

Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 24. A Potentiometric and ^{27}Al NMR Study of Polynuclear Aluminium(III) Hydroxo Complexes with Lactic Acid

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Equilibria between H^+ , aluminium(III) and lactic acid [$\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, HL] were studied within the limits $0.95 \leq Z_c \leq 3.5$; $-\log [\text{H}^+] \leq 5.5$; $0.0003 \leq B \leq 0.010$ M; $0.0007 \leq C \leq 0.010$ M and $1 \leq B/C \leq 5$, where Z_c is the average number of OH^- reacted per HL and B and C stand for the total concentrations of aluminium and lactic acid, respectively. The measurements were performed at 25°C in a constant ionic medium of 0.6 M NaCl. As the attainment of equilibria in this area was very slow, the measurements were performed as batch potentiometric (glass electrode) measurements combined with quantitative ^{27}Al NMR measurements. In addition to the mononuclear aluminium–lactate complexes AlL^{2+} , AlL_2^+ , AlL_3^0 and $\text{Al}(\text{H}_{-1}\text{L})^0$ dominating at $Z_c \leq 0.95$, all data could be explained with the complexes $\text{Al}_2(\text{OH})_2\text{L}^{3+}$, $\text{Al}_2(\text{OH})_2(\text{H}_{-1}\text{L})_2^0$ and a species of high nuclearity which tentatively has been given the composition $\text{H}_{-36}\text{Al}_{13}(\text{HL})_4^{3+}$. Equilibrium constants, defined according to the following reaction



are $\log \beta_{-3,2,1} = -6.86 \pm 0.044$, $\log \beta_{-6,2,2} = -16.79 \pm 0.055$ and $\log \beta_{-36,13,4} = -106.9 \pm 0.25$. The hydrolysis constant for $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ was determined from separate solutions aged for prolonged periods, giving the result $\log \beta_{-32,13,0} = -105.5 \pm 0.20$. Data were analysed with the least-squares computer program LETAGROPVRID. To demonstrate the complexing ability of lactate ions to Al^{3+} , the results of some model calculations are presented and discussed.

In part 14 of this series,¹ equilibria in the three-component system H^+ – Al^{3+} –lactic acid (2-hydroxypropionic acid) were studied in the area $0 \leq Z_c \leq 0.95$, where Z_c is the average number of OH^- reacted per HL. These measurements were performed as potentiometric titrations at 25°C in 0.6 M NaCl medium. The titrations were characterized by rapid attainment of equilibria, and data could all be explained with the mononuclear species AlL^{2+} , AlL_2^+ , AlL_3^0 and $\text{Al}(\text{H}_{-1}\text{L})^0$. It was also found that for $C/B \leq 5$ and $Z_c > 0.95$, additional effects, caused by other soluble ternary species, appeared. As these reactions were characterized by very slow kinetics, with equilibration times of up to several months, the ordinary titration technique did, however, prove inadequate. The present investigation, which aims at interpreting the complexation in this area, is therefore based on data from batch solutions, equilibrated at 25°C in periods of up to 7 months. Since the present measurements are conducted in an area where the slow-forming hydrolytic species $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ can be expected to form, a redetermination of its formation constant under

comparable conditions (i.e. equilibration times of several months) was also performed.

Experimental

Chemicals and analysis. All stock solutions used [NaCl, HCl, NaOH, DL- $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, AlCl_3] were prepared and analyzed as described earlier.¹

Apparatus. The automatic system for precise EMF measurements, the thermostat and the electrodes are fully described in Ref. 1. The calibration of the glass electrode was performed separately in solutions of known $[\text{H}^+]$ before and after each measurement. The turbidimetric measurements were performed using a Hach model 18900 ratio turbidimeter. The ^{27}Al NMR spectra were measured on a Bruker AC-250 spectrometer equipped with a 10 mm multinuclear probehead.

Methods

Potentiometric measurements. Owing to the extreme slowness by which equilibria are attained in this area, the pre-

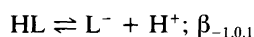
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sent investigation is based on measurements performed on batch solutions. Approximately 30 stock batches of aluminium lactate solutions within the ranges: $0.004 \leq B \leq 0.010$ M; $0.008 \leq C \leq 0.015$ M; $C/B = 1, 2, 3$ and 5 ; $1.2 \leq Z_c \leq 4.0$ (where B and C represent the total concentrations of aluminium and lactic acid, respectively) were prepared and stored for 2 weeks. After that time, turbidimetric measurements were undertaken, and all solutions containing precipitates were discarded. The remaining 19 clear solutions were then used to prepare series of solutions at constant C/B and Z_c by mixing known volumes of the solutions with various volumes of pure ionic medium. Through this procedure, a total of 137 batches were prepared. The attainment of equilibrium in these solutions were followed through repeated measurements of the free H^+ concentration. Depending on C/B and Z_c , the equilibration time varied from a few days up to almost 3 months. The final $-\log [H^+]$ values, on which the present data analysis is based, were obtained from solutions aged for 7 months.

