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Hydrogen bonded associates in the Bayer process (in concentrated aluminate lyes): the mechanism of gibbsite nucleation

Ágnes Buvári-Barcza, Márta Rózsahegyi and Lajos Barcza*

Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest-112, P.O.Box 32, 1518 Hungary

The highly alkaline aluminate lye, which is produced in the first step of Bayer process, is characterized by low water activity and strong competition for water molecules. The consequence of these effects is that two (or more) negatively charged species can be brought together and stabilized in the form of anionic hydrogen bonded complexes. Depending on temperature, total concentration and aluminate to hydroxide ratio, aluminate–hydroxide as well as aluminate–aluminate associates can be formed. Among the oligomerized aluminates, the cyclic hexamer seems to play a key role, as it contains octahedrally coordinated aluminate ions and is able to form nuclei in further polymerization for the partial precipitation of $Al(OH)_3$. The interactions have been experimentally investigated using specially developed methods and a detailed computational analysis.

Alumina is produced in several million tons per year by the Bayer process. The first step of this method is the extraction of bauxite using concentrated NaOH at high temperature.[1,2] When the bauxite contains 'monohydrates' (AlOOH: boehmite and diaspore, minerals from temperate zones) the extraction requires higher concentration (20–30% NaOH) and higher temperature (200–250 °C under 3.5 MPa pressure), while bauxite containing 'trihydrates' [$Al(OH)_3$: gibbsite and hydrargillite, minerals from the tropics] can be extracted at lower temperature (120–140 °C) and with less concentrated caustic soda (*ca.* 15% NaOH).[1–3] The highly alkaline solution is metastable at any temperature and can be decomposed to form $Al(OH)_3$ precipitate. [The symbol $Al(OH)_3$ represents here the amorphous→pseudo-boehmite→bayerite→gibbsite series.[4]] The separated product is always contaminated by some free alkali, which is attributed to the unwashable mother-liquor. All forms of the precipitated $Al(OH)_3$[4,5] consist of octahedrally coordinated aluminiums connected by bridging hydroxide ions in a layered structure of six-membered rings[6,7] (like the honeycomb structure of the carbon atoms in graphite layers), and the layers are held together by hydrogen bonds.[3] It is generally known that the production of $Al(OH)_3$ is influenced both qualitatively and quantitatively by the total concentration, the alumina/sodium hydroxide ratio and the temperature of the aluminate lye.[1,2] In spite of the fact that several empirical and semi-empirical rules are known concerning alkaline aluminate solutions, further work is of importance.

The interaction between aluminium and hydroxide ions has been mainly investigated in terms of hydrolysis, *i.e.* in more or less acidic solutions,[10–14] where the main component is the octahedral $Al(H_2O)_6{}^{3+}$ ion itself, however the relative stability of a terdecamer cation $Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$ (containing twelve [AlO_6] octahedra joined together by common edges) is of note.[15]

The composition of alkaline aluminate solutions and the structure of the aluminate anion have been investigated by several workers,[9,16–22] the definitive review is that of Eremin *et al.*,[23] who analysed UV, IR, Raman and NMR spectra, as well as electrochemical, thermodynamic and kinetic properties. Similarly, the formation constants for the $Al(OH)_3$–$Al(OH)_4{}^-$ equilibrium system have been measured by several workers;[10–14] the definitive review of earlier work is that of Baes and Mesmer.[12] In solid state, the $Al_2O(OH)_6{}^{2-}$ unit (built up from two [AlO_4] tetrahedra) was identified in a crystalline solid[24] (and detected later in concentrated solutions by IR, NMR and Raman methods[25,26]) while the structure of solid $CaO{\cdot}Al_2O_3{\cdot}10H_2O$ [27] points to the existence of polymeric $Al_6(OH)_{24}{}^{6-}$ species, containing six edge-linked, octahedrally coordinated aluminate ions. Based on solid state ^{27}Al NMR investigations,[28–30] more and more data have been accumulated on concentrated aluminate solutions containing not only tetrahedral but also octahedral species.[31–33] Concerning the composition of aluminate lye, similar semi-empirical results can be deduced using molecular modelling.[34]

According to our earlier work, the viscosity of a solution with strictly constant cation concentration and temperature is sensitive to any association, and the conductivity (under the same circumstances) is very sensitive to the hydroxide ion concentration.[35] (When either the total concentration or the temperature is changed, no theory is able to accurately predict their effect on concentrated solutions.) To elucidate the differences between the two main versions of the Bayer process, the investigation of the corresponding systems has been conducted, combining the experimental methods mentioned above with the most efficient computer simulation. Two model series were chosen which resemble the processes used in practice: (i) a system with constant 6 M sodium (hydroxide) concentration at 25 °C and (ii) a system with constant 4 M sodium (hydroxide) concentration at 65 °C. In both series, the molar ratios (conventionally: $r = Na_2O/Al_2O_3$) were varied down to rather low values ($r \approx 1.35$, *i.e.* the concentration of aluminate in such solutions was very high).

