



Review

The structure of Al(III) in strongly alkaline aluminate solutions – A review

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ABSTRACT

Research papers dealing with the identity and abundance as well as the structure of aluminium-bearing species present in pure and homogeneous, strongly alkaline aluminate solutions (often called synthetic Bayer liquors) published in the open literature since the 1970's have been reviewed. On the basis of critical evaluation of the data, four solution species (all aquated), *i.e.*, Na⁺, OH⁻, Al(OH)₄⁻ and a dimeric complex (most probably (OH)₃Al–O–Al(OH)₂²⁻) along with their ion pairs, are sufficient to account qualitatively and, where appropriate, quantitatively for all the experimental observations collected for concentrated alkaline aluminate solutions at temperatures up to 100 °C. An extended network of these entities held together by electrostatic forces and hydrogen bonds seems also to be likely. The presence of other species, like the dehydrated monomers (AlO₂⁻ or AlO(OH)₂⁻) or higher complexes (Al(OH)₅²⁻ and Al(OH)₆³⁻) in significant concentrations can be excluded. Aluminate species formed *via* release of hydroxide from Al(OH)₄⁻ and subsequent oligomerization are also conclusively eliminated. Hexameric aluminate complexes, believed to be the docking species during gibbsite crystallization were also found to be experimentally undetectable. If such species exist at all, they can only be present in very small quantities and are therefore “invisible” for the currently available experimental techniques. The question, whether the T_d → O_h transformation of aluminium involves a (minor) solution species or it takes place on the surface of the gibbsite during crystallization, appears to remain unresolved.

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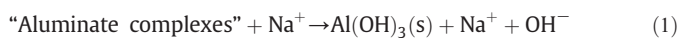
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1. Introduction and overview

1.1. The importance of the chemical speciation of Bayer liquors and the uncertainties associated with it

The principal way of mass-producing pure alumina ($\text{Al}_2\text{O}_3(\text{s})$) from bauxite has been invented by Karl Bayer in 1888. The first alumina plant using the Bayer process was opened in 1893, and since then alumina production became a multi-billion dollar industry [1–4]. During the Bayer process, first, the aluminium-bearing minerals in bauxite are selectively extracted from the insoluble components (mostly iron-oxides and silica) by dissolving them in extremely alkaline ($\text{pH} > 14$), concentrated aqueous solution of sodium hydroxide ($[\text{NaOH}]_T \leq 7 \text{ M}$)¹, at elevated temperatures (140 °C–270 °C) and pressures (up to 35 atm). Crystalline gibbsite ($\text{Al}(\text{OH})_3(\text{s})$) is then precipitated from the digestion liquor in a process reverse of the extraction, according to



where “aluminate complexes” represents the various aluminium-bearing hydroxo-complexes (anionic or neutral) present in the liquor. Gibbsite is then calcined to form alumina ($\text{Al}_2\text{O}_3(\text{s})$) for the smelting of aluminium.

Because of its industrial importance, the composition and abundance of these aluminate complexes present in Bayer liquors (*i.e.*, the chemical speciation) as well as their structure is among the most intensely investigated questions in the chemistry of aluminium over the last 120 years. The estimated number of scientific publications dealing with this particular question is well over a thousand. Despite the tremendous scientific effort and resources deployed, well-established knowledge of the speciation in Bayer-liquors is limited. A wide variety of experimental techniques has been used, but the conclusions are most often contradictory. This might be associated either with the dubious methodology employed or with the well-known practical difficulties (*e.g.*, dealing with extremely high concentrations and alkalinity) of studying these solutions (or in some cases with both). Furthermore, due to the lack of a suitable

model of chemical interactions occurring in Bayer liquors, reliable interpretation of the experimental data is often impossible. In the realm of the extremely concentrated aqueous solutions, the experimental parameters influencing the interactions in solution cannot be varied independently, therefore the individual contribution of each parameter is not known, which makes understanding of the results at least complicated.

The Bayer process can be considered an industrial scale recrystallization of gibbsite in presence of various organic (*e.g.*, oxalate, succinate, acetate, *etc.*) and inorganic (*e.g.*, carbonate, chloride, sulphate, *etc.*) impurities. “Real” liquors also contain particulate matters, *e.g.*, crystals, seeds, and other macroscopic inhomogeneities. Relatively little work has been done on the chemical speciation of these multicomponent and inhomogeneous “real” liquors. The majority of published works are concerned with the (seemingly!) less complicated “synthetic” Bayer liquors, which are homogeneous, and consist only of three components: H_2O , NaOH and dissolved $\text{Al}(\text{III})$.

The current review deals with these “synthetic” Bayer liquors in the context of chemical speciation and structure of aluminium in them. Beside the critical assessment of the available experimental observations published in the open literature, we will attempt to construct a robust speciation model of precipitate free Bayer liquors.² To the best of our knowledge, the last critical review in this field with extensive number of citations appeared in 1970 [5], therefore the relevant literature back to the early 70’s will be elaborated here. Where appropriate, the discussion will be extended to alkaline aluminate solutions containing cations other than Na^+ (*i.e.*, K^+ , Cs^+ , Li^+ and $(\text{CH}_3)_4\text{N}^+$). The majority of the data available are related to ambient conditions, but certain critical measurements have been carried out at $T > 25 \text{ °C}$, which will also be included. Finally, the behaviour of $\text{Al}(\text{III})$ in alkaline conditions will be briefly compared with that of structurally related trivalent cations, such as $\text{Ga}(\text{III})$ and $\text{Fe}(\text{III})$.

¹ The square brackets denote concentration and the subscript T signifies total or analytical values.

² The data presented in this review will include (beside a selection of works in this field) the already published findings of a collaborative research project (AMIRA P380 “Fundamentals of Alumina Precipitation”) jointly sponsored by the largest alumina producing companies in Australia. The author of this review participated in one of the three modules of the project, “Chemical speciation of synthetic Bayer liquors”.

1.2. The nature of alkaline aluminate solutions

Even the fundamental nature of the alkaline aluminate solutions (i.e., whether they are colloidal or true solutions) has been debated from as early as 1913. The school represented by Mahin considered them colloidal systems [6], while Blum et al. argued, that they are true solutions [7]. At the early ages of Bayer liquor chemistry, the colloidal [8–12] and the true solution [4,13–16] model was discussed for a couple of decades. Nowadays it is well accepted, that quantitative dissolution of high purity aluminium metal in carbonate free base, followed by the appropriate filtration results in true (molecularly dispersed) aluminate solutions [17,18].

Several aluminate solution species, as possible and probable aluminium hydroxo-, or oxo-complexes, have been postulated in the literature. In the first overview of this field, Glastonbury [16] suggested, that in solutions of up to ca. 30 m/m% NaOH, the tetrahedral $\text{Al}(\text{OH})_4^-$ ion predominates. At “higher”³ concentrations of base, the monomeric aluminate ion was suggested to be dehydrated to AlO_2^- , and at “moderate” concentrations, the $\text{Al}(\text{OH})_4^-$ ions to form a “quasi-crystalline structure” via hydrogen bonding. In the more comprehensive review of Eremin et al. [5], several mono- and polynuclear species have been proposed. All the mononuclear ones are related to $\text{Al}(\text{OH})_4^-$ (i.e., $\text{AlO}(\text{OH})_2^-$, AlO_2^- , $\text{Al}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$), while the formation of measurable amounts of $\text{Al}(\text{OH})_5^{2-}$ and $\text{Al}(\text{OH})_6^{3-}$ have been challenged. Eremin et al. also pointed out [5] the contradictions existing among the published information regarding polynuclear aluminate species. In reviewing the multidisciplinary collaborative effort of many Hungarian chemists in the 1970's and 1980's, Zámbo suggested the existence of 10 different possible species (7 of them are mononuclear), that are likely to exist in alkaline aluminate solutions [19], and listed a further 6, as “assumed but improbable”. From Zámbo's compilation [19], a multi-species speciation picture emerges, which is very different of that suggested by Glastonbury [16] or Eremin [5].

In the following section, a short summary is attempted to be given about the most often suggested aluminate species, together with the techniques employed and with some (but not all) of the relevant literature sources in which they were suggested.

1.3. Mononuclear aluminate species

1.3.1. $\text{Al}(\text{OH})_4^-$

It is generally agreed, that the predominant species in alkaline aluminate solutions is the mononuclear, tetrahedral aluminate ion, $\text{Al}(\text{OH})_4^-$. This has been confirmed by a range of spectroscopic techniques, such as NMR [20–29], vibration spectroscopic [24,30–38], solution X-ray diffractometric [39] and ultrasound [40] measurements. From Raman/IR measurements, formation of $\text{AlO}(\text{OH})_2^-$ [34] and AlO_2^- [37,41] as dehydration product of $\text{Al}(\text{OH})_4^-$ has also been proposed and was employed to explain the results of vapour pressure measurements [42]. From potentiometric measurements, in solutions of $[\text{NaOH}]_{\text{T}} < 1$ M, the predominance of the $\text{Al}(\text{OH})_4^-$ has been postulated [43,44].⁴ From conductivity measurements, the predominance of $\text{Al}(\text{OH})_4^-$ ions is also evident [45,46]. The volume contraction due to dissolution of Al metal in NaOH is also consistent with the formation of variously hydrated $\text{Al}(\text{OH})_4^-$ [47–49]. NMR spectroscopic results strongly indicated the formation of various ion pairs (such as NaOH^0 [21] and NaAlOH_4^0 [22,27,50] in strongly alkaline aluminate solutions.

1.3.2. $\text{Al}(\text{OH})_5^{2-}$

The existence of the pentacoordinated $\text{Al}(\text{H}_2\text{O})_4\text{OH}^{2+}$ species at $4.3 < \text{pH} < 7$ has recently been established [51]. Aluminate species in

alkaline media with similar coordination geometry (i.e., $\text{Al}(\text{OH})_5^{2-}$) has been suggested from electric conductance measurements [45,46,52] and from *ab initio* quantum mechanical calculations [53].

1.3.3. $\text{Al}(\text{OH})_6^{3-}$

The existence of this species has been suggested from ²⁷Al NMR measurements [54], from Raman studies [55], from conductivity [45,46,52] and from potentiometry [56]. Quantum chemical calculations also provided some support to its existence in Na^+ -ion paired form [53].

1.4. Polynuclear aluminate species

1.4.1. Dimeric species

An oxo-bridged dimeric aluminate species with the formula of $(\text{OH}_3)\text{Al}-\text{O}-\text{Al}(\text{OH})_3^-$ has been deduced from Raman [24,32,57], NMR [20,22,24] and conductivity [45,46] measurements. Postulation of such species was proven to be necessary for the interpretation of the results of vapour pressure measurements [43]. Early quantum chemical calculations also supported the formation of this complex [58], but in a recent work, the di- μ -hydroxo-bridged dimer (first suggested by Brintzinger [59]) $(\text{OH}_3)\text{Al}(\text{OH})_2\text{Al}(\text{OH})_3^{2-}$ was demonstrated to be energetically more favoured [53]. Further dimeric species with the formulae of $\text{Al}_2(\text{OH})_8^{2-} \cdot 2\text{H}_2\text{O}$, $\text{Al}_2\text{O}_2(\text{OH})_4^{2-}$ [19] and $(\text{OH})_3\text{Al}-\text{O}-\text{Al}(\text{OH})_3^- \cdot \text{OH}^-$ [46,52] have also been suggested.

