Translated from *Uspekhi Khimii*, 43, 224-251 (1974) U.D.C. 546.623'33

Structure and Behaviour of Aluminate Ions in Solution

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The most important published data on the composition and structure of aluminate ions in solutions of different concentrations and pH values are systematised and analysed. The views of various workers on the types of interaction present in aluminate solutions are discussed. The significance of different hypotheses and models of mononuclear and polynuclear aluminate ions is examined in the light of the results of recent physicochemical investigations.
The bibliography includes 154 references.

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I. INTRODUCTION

The structure of aluminate ions in solution is among the most important problems in the chemistry of aluminium and also in the production of alumina by alkali methods [1,2]. Even the fundamental nature of these solutions (colloidal [3-14], or true solutions [15-25]) remained controversial until quite recently. The lack of general agreement on the nature and structure of aluminate ions in solution is due to the complexity of their behaviour and to the inconsistency of many of the experimental results which have been reported. Nevertheless, the most reliable experimental results appear to be consistent with the ionic model of aluminate solutions [1,2,19-25].

However, the problem of the composition and structure of the aluminate ion in solutions of different concentrations and pH values is still not finally settled. Hence, the structural differences between unsaturated and supersaturated solutions, and the decomposition mechanism of aluminate solutions, are also still unclear [1,2,19-23,26-28].

It is generally agreed that the predominant species in aluminate solutions (at least, in unsaturated solutions at high pH) is the mononuclear aluminate ion [22-26,29-32], although divergent views are held on the structure of this ion. The following compositions have been proposed: AlO_2^-, [22,29-31,33-41] $AlO(OH)_2^-$, [22,29-30,33] $Al(OH)_4^-$, [22,24-26,29-31,33,42-65] and $Al(OH)_4.2H_2O^-$. [19,51,66] Several workers [22,29,30,33] believe that the first three types of mono-aluminate ion can coexist in aluminate solutions as singly-charged anions with different degrees of hydration:

$$Al(OH)_4^- \rightleftharpoons AlO(OH)_2^- + H_2O \rightleftharpoons AlO_2^- + 2H_2O, \qquad (1)$$

the equilibrium being shifted towards the right by increase of temperature and concentration.

The formation of measurable amounts of ions of the $Al(OH)_5^{2-}$ and $Al(OH)_6^{3-}$ type, reported in most of the textbooks and monographs on the chemistry of aluminium, is not confirmed by experimental results [23,24].

Published information on the presence and on the existence region of poly-nuclear hydroxo aluminium complex anions in alkaline solutions is scarce, and contradictory [22,25,28,31,32]. However, this type of information is highly relevant both to the behaviour of metastable aluminate solutions and to the more general problem of poly-nuclear complex formation in solutions [67,68]. Furthermore, the control of industrial processes for the production of alumina requires a full understanding of the structure of the aluminate ions and of the phenomena which occur in supersaturated solutions.

The aim of this review is to survey and discuss critically the most important recent work which can serve as a basis for the further development of our views on the structure and behaviour of aluminate solutions.

II. RESULTS OF SPECTROSCOPIC INVESTIGATIONS

A wide range of spectroscopic methods has been applied to the study of the composition and structure of aluminate ions: Raman spectroscopy (RS), [31,39-41,52,62,63] infrared spectroscopy (IRS), [39,63,69,70] ultraviolet spectroscopy (UVS), [28,32,53,57,58,66] nuclear magnetic resonance (NMR), [30,51,60,61,63,71,72] and also X-ray [73,74] and acoustic (ultrasonic) spectroscopy [71,75].

The earliest reported (1952) RS spectra of dilute aluminate solutions [52] contained two lines (310 cm^{-1} and 615 cm^{-1} respectively) with relative intensities in the ratio of 1 : 5. The authors did not comment on the polarisation of these lines. From these results, they concluded that the $Al(OH)_4^-$ ion corresponds to the T_d model, although they were unable to observe the $\nu_3(F_2)$ line at 720 cm^{-1} which that model predicts. They merely state that the line is too weak to be observed experimentally. Further evidence in favour of the tetrahedral configuration was obtained from the values of the force constants calculated [76] by Hertzberg's method from the T_d model, which agreed satisfactorily with the values calculated from Gordy's equation [77] relating force constants and electronegativities in tetrahedral molecules. It should be noted, however, that neither the T_d nor the O_h symmetry is fully consistent with the observed [52] spectra of the aluminate ion, since the former symmetry should give four Raman-active (normal) vibrations (including two at similar energies), and the latter symmetry should give three active vibrations [52,78]. In any case, conclusions made from Raman spectra should be confirmed by IR spectroscopy whenever possible.

Lanaspeze and Eyraud[62] agreed with these conclusions[52], although they observed only one ν_1 line (at 615 cm^{-1}) in the Raman spectra of their aluminate solutions. They, also, did not comment on the polarisation of this line.

More recent work[31,39-41,63] on the Raman spectra of aluminate solutions covers a range of pH values and concentrations, as well as exploiting the helium–neon laser as a source of radiation. Only one of these investigations[63] is in partial agreement with the previous work[52,62]. Carreira and coworkers[39] found that at pH $\geqslant$ 13 the Raman spectra contain only one line, at 628 cm^{-1}, with a depolarisation ratio close to zero. At lower pH values they observed three lines (540, 625, and 830 cm^{-1}) and they found that the 830 cm^{-1} line is polarised. All these findings were confirmed (within measurement error) by other workers[40,41], who reported lines at 530, 620, 630, and 825 cm^{-1}. Some experimental data, together with the vibrations expected for the most likely symmetries with allowance for the selection rules and for line polarisation, are shown in Tables 1–4 and in Fig. 1.

Table 1. Raman and i.r. spectra of 4 M aluminate solutions (after Carreira and coworkers[39]).

pH	ν, cm^{-1} exper.	ν, cm^{-1} calc.	Depolarisation ratio	Line width $\Delta\nu$, cm^{-1}	Symmetry and activity of vibrations in Raman or i.r. spectra	
10.2	830	910	0	25	ν_1 (A_{1g} Raman)	O_h
	625	—	6/7	40	ν_2 (Eg Raman)	
	1240	1209	—	35	ν_3 (F_{1u} i.r.)	
	—	606	—	—	ν_4 (F_{1u} i.r.)	
	540	—	6/7	30	ν_5 (F_{2g} Raman)	
	—	—	—	—	ν_6 (F_{2u} i.r. inactive)	
13	628	—	0	35	ν_1 (A_1 Raman)	

The results given in Table 2 show a spontaneous change in the intensity of the Raman spectra, accompanied by a change in pH, if the pH of the solution is below 12.5–13.0. According to Tables 2 and 3, and Fig. 1, the bands at 530 and 825 cm^{-1} become weaker, and the band at 620 cm^{-1} becomes stronger, as the solution becomes progressively more alkaline. It is evident from Table 4 that in the pH region 8.3–13 the presence of three Raman lines cannot be reconciled with the $D_{\infty h}$ symmetry of the AlO_2^- ion for any of the models considered. Since none of the RS lines is found in the IRS (Table 1), we may assume that the aluminate ion is centrosymmetric[76,79]. Hence, the presence of $AlO_2^-(C_{2v})$ and $Al(OH)_4^-(Td)$ anions in solutions of pH $\leqslant$ 13 is not experimentally confirmed. The existence of aluminate ions having the O_h symmetry in weakly alkaline solutions is not eliminated by the spectra, but it is not confirmed by the vast majority of experimental results[23,24].

Thus, by comparing experimental results[31,39-41] with the calculated results of Table 4 we are led to the conclusion that solutions of pH $\leqslant$ 13 contain either $Al(OH)_4^-$ ions with the D_{4h} symmetry or polymeric associations, for which the linear group factor is isomorphous with the $D_{2h}(XY_4Z_2)$ or $D_{4h}(XY_4Z_2)$ point group. In the latter case the vibrations should be the same as in the octahedral $Al(OH)_6^{3-}(O_h)$ molecule if the transition from the octahedron to the polymer does not produce splitting of the degenerate vibrations or if the splitting is masked by solvent effects.

The presence of a planar $D_{4h}(XY_4Z_2)$ polymer in aluminate solutions seems unlikely. Therefore, the experimental results indicate an $Al(OH)_4^-$ structure, with D_{4h} symmetry, or an octahedral polymeric structure, $[Al(OH)_4]_n(OH)_2^{(n+2)-}$, with D_{2h} symmetry. However, the observed ageing of aluminate solutions accompanied by slow changes in pH,[30,31,48,49] and also the electrochemical measurements reported by Plumb and Swaine[78], convincingly point to the presence of polymeric aluminate ions in weakly alkaline solutions (pH $\leqslant$ 13).

Table 2. Raman spectra of 3 M aluminate solutions as a function of ageing time[40].

Time, h	pH	ν, cm^{-1}	I*
0.5	8.30	530	45
		825	20
		620	12
8.0	8.46	530	43
		825	18
		620	17
30	9.50	530	41
		825	12
		620	29
50	10.0	530	40
		825	10
		620	35
60	10.0	530	40
		825	10
		620	34

*Intensities relative to that of the 630 cm^{-1} line (taken as 100) for solutions of pH 13.0.

