

on the acid dissociation constants of several amino acids which are similar to the dithiocarbamic acids but have a zwitterion character. These studies^{19,20} on the amino acids indicate that the separation between the charges in the zwitterion has a definite influence on the variation of pK with ionic strength. In order to substantiate the

above interpretations further work on several other dithiocarbamates is in progress.

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The Structure of the Aluminate Ion in Solutions at High pH

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Infrared and Raman spectra of sodium aluminate dissolved in H₂O and D₂O and ²³Na and ²⁷Al nmr spectra of sodium aluminate dissolved in H₂O have been obtained in the concentration range 0.5 to 6 M. At aluminum concentrations below 1.5 M, four vibrational bands were observed in H₂O, two of them infrared active at ~950 and 725 cm⁻¹, and three Raman active at 725, 625, and 325 cm⁻¹. The ²⁷Al nmr showed a narrow resonance line. These data are consistent with the existence of the tetrahedral Al(OH)₄⁻ as the predominant aluminum-bearing species in solution. At aluminum concentrations of about 1.5 M and above, new vibrational bands appeared at 900 (ir), 705, and 540 cm⁻¹ (R). The ²⁷Al nmr resonance was considerably broadened, but no change in chemical shift was noted. These observations are interpreted in terms of the condensation of Al(OH)₄⁻ with increasing concentration to form Al₂O(OH)₆²⁻, such that in 6 M solution the two forms coexist.

Introduction

The nature of cationic aluminum species in acid solution and in mixed solvents has recently been elucidated by the use of nuclear magnetic resonance measurements. In studying ¹⁷O-enriched acidified aqueous solutions of AlCl₃, Connick and Fiat¹ concluded that the aluminum ion was octahedrally coordinated. Similar results have been obtained for Al^{III} in aqueous mixtures of various solvents using proton magnetic resonance.^{2,3} The nature of the aluminum species during the process of neutralization has been inferred from crystallographic studies of various basic salts. For example, Johansson⁴ described the structure of the [Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺ ion existing in certain basic aluminum salts as having the aluminum octahedrally surrounded by oxygens, some of which form oxo bridges to other Al^{III} ions. It was inferred that the Al(H₂O)₆³⁺ ion in solution undergoes hydrolysis and polymerization as the solution pH is raised, but still retains octahedral coordination. Recent potentiometric measurements on Al^{III} solutions around pH 3 have supported this conclusion.⁵

The dissolution of Al(OH)₃ in aqueous NaOH is well known, and serves as a key step in the extractive metallurgy of aluminum. However, the nature of the Al-bearing ion in basic solution continues to be a subject of considerable controversy. In early studies of the

nature of alkaline aluminate solutions⁶⁻⁸ it was concluded that discrete, nonpolymeric, nonhydrolyzed anionic species were present. However, later studies^{9,10} led some workers to postulate the existence of polymeric ions such as Al₂(OH)₁₀⁴⁻, Al₂O₂(OH)₈⁶⁻, etc. Recently, polyvalent ions such as Al(OH)₅²⁻ and AlO(OH)₃²⁻ have been suggested.¹¹

Raman studies by Lippincott and coworkers¹² were

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interpreted in terms of a tetrahedrally coordinated $\text{Al}(\text{OH})_4^-$ ion. Later, Plumb, and coworkers,¹³ using both Raman and infrared data, concluded that two aluminate species exist; one, predominant in the pH range 8–12, whose vibrational spectrum was interpreted to indicate either a square-planar $\text{Al}(\text{OH})_4^-$ or a polymeric six-coordinate aluminate ion, and another, predominant in more strongly alkaline solutions, was indicated to be the linear AlO_2^- ion. The lower pH species was studied in a metastable region highly supersaturated in aluminum, and apparently is the only reported spectroscopic work in this pH range. Attempts to prepare solutions with an appreciable aluminum concentration in this pH range were unsuccessful in the present investigation.

In a detailed study of the vapor pressure of aqueous sodium aluminate solutions,¹⁴ formation of $\text{Al}(\text{OH})_4^-$ at low alumina concentrations, followed by gradual dehydration to AlO_2^- as the alumina concentration increased, was reported. Mal'tsev and coworkers¹⁵ found a correlation between the proton chemical shift in aqueous aluminate solutions of varying concentration and the corresponding vapor pressure changes. This observation was interpreted as added support for the dehydration of the aluminate ion at high concentration. Furthermore, increasing the Al_2O_3 concentration caused a slight increase in ^{23}Na nuclear magnetic resonance line width, but no chemical shift was observed. Similar results had been reported on the concentration dependence of the ^{23}Na line width in aqueous NaOH .^{16,17} On the basis of this similarity, Mal'tsev and coworkers reasoned that ion pairing in concentrated sodium aluminate solutions occurred as it is believed to in concentrated aqueous NaOH .