1.4.2. Polymeric species

Perhaps the most controversy surrounds the problem of the existence and identity of various polymeric species in alkaline aluminate solutions. NMR [21,22,26,54], Raman/IR [5,30,33,35,36,41,55,60], UV [5] potentiometric [56] and conductometric [46,52] measurements appeared to support their formation. Rheological data were also interpreted in terms of polymerization of the aluminate ion [61].

A particularly interesting polymeric solution species is the hexameric one, as a species with six aluminium ions is thought to be the primary growth unit of gibbsite [62–64]. Hexameric aluminate species with a formula of $\text{Al}_6(\text{OH})_{24}^{6-}$ was deduced from conductivity measurements in homogeneous [46,52] and from ultracentrifugation in heterogeneous [65] solutions. Potentiometric [17] and spectroscopic measurements [66] were rationalized by postulating the $\text{Al}_6(\text{OH})_{22}^{4-}$ hexamer, forming from six monomeric aluminates via the release of two OH^- .

In the following, we will assume the presence of $\text{Al}(\text{OH})_4^-$, as a basis species, and will systematically investigate the proofs of its possible transformations to various other species listed above. The various sections below will focus on (i) dimerization; (ii) formation of $\text{Al}(\text{OH})_5^{2-}$ and $\text{Al}(\text{OH})_6^{3-}$; (iii) formation of various ion pairs, like NaOH^0 and $\text{NaAl}(\text{OH})_4^0$; (iv) formation of the hexameric species and (v) formation of an extended polymeric network.

2. Formation of the dimeric aluminate species, with particular emphasis on the Raman spectroscopic results

2.1. Raman spectra of alkaline aluminate solutions

It is well established [5,24,30,31,31,55,60,67–71] that, apart from the various bands associated with NaOH and water, the Raman spectra of alkaline aluminate solutions at $[\text{Al}(\text{III})]_{\text{T}} < 0.5$ M show only one significant band, centred on ~ 620 cm^{-1} (Fig. 1). This highly polarised mode has been assigned to the symmetric ν_1 - AlO_4 stretching of the pseudotetrahedral $\text{Al}(\text{OH})_4^-$. A weak depolarised band due to the antisymmetric ν_3 - AlO_4 stretching of $\text{Al}(\text{OH})_4^-$ has also been observed [24,31,41,67] at ~ 710 – 720 cm^{-1} . The weak depolarized ν_2 - and ν_4 - AlO_4 antisymmetric bending modes occur at ~ 325 cm^{-1} but they overlap with the broad librational modes of OH^- .

At $[\text{M}'\text{OH}]_{\text{T}} \leq 10$ M and $[\text{Al}(\text{III})]_{\text{T}} \geq 0.5$ M, the concentration ranges of greatest industrial relevance, two new modes (often but loosely called

³ Note, that the terms “higher” and “moderate” are not defined in Ref. [16].

⁴ Of course, for thermodynamic techniques, like potentiometry, the species $\text{Al}(\text{OH})_4^-$, $\text{AlO}(\text{OH})_2^-$ and AlO_2^- are indistinguishable.

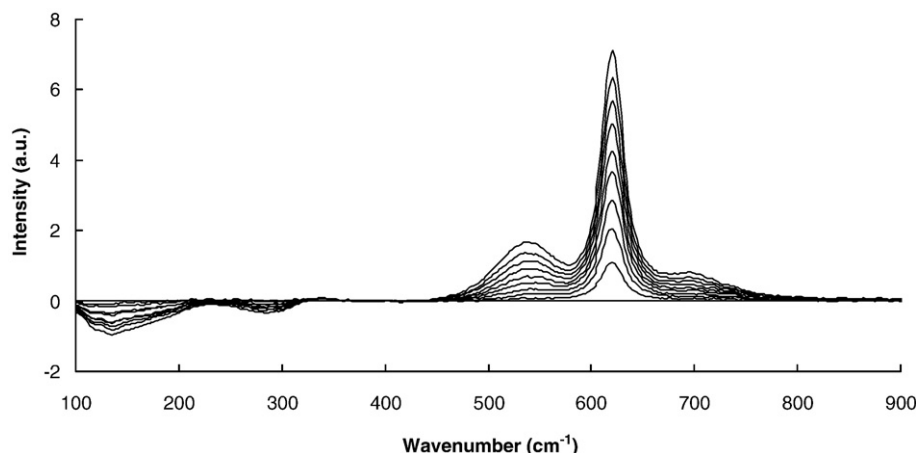


Fig. 1. Background-corrected Raman spectra of alkaline sodium aluminate solutions at 25 °C and $a_w=0.6$, with $[\text{NaOH}]_T=7.30\text{--}7.78$ M and, from bottom to top in ca. 0.5 M increments, $[\text{Al(III)}]_T=0\text{--}4.702$ M. From Ref. [72] reproduced with the permission of the Royal Society of Chemistry.

'sidebands') appear on both sides of the Al(OH)_4^- band. These modes, centred on $\sim 705\text{ cm}^{-1}$ and $\sim 535\text{ cm}^{-1}$ [60,55,24,5,68,30,71] are broad, asymmetric [55] and polarized [24]. Upon deuteration both the $\sim 620\text{ cm}^{-1}$ and the $\sim 705\text{ cm}^{-1}$ bands are shifted (to $\sim 600\text{ cm}^{-1}$ and $\sim 730\text{ cm}^{-1}$ respectively), while the $\sim 535\text{ cm}^{-1}$ band remains practically unchanged [24,60,70] indicating this mode does not involve hydrogen atoms. At $[\text{NaOH}]_T \geq 10$ M and $[\text{Al(III)}]_T \geq 1.0$ M, a band was reported by Watling et al. [55] at $\sim 555\text{ cm}^{-1}$ that was attributed to small concentrations of Al(OH)_6^{3-} . Similarly, the asymmetric $\sim 535\text{ cm}^{-1}$ mode shifted to lower wavenumbers at extremely high $[\text{Al(III)}]_T$ and therefore it has been suggested that it might consist of more than one band [55,60].

2.2. Possible ways of interpreting the Raman spectra

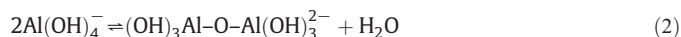
Most Raman studies report that the intensity of the two sidebands increases with increasing $[\text{Al(III)}]_T$, both at constant alumina-to-caustic ratios and at constant $[\text{M}'\text{OH}]_T^{5}$. A number of investigations [24,60,67] confirm that these bands are formed at the expense of Al(OH)_4^- , which is an essential criterion for a speciation change involving Al(III). In a recent work, the effect of $[\text{OH}^-]$, the nature of the cation M'^+ , and the water activity on this speciation change have been systematically studied [72].

It is possible, that these sidebands arise from contact ion pairing between Na^+ and Al(OH)_4^- . Moolenaar et al. [24] inferred that the ~ 705 and $\sim 535\text{ cm}^{-1}$ modes could not be due to contact ion pairs (CIPs) involving Al(OH)_4^- because of the magnitude of the shifts (from $\sim 620\text{ cm}^{-1}$). This is consistent with observations for anions other than aluminate [73] and also with Tossell's quantum mechanical calculations [74] which predict that formation of a NaAl(OH)_4^0 CIP should cause only a 3–6 cm^{-1} shift in $\nu_{\text{max}}(\text{Al(OH)}_4^-)$. Furthermore, Raman spectra of alkaline aluminate solutions containing both Al(OH)_4^- and the species responsible for the sidebands do not change significantly with the background cation (i.e., Na^+ , K^+ , Cs^+ and $(\text{CH}_3)_4\text{N}^+$). If a CIP, for example, $(\text{CH}_3)_4\text{NAl(OH)}_4^0$, were responsible for the sidebands, Raman spectrum of the $(\text{CH}_3)_4\text{NOH}/\text{Al(OH)}_3$ mixtures would be expected to differ significantly from equivalent $\text{NaOH}/\text{Al(OH)}_3$ solutions (Fig. 2). The intensities and locations of the sidebands were found to be independent of the temperature at $25\text{ °C} \leq T \leq 100\text{ °C}$ [72]. Since it is known that the formation constants of the NaOH^0 and NaAl(OH)_4^0 ion pairs show a ca. 2-fold increase when the temperature is increased from 25 °C to 100 °C [75] this again argues against the sidebands being associated with ion pairing.

⁵ In order to distinguish them from the unit of concentration, M , univalent metal ions will be denoted by M'^+ throughout the text.

Raman spectra obtained for a series of solutions at constant ionic strength and $[\text{Al(III)}]_T$, but changing hydroxide excess were found to be virtually identical [76]. Therefore it is reasonable to conclude, the sidebands are not associated with a species, which is formed in an equilibrium that includes free OH^- (e.g., formation of Al(OH)_5^{2-} or Al(OH)_6^{3-} or formation of a species with the formula $\text{Al}_n(\text{OH})_{4n-p}^{n-p-}$; for latter, see Section 5.3 for more details).

The most widely accepted interpretation, due to Moolenaar et al. [24], is that the Raman sidebands arise from the formation of an oxygen-bridged dimer:



This assignment [24], was essentially based on the similarity between the IR and Raman spectra of concentrated alkaline aluminate solutions and the crystalline solid $\text{K}_2[\text{Al}_2\text{O(OH)}_6]$ [77] which, as shown by X-ray diffraction, contains this dimeric anion. However, a detailed study [78] of a series of hydroxy aluminates using solid state and solution NMR, Raman and IR spectroscopies, showed that samples with different (four- or six-fold) coordination in the solid state, as shown by their ^{27}Al -MAS NMR spectra, gave similar or in some cases almost identical IR and Raman traces in solution. This indicates that solid state Raman and IR spectra of aluminate compounds *cannot* be used to deduce unambiguously the structure of aluminate species in solution [78].

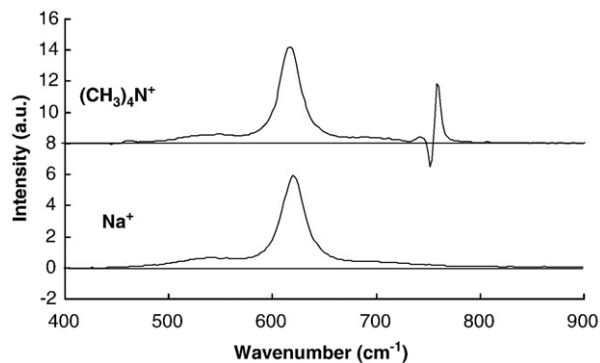


Fig. 2. Comparison of the Raman spectra of Na^+ - and $(\text{CH}_3)_4\text{N}^+$ -aluminate solutions at $[\text{M}'\text{OH}]=4.32$ M, $[\text{Al(III)}]_T=2.33$ M. Matrix-matched backgrounds have been subtracted. The double peak in the $(\text{CH}_3)_4\text{N}^+$ spectrum is an artefact. From Ref. [72] reproduced with the permission of the Royal Society of Chemistry.