Table 3. Raman spectra of 3 M aluminate solutions[40].

pH	J_{630}	Line width $\Delta\nu$, cm^{-1}	J_{620}	Line width $\Delta\nu$, cm^{-1}	J_{630}	Line width $\Delta\nu$, cm^{-1}	J_{825}	Line width $\Delta\nu$, cm^{-1}
10.05	35	30	20	45	—	—	20	26
10.52	33	—	24	—	—	—	20	—
10.74	32	—	30	—	—	—	19	—
11.03	31	30	35	90	—	—	18	35
11.21	29	—	40	—	—	—	17	—
11.50	28	—	46	—	—	—	16	—
11.75	27	—	50	—	50	—	14	—
12.02	26	25	60	80	60	80	—	—
12.23	22	—	66	—	66	—	12	48
12.49	18	—	—	—	74	—	9	—
12.71	8	—	—	—	82	—	6	—
12.98	0	—	—	—	99	—	0	—
13.90	0	—	—	—	100	65	0	—

In the region of pH $\geqslant$ 13, the requirement of a single, polarised line at 630 cm^{-1} is satisfied only by the AlO_2^- structure with $D_{\infty h}$ symmetry (Tables 1 and 4, Fig. 1). This conclusion is confirmed by the absence of isotopic shifts in the spectra of deuteriated aluminate solutions at pH $\geqslant$ 13 (Fig. 1), which shows that in these solutions practically none of the protons are combined with aluminium through oxygen. On the other hand, the shift of the Raman bands towards lower frequencies following deuteriation at pH $\leqslant$ 13 (Fig. 1) justifies the conclusion[31,39-41] that under these conditions the Al ligands are hydroxyl ions.

The Raman spectra of potassium aluminate solutions[41] are practically indistinguishable from those of sodium aluminate. This suggests that the AlO_2^- and $[Al(OH)_4]_n(OH)_2^{(n+2)-}$ ions undergo only outer-spher interactions[80] with the alkali metal cations. Outer-sphere complex formation in aluminate solutions can be represented by the reactions

$$x\,M(H_2O)_y^+ + (OH)_2[Al(OH)_4]_n^{(n+2)-} \rightleftharpoons \{[M(H_2O)_y]_x(OH)_2[Al(OH)_4]_n^{x-n-2}\}, \quad (2)$$

$$M(H_2O)_y^+ + AlO_2^- \rightleftharpoons [M(H_2O)_y]AlO_2, \quad (3)$$

where M is an alkali metal cation.

Table 4. Symmetry and spectroscopic data according to the selection rules for structures similar to the aluminate ion[31,39].

Chemical formula	Точечная группа	I.r. active vibrations	Raman active vibrations	Inactive vibrations
AlO_2^-	C_{2v}	$\nu_1(A_1)$ $\nu_2(A_1)$ $\nu_3(B_2)$	$\nu_1(A_1)$ $\nu_2(A_1)$ $\nu_3(B_2)$	
	$D_{\infty h}$	$\nu_1(E_{1u})$ $\nu_3(A_{1u})$	$\nu_1(A_{1g})$	
$Al(OH)_4^-$	T_d	 $\nu_3(F_2)$ $\nu_4(F_2)$	$\nu_1(A_1)$ 615 cm^{-1}* $\nu_2(E)$ 310 cm^{-1} $\nu_3(F_2)$ 720 cm^{-1} $\nu_4(F_2)$ 300 cm^{-1}	
	D_{4h}	$\nu_4(A_{2u})$ $\nu_6(E_u)$ $\nu_7(E_u)$	$\nu_1(A_{1g})$ $\nu_3(B_{1g})$ $\nu_3(B_{2g})$	$\nu_5(B_{2u})$
$Al(OH)_6^{3-}$ (XY_4Z_2)	O_h	$\nu_3(F_{1u})$ $\nu_4(F_{1u})$	$\nu_1(A_{1g})$ $\nu_3(E_g)$ $\nu_5(F_{2g})$	$\nu_6(F_{2u})$
	D_{4h}	$\nu_3(A_{2u})+\nu_3'(E_u)$ $\nu_4(A_{2u})+\nu_4'(E_u)$	$\nu_1(A_{1g})$ $\nu_2(A_{1g})+\nu_2'(B_{1g})$ $\nu_5(B_{2g})+\nu_5'(E_g)$	$\nu_6(B_{2u})+\nu_6'(E_u)$
	D_{2h}	$\nu_3(B_{1u})$ $\nu_3'(B_{2u})$ $\nu_3''(B_{3u})$ $\nu_4(B_{1u})$ $\nu_4'(B_{2u})$ $\nu_4''(B_{3u})$	$\nu_1(A_g)$ $\nu_2(A_g)$ $\nu_2'(B_{1g})$ $\nu_5(A_g)$ $\nu_5'(B_{2g})$ $\nu_5''(B_{3g})$	$\nu_6(A_u)$ $\nu_6'(B_{2u})$ $\nu_6''(B_{3u})$

*These lines were predicted by Lippincott and coworkers[52].

The large charge of the $[Al(OH)_4]_n(OH)_2^{(n+2)-}$ ion could lead to association of this anionic ligand with several cations. Hence, we could discuss these systems from the standpoint of polynuclear outer-sphere complex formation[81], possibly complicated by inner-sphere interactions in concentrated solutions, which may become significant when the system passes through the full solvation boundary[82].

Moolenaar and coworkers[63] also studied the state of aluminium in alkaline aqueous and deuteriated solutions by RS and IRS methods. They also examined the NMR spectra of ^{23}Na and ^{27}Al, covering the concentration range 0.5–6.0 g-ion $litre^{-1}$ of Al. They were unable to prepare solutions containing appreciable quantities of aluminium at pH $\leqslant$ 13, such as had been prepared by earlier workers[39–41], and, therefore no comparison is possible outside the strongly

The RS and IRS results obtained[63] in aqueous and in deuteriated aluminate solutions at pH > 13 are summarised in Table 5. At aluminium concentrations below 1.5 g-ion $litre^{-1}$ we find four vibrational bands, two of which correspond to infrared-active vibrations (950 and 725 cm^{-1}) and three to Raman-active vibrations (725, 625, 325 cm^{-1}). However, on raising the concentration of aluminate ions beyond 1.5 g-ion $litre^{-1}$ new spectral bands are observed (900 cm^{-1} in the IRS and 705 and 540 cm^{-1} in the RS). The additional, weak Raman lines, which had not been observed by earlier workers[39–41,52], are ascribed[63] to the use of a more powerful source of radiation. None of the strongly alkaline aluminate solutions studied in this work[63] showed any significant ageing effects.

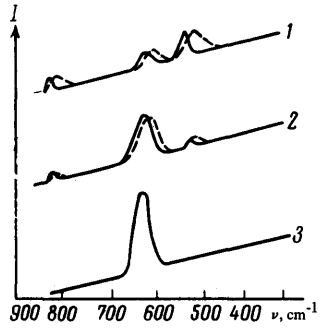


Figure 1. Raman spectra of 3 M aqueous solutions of sodium aluminate[41]: *1*) pH 10.5, *2*) pH 12.7, *3*) pH 12.9. The broken lines correspond to 80% deuteriated samples.

The Raman spectra of strongly alkaline aluminate solutions containing less than 1.5 g-ion $litre^{-1}$ of aluminium are claimed[63] to be consistent with the tetrahedral model of the $Al(OH)_4^-$ ion predicted by Lippincott[52] (see Table 4). The IRS results only partly confirm this claim. According to Table 4, aluminate ions with T_d symmetry should give rise to two lines, both IRS and RS active. One line at 725 cm^{-1} (Table 5) satisfies this condition, but the second broad and weak IR line at 950 cm^{-1} is absent in the RS. This band cannot be seen in the deuteriated solutions because its new position (close to 700 cm^{-1}) is obscured by the strong line at 745 cm^{-1}. The R line at 950 cm^{-1} is assigned[63] to Al–O–H bending vibrations. The solvent isotope effect on the position of the spectral lines (Table 5) suggests that linear AlO_2^-, non-linear AlO_2^-, or indeed any solvated form of AlO_2^- containing the O–Al–O structural element cannot be present in significant amounts in aluminate solutions. NMR studies of ^{27}Al confirm that the aluminate ion has a tetrahedral configuration.

Additional evidence in favour of the T_d symmetry of the $Al(OH)_4^-$ anion in dilute solutions is obtained[63] by interpreting the spectra of concentrated aluminate solutions. Increasing the concentration of aluminate and of sodium hydroxide should favour the formation of ion pairs between $Al(OH)_4^-$ and hydrated sodium ions, with very little effect on the shape of the spectra[80]. However, this interaction could assist the formation in solution of mononuclear $AlO(OH)_2^-$ ions[29,30] or dinuclear dehydrated $Al_2O(OH)_6^{2-}$ ions. The latter were discovered and studied by Johansson[74] in crystalline potasium aluminate using X-ray diffraction spectroscopy. The $AlO(OH)_2^-$ and $Al_2O(OH)_6^{2-}$ ions have a lower symmetry than the T_d $Al(OH)_4^-$ ion, and therefore they could be responsible for the appearance of additional spectral lines in concentrated solutions (Table 5).

The monomeric, singly charged $AlO(OH)_2^-$ ion is probably the most convenient species for interpreting the vapour pressure, osmotic, and other properties of aluminate solutions [23]. However, Moolenaar and coworkers [63] prefer to discuss their results in terms of the dimeric, doubly charged $[(HO)_3Al-O-Al(OH)_3]^{2-}$ ion.