A study of the ^{27}Al nuclear magnetic resonance line widths of a variety of aluminum-containing species led O'Reilly and later Haraguchi and Fujiwara¹⁸ to conclude that the aluminate ion has cubic symmetry. The large negative chemical shift of the ^{27}Al in basic solution, as compared to that for octahedral Al^{III} in acid solution, suggests a coordination number less than 6 for the aluminate ion. These observations are best interpreted in terms of the tetrahedral $\text{Al}(\text{OH})_4^-$ as the predominant aluminum-bearing species in alkaline solution.

A recent review by Glastonbury¹⁹ summarizes much of the remaining work on the structure of dissolved aluminates.

The need for the present spectroscopic study (Raman, infrared, and nmr) of the aluminate ion in highly basic aqueous solutions became apparent when solubility studies of $\text{Al}(\text{OH})_3$ in such solutions containing other salts required interpretation;²⁰ although there appears to be general agreement that the predominant species is $\text{Al}(\text{OH})_4^-$, the discordant conclusion that linear AlO_2^- is the predominant anion was reached from a Raman study which is likely the most direct method of studying the problem.

Experimental Section

Reagent grade NaOH and $\text{Al}(\text{OH})_3$ were used in all experiments. Solution concentrations were determined using standard volumetric methods. Deuterated solutions of sodium aluminate were prepared by dissolution of metallic sodium and aluminum wire in D_2O . The 6 M Al solution was prepared at 200°, cooled rapidly to 52°, and filtered quickly through a medium sintered glass frit. The resulting supersaturated solution remained clear at room temperature for ~1 week. No aging effects were noted in the spectra of any of these high pH solutions. Prior to recording Raman spectra, the solutions were again filtered through an ultrafine sintered glass frit.

Potassium aluminate, $\text{K}_2[\text{Al}_2\text{O}(\text{OH})_6]$, was prepared following Johansson's procedure,²¹ and the X-ray powder diffraction pattern of the product confirmed that the same phase was obtained.²² The deuterium substituted salt was prepared by exchange with D_2O .

Raman spectra were recorded photoelectrically, initially with a Perkin-Elmer LRI instrument and later with a Spex Ramalog instrument, using for excitation in both cases a Spectra-Physics 125 helium-neon laser emitting approximately 70 mW at 6328 Å; most recently, an argon-krypton laser (Coherent Radiation Lab) emitting approximately 200 mW at 4880 Å was used. The polarized output of the laser and an analyzer between sample and spectrometer ensured that spectra proportional to $(45\alpha^2 + 4\beta^2)$ and to $3\beta^2$ were obtained using the two standard orientations of the analyzer; α^2 and β^2 are, respectively, the isotropic and anisotropic parts of the derived polarizability tensor.

Only semiquantitative intensity measurements were made when it was found that the spectra were concentration dependent. Since the primary interest was in the lower concentration solutions, which contain one aluminate species, detailed quantitative intensity studies using internal standards were not employed to elucidate the higher concentration equilibria.

Infrared absorption spectra of thin films of solution between silver chloride plates were recorded using Herscher prism-grating instruments and a Beckman IR9 instrument. The region of interest is largely

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overlapped by the broad absorption band of water, which is assigned to the liquid's librational modes, but good spectra were obtained with the more concentrated solutions and with solutions in D_2O for which the librational modes appear at a lower wave number. Solvent-absorption compensation was used in attempting to improve the spectra of the dilute solutions in H_2O .

^{27}Al nmr measurements were made at 15.63 MHz on the spectrometer described by Baker and Burd.²³ Spectra were recorded in the absorption mode and were characterized by well defined Lorentzian lines. A 3 M $AlCl_3$ solution was used as an external reference. Chemical shifts are precise to ± 0.2 ppm and line widths to ± 0.004 G. Owing to improved instrumentation, these measurements are taken to be substantially more accurate and precise than previously reported values.¹⁸ ^{23}Na spectra were run at 15.87 MHz in the absorption mode. Chemical shifts are precise to ± 0.05 ppm and line widths to ± 0.001 G. A 1 M $NaCl$ solution was used as an external reference.

Results

Typical infrared and Raman spectra of the solutions are illustrated in Figures 1–4. Spectra are concentration dependent, the intensity changes being consistent with the presence of a single aluminate species at lower concentration (approximately 1 M), and the formation of a new species as the concentration of aluminate is increased. The addition of more $NaOH$ to solutions containing the new species enhanced its concentration, but attempts to observe the effects of other added salts (perchlorate, nitrate, and chloride) were frustrated by overlapping perchlorate bands and limited solubility of the nitrates and chlorides.