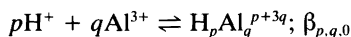
NMR measurements. Time-dependent as well as equilibrium ^{27}Al -NMR measurements were carried out at 295 ± 1 K with the instrument operated in the absolute intensity mode. By calibrating the instrument versus a 5.00×10^{-3} M Al^{3+} solution at $-\log [H^+] = 2.30$, quantitative measures of free Al^{3+} and $\text{AlO}_4[\text{Al}_{12}(\text{OH})_{24}]^{7+}$ were obtained. Owing to the high stability of the spectrometer and the quadrupolar properties of ^{27}Al , resulting in relatively short acquisition times, these spectra were collected without having a D_2O lock on the instrument.

Data treatment. The different types of equilibria which must be considered in the present study can be divided into groups as follows.

(i) The binary lactic acid equilibrium

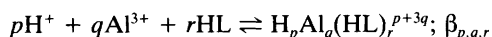


(ii) The hydrolytic equilibria of Al^{3+}



For these equilibria, results evaluated earlier in this series^{1,2} will be used. Dominating species and corresponding equilibrium constants, valid in 0.6 M NaCl medium, are given in Table 1.

(iii) Three-component equilibria of the general form



In part 14 of this series formation constants for complexes appearing in the area of $0 \leq Z_c \leq 0.95$ were determined. These constants are also given in Table 1. In the following calculations all of these constants, except the one for $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$, will be considered as known and no at-

Table 1. Binary and ternary complexes in the three-component system $\text{H}^+ - \text{Al}^{3+} - \text{lactic acid}$. The formation constants are related according to the reaction $p\text{H}^+ + q\text{Al}^{3+} + r\text{HL} \rightleftharpoons \text{H}_p\text{Al}_q(\text{HL})_r^{p+3q}$.

p,q,r	Tentative formula	$\log(\beta_{pqr} \pm 3\sigma)$	Ref.
-1,1,0	$\text{Al}(\text{OH})^{2+}$	-5.52	2
-2,1,0	$\text{Al}(\text{OH})_2^+$	-11.3	2
-3,1,0	$\text{Al}(\text{OH})_3$	-17.3	2
-4,3,0	$\text{Al}_3(\text{OH})_4^{5+}$	-13.57	2
-32,13,0	$\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$	-109.2	2
-4,1,0	$\text{Al}(\text{OH})_4^-$	-23.46	2
-1,0,1	L^-	-3.572 ± 0.001	1
-1,1,1	AlL^{2+}	-1.21 ± 0.017	1
-2,1,2	AlL_2^+	-2.72 ± 0.028	1
-3,1,3	AlL_3^0	-4.92 ± 0.14	1
-3,1,2	$\text{Al}(\text{H}_{-1}\text{L})^0$	-6.17 ± 0.012	1
-32,13,0	$\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$	-105.5 ± 0.20	This work
-3,2,1	$\text{Al}_2(\text{OH})_2\text{L}^{3+}$	-6.86 ± 0.044	This work
-6,2,2	$\text{Al}_2(\text{OH})_2(\text{H}_{-1}\text{L})_2^0$	-16.79 ± 0.055	This work
-36,13,4		-106.9 ± 0.25	This work

tempts to vary them will be made. In the evaluation of the experimental data, the least-squares computer program LETAGROPVRID³ (version ETITR)^{4,5} was used. pqr -triplets and corresponding equilibrium constants that "best" fit the experimental data were determined by minimizing the error squares sum $U = \sum (H_{\text{calc}} - H_{\text{exp}})^2$. The LETAGROP calculations also give standard deviations $\sigma(\text{H})$ and $3\sigma(\log \beta_{pqr})$ defined according to Sillén.^{6,7} The computations were performed on a CD CYBER 850 computer.

