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Abstract	In this work we report the results of an investigation on the hydrolysis of Al^{3+} aged in 3.0 mol·L^{-1} (Na)Cl ionic medium at 25 °C, in the ranges of Al(III) concentration $0.0125 \leq B \leq 0.1000$ mol·L^{-1} and average number of H$^+$ released, or OH$^-$ bound per metal atom of $0.1 \leq Z \leq 1.5$. The analysis of the emf(H) data, first in terms of the core + links hypothesis and, subsequently, by using the generalized least-squares program LETAGROP, indicates formation of the complexes $[Al_2(OH)_2]^{4+}$, $[Al_3(OH)_4]^{5+}$, $[Al_{13}(OH)_{30}]^{9+}$, $[Al_{13}(OH)_{32}]^{7+}$ and $[Al_{13}(OH)_{34}]^{5+}$. The species distribution diagrams are briefly discussed.

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3 Studies on Aluminum Chemistry: 1. Hydrolysis of Al³⁺
4 Aged in Acidic 3.0 mol·L⁻¹ (Na)Cl Solution at 25 °C

5 **A. Marín[1] · M. L. Araujo[1] · J. D. Martínez[1] · V. Lubes[2] ·**
6 **F. Brito[1]**

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10 aged in 3.0 mol·L⁻¹ (Na)Cl ionic medium at 25 °C, in the ranges of Al(III) concentration
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16 briefly discussed.

17 **Keywords** Aluminum(III) hydrolysis · Aged solutions · Emf(H) measurements · Stability
18 constants · Core + links hypothesis · LETAGROP program
19

20 1 Introduction

21 **AQ2** Aluminum is the most abundant metal in the earth's crust. Its compounds are present in
22 most rocks, generally as silicates. Aluminum is only extracted from bauxite by a sequence
23 of transformations, first as alumina using Bayer's process, followed by electrolysis to
24 prepare the metal [1].

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25   This metal possesses a combination of properties that make it very useful in the
26 engineering of materials. Indeed, aluminum is the second most used metal after steel,
27 because it is so versatile. Aluminum is used by several industries including high voltage
28 transmission lines, electrical products, TV and satellite antennas, automotive and aerospace
29 industries, building and construction, packaging, etc. [2].
30   Its impact on biological systems has been the subject of much controversy in the past
31 decades, and a profuse amount of research has shown that it can produce adverse effects on
32 plants, aquatic animals and human beings [3].
33   Aluminum is found in the trivalent state in its compounds and in solution. With an ionic
34 radius of 0.6 Å, the regular octahedral $[Al(H_2O)_6]^{3+}$ ion, denoted here by Al^{3+}, has a
35 hydration number of six. Its small ionic size leads to extensive hydrolysis of its aqueous
36 solutions starting at pH ≥ 3.
37   We define hydrolysis in terms of the formation function Z, the average number of OH^-
38 bound, or H^+ released, per Al atom according to Eq. 1:

$$p\mathrm{H_2O} + q\mathrm{Al}^{3+} \rightleftarrows \mathrm{Al}_q(OH)_p^{(3q-p)+} + p\mathrm{H}^+. \tag{1}$$
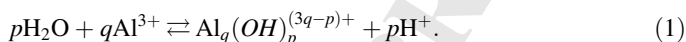
40
41   We write each hydrolysis product in the general form $Al_q(OH)_p^{(3q-p)+}$, briefly $(p,$
42 $q)$ species (complex), and define a stability constant β_{pq} for each reaction (1). If c_{pq} is the
43 concentration of the (p, q) complex, $h = [H^+]$ and $b = [Al^{3+}]$, and assuming the con-
44 stancy of the activity factors of reactants and products in high concentration ionic media
45 [4], then we have the law of mass action in the following form:

$$c_{pq} = \beta_{pq}h^{-p}b^q. \tag{2}$$

47
48   The hydrolysis of Al^{3+} has been extensively investigated over the last 70 years. A
49 number of researchers have studied Al–OH solutions, obtained by mixing Al^{3+} and OH^- in
50 various proportions and allowed the mixture to be exposed to an increase in temperature or
51 aged for different times, because achieving equilibrium for the complexes takes a long time
52 at room temperature. As a matter of fact, due to the slowness of the involved reactions, it is
53 difficult to apply equilibrium analysis [5] and it is therefore assumed that such a system can
54 achieve equilibrium conditions either by increasing the temperature or by ageing of the
55 solutions.
56   Emf(H) measurements performed by Brosset in 2.0 mol·L^{-1} NaClO$_4$ at 40 °C [6],
57 Biedermann in 3.0 mol·L^{-1} NaClO$_4$ at 50 °C [7], Aveston in 1.0 mol·L^{-1} NaClO$_4$ at
58 25 °C [8], Baes and Mesmer in 1.0 mol·L^{-1} KCl at 62–150 °C, [9, 10], Öhman and
59 Forsling in 0.6 mol·L^{-1} at 25 °C [11], and Brown et al. in 0.1 mol·L^{-1} NaNO$_3$ at 25 °C
60 [12] indicate formation of more or less large polynuclear complexes through very slow
61 reactions. The ^{27}Al and ^{1}H NMR measurements of Akitt et al. [13] and Bottero et al. [14]
62 lead to the same conclusions.
63   On the other hand, from studies on the crystal structure by X-ray diffraction of the basic
64 aluminum salts Al$_2$O$_3$·2SO$_3$.11H$_2$O, Al$_2$O$_3$.2SeO$_3$·11H$_2$O and Na$_2$O·13Al$_2$O$_3$·6SO$_3$.
65 (68–76)H$_2$O and Na$_2$O·13Al$_2$O$_3$·6SeO$_3$·(68–76)H$_2$O, obtained from solutions with inter-
66 mediate acidity, Johansson found the complexes $[Al_2(OH)_2(H_2O)_8]^{4+}$ [15] and
67 $[Al_{13}(OH)_{32}(H_2O)_{12}]^{7+}$ [16]. The complex $[Al_2(OH)_2(H_2O)_8]^{4+}$ has two octahedra sharing
68 an edge with two OH^- groups, and complex $[Al_{13}(OH)_{32}(H_2O)_{12}]^{7+}$, which may be written
69 as $\left[Al^{IV}O_4Al_{12}^{VI}(OH)_{32}(H_2O)_{12}\right]^{7+}$; it is spherical and in the center is one Al atom sur-
70 rounded by a tetrahedron of oxygens and around it are 12 more Al atoms, which are nicely

71 packed with 36 more oxygens [17]. X-ray data obtained in solution by Rausch and Bale
72 [18] indicate that the complex $[Al_{13}(OH)_{32}(H_2O)_{12}]^{7+}$ exists.

