Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 1. The Formation of Ternary Mononuclear and Polynuclear Complexes in the System Al^{3+} – Gallic Acid – OH^-. A Potentiometric Study in 0.6 M Na(Cl)

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Three-component equilibria between aluminium-(III), gallic acid ($C_7H_6O_5.H_3L$) and OH^- were studied by means of emf titrations at 25 °C in an ionic medium of 0.6 M Na(Cl). The total concentrations of aluminium, B, and gallic acid, C, were varied within the limits $0.0005 \leq B \leq 0.01$ M and $0.007 \leq C \leq 0.032$ M and the ratios C/B between $3 \leq C/B \leq 25$. Data can be explained with the mononuclear complexes $AlHL^+$, $Al(OH)(HL)$ or AlL, AlL_2^{3-} and AlL_3^{6-} together with a series of dinuclear species $Al_2(OH)_2(HL)_3^{2-}$, $Al_2(OH)_2(HL)_2L^{3-}$, $Al_2(OH)_2(HL)L_2^{4-}$ and $Al_2(OH)_2L_3^{5-}$. (These compositions are tentative.) The equilibrium constants with standard deviations are given in Table 2. This table also contains the first three dissociation constants of gallic acid. Data were analyzed with the least-squares computer program LETAGROPVRID. The ability of this complexation to increase the solubility of a clay mineral (kaolinite, $Al_2(OH)_4Si_2O_5$) is demonstrated in a model calculation.

In a newly started project at this department we have directed our interest to two of the most abundant elements in the earth's crust, silicon and aluminium. In spite of the great importance of these elements in the understanding of many geochemical and geological processes (*e.g.* weathering of minerals, formation of clay minerals) the literature concerning speciation and concentration of these ions in natural waters is rather meagre, probably due to experimental difficulties. The aim of our project is to investigate the ability of Si(IV) and Al(III) to form aqueous three-component complexes with naturally occurring inorganic and organic ligands with special reference to mixed hydroxo complexes in sea water medium. Concerning the organic ligands, we will treat naturally occurring low-molecular weight substances such as polyalcohols and polyhydroxycarboxylic acids as well as potential metal-chelating subgroups found in humic and fulvic acid analysis, *e.g.* o-diphenols and o-dimetoxybenzenes.

In the first part in this new series we will report and discuss complex formation between aluminium-(III) and gallic acid (3,4,5-trihydroxy benzoic acid). This ligand which contains o-diphenolic groups, has been described as a degradation product of lignin and humic acids.[1]

EXPERIMENTAL

Chemicals and analysis. Sodium chloride (Merck *p.a.*) was dried at 180 °C and used without further purification. Fresh sodium chloride solutions were always used in the measurements to avoid contamination by bacteria.

The dilute *hydrochloric acids* (Merck *p.a.*) were standardized against tris(hydroxymethyl)amino-methane (TRISMA-base).

Dilute *sodium hydroxide* was prepared from "oljelut" (50 % NaOH and 50 % H_2O) and standardized against acid or hydrazine sulfate.

Gallic acid, (3,4,5-trihydroxy benzoic acid), $C_7H_6O_5 \cdot H_2O$ (Baker grade) was used without further purification, as every attempt to recrystallize it from hot water resulted in a pale grey, partly oxidized, product.

Stock solutions of $C_7H_6O_5$ were prepared by dissolving $C_7H_6O_5 \cdot H_2O$ in standardized HCl. The $C_7H_6O_5$-content was determined potentiometrically using the Gran extrapolation method.[2] The titrated amount was always higher than that expected from the weighed amount ($\sim 3.5\%$) due to a water content of less than unity in the solid phase. The value obtained from titration has been assumed to be correct. After standardization, the solution was used within a few days to avoid effects from the slow oxidation which occurs in acidic solution.

Stock solutions of *aluminium chloride* were prepared by dissolving $AlCl_3.6H_2O$ (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 (~ 0.1 M) of the stock solutions was determined by precipitation with 8-hydroxyquinoline according to Kolthoff[3] 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[2] 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.

