Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. Part 9.† A Potentiometric Study of Mono- and Poly-nuclear Aluminium(III) Citrates

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Complexation in the Al^{3+}–H_3L–OH^- system (H_3L = citric acid) has been studied within the limits $2 \leqslant -\log [H^+] \leqslant 8$, $0.000\,25 \leqslant B \leqslant 0.016$ mol dm^{-3}, and $0.000\,25 \leqslant C \leqslant 0.016$ mol dm^{-3} with $C:B$ ratios equal to 1, 2, 4, 8, 16, and 32 (B and C represent the total concentrations of Al^{3+} and citric acid respectively). The measurements were performed as potentiometric (glass electrode) titrations in 0.6 mol dm^{-3} NaCl at 25 °C. Data are explained with the mononuclear species $[Al(HL)]^+$, $[AlL]$, and $[AlL_2]^{3-}$ together with a very stable trinuclear complex $[Al_3(OH)_4L_3]^{4-}$. Equilibrium constants including acidity constants of H_3L have been obtained. Data were analyzed using the least-squares computer program LETAGROPVRID. To demonstrate the complexing ability of citrate ions to Al^{III} in natural waters, the solubility of a clay mineral (kaolinite) was calculated within the range $4 \leqslant pH \leqslant 9$.

At present, there is a growing interest in the environmental chemistry of aluminium. This metal has generally been considered non-toxic. However, this situation has changed with the suspicion that Al^{III} is toxic to aquatic life in acidified natural waters. Elevated levels of aluminium in these waters have been found seriously to affect fish and other aquatic biota.[1]

It is generally accepted that complexation alters both the distribution and toxicity of trace metals, a conclusion which also is applicable to aluminium.[1] Knowledge of the speciation of Al^{III} in a natural water system is thus necessary for the study of its toxicity as well as for a better understanding of its transport in soils and freshwaters.

In preceding papers of this series, equilibrium studies of different Al^{3+} systems including inorganic $[CO_2(aq)]$ [2] and organic (gallic acid,[3,4] salicyclic acid,[5] and 3,4-dihydroxynaphthalene-1-sulphonate [6]) ligands have been performed. It has been shown that besides pure binary Al^{3+}–L, protonated Al^{3+}–HL as well as mixed mono- and poly-nuclear hydroxo Al^{3+}–OH^-–L species are significantly formed.

The aim of the present investigation is to interpret complexation in the Al^{3+}–citric acid (H_3L)–OH^- system. Earlier equilibrium studies of aqueous aluminium citrates (Pattnaik and Pani,[7] 33 °C, 0.25 mol dm^{-3} $NaClO_4$ medium) show the formation of a neutral complex [AlL] in acidic solutions. At a higher pH (pH > 3.1) this complex behaves like a dibasic acid with pK_a values of 3.49 and 6.79 respectively. The evaluation of the equilibrium model was, however, based on a very restricted number of experimental data. Furthermore, the hydrolysis of the Al^{3+} ion and probable formation of polynuclear complexes were neglected. Wiese and Veith,[8] on the other hand, have suggested that complexation in the Al^{3+}–citrate–OH^- system is to be explained by several polynuclear complexes. Although no formation constants were evaluated, a simple mathematical method based on inflection points of titration curves yielded the compositions of three polynuclear complexes, *viz.* $[Al_3(OH)L_3]^-$, $[Al_3(OH)_4L_2]^-$, and $[Al_{10}(OH)_{15}L_6]^{3-}$. In alkaline solutions (pH > 9) formation of the aluminate ion $[Al(OH)_4]^-$, was suggested.

Considering the inconsistency in earlier interpretations and the basic importance of this system a precise potentiometric method in combination with computer assisted equilibrium analysis would be of great interest. In these measurements as wide concentration ranges as possible will be studied, so that the formation of binary as well as ternary mono- and polynuclear complexes can be examined.

Experimental

Chemicals and Analysis.—Citric acid monohydrate $[HOOCCH_2C(OH)(CO_2H)CH_2COOH \cdot H_2O$, $H_3L \cdot H_2O]$ (Merck p.a.) was used without further purification. Stock solutions were prepared by dissolving $H_3L \cdot H_2O$ in water and the L content determined potentiometrically. The titrated amount was somewhat lower (0.3%) than that expected from weighing and the titrated value was assumed to be correct.