73 Johansson has also made ^{27}Al NMR studies in solutions with varying Z values (quoted
74 by Sillén [5], p. 71). The resonance peaks registered may be ascribed to ^{27}Al in $Al^{IV}O_4$ and
75 $Al^{VI}O_6$ octahedra. In acidic solutions at pH ≤ 3 and $Z = 0$, all aluminum present has a
76 coordination number of six; in alkaline solution at pH ≥ 9 and $Z = 3–4$, it is all four
77 coordinated, and in solutions corresponding to the Al_{13} complex at pH ~ 5.5 and $Z \sim 2.5$,
78 both coordination's numbers are present, as verified by further research [13, 14].

79 These results constitute an important foundation for the interpretation of the hydrolysis
80 of Al^{3+}, based on the particular slowness of the involved reactions at room temperature,
81 and the low accuracy of the emf(H) data at high temperature, since there are many
82 experimental difficulties in this regime [7].

83 Brosset [6] published a study on the hydrolysis of Al^{3+} in 2.0 mol·L^{-1} NaClO$_4$ of
84 varying acidity at 40 °C, for total concentrations of metal **B** = 2.21, 11.07 and
85 55.41 mmol·L^{-1}, respectively, and measured pH using a hydrogen electrode versus a
86 Hg$_2$Cl$_2$–Hg electrode in 2.0 mol·L^{-1} NaClO$_4$ at 40 °C. He interpreted the data assuming
87 that the species $[Al_2(OH)_3]^{3+}$, $[Al_3(OH)_6]^{3+}$ and $Al_n(OH)_{3(n+1)}^{3-}$ are present in acidic media
88 ($Z = 0–3$), and the complex $Al(OH)_4^{-}$ forms in alkaline medium ($Z = 3–4$).

89 Later on, these data were reinterpreted by Brosset et al. [19] in terms of Sillén's
90 core + links hypothesis (1954) [20, 21], assuming that in the acid range ($Z = 0–2.5$) either
91 a single species such as $[Al_6(OH)_{15}]^{3+}$, $[Al_8(OH)_{20}]^{4+}$, or $[Al_{13}(OH)_{33}]^{6+}$, or a series of
92 complexes of general formula $Al(Al_2(OH)_5)_n^{n+3}$, are present and confirmed that a single
93 complex $[Al(OH)_4]^{-}$ is present in the alkaline range ($Z = 3–4$).

94 Biedermann [7] made a careful study of the hydrolysis of Al^{3+} in 3.0 mol·L^{-1} NaClO$_4$
95 at 50 °C for **B** = 5–50 mmol·L^{-1} by measuring the concentrations of free H$^+$ ions, h,

Table 1 Literature values of stability constants for Al(III) hydrolysis in different ionic media and temperatures according to reaction (1)

Species	$-\log_{10} \beta_{pq}$						
$[AlOH]^+$						5.52 (4)	5.33 (1)
$[Al(OH)_2]^+$							10.91 (4)
$[Al_2(OH)_2]^{4+}$	7.07 (6)	5.90	4.8 (2)	3.95 (7)			
$[Al_3(OH)_4]^{5+}$		10.74	8.2 (1)	7.01 (9)		13.57 (2)	13.13 (1)
$[Al_7(OH)_{17}]^{4+}$					48.8 (1)		
$[Al_{13}(OH)_{32}]^{7+}$	104.50 (6)		64.3	52.9		109.2 (1)	107.41 (4)[a]
$[Al_{13}(OH)_{34}]^{7+}$					97.6 (1)		
$\sigma(Z)$		0.006	0.028	0.014			
Ionic medium/mol·L^{-1}	1.0 (NaClO$_4$)	1.0 (KCl)	1.0 (KCl)	1.0 (KCl)	3.0 (NaClO$_4$)	0.6 (NaCl)	0.1 (NaNO$_3$)
°C	25	62.5	99.6	124.8	50	25	25
B/mmol·L^{-1}	2.7–99.2	5–45	5–45	5–45	5–50	2.5–20	0.99–0.992
Z range	≤ 2.43	≤ 2.4	≤ 2.0	≤ 2.0	≤ 2.5		≤ 2.5
References	[8]	[9, 10]			[7]	[11]	[12]

[a] Among other possible polymers whose stability constant follows the expression $-\log_{10} \beta_{pq} = 5.73 - 3.6q + 4.64p$ with $p = 12–34$ and $q = 5–14$

