

# Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 14. Speciation and Equilibria in the Aluminium(III)-Lactic Acid-OH<sup>-</sup> System

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Three-component equilibria between H<sup>+</sup>, aluminium (III) and lactic acid (CH<sub>3</sub>CH(OH)COOH, HL) were studied by means of potentiometric (glass electrode) titrations at 25 °C in an ionic medium of 0.6 M NaCl. The total concentrations of aluminium, *B*, and lactic acid, *C*, were varied within the limits 0.010 ≥ *B* ≥ 0.001 M and 0.035 ≥ *C* ≥ 0.0025 M and the ratios *C/B* between 30 ≥ *C/B* ≥ 1. Data with *Z<sub>c</sub>* ≤ 0.95 (where *Z<sub>c</sub>* is the average number of OH<sup>-</sup> reacted per *C*) were explained with the following species (defined according to the reaction  $p\text{H}^+ + q\text{Al}^{3+} + r\text{HL} \rightleftharpoons \text{H}_p\text{Al}_q(\text{HL})_r^{p+3q}$ ;  $\beta_{pqr}$ ) and corresponding equilibrium constants:  $\text{AlL}^{2+}$ ,  $\lg \beta_{-111} = -1.21 \pm 0.017$ ;  $\text{AlL}_2^+$ ,  $\lg \beta_{-212} = -2.72 \pm 0.028$ ;  $\text{AlL}_3$ ,  $\lg \beta_{-313} = -4.92 \pm 0.14$ ; and  $\text{Al}(\text{H}_{-1}\text{L})\text{L}$ ,  $\lg \beta_{-312} = -6.17 \pm 0.012$ . The standard deviations were  $3\sigma(\lg \beta_{pqr})$ . The carboxylic acid dissociation constant  $\text{HL} \rightleftharpoons \text{H}^+ + \text{L}^-$  was studied in separate titrations and was found to be  $\lg \beta_{-101} = -3.572 \pm 0.001$ . Data were analyzed with the least-squares computer program LETAGROPV-RID.

During the last decades, precipitation in the industrialized parts of the world has become increasingly acidic due to the extensive use of sulfur-containing fossil fuels. In areas of poorly buffered bedrocks (e.g. northeastern North America and Scandinavia) this has resulted in a marked increase in the geochemical mobility of aluminium. The resulting elevated aluminium concentrations in stream and lake waters have been shown to cause severe damage to fish and other biota.<sup>1</sup> In fact, according to the SWAP\*\* background document,<sup>2</sup> "the most important ecological effect of increasing the acidification of surface waters is the mobilization of aluminium which is toxic to aquatic life". Recently, in-

creased aluminium concentrations have also been shown to be connected to two human pathological conditions. Specific increased aluminium levels have been detected in Alzheimer's disease, the prevalent form of senile dementia, and dialysis encephalopathy, resulting from renal dialysis.<sup>3</sup> However, neither in aquatic systems nor in terrestrial organisms, has any direct correlation been found between total aluminium loading and toxicity. Thus, in lakes and streams containing high concentrations of dissolved organic carbon (humic substances), fish production can commence at considerably higher aluminium concentrations than in lakes with low DOC. It has also been shown in a laboratory experiment that aluminium became nontoxic to fish when an excess of citrate was added to the water.<sup>4</sup> On the contrary, Slanina *et al.*<sup>5</sup> have recently shown that rats fed on an aluminium-rich diet accumulated aluminium in the brain and bone tissue when aluminium was administered as citrate, but not when it was administered as hydroxide. An understand-

\*\*SWAP: Surface Waters Acidification Programme. A joint project among the Royal Society of London, the Norwegian Academy of Science and Letters and the Royal Swedish Academy of Sciences.