Table 5. Raman and i.r. spectra of aluminate solutions [63]*.

Composition of solution	Raman ν, cm^{-1}		I.r. ν, cm^{-1}	
	in H_2O	in D_2O	in H_2O	in D_2O
1 g-ion Al $litre^{-1}$	–	–	~950	–
1 mole $litre^{-1}$ NaOH (excess)	725 ± 5 vw, dp	745 ± 5 vw, dp	725 ± 5 s	745 ± 5 s
	625 ± 2 s, p	605 ± 2 s, p	–	–
	325 ± 10 vw, dp	320 ± 10 vw, dp	–	–
6 g-ion Al $litre^{-1}$	–	–	900 ± 5 s	895 ± 5 s
	705 ± 10 p	725 ± 10 p	–	–
2.3 mole $litre^{-1}$ NaOH (excess)	–	–	725 ± 5 s	745 ± 5 s
	625 ± 2 s, p	605 ± 2 s, p	625 ± 3 v.w.	–
	540 ± 5 p	534 ± 5 p		
	330 ± 10 w, dp	316 ± 10 w, dp		

*s = strong, w = weak, vw = very weak, p = polarised line, dp = depolarised line.

Their only evidence for this choice is the similarity between the spectra of the solutions (Table 5) and the IR and Raman spectra of the dimeric ion in the solid state. A comparison of the spectra for the solid and the liquid phase, allowing for the spectral effects of the phase itself, has shown that all the bands found in concentrated solutions (Table 5) appear also in the spectra of the solid material. However, the latter contain additional bands at wavelengths which are obscured in aluminate solutions by strong bands from the solvent and from the $Al(OH)_4^-$ monomer. Hence, the conclusion [63] is that two types of ion coexist in concentrated aluminate solutions: $Al(OH)_4^-$ and $Al_2O(OH)_6^{2-}$, having T_d and C_s symmetry respectively.

Moolenaar and coworkers [63] also made another interesting observation: the IR, Raman, and NMR spectra of 2 M aluminate solutions containing ions of both types remain unchanged at temperatures up to 150°. Obviously, the equilibrium is relatively independent of temperature, or the concentration of dimeric ions is not large enough to influence the spectra significantly. If the first explanation is correct, the effect of temperature on the stability of metastable aluminate solutions cannot be ascribed to a structural rearrangement of the aluminate ion.

It should be noted that most of the concentrated aluminate solutions examined by Moolenaar and coworkers [63] were supersaturated with respect to aluminate ions, and therefore some caution is needed in extending their results and conclusions to the structure of unsaturated aluminate solutions. So far, the only (indirect) confirmation of the existence of polymeric ions with a single Al–O–Al oxygen bridge in supersaturated solutions of hydrated sodium aluminate comes from the work of Ni and coworkers [69,70], who also observed lines at 900, 740, 635, and 540 cm^{-1} in the IR spectra of their aqueous solutions. By comparing these spectra with those of the solid salt $K_2O.Al_2O_3.3H_2O$, whose lattice is known to consist of double $Al(OH)_4^-$ tetrahedra [83] joined by a single oxygen bridge, those workers concluded that a similar structure must be present in solution. Their Raman spectra [70] were not fully consistent with those of Moolenaar [63].

Thus, a search of the literature on the vibrational spectra of aluminate solutions suggests that monomeric aluminate ions with T_d symmetry are present in moderately concentrated solutions at pH > 13. The problem of polynuclear aluminium complexes, and of their existence regions, requires further study.

Studies of the NMR spectra of aluminate solutions also led a number of workers [51,60,61,63,71,72,84] to the conclusion that the aluminate ion has tetrahedral symmetry. The large negative chemical shift of ^{27}Al in alkaline solutions [51,60,61,63,71] as compared with the octahedrally hydrated Al ion in acid solutions [85–88] suggests that the coordination number of aluminium in the aluminate ion is less than six.

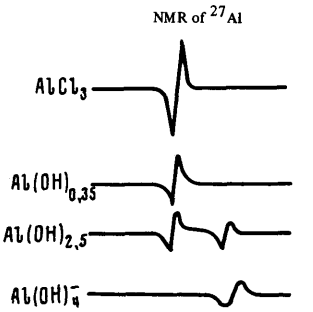


Figure 2. NMR spectra of ^{27}Al for solutions with different OH : Al ratios [51].

Fig. 2 shows the NMR spectrum of ^{27}Al in solutions with different OH : Al ratios [51]. In the acid solutions the resonance peaks are assigned to ^{27}Al in the AlO_6 group, whereas in alkaline solutions (OH/Al > 4) they are assigned to AlO_4. However, it appears from the spectra that both six- and four-coordinated aluminium ions can exist in solutions with an OH/Al ratio close to 3. This conclusion has been confirmed [89].

According to O'Reilly [60], the small width of the quadrupole line in aluminate solutions indicates a high degree of symmetry of the field surrounding the aluminium nuclei. The $Al(OH)_4^-$ ion has the required symmetry, whereas the AlO_2^- ion should give a broader line.

Mal'tsev and coworkers [30,90] used the NMR method (with ^1H and ^{23}Na) to study aluminate solutions containing up to 24% of Na_2O, and they observed a correlation between the chemical proton shift and the vapour pressure [29,30]. This work confirmed Dibrov's suggestion [29] that the tetrahydroxoaluminate ion becomes dehydrated at high concentrations according to reaction (1).

More recent work [63] also confirmed the dehydration of the $Al(OH)_4^-$ ion with increasing concentration of Na_2O and Al_2O_3, but to give the dimeric complex $Al_2O(OH)_6^{2-}$ rather than ions of the $AlO(OH)_2^-$ or AlO_2^- type. It is pointed out that the chemical shift of the ^{27}Al NMR line of the $[(HO)_3Al-O-Al(OH)_3]^{2-}$ ion should not differ significantly from that of $Al(OH)_4^-$, as is found in practice. If, on the other hand, a dehydrated ion of $AlO(OH)_2^-$ type had been

formed, no resonance would have been observed because of the line broadening caused by the asymmetric electric field gradient surrounding the nucleus of the aluminate ion. The insensitive dependence of the chemical shift of ^{27}Al on the concentration of alkali and of aluminate ions in solution can be ascribed[71] to the strong screening effect of the OH ions on the aluminium ion. Hence, the various interactions between the components of the solution and the $Al(OH)_4^-$ ion have only a minor effect on the electron density around the ^{27}Al ion.

The formation of ionic associations between sodium and aluminate ions has been convincingly demonstrated[30,63,71,90]. The increasing concentration of these associations with concentration of Na^+ ions in solution is revealed by a broadening of the ^{27}Al and ^{23}Na lines. This observation is consistent with analogous studies of the ^{23}Na line width in aqueous solutions of NaOH and certain salts[30,91,92]. Ion-pair formation significantly affects the time of half-exchange between free and associated ions in solution[30], and therefore the concentration dependence of the ^1H relaxation time observed in NMR cannot be ascribed wholly to polymerisation of the aluminate ions, as suggested by Romanov and Ni[72].

There is a single report[71], not supported by other published work[30,90,91], that the ^{23}Na resonance signal is shifted towards weaker fields in alkali as well as in aluminate solutions. The large changes in the chemical shift of ^{23}Na with Al concentration suggest that the interaction of the aluminate ions is stronger with sodium cations than with OH ions. It is important to take account of this interaction in any discussion of the bulk properties of the solution (electrical conductivity, viscosity[1,2]), and also when considering the dissociation mechanism of aluminate solutions.

The line widths and nuclear relaxation times of ^{23}Na and ^{27}Al, and also the results of ultrasonic and refractometric investigations[71], are consistent with the conclusions reached by analysing the chemical shifts of ^{23}Na and ^{27}Al. The NMR spectra indicate[71] the formation of dimeric complexes of the $Al_2O(OH)_6^{2-}$ type[63] at concentrations of aluminium above 1.5–2.0 g-ion litre^{-1}.

U.v. spectral studies of aluminate solutions over a wide range of concentrations[23,28,53,57,58,66] have identified two absorption bands at wave lengths 230 and 265 nm[32,66]. The overall absorption band[93] of aluminate solutions[32] is shown in Fig. 3 together with its expansion into two Gaussian components.

According to Taichi[66], the absorption bands at 230 and 265 nm are due to the presence of the ions $Al(H_2O)_6^{3+}$ and $Al(OH)_4.2H_2O^-$ in aluminate solutions. This assignment of the first absorption band to the hexa-aquo Al ion is not convincing, since optical studies of acid solutions of Al have shown that this ion does not absorb at wave lengths greater than 200 nm.[32,94] Equally, the presence of the $Al(OH)_4.2H_2O^-$ ion in aluminate solutions has not been confirmed experimentally[23]. Hence, we cannot accept Taichi's explanation of the anomalously high viscosity of aluminate solutions in terms of hydrogen-bond formation between these two non-existent species.

It can be seen from Fig. 3 that the relationship between optical density and concentration of the aluminate ion in solution follows the Lambert–Beer law[93]. The law is obeyed in solutions both undersaturated and supersaturated with respect to hydrargillite. This behaviour suggests that one particular type of aluminate ion (which could not be identified from u.v. spectra alone) is predominantly present in the solutions examined. Because of the low values of the extinction coefficients, structural rearrangements of the aluminate ion as between undersaturated and supersaturated solutions cannot be detected.