Experimental

Sodium hydroxide and water were purified to eliminate any carbonate. Aluminate solutions were prepared by dissolving high purity (99.99%) aluminium metal in sodium hydroxide solution. Contamination by silicate and carbonate were carefully avoided: the solutions were prepared and stored in polythene vessels under carbon dioxide free nitrogen.

To check whether the properties of solutions depend on their preparation, freshly prepared or aged, heated and/or mixed and/or diluted solutions of identical composition were studied. Disregarding some solutions of very low molar ratio ($r < 1.3$, *i.e.*, with extremely high aluminate concentration), the results are very reproducible, which means that the equilibria between the different species must be fast and reversible.

The viscosities were measured in Ostwald type viscometers constructed of alkali resistant glass and having capillary diameters of 0.47, 0.53, 0.63 or 0.84 mm. They were calibrated with

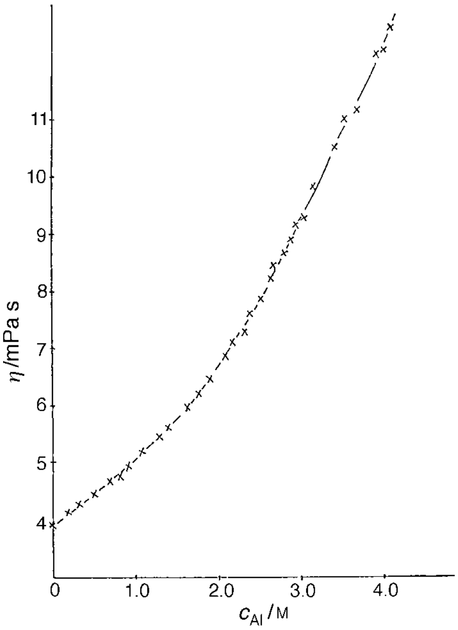

Fig. 1 Viscosities (× = every fifth data point, — = calculated curve) measured in 6 M solutions and at 25 °C

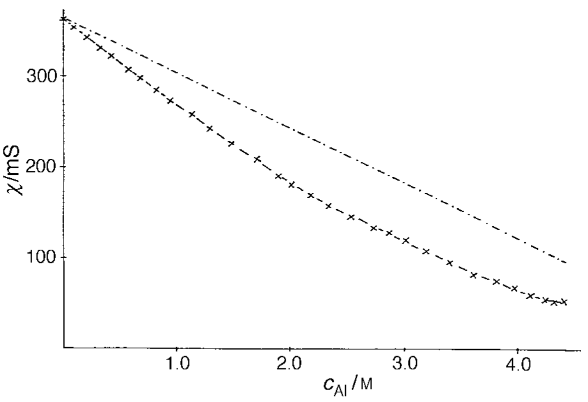

Fig. 2 Conductivities (× = every tenth data point, — = calculated data, -·- = the calculated conductivity of the free sodium hydroxide content) measured in 6 M solution and at 25 °C

glycerol solutions of known concentration and viscosity.[36] The flow-time varied from 60 to 150 s, measured with an accuracy of ±0.05 s. Conductivity data were recorded with a Radiometer CDM-2d type conductometer using CDC-104 or other, specially adapted electrodes.[36,37] The reproducibility of measured data was better than ±0.5%. The temperature was kept strictly constant (within ±0.02 °C), as was the sodium ion concentration (variation < ±0.1%).

The data were measured in different ranges of molar ratios ($r > 6$, $r = 6$–3, $r = 3$–2 and $r = 2$–1.35), *i.e.* starting with low aluminate content and increasing the concentration up to the highest values. The measurements were repeated several times. Some of the viscosity data measured in 6.000 M solutions and at 25.0 °C are presented in Fig. 1 and those of conductivities in Fig. 2. (The data measured in 4.000 M solutions and at 65.0 °C show no special characteristics, the trends of data are similar.)