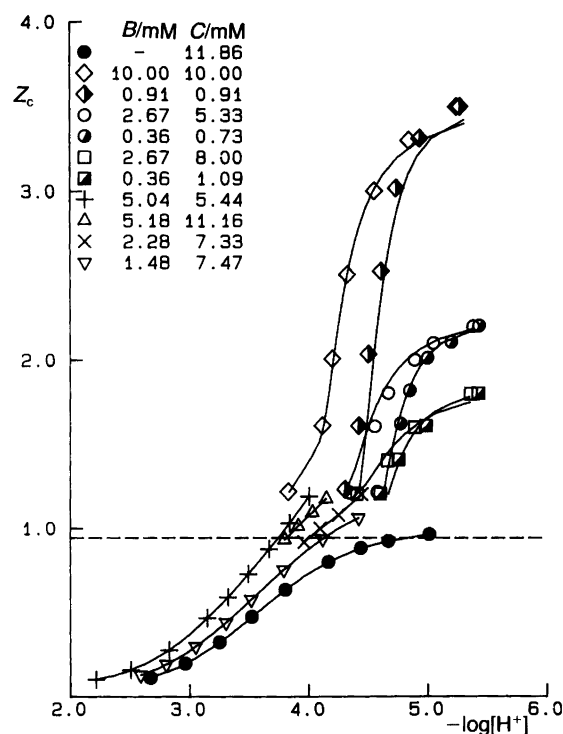


Fig. 1. Experimental data in the $\text{H}^+ - \text{Al}^{3+} - \text{lactic acid}$ system plotted as Z_c vs. $-\log [H^+]$. The drawn curves have been calculated with the equilibrium constants proposed in Table 1.

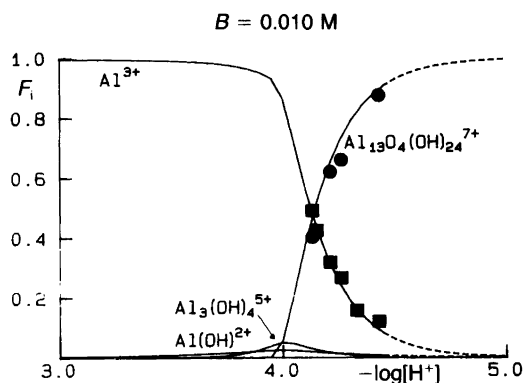


Fig. 2. Distribution diagram $F_i(-\log[H^+])$ in the H^+-Al^{3+} system. F_i is defined as the ratio between aluminium(III) in a species and total aluminium(III). The broken curves denote extrapolated values. Some of the ^{27}Al -NMR measurements are illustrated in the figure.

Data, calculations and results

The analysis of the present data was started by calculating the average number of OH^- groups reacted per C , Z_c , as a function of C , B , C/B and $-\log[H^+]$. Z_c is given by the expression $Z_c = (h - H - k_w h^{-1})/C$, where h denotes the free H^+ concentration, k_w denotes the ionic product of water in 0.6 M NaCl medium and H denotes the total concentration of protons using H_2O , Al^{3+} and HL as zero level. Some of these data are given in Fig. 1.

From the very strong concentration dependence and the "steepness" of these data, it can be concluded that the additional complex/complexes are probably polynuclear. By applying the equilibrium model given in Table 1 to these data, a clear indication of the presence of one or several additional aqueous species was obtained. Through this calculation it was, however, also indicated that the slow-forming hydrolytic species $Al_3(OH)_4^{5+}$ was probably a predominating species in some of the data, especially at low C/B quotients and high Z_c . As such, and as the formation constant used for this species was evaluated from data where it was formed in very minor amounts,⁸ we found it necessary to supplement our data with some binary

H^+-Al^{3+} data from solutions stored and analysed in a manner identical to the ternary H^+-Al^{3+} -lactic acid solutions.

The H^+-Al^{3+} system. These data consist of 16 batch solutions at four different total concentrations ($0.0009 \leq B \leq 0.010$ M) with Z_B , i.e. the average number of OH^- reacted per Al^{3+} , ranging from 1.20 to 2.20. All attempts to prepare solutions at higher Z_B values resulted in the precipitation of $Al(OH)_3$. The $-\log[H^+]$ values of these solutions were repeatedly measured until stable readings were obtained. The evaluation of the equilibrium constant is based on data from solutions aged for more than 2 months. This calculation ended at $\sigma(H) = 0.25 \times 10^{-3}$ M, and the equilibrium constant obtained was $\log \beta_{-32,13,0} = 105.5 \pm 0.20$. This value was hereafter used in all calculations.

As an indication of the difficulty in determining this equilibrium constant, it can be pointed out that the resulting difference in measured $-\log[H^+]$ between the present value of $\beta_{-32,13,0}$ and the previous⁸ value, $10^{-109.2}$, is 0.11 units. In view of the much lower value previously reported it must, however, be concluded that the formation of this species is kinetically hindered in solutions containing complex forming/buffering substances.

An independent validation of the present equilibrium constant was also obtained from series of quantitative ^{27}Al NMR measurements, some of which are illustrated in Fig. 2. Through these measurements it was found that the registered concentrations of Al^{3+} as well as of $Al_3(OH)_4^{5+}$ were in full agreement with those predicted by the potentiometric model. However, even with this revised value for the equilibrium constant of $Al_3(OH)_4^{5+}$, considerable effects remained to be explained in the three-component system.