However, in supersaturated solutions a decrease in the concentration of alkali and aluminium (at a constant $Na_2O : Al_2O_3$ ratio of 2.0) produces a bathochromic shift of both u.v. bands by 3–5 nm. This effect is absent in undersaturated aluminate solutions. The bathochromic shift observed in supersaturated solutions could be due to the formation of small amounts of polymeric aluminate ions.

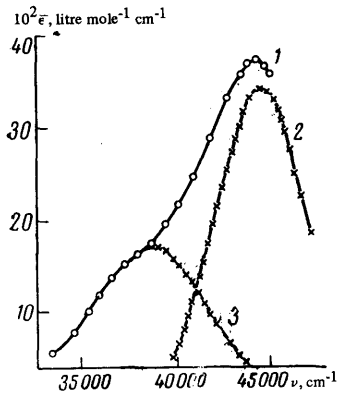


Figure 3. Absorption spectrum of aluminate solutions (*1*) resolved (*2*, *3*) according to Volokhov[32]: Na_2O concentration 0.5–2.51, alkalinity modulus α (Na_2O/Al_2O_3) 2–10.

Thus, some published work[31,39–41,78] suggests that polynuclear anions may be present in aluminate solutions of pH < 12–13, but when the pH is greater than 13 spectroscopic methods indicate that monomeric aluminate ions are predominant in concentrated solutions. Very accurate measurements of electrical conductivity and of diffusion coefficients[57,58], and also by the anion exchange method[84], have confirmed this conclusion, but unfortunately these measurements have been confined to aluminate solutions with a total electrolyte concentration not greater than 2 M.

III. ELECTROCHEMICAL INVESTIGATIONS

Studies of the chemistry of aluminium in aqueous solutions are complicated by the lack of simple and reliable methods for determining equilibrium concentrations of aluminium ions[78,95,96]. For this reason the Al–OH system has been studied by the very convenient pH method[97], which allows the composition of the aluminate ions to be determined from the measured concentration of hydroxyl ions[98]. However, the study of concentrated aluminate solutions in which the concentration of alkali is greater than 1 M is precluded by the large errors attending the use of glass or hydrogen electrodes in strongly alkaline solutions[97]. Not surprisingly, therefore, the solutions studied by the pH method have been more dilute, on the whole, than those studied by spectroscopic methods.

Brosset[48] reported, in 1952, one of the most important investigations of the chemistry of hydroxo-complexes of aluminium. He studied the hydrolysis of aluminium ions at concentrations between 2.21×10^{-3} and 1.11×10^{-2} g-ion litre^{-1} by a potentiometric method, using hydrogen electrodes. The measurements were made at a constant ionic strength of 2, maintained by sodium perchlorate[99,100]. Brosset concluded, from his results, that the main products of the hydrolysis of aluminium ions in alkaline solutions are polynuclear hydroxo complexes of $[Al(OH)_3]_n(OH)^-$ type.

However, a recalculation of these results by the method developed by Sillén to establish the mechanism of polynuclear hydrolysis[101-103] led to the conclusion[49] that the main hydrolysis product is the mononuclear $Al(OH)_4^-$ complex. The following reactions were suggested for the formation of these ions:

$$Al(OH)_{3(s)} + H_2O \overset{K'}{\rightleftharpoons} Al(OH)_4^- + H^+ , \quad (5)$$

or

$$Al(OH)_{3(s)} + OH^- \overset{K}{\rightleftharpoons} Al(OH)_4^- . \quad (6)$$

The logarithms of the constants for these equilibria are 12.5 ± 0.2 and 1.0 ± 0.2 respectively. Ageing of an $Al_2O_3 . xH_2O$ precipitate may result in the transformation of amorphous aluminium hydroxide into a more stable form, for which [according to Eqn. (6)] $\lg K = 0.5 \pm 0.2$.

It is stressed[49] that the precision of the measurements is relatively low, and there is no really convincing evidence of the absence of polynuclear anions in the solution.

After a more detailed analysis[51] of the data for these hydrolytic equilibria Sillèn concluded that alkaline aluminate solutions contain predominantly mononuclear anions with a tetrahedral $[Al(OH)_4^-]$ or octahedral $[Al(OH)_4 . 2H_2O^-]$ configuration.

Most of the published potentiometric investigations[24,26,55,65,104] confirm Sillèn's conclusion that the most abundant species in dilute aluminate solutions are mononuclear tetrahydroxo or dioxo complexes of aluminium.

Table 6 lists the published data for the equilibrium constant of reaction (5), assuming different modifications of aluminium hydroxide. It is evident that the equilibrium in the heterogeneous aluminate system depends very significantly on the structure of the solid aluminium hydroxide. The differences (Table 6) between the constants for a given modification of aluminium hydroxide suggest that in some of the work the crystalline form of the solid phase was not identified with sufficient care. In some cases the solid aluminium hydroxide was prepared under conditions different from those chosen for the equilibrium study. The criterion adopted as an indication of the establishment of equilibrium, and possibly also the presence of aluminate ions of composition other than $Al(OH)_4^-$, may have influenced the results.

Berecz and Szita[26] used as their equilibrium criterion for the dissolution of hydrargillite in alkali an electrochemical cell containing two mercury–oxide electrodes:

$$-Hg\,|\,HgO\,|\,OH^-,\ Na^+,\ Al(OH)_4^-\,|\,Al(OH)_3(s)\,HgO\,|\,Hg^+. \quad (7)$$

The electromotive force of this cell decreases with time as the $Al(OH)_3$ dissolves, and vanishes when equilibrium between the solution and the solid phase is established. This method has the advantage that the cell e.m.f. does not include a diffusion potential, and it gives reliable results with concentrated as well as with dilute NaOH solutions. Hence, the equilibrium constants can readily be extrapolated to zero ionic strength (Table 6).

These workers[26] did not observe a break in their plots of e.m.f. against time, and they showed that the rate of change of potential is practically independent of alkalinity, and hence of the concentration of aluminate ions. By combining this observation with other published data they concluded that the dissolution of hydrargillite in NaOH produces only $Al(OH)_4^-$ anions. However this conclusion[26] applies only to solutions with pH > 12.5.

Table 6. Thermodynamic equilibrium constants of reaction (5) for different modifications of aluminium hydroxide.

Solid phase	lg K'	t°C	References
Freshly precipitated hydroxide	−12.71	25	24
	−12.50*	40	49
Boehmite (AlOOH)	−12.45	25	55
Bayerite ($Al_2O_3.3H_2O$)	−13.84	25	55
	−13.95	25	24
	−14.52	25	56
Gibbsite ($Al_2O_3.3H_2O$) (hydrargillite)	−14.57	25	55
	−15.26	25	
	−14.72	35	26
	−14.04	50	
	−13.65	60	

*This value was obtained at a constant ionic strength of 2.

Except for the paper by Stefanowicz and Kiziak[65], there are no data on the stability of tetrahydroxoaluminate ions in aqueous solutions. These workers studied the state of the aluminate ions by potentiometric titration with a glass electrode, using an ionic strength of 0.1 and varying the pH from 1 to 10–11. They interpreted their results in terms of monomer hydrolysis only, to give complexes of the $Al(OH)_n^{3-n}$ type with $n = 1$, 3, and 4 and stability constant logarithms of 12.30 ± 0.3, 31.98 ± 0.3, and 36.58 ± 0.3 respectively.

The complex $Al(OH)_2^+$ does not appear to be formed in the solutions examined[65]. This fact is contrary to the principle of stepwise complex formation[105] and needs to be confirmed. Furthermore, the large difference between the stability constant of the $AlOH^{2+}$ ions and the values reported by other workers[25,32], and also the convincing evidence for the presence of polymeric associations in weakly acid solutions of aluminium salts[24,25,89,106,107], raise some doubts on the reliability of the stability constant obtained for the $Al(OH)_4^-$ ion.

Plum and Swaine[78] obtained some interesting results on the composition and structure of aluminate ions in their study of dilute aluminate solutions with a special electrode[108] reversible towards aluminium ions. They found[78] a definite relationship between the electrode potential and the concentration and pH of the aluminate solution. At pH > 12.4 the potential of the aluminium electrode against the saturated calomel electrode becomes independent of the concentration of aluminate ions and varies less steeply with pH. Under these conditions only four protons take part in the electrode reaction, and the experimental results are described by the empirical equation

$$E_{SCE} = 0.962 + {}^4/_3(0.059)\,pH . \quad (8)$$

However, in solutions of pH < 12.4 the potential depends on the concentration of aluminate ions, and is described by the equation

$$E_{SCE} = 0.5099 + \frac{0.059}{3} \lg [\text{aluminate}] + 2(0.059)\text{pH}. \quad (9)$$

The authors assumed the electrode reaction

$$Al + 4H_2O \rightleftharpoons Al(OH)_4^- + 4H^+ , \quad (10)$$

whose potential should be given by

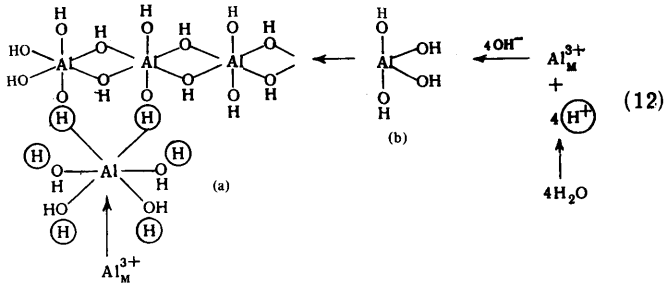
$$E = E^0 - \frac{0.059}{3} \lg [Al(OH)_4^-] + \frac{4}{3}(0.059)\,\text{pH} . \quad (11)$$

However, Eqn.(11) is inconsistent with the empirical equations (8) and (9). Hence, the hypothetical electrode reaction (10) cannot be correct. But if we assume that the formation of the products of the electrode reaction is independent of the total concentration of aluminate ions in solutions of pH > 12.4, and is determined only by the concentration of OH^- ions, Eqns.(8) and (11) become identical. Under these conditions, as can be seen from Eqn.(8), we have a direct reaction between four hydroxyl ions and one aluminium ion from the metal electrode.