Results

The measured viscosity data could be fitted in a computer simulation [based on equations similar to eqn. (2) and (5),[36,37] with coefficient(s) characterising the contribution(s) of the individual species to the viscosity measured] assuming monomeric species alone only at relatively low aluminium concentration ($r > 6$ in 6.0 M and $r \geqslant 10$ in 4.0 M solutions, respectively), while a mixture of monomeric and dimeric aluminate species is assumed if $r \geqslant 2$ in 6.0 M solutions at 25 °C or $r \geqslant 4$ in 4.0 M solutions at 65 °C (which means that the aluminium concentrations are < 3 or 1 M, respectively). The viscosities of solutions with higher aluminate content can be best approached (in 4.0 M solutions at 65 °C) assuming monomeric, dimeric and hexameric aluminate species, while any combination of polymeric species (including the variation mentioned as the simplest case) fits well for 6.0 M solutions, too.

The measured conductivities show a very interesting trend, characteristic for complex formation.[35] Namely, when we suppose a single monomeric aluminate component [*i.e.* $Al(OH)_4^-$] at relatively low total aluminate concentration, the equilibrium concentration of monomeric aluminate can be presumed to be equal to the total aluminium concentration (c_{Al}):

$$c_{Al} = [NaAl(OH)_4] \tag{1}$$

and we can assume:

$$\kappa = \lambda_{NaOH}\,[NaOH] + \lambda_{Na\text{-}aluminate}\,[NaAl(OH)_4] \tag{2}$$

where κ is the measured conductivity, λ is the molar conductance of a given species (in the given media), while [ ] denotes equilibrium concentrations [eqn. (2) reflects the well known rule of additivity]. According to our experiences, this rule is valid also for the conductivity of rather concentrated electrolyte mixtures with constant common cation concentration, *e.g.* for that of NaOH–$NaClO_4$ solutions with constant 6.0 M sodium ion concentration, or even for that of KOH–K_2CO_3 mixtures with constant 5.0 M potassium ion concentration.[35]

As λ_{NaOH} can be measured in pure NaOH solutions ($c_{Al} = 0.0$ M) very precisely, the 'free' sodium hydroxide concentrations and its conductivity [based on eqn. (2), disregarding the conductivity of sodium aluminate] can be calculated in the concentration range under discussion. The calculated, hypothetical values give a straight line, as shown in Fig. 2.

The (negative) difference between the measured and hypothetical conductivities can not be explained by assuming completely undissociated sodium aluminate ion pairs (since the molar conductance can never be negative) but only by interactions which decrease the hydroxide ion concentration, such as the formation of a hydrogen bonded hydroxide–aluminate complex $Al(OH)_4^- \cdot OH^-$. Extremely low water activity is characteristic for aluminate lyes[8,17,23] and therefore strong competition exists for water molecules, which can bring the two negatively charged species together. (Of course, the associate can bind some water molecules, also, but the total quantity of bound water is surely decreased. The role of low water activity has been previously discussed by Scotford and Glastonbury[17] and by Eremin *et al.*[23])

The oligomerization equilibria of tetrahydroxo aluminate anions and their background (OH^- here) can be explained similarly. Further, both possibilities have been considered. Since the formation constant of the $Al(OH)_4^-$ ion ($\beta_4 = [Al(OH)_4^-]/[Al^{3+}][OH^-]^4$) is extremely high (at 25 °C and at ionic strength extrapolated to 0.0: $\log \beta_4 \geqslant 33$[13,14]), it must be regarded as the basic component for all species containing aluminium in alkaline solution:

$$p\,Al(OH)_4^- + q\,OH^- \rightleftharpoons (Al(OH)_4^-)_p(OH^-)_q \tag{3}$$

The general definition of the formation constant for this equilibrium is as follows:

$$\beta_{pq} = [(Al(OH)_4^-)_p(OH^-)_q]/[Al(OH)_4^-]^p\,[OH^-]^q \tag{4}$$

We can define a parameter Y[35,36] (in general form, similarly to the simpler case represented by eqn. (2), at constant cation concentration and temperature) as

$$Y = \sum\sum f_{pq}\beta_{pq}\,[Al(OH)_4^-]^p\,[OH^-]^q \tag{5}$$

where f_{pq} symbolizes the linear contribution of a (p,q) species to the given property. It follows that f_{pq} is a constant valid only for the given electrolyte and temperature (such as molar conductance in the case of conductometric measurements).

