Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. Part 13.† A Potentiometric and ^{27}Al Nuclear Magnetic Resonance Study of Speciation and Equilibria in the Aluminium(III)–Oxalic Acid–Hydroxide System

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Equilibria between Al^{3+}, oxalic acid (H_2L), and OH^- were studied in 0.6 mol dm^{-3} NaCl medium at 25 °C. Potentiometric titrations (glass electrode) and ^{27}Al n.m.r. measurements were performed to study speciation and equilibria within the concentration ranges $0.2 \leqslant -\log [H^+] \leqslant 7.2$, $0.0005 \leqslant b \leqslant 0.02$ mol dm^{-3}, $0.0005 \leqslant c \leqslant 0.025$ mol dm^{-3}, and $0.5 \leqslant c/b \leqslant 16$ [b and c are the total concentrations of aluminium(III) and oxalic acid respectively]. Besides a series of $[AlL_n]^{3-2n}$ complexes with n = 1, 2, and 3, the formation of the polynuclear mixed hydroxo-complexes $Al_3(OH)_3L_3$ and $[Al_2(OH)_2L_4]^{4-}$ were established. N.m.r. data also indicated the formation of an $[AlHL]^{2+}$ complex in strongly acidic solutions: $pK_a([AlHL]^{2+}) \approx 0.0$. The significance of the different Al complexes to conditions prevailing in natural waters is discussed, including a model calculation of the solubility of a clay mineral (kaolinite) in the presence of oxalate. Data were analysed using the least-squares computer program LETAGROPVRID.

In a current project at this department, speciation and equilibria in different Al^{III} systems are being investigated. In these systems, the complexing ability of different organic ligands of relevance to natural water conditions have been studied, and special attention paid to the detection of the possible formation of mixed hydroxo-complexes.

Oxalic acid has been reported to be one of the most abundant low-molecular-weight organic acids present in solution of a 'mor humus layer'.[1,2] Oxalate is also a common component of soil solutions and a concentration of 10^{-5} mol dm^{-3} has been reported.[3] Furthermore, the minerals whewellite $[Ca(C_2O_4)\cdot H_2O]$ and weddellite $[Ca(C_2O_4)\cdot 2H_2O]$ have been found in the 'litter layer' of several different soils,[3] indicating that oxalate is a major metabolic product of fungi in natural environments. Many species of fungi also produce oxalate in laboratory culture.[4] It is, however, important to realise that the biodegradability of oxalate is high and that its abundance in natural systems is governed by dynamic equilibrium between formation and destruction rates.

Besides forming sparingly soluble salts with Ca^{2+}, oxalate forms strong complexes with aluminium. This complexation tends to increase the concentrations of the nutrients K, Mg, and Ca, due to increased weathering of silicate minerals. Here kinetic and equilibrium effects are of importance. According to Boyle *et al.*[5] oxalic acid has been found to weather biotite more rapidly than other low-molecular-weight organic acids as well as HCl.

The presence of oxalate in natural environments thus affects nutrient as well as geochemical cycles. An understanding of these coupled processes necessitates a knowledge of the complexation behaviour of oxalate in natural waters, especially with respect to Al and Fe. According to earlier studies (*cf.* ref. 6) speciation in the Al^{3+}–oxalate system is characterized by the formation of a series of mononuclear complexes $[AlL_n]^{3-2n}$, with n = 1, 2, and 3. However, the results with respect to the stability of these species are confusing as variations of several orders of magnitude are found in the stability constants. This uncertainty is especially pronounced for log β_1, probably due to the fact that $[AlL]^+$ is formed in acidic solutions ($-\log [H^+] \lesssim 1$), where the use of a potentiometric method, measuring $[H^+]$, is very uncertain.

In a careful study by Bottari and Ciavatta[7] (25 °C, 1 mol dm^{-3} $NaClO_4$) complex formation was studied using the method of competitive reactions. As auxiliary species the copper(II) ion, which forms oxalate complexes of known composition and stability, was used. By using a copper amalgam electrode, the free Cu^{2+} concentration could be measured. This made it possible to calculate the free ligand (oxalate) concentration. The following results were obtained: log β_1 = 6.0, log β_2 = 11.09, log β_3 = 15.12. In the present study complexation reactions are studied by measuring the free Al^{3+} and H^+ concentrations (B and H respectively) using ^{27}Al n.m.r. and potentiometric techniques respectively. Furthermore, the possible formation of Al^{3+}–HL^- and Al^{3+}–L^{2-}–OH^- complexes will be investigated by performing measurements at very high and low acidities. In earlier papers of this series it has been shown that mono- as well as poly-nuclear mixed hydroxo-complexes with Al^{III} are frequently formed. Although these types of complex can be expected to be significant in natural water systems, they have been much overlooked in earlier investigations.