In order to explain the dependence of the potential on the concentration of aluminate ions in solution of pH < 12.4 the authors assume that the aluminate ion takes part in the electrode reaction. In other words, the aluminium ion transferred to the solution from the metal electrode must react with aluminate ions to give some form of polynuclear association. It would appear from the experimental results [Eqn.(9)] that six protons are set free when an aluminium ion goes into solution.

Plumb and Swaine [78] considered the most probable structures of aluminate ions in which the Al can have a coordination number of four or six. By combining their own results with those of others [49,52] they concluded that the anion has a polymeric structure of the type $[Al(OH)_4]_n.(OH)_2^{(n+2)-}$. They assume, with little justification, that the same polymer must exist also in solutions of high pH, in which the monomeric ions are thought to be in equilibrium with the ends of polymer chains. If the chains are sufficiently long, the electrode potential will be independent of the total concentration of aluminate ions in solution.

According to Plumb and Swaine [78], the two reactions in solutions of low and high pH respectively can be described by the following scheme:



(12)

where the circles denote replaceable protons.

The reaction between active centres on the side of the polymer chain and an aluminium ion hydrated by four water molecules gives a branched structure in which bonding is by two adjacent oxygen bridges [Eqn.(12a)]. A linear polymer with n aluminium ions will have $(n-1)$ such positions, and therefore the electrode reaction leading to the formation of the branched polymer will depend on the concentration of aluminate ions in solution [see Eqn.(9)].

However, at high pH the concentration of OH ions exceeds the number of active centres in the polymer, and $Al(OH)_4^-$ ions are formed (probably in equilibrium with the ends of polymer chains). In this case, according to mechanism (12b), the coordination number of the aluminium should change from four to six. We can expect the branched polymer to be metastable with respect to the linear polymer, since the former should have a greater density of negative charges than the latter. A thermodynamic analysis of experimentally observed standard electrode potentials [78] has confirmed this expectation.

The polymeric model of the aluminate ions, $[Al(OH)_4]n(OH)_2^{(n+2)-}$, is formally consistent with the observation [49] that the mean Bjerrum number $\bar{n}$ [105] in dilute aluminate solutions is slightly greater than four. Using published [49] values of $\bar{n}$ for different Al concentrations, Plumb and Swaine calculated that the number of monomer units (n) in the polymer chain increases with concentration and can reach a value of 100 at an Al concentration of 1.1×10^{-2} g-ion litre^{-1}. However, this calculation is possible only for the unlikely case of a solution containing only polymeric anions of uniform composition.

The reaction of the $Al(OH)_4^-$ ion with a polymer (mechanism 12b) does not explain the well known increase of pH with time in freshly prepared aluminate solutions [49]. The effect could be due to the migration of branches in a metastable (highly branched) polynuclear structure towards the ends of the chain, the oxygen bridges taking up a proton from the solution, or to mutual interaction of the polymer chains according to the equation

$$[Al(OH)_4]_n(OH)_2^{(n+2)-} + [Al(OH)_4]_m(OH)_2^{(m+2)-} \rightleftharpoons [Al(OH)_4]_{m+n}(OH)_2^{(n+m+2)-} + 2OH^- . \quad (13)$$

If the increase of pH with time is due to polymerisation of the aluminate anions, and each elementary step is accompanied by the generation of two free OH ions, it can easily be shown from Brosset's results [49] that in solutions with $\bar{n} > 4$ the amount of polymer does not exceed 2%. If this is so, the disagreement between the results of pH measurements [24,48,49] and those of electrochemical measurements [78] is not surprising.

Plumb and coworkers [39] have recently confirmed by spectroscopic methods that polymeric species are present also in concentrated aluminate solutions of pH < 13.

IV. MONONUCLEAR AND POLYNUCLEAR ALUMINATE IONS IN STRONGLY ALKALINE SOLUTIONS

The existence of polymeric aluminate ions in solutions of different concentrations but pH $\leqslant$ 12–13 has been proposed in a number of publications [31,39–41,78] discussed in the previous sections of this review. However, information on the presence of polynuclear structures in strongly alkaline solutions is controversial, and erroneous in parts.

The first report of the polymerisation of aluminate ions in alkaline solutions is due to Brintzinger [109], who concluded from dialysis results that the two polymeric structures $[Al_2(OH)_{10}]^{4-}$ and $[Al_2O_2(OH)_8]^{8-}$ were present in his solutions. Because of the difficulty of interpreting dialysis data correctly, the equivalent weights of the ions cannot be established with confidence [110]. In our system the problem is further complicated by the fact that the equivalent weights of the dimeric anions are almost identical. Brintzinger's results [109] are also inconsistent with more recent work which suggests that the formal

charge on the aluminate ion, at least in equilibrium solutions at high pH, is unity [22-26,29-31,33,66]. However, the former of the above ions, $[Al_2(OH)_{10}]^{4-}$, agree in composition with the general polymer formula $[Al(OH)_4]_n \cdot (OH)_2^{(n+2)-}$, with $n = 2$, proposed for solutions of pH < 12.5. [31,39-41,78]

Calvet and coworkers [12] have shown, by diffusion measurements, that the calculated apparent radius of the aluminate ions decreases by about a factor of two on raising the temperature of the solution from 20° to 50°. This effect could be due to dissociation of ion pairs and polymeric ions, or to the dehydration of aluminate ions, but the diffusion method lacks the power to distinguish between these processes.

Jahr and Plaetschke [53] also used the diffusion method to study aluminate solutions. By referring to some earlier and unconfirmed diffusion measurements they concluded that the size of the aluminate ion is determined mainly by the alkalinity of the solution. Weakly alkaline solutions contain polymeric aluminate ions whose size decreases with increasing concentration of OH^- ions according to the reaction

$$[(H_2O)_2(OH)_3Al{-}OH{-}Al(OH)_3(H_2O)_2]^- + OH^- \rightleftharpoons 2[Al(OH)_4 \cdot 2H_2O]^- , \quad (14)$$

The resulting mononuclear aquohydroxoaluminate ions are dehydrated if the concentration of OH^- ions is increased from 6.5 to 20 (expressed as OH : Al ratio), giving rise to water-free polymers of general formula $[Al_n(OH)_{3n+1}]^-$, for example by the reaction

$$2[Al(OH)_4^-] \rightleftharpoons [(HO)_3Al{-}OH{-}Al(OH)_3]^- + OH^- , \quad (15)$$

with an average degree of polymerisation not greater than four. Further increase in alkalinity leads to decomposition of the $[Al_n(OH)_{3n+1}]^-$ complexes, and $Al(OH)_4^-$ ions become the predominant species in solution.

The polymerisation scheme proposed by Jahr and Plaetschke[53] is in general agreement with other experimental results obtained at about the same time, and is not incompatible with the growing belief that the aluminate ion carries a unit charge. However, later work has not produced any convincing evidence in favour of the formation of polymers by reactions of the type of (14) and (15).

Indeed, Jahr and Pernoll [57,58] made a series of high-precision measurements in 1965 but they were unable to confirm the earlier conclusions [53]. Their measurements of OH^- ion activity [57] indicated that only monomeric $Al(OH)_4^-$ complexes are present in alkaline solutions of pH $\geqslant$ 11.5. Their measurements of diffusion coefficient and electrical conductivity [58] also suggested that the composition of the aluminate ions is independent of the OH : Al ratio, and that polymeric anions cannot exist in strongly alkaline solutions.

An improved anion exchange method [64] has been used to show that aluminate ions in 1 M NaOH solution are always present as the monomer $Al(OH)_4^-$. The composition of the ions is independent of the ageing time of the solution, and remains unchanged up to the onset of visible decomposition of the aluminate solutions. It should be noted that these conclusions [57,58,64] apply to solutions in which the overall concentration of the components is less than 2 M, i.e. to dilute and moderately concentrated solutions.

The work of Kuznetsov [2,20-22,111] has had a profound effect on the development of our views on the structure of alkaline solutions of aluminium. According to Kuznetsov, aluminate solutions with a high alkalinity modulus ($\alpha = \frac{Na_2O}{Al_2O_3}$) contain $Al(OH)_4^-$ ions, which can form polymeric groupings in low-modulus solutions containing less than 150–180 g litre^{-1} of Na_2O according to the scheme

$$Al(OH)_4^- \rightarrow Al_n(OH)_{4n}^{n-} \rightarrow Al_6(OH)_{24}^{6-} \rightarrow \underset{\text{(Gibbsite)}}{\text{hydrargillite}} . \quad (16)$$

The formation of hydrargillite from ring structures of the $Al_6(OH)_{24}^{6-}$ type is explained by assuming that aluminate ions in solution have the same structure as the elements of the crystal lattice of hydrargillite, and also from electrical conductivity and viscosity data [20-22,111].

