Aluminium-27 Nuclear Magnetic Resonance Studies of Sulphato-complexes of the Hexa-Aquo Aluminium Ion

By **J. W. Akitt, N. N. Greenwood,*** and **B. L. Khandelwal,** Department of Inorganic and Structural Chemistry, The University of Leeds, Leeds LS2 9JT

A sulphato-aluminium complex and a small amount of dimeric aluminium cation have been detected in aqueous aluminium sulphate solutions by means of ^{27}Al n.m.r. spectroscopy. The sulphato-complex is probably formed from the SO_4^{2-} rather than the HSO_4^- ion. The results emphasise the complexity of aluminium sulphate solutions and may throw light upon the old controversy over the exact proportion of water present in aluminium sulphate crystals.

THE ^{27}Al n.m.r. spectrum obtained from aqueous aluminium sulphate solutions consists of a strong resonance due to $Al(H_2O)_6^{3+}$ and a weaker one 3·3 p.p.m. to high field due to a complex with some form of the sulphate ion.[1,2] We report here more detailed n.m.r. studies of the system using an increased magnetic field and relate our results to the several previous studies of aluminium sulphate complexes.

EXPERIMENTAL

^{27}Al and ^{1}H N.m.r. spectra were obtained using a Bruker HFX spectrometer with a magnetic field of 21·1 kG and operating at 23·45 and 90·0 MHz respectively. The solutions were made up by weight using AnalaR reagents. Peak areas were measured using a Du Pont 310 curve analyser.

RESULTS

It was found previously that the proportion of sulphate complex could be increased by the addition of sulphuric acid. This work was repeated and the relative peak areas obtained are plotted in Figure 1. A typical ^{27}Al spectrum is shown in Figure 2. Small additions of acid do not appreciably affect the area of the peak due to the complex; this increases only when the concentration of acid exceeds 4 mol l^{-1}. Above 9 mol l^{-1} a third resonance emerges at still higher field with a chemical shift of 7·0 p.p.m. This was not observed previously due to overlap of peaks at the lower magnetic field used (13·5 kG).

The area of the peak at 3·3 p.p.m. increases roughly linearly if the sulphate concentration is increased either by adding sodium sulphate or further aluminium sulphate in the absence of sulphuric acid. The sodium salt is the more effective. These results are also plotted on Figure 1. The area of this peak diminishes if hydrochloric acid is added and the complex is undetectable if this acid is added in excess. This observation suggests that the complex is not formed from the bisulphate ion.

The complex peak at +3·3 p.p.m. is present in the ^{27}Al spectra of solutions of alums and is somewhat intensified if ammonium sulphate is added to an aluminium sulphate solution, although rapid crystallisation of ammonium alum makes measurement difficult.

---

[1] J. W. Akitt, N. N. Greenwood, and G. D. Lester, *J. Chem. Soc.* (*A*), 1969, 803.

[2] B. E. Epperlein and O. Lutz, *Z. Naturforsch.*, 1968, **23a**, 1413.

The observation of two ^{27}Al resonances for complex and for $Al(H_2O)_6^{3+}$ separated by only 3·3 p.p.m. indicates that interconversion between the two species is slow. A temperature-dependence study indicated that collapse of the two lines occurred at about 330 K implying a rate of interconversion of *ca.* 330 s^{-1} at this temperature.

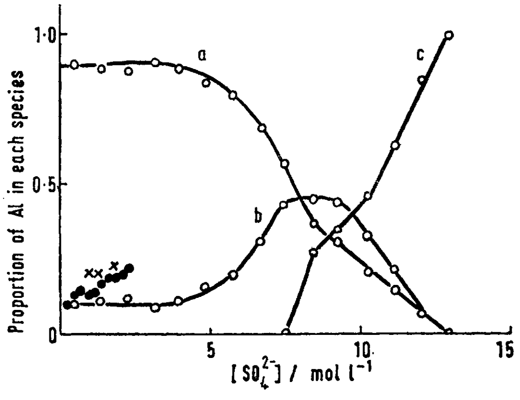

FIGURE 1 Mole fractions of aluminium present as various species in aluminium sulphate solutions: ○ = 0·3M in Al with added sulphuric acid; ● = various concentrations of aluminium sulphate only, [Al] = 0·15 to 1·5M; × = 0·3M in Al with added sodium sulphate. The letters indicate which resonance gives rise to the results (Figure 2)