96　using the cell without junction potential: glass electrode/test solution, Ag^+ 1.0 mmol·L^{-1}/
97　Ag. The data were also analyzed in terms of Sillén's core + links hypothesis [20, 21] that
98　could explain the observed results by assuming the formation of $[Al_7(OH)_{17}]^{4+}$ and
99　$[Al_{13}(OH)_{34}]^{5+}$ species. Table 1 (column 6) shows the corresponding stability constants.
100　　Aveston [8] published the results of the hydrolysis of the Al^{3+} in 1.0 mol·L^{-1} $NaClO_4$
101　at 25 °C in the region $Z \leq 2.43$ using solutions that were first hydrolyzed at 50 °C, held
102　there for 15 min and, finally, stored for 2 weeks at 25 °C. He explained the data satis-
103　factorily in terms of species $[Al_2(OH)_2]^{4+}$ and $[Al_{13}(OH)_{32}]^{7+}$, in accordance with those
104　reported by Johansson [15, 16] (vide supra) for crystalline solids that precipitated from
105　hydrolyzed Al(III) solutions. Table 1 (column 2) contains the respective stability constants
106　and the experimental conditions.
107　　Baes and Mesmer [9, 10] studied the hydrolysis of Al^{3+} in 1.0 mol·L^{-1} KCl at
108　25–150 °C for $\mathbf{B} = 5$–45 mmol·L^{-1}, using a hydrogen electrode in a concentration cell,
109　allowing precise acidity measurements at elevated temperatures [22]. They found that the
110　model formed by the species $[Al_2(OH)_2]^{4+}$, $[Al_3(OH)_4]^{5+}$, and $[Al_{14}(OH)_{34}]^{8+}$ or
111　$[Al_{13}(OH)_{34}]^{5+}$ represented their data well [9]. However, later on they concluded that the
112　model formed by the species $[Al_2(OH)_2]^{4+}$, $[Al_3(OH)_4]^{5+}$ and $[Al_{13}(OH)_{32}]^{7+}$ is the most
113　probable scenario [10]. Table 1 (columns 3–5) contains the respective stability constants
114　and dispersions $\sigma(Z)$ at 62.5, 99.6 and 124.8 °C for the latter model. It can be observed that
115　the stability constants vary considerably with temperature, from which they calculated the
116　thermodynamic parameters ΔH_{pq} and ΔS_{pq}.
117　　Akitt et al. [13] studied the hydrolysis of Al^{3+} in solutions prepared by different
118　methods, concentrations and temperatures in the range $0 \leq Z \leq 2.5$, using ^1H and ^{27}Al
119　NMR spectroscopy and pH measurements. They postulated that the species $[AlOH]^{2+}$,
120　$[Al_2(OH)_2]^{4+}$, and $[Al_{13}(OH)_{32}]^{7+}$ were present and, with less certainty, $[Al_8(OH)_{20}]^{4+}$.
121　　Bottero et al. [14] studied the hydrolysis of Al^{3+} in solutions with total concentration
122　$\mathbf{B} = 0.1$ mol·L^{-1} in the range $0.5 \leq Z \leq 2.5$ with a 24 h aging time at 25 °C by ^{27}Al
123　NMR spectroscopy and pH titration techniques. A comparison of their experimental curve
124　$Z(\log_{10} h)_\mathbf{B}$ (their curve I, Fig. 4, p. 2937) with several theoretical curves shows that curves
125　V (for species $[AlOH]^{2+}$, $[Al(OH)_2]^+$, $[Al_2(OH)_2]^{4+}$, $[Al_2(OH)_x]^{(6-x)+}$ and $[Al_{13}(-$
126　$OH)_{36}]^{3+}$) and VI (all of these species plus $Al(OH)_{3)}$ were the ones that gave the best
127　agreement.
128　　Öhman and Forsling [11] also investigated the hydrolysis of Al^{3+}, covering ranges
129　$2.5 \leq \mathbf{B} \leq 20$ mmol·L^{-1} and $1.5 \leq pH \leq 4.3$, in connection with studies of hydroxo
130　carbonates of Al(III) in 0.6 mol·L^{-1} NaCl at 25 °C. They found the species $[AlOH]^{2+}$,
131　$[Al_3(OH)_4]^{5+}$ and $[Al_{13}(OH)_{32}]^{7+}$ to be present, whose stability constants are given in
132　Table 1 (column 7).
133　　Brown et al. [12] studied the hydrolysis of Al^{3+} in 0.1 mol·L^{-1} $NaNO_3$ at 25 °C
134　covering the range $0.099 \leq \mathbf{B} \leq 0.992$ mmol·L^{-1} and $4.0 \leq pH \leq 4.9$. They validated
135　the presence of species $[AlOH]^{2+}$, $[Al(OH)_2]^+$, $[Al_3(OH)_4]^{5+}$ and a high-molecular-weight
136　polymer $Al_q(OH)_p^{(3q-p)}$ with ratio $p/q \sim 2.46$ and $q = 6$–14. Table 1 (column 8) contains
137　the stability constants for the first three species and the polymer $[Al_{13}(OH)_{32}]^{7+}$.
138　　Regarding the hydrolysis of Al^{3+} in the alkaline range ($Z = 3 \leq 4$), the species
139　$Al(OH)_4^-$ and a dimeric complex {most probably $(OH)_3AlOAl(OH)_3^{2-}$ $OH)_3$} are suffi-
140　ciently to account for all the experimental observations collected for concentrated alkaline
141　solutions at temperature up to 100 °C. The presence of other species in significant con-
142　centrations, like AlO_2^-, $AlO(OH)_2^-$, $Al(OH)_5^{2-}$, or $Al(OH)_6^{3-}$, can be excluded [23].

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143   One can see that the general tendency is the preferential formation of polynuclear
144 complexes, besides one and/or two mononuclear species. The lack of agreement in the
145 results obtained by different authors about the composition of the system can be attributed
146 partly to the fact that the reactions are very slow and there is frequently not true equi-
147 librium, but rather time-dependent transient equilibria, or that the formed products can be
148 influenced by the type of the anion present in the ionic medium or the way in which the
149 Al(III) solutions were prepared.
150   The present work reports the results of a study of the hydrolysis of Al^{3+}, aged in
151 3.0 $mol \cdot L^{-1}$ (Na)Cl ionic medium at 25 °C, by emf(H) measurements. It was carried out to
152 try to get a model that better explains the behavior of the Al–OH system using aged
153 solutions prepared far from the area of general disagreement $Z \geq 1.5$, where most of the
154 time precipitates of basic salts are formed and slow reactions occur for several reasons.
155 Emf(H) measurements are a well-established method for studying equilibria in solution [7,
156 20, 24–26].
157   The symbols used in this article are the same as those adopted in previous work [25, 26].

2 Experimental

2.1 Materials, Solutions and Methods

160 As reagents HCl and NaOH Sigma–Aldrich (Fixanal 0.100 $mol \cdot L^{-1}$ ampoules), NaCl
161 (99.8 %), Na_2CO_3 (99.5 %), KHI_2O_6 (99.0 %) and 8-hydroxiquinole (99.0 %) Merck p.a.,
162 CO_2-free triply-distilled water, and argon were used. The source of aluminum was Merck
163 p.a. $AlCl_3 \cdot 6H_2O$ (95.0 %) recrystallized three times.
164   Solutions: 3.0 $mol \cdot L^{-1}$ NaCl ionic medium, $T_1 = 100$ $mmol \cdot L^{-1}$ (Na, H)Cl in H^+ and
165 $T_2 = 3.0$ $mol \cdot L^{-1}$ Na(OH, Cl) in 100 $mmol \cdot L^{-1}$ OH^- were prepared by weighing dry
166 NaCl and, where appropriate, by adding HCl and NaOH that had been standardized versus
167 Na_2CO_3 and KHI_2O_6 [27], respectively.
168   A stock solution of Al(III), whose concentration $S_o = 2.129$ $mol \cdot kg^{-1}$, was prepared
169 and analyzed by precipitation with 8-hydroxiquinoleine [27], containing ≤ 10 ppm Fe(III)
170 as determined by atomic absorption, from which was prepared the more dilute solution
171 $S_1 = 303.5$ $mmol \cdot L^{-1}$ Al(III), 6.798 $mmol \cdot L^{-1}$ H^+, 2.083 $mol \cdot L^{-1}$ Na^+ and 3.0 $mol \cdot L^{-1}$
172 Cl^-, and whose exact acid content was determined by potentiometric titration with the T_1
173 solution [28].
174   For the emf(H) measurements, four sets of solutions with total concentrations of
175 **B** = 12.5, 25.0, 50.0 and 100.0 $mmol \cdot L^{-1}$ Al(III) were used. For each set, using solutions
176 S_1 and T_2, and special glass bottles as containers, fifteen solutions with Z values distributed
177 in the range $0.1 \leq Z \leq 1.5$ were prepared and aged for 15 days.