The different Al^{3+} and $C_7H_6O_5$ solutions used in the titrations were prepared from different stock solutions in order to detect possible systematic errors caused by impurities and analytical errors.

Apparatus. The potentiometric titrations were performed with an automatic system for precise emf titrations constructed and built at this institute by O. Ginstrup.[4] The cell arrangement, which was immersed in an oil thermostat at $25.00 \pm 0.05\,°C$, was similar to that described by Forsling *et al.*[5]

The Ag, AgCl electrodes were prepared according to Brown[6] and the hydrogen electrodes according to Bates.[7]

The glass electrodes (Ingold type 201-NS) were tested against the hydrogen electrode and showed constant and reproducible potentials within ± 0.2 mV for $-\lg h \lesssim 9$.

Special precautions. Since gallic acid is extremely sensitive to oxidation in neutral and alkaline solution, special efforts had to be made to protect it from oxygen. Therefore, during the titrations, performed in airtight vessels with gas outlet beneath a liquid surface, a stream of argon or hydrogen was bubbled through the solution for stirring and for maintaining an inert and reducing atmosphere. The gas, from a cylinder, was first bubbled through a vanadium(V^{III}, V^{IV}) solution in order to remove traces of oxygen and then through solutions of 10% NaOH and 10% H_2SO_4 in order to remove acid and alkaline impurities. Finally, before the gas came into contact with the equilibrium solution, it was passed through pure ionic medium.

Before the addition of OH^- ions, the vessel was deaerated with argon for at least two hours. In the case of backward titrations, two burettes containing OH^- resp. H^+ ions were mounted on the vessel before the experiment and $-\lg h$ was raised to a proper value with OH^- ions before the titration with H^+ ions.

With these precautions, no discolouring of the solution due to oxidation could be observed during the measurements. Without them, the solutions were immediately dark brown coloured and no stable potentials could be obtained.

METHOD

The present investigation has been carried out through a series of titrations at 25 °C. In order to avoid activity coefficient variations, a constant ionic medium of 0.6 M Na(Cl) was used.

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

$$-RE \,\|\, \text{equilibrium solution} \,|\, ME +$$
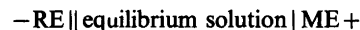
where ME denotes a glass or hydrogen electrode and $RE = Ag,AgCl|0.01$ M Cl^-, 0.59 M ClO_4^- ‖0.60 M NaCl. Assuming the activity coefficients to be constant, the expression (1) is valid for the measured

$$E = E_o + 59.157 \lg h + E_j \qquad (1)$$

emf, where E_0 is a constant determined at each titration in acid (H^+, Al^{3+}, $C_7H_6O_5$) solution of known composition where complex formation can be neglected ($-\lg h \lesssim 2$). For the liquid junction potential we have used $E_j = -77h + 42k_w h^{-1}$ mV, where $k_w = 1.875 \times 10^{-14}$ M^2 is the ionic product of water in 0.6 M Na(Cl).[8]

The binary titrations concerning the acidity constants of gallic acid were performed in separate experiments comprising totally 469 experimental points within the concentration range 0.03 M -0.002 M covering the $-\lg h$ range $1.5 \leq -\lg h \leq 11.5$ by adding hydroxide or hydrogen ions. During the titrations [H^+] = h was measured with both glass and hydrogen electrodes. This was

absolutely necessary since the hydrogen electrode was disturbed in acid solution ($-\lg h < 4$) while the glass electrode gave unreliable values for $-\lg h \gtrsim 9$. The middle region, $4 \lesssim -\lg h \lesssim 9$, was used to evaluate E_0 for the hydrogen electrode, exploiting the constant emf difference between the electrodes.