According to eqn. (5) and using the expressions of mass balances:

$$c_{\mathrm{Al}}=\sum\sum p\,\beta_{pq}\,[\mathrm{Al(OH)_4}^-]^p\,[\mathrm{OH}^-]^q \tag{6}$$

$$c_{\mathrm{OH}^-}=\sum\sum q\,\beta_{pq}\,[\mathrm{Al(OH)_4}^-]^p\,[\mathrm{OH}^-]^q \tag{7}$$

both the viscosity and conductivity data can be evaluated in parallel and step by step in the whole concentration range investigated.

With the aid of eqn. (6) and (7), some relations, used earlier, can be defined more exactly, as

$$c_{\mathrm{Na}^+}=c_{\mathrm{OH}^-}+c_{\mathrm{Al}}=\mathrm{const} \tag{8}$$

and

$$r=c_{\mathrm{Na}^+}/c_{\mathrm{Al}} \tag{9}$$

In systems of low aluminate content (at higher r values: $r \geqslant 6$ or $r \geqslant 10$, respectively, for $[\mathrm{Na}^+]=6$ or 4 M) the viscosity data can be interpreted by monomeric aluminate species [which can be either $Al(OH)_4^-$ or $Al(OH)_4^-{\cdot}OH^-$; *viz.* *(1,0)* and *(1,1)* species]. In the same concentration range, the conductivity data indicate both *(1,0)* and *(1,1)* species and their stability constants can be computed using eqn. (5)–(7). Correlating the viscosity data with these constants using eqn. (5)–(7) leads to a perfect fit of measured and calculated data. (We should mention here that constants calculated in the range of lower aluminate concentrations were kept unchanged for the subsequent computer calculations.)

The evaluation of viscosity data in themselves shows the increasing presence of dimeric species with increasing c_{Al} (with decreasing r, between $r=6$–2 and $r=10$–4, respectively for $[\mathrm{Na}^+]=6$ and 4 M), corresponding to $Al_2O(OH)_6^{2-}$, indicated here as $\{Al(OH)_4^-\}_2$ or *(2,0)*. [However, the formation of an $Al(OH)_4^-{\cdot}Al(OH)_4^-$ species could also be rationalized similarly to the formation of $Al(OH)_4^-{\cdot}OH^-$ species, and it may have a similar Raman spectrum to that of $Al_2O(OH)_6^{2-}$.[34]]

Computation of the conductivity data does not give a good fit assuming only *(1,0)*, *(1,1)* and *(2,0)* species, and hydroxide associate *(2,1)* has to be introduced. It is remarkable that no *(2,2)* complex exists:[38] repulsion among the four negatively charged ions (two of them being hydroxide ions) seems to be too strong.

Both viscosity and conductivity data can be well fitted down to $r=2.1$ (6 M, 25 °C, $c_{\mathrm{Al}} \leqslant 2.86$ M) or $r=4.3$ (4 M, 65 °C, $c_{\mathrm{Al}} \leqslant 0.93$ M), respectively, with the series of *(1,0)*, *(1,1)*, *(2,0)* and *(2,1)* species. Below these r values (at higher c_{Al}), many combinations were tried but the simplest (*i.e.* using the lowest number of constants) and best fit was achieved when a hexameric *(6,0)* species was added to the series.

The calculated stability constants are summarized in Table 1. It must be emphasized that these values are only valid for the given environment: for the constant cation concentration and temperature (and may also involve ion pair and other formation constants). The association constants are much higher in 6 M NaOH (25 °C) than in 4 M (65 °C), the differences being reasonable considering the temperatures and the mainly hydrogen bonded character of the interactions. The mole fractions of different species as a function of c_{Al} are presented in Figs. 3 and 4.