2.2 Emf(H) Measurements

179 The concentration h of each aged solution was measured every 2 days until reaching a
180 constant value, by means of cell (3), where REF**//**= 3.0 $mol \cdot L^{-1}$ NaCl**/**3.0 $mol \cdot L^{-1}$ NaCl,
181 Hg_2Cl_2 (saturated)**/**Hg_2Cl_2–Hg(Pt), and **S** = **B** $mmol \cdot L^{-1}$ Al^{3+}, **H** $mmol \cdot L^{-1}$ H^+ (3.0 –
182 **H** – 3 **B**) $mol \cdot L^{-1}$ Na^+, and 3.0 $mol \cdot L^{-1}$ Cl^-.

$$\text{REF} //\mathbf{S}/ \text{ glass electrode.} \tag{3}$$

184 The potential E (mV) of cell (3) at 25 °C is given by Nernst's equation, Eq. 4:

$$E = E_0 + Jh + 59.16 \log_{10} h. \tag{4}$$

188 Before measuring E, the standard potential E_0 and the parameter J were determined
189 using solutions of 3.0 mol·L^{-1} (H, Na)Cl of well known H$^+$ concentration. Estimates of
190 the precisions of emf(H) measurements is 0.1 mV/0.002 pH units.
191 Once h was determined for each solution after reaching a constant value, the formation
192 function Z was calculated using Eq. 5, where K_w is the water dissociation constant:

$$Z = \left(h - \mathbf{H} - Kw \cdot h^{-1}\right). \tag{5}$$

195 The ageing process and the emf(H) measurements were carried out under argon
196 sweeping in a special chamber, thermostatically regulated at 25.0 (1) °C, placed inside a
197 thermostatted air room environment at 25 (1) °C.
198 The resulting data for $Z(\log_{10} h)_{\mathbf{B}}$ are shown in Fig. 1 and also are given in Table 2.

3 Result and Discussion

200 According to reaction (1), the balances of reagents H$^+$ and Al^{3+} are given by Eqs. 6 and 7,
201 respectively:

$$\mathbf{B}Z\left(= h - \mathbf{H} - Kwh^{-1}\right) = \sum_p \sum_q p\beta_{pq}h^{-p}b^q \tag{6}$$
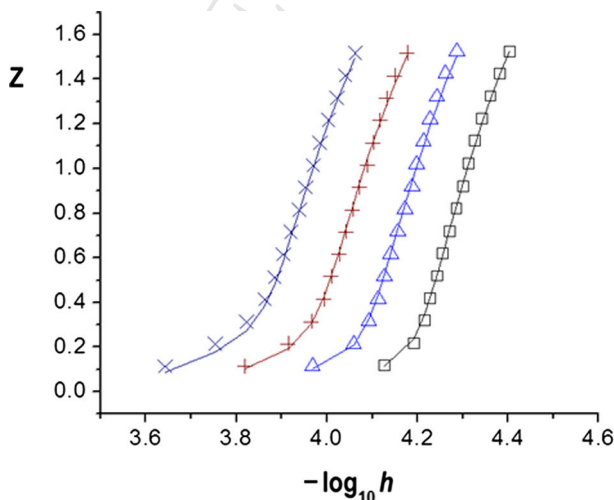
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Fig. 1 Z, average number of OH$^-$ groups bound or H$^+$ split off per Al^{3+} according to reaction (1), as a function of $-\log_{10} h$ in 3.0 mol·L^{-1} (Na)Cl ionic medium at 25 °C, for four different total concentration $\mathbf{B} = 12.5$ (*square*), 25 (*triangle*), 50 (*plus*) and 100 (*times*) mmol·L^{-1}. The *solid lines* represent theoretical *curves* calculated with the stability constants of Table 3 (column 7)

Table 2 Experimental data $Z(\log_{10} h)_{\mathbf{B}}$ for Al(III) hydrolysis in 3.0 mol·L^{-1} (Na)Cl ionic medium at 25 °C, for **B** 12.5, 25.0, 50.0 and 100.0 mmol·L^{-1} (aged solutions)

B = 12.5 mmol·L^{-1}. $-\log_{10} h$, Z: 4.128, 0.1164; 4.193, 0.2162; 4.216, 0.3167; 4.228, 0.4173; 4.245, 0.5169; 4.257, 0.6183; 4.272, 0.7172: 4.287, 0.8192: 4.301, 0.9199; 4.313, 1.021; 4.328, 1.122; 4.343, 1.222; 4.362, 1.323; 4.382, 1.422; 4.404, 1.523

B = 25.0 mmol·L^{-1}. $-\log_{10} h$, Z: 3.968, 0.1148;b 4.059, 0.2146; 4.093, 0.3150; 4.113, 0.4155; 4.127, 0.5160; 4.141, 0.6166; 4.157, 0.7172; 4.172, 0.8176; 4.188, 0.9182; 4.198, 1.019; 4.213, -1.120; 4.228, 1.220; 4.243, 1.321; 4.262, 1.424; 4.287, 1.525

B = 50.0 mmol·L^{-1}. $-\log_{10} h$, Z: 3.819, 0.1135; 3.915, 0.2136; 3.966, 0.3138; 3.994, 0.4746; 4.010, 0.5149; 4.027, 0.6156; 4.042, 0.7163: 4.057, 0.8138: 4.072, 0.9141: 4.090, 1.014; 4.103, 1.115; 4.117, 1.215; 4.132, 1.315; 4.150, 1.415; 4.178, 1.516

B = 100.0 mmol·L^{-1}. $-\log_{10} h$, Z: 3.643, 0.1124; 3.753, 0.2122; 3.822, 0.3124; 3.863, 0.4125; 3.885, 0.5128; 3.903, 0.6132; 3.920, 0.7135; 3.939, 0.8138: 3.953, 0.9138: 3.970, 1.014; 3.985, 1.114; 4.003, 1.215; 4.022, 1.316; 4.041, 1.415; 4.062, 1.515

$$\mathbf{B} = b + \sum_p \sum_q p\beta_{pq} h^{-p} b^q. \tag{7}$$

If **H** and **B** are known from analytical data and h is measured as stated in the previous section, then it is possible to calculate the stability constants β_{pq} of the formed complexes using the appropriate values of p and q [17, 29, 30].

Now, since the $Z(\log_{10} h)_{\mathbf{B}}$ curves shown in Fig. 1 for different values of **B** are parallel, it is apparent that at least one polynuclear complex $\mathrm{Al}_q(\mathrm{OH})_p^{(3q-p)+}$ is formed, so Sillén's core + links hypothesis [20, 21] may be applied.

In order to deduce the sets of parameters (p, q, β_{pq}) for the formed complexes, we treated the $Z(\log_{10} h)_{\mathbf{B}}$ data, Table 2 and Fig. 1, first in terms of the core + links hypothesis and, subsequently, by using the generalized least-squares program LETAGROP [25, 31], whose principles are based on the functional behavior of the minimum error square sum, and the standard deviations in Z and the stability constants, as given in references [17, 29, 30].

The results of these analyses are summarized in Table 3.

3.1 Core + Links Analysis

Systems presenting parallel $Z(\log_{10} h)_{\mathbf{B}}$ curves can be analyzed in terms of a series of species constituted by a central group, denominated core and several hypothetical composite ligands that also contain the central group, referred to as links. This means that the species formed may be written in the core + links form as $\mathrm{Al}(\mathrm{Al}(\mathrm{OH})_t)_n^{3(n+1)-nt}$, where t is a constant not necessarily an integer, and where n may be a unique integer N or a series of n integers such that the product nt is also an integer.