2.3. The formation constant of the dimeric aluminate species

Very few attempts have been made to quantitatively interpret the Raman spectra in terms of the population of species in solution. For example, Wajand et al. [57] calculated the formation constant of the oxo-bridged dimer' (K_{dim}) from Raman and water activity (a_w) measurements, [79,80] at one ionic strength ($I=5.8$ M) at room temperature. Johnston et al. [67] also attempted to derive K_{dim} from their thorough Raman investigation. However, their results are difficult to interpret quantitatively because they held neither the ionic strength nor a_w constant. For this reason, in calculating K_{dim} , they were obliged to assume arbitrarily that the ratio of the activity coefficients of the monomer and the dimer was constant and independent of a_w . Given the differences in charge and size of these ions and the variations in conditions, these assumptions are questionable. A further attempt to determine K_{dim} is described in Zhou's unpublished work [71]. This thesis reports very good quality Raman spectra, for about 15 solutions at an approximately constant $[\text{NaOH}]_{\text{T}}/[\text{Al(III)}]_{\text{T}}$ ratio of 4.2. Zhou derived an approximately constant value of K_{dim} at $I=4$ and 9 M, although using an incorrect activity coefficient expression. Buvári-Barcza et al. [52] also gave an estimate of K_{dim} based on viscosity and conductivity data. In a recent work [72], the formation constant of the dimeric aluminate species was determined from a series of Raman spectra of solutions with constant a_w and varying $[\text{Al(III)}]_{\text{T}}$. Because a_w does not change dramatically when OH^- is exchanged for Al(OH)_4^- [81], there is little variation in the ionic strength within the series investigated. The integrated intensities of the individual bands in the 400 to 900 cm^{-1} region were found to increase non-linearly with $[\text{Al(III)}]_{\text{T}}$ and the relative contribution of the Al(OH)_4^- band to the overall integrated intensity of the 400 to 900 cm^{-1} envelope decreased significantly with increasing $[\text{Al(III)}]_{\text{T}}$ (Fig. 3). This behaviour suggests that the sidebands are probably associated with polynuclear complex formation since, if they resulted from an interconversion between mononuclear aluminate species, all the individual Raman intensities would increase strictly linearly with $[\text{Al(III)}]_{\text{T}}$. Therefore the formation of dehydrated, mononuclear aluminate species, such as AlO(OH)_2^- and AlO_2^- [4,5,16,19] is not suitable for the interpretation of the Raman sidebands. The formation constant of the species $(\text{Al(OH)}_4)_n^{n-}$ for various n -s were determined by assuming, that the intensity of the monomer's band is linearly proportional with $[\text{Al(OH)}_4^-]$. The data were found to be inconsistent with $n=1$ and $n \geq 3$, but the $n=2$ case gave excellent agreement. Hence the Raman observations can be reasonably

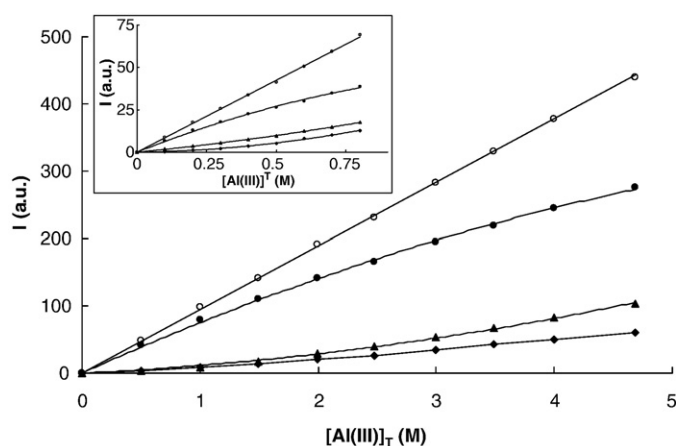


Fig. 3. Integrated intensity of the Raman modes as a function of $[\text{Al(III)}]_{\text{T}}$ at 25 °C. Main figure: $a_w = 0.6$; insert: $[\text{NaOH}]_{\text{T}} = 18.0$ M. Combined peak area in 400–900 cm^{-1} range: ○; peak area of the ~620 cm^{-1} band: ●; peak area of the ~530–550 cm^{-1} band: ▲; peak area of the ~700–720 cm^{-1} band: ◆. From Ref. [72] reproduced with the permission of the Royal Society of Chemistry.

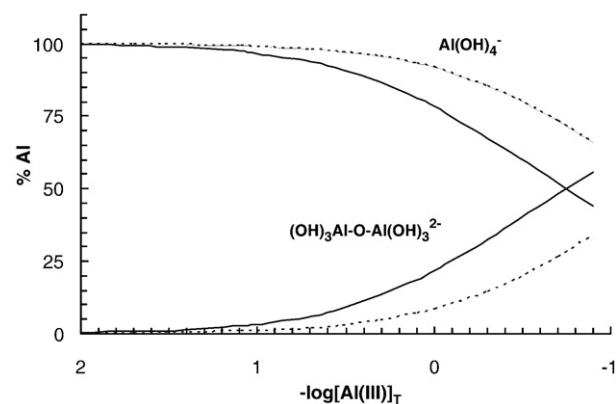


Fig. 4. Species distribution diagram of sodium aluminate solutions at various water activities. Dotted line: $a_w = 0.8$ ($I = 4.4\text{--}4.7$ M). Solid line: $a_w = 0.4$ ($I = 10.2\text{--}10.5$ M). Calculated by using the formation constants obtained at constant water activities, published in Ref. [72].

interpreted by assuming only the formation of a dimer. On this basis, $[\text{Al(OH)}_4^-]$ was calculated at various a_w and in different media. These values indicate that the Al(OH)_4^- solution species is the predominant form of Al(III) at all concentrations of industrial relevance. The formation constant of the dimer increases with decreasing a_w , and at constant a_w but in presence of various cations, it decreases in the order: $\text{Na}^+ > \text{K}^+ > \text{Cs}^+$. Coupled with the lack of temperature dependence of the spectra in the temperature range of 25 °C $\leq T \leq$ 100 °C, the formation constants of the dimeric aluminate species thus obtained can be used for calculating species distributions in concentrated alkaline aluminate solutions up to 100 °C (Fig. 4).

2.4. The structure of the dimeric aluminate species

Most authors, following Moolenaar et al. [24], have preferred to designate the structure of the dimeric aluminate species as $(\text{HO})_3\text{Al-O-Al(OH)}_3^{2-}$. However, a combination of solid state and solution NMR and Raman evidence [78] has shown that it is not possible to unequivocally infer solution species from solid state spectra as assumed by Moolenaar et al. [24] It is difficult to find complementary experimental techniques that support this assignment. Solution X-ray diffraction measurements [39] demonstrated a small but significant shortening of the Al–O distances in solutions with increasing aluminate concentration. On the basis of crystallographic data of solid aluminates, Al–OH distance is somewhat longer, than Al–O in which an O is shared by two Al ions. Therefore these observations provide an indirect proof for the oxo-bridged dimer. Results from dielectric relaxation spectroscopy [82] can only be explained by assuming a solute species, which has a dipole moment close to that calculated for the Moolenaar dimer. UV–Vis spectra of aluminate solutions was also found to be uninformative, but for another reason: aluminate ions in rigorously pure solutions (contrary to the *ab initio* quantum chemical predictions of Chen et al. [83] and to other, more recent reports [84,85]) have no UV-absorption at all [86]. As noted above, from the purely thermodynamic viewpoint there is no distinction in aqueous solution between the oxo-bridged dimer and its hydrated analogue, the di- μ -hydroxo species $(\text{HO})_3\text{Al(OH)}_2\text{Al(OH)}_3^{2-}$ or, indeed, with any other solution species that differs only in its level of hydration. In this context, *ab initio* quantum-mechanical calculations [53] suggest that a hydrated form, $[(\text{OH})_3\text{Al(OH)}_2\text{Al(OH)}_3(\text{H}_2\text{O})_2]^{2-}$, and not the (dehydrated) oxo-bridged dimer is the energetically-favoured dimeric species in concentrated alkaline aluminate solutions. Note, however, that from the IR spectra derived from these calculations, the most favoured dimer species is not distinguishable from the CIP, NaAl(OH)_4^- .

3. The possible formation of $\text{Al}(\text{OH})_5^{2-}$ and $\text{Al}(\text{OH})_6^{3-}$ solution species

It was pointed out first by Eremin et al. [5] that “the formation of measurable amounts of ions of the $\text{Al}(\text{OH})_5^{2-}$ and $\text{Al}(\text{OH})_6^{3-}$ type ... is not confirmed by experimental results”. However, the formation of such species have been claimed in numerous publications since then [45,46,52–56] and reported in most of the textbooks and monographs on the chemistry of aluminium (e.g., Ref. [87]).

From solution XRD [39] and (in an indirect way) from EXAFS spectroscopy [88], the presence significant amounts of aluminate species with coordination number higher than 4 was found to be unlikely. However, these techniques are not suitable for dealing with species present in minor concentrations. More sensitive methods, like ^{27}Al NMR and Raman spectroscopies, were also used in an attempt of detecting such species at very high concentrations of base [76,89,90].

3.1. The ^{27}Al NMR and Raman spectra at very high concentrations of the base ($[\text{NaOH}]_{\text{T}} > 10 \text{ M}$)

In alkaline aluminate solutions at industrial concentrations usually only one ^{27}Al NMR line is seen and the chemical shift is always around 80 ppm [23–25,29,54,91] (relative to $\text{Al}(\text{H}_2\text{O})_6^{3+}$ set at 0 ppm); this is typical of four coordinate aluminium [23,25]. The invariance in the chemical shift observed in alkaline aluminate solutions proves that the aluminium is predominantly in a tetrahedral environment. That is, $\text{Al}(\text{OH})_4^-$ [23–25,29,54] or closely related coexisting species whose interconversion causes only subtle variations in the observed ^{27}Al NMR chemical shifts [29].

On the ^{27}Al NMR spectra of aluminate solutions with $0.005 \text{ M} \leq [\text{Al}(\text{III})]_{\text{T}} \leq 3 \text{ M}$ only one broad peak was observed, and the second weak band at $\sim 0 \text{ ppm}$ published in [55] was not seen in any of the solution spectra recorded. For $[\text{NaOH}]_{\text{T}} \leq 5 \text{ M}$ (i.e., solutions of industrial composition), the chemical shift is practically independent of $[\text{Al}(\text{III})]_{\text{T}}$ and constant at a value of $80.3 \pm 0.2 \text{ ppm}$ in accordance with literature data [23–25,29,54,91]. The single peak is assigned to the tetrahedral $\text{Al}(\text{OH})_4^-$ and/or other possible species with tetrahedral coordination geometry around the Al (cf., $\text{NaAl}(\text{OH})_4^0$ ion pairs [76,92] or the dimeric aluminate species $(\text{OH})_3\text{Al}-\text{O}-\text{Al}(\text{OH})_3^-$ [24], etc.) As $[\text{NaOH}]_{\text{T}}$ increases beyond 5 M, however, the chemical shifts show systematic variations both with $[\text{NaOH}]_{\text{T}}$ and $[\text{Al}(\text{III})]_{\text{T}}$. In solutions of $[\text{Al}(\text{III})]_{\text{T}} \leq 0.8 \text{ M}$, the chemical shift moves systematically upfield with the increasing $[\text{NaOH}]_{\text{T}}$. For $0.005 \text{ M} \leq [\text{Al}(\text{III})]_{\text{T}} \leq 0.1 \text{ M}$ the δ_{obs} vs. $[\text{NaOH}]_{\text{T}}$ functions are independent of $[\text{Al}(\text{III})]_{\text{T}}$. On the other hand, there are no such variations in δ_{obs} at $[\text{Al}(\text{III})]_{\text{T}} \geq 1.2 \text{ M}$. Measurements performed in LiOH and KOH medium using $[\text{Al}(\text{III})]_{\text{T}} = 0.005 \text{ M}$, (due to the very low solubility of Al(III) in LiOH) showed, that the chemical shift variation depends strongly on the cation of the system and follows the order of $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ [89,90].