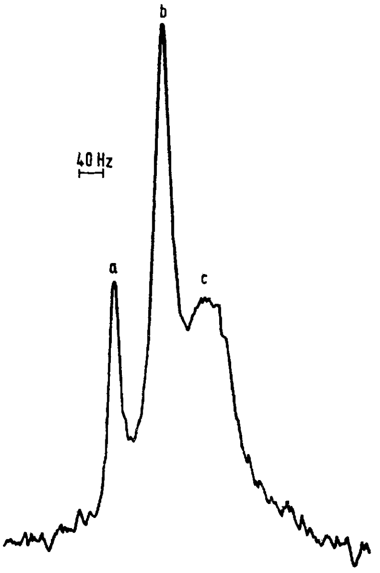

FIGURE 2 ^{27}Al N.m.r. trace of a solution of aluminium sulphate containing a large excess of sulphuric acid (a) $Al(H_2O)_6^{3+}$, (b) probably $Al(H_2O)_5(SO_4)^+$, (c) complex containing co-ordinated sulphuric acid or bisulphate ion or ions

We have previously pointed out that because of the ready formation of a dimer cation in aqueous aluminium nitrate or chloride solutions, which is accompanied by the liberation of two protons from hydrolysis, the anions are appreciably protonated to form the un-ionised acids, which indeed can be removed by distillation or purging.[3,4] Because of the relatively small second dissociation constant for sulphuric acid, one would likewise expect that in aluminium sulphate solutions the sulphate anion would become protonated to form the bisulphate anion and that dimer cation would be generated to an even greater extent. A search for the broad, low-field resonance of the dimer at high gain and high power revealed the typical asymmetry on the low-field side of the $Al(H_2O)_6^{3+}$ resonance, indicating the presence of a small quantity of the dimer ion.[3]

Low-temperature proton spectra, down to −30°, were also obtained on aluminium sulphate solutions which contained sulphuric acid in an attempt to measure the average hydration number of the aluminium and so estimate the number of sulphate ligands in the complex.[5] A single resonance was observed at all temperatures so that proton exchange between hydrated ions and acidic solvent is fast.

DISCUSSION

The existence of sulphato-complexes of aluminium has been discussed for some years though there is some dispute as to whether the sulphate is bound to the metal and resides in the first hydration sphere or whether it resides primarily in the second hydration sphere. Several different techniques have been used in the investigations and are summarised briefly below. Thus, sulphate ion has a large effect on the pH of solutions containing cationic polymers.[6] The ultrasonic absorption of aluminium sulphate solutions is greater than that of solutions of the chlorides, and stepwise formation of sulphate complexes has been inferred.[7] Aluminium cations cause the coagulation of silver iodide sols but the presence of sulphate ion reduces the effectiveness of the aluminium; the formation of a complex with formation constant of $3·7 \times 10^2$ l mol^{-1} was suggested.[8,9] Temperature-jump and pressure-jump studies at different values of pH suggest that the rate of sulphate exchange is similar to that of the hydration water [10,11] while potentiometric results have been interpreted as indicating that most of the sulphate and aluminium are complexed as $Al(SO_4)^+$ and $Al(SO_4)_2^-$, plus an outer-sphere complex. Aluminium ions reduce the light absorption of cupric sulphate solutions and a thermodynamic stability constant of *ca.* 10^2 l mol^{-1} has been calculated for $Al(SO)_4)^+$.[12] Sodium hydrogen carbonate precipitates a solid phase, $5Al_2O_3,3SO_3,15H_2O$ from aluminium sulphate solutions which contains only anionic aluminium; this presumably can only arise if the sulphate ions form part of the aluminium polymeric clusters.[13] Conductivity measurements carried

---

[3] J. W. Akitt, N. N. Greenwood, B. L. Khandelwal, and G. D. Lester, *J.C.S. Dalton*, 1972, 604.

[4] J. W. Akitt, N. N. Greenwood, and B. L. Khandelwal, *Spect. Letters*, 1971, **4**, 139.

[5] A. Fratiello, R. E. Lee, V. M. Nishida, and R. E. Schuster, *J. Chem. Phys.*, 1968, **48**, 3705.

[6] A. W. Thomas and T. H. Whitehead, *J. Phys. Chem.*, 1931, **35**, 27.

[7] M. Eigen and K. Tamm, *Z. Elektrochem.*, 1962, **66**, 107.

[8] E. Matijevic, J. Leja, and R. Nemethy, *J. Colloid Interface Sci.*, 1966, **22**, 68.

[9] L. J. Stryker and E. Matijevic, *J. Phys. Chem.*, 1969, **73**, 1484.

[10] J. Miceli and J. Stuehr, *J. Amer. Chem. Soc.*, 1968, **90**, 6967.

[11] B. Behr and H. Wendt, *Z. Elektrochem.*, 1962, **66**, 223.

[12] A. K. Nanda and S. Aditya, *Z. phys. Chem.*, 1962, **35**, 139.