Sillén [20, 21] defined the parameter t, related to the spacing between the parallel $Z(\log_{10} h)_{\mathbf{B}}$ curves, according to Eq. 8:

$$t = -(\delta \log_{10} \mathbf{B} / \delta \log_{10} h)_z. \tag{8}$$

By making several slices at constant Z from our experimental $Z(\log_{10} h)_{\mathbf{B}}$ data, then Fig. 1 displays a plot of $\log_{10} \mathbf{B}$ $(\log_{10} h)_Z$ containing various straight lines (not shown for

232 simplicity), from whose slopes the values of parameter t were obtained, and which are
233 plotted against Z in Fig. 2.
234 As we can see from this figure, the values of t range approximately between $t = 2.0$ for
235 $Z \leq 0.25$ and $t = 2.5$–2.7 for $Z \geq 0.8$.
236 According to the literature (vide supra), one can assume that it is probable that in
237 solution the following species could be present: $Al(Al(OH)_2)_2^{5+}$ ($t = 2$, $p = 4$, $q = 3$) for
238 low Z values and the species $Al(Al(OH)_{2.5})_{12}^{9+}$ ($t = 2.5$, $p = 30$, $q = 13$),
239 $Al(Al(OH)_{2.67})_{12}^{7+}$ ($t = 2.67$, $p = 32$, $q = 13$), and $Al(Al(OH)_{2.83})_{12}^{5+}$ ($t = 2.83$, $p = 34$,
240 $q = 13$) for higher Z values.
24 **AQ3** The $Z(\log_{10} h)_{\mathbf{B}}$ data, Fig. 1, are plotted as Z/t versus x ($= \log_{10} \mathbf{B} - t \log_{10} h$) for $t = 2$,
242 2.5, 2.67 and 2.83, respectively, in Figs. 3, 4, 5, 6.
243 In the first place, it can be seen that for $t = 2$, Fig. 3, the dispersion of the plotted points
244 is very large, although the spread is reduced for $Z \leq 0.25$. This is an indication that, for
245 this interval, at least one $Al(Al(OH)_2)_N^{N+1}$ species ($p = 2 N$, $q = N + 1$) is formed.
246 General balances using Eqs. 6 and 7 yield Eqs. 9 and 10,

$$\mathbf{B} = b + q\beta_{pq}h^{-p}b^q \tag{9}$$

248
$$\mathbf{B}Z = p\beta_{pq}h^{-p}b^q \tag{10}$$

250 and give Eqs. 11 and 12 when they are combined:

$$\mathbf{B}^{(1-q)}Z(1 - qZ/p)^{-q} = p\beta_{pq}h^{-p} \tag{11}$$

252
$$(1-q)\log_{10}\mathbf{B} + \log_{10}Z - q\log_{10}(1 - qZ/p) = \log_{10}(p\beta_{pq}) - p\log_{10}h. \tag{12}$$

254
255 Now, plotting the first member of Eq. 12 as a function of $-\log_{10} h$ for different possible
256 values of p and q, it is found that only for $p = 4$ and $q = 3$ are the points located on a
257 straight line, from which the stability constant of the $[Al_3(OH)_4]^{5+}$ complex was calcu-
258 lated, Table 3 (column 2) reports its stability constant value.

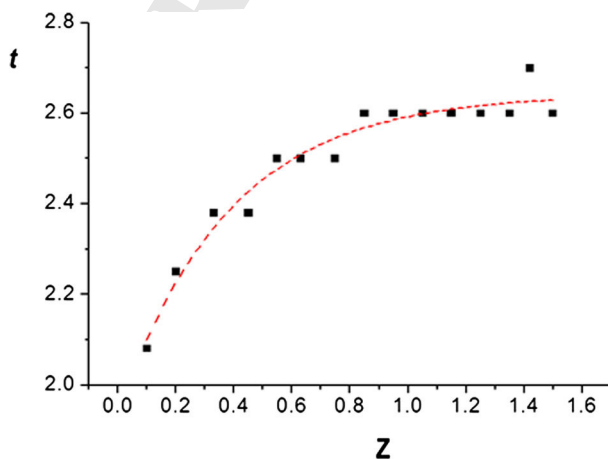**Fig. 2** Plot of the parameter t versus Z, for the system Al^{3+}–OH^- in 3.0 $mol \cdot L^{-1}$ (Na)Cl ionic medium at 25 °C

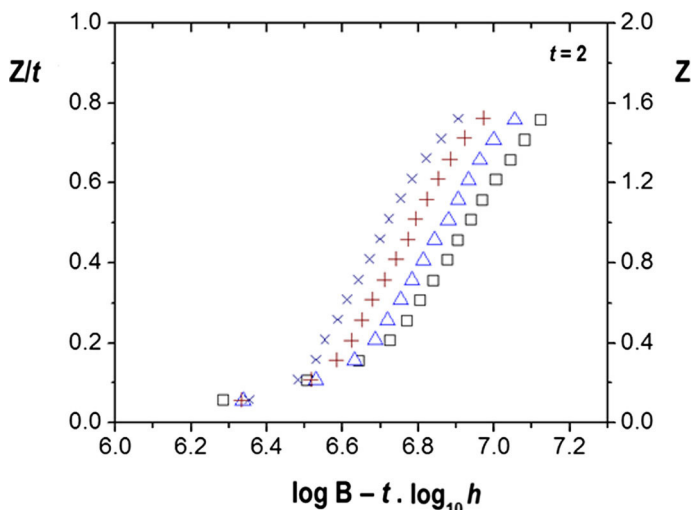J Solution Chem

Fig. 3 **a** Plot of Z/t versus $\log_{10} \mathbf{B} - t \log_{10} h$ for the system Al^{3+}–OH^- in 3.0 mol·L^{-1} (Na)Cl ionic medium at 25 °C, and $t = 2.00$ for $\mathbf{B} = 12.5$ (*square*), 25 (*triangle*), 50 (*plus*) and 100 (*times*) mmol·L^{-1}. **b** Z values are given on the y-axis to the right of the figure
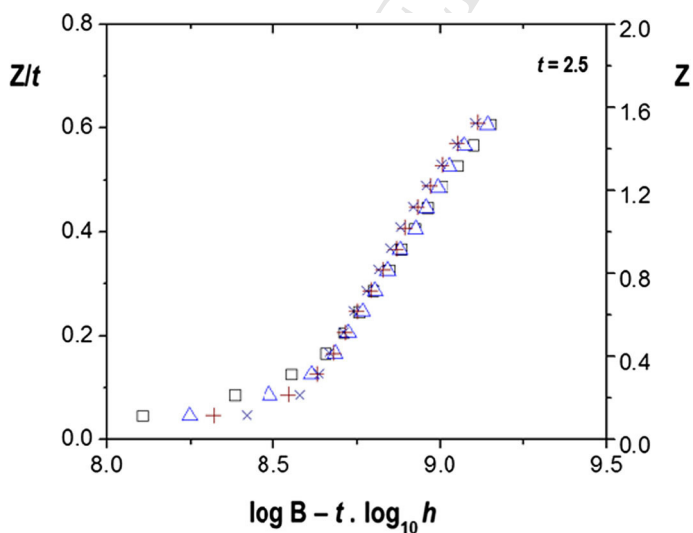