Given, that several of these solutions are supersaturated with respect to aluminium, these solutions are metastable and after preparation, usually in a slow process, $\text{Al}(\text{OH})_3(\text{s})$ precipitates from them. The possibility, that the interconversion of the solution species is slow and the slow formation of various solution species exists in the system has been checked in an extended series of experiments [17,39,66,72,89]. The Raman and ^{27}Al NMR spectra of these solutions were recorded several times over several weeks (or in some cases, months) [72,89]. It was found, that the spectra of these solutions did not change with time, and the spectra obtained for the same solution were superimposable (of course, this observation was valid only before the onset of the precipitation.) No time dependence was seen in the H_2/Pt -electrode potentiometric [17] and UV-Vis spectroscopic behaviour (using $\text{Tl}(\text{I})$ as $[\text{OH}^-]$ -sensitive indicator [66] or in the solution XRD patterns [39] of these systems. From these observations, it seems likely, that the interconversion of solution species in these supersaturated solutions is rapid and time dependent changes in solution speciation can only be observed in precipitating solutions. In this

context, the chemical speciation of certain alkaline aluminate solutions can be dependent on the way of preparation in a very peculiar way. If nuclei that are invisible to the naked eye and that are not removable even with the most sophisticated filtration technique are present in the system after the solution preparation (i.e., when liquors are made by dissolving $\text{Al}(\text{OH})_3(\text{s})$ or $\text{Al}_2\text{O}_3(\text{s})$), then this liquor is a precipitating solution from the very beginnings. In such systems, time dependent behaviours can easily be observed with various techniques, but they are most likely to be associated with the presence of the solid phase. When solutions are made by dissolving Al-metal in base [17], such complications were reported to be fully absent [17,39,66].

3.2. About the $\text{Al}(\text{OH})_6^{3-}$ solution species

Raman spectra of solutions with $[\text{Al}(\text{III})]_{\text{T}} = 0.8 \text{ M}$ and at $2 \text{ M} \leq [\text{NaOH}]_{\text{T}} \leq 10 \text{ M}$ showed only the $\sim 620 \text{ cm}^{-1}$ band with unchanged intensity and half width. However, at $[\text{NaOH}]_{\text{T}} \geq 10 \text{ M}$, ν_{max} shifted progressively from ~ 620 to $\sim 625 \text{ cm}^{-1}$ and decreased in intensity. In parallel, concentration-sensitive modes centred at ~ 710 to 720 and ~ 540 to 555 cm^{-1} (i.e., significantly different from the bands seen at ~ 705 and $\sim 535 \text{ cm}^{-1}$ at lower $[\text{NaOH}]_{\text{T}}$, see Section 2) appeared. The intensities of both bands increased with increasing $[\text{NaOH}]_{\text{T}}$. The gradual shifts in ν_{max} are similar in magnitude to the shifts observed for CO_3^{2-} and SO_4^{2-} ions in concentrated NaOH and CsOH solutions and therefore are likely to be associated with formation of CIPs [92].

The variation of ν_{max} from ~ 620 to $\sim 625 \text{ cm}^{-1}$ and the gradual downfield shift in δ_{obs} with increasing $[\text{NaOH}]_{\text{T}}$ occur in parallel (Fig. 5). Hence, the origin of these two effects is likely to be the same and thus the variations observed in the ^{27}Al NMR chemical shifts are associated with ion pairing rather than transformation of aluminium species with four-fold coordination geometry to five- or six-fold ones. This interpretation is further supported by the pronounced cation-dependence of the δ_{obs} vs. $[\text{M}'\text{OH}]_{\text{T}}$ functions and the observation, that for solutions with $[\text{Al}(\text{III})]_{\text{T}} \geq 1.2 \text{ M}$ (e.g., where the formation of CIPs are expected to be unfavourable due to the high $[\text{Al}(\text{III})]_{\text{T}}/[\text{NaOH}]_{\text{T}}$) δ_{obs} is practically independent of $[\text{NaOH}]_{\text{T}}$.

On the Raman spectra of solutions with $[\text{NaOH}]_{\text{T}} = 18.0 \text{ M}$ (const.) and $0.1 \text{ M} \leq [\text{Al}(\text{III})]_{\text{T}} \leq 0.8 \text{ M}$, the combined peak area increases linearly with $[\text{Al}(\text{III})]_{\text{T}}$ (insert in Fig. 3). However, the intensities of the ~ 720 and $\sim 555 \text{ cm}^{-1}$ bands increase at the expense of the $\sim 625 \text{ cm}^{-1}$ band in a non-linear manner. This behaviour is analogous to that observed

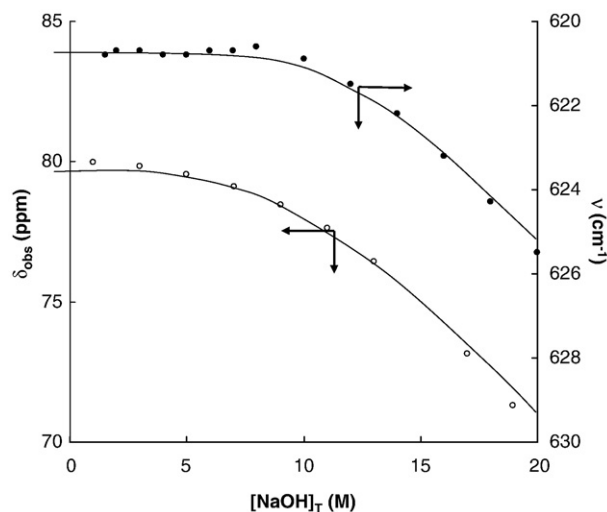


Fig. 5. ν_{max} of the Raman band of the $\text{Al}(\text{OH})_4^-$ ion around 620 cm^{-1} the δ_{obs} ^{27}Al NMR chemical shift for sodium aluminate solutions as a function of $[\text{NaOH}]_{\text{T}}$ at constant $[\text{Al}(\text{III})]_{\text{T}}$ (0.24 M). Figure was constructed on the basis of the data published in Ref. [89].

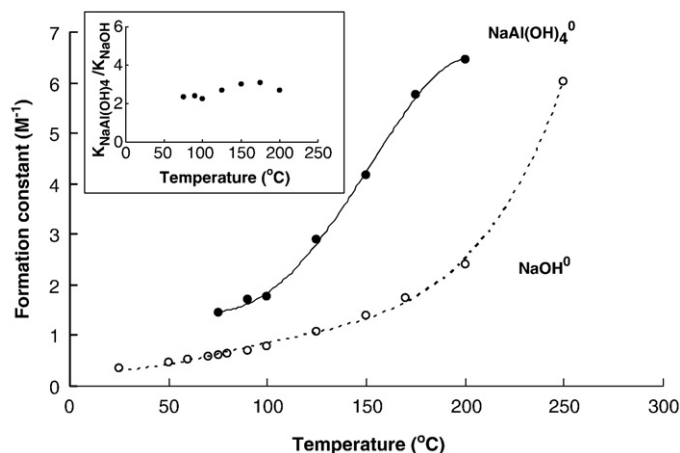


Fig. 6. Formation constants of the ion pairs $\text{NaOH}^0(\text{aq})$ (empty circles) and $\text{NaAl}(\text{OH})_4^0(\text{aq})$ (full circles), extrapolated to zero ionic strength, as a function of the temperature. The ratio between the two formation constants is shown in the insert. Figure was constructed on the basis of the data published in Ref. [75].

previously for the dimeric aluminate species [72] and strongly suggests that the ~ 720 and ~ 555 cm^{-1} bands correspond to the same polynuclear complex as the ~ 705 and ~ 535 cm^{-1} ones observed for aluminate solutions with lower $[\text{NaOH}]_{\text{T}}$ [72]. The band positions are supposedly shifted because of formation of CIPs. (Note, that under $[\text{NaOH}]_{\text{T}} = 18$ M (const.) conditions the water activity (a_{W}), $[\text{Na}^+]_{\text{T}}$ and $[\text{OH}^-]_{\text{T}}$, are practically constant and all these three components are in large excess relative to $[\text{Al}(\text{III})]_{\text{T}}$. If the development of the ~ 720 and ~ 555 cm^{-1} bands was the result of an interconversion between mononuclear aluminate species, then the Raman intensities would obey the Lambert–Beer law and the individual intensities would increase strictly linearly with $[\text{Al}(\text{III})]_{\text{T}}$. All the variations observed both in the ^{27}Al NMR and Raman spectra can be interpreted in terms of CIPs formed between the cation of the medium and the well-established $\text{Al}(\text{OH})_4^-$ or the dimeric aluminate species. Assumption of a higher aluminium hydroxo complex species, such as $\text{Al}(\text{OH})_3^{3-}$, is not necessary for the explanation of these spectroscopic effects nor is any such species detected by ^{27}Al NMR spectroscopy in solution. Note, that solid complex salts, crystallized from highly concentrated alkaline aluminate solutions and constructed of $\text{Al}(\text{OH})_6^{3-}$ building blocks are well known from the literature [78]. This finding points to the lack of direct correspondence between structure of the dominant solution species (i.e., tetrahedral environment) and that of the building blocks of crystals precipitating from them, at least for alkaline aluminate solutions.

4. Formation of ion pairs in Bayer liquors

More than likely, ion pairing interactions play a crucial role in highly concentrated aqueous aluminate solutions. It is reasonably well established that some alkali metal hydroxides are significantly ion paired even at room temperature and at relatively moderate electrolyte concentrations [92,94–96] and that their formation usually becomes favorable at higher temperatures [95,97,98]. It has been pointed out even in the earliest works [5], that ion pair formation must be taken into consideration, e.g., for interpreting the results of electrochemical studies on alkaline aluminate solutions. Clearly, at the extremely high concentration of these solutions, strong association between Na^+ and $\text{Al}(\text{OH})_4^-/\text{OH}^-$ will occur, and knowledge of the equilibrium constants is needed for the speciation picture of the system. Such data are, however, scarce partly because of the theoretical and experimental difficulties associated with weak interactions and partly because of a lack of suitable experimental techniques. There are only a few publications which address the thermodynamics of the interaction between sodium and hydroxide [75,94,99–101] or aluminate [75,92] ions. The structure of these ion pairs is also largely unexplored [39,82,102,103].

4.1. Formation constants of the ion pairs

From potentiometric measurements, by using a special high temperature ($T > 75$ °C) Na^+ -selective electrode, Diakonov et al. found [75] that both OH^- and $\text{Al}(\text{OH})_4^-$ form relatively stable ion pairs with Na^+ . The ratio of the two formation constants was found to be more or less constant (2.8 ± 0.3) from 70 to 200 °C (Fig. 6). At room temperature, a streaming amalgam electrode (Na/Hg) which is known to work reliably in concentrated caustic solutions [104,105] was used for measuring sodium activities in alkaline aluminate solutions at $I = 5$ M (TMA)Cl ionic strength.

The formation constant of the NaOH^0 ion pair, K_{NaOH} (calculated at each experimental point) exhibited a systematic variation with the analytical concentration of sodium ions but appear to be independent of the total concentration of hydroxide. Extrapolation to $[\text{Na}^+]_{\text{T}} \rightarrow 0$ M yields a value of $K_{\text{NaOH}} = 0.55 \pm 0.05$ M^{-1} , in good numerical agreement with the value reported in [94] (Fig. 7).