Experimental

Chemicals and Analysis.—Oxalic acid $[(COOH)_2\cdot 2H_2O, H_2L\cdot 2H_2O]$ (Merck *pro analysi*) was used without further purification after drying. Stock solutions were prepared by dissolving $H_2L\cdot 2H_2O$ in water and the L content determined potentiometrically. The titrated amount was found to be within 0.2% of that expected from weighing. The preparations of other solutions are fully described elsewhere.[8]

Apparatus.—The automatic system for precise e.m.f. titrations has been described in ref. 9. The ^{27}Al n.m.r. spectra were measured on a Bruker WM-250 spectrometer.

Temperature and Medium.—The present investigation was carried out at 25.00 ± 0.05 °C in a constant ionic medium of 0.6 mol dm^{-3} NaCl.

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† Part 12, S. Sjöberg, N. Ingri, A-M. Nenner, and L-O. Öhman, *J. Inorg. Biochem.*, 1985, **23**, in the press.

Methods.—The e.m.f. titration technique, combined with the use of solutions containing a constant ionic medium, has proved to be one of the most suitable methods in the study of complicated equilibria. However, as the complex formation is interpreted from the difference between analytical (h) and measured H^+ concentrations, the method becomes increasingly insensitive at low $-\log [H^+]$ values. Furthermore, in systems where the acid/base behaviour of the ligand coincides with the formation of ternary complexes, the method loses precision, especially at high ligand excesses. In the present system, both of these complications are simultaneously present, *i.e.* oxalic acid has a very high first acidity constant and aluminium oxalate complexes form at very low $-\log [H^+]$ values. It is therefore necessary to investigate this most acidic region with another, more direct method. We have thereby found quantitative measurements of $[Al^{3+}]$ by means of ^{27}Al n.m.r. to be most suitable.

N.M.R. Measurements.—The ^{27}Al n.m.r. measurements were carried out at 295 ± 1 K using a Bruker WM-250 spectrometer equipped with a 10-mm multinuclear probehead. The short spin-lattice relaxation times for the quadrupolar nucleus ^{27}Al and the high stability of the spectrometer made it possible to collect the data without D_2O lock of the instrument. The spectra were recorded without proton irradiation using 8 K data over a frequency domain of 2 000 Hz. Usually, 256 transients were collected and an exponential line-broadening function of 0.5 Hz was applied in order to improve the signal to noise ratio. By calibrating the instrument *versus* a 0.01 mol dm^{-3} Al^{3+} solution at $-\log [H^+] = 2$ and operating it in the absolute intensity mode, quantitative information about the concentration of each species could be determined. This evaluation, mainly on the Al^{3+} peak, was performed manually as (peak height × half-linewidth)/2 taking the half-linewidths from highly expanded parts of the spectra. In some spectra, we also estimated the concentration of each of the AlL_n species by cutting and weighing the different peaks.

Potentiometric Measurements.—The titration procedures, including a special procedure to calibrate the glass electrode, have been described in earlier papers.[8,10] The reproducibility and reversibility of equilibria were tested by performing both forward (increasing $-\log [H^+]$ coulometrically) and backward (decreasing $-\log [H^+]$ by means of addition of H^+) titrations. The acidity constants of oxalic acid were determined in separate titrations.

The three-component titrations were performed at a constant ratio between total concentration of aluminium (b) and oxalic acid (c). The upper $-\log [H^+]$ limits in these titrations were set by the formation of precipitates. By means of turbidity measurements, the precipitation boundaries have been determined. Furthermore, the precipitates have been characterized by i.r. spectra, *X*-ray powder data, and chemical analysis. According to these studies, two oxalate phases are formed with the stoicheiometric compositions $Al_3(OH)_7L$ and $NaAl(OH)_2L$. Structural characteristics and solubility products of these compounds will be reported in a forthcoming publication.[11]