Wave number data for the lower and higher concen-

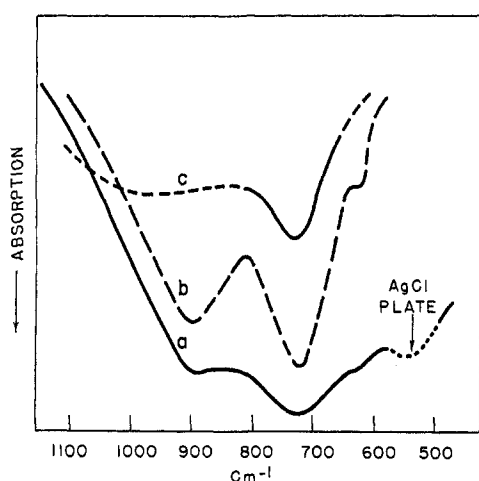


Figure 1. Infrared absorption spectra of thin films of H_2O solutions of sodium aluminate between $AgCl$ plates: (a) uncompensated spectrum of 6 M Al (2.3 M excess $NaOH$); (b) spectrum a corrected for solvent absorption using 6 M $NaOH$ as reference; (c) 1.28 M Al (1.34 M excess $NaOH$) compensated with film of H_2O in reference beam.

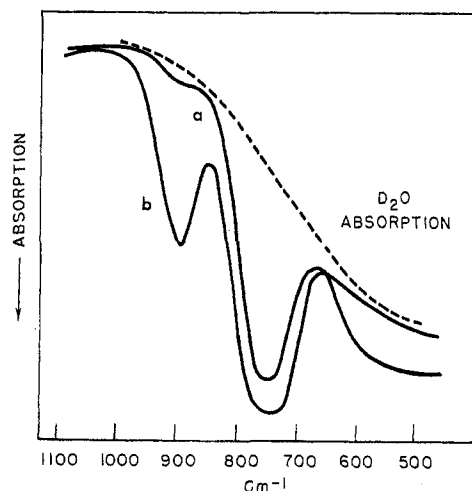


Figure 2. Uncompensated infrared absorption spectra of thin films of D_2O solutions of sodium aluminate between $AgCl$ plates: (a) 1.5 M Al (~ 1.5 M excess $NaOD$); (b) 6 M Al (3.15 M excess $NaOD$).

tration solutions with the estimated uncertainties arising largely from the broad nature or the low intensities are listed separately in Table I. Considerable uncertainty is associated with a broad band (definitely absent in D_2O solution) which is centered near 950 cm^{-1} in the infrared spectra of dilute solutions of aluminate in H_2O ; at higher concentrations, another sharper band arises near 900 cm^{-1} and obscures this region. The ambiguity arises because the band is broad and the solvent absorption not only rapidly changes with wave number in this region but also is, solute dependent. Previous studies have established, and exploratory spectra obtained here have confirmed, that solutes influence the position and intensity of the water librational bands. Compensated spectra obtained by using films of water or of sodium hydroxide solutions in the reference beam of the instrument showed a broad absorption but with a large uncertainty in its shape; 950 cm^{-1} is an estimate of its band center.

Another region of uncertainty is near 540 cm^{-1} where an impurity infrared-absorption band induced in the silver chloride plates by concentrated $NaOH$ solutions arose during the spectral scans.

Band intensities are low in the Raman but it was possible, with the use of the $4880\text{-}\text{\AA}$ line under high amplifier gain conditions, to demonstrate the Raman activity of the 725-cm^{-1} band (745 cm^{-1} in D_2O) in the $3\beta^2$ spectrum where the relatively more intense isotropic scattering of the adjacent 625 cm^{-1} is absent. Spectra e of Figure 3 and c of Figure 4 show that the anisotropic scatterings of the 625- and 725-cm^{-1} bands are approximately the same while the 745-cm^{-1} band is about twice as intense as the 605-cm^{-1} band. These measurements were made on dilute solutions which did not show the