Introduction of the aluminate, the electrode potential was found to be significantly lower than the one recorded in presence of equivalent amounts of free hydroxide but in the absence of aluminium, which indicates, that the formation constant of the $\text{NaAl}(\text{OH})_4^0$ is larger than that of the NaOH^0 . Similarly to the effect observed for NaOH^0 , $K_{\text{NaAl}(\text{OH})_4}$ increases systematically with the increasing $[\text{Na}^+]_{\text{T}}$ and also

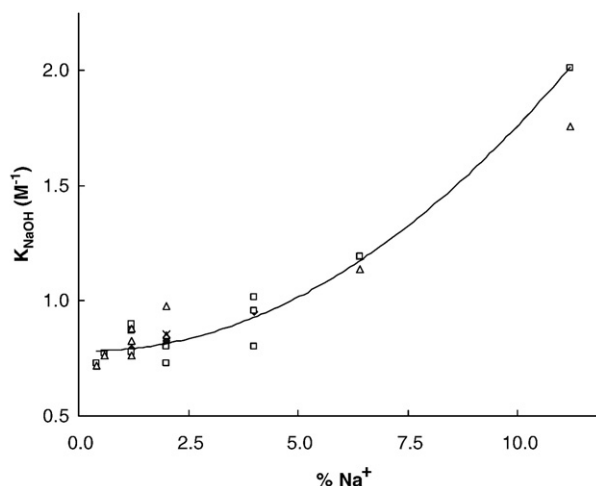


Fig. 7. Dependence of the formation constant of the NaOH^0 ion pair on the total concentration of sodium (expressed in terms of percentage substitution of the background cation, $(\text{CH}_3)_4\text{N}^+$) at constant ionic strength ($I = 5$ M (TMACl)), at various $[\text{OH}^-]_{\text{T}}$ (\diamond : 0.25 M; \square : 0.50 M; \circ : 0.75 M).

with the decreasing $[\text{Al(III)}]_{\text{T}}$ and has an average value of $1.8 \pm 0.4 \text{ M}^{-1}$ [106]. This is in good agreement with the data published by Diakonov et al. [75].

Based on these data, under typical Bayer conditions, the NaAl(OH)_4^0 ion pair is a dominant species (more than 50% of the aluminium can be in this form), and appreciable amounts of NaOH_0 (up to 10% of $[\text{Na}^+]_{\text{T}}$) is also present [92].

4.2. The structure of the ion pairs

As it was shown previously, in solutions of very high concentrations ($[\text{NaOH}]_{\text{T}} > 10 \text{ M}$), CIPs between the monomeric and dimeric aluminate ions are most likely to form, and their formation causes systematic variations in various spectral parameters, such as ^{27}Al NMR chemical shift or Raman band position. In less concentrated solutions, ion pairs with other structure, like SSIP or doubly solvent separated ion pairs (2SIP) may also be formed.

The structure of NaOH ion pairs have been discussed in a recent work of Megyes et al. [103], where the results of solution X-ray diffraction and simulation (MD and Car-Parrinello) have been compared. Formation of CIPs was deduced from solution X-ray diffraction experiments: both the increase in the $\text{Na}-\text{O}$ coordination number with increasing $[\text{NaOH}]_{\text{T}}$ and the variations of the peak heights on the pair distribution functions suggest, that CIPs are formed at high concentrations of base ($[\text{NaOH}]_{\text{T}} > 10 \text{ M}$). SSIPs were found to be dominant at lower concentrations (*i.e.*, where Na^+ ions are fully hydrated).

Solution X-ray diffraction studies [39] of alkaline aluminate solutions revealed, that in dilute ($[\text{NaOH}]_{\text{T}} \approx 2.7 \text{ M}$ and $[\text{Al(III)}]_{\text{T}} \approx 1.1 \text{ M}$) solutions the only species present are the Al(OH)_4^- monomer, the hydrated sodium ion and the bulk water. No direct evidence was found for the formation of sodium-aluminate CIP, however, the relatively low coordination number in the sodium hydration shell and the shortened value of the first neighbour $\text{H}_2\text{O}-\text{H}_2\text{O}$ distances give an indication of the influence of the aluminate ion on their structures. In more concentrated solutions ($[\text{NaOH}]_{\text{T}} \approx 8.6 \text{ M}$ and $[\text{Al(III)}]_{\text{T}} \approx 6.3 \text{ M}$), there is hardly enough water to completely hydrate any of the ions in solution. The existence of CIPs is thus ensured by simple stoichiometric and packing constraints. For these concentrated solutions, the ions are partly hydrated and partly in contact with each other. The shortening of the $\text{H}_2\text{O}-\text{H}_2\text{O}$ (or $\text{OH}^- - \text{H}_2\text{O}$) distances compared with the typical first neighbour distances in pure water points to an ordering effect attributable to the columbic interactions of the ions. The ions of opposite charge form CIPs and these species share the few water molecules in solution between them. These conclusions are in full accord with those obtained on the basis of Raman and ^{27}Al NMR spectroscopic measurements [89,90,101].

Buchner et al. studied the dielectric relaxation spectra of diluted ($[\text{NaOH}]_{\text{T}} < 2 \text{ M}$) [102] and concentrated [82] aluminate solutions. From the complex dielectric permittivity of the less concentrated systems, the concentration dependence of the effective hydration number of OH^- and Al(OH)_4^- as well as B(OH)_4^- as a function of NaOH -concentration was determined [102]. On the basis of the literature data [75,92,94,99–101,107,108], in these systems notable ion association is expected. However, relaxation processes corresponding to any type of ion pairs were not observed on the DR spectra. On the basis of the estimated amplitudes of solute relaxation processes [109], SSIPs and 2SIPs should show up on the spectra of NaOH solutions, and those, together with CIPs on the aluminate and borate containing ones. The most probable explanation for this is that the ion pair lifetimes (*ca.* 25 ps) are comparable or even smaller than the water relaxation time, therefore these ion pairs decompose, before DRS could observe them.

On the DR spectra of more concentrated aluminate solutions, in addition to the solvent relaxation, an additional low frequency Debye-dispersion with a relaxation time of 60–200 ps was observed, which can reasonably be assigned to a solution species [82] (Fig. 8). From the

Stokes–Einstein–Debye equation, an 82 pm effective rotational radius for this species was derived. This is consistent either with a very small relaxing particle, or with a species of spherical or cylindrical symmetry. Based on the results obtained for less concentrated solutions, simple species, like OH^- , Al(OH)_4^- or their ion pairs with Na^+ are not suitable to account for these observations. The dipole moment of the dimeric species suggested first by Moolenaar [24] is approximately 1.5 D [53], which is far too low to explain the dispersion amplitudes observed. However, the ion pair formed with the aluminate dimer (either SSIP or, less likely, 2SIP) would reasonably account for the DRS observations. Assuming, for example, and SIP rotating approximately around the $\text{Al}-\text{Al}$ axis, a dipole moment of *ca.* 32 D and up to 5–6% conversion of Al(III) in this ion pair can be estimated.

5. Aluminate oligomers and polymers

Variations observed in transport properties (*i.e.*, electric conductance) of alkaline aluminate solutions have been rationalized in terms of the formation of oligo- or polymeric aluminate species. Conductometric measurements of Barcza et al. (in combination with viscosimetry) [46,52] were interpreted in terms of the formation of a hexameric $[\text{Al(OH)}_4]_6^{6-}$ species (besides various associates between the monomer aluminate and the OH^- , which was also invoked by Maksimova et al. [45]). These conclusions must be, however, handled with caution, because the explanation of such titrations in terms of chemical speciation is always strongly model dependent.

Potentiometric titrations have frequently been used for identifying the stoichiometry of oligo- and polymeric solution species formed in alkaline aluminate solutions. The early work of Jahr et al. [43] already indicated, that in dilute aluminate solutions only Al(OH)_4^- exists and the lack of polymerization of Al(OH)_4^- was also observed during the dissolution of Al(OH)_3 [110,111]. Polymeric species with double OH^- bridges, such as $[\text{Al(OH)}_4]_n(\text{OH})_2^{(n+2)-}$ were suggested by Konenkova [56] and by Plumb et al. [112], however, the existence of such species (and in particular the supposed octahedral coordination of aluminium in these polymers) was not proven with an independent spectroscopic means.

Some potentiometric observations obtained for solutions of constant and extremely high ionic strength deserve some particular attention. These findings contributed to the creation and, as we will see, the refusal of a hypothesis including the formation of discreet polymeric (in particular hexameric) aluminate solution species in experimentally detectable amounts.

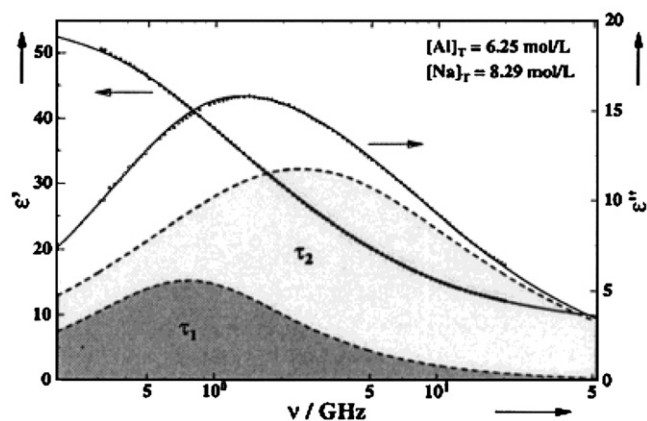


Fig. 8. Dielectric dispersion, $\varepsilon'(\nu)$ and loss, $\varepsilon''(\nu)$, spectrum of an alkaline aluminate solution with $[\text{Al(III)}]_{\text{T}} = 6.25 \text{ M}$ in aqueous NaOH at $[\text{Al(III)}]_{\text{T}}/[\text{NaOH}]_{\text{T}} = 0.75$ and 25°C . Experimental data (symbols) and superposition of a low-frequency Debye-process with a Cole-Cole equation (lines). Shaded areas indicate the contributions of processes 1 and 2 to $\varepsilon''(\nu)$. From Ref. [82] reproduced with the permission of the American Chemical Society.

5.1. Anomalism of $[\text{OH}^-]$ from potentiometry and the possible formation of $\text{Al}_6(\text{OH})_{22}^{4-}$

For a large number of alkaline aluminate solutions, from potentiometric titrations Szabó et al. [113,114] attempted to determine the equilibrium concentration of hydroxide ions, $[\text{OH}^-]$ at constant ionic strength ($I = 6 \text{ M NaNO}_3$) by using HgO electrode. They concluded, that up to a certain $[\text{NaOH}]_T$ and $[\text{Al(III)}]_T$, the results of the potentiometric titrations can be interpreted in terms of the formation of $\text{Al}(\text{OH})_4^-$. Beyond a certain $[\text{NaOH}]_T$ and $[\text{Al(III)}]_T$, they describe \bar{n} values of <4 (where \bar{n} is the average number of OH^- bound to Al(III)) were observed, however, the results were discounted as being “inconsistent with basic chemical principles” [113,114].