The H^+-Al^{3+} -lactic acid system. The data collected for the present investigation comprises a total of 19 groups with 137 experimental points. In the calculations, these data were supplemented with 10 groups containing 76 experimental points at $Z_c \leq 1.20$ from the previous investigation. During the collection of data, a marked increase in equilibration time was observed when Z_c exceeded 1.20. As a consequence, the evaluation of data was divided into two

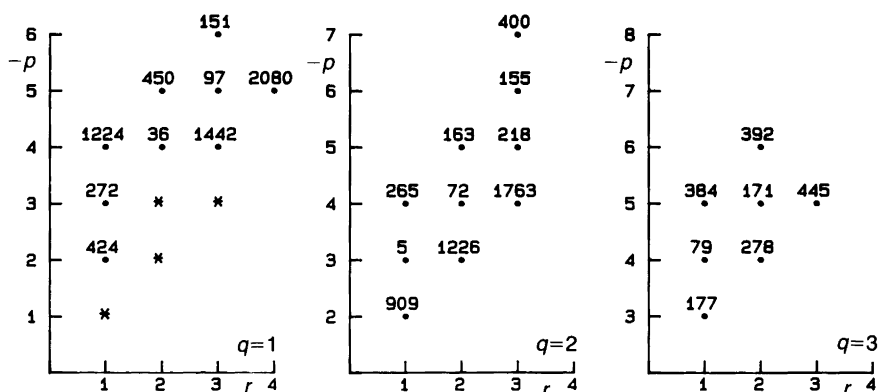


Fig. 3. Result of the (p,q,r) analysis on data with $C/B = 1$ and $Z_c \leq 1.20$. The figure gives error-sums $U_H(p,r) \times 10^3$ assuming one ternary complex. The calculations are based on 25 points giving $U_H(00)_0 \times 10^3 = 6211$.

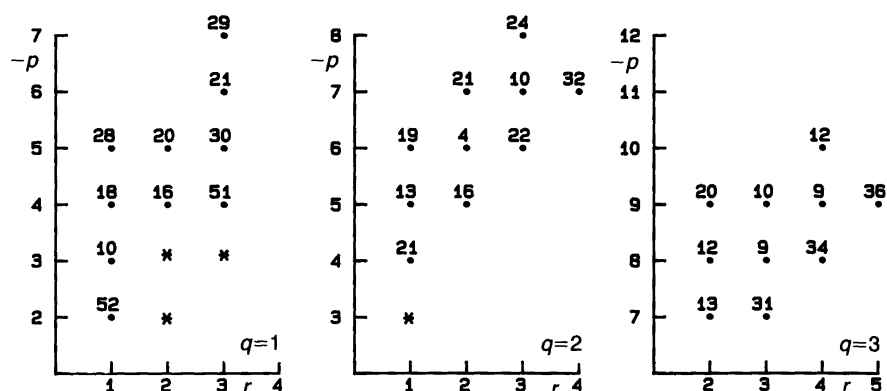


Fig. 4. Results of the second (p, q, r) analysis on data with $Z_c \leq 1.20$. The figure gives error-squares sums $U_H(pq)_q \times 10$ assuming the presence of $(-3, 2, 1)$ and one additional complex. In the calculations, the formation constant for $(-3, 2, 1)$ was refined together with that of the "new" complex. The calculations are based on 115 points giving $U_H(00)_0 \times 10 = 53$.

parts, corresponding to slow (days) and very slow (months) attainment of equilibria, respectively.

(a) *Three-component data with $Z_c \leq 1.20$.* The mathematical analysis of these data which, as a point of security, also contained some data from the previous investigation at $Z_c \leq 0.95$, was initiated through a (p, q, r) analysis assuming that only one new complex was present. The principle of this method is to vary successively the equilibrium constant for one (p, q, r) combination at the time until the combination which is able to provide the closest fit to experimental data, i.e. the lowest error squares sum $U = \sum (H_{\text{calc}} - H_{\text{exp}})^2$, is identified.

In the present case, the lowest error squares sum was obtained for a species $H_{-4}Al_2(HL)^{2+}$ but, as this species

also left considerable deviations in $\Delta H = H_{\text{calc}} - H_{\text{exp}}$ [$\sigma(H) = 0.14 \times 10^{-3} M$], it was obvious that the composition found was an average of two or several coexisting species. For this reason, a new (p, q, r) search was performed, now only on data with $C/B = 1$. The result of this analysis is illustrated in Fig. 3, and shows that a complex of the composition $H_{-3}Al_2(HL)^{3+}$ with $\log \beta_{-3,2,1} = -6.78 \pm 0.011$ gives a very good fit to these data.