During the three-component titrations, the ratio between the total concentration of aluminium B, and gallic acid, C, was held constant. The initial concentrations of B and C were varied within the limits $0.0005 \text{ M} \leq B \leq 0.01 \text{ M}$ and $0.007 \text{ M} \leq C \leq 0.032 \text{ M}$, convering the C/B ratios: 3, 4, 6, 8, 10, 16 and 25. The measurement of h was performed with a glass electrode in the range $1.5 \leq -\lg h \leq 9$. At $C/B = 3$ and 4, the available $-\lg h$ range was somewhat restricted due to the formation of a white, amorphous precipitate. The precipitation range appears from the broken lines in Fig. 1.
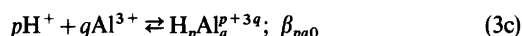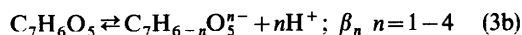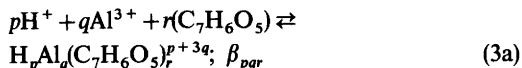
The reproducibility and reversibility of equilibria were tested by performing both forward (increasing $-\lg h$) and backward (decreasing $-\lg h$) titrations.

Data treatment. In the range of complex formation h was obtained for each point from the measured emf using eqn. 1. Since C and H (eqn. 6) are known from analysis we can calculate Zc for each point in a titration according to eqn. 2. This is the average

$$Z_c = (h - H - k_w h^{-1})/C \tag{2}$$

number of OH^- reacted per C. The experiments thus provide sets of data $Z_c(\lg h)$ at constant C/B. Such a plot is shown in Fig. 1.

We will assume the presence of three-component equilibria of the general form (3a) besides the two-component equilibria (3b) and (3c).

$$p\text{H}^+ + q\text{Al}^{3+} + r(\text{C}_7\text{H}_6\text{O}_5) \rightleftarrows$$
$$\text{H}_p\text{Al}_q(\text{C}_7\text{H}_6\text{O}_5)_r^{p+3q}; \ \beta_{pqr} \tag{3a}$$

$$\text{C}_7\text{H}_6\text{O}_5 \rightleftarrows \text{C}_7\text{H}_{6-n}\text{O}_5^{n-} + n\text{H}^+; \ \beta_n \ n = 1-4 \tag{3b}$$

$$p\text{H}^+ + q\text{Al}^{3+} \rightleftarrows \text{H}_p\text{Al}_q^{p+3q}; \ \beta_{pq0} \tag{3c}$$

The law of mass action and the conditions for the total concentrations then give eqns. $4-6$, where $b = [\text{Al}^{3+}]$ and $c = [\text{C}_7\text{H}_6\text{O}_5]$. The summation is taken over all species formed where β_{pqr}, β_n and β_{pq0}

$$B = b + \sum_{pqr} q\beta_{pqr} h^p b^q c^r \tag{4}$$

$$C = c + \sum_n \beta_n h^{-n} c + \sum_{pqr} r\beta_{pqr} h^p b^q c^r \tag{5}$$

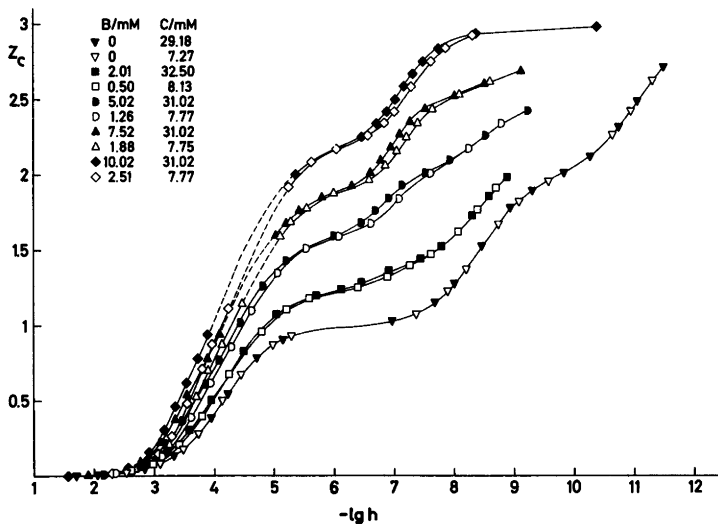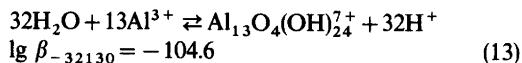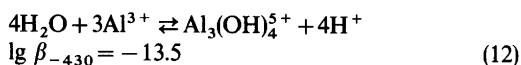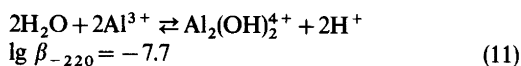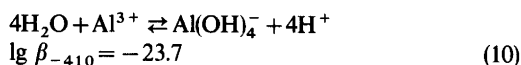$$H = h - \sum_n n\beta_n h^{-n} c + \sum_{pqr} p\beta_{pqr} h^p b^q c^r - k_w h^{-1} \tag{6}$$
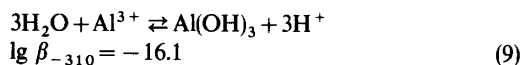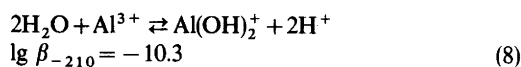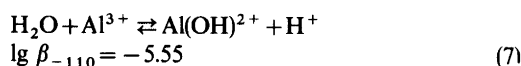