Data treatment. The equilibria under consideration in the present study can be divided into groups as follows: (1) ionization of oxalic acid, (2) hydrolysis of Al^{3+}, (3) general formation of three-component equilibria. For equation (1), we

$$H_2L \rightleftharpoons H_{2-n}L^{n-} + nH^+ \ (n = 1 \text{ or } 2); \quad \beta_{-1,0,1} \text{ and } \beta_{-2,0,1} \qquad (1)$$

will make use of results obtained in separate potentiometric titration experiments. For the hydrolytic equilibria of Al^{3+} [equation (2)] we will use the results obtained in earlier papers of this series,[12,13] 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 $[Al(OH)_4]^-$ ($\log \beta_{-4,1,0} = -23.46$).

$$pH^+ + qAl^{3+} \rightleftharpoons H_pAl_q{}^{p+3q}; \ \beta_{p,q,0} \qquad (2)$$

$$pH^+ + qAl^{3+} + rH_2L \rightleftharpoons [H_pAl_q(H_2L)_r]^{p+3q}; \ \beta_{p,q,r} \qquad (3)$$

In the evaluation of three-component data, these binary complex models were considered as known and all effects above this level treated as being caused by three-component species. The mathematical analysis of data was performed with the least-squares computer program LETAGROPVRID[14] (version ETITR [15]) using either measurements of $[Al^{3+}]$ (n.m.r. data) or $[H^+]$ (potentiometric data). The p,q,r triplets and corresponding equilibrium constants that best fit the experimental data were determined by minimizing the error-squares sum, $U = \Sigma(h_{calc.} - h_{exp.})^2$, where $h_{calc.}$ and $h_{exp.}$ denote calculated and experimental values of the analytical H^+ concentrations respectively. The LETAGROP calculations also give standard deviations $\sigma(h)$, $\sigma(\beta_{p,q,r})$, and $3\sigma(\log \beta_{p,q,r})$, defined and calculated according to Sillén.[16] The computations were performed on a CD CYBER 730 computer.

Calculations and Results

Binary H^+–H_2L *Equilibria*.—The data comprise 114 experimental points collected *via* four potentiometric titrations within the ranges $0.001 \leqslant c \leqslant 0.016$ mol dm^{-3} and $1.1 \leqslant -\log [H^+] \leqslant 4.5$. The LETAGROP calculation ended at $\sigma(h) = 0.06 \times 10^{-3}$ mol dm^{-3} and the following equilibrium constants were obtained: $\log (\beta_{-1,0,1} \pm 3\sigma) = -0.97 \pm 0.01$, $\log (\beta_{-2,0,1} \pm 3\sigma) = -4.54 \pm 0.01$. These values are in good agreement with comparable data in the literature.[6]

Ternary H^+–Al^{3+}–H_2L *Equilibria*.—*N.m.r. data*. Spectra (29) within the ranges $-0.0379 \leqslant h \leqslant 0.709$ mol dm^{-3}, $0.001\,57 \leqslant b \leqslant 0.0251$ mol dm^{-3}, $0.005\,80 \leqslant c \leqslant 0.0562$ mol dm^{-3}, and $0.5 \leqslant c/b \leqslant 4$ were collected. In these data, $\alpha_{Al^{3+}}$, defined as $[Al^{3+}]/b$, varied within the limits $0.013 \leqslant \alpha_{Al^{3+}} \leqslant 0.535$.

A LETAGROP calculation on these ($h,b,c,[Al^{3+}]$) data, assuming the formation of $[AlL]^+$, $[AlL_2]^-$, and $[AlL_3]^{3-}$ showed systematically too high values of $[Al^{3+}]$ at the highest h levels (*i.e.* the lowest $-\log [H^+]$ values). As this indicated the formation of additional complex(es) we therefore included the species $[AlHL]^{2+}$ into the model and performed a renewed LETAGROP calculation. With the result so obtained, $\log \beta_{-1,1,1} = 1.40 \pm 0.31$, $\log \beta_{-2,1,1} = 1.43 \pm 0.10$, $\log \beta_{-4,1,2} = 1.85 \pm 0.24$, and $\log \beta_{-6,1,3} = 1.50 \pm 0.45$, a quite satisfactory agreement between observed and calculated $[Al^{3+}]$ values was obtained in all 29 solutions. {An attempt was also made to include the species $[Al(HL)_2]^+$, however no improvement of the fit to data was obtained.} The rather high $3\sigma(\log \beta_{p,q,r})$ values obtained are due mainly to: (*i*) the accuracy of the quantitative evaluation of $[Al^{3+}]$ from present n.m.r. data is estimated to be within ±10% of b; (*ii*) as many as four formation constants were covaried on a data set with relatively few data points (29).