The preparation of other solutions, cell arrangement, and experimental details of the e.m.f. measurements are fully described elsewhere.[3]

Method.—The investigation was carried out as a series of potentiometric titrations at 25 °C in an ionic medium of constant $[Na^+] = 0.6$ mol dm^{-3} (NaCl). The titration procedures, including a special procedure to calibrate the glass electrode, have been described in earlier papers.[3,5] The acidity constants of citric acid were determined in separate titrations. It was found necessary to restrict the citric acid concentration, C, to $\lesssim 0.008$ mol dm^{-3} in order to obtain fully coincident titration curves. The concentration dependence was especially pronounced in citrate (L^{3-}) solutions and could be an effect due to complex formation with sodium ions in the medium, changes in the liquid junction potential (E_j), and/or variations in the activity coefficients. Ekström and Olin [9] (25 °C, 1 mol dm^{-3} $NaClO_4$) interpreted this concentration dependence as an E_j effect for which the following relation (1) was found. Applying (1) to present data implies that the E_j variation will at most amount to *ca.* 0.3 mV ($C = 0.008$ mol dm^{-3}). In the present investigation no correction for this variation was made as it definitely is too small to cause any significant changes in the equilibrium constants. During the three component titrations, the total concentrations of aluminium, B, and citric acid, C, were generally kept constant (by means of coulometric titrations), but dilution experiments with constant $C:B$ ratios were also carried out. The concentrations B and C were varied within the limits $0.00025 \leqslant B \leqslant 0.008$ mol dm^{-3} and $0.00025 \leqslant C \leqslant 0.008$ mol dm^{-3} covering the $C:B$ ratios: 1, 2, 4, 8, 16, and 32. At $C:B = 1:1$ where the amount of free citrate was estimated to be low, a titration with $B = C = 0.016$ mol dm^{-3}

$$E_j = -41.7[L^{3-}] - 21.3[HL^{2-}] - 6.1[H_2L^-] + 11.6[H_3L] \quad (1)$$

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† Part 8 is ref. 5.

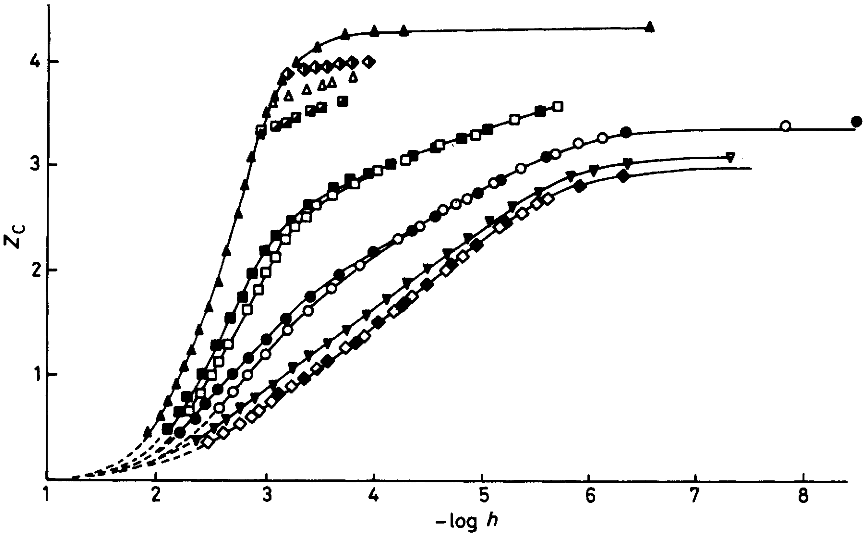


Figure 1. Part of experimental data plotted as curves of Z_C *versus* −log *h* for $C:B$ ratios of 1, 2, 4, 16, and ∞. $C = 8.00$ ($B = 0$) (◆); 2.00 (0) (◇); 8.00 (0.50) (▼); 8.00 (2.00) (●); 2.00 (0.50) (○); 8.00 (4.00) (■); 4.00 (2.00) (□); and 8.00 (8.00) (▲) mmol dm^{-3}. Titrations where burette solutions with $B = C = 0.016$ mol dm^{-3} and $Z = 3.3$ (◩), 3.6 (△), and 3.9 (◆), have been added to a slightly acidic ionic medium are also included. The full curves have been calculated using the set of proposed constants in the Table

was also performed; −log *h*, where $h = [H^+]$, was varied within the limits 2—8.