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ing of these coupled processes definitely necessitates a knowledge of the complexation behaviour of aluminium with respect to ligands occurring in appreciable amounts in natural water systems. Unfortunately, however, the strong tendency of the aluminium ion to undergo complex hydrolytic reactions has discouraged most investigators from performing measurements at pH values higher than  $\sim 3$ . Therefore, predictions of aluminium speciation in most natural systems suffers from large uncertainties since measurements performed in strongly acidic solutions are used to predict speciation at nearly neutral conditions. In a current project at this department, we are systematically investigating the ability of Al(III) to form complexes with ligands of relevance to natural water conditions. Within the project, special efforts are made to detect the possible formation of mixed hydroxo complexes, likely to occur in nearly neutral solutions.

The aim of the present investigation was to interpret complexation in the  $H^+ - Al^{3+}$ -lactic acid(HL) system. Being a metabolite in the microbial pathway of anaerobic fermentation, lactic acid has been found as a common constituent both in litter decay products as well as in reducing marine sediments. Also in the blood plasma of man, lactic acid constitutes one of the most important metal chelating components. However, due to the slow and complicated complexation behaviour registered in nearly neutral solutions, the present paper describes a model valid only for  $Z_c \leq 0.95$  ( $Z_c$  is defined as the average number of  $OH^-$  reacted per HL). The work at higher  $Z_c$  is well advanced and these results will be presented in the near future.

## Experimental

### *Chemicals and analysis*

Sodium chloride (Merck *p.a.*) was dried at  $180^\circ C$  and used without further purification. Dilute hydrochloric acids (Merck *p.a.*) were standardized against tris(hydroxomethyl)aminomethane (Trizma-base). Sodium hydroxide solutions were prepared from 50% aqueous NaOH and standardized against hydrochloric acid. DL-lactic acid (2-hydroxy-propanoic acid), (BDH), was distilled under vacuum and immediately diluted to  $\sim 1$  M to avoid polymerisation. The content of

the diluted lactic acid was determined potentiometrically.

Stock solutions of aluminium chloride were prepared by dissolving  $AlCl_3 \cdot 6H_2O$  (Fisher *p.a.*) in standardized hydrochloric acid. The stock solutions were filtered through a Jena G4 glass filter in order to remove dust particles and then carefully tested for impurities, especially Fe(III) and Si(IV). Tests for these ions were negative. The Al(III) content ( $\sim 0.1$  M) of the stock solutions was determined by precipitation with 8-hydroxy-quinoline according to Kolthoff<sup>6</sup> and by indirect titration with  $EDTA - Pb(NO_3)_2$  using xylenol orange as indicator. The agreement between these two methods was within 0.2%. The  $Cl^-$  content of the stock solutions was determined as  $AgCl$  in a potentiometric (Ag,  $AgCl$  electrode) titration using the Gran extrapolation method<sup>7</sup> to evaluate the equivalence point. The difference in  $[Cl^-]$  between this determination and the value obtained from the sum  $[H^+] + 3[Al^{3+}]$  was less than 0.2%. All solutions were prepared using distilled and boiled water.

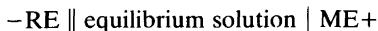
### *Apparatus*

The potentiometric titrations were performed with an automatic system for precise emf titrations constructed and built at this institute by O. Ginstrup.<sup>8</sup> The measurements were made at  $25.00 \pm 0.05^\circ C$ . The cell arrangement, which was immersed in an oil thermostat, was similar to that described by Forsling *et al.*<sup>9</sup> During the experiments, a stream of argon was bubbled through the solution for stirring and for maintaining an inert atmosphere. The gas, from a cylinder, was first bubbled through solutions of 10% NaOH and 10%  $H_2SO_4$  to remove acid and alkaline impurities. Finally, before the gas came into contact with the equilibrium solution, it was passed through a pure ionic medium. The Ag,  $AgCl$  electrodes were prepared according to Brown;<sup>10</sup> the glass electrodes were of the Ingold 201-NS type.