Fig. 1. A part of experimental data plotted as curves $Z_c(\lg h) = (h - H - k_w h^{-1})/C$ for C/B ratios 3, 4, 6, 16 and ∞. All symbols represent starting concentrations. The full curves have been calculated using the set of proposed constants in Table 2. Broken lines denote ranges where no measurements have been performed due to precipitation.

are the equilibrium constants for the reactions 3a, 3b and 3c, respectively.

Concerning the binary proton gallic acid equilibria (3b) we will make use of the results obtained from separate experiments.

The two-component hydrolysis equilibria according to eqn. (3c) has been studied by several workers. The main conclusions from these studies are given and discussed by Baes and Mesmer.[9] The complexes and equilibrium constants (7)−(13) are proposed (recalculated values valid in 0.6 M medium).

$$H_2O + Al^{3+} \rightleftarrows Al(OH)^{2+} + H^+$$
$$\lg \beta_{-110} = -5.55 \tag{7}$$

$$2H_2O + Al^{3+} \rightleftarrows Al(OH)_2^+ + 2H^+$$
$$\lg \beta_{-210} = -10.3 \tag{8}$$

$$3H_2O + Al^{3+} \rightleftarrows Al(OH)_3 + 3H^+$$
$$\lg \beta_{-310} = -16.1 \tag{9}$$

$$4H_2O + Al^{3+} \rightleftarrows Al(OH)_4^- + 4H^+$$
$$\lg \beta_{-410} = -23.7 \tag{10}$$

$$2H_2O + 2Al^{3+} \rightleftarrows Al_2(OH)_2^{4+} + 2H^+$$
$$\lg \beta_{-220} = -7.7 \tag{11}$$

$$4H_2O + 3Al^{3+} \rightleftarrows Al_3(OH)_4^{5+} + 4H^+$$
$$\lg \beta_{-430} = -13.5 \tag{12}$$

$$32H_2O + 13Al^{3+} \rightleftarrows Al_{13}O_4(OH)_{24}^{7+} + 32H^+$$
$$\lg \beta_{-32130} = -104.6 \tag{13}$$

The results on the two-component equilibria will be considered as known in the following calculations and no attempts will be made to adjust their equilibrium constants. (In a special calculation after the final model had been evaluated, it was furthermore proved that the Al^{3+}-hydrolysis was quite negligible under our conditions.)

The computational problem involves 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[10] (version ETITR[11]) was used. The "best" model or models are those giving the lowest error squares sum $U = \Sigma[Z_c - Z_c(\text{calc.})]^2$. The LETAGROP calculations also give standard deviations $\sigma(Z_c)$, $\sigma(\beta_{pqr})$ and $\sigma(\lg \beta_{pqr})$. For the definitions of these errors the reader is referred to Sillén.[12] The computations were performed on a Cyber 172 computer.