To test the reproducibility and reversibility of equilibria, both forward (increasing −log *h*) and backward (decreasing −log *h*) titrations were performed.

Data Treatment.—In order to visualize experimental results, data sets Z_C *versus* −log *h* were calculated and some of them are given in Figure 1; Z_C is defined as the average number of OH^- ions reacted per citric acid and is given by the relation $Z_C = (h - H - k_w h^{-1})/C$, where *H* denotes the total concentration of protons calculated over the zero level H_2O, Al^{3+}, and H_3L. The term $k_w h^{-1}$, where k_w is the ionic product of water, can be neglected in the present study. These curves reflect the total complexation behaviour in the system, comprising binary [equations (2) and (3)] as well as ternary [equation (4)] equilibria. Regarding the acidity constants of citric acid [*i.e.* equation (2)] we will, as mentioned earlier,

$$H_3L \Longleftrightarrow H_{3-n}L^{n-} + nH^+ \ (\beta_{-n,0,1};\ n = 1, 2, \text{and } 3) \quad (2)$$

$$pH^+ + qAl^{3+} \Longleftrightarrow [Al_qH_p]^{p+3q} \ (\beta_{p,q,0}) \quad (3)$$

$$pH^+ + qAl^{3+} + r(H_3L) \Longleftrightarrow [Al_qH_p(H_3L)_r]^{p+3q} \ (\beta_{p,q,r}) \quad (4)$$

make use of results obtained in separate experiments. For the hydrolytic equilibria of Al^{3+} [*i.e.* equation (3)], we will use the results obtained in earlier papers [2,6] of this series, showing the occurrence of $[Al(OH)]^{2+}$ (log $\beta_{-1,1,0} = -5.52$), $[Al_3(OH)_4]^{5+}$ (log $\beta_{-4,3,0} = -13.57$), $[Al_{13}O_4(OH)_{24}]^{7+}$ (log $\beta_{-32,13,0} = -109.2$), and $[Al(OH)_4]^-$ (log $\beta_{-4,1,0} = -23.46$). In the evaluation of the three-component experimental data [*i.e.* equation (4)] the binary complex models were considered as known and all effects above this level treated as being caused by ternary species. The mathematical analysis of the data was performed with the least-squares computer program LETAGROPVRID [10] (version ETITR [11,12]). The *p,q,r* triplets and corresponding equilibrium constants that ' best ' fit the experimental data were determined by minimizing the error squares sum $U = \Sigma(H_{calc.} - H_{exp.})^2$. The LETAGROP calculations also give the standard deviations $\sigma(H)$, $\sigma(\beta_{p,q,r})$, and $3\sigma(\log \beta_{p,q,r})$. For the definitions of these errors the reader is referred to Sillén.[13,14] The computations were performed on a CD CYBER 730 computer.

Results

Binary H^+–H_3L *Equilibria.*—The data used to determine the acidity constants of citric acid comprise four titrations including 105 experimental points. The LETAGROP calculations ended at $\sigma(H) = 0.01 \times 10^{-3}$ mol dm^{-3} and the following equilibrium constants were obtained: log $\beta_{-1,0,1} = -2.769 \pm 0.003$; log $\beta_{-2,0,1} = -6.850 \pm 0.003$, and log $\beta_{-3,0,1} = -12.067 \pm 0.004$. [The errors given correspond to $3\sigma(\log \beta_{-n,0,1})$.]

Ternary H^+–Al^{3+}–H_3L *Equilibria.*—Data in this three-component system have been divided into two main parts: data with excess ligand, *i.e.* $C:B \geqslant 2:1$ and data with $C:B = 1:1$. In the following these data will be denoted Data 1 and Data 2, respectively.

Data 1. As an attempt to suppress possible formation of binary and ternary hydroxo-complexes, data were at first collected with excess ligand, *i.e.* with $C:B = 2, 4, 8, 16$, and 32. At these ratios rapid equilibria were found in acid solutions (−log $h \leqslant 3$). In less acid solutions, and especially at low $C:B$ ratios, stable potentials were not obtained until approximately 6 h had elapsed.