Sipos et al. [17] performed an extended series of potentiometric titrations using H_2/Pt indicator electrode at $I = 8 \text{ M NaClO}_4$ (constant ionic strength in the electrochemical cell

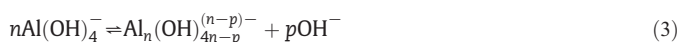


From the various reproducibility tests performed, it was proven, that the potentiometric effects recorded are independent of time, reasonably reproducible, and occur when the titrations are performed in reverse, therefore they can be considered as real effects.

From the titration curves obtained (Fig. 9), it is apparent that at relatively low $[\text{Al(III)}]_T$ the data show very little departure from that expected (i.e., if $\text{Al}(\text{OH})_4^-$ was assumed to be the only significant aluminium-containing species present in solution, indicated by the dashed lines in the Fig. 9). However, as $[\text{Al(III)}]_T$ increases, there is an increasing departure of the experimental curves from those which assume only $\text{Al}(\text{OH})_4^-$.

The truly remarkable feature of these titrations is that they indicate a release of OH^- as $[\text{OH}^-]_T$ increases, apparently contradicting the Le Chatelier's principle. This is not only very interesting but it also corroborates the discounted observations of Szabó et al. [113,114].

The observed variations of the electrode potentials were explained in terms of chemical speciation changes, consistent with the release of OH^- with increasing Al(III) and OH^- concentrations, i.e., via the formation of polymeric species, according to the equilibrium



Calculations using the ESTA suite of computer programmes [115–117] demonstrated that an acceptable fit could not be achieved with complexes of low stoichiometries (e.g., $n < 3$). However, when the model included any of the family of polymeric species related to $\text{Al}_6(\text{OH})_{22}^{4-}$ the objective function improved significantly. The best fit was achieved when the model included $\text{Al}_6(\text{OH})_{22}^{4-}$. There is, however, no single stoichiometry which best satisfies all the optimization criteria, i.e., any of the species with $n = 4-7$ and $p = 1$ or 2 provide an acceptable fit of the data. The species $\text{Al}_6(\text{OH})_{22}^{4-}$ can be thought of as the condensation product of six $\text{Al}(\text{OH})_4^-$ units which has lost two hydroxide ions. One might speculate, that progressive association of monomers may occur, with a corresponding build-up of charge that is relieved by the ejection of OH^- . Clearly, the formation of such associates requires the rearrangement of the coordination sphere of the participating Al(III) ions.

5.2. Anomalism of $[\text{OH}^-]$ proven by various spectroscopies

Because of strong correlation between the adjusted parameters during the optimization of the H_2/Pt electrode potentiometric results, possible ion pairing effects and (albeit minimized) variations in liquid junction potentials and activity coefficients, further evidence was needed to corroborate the existence of the anomalism of $[\text{OH}^-]$ variation and thus the species $\text{Al}_n(\text{OH})_{4n-p}^{(n-p)-}$.

First, an indirect spectroscopic technique involving the use of Tl(I) ion as $[\text{OH}^-]$ sensitive inorganic indicator was employed to indepen-

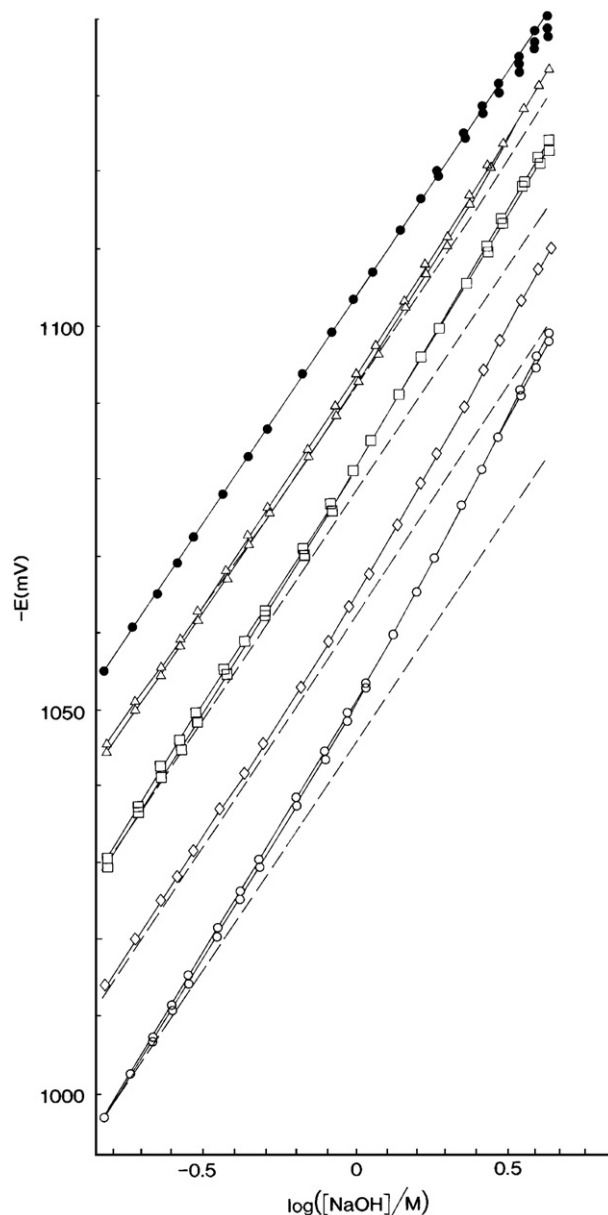


Fig. 9. Cell potentials as a function of $[\text{NaOH}]_T$ at various $[\text{OH}^-]_T/[\text{Al(III)}]_T$ ratios. Calibration titrations: ●; aluminate titrations at $[\text{OH}^-]_T/[\text{Al(III)}]_T$ ratios of 6.92 (△), 4.92 (□); 4.52 (◇) and 4.30 (○). Dashed lines represent calculated cell potentials assuming, that $\text{Al}(\text{OH})_4^-$ is the only aluminium containing species present in the system. The aluminate titration curves have been shifted by +5 mV for representational convenience. From Ref. [17] reproduced with the permission of CSIRO Australia.

dently prove the existence of the “ OH^- -release” effect observed potentiometrically [17]. The formation of TlOH^0 and $\text{Tl}(\text{OH})_2^-$ solution species is significant only at very high pH ($[\text{OH}^-] \geq 0.1 \text{ M}$), and these equilibria can be followed both by UV-Vis and ^{205}Tl NMR spectroscopy [66,118]. The sensitivity of both spectroscopic techniques is reasonable, as significant changes occur at 230–270 nm in the UV-spectrum and ^{205}Tl NMR chemical shift changes by hundreds of ppm.

Both ^{205}Tl NMR and UV-spectra recorded for alkaline aluminate solutions spiked with Tl(I) [66] qualitatively indicated the anomalous variation of $[\text{OH}^-]$ in a fashion similar to that observed during the potentiometric measurements (Fig. 10). Observed ^{205}Tl NMR chemical shifts were found to be higher in presence of Al(III) than the calculated ones, and the UV-spectra showed characteristic variations consistent with the “ OH^- -release”. Quantitative analysis of the spectra was somewhat hindered by the formation of $\text{TlAl}(\text{OH})_4^0$ solution species. However, analysis of the spectra by assuming the formation of an

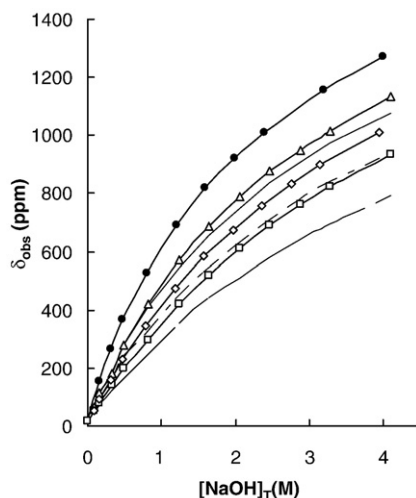


Fig. 10. Variation of ^{205}Tl NMR chemical shift with $[\text{NaOH}]_T$ at different $[\text{OH}^-]_T/[\text{Al(III)}]_T$ ratios. Al(III)-free system: ●; aluminate titrations at $[\text{OH}^-]_T/[\text{Al(III)}]_T$ ratios of 6.08 (▲), 5.06 (◇) and 4.59 (□). Dotted lines are calculated assuming, that $\text{Al}(\text{OH})_4^-$ is the only aluminium containing species present in the system. From Ref. [66] reproduced with the permission of the Royal Society of Chemistry.

oligomeric species forming according to Eq. (3) proved, that both series of spectra can be best fitted with any of the $\text{Al}_n(\text{OH})_{4n-p}^{(n-p)-}$ species with $n=4-7$ and $p=1$ or 2. A gratifying agreement between the formation constants derived from the two spectroscopic techniques [66] and the previous potentiometric investigations [17] was achieved. However, because of the necessarily indirect and limited nature of the spectral information (both UV-Vis and ^{205}Tl NMR) obtainable and the correlation of errors, precise stoichiometry cannot be derived. This was assigned to the very high ionic strength and, more important, the high level of replacement of the ionic medium by the interacting species which was necessary to obtain significant experimental effects [17,66].

5.3. Raman and ^{27}Al NMR spectrum of the $\text{Al}_6(\text{OH})_{22}^{4-}$ solution species

Any species with the stoichiometry of $\text{Al}_n(\text{OH})_{4n-p}^{(n-p)-}$ with $n=4-7$ and $p=1$ or 2 is expected to have geometries around the Al(III) ions different from that present in the $\text{Al}(\text{OH})_4^-$ ion. Accordingly, the formation of such species must show up in the Raman spectra of alkaline aluminate solutions. Conversely, if there are no spectral changes in the concentration range, where the formation of this/these species was observed by potentiometry and by two spectroscopies (all sensitive only to $[\text{OH}^-]$), then the anomalous variation of $[\text{OH}^-]$ is *not associated* with the formation of the $\text{Al}_n(\text{OH})_{4n-p}^{(n-p)-}$ and alternative interpretation has to be sought [76].

To investigate this question, Raman spectra of alkaline aluminate solutions with constant ionic strength ($I=8\text{ M NaClO}_4$) and $[\text{Al(III)}]_T$ (3 M) but changing $[\text{OH}^-]$ (from 1 M to 5 M) was investigated (*i.e.*, within the solution series, ClO_4^- ions were exchanged for OH^- ions) [76]. Similar measurements were performed at $I=7\text{ M CsCl}$ ionic strength [101]. The rationale of these experiments is, that increasing $[\text{OH}^-]$ in the system shift the equilibrium (3) to the left, that is, the formation of the $\text{Al}_n(\text{OH})_{4n-p}^{(n-p)-}$ would become unfavourable. Accordingly, with increasing $[\text{OH}^-]$ the signal corresponding to the monomeric aluminate ion should increase, while that of the oligomer should decrease. On the basis of the formation constants derived from the H_2/Pt electrode potentiometry and from the Tl(I)-spiked solutions' spectra, under the conditions detailed above, the conversion of $\text{Al}(\text{OH})_4^-$ to $\text{Al}_n(\text{OH})_{4n-p}^{(n-p)-}$ would change from 40% to 15% between the two end members of this series. The Raman spectra did not show any such variations. Clearly, this invariance refutes the hypothesis, that the equilibrium resulting in an oligomeric aluminate species

according to Eq. (3) does not take place. (Note that parallel ^{27}Al NMR measurements led to the same conclusion [76].) Accordingly, the formation of the species is inconsistent with the above Raman observations and alternative explanation has to be found to account for the anomalous variation of $[\text{OH}^-]$ [76].