Potentiometric Data.—These data comprise 33 titrations (538 experimental points) within the ranges $0.0005 \leqslant b \leqslant 0.02$ mol dm^{-3}, $0.0005 \leqslant c \leqslant 0.025$ mol dm^{-3}, and $1.6 \leqslant -\log [H^+] \leqslant 7.3$. The following c/b ratios have been covered: 0.50, 1, 2, 2.5, 4, 8, and 16. In order to visualize experimental data Z_c *versus* $-\log [H^+]$ were calculated and some of these data are given in Figure 1.* This function, which gives the average number of

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* $Z_c = ([H^+] - [OH^-] - h)/c$.

OH^- reacted per ligand, shows the formation of binary and ternary complexes in the system. $Z_c > 2$ is direct evidence for the formation of ternary Al–oxalate–OH^- and/or Al hydrolysis products. At lower Z_c values, the n.m.r. measurements had shown the presence of the species $[AlHL]^{2+}$, $[AlL]^+$, $[AlL_2]^-$, and $[AlL_3]^{3-}$. Out of these, the present data set mainly covers the formation of $[AlL_2]^-$ and $[AlL_3]^{3-}$. By considering the values of log $\beta_{-1,1,1}$ and log $\beta_{-2,1,1}$ (evaluated from n.m.r. data) as known, formation constants for $[AlL_2]^-$ and $[AlL_3]^{3-}$ were determined using data with $Z_c \lesssim 1.9$. This calculation ended at $\sigma(h) = 0.05 \times 10^{-3}$ mol dm^{-3} giving log $\beta_{-4,1,2} = 1.85 \pm 0.036$ and log $\beta_{-6,1,3} = 1.26 \pm 0.029$. The value of $\beta_{-4,1,2}$ is in very good agreement with the corresponding one determined from n.m.r. data, and thus confirms their interpretation.

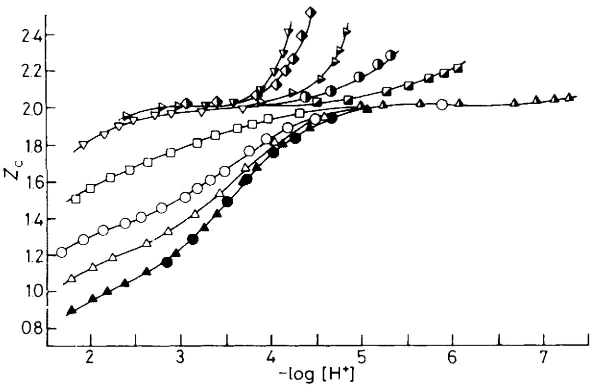

Figure 1. Part of the experimental data plotted as Z_c *versus* $-\log [H^+]$. The full curves have been calculated using the set of proposed constants. Combinations of concentrations *b*,*c* (10^{-3} mol dm^{-3}): (●) 0, 1; (▲) 0, 16; (△) 1, 16; (○) 2, 16; (□) 2, 8; (▽) 2, 4; (▲) 3, 24; (◩) 10, 25; (◑) 10, 20; (◆) 10, 10; (▼) 10, 5; and (▶) 1, 1

The search for composition and stability of species formed within the range $1.9 \leqslant Z_c \leqslant 2.5$ was performed as a *p*,*q*,*r* analysis. This is a procedure which is based on the assumption that, within the new data area considered, only one additional complex, $[H_pAl_q(H_2L)_r]^{p+3q}$, is present. Through a series of LETAGROP calculations, different *p*,*q*,*r* combinations are systematically tested one by one until the complex which gives the best fit to data, *i.e.* the lowest error-squares sum, *U*, is found. As preliminary calculations had indicated the formation of mixed hydroxo-complexes with $r/q \lesssim 1$ and 2 respectively, the calculations were started on data with $c/b = 0.5$ and 1. The systematic search performed on these data [see Figure 2(*a*)] clearly showed that the main hydroxo-complex is polynuclear. The best fit was obtained for an uncharged complex, *viz.* −9,3,3 $[Al_3(OH)_3L_3]$, whereas the −6,2,2, −8,3,2, and −10,4,3 species give somewhat higher *U* values. By including the −9,3,3 complex in the equilibrium model, another systematic search was performed on the whole data. As can be seen from Figure 2(*b*), these calculations favoured the formation of a −10,2,4 complex, with the tentative formula $[Al_2(OH)_2L_4]^{4-}$.