Table 1 Main species in aluminate lyes and their formation constants

		stability constant, β_{pq}	
p,q	species	6 M, 25 °C	4 M, 65 °C
1,0	$Al(OH)_4^-$	1	1
0,1	OH^-	1	1
1,1	$Al(OH)_4^-{\cdot}OH^-$	3.9±0.2	0.25±0.01
2,0	$[Al(OH)_4]_2^{2-}$	1.9±0.2	0.38±0.04
2,1	$[Al(OH)_4]_2^{2-}{\cdot}OH^-$	26.7±3.1	1.0±0.1
6,0	$[Al(OH)_4]_6^{6-}$	33.0±4.3	15.0±2.0

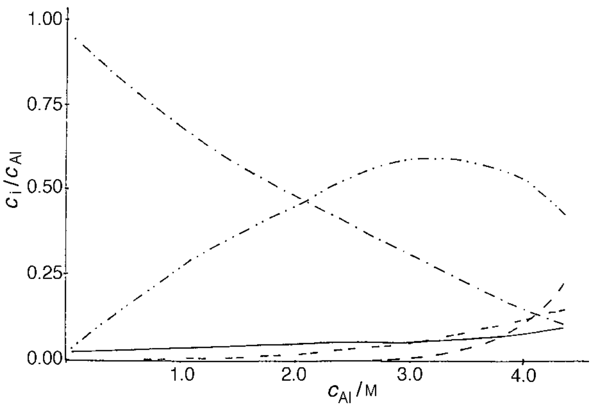

Fig. 3 Molar speciation in 6 M solutions at 25 °C as a function of the total aluminium concentration (c_i expressed as molar concentration of Al in the form of the given species; ——=$Al(OH)_4^-$; – –=$[Al(OH)_4]_2^{2-}$;— —=$Al_6(OH)_{24}^{6-}$; –·–·–=$Al(OH)_4^-{\cdot}OH^-$; —··—=$[Al_2(OH)_8^{2-}{\cdot}OH^-]$)

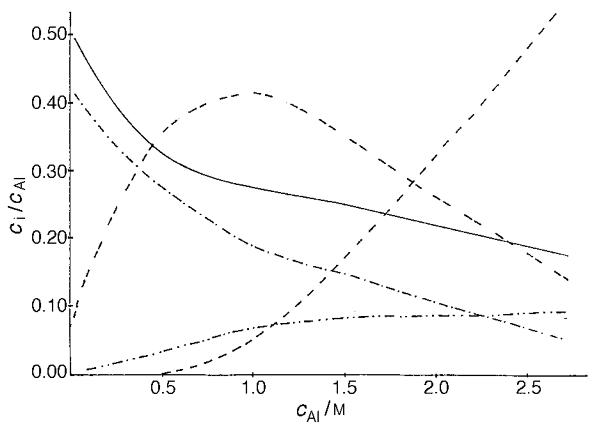

Fig. 4 Molar speciation in 4 M solutions at 65 °C as a function of the total aluminium concentration (see Fig. 3 caption for key)

It should be mentioned that the existence of tri-, tetra-, penta-, hepta- and higher oligomeric species can be neglected as minor components, when we characterize the system assuming a minimum number of species present, however, the possibility of their existence at low concentrations is not ruled out, in contrast to *(1,2)* $Al(OH)_6^{3-}$ or *(2,−1)* $Al_2(OH)_7^-$ species, which were, among others, also tested.

Discussion

The key species in the aluminate lye seems to be the (cyclic) hexamer, since this is the smallest oligomer where octahedral coordination can be fulfilled for every aluminium (Fig. 5). The ring contains six octahedrally coordinated aluminiums connected by two bridging hydroxide ions and the aluminium atoms are in a planar arrangement. This structure is identical with the basic unit of both bayerite and gibbsite[3,6,7] determined in the solid phase, therefore the olation type polymerization by O^{2-} bridging ligand seems less probable.

If we assume that (four) monomeric $Al(OH)_4^-$ units are able to attach in-plane to the hexameric aluminate (see Fig. 5), a second six-membered ring could be formed (*cf.* naphthalene $C_{10}H_8$) with formula $Al_{10}(OH)_{38}^{8-}$. Similarly, a condensed three ring system (like anthracene or phenanthrene, $C_{14}H_{10}$): $Al_{14}(OH)_{52}^{10-}$ could also be formed. The oligomer corresponding to coronene ($C_{24}H_{12}$), consisting of seven rings can also be