[13] M. Le Peintre, *Compt. rend.*, 1964, **223**, 1004.

out on potassium alum solutions have been interpreted as indicating the formation of an outer-sphere complex with a formation constant of $5{\cdot}4 \times 10^3$ l mol^{-1} at zero ionic strength.[14] Equilibrium elution of aluminium from an ion-exchange resin by various acids indicates that an aluminium sulphate complex is formed fairly strongly.[15] Raman spectroscopy however gives no evidence to support the formation of an inner-sphere complex.[16]

The observation of a second ^{27}Al resonance in aqueous aluminium sulphate solutions provides for the first time unequivocal evidence for the formation of an aluminium sulphato-complex. The new resonance is narrow so that the aluminium must remain in an almost regular octahedral environment while the variable-temperature results indicate that the complex is relatively long-lived at 25° with a lifetime that must exceed 20 ms. The existence of a chemical shift of 3·3 p.p.m. in the ^{27}Al resonance is evidence of a change in the type of ligand co-ordinating the aluminium. The destruction of the complex by an excess of hydrochloric acid indicates that, contrary to our previous suggestion,[1] the bisulphate ion almost certainly is not the ligand and that the complex is formed from the fully dissociated sulphate ion. These observations are only consistent with an inner-sphere complex in which some of the hydration water has been replaced by sulphate, $Al(H_2O)_{6-x}(SO_4)_x^{(3-2x)+}$. If an outer-sphere complex is formed ^{27}Al n.m.r. would not be expected to detect it.

In contrast with the results of previous workers, the formation quotient Q, calculated on the assumption that $x = 1$, is quite small. Several values are given in the Table. These were calculated ignoring the dimer equilibrium since the broad dimer resonance does not affect the ^{27}Al spectra used for measurements. The free sulphate concentration would be a few percent less than shown due to protonation but the correction is too small to effect the Q values significantly.

Formation quotient Q for the sulphate-complex $Q = [Al(H_2O)_5(SO_4)^+]/[SO_4^{2-}][Al(H_2O)_6^{3+}]$ in aluminium sulphate solutions

[Al] (mol l^{-1})	0·15	0·3	0·6	1·05	1·5	0·3 [a]
$[SO_4^{2-}]_4$(mol l^{-1})	0·21	0·41	0·82	1·37	1·92	1·19
Q/(l mol^{-1})	0·53	0·36	0·19	0·17	0·15	0·22

[a] Plus 0·8 mol l^{-1} Na_2SO_4.

The fair constancy of the figures for Q seem to justify the assumption that $x = 1$, particularly as the adoption of other stoicheiometries leads to more variable values of Q. Q Is several orders of magnitude smaller than some previous values and our results show that the concentration of the complex is less than would have been anticipated. There are probably two reasons for this discrepancy. In some cases the previously used techniques involved changes in pH but the buffering effect of the presence and formation of dimeric aluminium ions was ignored. The dimer undergoes exchange reactions at a similar rate to the sulphato-complex [3] and so would also contribute to relaxation effects.[7,10,11] Even results obtained in 'neutral' salt solutions will contain a contribution due to the dimer which is inevitably present.[16,17] The conductivity results are also probably confused by the presence of dimer which may be increasingly formed in dilute solution [17] and by the associated tendency for the sulphate ion to be protonated to give extra HSO_4^-. In addition, the conductivity [14] will be sensitive to the presence of both inner- and outer-sphere complexes and may merely indicate that the sulphate ions spend a large proportion of the time in close proximity to the aluminium ions. In moderately concentrated aluminium sulphate solutions (*ca.* 0·9M) the anions and cations are separated on average by only two water molecules (including the cation hydration water). It is therefore not surprising to note that Behr and Wendt find the ratio $[AlSO_4^+]/[AlH_2OSO_4^+]$ to be 10^{-1} to 10^{-2}, very close to our Q value and that only *ca.* 5% of the Al^{3+} is truly free.[11]

The behaviour of the aluminium complex in the presence of sulphuric acid is more complicated than originally realised.[1] Small additions of acid produce no effect and this may indicate that the acid is highly associated in the already acidic/sulphate solution of aluminium. The amount of complex is considerably increased when the concentration of acid is increased above 4M and a second complex peak appears at 7·0 p.p.m. which becomes the dominant species as the acid concentration is further increased. Solutions in this composition range tend to solidify rapidly and to precipitate salts usually formulated as containing sulphuric acid [18,19] but which may perhaps be bisulphate complexes. Proton exchange is fast and the state of protonation of the acid ligands probably varies with acid concentration. There is no evidence to suggest that this complex is the bis-sulphato-complex $Al(SO_4)_2^-$ since the amount of sulphate ion in sulphuric acid solutions actually decreases above 8M acid. The spectra which we obtained at lower frequency [1] apparently contained only a single complex peak since the two reported here overlapped. The combined intensity increases with HSO_4^- concentration and this led us to believe that this was the ligand in all cases. However these new results indicate that the formation of a complex with a protonated sulphate ligand occurs only in the presence of an excess of sulphuric acid and the loss of intensity of the 3·3 p.p.m. peak with increasing acid concentration confirms this as arising from a complex with the SO_4^{2-} ligand.