5.4. Is ion pairing suitable to explain the anomalism of $[\text{OH}^-]$?

As the $\text{NaAl}(\text{OH})_4^0$ ion pair is most likely to be more stable than the NaOH^0 [75,92,106] the equilibrium



may be shifted towards the right hand side with increasing $[\text{Al}(\text{OH})_4^-]_T$ and $[\text{NaOH}]_T$. In this way the observed unusual increase in $[\text{OH}^-]$ could be due to the competition between OH^- and $\text{Al}(\text{OH})_4^-$ for Na^+ . To check this hypothesis, identical sets of H_2/Pt potentiometric titrations were carried out in $M'\text{OH}/M'\text{Al}(\text{OH})_4/M'\text{Cl}$ solutions in presence of three different background ions ($M'^+=\text{Na}^+, \text{K}^+$ and Cs^+) at constant ionic strength ($I=4\text{ M}$) [101]. The observed cell potentials as a function of $\lg([M'\text{OH}]_T)$ show significant deviation from the experimental curves obtained for the Al(III)-free systems. These deviations are apparently independent of the cation present in the solution (Fig. 11).

Model calculations [101] carried out with the PSEQUAD suite of computer programs [119] proved that the formation of the $M'\text{Al}(\text{OH})_4^0$ ion pair *in itself* does not result in the potential patterns observed and results in linear plots and the assumption of the formation of the $M'\text{OH}^0$ ion pair in significant amounts is necessary for a successful simulation. The second assumption is true only for NaOH, but not for

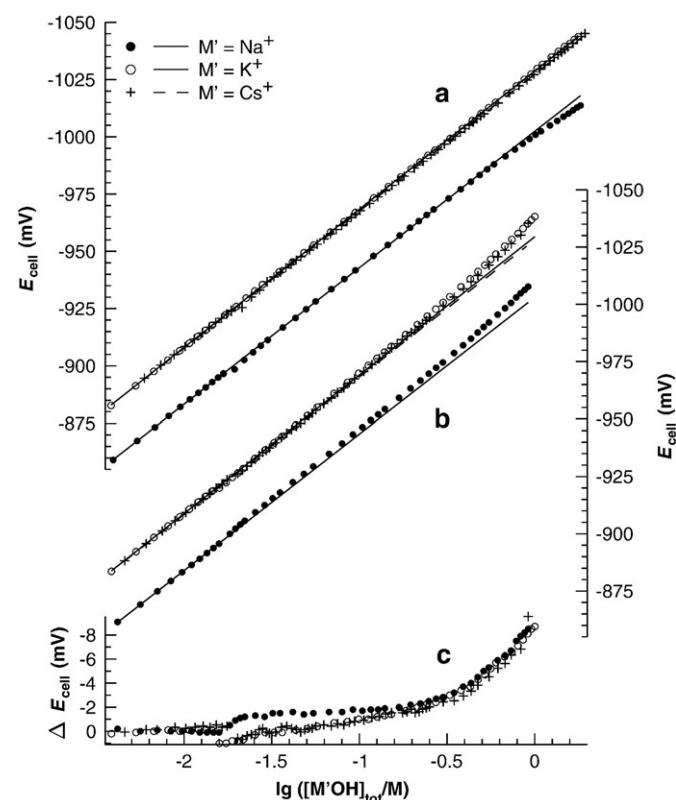


Fig. 11. Observed electrode potentials of the H_2/Pt electrode (E_{cell} in mV as a function of $\lg([M'\text{OH}]_T)$ at $25\text{ }^\circ\text{C}$ and $I=4\text{ M}$) (a) in $M'\text{OH}/M'\text{Cl}$ mixtures ($[\text{Al}(\text{OH})_4^-]=0\text{ M}$); (b) in $M'\text{OH}/M'\text{Al}(\text{OH})_4/M'\text{Cl}$ mixtures ($[M'\text{OH}]_T=[M'\text{Al}(\text{OH})_4]_T$). Set (c) shows the differences between the observed points of sets (b) and (a). Lines are fitted by using the Nernst equation on the linear section of the experimental curves. From Ref. [101] reproduced with the permission of the Royal Society of Chemistry.

KOH or CsOH. Therefore, the ion pair formation between the hydroxide/aluminate ion and the background cation cannot explain the observed uniform, cation-independent potentiometric patterns.

To interpret these deviations in terms of variations in activity coefficients caused by ion pairing, it needs to be considered, that the formation of $\text{NaAl}(\text{OH})_4^0$ ion pair (similarly to the NaOH^0) decreases the ionic strength of the solution. Therefore, the direction of the deviation from the linearity should be the same both for $\text{NaAl}(\text{OH})_4^0$ and for NaOH^0 , which is just the opposite of the experimentally observed direction (Fig. 11). Thus the observed deviations can not be explained solely in terms of activity coefficient variations caused by ion pair formation.

5.5. Changes of activity coefficient due to dimer formation to explain variations in $[\text{OH}^-]$

Mean activity coefficient (γ_{\pm}) variations caused by the formation of the $(\text{OH})_3\text{Al}-\text{O}-\text{Al}(\text{OH})_3^{2-}$ dimer can increase the ionic strength in the investigated solutions, as the formation of the doubly charged dimeric species results in a dramatic increase in the ionic strength of the solutions leading to higher activity coefficients. If the increase in γ_{\pm} caused by the dimerization overcompensates the decrease in γ_{\pm} originated from the formation of ion pairs (which is a necessary assumption only for Na^+ -containing systems), then this effect can account for the deviation occurring in aluminate-containing solutions, in presence of any M^+ . The $\gamma_{\pm}(c)$ function was optimized together with the formation constant (expressed in terms of activities) of the dimer (β_D) and it was found, that values in the range of $0.2 \leq \beta_D$ correspond to chemically realistic γ_{\pm} values. Although direct comparison with the data obtained by Raman spectroscopy [72] is not possible (this method yields β_D , while Raman spectroscopy results in formation constant expressed in terms of concentrations), it is important to mention that the two values are in the same order of magnitude.

These data show that the observed electrochemical patterns can be interpreted quantitatively by relatively small changes in the γ_{\pm} values (10–25%) and these changes in γ_{\pm} can be derived from the formation of NaOH^0 ion-pair and the dimeric aluminate species. The same speciation is capable of interpreting the observed Raman spectroscopic- and electrochemical data. This way it resolves the virtual contradiction between these two methods previously experienced. At the same time, it proves the non-existence of the oligomeric (hexameric) aluminate species previously postulated to form in alkaline aluminate solutions [101].

6. The possible formation of an extended polymeric network in Bayer liquors

Formation of associates between the OH^- and other negatively charged aluminate species such as $\text{Al}(\text{OH})_4^-$ or $(\text{OH})_3\text{Al}-\text{O}-\text{Al}(\text{OH})_3^{2-}$ via hydrogen bridges to form the species $\text{Al}(\text{OH})_4^-\cdot\text{OH}^-$ or $(\text{OH})_3\text{Al}-\text{O}-\text{Al}(\text{OH})_3^{2-}\cdot\text{OH}^-$ was first suggested by Barcza et al. [46,52] on the basis of conductometric and viscosimetric measurements. These species are rather peculiar and are implicitly based on the assumption that the hydrogen bond formation may occur even between ions of the same charge under “crowded” conditions [120].

The rheological behaviour of the alkaline aluminate solutions is also rather peculiar. Kuznetsov et al. [61] interpreted their early rheological observations in terms of the formation of polymeric aluminate ions. Sipos et al. [121] and Hefter et al. [122] have determined the viscosities of the hypothetical pure ‘ $\text{NaAl}(\text{OH})_4$ ’ solutions at 25 °C by fitting each data set obtained for $\text{NaOH}/\text{NaAl}(\text{OH})_4$ mixtures at a given (constant) ionic strength to a quadratic equation and extrapolation to 100% substitution of NaOH with $\text{NaAl}(\text{OH})_4$. The shape of the η vs. $[\text{NaAl}(\text{OH})_4]_{\text{T}}$ curve (Fig. 12) is typical of other aqueous electrolyte solutions [123,124], but it is notable, that the

extrapolated values of η (‘ $\text{NaAl}(\text{OH})_4$ ’) are unusually high, i.e., much higher than that of analogous NaOH solutions, which are also known to be highly viscous at high electrolyte concentrations.

One of the possible explanations for this unusually high viscosity values is, that aluminate ions in aqueous solution form an extended network of ions (both same and opposite charges) which is held together with bridging counterions and possibly hydrogen bonds as suggested by Barcza et al. [46,52]. Such extended network could conveniently explain the variations observed in the transport properties (conductance, viscosity) of these solutions. However, it can not be defined as individual polymer, it is rather a diffuse network of (fully or partially) hydrated and densely packed (crowded) ions.

7. Comparison of the behaviour of Al(III) with that of Ga(III) and Fe(III) in alkaline solutions

7.1. Alkaline Ga(III) solutions

The aqueous chemistry of Al(III) and Ga(III) up to $\text{pH} = 13$ is known to be very similar [91,125,126]. Starting from the strongly acidic region, with increasing pH both metal ions hydrolyse with the progressive formation of mono-, di and trihydroxo complexes [127–130] and a tridecameric species (the so-called Keggin polymer [91,94,126,131–134]). Around neutral pH both metal ions form trihydroxide or oxo-hydroxide precipitates which dissolves in slightly basic solutions in the form of tetrahydroxo complexes, which, similarly to analogous Al(III)-containing systems, is the predominant form of Ga(III) in these solutions [125,128,130,135,136].

Relatively little is known about the structure of other Ga(III)-bearing species forming in strongly alkaline ($\text{pH} > 13$) solutions (i.e., in solutions with compositions characteristic to Bayer liquors), therefore direct comparison of the Ga(III) and Al(III) hydroxo complexes forming in these systems is not straightforward. A series of solid compounds containing the dimeric unit $(\text{OH})_3\text{Ga}-\text{O}-\text{Ga}(\text{OH})_3^{2-}$ have been prepared and their crystal structure is known [137–139]. It is however not well established if this species exists in solution. On the IR spectra of aqueous alkaline gallate solutions, vibrations characteristic to the Ga–O–Ga bonds were identified [140] from which the existence of oxo-bridged oligomers in solution was postulated. Dialysis experiments [141] on gallate solutions with total concentration of the base, $[\text{NaOH}]_{\text{T}} = 0.4$ M yielded a molecular mass of 270 for the gallium bearing species, indicating the possible presence of di- or oligomeric gallate complexes in the system. Conductivity measurements on gallate solutions (like those for analogous aluminates [45,46,52]) also appeared to indicate the formation of polynuclear aggregates [142,143].

Several solid state Ga(III) hydroxo complex salts with $\text{Ga}(\text{OH})_6^{3-}$ [144–148] structural units have been synthesized and characterized. It was suggested that the hexahydroxo complex of Ga(III) might exist not

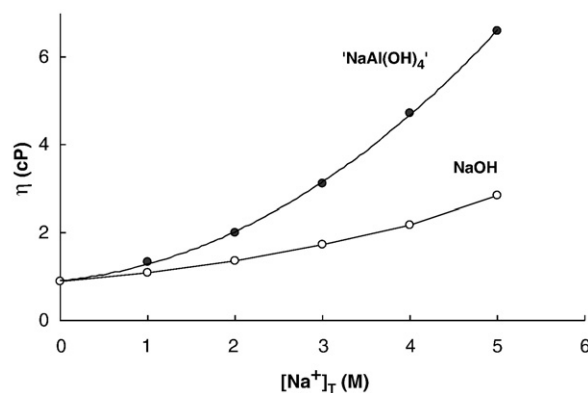


Fig. 12. Viscosities (η) of NaOH and the hypothetical pure ‘ $\text{NaAl}(\text{OH})_4$ ’ aqueous solutions as a function of the molar ionic strength. From Ref. [121] reproduced with the permission of the American Chemical Society.

only in solids but also in strongly alkaline solution [149]. The formation of $\text{Ga}(\text{OH})_6^{3-}$ solution species in concentrated alkaline gallate solutions has also been suggested from conductivity [142] and solubility [150] experiments.