As final calculations, a number of models including two or three mixed hydroxo-complexes were tested. These calculations show that the best combination is given by the −9,3,3 and −10,2,4 complexes with log $\beta_{-9,3,3} = -4.28 \pm 0.02$, log $\beta_{-10,2,4} = -4.62 \pm 0.04$, and $\sigma(h) = 0.09 \times 10^{-3}$ mol dm^{-3}. These two species were also found to give the best fit to

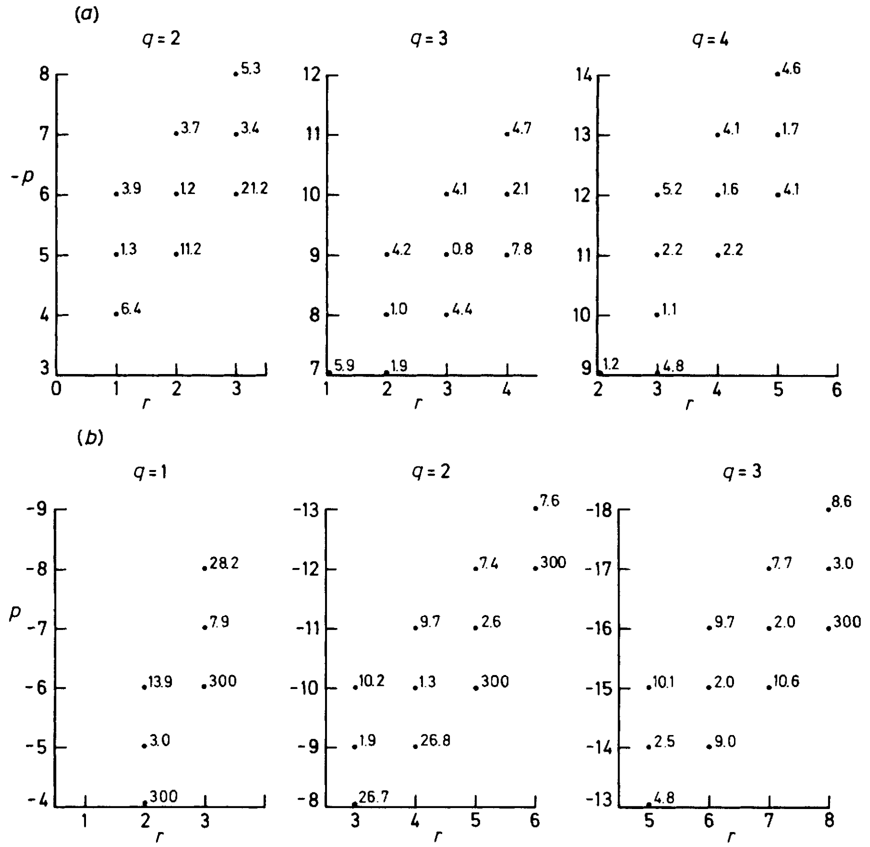

Figure 2. Results of a *p*,*q*,*r* analysis on data with $0.5 \leqslant c/b \leqslant 1$ (*a*) and $0.5 \leqslant c/b \leqslant 8$ (*b*). The figures give error-squares sums, $U_h(pr)_q$, assuming one new ternary complex

Table. Binary and ternary complexes in the H^+–Al^{3+}–oxalic acid (H_2L) system[a]

p,q,r	Tentative structure	$\log (\beta_{p,q,r} \pm 3\sigma)$
$-1,0,1$	HL^-	-0.97 ± 0.01
$-2,0,1$	L^{2-}	-4.54 ± 0.01
$-1,1,1$	$[AlHL]^{2+}$	1.40 ± 0.31
$-2,1,1$	$[AlL]^+$	1.43 ± 0.10
$-4,1,2$	$[AlL_2]^-$	1.85 ± 0.04
$-6,1,3$	$[AlL_3]^{3-}$	1.26 ± 0.03
$-9,3,3$	$Al_3(OH)_3L_3$	-4.28 ± 0.02
$-10,2,4$	$[Al_2(OH)_2L_4]^{4-}$	-4.62 ± 0.04

[a] The formation constants ($\beta_{p,q,r}$) are defined according to the reaction $pH^+ + qAl^{3+} + rH_2L \rightleftharpoons [H_pAl_q(H_2L)_r]^{p+3q}$.

solubility data, results which will be presented in a forthcoming publication.[11] It was also found that the mononuclear mixed hydroxo-complexes, *e.g.* Al(OH)L, $[Al(OH)_2L]^-$, $[Al(OH)L_2]^{2-}$, or $[Al(OH)_2L_2]^{3-}$ give no significant improvement to the present data.