### **Method**

The present investigation was carried out through a series of titrations at  $25^\circ C$ . In order to avoid activity coefficient variations, a constant ionic medium of 0.6 M  $NaCl$  was used. The

free  $H^+$  concentration,  $h$ , was determined by measuring the emf of the cell:



where ME denotes a glass electrode and RE = Ag, AgCl | 0.6 M NaCl. Assuming the activity coefficients to be constant, expression (1) is valid for the measured emf:

$$E = E_o + 59.157 \lg h + E_i \quad (1)$$

where  $E_o$  is a constant determined at each titration. For the liquid junction potential, we have used  $E_i = -77h + 42k_w h^{-1}$  mV,<sup>12</sup> where  $k_w = 1.875 \cdot 10^{-14}$  M<sup>2</sup> is the ionic product of water in 0.6 M NaCl. As the carboxylic pKa for lactic acid is too low to permit the customary procedure in calibrating the electrode,<sup>11</sup> the following titration procedure was used: to  $V_o$  ml of  $\sim 10$  mM HCl in 0.6 M NaCl, approximately 6 successive additions of  $OH^-$  with intervening emf recordings were made until the solution was nearly neutralized. Then,  $V_i$  ml of HL or  $Al^{3+}/HL$  solution was added to the vessel and the titration continued. With this procedure, the electrode calibration could be evaluated as the mean of several measurements within the titration which, in our opinion, gave a more accurate calibration than by using separate solutions of known  $H^+$  concentration.

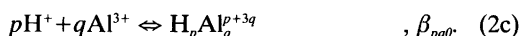
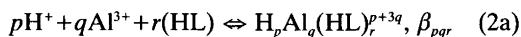
The binary titrations concerning the acidity constant of lactic acid were performed in separate experiments ( $B = 0$ ) within the concentration range 0.041–0.008 M covering the  $-\lg h$  range 2.5  $\leq -\lg h \leq 5.7$ . No attempts were made to evaluate the hydroxylic acidity constant of lactic acid. During the three-component titrations, the ratio between the total concentration of aluminium,  $B$ , and lactic acid,  $C$ , was held constant. The initial concentrations of  $B$  and  $C$  were varied within the limits  $0.010 \geq B \geq 0.001$  M and  $0.035 \geq C \geq 0.0025$  M, covering the  $C/B$  ratios 1, 2, 3, 5, 10, 15 and 30.

The present study was limited to  $Z_c \leq 0.95$  and  $2 \leq -\lg h \leq 5$ . Within these ranges, rapid equilibria were attained. At higher  $Z_c$  and  $-\lg h$  values, the reactions are characterized by slow kinetics and the conventional titration technique was not found suitable. Instead, point solutions were prepared and allowed to equilibrate. The measure-

ments showed that equilibration times amounting to several weeks were necessary. The results of these measurements will be presented in a forthcoming publication.

#### Data treatment

Assuming the presence of three-component equilibria of the general form (2a) besides the two-component equilibria (2b) and (2c), we have:



The law of mass action and the conditions for the total concentrations then give equations 3–5, where  $b = [Al^{3+}]$  and  $c = [HL]$ . The summation is then taken of all species formed where  $\beta_{pqr}$ ,  $\beta_{-101}$ , and  $\beta_{pq0}$  are the equilibrium constants for the reactions 2a, 2b and 2c, respectively.

$$H = h - \beta_{-101} h^{-1} c + \frac{\sum p \beta_{pqr} h^p b^q}{\sum p \beta_{pqr} h^p b^q c^r - k_w h^{-1}} \quad (3)$$

$$B = b + \sum q \beta_{pqr} h^p b^q + \sum q \beta_{pq0} h^p b^q c^r \quad (4)$$