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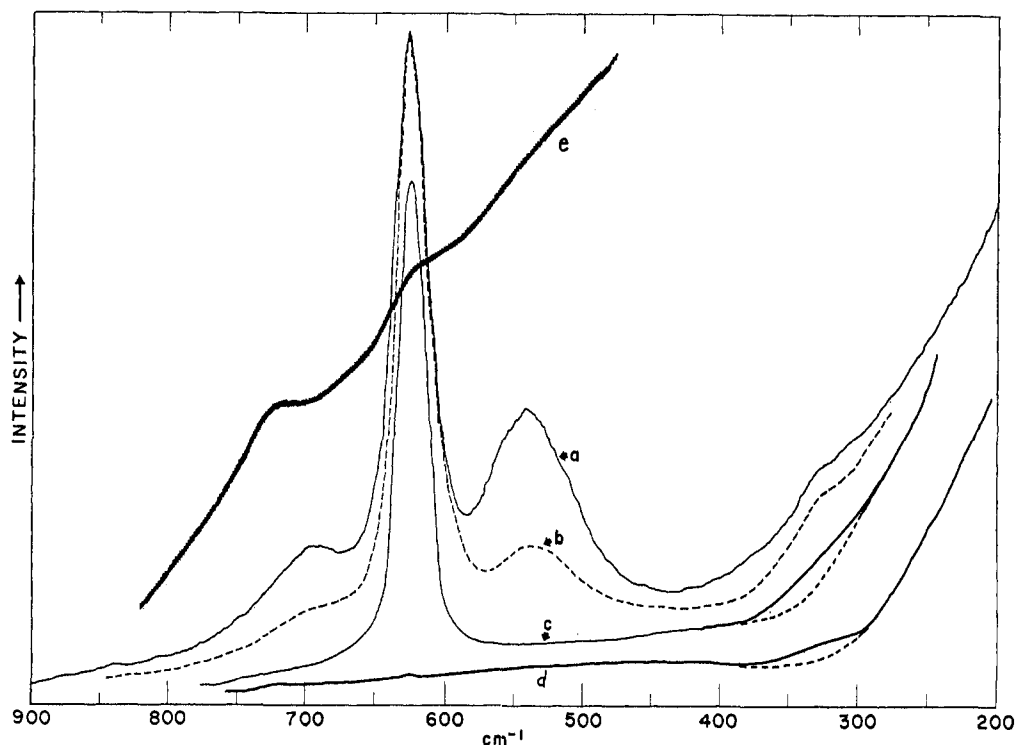


Figure 3. Raman spectra of sodium aluminate solutions in excess NaOH: (a) 5.3 *M* Al (2.5 *M* excess NaOH); (b) 2.6 *M* Al (1.3 *M* excess NaOH); (c) 0.5 *M* Al (0.75 *M* excess NaOH); (d) 1 *M* Al (1 *M* excess NaOH); (e) 1 *M* Al (1 *M* excess NaOH). Slit widths were approximately 8 cm^{-1} . Spectra a, b, and c are proportional to $45\alpha^2 + 4\beta^2$ while spectra d and e are proportional to $3\beta^2$. Spectrum e obtained under high gain illustrates the weak band near 725 cm^{-1} and the dotted lines drawn in the 300–400- cm^{-1} region under spectra c and d demonstrate the presence of a weak band occurring there in dilute solutions.