The data evaluation was then continued with a renewed (p, q, r) search on all data, in which the equilibrium constant for $(-3, 2, 1)$ was refined together with the equilibrium constant for an additional (p, q, r) species. The result of these calculations is illustrated in Fig. 4, and shows that the best explanation of data is obtained assuming the presence of a species $H_{-6}Al_2(HL)_2^0$ ($\log \beta_{-6,2,2} = -16.79 \pm 0.055$), together with $H_{-3}Al_2(HL)^{3+}$ ($\log \beta_{-3,2,1} = -6.86 \pm 0.044$). With these two species, the remaining average residual $\sigma(H)$ became $0.06 \times 10^{-3} M$, indicating a good fit to experimental data. These equilibrium constants were then included in the model when data at higher Z_c were examined.

(b) *Three-component data at $Z_c > 1.20$.* The analysis of data in this region was initiated in the same way as in the $Z_c \leq 1.20$ range, i.e. with a (p, q, r) search assuming one new complex to be formed. This analysis did, however, turn out to be very discouraging as it was found that a large number of (p, q, r) combinations yielded approximately the same fit to experimental data. This is exemplified in Fig. 5, which gives the best possible error squares sums for species containing two lactic acid molecules. The only definitive conclusions which it was possible to draw from these calculations were that the complex formed was of a high nuclearity, contained ca. -2.57 protons per aluminium and that the number of coordinated ligands was much lower than the number of aluminium ions.

As these qualities closely resemble those for the species $Al_{13}O_4(OH)_{24}^{7+}$, we found it necessary to question once again the formation constant for this species. This calculation ended with $\log \beta_{-32,13,0} = -102.5 \pm 0.26$ and with an error squares sum of 17. Compared to the error squares sums reported in Fig. 5, it can thus be concluded that the species with $r > 0$ give a better fit to the experimental data.

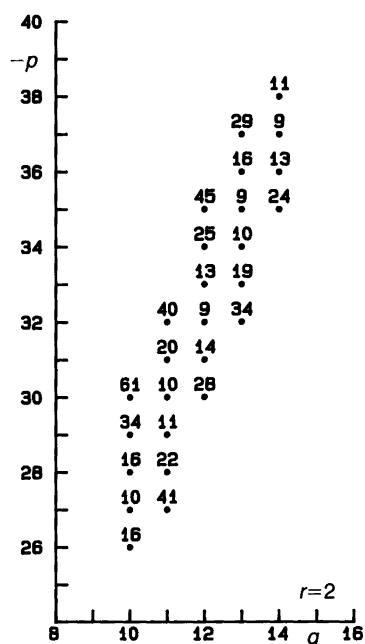


Fig. 5. Result of the (p, q, r) analysis on data with $Z_c > 1.20$. The figure gives $U_H(pq)_2$ assuming one additional complex. In the calculations, the species $(-3, 2, 1)$ and $(-6, 2, 2)$ were treated as known. The calculations are based on 98 points giving $U_H(00)_0 = 83$.

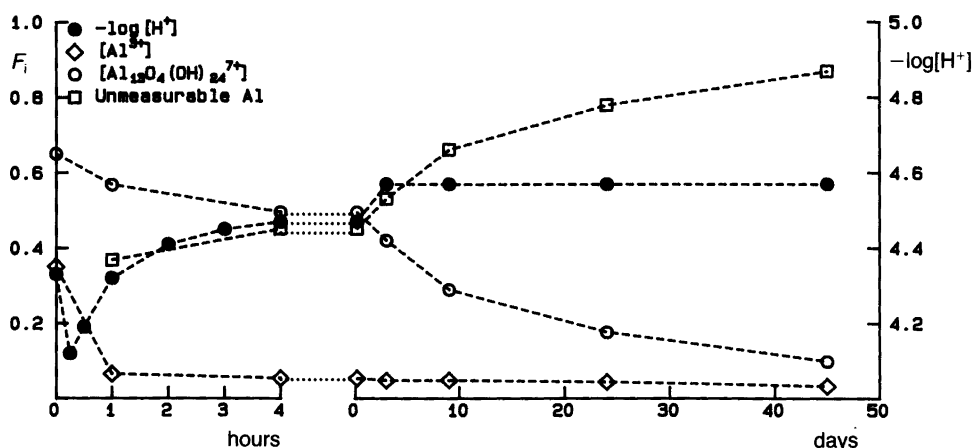


Fig. 6. The distribution of Al^{3+} and $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ as a function of time when a highly hydrolysed aluminium solution ($Z_B = 2.0$) is mixed with an equimolar concentration of lactate. The measurements were performed using ^{27}Al -NMR.

The final objection towards the assumption of a higher stability of $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ was, however, obtained from the ^{27}Al NMR spectra of solutions with $B = C = 0.010 \text{ M}$ and $2.0 \leq Z_c \leq 3.5$. In these spectra, only a gradually weakening signal corresponding to the free Al^{3+} ion could be observed, i.e. the concentrations of $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ in these solutions proved to be negligible. These spectra also showed that the linewidth of the "new" species formed was too wide to be detectable.