$$C = c + \beta_{-101} h^{-1} c + \sum r \beta_{pqr} h^p b^q c^r \quad (5)$$

For the two-component hydrolysis equilibria according to eqn. (2c), we used the results obtained by Öhman and Forsling.<sup>13</sup> The computational problem involved determination of sets of pqr triplets and the corresponding equilibrium constants that “best” fit the experimental data. In the calculations, the least-squares computer program LETAGROPVRID<sup>14</sup> (version ETITR<sup>15</sup>) was used. The “best” model or models were those giving the lowest sum of the errors squares,  $U = \sum [H_{\text{calc}} - H_{\text{exp}}]^2$ . The LETAGROP calculations also gave the standard deviations  $\sigma(H)$ ,  $\sigma(\beta_{pqr})$  and  $3\sigma(\lg \beta_{pqr})$ . For the definitions of errors, the reader is referred to Sillén.<sup>16</sup> The computations were performed on a Cyber 172 computer.

#### Data, calculations and results

##### The $H^+$ -lactic acid system

The data used to determine the carboxylic acidity constant of lactic acid comprise 18 titrations and

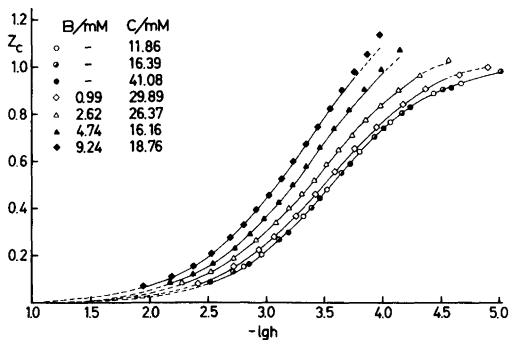


Fig. 1. A part of experimental data plotted as  $Z_c(-lgh)$ . The full curves have been calculated using the set of proposed constants. The broken curves denote an extrapolation of the present model.

630 experimental points. The analysis gave  $\lg(\beta_{-101} \pm 3\sigma) = -3.572 \pm 0.001$  with  $\sigma(H) = 0.09$  mM.

*The  $H^+ - Al^{3+}$ -lactic acid system*

In order to visualize the experimental results,  $Z_c$  for each point in a titration was calculated using equation (5).

$$Z_c = (h - H - k_w h^{-1}) / C \tag{5}$$

This is the average number of  $OH^-$  reacted per

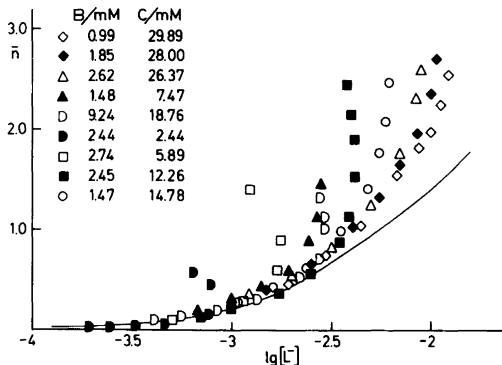


Fig. 2. Experimental data plotted as curves  $\bar{n}(\lg[L^-])$ . The full curve has been calculated with  $\lg \beta_{-111}$ ,  $\lg \beta_{-212}$  and  $\lg \beta_{-313}$  according to Table 1.

$C$ . The experiments thus provided sets of data for  $Z_c(-lgh)$  at constant  $C/B$ . Such a plot is shown in Fig. 1. As can be seen from this figure, the different  $Z_c$  curves do not show limiting values at  $Z_c = 1$ . This is direct proof that mixed hydroxo complexes, or species where the  $OH$  group of the lactate ion is deprotonated, are formed. In an attempt to find out whether specified ranges exist where the formation of binary  $Al^{3+} - L^-$  complexes prevail,  $\bar{n}(\lg[L^-])$  curves were plotted (see Fig. 2), where  $\bar{n}$  corresponds to the average number of ligands bound per  $Al$ . Coinciding curves are found if predominating mononuclear  $AlL_n$