In order to visualize the speciation in the present system, distribution diagrams have been calculated using proposed constants given in the Table (see Figure 3). In these calculations the computer program SOLGASWATER[17] was employed.

Discussion

Speciation and Equilibria.—Complexation in the present system is characterized by the formation of binary as well as ternary Al^{3+} complexes. By means of potentiometric and ^{27}Al n.m.r. measurements, it has become possible to determine the successive formation of the complexes $[AlL_n]^{2n-3}$, with $n = 1, 2,$ and 3. These mononuclear complexes are all formed in significant amounts, and predominate within the concentration ranges as shown in Figure 3. The values of the stepwise constants ($\log k_n$) are 6.03, 4.90, and 3.99 respectively. These values are in very good agreement with those reported by Bottari and Ciavatta[7] (6.0, 5.09, 4.03; 25 °C, 0.5 mol dm^{-3} $NaClO_4$).

Close to the precipitation boundary (see Figure 3) hydrolysis of the different Al^{3+}–L^{2-} complexes occurs. An equilibrium analysis of the present data clearly indicated the formation of polynuclear mixed hydroxo-complexes. Similar complexes with Al^{3+} have been demonstrated in earlier papers of this series.[1,2,18–20] Dinuclear as well as trinuclear complexes were found in corresponding systems with pyrocatechol,[18] and carbonic,[12] gallic,[1,19] and citric acids.[20] In the present system the best fit was obtained for $Al_3(OH)_3L_3$ ($c/b \leqslant 1$) and $[Al_2(OH)_2L_4]^{4-}$ ($c/b \geqslant 2$). These two complexes predominate along parts of the solubility boundary (Figure 3). As $Al_3(OH)_3L_3$ is formed close to the precipitation range of $Al_3(OH)_7L$, it seems reasonable to assume this phase to be formed where an exchange of L^{2-} with OH^- takes place: equation (4). The dinuclear complex, $[Al_2(OH)_2L_4]^{4-}$, is

$$Al_3(OH)_3L_3 + 4H_2O \rightleftharpoons Al_3(OH)_7L(s) + 2L^{2-} + 4H^+ \quad (4)$$

formed in solutions with excess of ligand. Tentatively it may be assigned as a dihydroxo-bridged complex with the oxalate ligands bound in a bidentate manner to complete the octahedral co-ordination sphere. A more detailed description of the structure of this complex may be obtained, as single crystals have been obtained with the stoicheiometric composition $Na_2Al(OH)L_2$, *i.e.* the same as in the aqueous complex. Work is now in progress to determine the crystal structure of this phase.