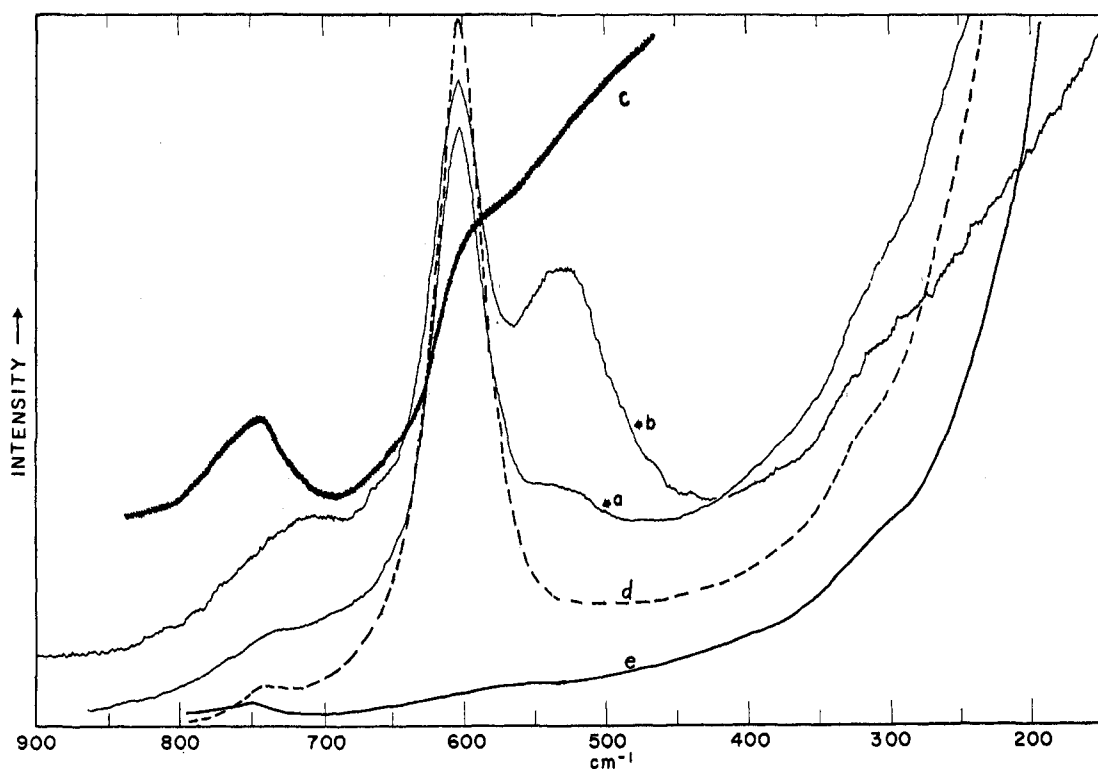


Figure 4. Raman spectra of sodium aluminate solutions in excess NaOD: (a) 1.5 *M* Al (1.5 *M* excess NaOD); (b) 6 *M* Al (3.2 *M* excess NaOD); (c), (d), and (e) 0.9 *M* Al (0.9 *M* excess NaOD). Spectra a, b, and d are proportional to $45\alpha^2 + 4\beta^2$ while c and e are proportional to $3\beta^2$; c obtained under high gain illustrates the band at 745 cm^{-1} .

Table I: Raman and Infrared Data for Sodium Aluminate Solutions^a

Raman		Infrared	
H ₂ O	D ₂ O	H ₂ O	D ₂ O
(a) 1 M in Al (~1 M in NaOH)			
725 ± 5, vw, dp	745 ± 5, vw, dp	~950 ?	
625 ± 2, s, p	605 ± 2, s, p	725 ± 5, s	745 ± 5, s
~325 ± 10, vw, dp	~320 ± 10, vw, dp		
(b) 6 M in Al (~2.3 M in NaOH)			
705 ± 10, m, p	725 ± 10, m, p	900 ± 5, s	895 ± 5, s
625 ± 2, s, p	605 ± 2, s, p	725 ± 5, s	745 ± 5, s
540 ± 5, m, p	534 ± 5, m, p	625 ± 3, vw	
		Obscured by AgCl plate absorption	
330 ± 10, w, dp	316 ± 10, w, dp		

^a s = strong; w = weak; p = polarized; dp = depolarized.

bands of the new species present at higher concentration.

The depolarization ratio, ρ , of the 625-cm⁻¹ band in dilute solution (1 M, Al) was also obtained more precisely using the argon laser line at 4880 Å. In H₂O, $\rho = 0.007 \pm 0.003$ and in D₂O $\rho(605 \text{ cm}^{-1}) < 0.005$. At higher concentrations, *e.g.*, at 5 M in Al, ρ was still small, 0.10, and overlapping by the adjacent, less polarized bands of the new species probably contributes much to this value.

Infrared and Raman spectra of potassium aluminate obtained for comparison purposes are shown in Figures 5 and 6.

Summarized in Table II are ²⁷Al and ²³Na nmr data. Line widths increase with increasing concentration in the expected manner. The change in $\delta^{23}\text{Na}$ with concentration contrasts previously reported data.¹⁵ The relatively high precision of the present measurements, however, permits detection of small chemical

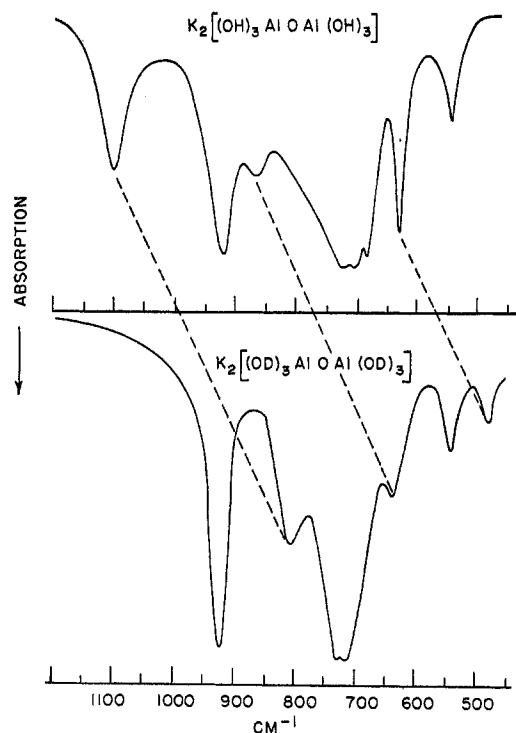


Figure 5. Infrared absorption spectra of Nujol mulls of the salt $\text{K}_2[(\text{OH})_3\text{AlOAl}(\text{OH})_3]$ and its deuterated analog. The dashed lines connect bands which are assigned to AlOH and AlOD bending modes.