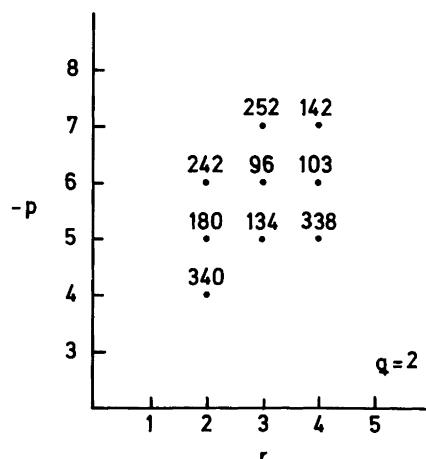
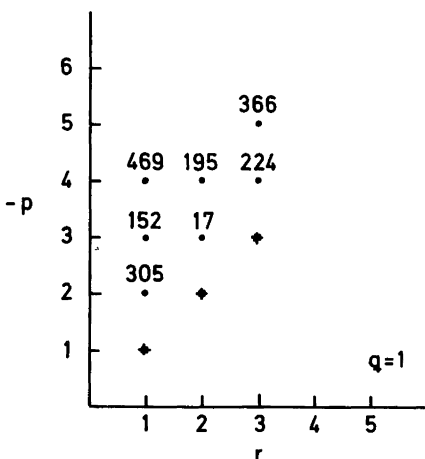


Fig. 3. The LETAGROP search for ternary  $H_p Al_q (HL)_r^{p+3q}$  complexes. The diagrams give error square sums  $U \times 10$  when one new ternary complex is varied together with  $(-3,1,3)$ . In the calculations,  $(-1, 1, 1)$  and  $(-2, 1, 2)$  and aluminium hydrolysis are assumed to be known.

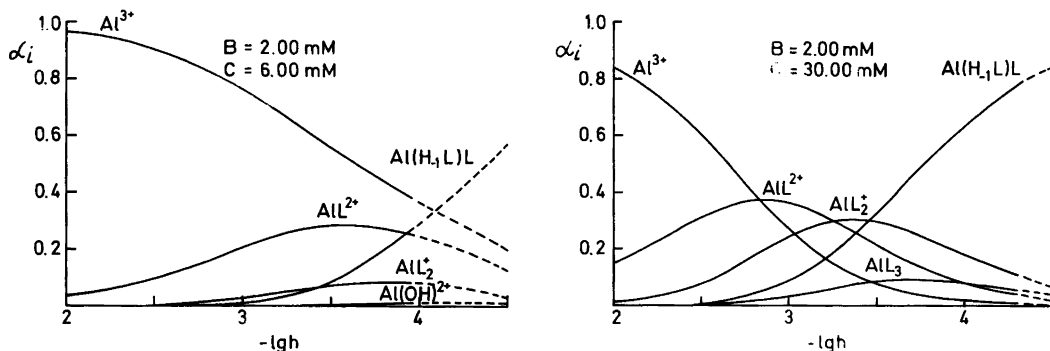


Fig. 4. Distribution diagrams  $\alpha_i(-\lg h)$  where  $\alpha_i$  is defined as the ratio between aluminium(III) in a species and total aluminium(III). The calculations have been performed using the computer program SOLGASWATER with constants given in Table 1. The broken curves denote extrapolated values.