DATA, CALCULATIONS AND RESULTS

The H^+ − gallic acid system. The analysis of the binary proton gallic acid data was divided into two parts corresponding to glass and hydrogen electrode measurements.
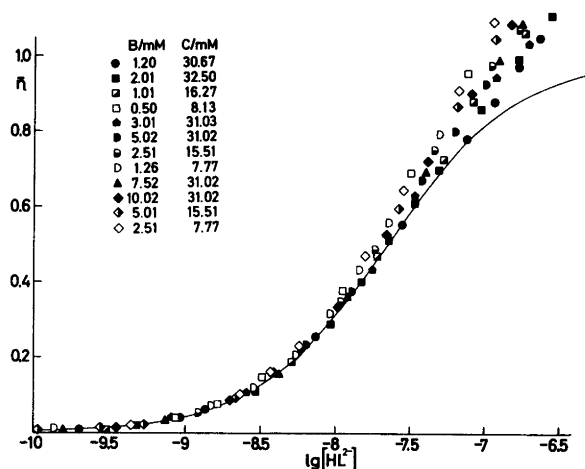

Fig. 2. Experimental data plotted as curves $\bar{n}(\lg[C_7H_4O_5^{2-}])$ for C/B ratios 3, 4, 6, 10, 16 and 25. The full curve has been calculated with $\lg \beta_{-211} = -4.93$.
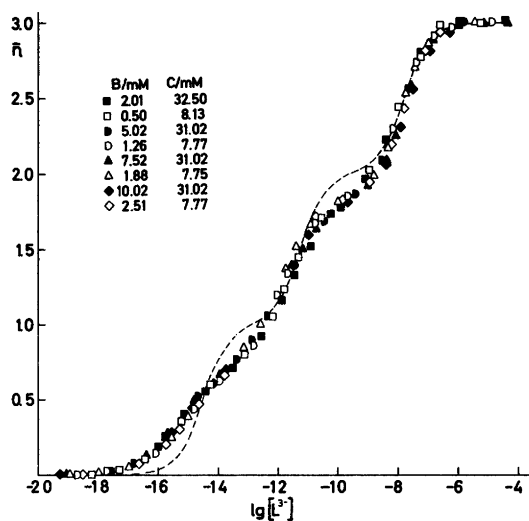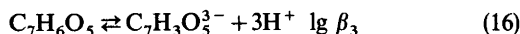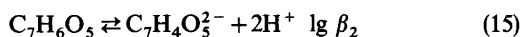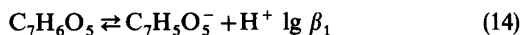
Fig. 3. Experimental data plotted as curves $\bar{n}(\lg[C_7H_3O_5^{3-}])$ for C/B ratios 3, 4, 6 and 16. The broken curve has been calculated assuming the formation of $Al(C_7H_3O_5)$, $Al(C_7H_3O_5)_2^{3-}$ and $Al(C_7H_3O_5)_3^{6-}$ and is a good illustration of this model's insufficience.

The glass electrode data were used to evaluate the first (carboxyl-) acidity constant, eqn. 14. The analysis ended at $\sigma(Z_c)=0.003$ giving $\lg(\beta_1 \pm 3\sigma)$ equal to -4.152 ± 0.002.

The hydrogen electrode data were used to evaluate the second and third (hydroxyl-) acidity constants, eqns. 15 and 16.

$$C_7H_6O_5 \rightleftharpoons C_7H_5O_5^- + H^+ \quad \lg \beta_1 \tag{14}$$

$$C_7H_6O_5 \rightleftharpoons C_7H_4O_5^{2-} + 2H^+ \quad \lg \beta_2 \tag{15}$$

$$C_7H_6O_5 \rightleftharpoons C_7H_3O_5^{3-} + 3H^+ \quad \lg \beta_3 \tag{16}$$

This analysis ended at $\sigma(Z_c)=0.007$ with $\lg(\beta_2 \pm 3\sigma)$ $= -12.590 \pm 0.005$ and $\lg(\beta_3 \pm 3\sigma) = -23.674$ ± 0.007. No attempts were made to evaluate the fourth acidity constant.