Perhaps the most important aspect of our results,

---

[14] T. Nishide and R. Tsuchaya, *Bull. Chem. Soc. Japan*, 1965, **38**, 1398.

[15] J. E. Salmon and J. G. L. Wall, *J. Chem. Soc.*, 1958, 1128.

[16] R. E. Hester and R. A. Plane, *Inorg. Chem.*, 1964, **3**, 769.

[17] E. Gundwald and Dodd-Wing Fong, *J. Phys. Chem.*, 1969, **73**, 650.

[18] S. Bretznajder and Z. Rojkowsek, *Bull.Acad. polon. Sci. Sér. Sci. chim.*, 1969, **17**, 133.

[19] J. V. Mather and A. W. Wylie, *Austral. J. Appl. Sci.*, 1950, **1**, 389.

however, is the degree of complexity which they reveal in solutions of the simple salt, aluminium sulphate. Thus we can recognise $Al(H_2O)_6^{3+}$, $Al(H_2O)_5(SO_4)^+$, $Al_2(OH)_2(H_2O)_8^{4+}$, and perhaps small quantities of $Al(H_2O)_x(H_2SO_4)^{3+}$. It would also be unwise to exclude the possibility that water in the dimer ion might also be replaced by sulphate.[13] Since the dimer exists in the solid crystals [20] and since other complex aluminium ions which are found in the crystalline state also exist apparently unchanged in solution,[3] it is of interest to consider how the complexity of the solutions may be further reflected in the structure of the associated solid phases.

The degree of hydration of solid aluminium sulphate $Al_2(SO_4)_3,xH_2O$ in contact with its solution has long been a source of controversy, and x has been given values between 16 and 26.[18,20-22] Bassett and Goodwin, on the basis of their extended study, hold strongly that $x = 16$ though their analytical results often suggest $x = 16{\cdot}5$. This discrepancy they feel, is due to absorption of moisture by the crystals. However, similar nonstoicheiometric results with x lower than the commonly accepted 17 or 18 might be obtained if the crystals contained a proportion of a sulphato-complex as well as of dimer since both ions contain less water per aluminium than does the hexa-aquo ion.[23] The presence for instance of 10% of sulphato-complex would reduce x by 0·6 without affecting the ratio $[Al]/[SO_4]$ in any way. Thus Bassett and Goodwin's results may actually indicate that $x = 17$ rather than 16.

The sulphato-complex is also present in solutions containing aluminium sulphate and sodium or ammonium sulphate. The alums, *e.g.* $NaAl(SO_4)_2,12H_2O$ obtained from such solutions are usually thought to have constant composition but recently a number of papers have appeared which suggest that the composition is variable [24] and that the crystal structure shows some disorder.[25-28] Thus we suggest that the alums may contain aluminium sulphate ion-pairs also. There is some precedent for this since it now seems well established that in certain solid materials the sulphate groups are co-ordinated directly to the aluminium.[29,30]

[1/2452 *Received, 22nd December,* 1971]

---

[20] H. Bassett and T. H. Goodwin, *J. Chem. Soc.*, 1949, 2239.

[21] Naray-Szabo Istvan, *Acta Chim.* (*Budapest*), 1969, **60**, 27.

[22] N. D. Smith, *J. Amer. Chem. Soc.*, 1942, **64**, 41.

[23] See also G. J. Johannsson, *Acta Chem. Scand.*, 1962, **26**, 403.

[24] V. G. Kugnetson and B. Imanakunov, *Zhur. strukt. Khim.*, 1962, **3**, 51.

[25] D. T. Cromer, M. I. Kay, and A. C. Larson, *Acta Cryst.*, 1967, **22**, 182.

[26] D. T. Cromer and M. I. Kay, *Acta Cryst.*, 1967, **22**, 800.

[27] A. C. Larson and D. T. Cromer, *Acta Cryst.*, 1967, **22**, 793.

[28] A. V. Belyustin, *Trudy, Inst. Krist. Akad. Nauk, S.S.S.R.*, 1956, 73.

[29] H. Tanabe, *J. Pharm. Soc. Japan*, 1957, **73**, 33, 68.

[30] Rong Wang, W. F. Bradley, and H. Steinfink, *Acta Cryst.*, 1965, **18**, 249.