complexes are formed. Accordingly in Fig. 2, an approximate limiting curve with  $\bar{n} \leq 1.5$  characterized by the  $B-C$  combination 0.99–29.89 mM can be seen. Data from this curve were used to evaluate the stability of the different  $AlL_n$  species ( $n = 1, 2, 3$ ). The following results were obtained:  $\lg\beta_{-111} = -1.18 \pm 0.03$ ;  $\lg\beta_{-212} = -2.84 \pm 0.16$ ; and  $\lg\beta_{-313} = -4.10 \pm 0.09$ . However, by calculating the values of the stepwise constants, it was found that  $\lg k_3(2.31) \sim \lg k_{-1}(2.39) > \lg k_2(1.91)$ . This high stability of  $AlL_3$ , compared to  $AlL^{2+}$  and  $AlL_2^+$ , probably is an artifact originating from difficulties in finding the proper “mononuclear wall”. In the search for composition ( $p, q, r$ ) and stability ( $\beta_{p,q,r}$ ) of the ternary species,  $\beta_{-313}$  was covaried with  $\beta_{p,q,r}$  to eliminate any misinterpretation due to this uncertainty. A trial and error procedure with the LE-TAGROPVRID program, called pqr analysis, was used to evaluate the ternary complexes. The principle behind this method is that complexes of different pqr compositions have been tested successively, one by one, and the complex that gives the lowest error square sum,  $U = \sum [H_{\text{calc}} - H_{\text{exp}}]^2$ , is considered to be the “best”. If there are still systematic deviations between calculated and experimental values of  $Z_c$ , additional complexes must be included and combinations of two and more pqr sets must be tested. The result of this analysis is given in Fig. 3. It was found that the lowest value of  $U$  was obtained for the complex  $Al(H_{-1}L)L$  with  $\lg(\beta_{-312} \pm 3\sigma) = -6.16 \pm 0.012$ , and  $\lg(\beta_{-313} \pm 3\sigma) = -4.86 \pm 0.16$ ;  $\sigma(H)$  ended at 0.08 mM.

It was not necessary to add any more com-

plex(es) to the model because the complex  $Al(H_{-1}L)L$  alone could explain the data. Thus, in the area  $Z_c \leq 0.95$ , our final proposal for the complexation consists of the species  $AlL^{2+}$ ,  $AlL_2^+$ ,  $AlL_3$  and  $Al(H_{-1}L)L$ . The final equilibrium constants, given in Table 1, were obtained by a covariation on the whole data set. The  $\sigma(H)$  value obtained in this calculation was 0.08 mM. No systematic deviations remained, with this set of equilibrium constants.

In order to visualize the amounts of the different species, we used the computer program SOLGASWATER,<sup>17</sup> equipped with plotting procedures, to calculate some distribution diagrams. These are presented in Fig. 4.

## Discussion

At  $-\lg h \leq 4.5$ , the speciation of the present Al system is characterized by a series of  $AlL_n^{3-n}$  com-

Table 1. Binary and ternary complexes in the  $H^+ - Al^{3+}$ -lactic acid(HL) system. The formation constants ( $\beta_{pqr}$ ) are defined according to the reaction  $pH^+ + qAl^{3+} + rHL \rightleftharpoons H_pAl_q(HL)_r^{p+3q}$

No. of titr./ No. of points	$pqr$	Proposed formula	$\lg(\beta_{pqr} \pm 3\sigma)$
18/630	-1 0 1	$L^-$	$-3.572 \pm 0.001$
16/444	-1 1 1	$AlL^{2+}$	$-1.21 \pm 0.017$
	-2 1 2	$AlL_2^+$	$-2.72 \pm 0.028$
	-3 1 3	$AlL_3$	$-4.92 \pm 0.14$
	-3 1 2	$Al(H_{-1}L)L$	$-6.17 \pm 0.012$

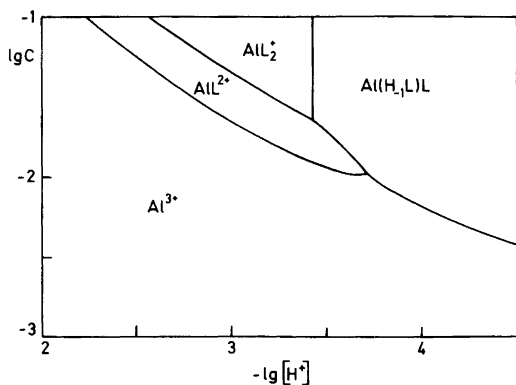


Fig. 5. Predominance area diagram for the different aluminium(III)-lactic acid complexes. The calculation is performed at a total aluminium(III) concentration of 2.00 mM using the computer program SOLGASWATER.