The $H^+ - Al^{3+} - $gallic acid system. The treatment of the three-component data was initiated by making the Bjerrum plots $\bar{n}(\lg[C_7H_5O_5^-])$; $\bar{n}(\lg[C_7H_4O_5^{2-}])$ and $\bar{n}(\lg[C_7H_3O_5^{3-}])$. The two latter are given in Figs. 2 and 3. From Fig. 3 we may conclude that the last step in complex formation is $Al(C_7H_3O_5)_3^{6-}$ as $\bar{n}$ reaches a limiting value of three. (For that reason we will denote $C_7H_3O_5^{3-} = L^{3-}$ and consequently gallic acid $= H_3L$ hereafter.) At lower $\bar{n}$-values the assumption of complexes AlL and AlL_2^{3-} is, however, insufficient. This appears clearly from the broken curve which is a theoretical $\bar{n}$-curve assuming the formation of AlL, AlL_2^{3-} and AlL_3^{6-} together with "best" equilibrium constants.

The first step in complex formation can be explained by the formation of $AlHL^+$, a conclusion

Table 1. Results of some LETAGROP calculations showing the inconsistance in the formation constant β_{-512}. The formation constants are related according to the relation $pH^+ + qAl^{3+} + rH_3L \rightleftharpoons (H)_p Al_q(H_3L)_r^{p+3q}$ where H_3L stands for $C_7H_6O_5$. The errors given are $3\sigma(\lg \beta_{pqr})$. If no 3σ is given the corresponding constant has not been varied.

No. of titr./ No. of points	C/B range	$\lg(\beta_{-211} \pm 3\sigma)$	$\lg(\beta_{-311} \pm 3\sigma)$	$\lg(\beta_{-512} \pm 3\sigma)$	$\lg(\beta_{-612} \pm 3\sigma)$	$\lg(\beta_{-913} \pm 3\sigma)$	$\sigma(Z_c)$
10/337	$10-25$	-4.94 ±0.016	-9.41 ±0.029	-16.44 ±0.028	-21.91 ±0.025	-37.67 ±0.028	0.0031
1/49	25	-4.94	-9.40 ±0.11	-16.59 ±0.09	-21.98 ±0.09	-37.67	0.0024
4/128	16	-4.94	-9.41 ±0.039	-16.49 ±0.037	-21.94 ±0.037	-37.67	0.0022
4/113	10	-4.94	-9.44 ±0.040	-16.39 ±0.037	-21.90 ±0.032	-37.67	0.0032
4/126	6	-4.94	-9.48 ±0.035	-16.25 ±0.028	-21.85 ±0.024	-37.67	0.0046

which might be drawn from Fig. 2. This plot also indicates that other complexes are formed as the function $\bar{n}(\lg[HL^{2-}])$ is dependent on B and C.

As these introductory graphical considerations gave us L^{3-} as well as HL^{2-} as ligands, it was then logical to test the complexes $Al(HL)_n L_m^{3-2n-3m}$ with $n,m \leq 3$ and $n+m \leq 3$ besides $AlHL^+$ and AlL_3^{6-} to a representative part of the data material, covering the whole $-\lg h$ range at relatively high C/B quotients. This was achieved in a procedure where the equilibrium constants of the different species were systematically varied by means of LETAGROPVRID. The analysis showed that the complexes $AlHL^+$, AlL, $Al(HL)L^{2-}$, AlL_2^{3-} and AlL_3^{6-} with equilibrium constants given in Table 1 could explain experimental data fairly well. There were, however, considerable deviations in the range $4 \lesssim -\lg h \lesssim 7$ and as these deviations seemed to depend on the quotient C/B, we decided to vary the AlL, $Al(HL)L^{2-}$ and AlL_2^{3-} equilibrium constants for one quotient at the time. The results of these calculations are given in Table 1, and the conclusions which might be drawn are:

(i) The constant values for AlL and AlL_2^{3-} are rather independent to quotient variation and seem to reach limiting values at high quotients.

(ii) The value for $Al(HL)L^{2-}$ is strongly and monotonically decreasing with increasing quotients, possibly indicating the formation of polynuclear species in the system.

On the basis of these conclusions we now found the complexes $AlHL^+$, AlL, AlL_2^{3-} and AlL_3^{6-} credible while the existence of $Al(HL)L^{2-}$ had to be questioned.