In Figure 1, some of the experimental data are visualized as Z_C *versus* −log *h* curves. Some characteristic features of these curves have to be pointed out. First, Z_C seems to reach limiting values in neutral or slightly acidic solutions. This implies that one predominating Al complex is formed at the end of these titrations. Secondly, the fact that these limiting Z_C values are all greater than 3 is direct proof that the predominating species is a mixed hydroxo-complex, or a species where the alcoholic group of the citrate ion is deprotonated. Thirdly, the steepness of the curves (especially for $C:B = 1:1$) indicates that polynuclear complex(es) are formed.

Concerning the low −log *h* (fast equilibrium) data, it was found that these could be explained assuming complexes with *p,q,r* notations of −2,1,1 and −3,1,1. The LETAGROP calculation ended at $\sigma(H) = 0.05 \times 10^{-3}$ mol dm^{-3}, with log $\beta_{-2,1,1} = -2.70 \pm 0.05$ and log $\beta_{-3,1,1} = -4.97 \pm 0.02$.

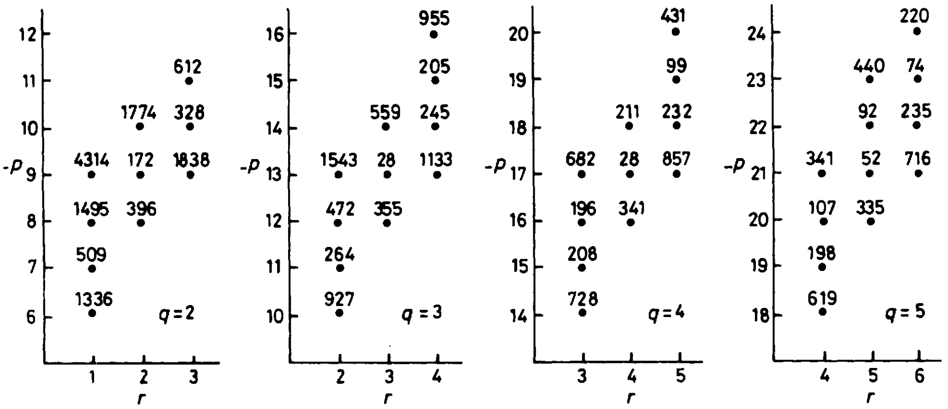


Figure 2. Result of a p,q,r analysis on data with $C : B \geqslant 2 : 1$ and $-\log h \gtrsim 3$. The figures give error square sums $U_H(pr)_q$ assuming one new ternary complex. In the calculations, $-2,1,1$ and $-3,1,1$ and aluminium hydrolysis have been assumed to be known. The calculations are based on 197 points giving $U_H(00)_0 = 6\,575$

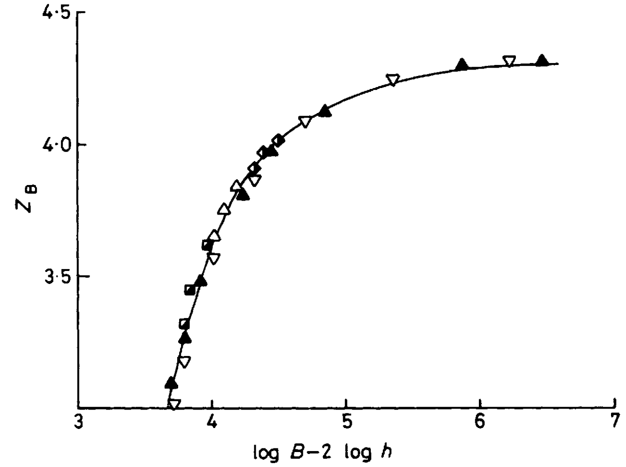


Figure 3. Plot of Z_B [$= (h - H)/B)$] *versus* log B − 2 log h. Data from $C : B = 1 : 1$ with symbols the same as in Figure 1. [In addition with $B = C = 0.016$ mol dm^{-3} (▽).] The full curve was calculated with proposed constants given in the Table

The search for the composition and stability of the predominating complex ($-\log h > 3$) was performed as a p,q,r analysis (systematic testing of p,q,r combinations) using the LETAGROPVRID program. The strategy was thereby to find that complex giving the lowest error-squares sum $U = \Sigma(H_{\text{calc.}} - H_{\text{exp.}})^2$. The results of this analysis are given in Figure 2 and it is seen that equal values of U were obtained assuming either the $-13,3,3$ (log $\beta = -21.73$) or $-17,4,4$ (log $\beta = -26.84$) species. As the Al^{3+}-H_3L ratio is 1 : 1 in both these complexes, they should be formed in optimum amounts at $C : B = 1 : 1$.