At Na_2O concentrations greater than 150–180 g litre^{-1} Kuznetsov assumes [2,20-22,111] that dehydrated polymers of the $[AlO(OH)_2]_n^{n-}$ type are present in solution. He suggests that changes in size of the polymer are due to fluctuations in the solutions, leading to changes in local concentration, temperature, density, etc. Hence, "conditions favourable to polymerisation are created in some microscopic regions, giving rise to hetero-phase fluctuations" [22]. Kuznetsov has not attempted to confirm his hypothesis experimentally, particularly since the problem of homogeneity or microheterogeneity in supersaturated solutions in general is still highly controversial [112].

Measurements of the electrical conductivity and viscosity of aluminate solutions [20-22,111] indicate a strong dependence of structure on concentration. Thus, the specific conductance of the alkali decreases very markedly when aluminate ions are introduced into the solution, but the electrical conductivities of aluminate solutions and of NaOH have very similar concentration dependences, going through a maximum as the concentration increases. The decrease in conductivity with increase in concentration occurs when the system has crossed the full solvation boundary [82,113], and can be explained by the formation of ion pairs [30] or by polymerisation of the aluminate ions [111].

In dilute aluminate solutions the activation energies for viscous flow ($E\eta$) and for electrical conduction ($E\lambda$) are small (less than 1 kcal mole^{-1}), and approximately equal. This suggests the presence of mobile ions, small in size, in dilute solutions. In aluminate solutions containing more than 150 g litre^{-1} of Na_2O the quantity $E\eta$ increases much faster than $E\lambda$. According to Kuznetsov [21,111], this behaviour could be associated with the appearance of large aluminate ions in solution, since viscosity is more sensitive than electrical conductivity to the presence of low-mobility ions.

Kuznetsov has also pointed out [22] that at some particular concentrations the solution develops a quasi-crystalline structure due to the formation of hydrogen bonds between aluminate ions. This effect is favoured by low temperature and low alkalinity.

Starting from the hydrated model of the aluminate ion, $Al(OH)_4.2H_2O^-$ (O_h), Pearson [19] also finds a correlation between the hydrogen bonding of aluminate ions and the viscosity of the solution. However, other work [26,30,57-59,63,64] has failed to confirm the presence of these ions, in which the aluminium should have a coordination number of six.

Kuznetsov and coworkers [114] found additional evidence in favour of hydrogen bond formation between hydroxo complexes in aluminium solutions in their study of the rheological properties of these solutions [115]. The deviations from Newtonian behaviour in aluminate solutions suggest that these liquids are structured, becoming quasi-crystalline beyond the full solvation boundary. It is pointed out [114] that structural ordering is more marked in solutions with a high content of aluminate ions and at low OH : Al ratios. Hence, plots of the stability of the structure (said [114] to be related to the degree of polymerisation)

against the alkalinity modulus at constant Al_2O_3 concentration go through a maximum at a $Na_2O : Al_2O_3$ ratio of 1.6.

Unfortunately, the authors [114] do not comment on the similarity between the concentration dependences of electrical conductivity [111] and structural stability in aluminate solutions, and they offer no explanation for the appearance of a stability maximum at that particular value (1.6) of the alkalinity modulus. Furthermore, the interpretation of the rheological properties of aluminate solutions is complicated by the lack of data on the rheological properties of concentrated solutions of pure alkalies, which are also known [116,117] to have a quasi-crystalline structure.

Thus, Kuznetsov's views on the presence of polymeric aluminate ions formed by hydrogen bonding in alkaline solutions of aluminium salts are based essentially on measurements of electrical conductivity, viscosity, and rheological properties, although the concentration dependence of these parameters could equally well be explained by postulating the formation of ion pairs or associated ionic species with a more complex structure.

Firstly, the electrical conductivity of aluminate solutions varies with concentration in the same way as in pure alkali solutions [1,2,30,111]. The conductivity of NaOH solutions begins to decrease beyond the full solvation boundary as a result of a decrease in the concentration of Na^+ and OH^- ions, due to ion pair formation [29,30,117]. The analogous trend of the conductivity changes in aluminate solutions could also be due to the formation of ionic associations between aluminate and hydroxyl anions, on the one hand, and sodium cations [30,71]. Of course, hydrogen bonding between the water molecules of the hydration shell surrounding the Na^+ cations and the hydroxyl groups of the aluminate ions could assist the formation of ionic associations of the $[Na(H_2O)_x^*]_yAl(OH)_4^-$ type, where y cannot be greater than 4. But in this case the formation of significant amounts of large polynuclear aluminate ions is unlikely, because ion pairs held by strong hydrogen bonds do not readily polymerise [118]. The increase in the viscosity of alkali solutions following the addition of aluminate ions can be ascribed to the same interactions. Furthermore, electrostatic considerations suggest that aluminate anions in alkali solutions should more easily form bonds with the oppositely charged Na^+ cations than interact with each other. Only when the concentration of aluminate ions is not very different from the concentration of Na^+ ions are conditions favourable to the formation of polynuclear aluminate structures, particularly in supersaturated solutions.

Secondly, reactions leading to the formation of complicated polymeric structures are kinetically slower than simple hydrolysis reactions [32,68], because they involve a number of separate steps. However, equilibrium is established very rapidly both in the dissolution of metallic aluminium in NaOH solutions and in the dilution of aluminate solutions with solutions of alkali, and the properties of supersaturated aluminate solutions (electrical conductivity, density, viscosity, pH,[119] optical density [32,63], velocity of ultrasonic waves [71,120]) remain constant up to the onset of visible decomposition. If, on the other hand, mononuclear and polynuclear anions of different degree of condensation were present in aluminate solutions of high pH, and if their composition were changing with time during the ageing period of the solution, none of the above properties would remain constant during the period preceding the precipitation of aluminium hydroxide.

Thirdly, the stability of supersaturated and undersaturated aluminate solutions as a function of temperature, concentration, and alkalinity modulus [2,121] can be explained not only in terms of polynuclear complex formation but also by considering the formation of ionic associations between aluminate anions and sodium cations [28], particularly since these associations are fairly stable [71] and they appear to be of the outer-sphere complex type [122], whose formation in concentrated salt solutions is known to be endothermic. Hence, increase of temperature may produce not only a rearrangement of the structure of the aluminate ions but also a blocking of those ions by sodium cations, thus increasing the stability of the solutions. Differences in behaviour between potassium and sodium aluminate solutions [41,123] lend some support to these views.

Many other published results [26,29,30,39-41,57-61,63] are also inconsistent with the presence of significant amounts of highly complex polymeric aluminate ions in strongly alkaline and concentrated solutions. An analysis of data on polynuclear hydroxo complexes of various metal ions [25] suggests that the stability of these complexes is, in general, low, and therefore their concentration must be small. Evidently, aluminate solutions are not exceptional in this respect. To some extent, this is confirmed by the low intensities of the i.r. and Raman lines obtained [63] with supersaturated solutions. It seems likely that the formation of aluminium hydroxide from alkaline solutions does not require large numbers of large polynuclear aluminate ions to be formed during the induction period.

V. THERMODYNAMIC PROPERTIES

The fullest and most reliable thermodynamic data on alkaline and aluminate solutions of composition $NaOH-H_2O$, $KOH-H_2O$, $Na_2O-Al_2O_3-H_2O$, $K_2O-Al_2O_3-H_2O$, and also $Na_2O-K_2O-Al_2O_3-H_2O$, were obtained in the Physical Chemistry Department of the Lensovet Leningrad Technical Institute. Measurements of density, equilibrium water vapour pressure, and specific heat were made over a wide range of concentrations and at temperatures between 25° and 300°. Details of the apparatus, procedures, and results obtained have already been given [29,30,33,90,117,124-140]. Most of the results relate to stable aluminate solutions. Only one publication [141] deals with the saturated vapour pressure and relative partial molar enthalpy of water in a small range of metastability. Some workers have calculated the thermodynamic characteristics of aluminate solutions by taking the aqueous solutions of pure alkali (NaOH or KOH) as the solvent [142], since their thermodynamic properties are known with sufficient precision [143-145]. The validity of this approach has been demonstrated by Karapet'yants [146].

Mal'tsev and Mashovets [30,128] obtained a large amount of valuable experimental data on the specific heat of alkali and aluminate solutions in the temperature range 25-90°. They showed that the specific heat is fairly high at low temperatures, and decreases with increasing temperature. This effect is more marked in aluminate solutions than in pure alkali solutions. The decrease in heat capacity observed on adding aluminium to a solution of sodium hydroxide is ascribed [128] to the formation of polymers or complex ions.

The theoretical interpretation of the results is extremely difficult, because of the complexity of the processes which can take place in aluminate solutions. Negative deviations from additivity of the specific heat may arise through changes in the structure of water under the influence of the dissolved ions and their hydration processes, since water is known to have a lower specific heat when in

a bound state. Positive deviations from additivity indicate predominantly interionic interactions (formation of ion pairs or polymeric associations). Using this type of argument, Mal'tsev and Mashovets [128] ascribed the small changes in specific heat at 75–90° to decomposition or dehydration of polymeric aluminate ions. Increase in concentration is also thought [128] to assist the degradation of polymeric structures at all temperatures.