plexes ( $n = 1, 2, 3$ ) and one ternary species  $\text{Al}(\text{H}_{-1}\text{L})\text{L}$ . According to a predominance area diagram,  $\text{AlL}_2^{2+}$ ,  $\text{AlL}_3$  and  $\text{Al}(\text{H}_{-1}\text{L})\text{L}$ , all predominate within specified ranges as shown in Fig. 5. The standard deviations ( $3\sigma(\lg\beta_{\text{par}})$ ) of the corresponding formation constants are better than 0.03 units, which shows that composition and stability of these species are well determined. On the other hand,  $\text{AlL}_3$  is formed in small amounts (<10% B, see Fig. 4), which explains the rather high uncertainty in its formation constants (cf. Table 1).

The values of the stepwise constants ( $\lg k_1 = 2.36$ ,  $\lg k_2 = 2.06$  and  $\lg k_3 = 1.37$ ) show the different  $\text{Al}^{3+}-\text{L}^-$  species to be of intermediate stability, i.e. a 5–10-fold excess of ligand is necessary to yield significant amounts of  $\text{AlL}_2^{2+}$  and  $\text{AlL}_3$ , see Fig. 5. A comparison between the present results and those reported by Hurnik (20°C, 0.2 M  $\text{NaNO}_3$ )<sup>18</sup> shows a good agreement in  $\lg k_1$  (2.38) and  $\lg k_2$  (2.18). However, Hurnik claimed the stability of the  $\text{AlL}_3$  complex ( $\lg k_3 = 2.11$ ) to be of the same magnitude as for  $\text{AlL}_2$ . This high value is probably due to the fact that the formation of ternary species, e.g.  $\text{Al}(\text{H}_{-1}\text{L})\text{L}$  was neglected.

To find out whether the lactate ion acts as a mono or bidentate ligand, corresponding stepwise constants with propionate (monodentate) and oxalate (bidentate) were looked for. For propionate,<sup>19</sup> a value of  $\lg k_1$  equal to 1.69 was found, while the corresponding value for oxalate<sup>20</sup> was

5.97. Since  $\lg k_1 = 2.36$  for lactate, it seems plausible to suggest that the undissociated hydroxyl group forms a weak bond in bidentate sites of the different  $\text{AlL}_n^{3-n}$  complexes.

An answer to the question whether the (-3, 1, 2) species is a mixed hydroxo complex ( $\text{Al}(\text{OH})\text{L}_2$ ) or a complex where the OH group in the lactate ion is deprotonated, cannot be given from present data. However, by comparing acidity constants of different  $\text{Al}^{3+}-\text{L}$  complexes where mixed hydroxo species have been postulated, some conclusions can be drawn. With the ligands salicylate,<sup>21</sup> pyrocatechol<sup>22</sup> and 1,2-dihydroxynaphthalene-4-sulfonate,<sup>23</sup> an  $\text{Al}(\text{OH})\text{L}_2^{2-}$  complex was found and acidity constants,  $\text{p}k_a$  ( $\text{AlL}_2(\text{H}_2\text{O})^+$ ) = 7.60, 8.01 and 8.04 were reported. These rather high  $\text{p}k_a$  values, in comparison with  $\text{p}k_a$  ( $\text{AlL}_2$ ) = 3.45 in the present system, indicate that the deprotonation originates from the OH group of the lactate ligand. This hypothesis is supported by findings from the boric acid-lactate system.<sup>24</sup> Here a  $\text{B}(\text{OH})_2\text{L}$  as well as a  $\text{B}(\text{OH})_2(\text{H}_{-1}\text{L})$  complex were found.  $\text{p}k_a$  ( $\text{B}(\text{OH})_2\text{L}$ ) = 3.4 was calculated, a value in good agreement with the corresponding one of the present system. The interpretations of the  $\text{B}(\text{OH})_2$  system were based on IR measurements. Spectra were recorded at pH = 2 and 6, and the absence of a  $\delta\text{OH}$  band at pH = 6 clearly showed a deprotonation of the lactate OH group.

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