To study the transformation of $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ into this "new" species, we performed an experiment in which lactate ions were added to a highly hydrolysed ($Z_B = 2.0$) aluminium solution. The concentrations of Al^{3+} and $\text{AlO}_4[\text{Al}_{12}(\text{OH})_{24}]^{7+}$ in this solution were monitored as a function of time via repeated ^{27}Al -NMR measurements. Also, the evolution of $-\log [\text{H}^+]$ with time was monitored. The result of this experiment is illustrated in Fig. 6 and shows that, followed by a very fast decrease in the free Al^{3+} concentration, the concentration of $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ slowly decreases during tens of days. During this slow transformation process, neither the concentration of Al^{3+} nor the $-\log [\text{H}^+]$ in the solution changes. It can therefore be concluded that the "new" unmeasurable species contains approxi-

mately the same number of aluminium ions and the same average number of hydroxyl groups per aluminium as the vanishing $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$. On the other hand, this experiment does not provide any information concerning the number of lactate ions coordinated in the complex.

A renewed (p, q, r) search on EMF data, in which the number of aluminium ions was fixed at 13, was therefore conducted. The result of these calculations is given in Fig. 7 and shows, once again, that several (p, q, r) combinations give rise to more or less identical error squares sums. Our final conclusion is therefore that using our present data, we have no possibilities to determine the stoichiometry of this complex uniquely. To be able to illustrate the significance of the species formed we have, however, tentatively chosen the composition $\text{H}_{-36}\text{Al}_{13}(\text{HL})_4^{3+}$ to represent this complex. The choice is not critical, as also other choices result in almost identical distributions.

Our final suggestion for the complexation in the system $\text{H}^+ - \text{Al}^{3+} - \text{lactic acid}$ is given in Table 1. The computer program SOLGASWATER,⁹ equipped with plotting procedures, has been used to prepare a series of distribution diagrams presented in Fig. 8.

Discussion

Equilibria and structures. The present study completes the investigation of the ability of lactic acid to form complexes with the Al^{3+} ion. A tabulation of proposed complexes and corresponding formation constants from this and the previous investigation is given in Table 1.

In the present study, clear evidence for the formation of ternary polynuclear complexes have been given and, as shown in the distribution diagrams of Fig. 8, these species are all formed in significant amounts at $-\log [\text{H}^+] \geq 3.5-4$. A comparison between the speciation at $C/B = 1$ and 5 reveals that the relative importance of the two species $\text{H}_{-3}\text{Al}_2(\text{HL})^{3+}$ and $\text{H}_{-6}\text{Al}_2(\text{HL})_2^0$ is strongly dependent on this ratio. This gives an explanation of the problem we encountered when we tried to explain all data at $Z_c \leq 1.20$ with one single complex. These diagrams also illustrate the profound importance of the highly condensed, slow-form-

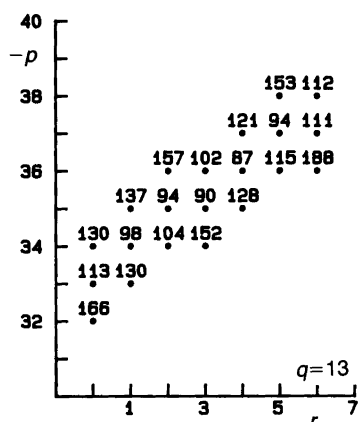


Fig. 7. Result of the second (p, q, r) analysis on data with $Z_c > 1.20$. The figure gives $U_H(p, r)_{13} \times 10$ with the same assumptions as in Fig. 5.

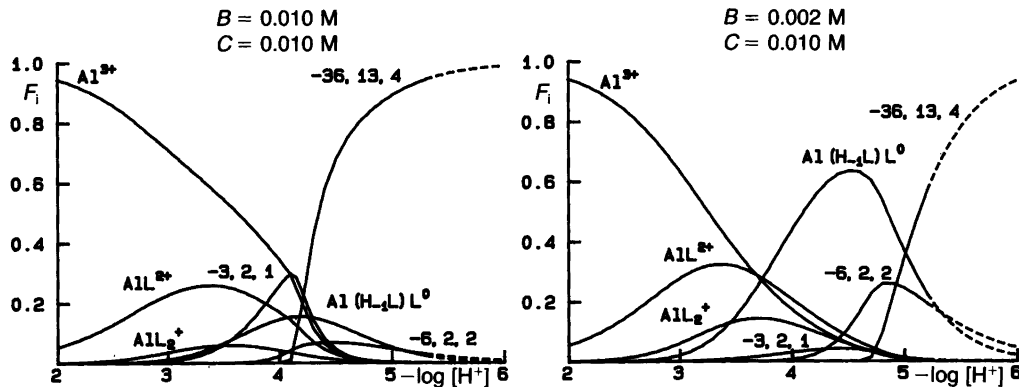


Fig. 8. Distribution diagrams $F_i(-\log [H^+])$, defined as in Fig. 2. The calculations have been performed using the computer program SOLGASWATER using equilibrium constants given in Table 1. The broken curves denote precipitation ranges.

ing species for which we failed to determine a unique stoichiometry. In fact, this species suppresses the formation of $Al_{13}O_4(OH)_{24}^{7+}$, which otherwise would have formed close to the precipitation boundary of $Al(OH)_3(s)$.