More recently, Mal'tsev and coworkers [30,90] have tried to explain the measured specific heats of aluminate solutions by postulating monomeric aluminate ions of different degree of hydration. Positive deviations of the measured specific heats from the linearly interpolated values are ascribed to the formation of ionic association or ion pairs by the reactions

$$Na^+ + Al(OH)_4^- \rightleftharpoons Na^+[Al(OH)_4^-] \rightleftharpoons Na^+\left[O{-}Al\begin{matrix}OH\\OH\end{matrix}\right]^- + H_2O \rightleftharpoons Na^+AlO_2^- + 2H_2O\ . \quad (17)$$

This equilibrium should be shifted towards the right by increasing the concentration. In addition to the heat capacity measurement, data on the electrical conductivity of aluminate solutions [30,90] and the NMR spectra of ^{23}Na [30,90] provide indirect support for the suggested interionic interactions [Eqn.(17)]. Direct proof of the very strong interaction of aluminate ions with sodium cations is given in Ref. 71. Other workers [130,139–141] have critically assessed the experimental vapour pressure data, and have proposed new formulae and graphical methods for determining the vapour pressure of sodium and potassium aluminate solutions over a wide range of concentrations and temperatures. Mal'tsev [30] concludes from the dependence of vapour pressure on Al content that the total number of ions in a sodium aluminate solution is almost the same as in the corresponding solution of pure alkali, and that the two solutions have very similar structures. The dehydration mechanism of aluminate ions is consistent with the observed increase in water vapour pressure with concentration of aluminate ions [29,30]. Eqn.(17) predicts a sharp decrease in the symmetry of the aluminate ion after dehydration: the prediction is not borne out by the NMR spectra of ^{27}Al [51,60,61,63,71] or by other spectroscopic observations [52,62,63,71]. This discrepancy between the vapour pressure data and the NMR spectra of ^{27}Al can be resolved [63] by postulating the presence of partly dehydrated anions (e.g. $[Al_2O(OH)_6]^{2-}$) in concentrated solutions, since in these anions the tetrahedral configuration of the aluminate point group is distorted to a negligibly small extent.

Chakhal'yan [141] has carried out a thermodynamic assessment of the structure of aluminate solutions and of various models of the aluminate ion by combining thermochemical data with vapour pressure data for the stable and the metastable regions of these solutions. Using specially designed apparatus, he obtained some important experimental results:

1. The relative partial molar and specific enthalpies of water and of the defined solvent [aqueous alkali with a constant $(Na_2O)/(Na_2O + H_2O)$ ratio] were measured in sodium and potassium aluminate solutions at 25°, and also the heats of dilution of these solutions with solutions of pure alkali.

2. The differential heats of dissolution of hydrargillite in $R_2O{-}Al_2O_3{-}H_2O$ systems (where $R = Na^+$ or K^+) and in pure alkali solutions with a ratio $(R_2O)/(R_2O + H_2O) = 0.23243$ by weight were measured at 85°.

3. The saturated water vapour pressure was measured only over sodium aluminate solutions, for nine values of the alkalinity modulus [$\alpha = (Na_2O)/(Al_2O_3)$] in the Na_2O concentration range 5–25 wt.% and at two temperatures (25° and 75°).

From his experimental results he calculated the integral heats of dissolution of hydrargillite at three constant $(Na_2O)/(Na_2O + H_2O)$ ratios, the relative partial molar entropic terms of water in sodium and potassium aluminate solutions at 25°, and some other parameters, and he compiled an enthalpy–concentration diagram for the $Na_2O{-}Al_2O_3{-}H_2O$ ternary system.

Because of the profound influence of water on the behaviour of aluminate solutions, Chakhal'yan [141] calculated the activity of water as a function of $1/\alpha$ at various concentrations of R_2O, using vapour pressure data for solutions of sodium and potassium aluminates, and of pure alkalies. The data for 300° and for the $K_2O{-}Al_2O_3{-}H_2O$ system, were taken from the work of Mashovets and coworkers [126,130,140]. As an example, the activity of water in the $Na_2O{-}Al_2O_3{-}H_2O$ system (a_{AR}) is compared in Fig.4 with the same parameter for a pure alkali solution (a_R) as a function of the alkalinity modulus and of the Na_2O content at 25°.

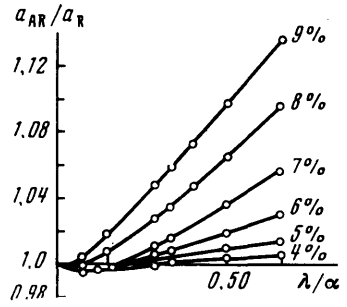


Figure 4. Ratio of the activities of water in sodium aluminate solutions (a_{AR}) and in alkali solutions (a_R) against $1/\alpha$ at 25°. [141] The numbers against each curve denote mol.% of Na_2O.

It is evident from the Figure that the activity of water in aluminate solutions with a high alkalinity modulus drops below the value for solutions of pure alkali at first, but it then crosses the horizontal axis and begins to increase at a rate depending on the Na_2O content. This type of curve is believed [141] to indicate the existence of two regions in which the structure of the aluminate ion is different, and therefore the degree of hydration is also different: for example, $Al(OH)_4^-$ and $AlO(OH)_2^-$. However, no allowance was made for the possible formation of hydrates such as $[Al(OH)_4^-](H_2O)_X$.

In order to investigate further the structure of the aluminate ion, the $a_{AR}/a_R = f(1/\alpha)$ curves (Fig. 4) were compared with $n_{AR}/n_R = f(1/\alpha)$ curves (where n_{AR} and n_R are the mole fractions of water in the aluminate and the pure alkali solutions respectively) calculated for

various proposed models of the aluminate ion. The calculations showed that the mole fraction of water decreases with increase in $1/\alpha$ in the following sequence:

$$[AlO(OH)_2]_n^{n-} > [AlO(OH)_2]_6^{6-} > Al(OH)_4^{3-} > [Al(OH)_4]_6(OH)_2^{8-} >$$
$$> AlO_2^- = [Al(OH)_4]_n^{n-} = [Al(OH)_4]_n(OH)_2^{(n+2)-} > [Al(OH)_4]_6^{6-} =$$
$$= [Al_6(OH)_{24}]^{6-} > AlO(OH)_2^- > [Al_6(OH)_{18}](OH)_6^{6-} >$$
$$> Al(OH)_4^- = [Al_6(OH)_{18}]_n(OH)_6^{6-} \quad (\text{for } n \gg 6).$$

The mole fractions of water in aluminate and in pure alkali solutions become the same if the aluminate solution is assumed to contain only monomeric AlO_2^- ions or polymeric $[Al(OH)_4]_n^{n-}$ and $[Al(OH)_4]_n(OH)_2^{(n+2)-}$ ions. In other words, these calculations [141] suggest that the hydration properties of Al_2O^- and OH^- ions are identical. This surprising result can be explained by the failure to take account, in the calculation of n_{AR} and n_R, of the water molecules in the hydration shells of the components of the solution, and also of the trans-solvation effects accompanying the formation of various ion pairs or ionic associations between sodium cations and hydroxyl or aluminate anions [30,71,90,117]. Furthermore, it is not easy to distinguish "physical" from "chemical" phenomena in these solutions without *a priori* knowledge of the final result [147], though some allowance for the "chemical" contribution to the phenomenon can be made by choosing the correct model for the aluminate ion.

Evidently, still greater complications can be expected in the calculation of the mole fraction of water in concentrated solutions, where the composition of the aluminate ions can be even more complex. In particular, the increase in the activity of water with concentration (Fig. 4) could be due not only to dehydration and polymerisation of the aluminate ion [141], but also to interactions between aluminate anions and sodium cations stronger than the corresponding interactions between Na^+ and OH^-. [71] Hence, the real composition of the aluminate ion cannot readily be inferred from integral properties of the system such as the activity of water.

From his comparison of the $a_{AR}/a_R = f(1/\alpha)$ plots (Fig. 4) with calculated plots of $n_{AR}/n_R = f(1/\alpha)$ Chakhal'yan concludes [141] that $Al(OH)_4^-$ ions are present in solutions with a high concentration of Na_2O (>8 mol.%) but a low concentration of aluminium. Increasing concentration apparently leads to dehydration of these anions and formation of polymers of the $[AlO(OH)_2]_n^{n-}$ type, or even $[AlO_2]_n^{n-}$. The existence of these polymers is not inconsistent with the thermodynamic measurements carried out by the author, or with his calculations [141] of the equilibrium constants of aluminate solutions saturated with hydrargillite at 25°. But his analysis of the equilibrium constants involve the doubtful assumption that ions of the same charge have the same activity coefficient in a given solution, although quite different numerical values have been reported for concentrated electrolytes of the same type [148].

Chakhal'yan's model [141] resembles Kuznetsov's theory [2,21,22] most closely. However, the presence of polymers of composition $[AlO(OH)_2]_n^{n-}$ and $[AlO_2]_n^{n-}$ is not confirmed by the spectroscopic results [5,52,60-63,71], or by the very low heats of dilution of aluminate solutions by solutions of alkali [141], since the degradation of these polymers should require a fairly large expenditure of energy.