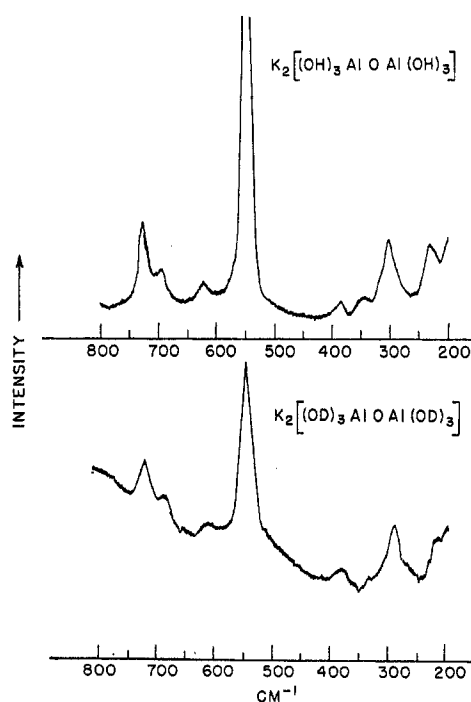


Figure 6. Raman spectra of solid samples of $\text{K}_2[(\text{OH})_3\text{AlOAl}(\text{OH})_3]$ and $\text{K}_2[(\text{OD})_3\text{AlOAl}(\text{OD})_3]$. The salts are weak scatterers and show some background due to fluorescent impurities, particularly the D compound. No bands were observed above 800 cm⁻¹.

Table II

Sample	Concn, <i>M</i>		Temp, °C	$\delta_{\text{AlCl}_3}^{27\text{Al}}$, ppm	Width, G	$\delta_{\text{NaCl}}^{23\text{Na}}$, ppm	Width, G
	Al	NaOH					
AlCl ₃	3		27	0	0.054		
Al(OH) ₃	0.5	0.75	27	-79.8	0.021	-0.45	0.008
Al(OH) ₃	1.28	1.34	27	-80.0	0.041	-1.10	0.012
Al(OH) ₃	6.0	2.0	80 ^a	-79.5	> 0.2		

^a Resonance line was too broad to observe at 27°. Substantial narrowing with increasing temperature was observed.

shift changes. In both tables, the NaOH concentrations are the quantities in excess of that necessary to form NaAl(OH)₄ from Al(OH)₃ and NaOH.

Discussion

Lower Concentration Solutions. The tetrahedral structure, Al(OH)₄⁻, was proposed to accommodate the data obtained from the initial Raman study by Lippincott and coworkers¹² of high pH sodium aluminate solutions. The aluminate concentration was not specified. A strong band near 615 cm⁻¹ and a weaker band near 310 cm⁻¹ were observed. In a more recent study by Plumb and coworkers,¹³ high aluminum concentrations, reportedly 4 *M*, were used in the pH range 8–13. Only the strong band at 628 cm⁻¹ in both H₂O and D₂O solutions was observed. These findings prompted a reassignment; the strong, highly polarized, solvent insensitive Raman band was assigned to the totally symmetric stretching mode of a linear AlO₂⁻ (*D_{∞h}*). No infrared data were reported by either worker.

In this study, stable solutions containing appreciable amounts of aluminum at pH below 13 could not be prepared; so, only those solutions of immediate practical interest with pH above 13 were examined. Comparison with Plumb and coworkers' data can thus be made only for the high pH spectra, and here there are some points of disagreement. The spectra illustrated in Figure 3 show the 628-cm⁻¹ band, but it is significantly shifted (20 cm⁻¹) between H₂O and D₂O. Additionally, the spectra show a number of other bands which must be assigned to a new species favored by high aluminum and hydroxide concentrations. This species will be discussed in the next section. These discrepancies may be explained in part by the use of a much more powerful light source for the Raman measurements in this work.

The data for the dilute solution species above pH 13 show that: (1) a prominent Raman band at 625 cm⁻¹ is highly polarized with a ρ value barely distinguishable from zero and is also distinctly solvent isotope dependent; (2) two other depolarized Raman bands occur near 320 and near 725 cm⁻¹ which are also shifted in D₂O; (3) a strong infrared band coincides with the 725-cm⁻¹ (745 cm⁻¹ in D₂O) Raman band; (4) a second, broad infrared band near 950 cm⁻¹ in H₂O is absent in D₂O solution, but its expected new location, near 700 cm⁻¹, is obscured by the strong 745-

cm⁻¹ band; (5) the ²⁷Al resonance is narrow and the chemical shift is in accord with a tetracoordinate species.¹⁸