In order to do this, we chose a representative data material covering $3.8 \lesssim -\lg h \lesssim 4.5$ and the whole quotient range, and tried the simple hypothesis that only one additional complex, $H_p Al_q(H_3L)_r^{p+3q}$, was present. A trial and error procedure with the LETAGROPVRID program was used to determine the composition and equilibrium constant of the additional complex, which provided the closest fit to the data. The principle of this method has been that complexes of different pqr-compositions have successively been tested one by one, and the complex that gives the lowest error squares sum U
$$= \sum[Z_c - Z_c(\text{calc.})]^2$$
will be considered as the best explanation of data.

The error squares sums U obtained for the tested combination are given in Fig. 4. It was found that the lowest values of U was obtained for the complex $H_{-8}Al_2(H_3L)_3^{2-}$ with $\lg \beta_{-823} = -22.58 \pm 0.03$. Furthermore, $Al(HL)L^{2-}$ was rejected in a variation with the $(-8,2,3)$ complex.

This complex alone could not, however, explain the whole $4 \lesssim -\lg h \lesssim 7$ range and the data material was subsequently expanded to cover $3.8 \lesssim -\lg h \lesssim 5.5$ and the above procedure repeated, now assuming $(-8,2,3)$ together with $AlHL^+$, AlL, AlL_2^{3-} and AlL_3^{6-} to be known. The result of this second pqr-analysis is given in Fig. 5. It can be seen that the complexes $H_{-10}Al_2(H_3L)_3^{4-}$ with $\lg \beta_{-1023} = -32.74 \pm 0.03$ and $H_{-14}Al_3(H_3L)_4^{5-}$ with $\lg \beta_{-1434} = -43.71 \pm 0.05$ give error squares sums of comparable size.

When the whole $-\lg h$ range now was examined, assuming either of these polynuclear complexes to be present it was found that, with $(-10,2,3)$, only
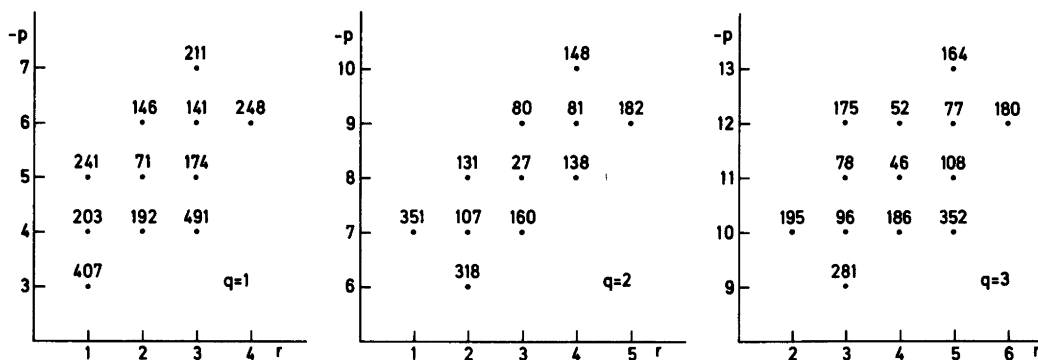
Fig. 4. The first LETAGROP-search for ternary $H_p Al_q(H_3L)_r^{p+3q}$ complexes in the region $3.8 \lesssim -\log h \lesssim 4.5$. The diagrams give error square sums $U_{Z_c}(pr)_q \times 10^{-2}$ assuming only one complex. In the calculations $AlHL^+$, AlL, AlL_2^{3-}, AlL_3^{6-} and aluminium hydrolysis have been assumed to be known. The calculations are based on 137 points giving $U_{Z_c}(00)_o = 666 \times 10^2$, chosen to cover as great a concentration range as possible.
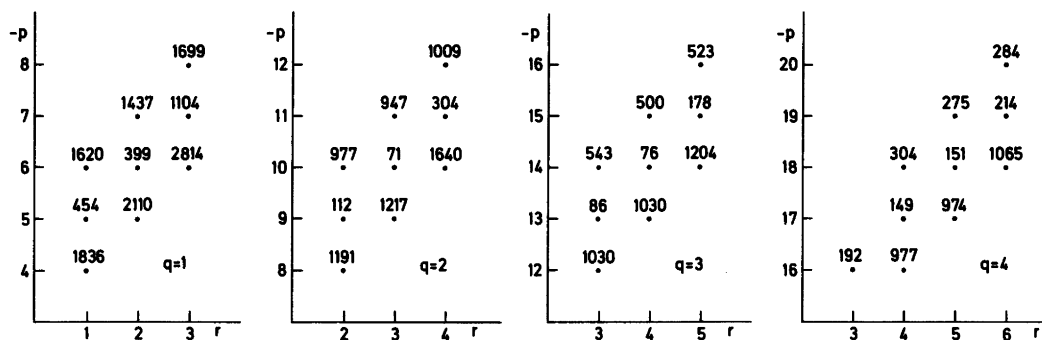
Fig. 5. The second LETAGROP-search for ternary $H_pAl_q(H_3L)_r^{p+3q}$ complexes in the region $3.8 \lesssim -\lg h \lesssim 5.5$. The diagrams give error square sums $U_{Z_c}(pr)_q \times 10^{-2}$ assuming one new complex. Mononuclear species, aluminium hydrolysis and $H_{-8}Al_2(H_3L)_3^{2-}$, found in the first pqr-search, have been assumed to be known. These calculations are based on 224 points giving $U_{Z_c}(00)_o = 3539 \cdot 10^2$.