A comparison of the relative partial molar entropies of water in solutions of aluminates and of pure alkalies respectively has shown [141] that water is more strongly bound in aluminate solutions (containing not more than 8 mol.% of Na_2O) than in solutions of sodium hydroxide. This finding agrees with conclusions reached by other methods [19,71], but it is given a different interpretation: some assume [19,141] that the water is built into the "intrinsic" structure of the aluminate ion ($[Al(OH)_4^-]$ (T_d) [141] or $[Al(OH)_4 \cdot 2H_2O]^-$ (O_h) [19]), whereas others [71] believe that the aluminate ion itself can form hydrates of the $[Al(OH)_4^-](H_2O)_X$ type, in which the tetrahedral (T_d) configuration is retained.

VI. KINETIC DATA ON THE BEHAVIOUR OF THE $Na_2O-Al_2O_3-H_2O$ SYSTEM

In contrast to the hydrolysis of Al ions in acid solutions, the hydrolysis of this metal in the alkaline region usually produces an increase of pH with time [48]. The decomposition of aluminate solutions is an autocatalytic process in which the resulting aluminium hydroxide (and various salt additives [1,2]) can act as catalysts [22].

Brosset [48] studied the rate of hydrolysis of aluminium ions in alkaline solutions, but he was unable to obtain reproducible results. He ascribed the varying rates to the slow establishment of equilibrium potentials on the hydrogen electrode. The errors in the measured pH were particularly serious during the first hour after mixing of the Al and alkali solutions.

This problem was avoided [32,149] by using glass electrodes, whose equilibrium potentials are developed almost instantaneously [97]. Mironov [81] monitored the hydrolysis of Al in alkaline solutions by pH measurements at a constant ionic strength of 3, maintained by adding sodium perchlorate, at 40°. The total concentration of aluminium was varied between 10^{-3} and 10^{-1} g-ion litre^{-1}, but most of the measurements were made at an aluminium concentration of 1×10^{-2} g-ion litre^{-1}.

Measurements of pH, combined with Raman spectral studies, have shown [149] that the ratio of the total concentrations of alkali and aluminium (OH : Al) has a profound effect on the hydrolytic reactions. We can distinguish three regions of OH : Al values, corresponding to different hydrolysis rates and mechanisms.

Region No. 1 (OH : Al $\simeq$ 4.4, pH $\geqslant$ 13.0) is a region of stable solutions, where equilibrium is established very rapidly.

Region No. 2 (OH : Al $\simeq$ 3.3–4.4, pH $\simeq$ 9.3–12.8) gives pH–time curves of the type shown as curve *a* in Fig. 5).

Region No. 3 (OH : Al $\simeq$ 3.01–3.3, pH $\simeq$ 8.2–9.3, curves *b* and *c* of Fig. 5). There seems to be general agreement [24-26,29-31,33-65] that monomeric aluminate ions are the predominant species in solutions within region No. 1.

In region No. 2, polymers of composition $[Al(OH)_4]_n \cdot (OH)_2^{(n+2)-}$ are formed as soon as sodium hydroxide is added to the solutions [31,39-41,78]. Migration of the polymer chains leads to gradual chain breaking and formation of hydroxyl ions, so that the pH of the solution increases with time.

Solutions prepared within region No. 3 show a rapid formation of a mixture of aluminium hydroxide and polymers of the $[Al(OH)_3]_n(OH)^-$ and $[Al(OH)_4]_n(OH)_2^{(n+2)-}$ type (sections *1* and *2* of the curves in Fig. 5*b* and 5*c*), the former consisting of fine colloidal particles. The transformation of these polymers into aluminium hydroxide (sections *2–3–4–5* in Fig. 5*b* and 5*c*) causes a gradual release of OH^- ions into the solution.

The apparent first-order rate constants for the generation or disappearance (region No. 3) of OH^- ions, calculated for sections *1* and *2*, are $(5.5 \pm 0.7) \times 10^{-2}$, $(3.0 \pm 0.5) \times 10^{-2}$, and $(3.6 \pm 0.4) \times 10^{-2}$ min^{-1} respectively. The rate constants calculated from Figs. 5*b* and 5*c* are the same within experimental error: this is not surprising, since the two curves refer to systems within the same region.

Scotford and Glastonbury [150] studied the effect of temperature on the rate of dissolution of gibbsite and boehmite in NaOH solutions at temperatures between 25° and 100°. They assumed the following reactions

$$\underset{\text{(gibbsite)}}{Al(OH)_3} + OH^- \rightleftarrows Al(OH)_4^- \qquad (18)$$

$$\underset{\text{(boehmite)}}{AlOOH} + OH + H_2O \rightleftarrows Al(OH)_4^- \ . \qquad (19)$$

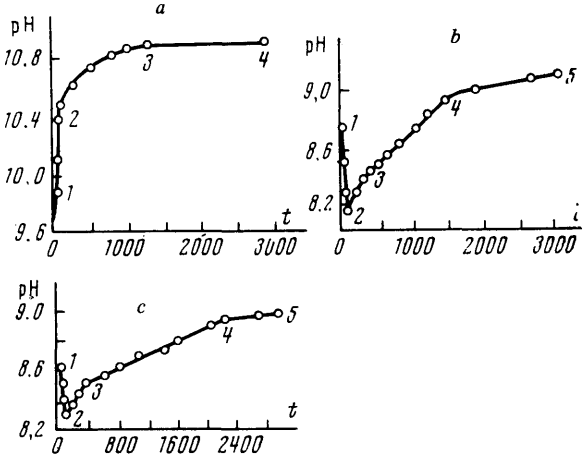


Figure 5. Changes of pH with time [149] t, min, for different OH : Al ratios: *a*) 3.5, *b*) 3.1, *c*) 3.01.

The activation energies, calculated from the initial rates of dissolution, were found to be (30.6 ± 0.9) and (29.4 ± 1.3) kcal $mole^{-1}$ respectively.

The heat of reaction (18), according to Sato [151], lies between 5.88 and 7.34 kcal $mole^{-1}$. However, most workers prefer to use the higher value (approximately 7.3 kcal $mole^{-1}$) obtained by Russell and coworkers [37], who also estimated the heat of dissolution of boehmite as ~4.8 kcal $mole^{-1}$. By combining these values with the activation energies obtained for the forward reaction (18) and (19), Scotford and Glastonbury [150] calculated the activation energies for the reverse reactions (23 and 25 kcal $mole^{-1}$ for gibbsite and boehmite respectively).

The high activation energies obtained for both the forward and the reverse reactions suggest that the lixiviation of alumina and the decomposition of aluminate solutions are both activation controlled. Herrmann [13] on the other hand concludes that these reactions are diffusion controlled, but his views on the nature of aluminate solutions have been severely criticised, in particular by Kuznetsov [22].

The calculation [150] of the activation energy from the initial rates of dissolution of alumina avoids the difficulties arising from the reversibility of reactions (18) and (19) and from the need to find the true rate constants, particularly since the latter cannot be determined unless the correct kinetic equations and the complex mechanisms of the dissolution and precipitation of alumina are known. Furthermore, activation energies obtained from the temperature dependence of rate constants are valid only on the assumption of constant composition of the components of the solution, and of the solid phase, at different temperatures. This condition, of course, is not fulfilled in the present system, since both the composition and the structure of the aluminate ions may vary with temperature [23,30]. An incorrect value of the activation energy will be obtained from the temperature dependence of the rate of reaction also if the surface area of the precipitate after a given time is different at different temperatures.

The latter effect is probably responsible for the low activation energy attending the dissolution of gibbsite in alkali, previously reported [152,153] as 23.8 kcal $mole^{-1}$, determined from the temperature dependence of the reaction rate measured over long time intervals (and therefore possibly affected by changes in the specific surface area of the alumina).

Elson and coworkers [154] reported an even lower value of the activation energy (19.6 kcal $mole^{-1}$). This value was calculated from the following empirical kinetic equations, which relate the reaction rate to the surface area of the solid phase and the composition of the aluminate solution:

$$\frac{dx}{dt} = k_2 A_t \left(\frac{x_\infty - x_t}{a_\infty + x_\infty} \right)^2 \qquad (20)$$

$$\frac{d\lambda}{dt} = k_1 A_t (x_\infty - x_t)^2 \ , \qquad (21)$$

where $k_2 = k_1(a_\infty + x_\infty)^2$; x_t and x_∞ are the molar concentrations of aluminium at time t and at equilibrium; a_∞ is the molar concentration of sodium expressed as NaOH at equilibrium; A_t is the surface area of the solid phase at time t; k_1 and k_2 are the rate constants.

These workers [154] did not attempt to justify theoretically their choice of Eqns. (20) and (21): some of the arguments against the use of these equations are discussed briefly above, and in greater detail by Scotford and Glastonbury [150]. The latter recalculated previous results [152–154] by the initial dissolution rate method, and they showed that the resulting value of the activation energy for the dissolution of gibbsite in alkali is close to their value of (30.6 ± 0.9) kcal $mole^{-1}$. Hence the activation energy is essentially independent of the initial particle size of the solid phase (20–120 μm) and of the concentration of alkali (30–210 g $litre^{-1}$ of Na_2O).

In spite of the fairly large effort devoted to the study of the kinetics of the lixiviation of alumina and of the decomposition of aluminate solutions [1,2], the mechanism of these processes is still far from clear. A full understanding of the processes taking place in metastable aluminate solutions must await the final resolution of the structural problem presented by aluminate ions under different conditions.

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