Data 2. To obtain as accurate a determination of the polynuclear complex as possible, it was necessary to collect experimental data with as great variation in B as possible. As the formation of this complex was found to be rather slow, solutions with $B = C = 0.016$ mol dm^{-3} and $Z = 3.3$, 3.6, and 3.9, respectively, were prepared. They were then allowed to stand for several days before they were used as burette solutions in a number of titrations. These solutions were added to a slightly acidic ionic medium ($B = C = 0$ mol dm^{-3}, $-\log h \approx 4$) and the equilibria were rapidly attained. In this way the range $0.00025 \leqslant B \leqslant 0.008$ mol dm^{-3} was covered and some of these data are visualized in Figure 1. It was found that no mononuclear curve was obtained at low B. In fact, the Z *versus* (log $h)_B$ curves appeared to be parallel. This would indicate that the polynuclear complex can be written in a ' core + links ' form $[AlL(AlLH_{-t})_n]^{nt-}$ where t is constant and n may assume several values. (For details of the ' core + links ' mechanism the reader is referred to papers by Sillén.[15,16]) From experimental Z *versus* (log $h)_B$ data, values for the derivative (5) equal to 2.0 ± 0.1 were obtained.

Table. Binary and ternary complexes in the three-component system, Al^{3+}-OH^--citric acid. The formation constants are related according to the reaction $pH^+ + qAl^{3+} + rH_3L \Longleftrightarrow [Al_qH_p(H_3L)_r]^{p+3q}$, where H_3L = citric acid

p, q, r	Tentative formula	log ($\beta_{p,q,r} \pm 3\sigma$)
−1, 0, 1	H_2L^-	−2.769 ± 0.003
−2, 0, 1	HL^{2-}	−6.850 ± 0.003
−3, 0, 1	L^{3-}	−12.067 ± 0.004
−2, 1, 1	$[Al(HL)]^+$	−2.68 ± 0.024
−3, 1, 1	$[AlL]$	−4.925 ± 0.008
−6, 1, 2	$[AlL_2]^{3-}$	−12.53 ± 0.12
−13, 3, 3	$[Al_3(OH)_4L_3]^{4-}$	−21.77 ± 0.019

$$\left(\frac{\partial \log B}{\partial \log h}\right)_Z \qquad (5)$$

This implies that the complex should be written as $[AlL(AlLH_{-2})_n]^{n2-}$. Furthermore Z is a function of $[AlL]h^{-2}$ only, *i.e.* if Z is plotted against log B − 2 log h, coinciding curves should be obtained. As can be seen from Figure 3, the points lie on a single curve with a limiting Z value equal to 4.35 ± 0.05. This implies that the composition of the complexes is defined as $[Al_2L_2H_{-2}]^{2-}$ and/or $[Al_3L_3H_{-4}]^{4-}$. In a LETAGROP calculation log $\beta_{-13,3,3} = -21.77 \pm 0.012$ was obtained, giving a very good fit to data with $Z > 3$ [$U = 1.66$, $\sigma(H) = 0.11 \times 10^{-3}$ mol dm^{-3}]. In a calculation where $\beta_{-13,3,3}$ and $\beta_{-8,2,2}$ were covaried, the latter species was shown to be quite insignificant. When the $-17,4,4$ complex was tested, $U = 14.8$ and $\sigma(H) = 0.34 \times 10^{-3}$ mol dm^{-3} were obtained, significantly higher values. Furthermore, while the formation constant for the $-13,3,3$ species was practically invariant compared with the calculation on data with $C : B \geqslant 2 : 1$ (a change in log $\beta_{-13,3,3}$ from −21.73 to −21.77) the value for $-17,4,4$ changed significantly (from log $\beta_{-17,4,4} = -26.84$ to log $\beta_{-17,4,4} = -27.12$).