In a recent work [151], highly concentrated alkaline gallate solutions with $0.23 \text{ M} \leq [\text{Ga}(\text{III})]_{\text{T}} \leq 2.32 \text{ M}$ and $1 \text{ M} \leq [\text{NaOH}]_{\text{T}} \leq 15 \text{ M}$ have been investigated by Raman and ^{71}Ga NMR spectroscopy and by solution X-ray diffraction. For all solutions investigated, a single ^{71}Ga NMR peak was observed at $225.0 \pm 1.5 \text{ ppm}$ corresponding to tetrahedral gallium hydroxo-complex species. The peak integrations are very close to 100%, and after viscosity correction, the full widths at half height were found to be practically constant. On the Raman spectra, only one dominant peak was seen on the spectra centred at $603\text{--}606 \text{ cm}^{-1}$. It is likely to correspond to the symmetric $\nu_1\text{-GaO}_4$ stretching of the pseudotetrahedral $\text{Ga}(\text{OH})_4^-$. The Raman peak area varies linearly with $[\text{Ga}(\text{III})]_{\text{T}}$ and the peak maximum (around 605 cm^{-1}) is somewhat shifted towards the higher wavenumbers with increasing $[\text{Ga}(\text{III})]_{\text{T}}$. Based on the magnitude of this shift ($<4 \text{ cm}^{-1}$) it is likely to be due to the formation of contact ion pairs [93]. Solution XRD [152] and EXAFS [153] measurements of such solutions also showed, that the central $\text{Ga}(\text{III})$ -ions are surrounded by four oxygen atoms in each solution and the primary Ga–O bond length was found to be 1.85 \AA , characteristic to tetrahedrally coordinated Ga-oxo compounds [154–155]. Both the Raman and ^{71}Ga NMR spectra as well as solution X-ray diffraction patterns are consistent with the presence of only one Ga-bearing species in the solutions studied: the well known tetrahedral hydroxo-complex $\text{Ga}(\text{OH})_4^-$. Hydroxo complexes with more than four hydroxide ligands (*i.e.*, $\text{Ga}(\text{OH})_5^{2-}$ or $\text{Ga}(\text{OH})_6^{3-}$) or species related to the oxo-bridged dimer forming in alkaline aluminate solutions of similar compositions (*i.e.*, $(\text{OH})_3\text{Ga-O-Ga}(\text{OH})_3^{2-}$) were not detected by any of these spectroscopic techniques.

7.2. Alkaline Fe(III) solutions

The identity and structure of water soluble Fe(III)-hydroxo complexes forming in strongly alkaline solutions is a particularly interesting question. The well known book of Baes and Mesmer [94] stated that the only water soluble mononuclear ferric hydroxo-complex at $\text{pH} \leq 13$ is the tetrahedral $\text{Fe}(\text{OH})_4^-$. This has been supported by a large number of observations [156–160]. For example, from UV-spectroscopic measurements, besides an unspecified polynuclear ferric-hydroxo complex, the formation of $\text{Fe}(\text{OH})_4^-$ was deduced [156,157]. Solubility measurements also strongly support, that $\text{Fe}(\text{OH})_4^-$ is the last member of the stepwise Fe(III)-hydroxo complexes [157–160]. However, Cotton and Wilkinson [161] mention the possible formation of $\text{Fe}(\text{OH})_6^{3-}$ in strong base solutions. In a recent paper, from a large number of accurate UV-Vis spectroscopic measurements, Perera et al. [162] reported the consecutive formation of $\text{Fe}(\text{OH})_5^{2-}$ and $\text{Fe}(\text{OH})_6^{3-}$ besides $\text{Fe}(\text{OH})_4^-$ with the exclusive presence of $\text{Fe}(\text{OH})_6^{3-}$ at $\text{pH} \geq 13$. As far as solid ferric hydroxo complexes are concerned, some naturally occurring minerals [163–165] are proven to consist of $\text{Fe}(\text{OH})_6^{3-}$ structural building blocks and various salts containing $\text{Fe}(\text{OH})_6^{3-}$, $\text{Fe}(\text{OH})_4^-$ and $\text{Fe}(\text{OH})_5^{2-}$ synthesised under laboratory conditions have been described both in the literature [166–168] and in university textbooks [169]. To the best of our knowledge, solid state complex salts consisting of $\text{Fe}(\text{OH})_4^-$ units has not been prepared and characterized in detail as yet. Kamnev et al. made a remarkable effort [170–172] to elucidate the Mössbauer spectrum of Fe(III)-hydroxo complex species forming in strongly alkaline aqueous solutions. In concentrated (15–17 M) NaOH solution, ferric ions were found to form a reddish-orange (supposedly colloidal and/or polynuclear) compound. When the solvent was evaporated, the colour of the complex disappeared. The singlet Mössbauer spectrum of the solid thus obtained (isomer shift: 0.68 mm s^{-1} ; half width: 0.72 mm s^{-1}) indicated the presence of a “symmetrically coordinated mononuclear hydroxo complex, statistically distributed in the $\text{NaOH}\cdot\text{H}_2\text{O}$ matrix” [170]. Upon heating, the symmetry of the complex has been found to be retained, and the

observed increase in the linewidth was attributed to the non-uniformity of the complexes' environment due to non-uniform drying [171]. The colloidal and/or polynuclear complex (during a 3.5 years aging period) was found to transform to a reddish brown solid complex with Mössbauer spectral parameters very similar to those of the solid obtained from evaporation [171]. From this, Kamnev et al. concluded, that (in accordance with their UV-Vis observations [156–157] obtained for solutions) the species responsible for the unique Mössbauer spectrum is most likely to be built up from $\text{Fe}(\text{OH})_4^-$ units in the solid state.

In a recent work, aqueous NaOH solutions supersaturated with respect to Fe(III) and the solid ferric-hydroxo complex salts precipitating from them have been characterized with a variety of experimental techniques [173]. The micro crystals obtained from such solutions were proven to be a new, so far unidentified solid phase. From EXAFS and XANES spectra, the environment of the ferric ion in *ca.* 20 M NaOH solutions (both native and quick-frozen) and in the complex salt was found to be different (Fig. 13). In the complex salt, the bond-lengths ($2.038 \pm 0.002 \text{ \AA}$) are consistent with octahedral coordination around the ferric centres [174]. In solution, the coordination geometry of Fe(III) is most probably tetrahedral (bond length were found to be $1.94 \pm 0.07 \text{ \AA}$), *i.e.*, the complex anion formed is $\text{Fe}(\text{OH})_4^-$. The singlet on the Mössbauer spectrum was argued to correspond to the octahedrally coordinated ferric hydroxo complex, and a sextet indicating magnetic interaction between the isolated $\text{Fe}(\text{OH})_4^-$ centres was also identified. From these results, in strongly alkaline aqueous solutions, ferric ions behave very similarly to Al(III) or Ga(III) [173].

8. The status of the speciation model of alkaline aluminate solutions

In concentrated alkaline aluminate solutions the predominant form of Al(III) is the pseudo-tetrahedral monomeric $\text{Al}(\text{OH})_4^-$ ion (including any of its ion pairs). Formation of dehydrated monomeric species (such as AlO_2^- or $\text{AlO}(\text{OH})_2^-$) or the occurrence of a significant fraction of higher complexes (such as $\text{Al}(\text{OH})_5^{2-}$ and $\text{Al}(\text{OH})_6^{3-}$) can be excluded. Furthermore, aluminate species formed *via* release of hydroxide from $\text{Al}(\text{OH})_4^-$ and subsequent oligomerization also conclusively eliminated.

Apart from $\text{Al}(\text{OH})_4^-$ (and its possible ion pairs), only one further Raman-distinguishable aluminate species appears to exist in significant concentrations. Analysis of band intensities indicates that this species is a dimer. An apparent formation constant of this dimer is

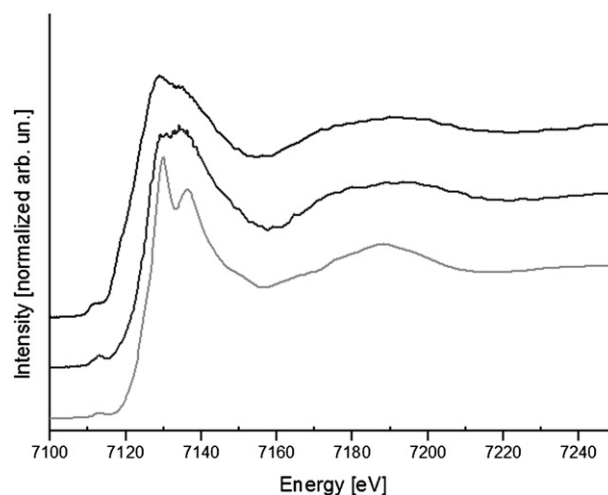


Fig. 13. XANES spectra of the solid ferric-hydroxo complex salt (lower spectrum), the strongly alkaline ($[\text{NaOH}]_{\text{T}} = 20 \text{ M}$) solution supersaturated with ferric ions (medium spectrum) and the same supersaturated solution after quick-freezing (upper spectrum). From Ref. [173] reproduced with the permission of the Royal Society of Chemistry.

now available for a wide range of water activities and Al(III) concentrations and has been shown to be relatively insensitive to temperature up to 100 °C.

The aluminate anion undoubtedly forms stable $\text{NaAl}(\text{OH})_4^0$ ion pairs, which are (depending on the concentrations) solvent-separated or contact; their relative contributions remain unknown at this stage. The presence of (somewhat less stable) NaOH^0 ion pairs is also well established but again their nature and extent of formation in concentrated solutions is unclear. Dielectric relaxation evidence was found to be consistent with (but did not prove) the formation of a solvent-shared ion pair between Na^+ and the dimeric aluminate ion. At extremely high caustic concentrations (> 10 M), where there will be a deficiency of water molecules, the presence of $\text{NaAl}(\text{OH})_4^0$ CIPs is likely, as would be expected on geometric (packing) effects alone. On the basis of the unexpectedly high viscosity of the hypothetical pure 'NaAl(OH)₄' solutions, the presence of an extended (most probably hydrogen-bonded) network of $\text{Al}(\text{OH})_4^-/\text{OH}^-/\text{Na}^+$ seems also to be likely. However, such species cannot be regarded as individual chemical entity, it is rather a loosely organised structure of the closely packed ions and molecules.

The species suggested here (all aquated): Na^+ , OH^- , $\text{Al}(\text{OH})_4^-$ and the dimeric aluminate along with their ion pairs, are sufficient to account qualitatively and, where appropriate, quantitatively for all the features observed for concentrated alkaline aluminate solutions at temperatures up to 100 °C. Other species, if they exist at all, can only be present in small quantities, and have only experimental effects which vanish in the baseline noise.

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