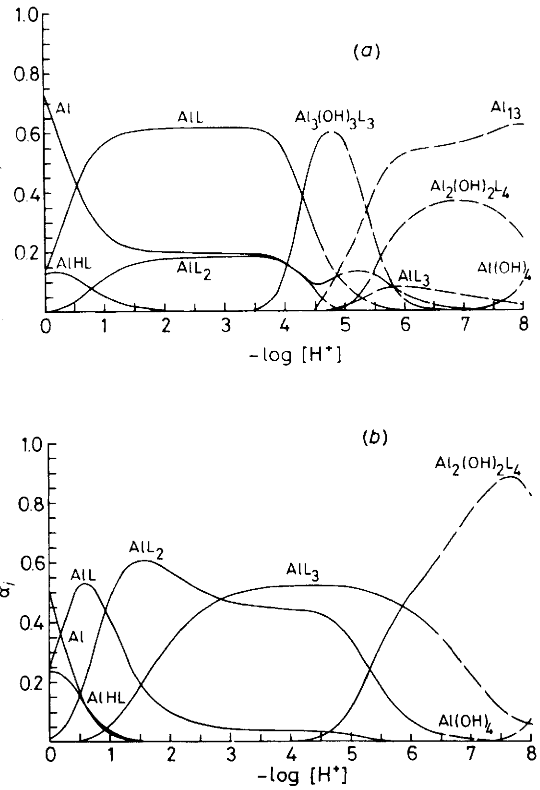

Figure 3. Distribution diagrams, α_i *versus* $-\log [H^+]$, with b,c 10, 10 (*a*); 10, 25 mmol dm^{-3} (*b*). Data with $-\log [H^+] \geqslant 4.5$ (*a*) and 6.2 (*b*) (— — —) denote precipitation ranges. The charges of the complexes are omitted $\{Al_{13} = [Al_{13}O_4(OH)_{24}]^{7+}\}$

In the most acidic solutions studied ($-\log [H^+] \approx 0.2$) protonation of $[AlL]^+$ to give $[AlHL]^{2+}$ takes place. The acidity constant, $pK_a([AlHL]^{2+}) \approx 0.0$, shows this complex to be more acidic than H_2L ($pK_a = 0.97$). The existence of protonated oxalate complexes is well documented. Formation constants of complexes with Fe^{3+}, Cr^{3+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Ca^{2+}, and Sr^{2+} have been reported.[6] A common feature of these species is that they are more stable than the corresponding acetate complexes. The same is true with Al^{3+} as $\log K (Al^{3+} + HL^- \rightleftharpoons [AlHL]^{2+}) = 2.37$, which can be compared with $\log K = 1.51$ with acetate as the ligand.[21] As the acetate ion functions as a unidentate ligand, this fact suggests some additional complexing ability for the hydrogen–oxalate species. It seems plausible to suggest that undissociated carboxyl group forms part of a bidentate site in protonated complexes.

Modelling on Natural Waters.—The presence of oxalate in natural waters implies that its complexing ability is important to consider when speciation, solubilities, and transportation of metal ions are discussed. Different model calculations have shown that the presence of ligands containing *o*-diphenolic groups[22] significantly increases the solubility of clay minerals, *e.g.* kaolinite, $Al_2(OH)_4Si_2O_5$. This increase takes place within the range $5 \leqslant pH \leqslant 9$. With the polycarboxylic acid citric acid[22] the increase is restricted to solutions with $4 \leqslant pH \leqslant 7$. A similar result is obtained with oxalate (see Figure 4). Using $c = 10^{-5}$ mol dm^{-3}, a value frequently found in soil solutions,[3] an increase of the solubility of kaolinite at pH 5 by a factor of

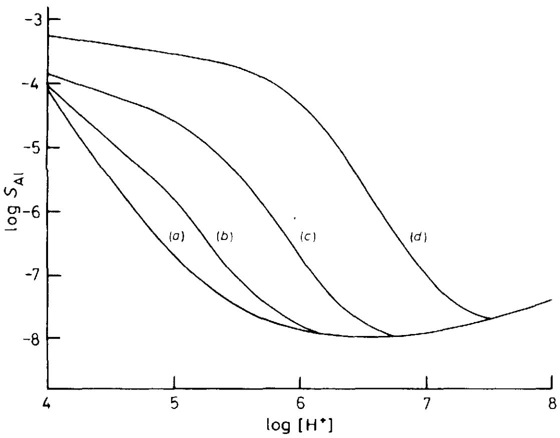

Figure 4. The solubility of kaolinite, log S_{Al}, *versus* $-\log[H^+]$ for $c = 0$ (*a*), 10^{-5} (*b*), 10^{-4} (*c*), 10^{-3} mol dm^{-3} (*d*). Formation constant for kaolinite is according to H. C. Helgeson, *Am. J. Sci.*, 1969, **266**, 729

eight is obtained. This increase is mainly due to the formation of $[AlL]^+$ and $[AlL_2]^-$ whereas the formation of $Al_3(OH)_3L_3$ and $[Al_2(OH)_2L_4]^{4-}$ is negligible at these concentrations. These results imply that in slightly acidic natural waters, increased concentrations of Al are to be expected in the presence of oxalate ions.

A practical application of Al^{3+}–oxalate complexes has been found within sulphite mills.[23] In these, calcium oxalate deposits have been a nuisance in the production of chemical pulp in mills with recovery plants. However, by adding aluminium sulphate to the spent sulphite liquor, soluble aluminium–oxalate complexes are formed, thus preventing the deposition of $Ca(C_2O_4)$.

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