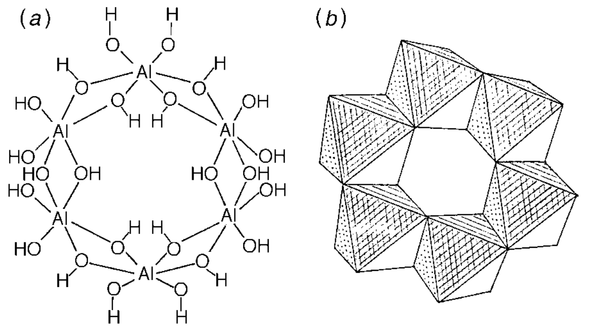

Fig. 5 The conventional atom-and-bond (*a*) and coordination polyhedral (*b*) model (omitting the charges) of the $Al_6(OH)_{24}{}^{6-}$ ion

supposed: $Al_{24}(OH)_{84}{}^{12-}$. (Theoretically this compound can exist, but it is mentioned only for demonstrating the relative decrease of charge as a function of the degree of in-plane polymerization.) The water solubility of such types of oligomer is surely influenced by their size and charge, and associates containing three to four hexameric units are probably at the limit of water-solubility. In-plane polymerization results in structures identical with the structure of layers in crystalline gibbsite.[3,6,7]

On the other hand, the growth of the hexameric core is possible not only in-plane but also on-plane. Two hexamers could attach by hydrogen bonds, since the shape of their surfaces and the positions of the appropriate functional groups fit well, like those of the parallel layers in gibbsite.[3] In this way polymers with general formula of $[Al_6(OH)_{24}]_n{}^{6n-}$ can be formed, which essentially copy the structure of bayerite or gibbsite, where the layers are held together in a similar manner.[3,6,7] The solubility limit can be set again as $n = 3$–4, but the further, insoluble species (the precipitate) will have undoubtedly higher charges than the product formed by the in-plane polymerization of the same number of Al atoms. It follows that the precipitate shall always contain a charge (compensated by Na^+ ions), which should be manifested, in good agreement with industrial experience, as the 'free caustic soda' content of the bayerite.

The type of polymerization (in-plane or on-plane or a mixture as the most probable case) depends on both the actual concentration of the hexaaluminate and its ratio to the concentration of $Al(OH)_4{}^-$. When this picture is considered from the standpoint of precipitation of gibbsite, the equilibria given in Fig. 6 can be deduced. The sign $\rightsquigarrow$ indicates irreversible precipitation (*via* in-plane or/and on-plane polymerization) while the symbol $Al(OH)_3$ represents the amorphous→pseudoboehmite→bayerite→gibbsite series. The main process proceeds *via* monomeric→dimeric→hexameric aluminates, while association with hydroxide ions (as it decreases the concentration of important species) only retards the main precipitation process.

High total concentration and relatively low temperature is known to promote the formation of hydrogen bridged associates as is demonstrated in Fig. 3: the hydroxide + aluminate associates are dominant in nearly the whole concentration range in 6.0 M NaOH solution (at 25 °C). It follows that the important hexameric species is only formed in a rather narrow range of c_{Al}, where $[Al(OH)_4{}^-]$ is very low. The consequence is that the on-plane polymerization will be predominant, leading to very small crystallite particles termed 'mealy' product industrially (with relatively high unwashable caustic soda content).

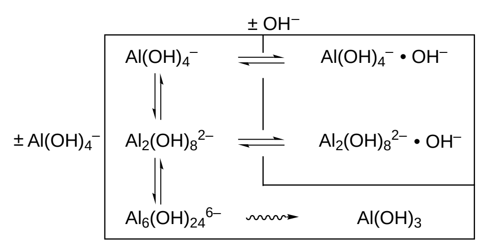

Fig. 6 The coherence of equilibria in highly alkaline solutions of aluminate [$\rightsquigarrow$: precipitation of $Al(OH)_3$]

Lower total concentration and higher temperature (4.0 M and 65 °C) hinder hydrogen bonded associations (Fig. 4): oligomerization is predominant over nearly the whole concentration range, but $[Al(OH)_4{}^-]$ is high enough to promote in plane polymerization. The main process is therefore the growth of nuclei, which occurs also at lower aluminate concentration resulting in the precipitation of larger particles (of 'sandy' texture).