Fig. 4 **a** Plot of Z/t versus $\log_{10} \mathbf{B} - t \log_{10} h$ for the system Al^{3+}–OH^- in 3.0 mol·L^{-1} (Na)Cl ionic medium at 25 °C, and $t = 2.50$ for $\mathbf{B} = 12.5$ (*square*), 25 (*triangle*), 50 (*plus*) and 100 (*times*) mmol·L^{-1}. **b** Z values are given on the y-axis to the right of the figure

259   On the other hand, for $Z \geq 0.8$ and $t = 2.5$, 2.67 and 2.83, Figs. 4, 5, 6, respectively, the
260 dispersion of the points is smaller, the best fit being found for $t = 2.5$ and 2.67, respec-
261 tively. In this case there in an indication that for $Z \geq 0.8$, $Al(Al(OH)_{2.5})_N$ ($t = 2.5$,
262 $p = 2.5\,N$, $q = N + 1$) and/or $Al(Al(OH)_{2.67})_N$ ($t = 2.67$, $p = 2.67\,N$, $q = N + 1$) can
263 be formed, among other possible species.

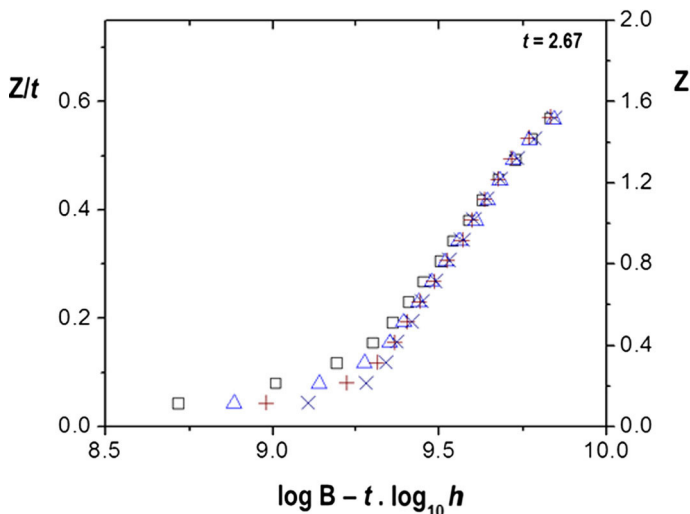**Fig. 5** **a** Plot of Z/t versus $\log_{10} \mathbf{B} - t \log_{10} h$ for the system Al^{3+}–OH^- in 3.0 mol·L^{-1} (Na)Cl ionic medium at 25 °C, and $t = 2.67$ for $\mathbf{B} = 12.5$ (*square*), 25 (*triangle*), 50 (*plus*) and 100 (*times*) mmol·L^{-1}. **b** Z values are given on the y-axis to the right of the figure

Fig. 6 **a** Plot of Z/t versus $\log_{10} \mathbf{B} - t \log_{10} h$ for the system Al^{3+}–OH^- in 3.0 mol·L^{-1} (Na)Cl ionic medium at 25 °C, and $t = 2.83$ for $\mathbf{B} = 12.5$ (*square*), 25 (*triangle*), 50 (*plus*) and 100 (*times*) mmol·L^{-1}. **b** Z values are given on the y-axis to the right of the figure
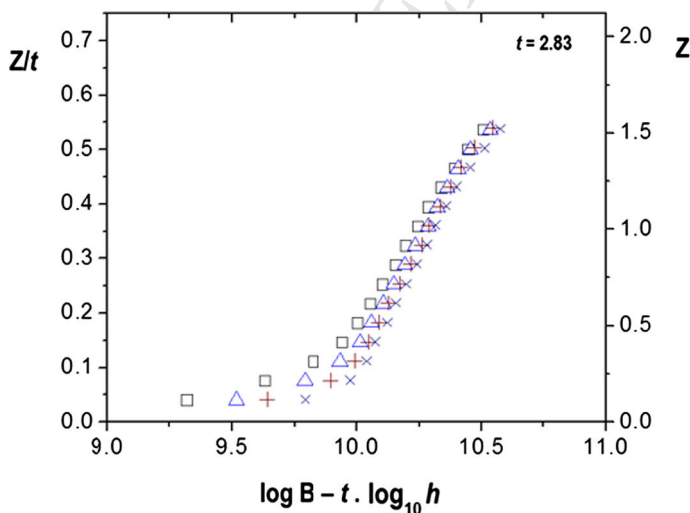
Then, the variable y (= Z/t) ($t = 2.5$ and 2.67) was plotted as the function x (= $\log_{10}$ $\mathbf{B} - t \log_{10} h$) and compared with the $Y(X)$ curves calculated using Eqs. 13 and 14 [20, 21]:

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$$Y = Ng[1 + (N + 1)g]^{-1} \tag{13}$$

268

$$X = N^{-1}\log_{10}g + \log_{10}[1 + (N + 1)g] - \log_{10}N + (1 + N^{-1})\log_{10}(N-1). \tag{14}$$

270
271   It can be seen that Y and X contain only N and the auxiliary variable g, and therefore
272 they are calculated giving the appropriate g values. Thus, a family of curves $Y(X)_N$ (not
273 shown for simplicity) was constructed for $N = 4$–18.
274   A good fit was found between the experimental points $y(x)$ and the calculated theoretical
275 curve $Y(X)$ for $N = 12$ and $t = 2.5$ and 2.67, corresponding to the complexes $[Al_{13}(-$
276 $OH)_{30}]^{9+}$ and $[Al_{13}(OH)_{32}]^{7+}$, respectively.
277   The $\log_{10} \beta_{pq}$ value was found from the lateral translation $(x - X)$ required to make the
278 experimental points coincide with the theoretical calculated curve. Table 3 (columns 3 and
279 4) reports the corresponding stability constant values.
280   Thus, from the analysis of $Z(\log_{10} h)_B$ data in terms of the core + links hypothesis, the
281 following stability constants $\beta_{43} = 10^{-14.1\ (3)}$, $\beta_{3013} = 10^{-104.8\ (2)}$ and $\beta_{3213} = 10^{-113.2\ (1)}$
282 were obtained, whose values are in good agreement with those obtained by LETAGROP
283 (vide infra)