These observations require an aluminate ion with approximately cubic symmetry and strongly bound hydroxy groups. Linear AlO₂⁻, bent AlO₂⁻, or any solvated form of AlO₂⁻ which retains the O–Al–O unit as the central structural feature are extremely improbable, if not conclusively eliminated, from consideration. On the other hand, no model accommodates the data as well as tetrahedral Al(OH)₄⁻. Although the AlO₄ unit is tetrahedral, the hydrogen atoms reduce the overall symmetry, and this explains the very small departure from zero observed for the depolarization ratio of the totally symmetric stretching motion; this mode's isotope dependence is also reasonable. The prominent infrared band at 725 cm⁻¹ is approximately described as the AlO₄ antisymmetric stretching mode but its upward shift to 745 cm⁻¹ in D₂O shows that mixing with OH bending motions occurs to different extents in the light and heavy species. An assignment of the observed bands to the modes of this model is given in Table III.

An additional indication that Al(OH)₄⁻ predominates in dilute solution is provided by the structure derived in the following section for the aluminate species which forms in more concentrated solutions.

Higher Concentration Solutions. In this study, the solutions of primary interest were in the lower concentration range, and the detailed Raman intensity measurements required to determine the concentration de-

Table III: An Assignment of the Raman and Infrared Bands Observed in Dilute Sodium Aluminate Solutions^{a,b}

Cm ⁻¹	Approximate description
~325	AlO ₄ antisymmetric bending
625	AlO ₄ symmetric stretching
725	AlO ₄ antisymmetric stretching
~950	Al–O–H bending

^a Descriptions are approximate only, solvent dependence shows that so-called AlO₄ modes include OH motions. ^b Lippincott, *et al.*,¹² observed the two lower wave number bands and calculated a value of 725 cm⁻¹ for the AlO₄ antisymmetrical stretch using these and the tetrahedral model.

Table IV: Bands Characteristic of the Higher-Concentration Aluminate Species^a

In H ₂ O, cm ⁻¹	In D ₂ O, cm ⁻¹	Spectrum
900 ± 10	895 ± 5	Infrared
705 ± 10	725 ± 10	Raman, polarized
540 ± 5	534 ± 5	Raman, polarized

^a Bands of this species may also occur in regions overlapped by bands of Al(OH)₄⁻, *i.e.*, near 330, 620 cm⁻¹ (Raman) and 725 cm⁻¹ (infrared).

pendence of the new species which was apparent in the spectra of solutions of concentrations greater than ~1.5 *M* were not made. It was, however, qualitatively established that the new species was characterized by the bands listed in Table IV, and that, although the addition of base enhanced the concentration of the new species, the degree of enhancement was not sufficient to be consistent with a proton abstraction process leading to OAl(OH)₂⁻ formation.¹¹

Another process, ion-pair formation between the Al(OH)₄⁻ and the solvated sodium ion, undoubtedly occurs, is enhanced by increasing concentrations of aluminate and sodium hydroxide, and must influence the spectra to some degree. However, this perturbation should, in itself, not influence the aluminate ion to the extent observed. It may, however, facilitate the abstraction of water from a single Al(OH)₄⁻ ion to yield OAl(OH)₂⁻¹⁴ or from a pair of Al(OH)₄⁻ ions to yield the divalent, single-bridged species (HO)₃AlOAl(OH)₃²⁻.

Monovalent, monomeric species are apparently favored for the interpretation of vapor pressure data, osmotic and other properties of the higher concentration aluminate solutions, as well as the lower concentration solutions;^{6,19} and, on this basis, the dehydration process yielding OAl(OH)₂⁻ at the first step would appear to be the more probable interpretation. The OAl(OH)₂⁻ ion presumably has a planar or nearly planar AlO₃ skeleton but, in either case, it possesses three skeletal stretching modes which may be described approximately as Al-O stretching, Al(OH)₂ antisymmetric stretching, and Al(OH)₂ symmetric stretching. The three bands in Table IV at 900, 705, and 540 cm⁻¹ may be reasonably assigned to these three modes, respectively. Analogous structures have been postulated, *e.g.*, in solutions of arsenious acid treated with base.²⁴