The present study has also shown that, in the 1–10 mM concentration range and C/B range of 1–5, the precipitation starts at $-\log [H^+] \approx 5.2$. Assuming aluminium hydroxide to be the solid phase, this precipitation boundary corresponds to a solubility product for $Al(OH)_3(s)$ of $\log^*K_{s0} \approx 10.5$, i.e. a value in good agreement with a value recently found (10.49 ± 0.08) in the $H^+-Al^{3+}-MoO_4^{2-}$ system.¹⁰ This value is considerably higher than the value reported for crystalline gibbsite (9.6),¹¹ and indicates the precipitate formed to be of an amorphous nature.

With regard to the structures of the different species formed, an investigation of this kind gives no direct information. In the previous article we made comparisons with other Al^{3+} -organic acid systems investigated, and concluded that the species $H_3Al(HL)_2^0$ probably could be written as $Al(H_{-1}L)L^0$, i.e. that it is a species in which the

hydroxy group of one of the lactate ions is deprotonated. The same assumption concerning the complex $H_6Al_2(HL)_2^0$ would then lead to the tentative formula $Al_2(OH)_2(H_{-1}L)_2^0$, i.e. to a dihydroxo-bridged species in which both lactate ions are deprotonated and bidentally bound. We have proposed this type of structure, consisting of a central $Al_2(OH)_2$ core surrounded by one or several ligands, in several of our previously investigated systems, and recently their existence in the solid state [as $Al_2(\mu-OH)_2(\text{nitrilotriacetate})_2^{2-}$]¹² has also been demonstrated. Also, we believe the species $H_3Al_2(HL)^{3+}$ to contain the same $Al_2(OH)_2$ core, i.e. this species should be written as $Al_2(OH)_2L^{3+}$. This assumption is based on the fact that a species with the same stoichiometry also forms with monocarboxylic (acetic and propionic) acids,¹³ in which the nature of the three leaving protons is quite unambiguous. Furthermore, by writing the formation of this species as follows:

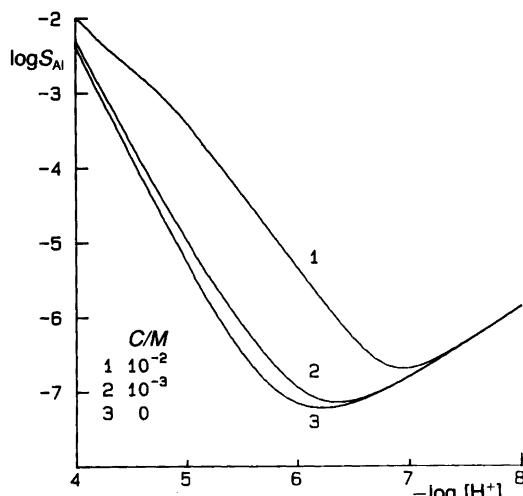
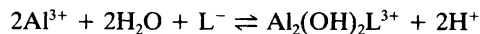


Fig. 9. The solubility of gibbsite ($\log^*K_{s0} = 9.6$) expressed as $\log S_{Al}$ vs. $-\log [H^+]$ for different total concentrations of lactic acid, C .

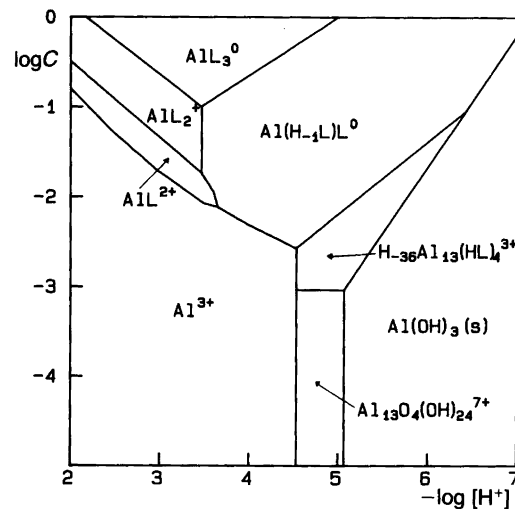


Fig. 10. Predominance area diagram showing dominating Al-containing species in a $B = 10^{-3}$ M solution in which amorphous aluminium hydroxide ($\log^*K_{s0} = 10.5$) is allowed to form.

with $\log K(\text{lactate}) = -3.29$, $\log K(\text{acetate}) = -3.49$ and $\log K(\text{propionate}) = -3.43$, its close similarity in stability in the three systems is emphasized.