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References

1 T. G. Pearson, *The Chemical Background to the Aluminium Industry*, Royal Institute of Chemistry, London, 1955.
2 S. I. Kuznetsov and V. A. Derevyakin, *The Physical Chemistry of Alumina Production in the Bayer Method*, Metallurgizdat, Moscow, 1964.
3 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, London–New York, 1984, p.273.
4 N. Dezelic, N. Dikinski and R. H. Wolf, *J. Inorg. Nucl. Chem.*, 1981, **33**, 791.
5 H. A. Van Straten and P. L. De Bruyn, *J. Colloid Interface Sci.*, 1984, **102**, 260.
6 V. R. Rothbauer, F. Zigan and H. O'Daniel, *Z. Kristallogr.*, 1967, **125**, 317.
7 H. Saalfield and M. Wedde, *Z. Kristallogr.*, 1974, **139**, 129.
8 J. Zámbó, *Light Metals*, 1986, 199.
9 J.R. Glastonbury, *Chem. Ind. (London)*, 1969, 121.
10 L. G. Sillén, *Quart. Rev.*, 1959, **13**, 146.
11 R. J. Stol, A. K. Van Helden and P. L. De Bruyn, *J. Colloid Interface Sci.*, 1976, **57**, 115.
12 C. F. Baes and A. Mesmer, Jr., *Hydrolysis of Cations*, J. Wiley, New York, 1976.
13 *Stability Constants of Metal-ion Complexes, Inorganic Ligands*, ed. E. Högfeldt, Pergamon, Oxford, 1982.
14 *Critical Stability Constants*, ed. R. M. Smith and E. Martell, Plenum, New York, 1976, vol. 4.
15 G. Johansson, *Acta Chem. Scand.*, 1960, **14**, 771.
16 K. F. Jahr and I. Pernoll, *Ber. Bunsen-Ges. Phys. Chem.*, 1965, **69**, 221, 226.
17 R. F. Scotford and J. R. Glastonbury, *Can. J. Chem. Eng.*, 1972, **50**, 754.
18 A. S. Russell, J. D. Edwards and C. S. Taylor, *J. Metals*, 1955, **7**, 1223.
19 R. C. Plumb and J. W. Swaine, Jr., *J. Phys. Chem.*, 1964, **68**, 2054.
20 L. A. Carriera, V. A. Maroni, J. W. Swaine, Jr. and R. C. Plumb, *J. Chem. Phys.*, 1966, **45**, 2216.
21 J. D. Hem, *Adv. Chem. Ser.*, 1968, **73**, 98.
22 K. Wefers, *Metall. (Berlin)*, 1967, **21**, 422.
23 N. I. Eremin, Yu. A. Volokhov and V. E. Mironov, *Usp. Khim.*, 1974, **43**, 224.
24 G. Johansson, *Acta Chem. Scand.*, 1966, **20**, 505.
25 R. J. Moolenaar, J. G. Evans and L. D. McKeever, *J. Phys. Chem.*, 1970, **74**, 3629.
26 R. J. Hill, G. V. Gibbs and R. C. Peterson, *Aust. J. Chem.*, 1979, **32**, 321.
27 W. Gessner, D. Müller, H. J. Behrens and G. Scheler, *Z. Anorg. Allg. Chem.*, 1981, **486**, 193.
28 D. Müller, W. Gessner, A. Samoson, E. Lipmaa and G. Scheler, *J. Chem. Soc., Dalton Trans.*, 1986, 1277.
29 S. F. Dec, G. E. Maciel, and J. J. Fitzgerald, *J. Am. Chem. Soc.*, 1990, **112**, 9069.
30 S. M. Bradley, R. A. Kydd and C. A. Fife, *Inorg. Chem.*, 1992, **31**, 1181.
31 J. W. Akitt and W. Gessner, *J. Chem. Soc., Dalton Trans.*, 1984, 147.
32 J. W. Akitt, W. Gessner and M. Weinberger, *Magn. Reson. Chem.*, 1988, **26**, 1047.
33 S. M. Bradley and J. V. Hanna, *J. Chem. Soc., Chem. Commun.*, 1993, 1249.

34 A. R. Gerson, J. Ralston and R. St. C. Smart, *Colloids Surf. A: Physicochem. Eng. Asp.*, 1996, **110**, 105.

35 M. Pálfalvi-Rózsahegyi, Á. Buvári, L. Barcza and Z. G. Szabó, *Acta Chim. Hung.*, 1979, **102**, 401.

36 P. W. Atkins, *Physical Chemistry,* Oxford University Press, Oxford, 4th edn., 1990.

37 M. Pálfalvi-Rózsahegyi, Z. G. Szabó and L. Barcza, *Acta Chim. Hung.*, 1980, **104**, 303.

38 L. Barcza and M. Pálfalvi-Rózsahegyi, *Mater. Chem. Phys.*, 1989, **21**, 345.

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