However, with $-\log h \gtrsim 4$ and $C : B \geqslant 2 : 1$ small deviations were observed. As the deviations were found within a

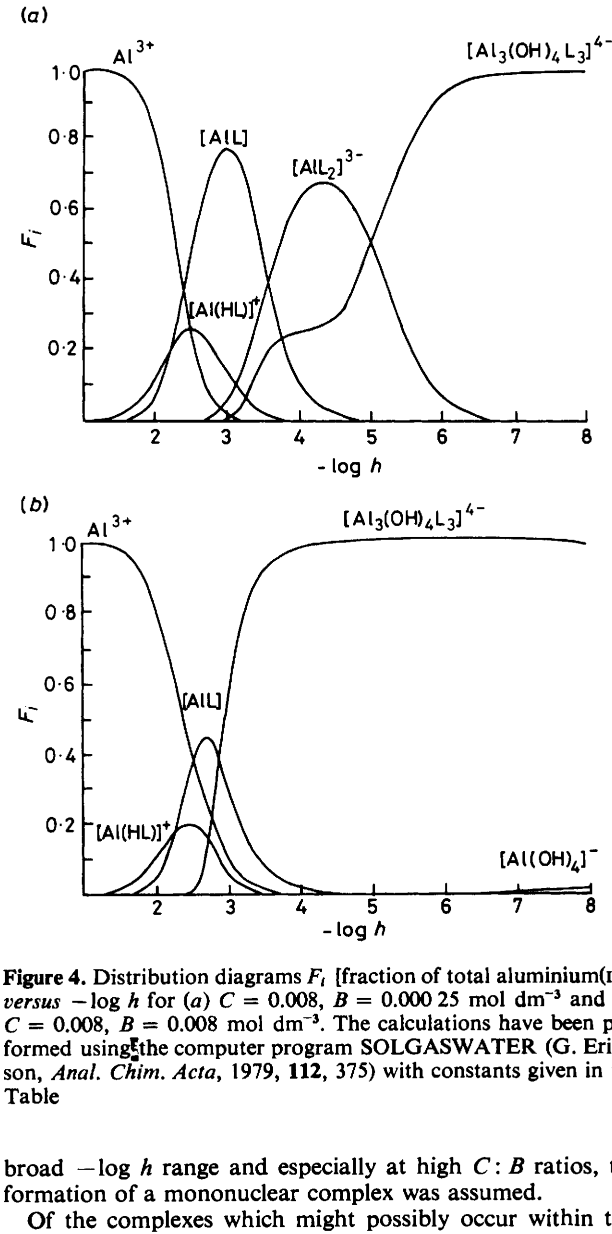


Figure 4. Distribution diagrams F_i [fraction of total aluminium(III)] *versus* $-\log h$ for (*a*) $C = 0.008$, $B = 0.000\,25$ mol dm^{-3} and (*b*) $C = 0.008$, $B = 0.008$ mol dm^{-3}. The calculations have been performed using the computer program SOLGASWATER (G. Eriksson, *Anal. Chim. Acta*, 1979, **112**, 375) with constants given in the Table

broad $-\log h$ range and especially at high $C:B$ ratios, the formation of a mononuclear complex was assumed.

Of the complexes which might possibly occur within this $-\log h$ range, $(-4,1,1)^-$, $(-5,1,1)^{2-}$, $(-5,1,2)^{2-}$, $(-6,1,2)^{3-}$, and $(-7,1,2)^{4-}$, we found that only $(-6,1,2)^{3-}$ ($\log \beta_{-6,1,2} = -12.60 \pm 0.16$) was accepted with any significant contribution to the model.

As a final model for the complexation between Al^{3+} and citric acid at $C:B \geqslant 1:1$ in the range $2 \leqslant -\log h \leqslant 8$ we therefore suggest: $(-2,1,1)^+$, $(-3,1,1)$, $(-6,1,2)^{3-}$, and $(-13,3,3)^{4-}$. The final equilibrium constants, obtained in a calculation on the whole data, comprising 17 titrations with 419 experimental points, are given in the Table. This calculation ended at $\sigma(H) = 0.09 \times 10^{-3}$ mol dm^{-3}.