284 ## 3.2 LETAGROP Analysis

285   Next, the $Z(\log_{10} h)_B$ data were analyzed by means of LETAGROP initially using these
286 prior results in terms of the hypothesis core + links (vide supra) analysis.
287   The model core + links formed by the species (3, 4), (30, 13) and/or (32, 13) gives an
288 acceptable $\sigma(Z)$ value, Table 3 (columns 5 and 6), which was improved when species (2, 2)
289 and (34, 13) were added, Table 3 (column 7), but the species (1, 1) was rejected.
290   According to the values of the standard deviation $\sigma(Z) = 0.013$ and the precision $(\pm 3\sigma)$
291 of the stability constants of the species involved, $\beta_{22} = 10^{-7.67\ (3)}$, $\beta_{43} = 10^{-14.34\ (4)}$,
292 $\beta_{3013} = 10^{-104.67\ (5)}$, $\beta_{3213} = 10^{-113.26\ (6)}$ and $\beta_{3413} = 10^{-123.6\ (2)}$, the goodness of fit
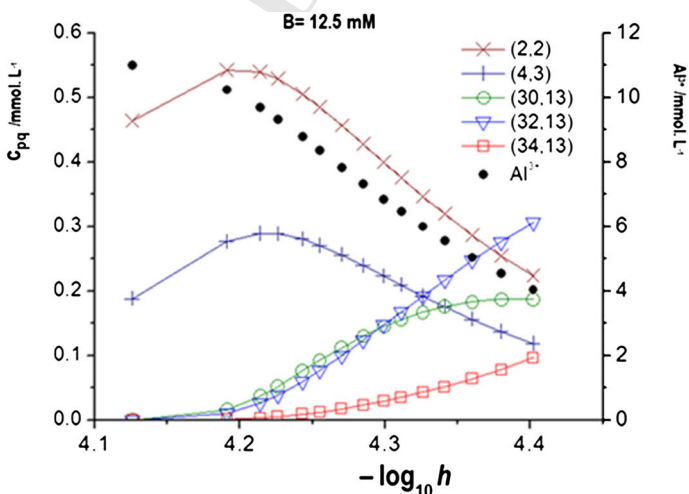

Fig. 7 Species distribution diagram for the system Al^{3+}–OH^- in 3.0 mol·L^{-1} (Na)Cl ionic medium at
25 °C and **B** = 12.5 mmol·L^{-1}

293 between the experimental $Z(\log_{10} h)_\mathbf{B}$ data and the proposed model is really good, such that
294 it satisfactorily explains the Al^{3+} hydrolysis present in our working conditions.

295 The solid lines of Fig. 1 represent the theoretical curves calculated with the stability
296 constants of Table 3 (column 7). Figures 7 and 8 show the species distribution diagram for
297 $\mathbf{B} = 12.5$ and 100 mmol·L^{-1}, respectively.

298 For $\mathbf{B} = 12.5$ mmol·L^{-1} the order of abundance for the complexes with 13 Al atoms is
299 (32, 13) > (30, 13) > (34,13), while for $\mathbf{B} = 100.0$ mmol·L^{-1} the order becomes (30,
300 13) > (32, 13) > (34,13). For the smallest species with 2 and 3 Al atoms the order is
301 always (2, 2) > (4, 3).

302 On the other hand, of the two species (34, 13) and (17, 7) postulated by Biedermann at
303 50 °C, [7], we only detected the first one that is especially abundant for
304 $\mathbf{B} = 12.5$ mmol·L^{-1} and pH ≥4.3, while the second one was not detected.

305 However, a few words must be said about those species, that according to Biedermann's
306 work (see reference 7, Fig. 1, p. 20), when all data for $\mathbf{B} = 5$–50 mmol·L^{-1} in
307 3.0 mol·L^{-1} NaClO$_4$ at 50 °C were plotted in terms of Z versus the variable x (= $\log_{10} \mathbf{B}$ −
308 2.83 $\log_{10} h$), they were fitted quite well in a single curve, giving in this way a great
309 evidence of the validity of his model. Moreover, assuming equilibrium conditions both for
310 the solutions aged at 25 °C (this work), and the solutions at 50 °C (Biedermann's work), it
311 can be seen that when increasing the temperature, there is a remarkable change in the value
312 of the stability constant of the (34, 13) species, which varies from $\beta_{34,13} = 10^{-122.6}$
313 (25 °C) to $10^{-97.6}$ (50 °C).

314 A similar effect is observed in Baes and Mesmer's work (Table 1, columns 3–5) [9, 10]
315 where with the change of temperature from 99.6 to 149.8 °C, for example, the values of the
316 stability constant of the species (32, 13) increases considerably from $\beta_{32,13} = 10^{-64.3}$
317 (99.6 °C) to $10^{-43.9}$ (149.8 °C).
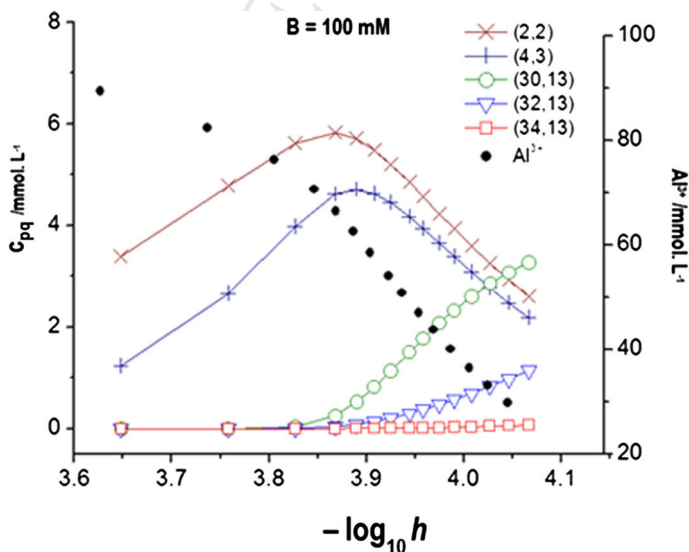
Fig. 8 Species distribution diagram for the system Al^{3+}–OH^- in 3.0 mol·L^{-1} (Na)Cl ionic medium at 25 °C and $\mathbf{B} = 100.0$ mmol·L^{-1}

Table 3 Equilibrium constants for Al(III) hydrolysis in 3.0 mol·L^{-1} (Na)Cl at 25 °C (aged solutions) according to reactions (1) (this work)

Species	$-\log_{10} \beta_{pq}$ (3σ)					
[AlOH]$^+$						(>6.1)
[Al$_2$(OH)$_2$]$^{4+}$						7.67 (3)
[Al$_3$(OH)$_4$]$^{5+}$	14.1 (3)			14.16 (4)	14.14 (6)	14.36 (4)
[Al$_{13}$(OH)$_{30}$]$^{9+}$		104.8 (2)		104.73 (3)	104.74 (5)	104.67 (5)
[Al$_{13}$(OH)$_{32}$]$^{7+}$			113.2 (1)	113.6 (1)	113.50 (7)	113.26 (6)
[Al$_{13}$(OH)$_{34}$]$^{5+}$						123.6 (2)
t	2.00	2.50	2.67			
σ(Z)				0.020	0.016	0.013
Method	*core + links*				LETAGROP	
ks/errors				=0	≠0^a	≠0^b

^{a} Errors in E_0 = −0.1, 0.0, −0.1, 0.2 mV, and **H** = 0.0, 0.0, 0.2, 1.2 mmol·L^{-1}

^{b} Errors in E_0 = −0.1, 0.1, 0.1, 0.3 mV, and **H** = 0.4, 0.3, −0.3, 2.63 mmol·L^{-1}

318 On the other hand, none of the three species (15, 6), (20, 8) and (33, 13) proposed by
319 Brosset et al. [19], the likely species (20, 8) considered by Akit et al. [13], or the four
320 species (2, 1), (x, 2), (36, 13) and (3.1) suggested by Bottero et al. [14] were detected in our
321 measurements.