Finally, with regard to the high-nuclearity species $\text{H}_{-36}\text{Al}_{13}(\text{HL})_4^{3+}$, we have no suggestions either as to its structure or as to its formula. However, since this complex does not give rise to a peak in the tetrahedral range of the ^{27}Al -NMR spectra, it is probably safe to conclude that this is *not* a species in which lactate ions have become coordinated to the hydrolytic species $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$.

Modelling calculations. In previous papers of this series, the potential ability of various ligands to affect the aquatic behaviour of aluminium has been indicated via computerized modelling¹⁴ in which crystalline gibbsite ($\log^*K_{s0} = 9.6$) has been used as a solubility-limiting phase. In the present system the corresponding calculation, which is illustrated in Fig. 9, shows that relatively high lactate concentrations are needed to cause any substantial solubilization of this phase. It can also be concluded that this influence is restricted to slightly acidic solutions and that (not illustrated) the solubilization mainly is caused by the formation of AlL^{2+} , AlL_2^+ and $\text{Al}(\text{H}_{-1}\text{L})\text{L}^0$, all determined in the previous paper on this subject.

In the present paper we have, however, shown that a more valid solubility for $\text{Al}(\text{OH})_3(\text{s})$ in mixtures with lactate is $\log^*K_{s0} = 10.5$. When this higher solubility is applied, all solubility curves are shifted upwards and, significantly, the species $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ and $\text{H}_{-36}\text{Al}_{13}(\text{HL})_4^{3+}$ both become predominating close to the precipitation boundary of $\text{Al}(\text{OH})_3(\text{s})$. This is illustrated in Fig. 10, which gives areas of predominating Al-containing complexes in a solution with $B = 10^{-3}$ M in which amorphous aluminium hydroxide is allowed to form.

To characterize the speciation in freshly prepared alu-

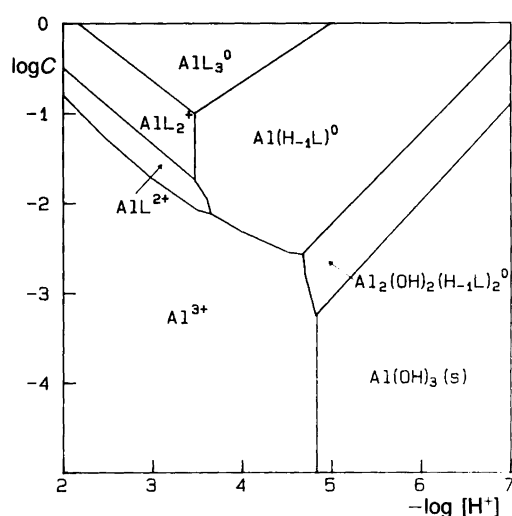


Fig. 11. Predominance area diagram in which the formation constants for $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ and $\text{H}_{-36}\text{Al}_{13}(\text{HL})_4^{3+}$ are set equal to zero and in which a highly amorphous aluminium hydroxide ($\log^*K_{s0} = 11.2$) is allowed to form.

minium–lactate mixtures, in which these highly condensed species have not had the time to form, we have prepared a type of “metastable” predominance diagram in which the solubility of $\text{Al}(\text{OH})_3(\text{s})$ was further increased to $\log^*K_{s0} = 11.2^{15}$ and in which the formation constants for $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ and $\text{H}_{-36}\text{Al}_{13}(\text{HL})_4^{3+}$ were put to zero. Under such circumstances it is found (cf. Fig. 11) that the species $\text{Al}_2(\text{OH})_2(\text{H}_{-1}\text{L})_2^0$ becomes the predominating aqueous species close to the precipitation boundary. The net neutral charge of this species, as well as of $\text{Al}(\text{H}_{-1}\text{L})\text{L}^0$, might be of importance when the bioavailability and toxicity of aluminium–lactates are considered. It should, however, be noted that even under these highly “metastable” conditions, a considerable excess of lactate ions is needed to form predominating amounts of these complexes.

With regard to conditions prevailing in the human body, it can be concluded that lactate complexes are of minor importance as a possible low molecular weight carrier of Al^{3+} in blood plasma. A model calculation, performed at pH 7.4 and a total concentration of lactate and aluminium of 10^{-4} and 10^{-6} M, respectively, showed that only 3% of the aluminium was bound in the complex $\text{Al}_2(\text{OH})_2(\text{H}_{-1}\text{L})_2^0$. The remaining 97% was found as the species $\text{Al}(\text{OH})_4^-$. Furthermore, even this minor amount of bound aluminium vanishes if the competitive complexation of citrate ions is taken into consideration.

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