Measurements are now planned to investigate possible hydrolysis of $[Al_3L_3H_{-4}]^{4-}$ in alkaline solutions. Furthermore, titrations at low ratios ($C:B < 1:1$) will be performed in order to study complexation in the presence of hydrolyzed Al^{3+} species.

Discussion

Speciation and Equilibria.—An equilibrium analysis of the present system has shown that besides a series of mononuclear species, *viz.* $[Al(HL)]^+$, [AlL], and $[AlL_2]^{3-}$, a very stable trinuclear complex is formed. Calculations based upon graphical ('core + links' mechanism) as well as least-squares refinements (LETAGROPVRID) have shown that the composition of this complex is $[Al_3L_3H_{-4}]^{4-}$. Whether this complex is a mixed-hydroxo-complex, $[Al_3(OH)_4L_3]^{4-}$, or a complex where the hydroxy group of the citrate ion is ionized is impossible to deduce from e.m.f. data. However, as the pK_a of the alcoholic group of the citrate ion is very high (p$K_a \gtrsim 13$, Bottari and Vicedomini,[17] Rajan *et al.*[18]) while hydrolysis of the Al^{3+} ion is found with $-\log h \gtrsim 4$, it seems more likely that this trinuclear complex is a mixed-hydroxo species. This hypothesis is supported by observations from the Pb^{2+}-H_3L system (Ekström and Olin [9]) where deprotonation of the hydroxy group was found to start at $-\log h > 6$. Distribution diagrams (Figure 4) as well as the predominance area diagram (Figure 5) shows $[Al_3(OH)_4L_3]^{4-}$ to be predominant in slightly acidic and neutral solutions. It can also be seen that this complex is formed to 100% of B with $-\log h \gtrsim 4$ and $C:B = 1:1$.

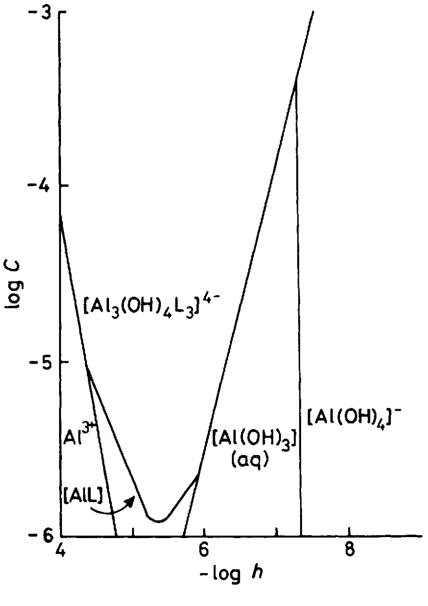


Figure 5. Predominance area diagram showing dominating Al species in equilibrium with kaolinite, $Al_2(OH)_4Si_2O_5$. Formation constants for the solid phase according to Helgeson, *Am. J. Sci.*, 1969, **266**, 729, and for soluble species according to this work

The mononuclear complexes are also formed in significant amounts with [AlL] and $[AlL_2]^{3-}$ predominating within the ranges as shown in Figure 4. Comparison of the stability constants reported here (Table) with published values is limited by the scarcity of previous work. The only comparison which can be made is $\log \beta_{-3,1,1} = -4.7$ according to Pattnaik and Pani,[7] in fair agreement with -4.925 ± 0.008 obtained in this study. The acidity constant of $[Al(HL)]^+$ (p$K_a = 2.25$) indicates increased acidities of the carboxylate groups. This probably is a consequence of the citrate ion acting as a tridentate ligand. Whether the alcoholic hydroxy group in the citrate ion is co-ordinated to Al^{3+} or not cannot be predicted from this type of data. However, it seems likely that this case is similar to citrate structures, *viz.* sodium and lithium dihydrogencitrates [19] and magnesium citrate decahydrate $[Mg(H_2O)_6{\cdot}Mg_2L_2(H_2O)_2{\cdot}2H_2O]$,[20] where the hydroxy group is actually co-ordinated to the metal ion. It is also interesting to note that the citrate ion bridges three Mg atoms acting as a terdentate ligand in the latter structure. It is