322 Definitely, our conclusion is that in 3.0 mol·L^{-1} NaCl ionic medium at 25 °C, in
323 solutions aged for 15 days, the main species are [Al$_2$(OH)$_2$]$^{4+}$, [Al$_3$(OH)$_4$]$^{5+}$, [Al$_{13}$(-
324 OH)$_{30}$]$^{9+}$, [Al$_{13}$(OH)$_{32}$]$^{7+}$ and [Al$_{13}$(OH)$_{34}$]$^{5+}$ over the whole ranges studied by us, that is
325 12.5 ≤ **B** ≤ 100 mmol·L^{-1} and 0.1 ≤ Z ≤ 1.5.

326 Complex (2, 2) must have a structure consisting of two AlO$_6$ octahedra sharing an edge with two
327 shared OH$^-$ groups, that is (H$_2$O)$_4$Al(OH)$_2$Al(H$_2$O)$_4^{4+}$, as inferred from the crystal structure of the
328 [Al$_2$(OH)$_2$(H$_2$O)$_8$]$^{4+}$ complex [15], or else a linear structure with two AlO$_6$ octahedra sharing an OH$^-$
329 bridge, that is (H$_2$O)$_5$Al(OH)AlOH(H$_2$O)$_4^{4+}$ (H$_2$O)$_5$Al(OH)AlOH(H$_2$O)$_4^{4+}$. By analogy,
330 complex (4, 3) must possess a similar structure with three octahedra sharing two edges with
331 two OH$^-$ groups for each of them, that is, (H$_2$O)$_4$Al(OH)$_2$Al(H$_2$O)$_2$(OH)$_2$Al(H$_2$O)$_4^{5+}$, or else
332 a linear structure consisting of three AlO$_6$ octahedra sharing two OH$^-$ bridges, that is
333 (H$_2$O)$_4$AlOH(OH)Al(H$_2$O)$_4$(OH)AlOH(H$_2$O)$_4^{5+}$.

334 On the other hand, the three homonuclear (30, 13), (32, 13) and (34, 13) species should
335 have structures with 12 AlO$_6$ octahedra with shared edges and OH$^-$ groups arranged
336 regularly around an AlO$_4$ tetrahedron, as deducted from the crystal structure of the
337 [Al$_{13}$(OH)$_{32}$(H$_2$O)$_{12}$]$^{7+}$ complex [16].

338 This model coincides with that of Baes and Mesmer [9, 10], partially with those of
339 Aveston [8], Öhman-Forsling [11], Biedermann [7] and other studies quoted in the
340 Introduction, in spite of the very different conditions used for most of these researchers'
341 work.

342 The novelty of our experimental approach was working in the area Z ≤ 1.5, quite far
343 from where very slow reactions of basic salts precipitation take place, covering a wide
344 range of Al(III) concentrations, using solutions aged for several days, and conducting the
345 final emf(H) measurements after the system had reached equilibrium, that is, when the pH
346 did not change over time.

347 In particular, for the $Z \gg 1.5$ area of disagreement among various authors, the three
348 homonuclear (30, 13), (32, 13) and (34, 13) complexes should predominate at $Z = 2.31$,
349 2.46 and 2.62, respectively, but whose much higher values purposely did not cross the
350 $Z = 1.5$ barrier at pH = 4.1–4.6, to avoid the region where slow precipitation of basic salts
351 takes place. However, for $Z \leq 1.5$ there is still sufficient quantity of the three species
352 present to allow fairly accurately determination of the corresponding stability constants.
353 Therefore, one can say that in our working conditions, the proposed model fully and
354 satisfactorily explains hydrolysis of the Al^{3+} ion.
355 Finally, we should add that our fundamental interest in studying Al^{3+} hydrolysis is that,
356 at the present time, we are also carrying out several studies of its reactions with ligands L
357 of different structure, and therefore we need to characterize the hydrolysis in order to
358 properly subtract the concentrations of $Al_q(OH)_{pr}]^{(3q-p)}$ species from the total system
359 contribution $Al_q(OH)_p]^{(3q-p)} + Al_x(OH)_y L_r]^{(3x-y)+}$ under similar experimental conditions
360 [25].

361 4 Conclusions

362 The hydrolysis of the Al^{3+} ion was studied by means of emf(H) measurements in
363 3.0 mol·L^{-1} NaCl ionic medium at 25 °C, in solutions aged 15 days, at total Al(III)
364 concentration $\mathbf{B} = 0.0125$–0.1000 mol·L^{-1}, and average number of bound OH^- or
365 released H^+ per Al atom $Z = 0.1$–1.5; the results show that the main species presents are
366 $[Al_2(OH)_2]^{4+}$, $[Al_3(OH)_4]^{5+}$ and the three homonuclear complexes $[Al_{13}(OH)_{30}]^{9+}$,
367 $[Al_{13}(OH)_{32}]^{6+}$ and $[Al_{13}(OH)_{34}]^{7+}$, and that this model fully explains hydrolysis of the
368 Al^{3+} ion.
369 For $\mathbf{B} = 0.012.5$ mol·L^{-1} the relative abundance for the complexes with 13 Al atoms is
370 (32, 13) > (30, 13) > (34, 13), while for $\mathbf{B} = 0.1000$ mol·L^{-1} the order becomes (30,
371 13) > (32, 13) > (34, 13). For the smallest species with 2 and 3 Al atoms the order is
372 always (2, 2) > (4, 3).
373 The stability constants obtained from the core + links hypothesis are in good agreement
374 with those obtained by using LETAGROP.
375 In dealing with solution equilibria, in order to find the stoichiometry and the stability
376 constants of the species formed, is very important to initially analyze the experimental data
377 by appropriate graphical methods, and subsequently by least-squares programs.
378 The aging method described here for Al^{3+} hydrolysis is recommended for studying
379 systems where slow reactions take place at ambient temperature, as well using wide ranges
380 of reactant concentrations and appropriate concentration ratios between them.

386

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