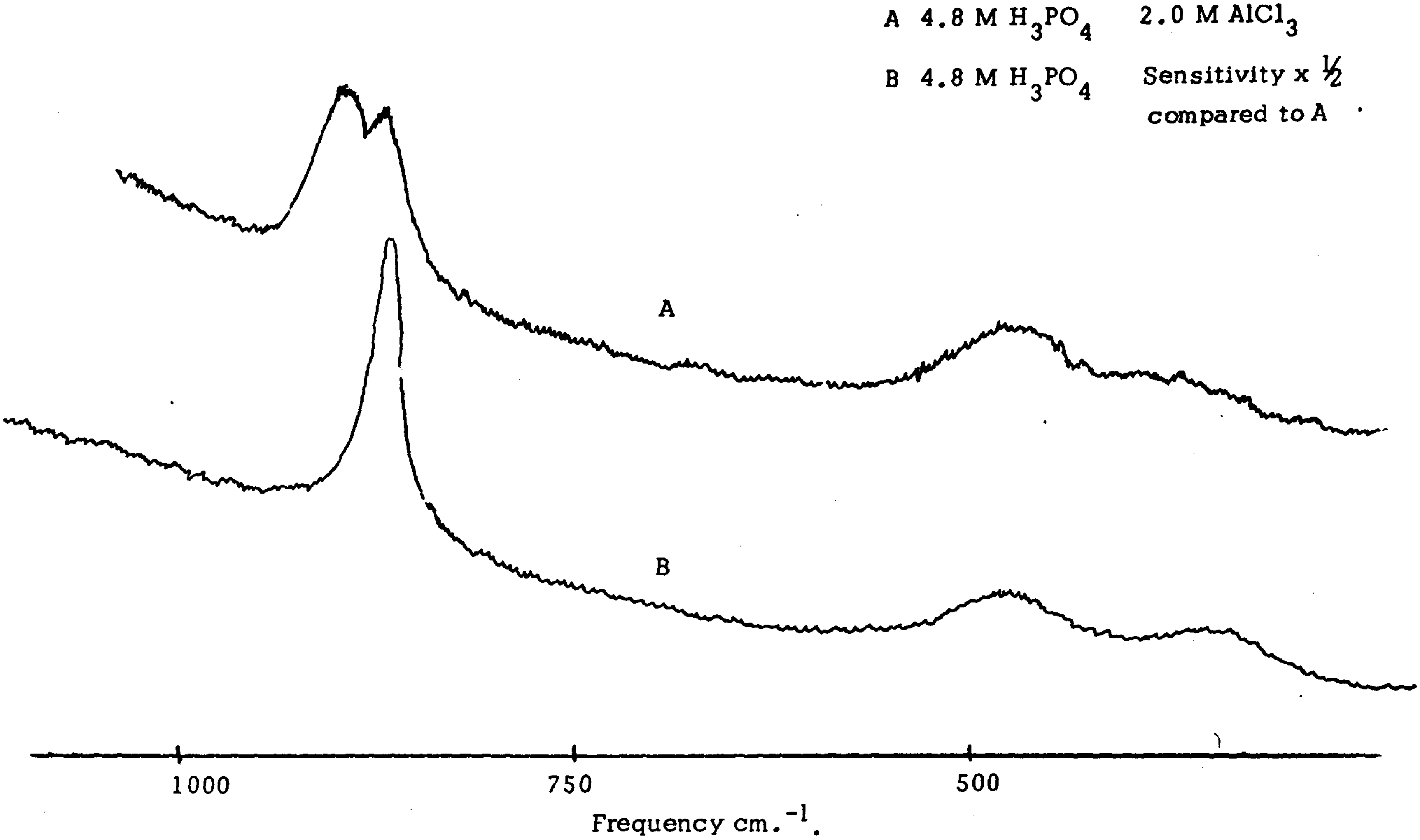
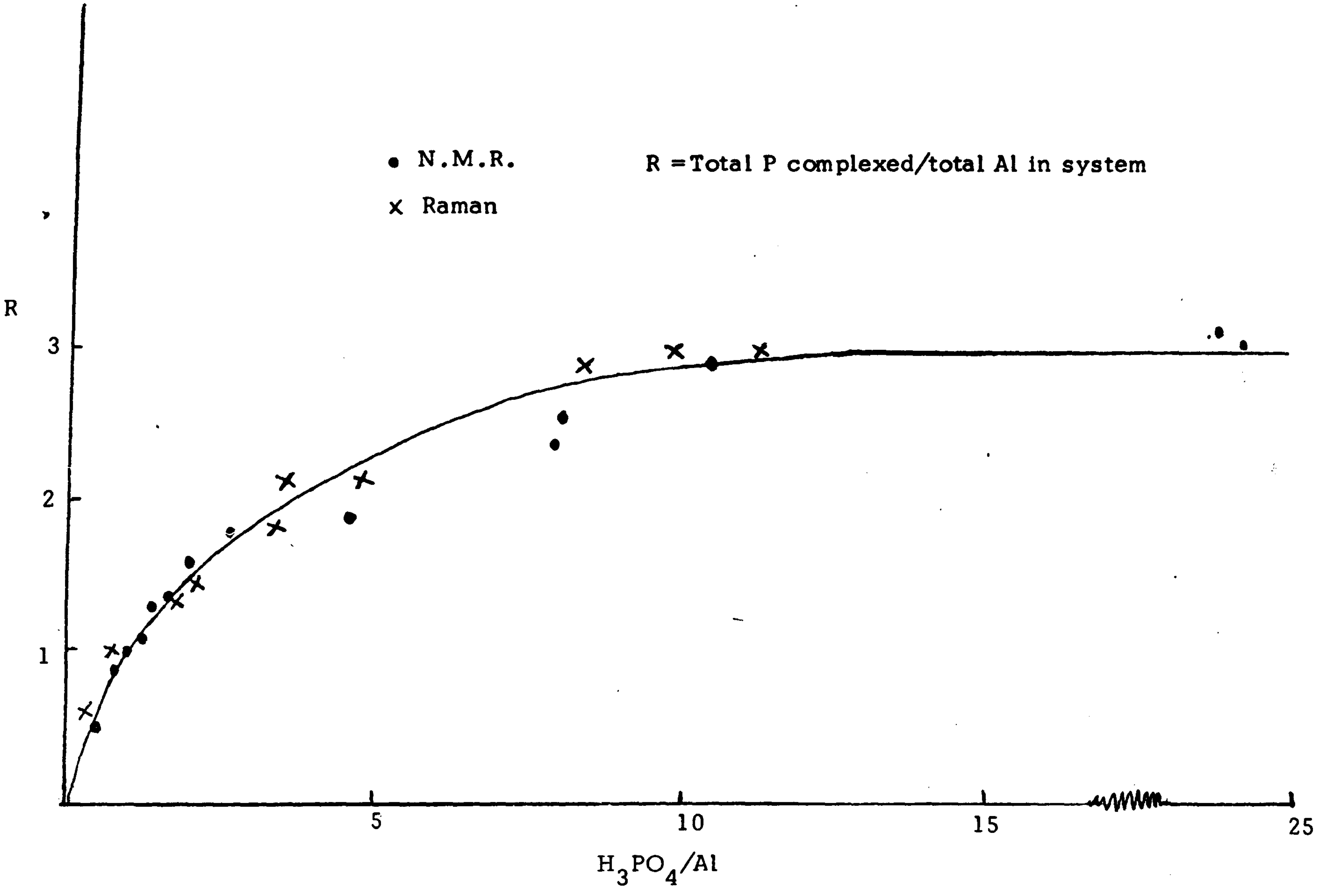


Figure 9 -3 Plot of total P complexed/total Al in system vs. H_3PO_4/Al ratio for N.M.R. and Raman investigations



stretching mode due to uncomplexed acid were compared to a standard calibration graph and from this the concentration was determined for unreacted H_3PO_4 at a particular ratio. The total concentration of phosphate complexed was easily determined from this value. In figure 9 - 3 the values of the ratio of $\bar{n} = \frac{\text{Total P Complexed}}{\text{Total Al in System}}$ obtained from this Raman study, at different H_3PO_4/Al ratios, is compared to similar values obtained in the n.m.r. investigations.

Agreement between the two techniques is good and the Raman studies confirm the aluminium species containing 3 phosphorus atoms to every aluminium as the only aluminium phosphate complex present at H_3PO_4/Al ratios greater than 10.

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