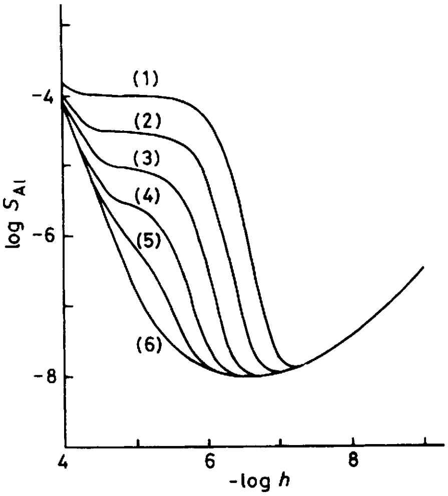
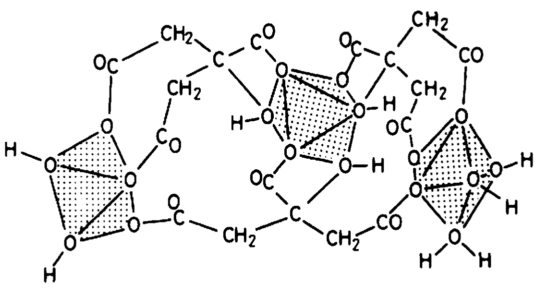


Figure 6. The solubility of kaolinite (with respect to Al) expressed as log S_{Al} *versus* $-\log h$ for different concentrations C of 10^{-4} (1), $10^{-4.5}$ (2), 10^{-5} (3), $10^{-5.5}$ (4), 10^{-6} (5), and 0 mol dm^{-3} (6)

tempting to assume the high stability of the trinuclear Al complex to be caused by the bridging capacity of the citrate ion. A possible six-co-ordination around the Al atoms might be as shown below. As a hypothesis the complex should thus be written as $[Al_3L_3(OH)_4(H_2O)_2]^{4-}$. Attempts are at present in progress to prepare single crystals suitable for a crystal structure determination, which might give structural information about the species in solution.



A potentiometric investigation of the corresponding gallium system (Kul'ba *et al.*[21]) has shown several similarities with the present system. Equilibria were studied within the ranges $1.3 \leqslant \mathrm{pH} \leqslant 3$ with $0.005 \leqslant B,C \leqslant 0.07$ mol dm^{-3} and $C: B = 0.5$, 0.7, 1.2 and 3. Besides the mononuclear species $[Ga(OH)_iL]^{i-}$, with $i = 0$—3, and $[GaL_2]^{3-}$ the trinuclear complex $[Ga_3(OH)_6L_3]^{6-}$ was proposed. The difference between the Al and Ga models seems to lie in the degree of hydrolysis, with the Ga species being more hydrolyzed. This is also in accordance with what has been found for pure binary hydrolysis of these two metals.[22]

Modelling on Natural Waters.—The presence of citrate in natural waters and biofluids implies that its complexing ability is of importance in such systems. It has earlier been shown [3,6] that the presence of ligands containing *o*-diphenolic groups significantly increases the solubility of clay minerals, *e.g.* kaolinite, $Al_2(OH)_4Si_2O_5$. With a total concentration of gallic acid and 3,4-dihydroxynaphthalene-1-sulphonate equal to 30 µmol dm^{-3}, the solubility of kaolinite with respect to aluminium was increased by an average factor of 3.4 and 4.8 respectively within the range $5 \leqslant \mathrm{pH} \leqslant 9$. In the present system, a corresponding calculation was performed and the results are shown in Figure 6. The strong complexing ability of citrate ions is clearly demonstrated and as can be seen there is a marked increase in the solubility, mainly due to the species [AlL] and $[Al_3(OH)_4L_3]^{4-}$. At pH 5 and 6 the solubilities have increased by factors 166 and 468 respectively, while at pH = 7 no increase is found. This implies that in slightly acidic natural waters high concentrations of Al are to be expected in the presence of citrate ions.

A practical application of stable Al^{3+} citrates could be in preventing the formation of scales and deposits consisting of different aluminosilicates in industrial processes. For instance, sodium aluminosilicates appear on tube walls and on evaporators in the final stages of black liquor evaporation in pulp mills.[23] Such scale formation might be eliminated or reduced by the addition of citrate ions.

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