However, in spite of this apparently satisfactory rationalization of the spectra, we prefer the alternative interpretation for the spectral changes observed in the higher concentration solutions, *i.e.*, condensation of two Al(OH)₄⁻ ions to form the divalent [(HO)₃AlOAl(OH)₃]²⁻ ion. The evidence is more direct and does not require major assumptions comparable to those necessarily made concerning water activities in interpreting osmotic and related data for concentrated

solutions. The evidence rests upon a direct comparison of the solution spectra and the solid state spectra of the dimeric ion (Figures 5 and 6). Johansson²¹ recently determined the structure of solid potassium aluminate *via* single crystal X-ray work, and demonstrated the presence of discrete [(HO)₃AlOAl(OH)₃]²⁻ ions built up from two AlO₄ tetrahedra which share an oxygen; the bridge AlOAl angle is 132°. Comparison of Figures 1 to 6, with due account being taken of the relatively small differences attributed to the phase difference (solution-solid), shows that all the bands of the higher concentration species appear in the solid spectra and that the additional bands in the solid phase spectra, which are shown by deuterium substitution to be Al-O modes of the dimer, occur in regions obscured in the aqueous solution by the strong bands of the monomer or by the solvent. Also prominent in the solid spectra, but understandably difficult to discern in the solution spectra from the solvent absorption, are the AlOH and AlOD bending modes; the wave number ratios, 1105/805 = 1.37, 870/640 = 1.36, and 630/480 = 1.31, are those expected for the bending modes of OH groups involved in hydrogen bonding but not in appreciable interaction with other skeletal modes. The three corresponding O-H stretching modes are also well defined. The simplest interpretation is that the three OH groups at each end of the ion form, in the solid phase, hydrogen bonds of different strengths and that each of these vibrates essentially independently of the others. In aqueous solution, of course, this is no longer the case and a broad absorption band near 950 cm⁻¹ which encompasses the bending vibrations of all the OH groups is a reasonable expectation. Table V summarizes the data for the solids and an approximate vibrational assignment which is based on the *C_s* model²¹ for the O₃AlOAlO₃ skeleton. The three main features observed in the solution spectra (Table IV) are assigned by comparison with Table V to the Al-O stretching modes: ~900 cm⁻¹ (two AlO₃ modes), ~700 cm⁻¹ (four AlO₃ modes), and 545 cm⁻¹ (one AlOAl mode).

The nmr data are also consistent with a dimeric aluminate species in concentrated solution. The chemical shift of (HO)₃AlOAl(OH)₃²⁻ would not be expected to be appreciably different from Al(OH)₄⁻ as observed. If the dehydrated species, OAl(OH)₂⁻, were formed, no ²⁷Al resonance is expected because of substantial line broadening owing to an asymmetrical electrical field gradient about the aluminum nucleus.

In accord with the expected increase in contact ion pair formation in these concentrated solutions, both the ²⁷Al and ²³Na resonances broaden. This observation is consistent with previously reported studies of line broadening in the sodium resonance of aqueous salts.^{15,17,25}

(24) T. M. Loehr and R. A. Plane, *Inorg. Chem.*, **7**, 1708 (1968).

(25) V. S. Griffiths and G. Socrates, *J. Mol. Spectrosc.*, **27**, 358 (1968).

Table V: Vibrational Spectra and Assignments for $[(\text{OH})_2\text{AlOAl}(\text{OH})_2]^{2-}$ and Its Deuterated Analog

$[(\text{OH})_2\text{AlOAl}(\text{OH})_2]^{2-}$		$[(\text{OD})_2\text{AlOAl}(\text{OD})_2]^{2-}$		Assignment ^a
Infrared	Raman	Infrared	Raman	
3540 m		2620 m		O'-H(D) stretch
3370 m		2510 m		O''-H(D) stretch
3275 m		2440 m		O'''-H(D) stretch
1105 m		805 m		O'''-H(D) bend
920 ms		920 ms		$\nu(\text{AlO}_3)$ A'(2)
870 mw		640 mw		O''-H(D) bend
725 s	725 mw	730 s	~725 w	$\nu(\text{AlO}_3)$ (4) A' and A'', overlapping O'-H(D) bend $\nu_{\text{antisymmetric}}(\text{AlOAl})$ A' $\nu_{\text{symmetric}}(\text{AlOAl})$ A'
700 s	695 w	710 s	~690 vw	
685 s		480 mw		Bending modes of skeleton
628 m		~620 w		
	625 w			
545 m	546 s	546 m	546 s	
385 sh	~385 w	380 m		
374 m		360 m		
344 m	~340 w	337 w		
325 m		310 m		
	302 mw	290 vw	~290 w	
270 m		265 m		
226 w	~226 w	225 vw		

^a These descriptions are approximate labels only since all skeletal modes will involve Al-OAl and Al-OH motions.

The evidence presented here for the existence of dimeric aluminate species in concentrated solutions also lends support to the arguments given earlier for tetrahedral $\text{Al}(\text{OH})_4^-$ at lower concentrations. If four-coordinate aluminum is present in solutions of high ionic strength, dilution would almost certainly not be expected to produce the dehydrated AlO_2^- ion. An additional interesting observation made in this study was that the spectrum of a 2 M aluminate solution

containing both aluminate species did not change at temperatures up to 150°. Apparently, the equilibrium is not highly temperature dependent.

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