minor residuals remained at low quotients and high $-\lg h$. With $(-14,3,4)$, the picture was much the same but the deviations were much more pronounced. As material for a third pqr-analysis we therefore chose a data set with its main point at a lower C/B quotient than earlier, covering the whole $-\lg h$ range. Assuming $(-14,3,4)$ to be known, it appeared that $H_{-11}Al_2(H_3L)_3^{5-}$ with $\lg \beta_{-1123} = -39.22 \pm 0.07$ gave the "best" fit. No sharp pit was obtained when we assumed $(-10,2,3)$ to be known, due to the fact that data were already rather well explained with this model.

Table 2. Results of LETAGROP calculations for some different assumptions concerning the complexes formed. The constants β_{pqr} are defined in Table 1 and the errors given are $3\sigma(\lg \beta_{pqr})$.

| No. of titr./ No. of points	p,q,r	$\lg(\beta_{pqr} \pm 3\sigma)$	p,q,r	$\lg(\beta_{pqr} \pm 3\sigma)$	p,q,r	$\lg(\beta_{pqr} \pm 3\sigma)$	p,q,r	$\lg(\beta_{pqr} \pm 3\sigma)$	$\sigma(Z_c)$
25/700	$-8,2,3$	-22.55 ± 0.037	$-14,3,4$	-43.71 ± 0.045	$-11,2,3$	-39.43 ± 0.057			0.0054
25/700	$-8,2,3$	-22.54 ± 0.040	$-10,2,3$	-32.80 ± 0.031					0.0067
25/700	$-8,2,3$	-22.53 ± 0.035	$-10,2,3$	-32.82 ± 0.029	$-11,2,3$	-39.83 ± 0.10			0.0059
25/700	$-8,2,3$	-22.68 ± 0.053	$-9,2,3$	-27.81 ± 0.092	$-10,2,3$	-32.89 ± 0.032	$-11,2,3$	-39.72 ± 0.073	0.0051
Proposed constants									
11/335	$-1,0,1$	-4.152 ± 0.0020							0.0033
9/134	$-2,0,1$	-12.590 ± 0.0053	$-3,0,1$	-23.674 ± 0.0073					0.0068
25/700	$-2,1,1$	-4.933 ± 0.0092	$-3,1,1$	-9.43 ± 0.018	$-6,1,2$	-21.98 ± 0.033	$-9,1,3$	-37.69 ± 0.015	0.0049
	$-8,2,3$	-22.65 ± 0.044	$-9,2,3$	-27.81 ± 0.074	$-10,2,3$	-32.87 ± 0.029	$-11,2,3$	-39.56 ± 0.053	
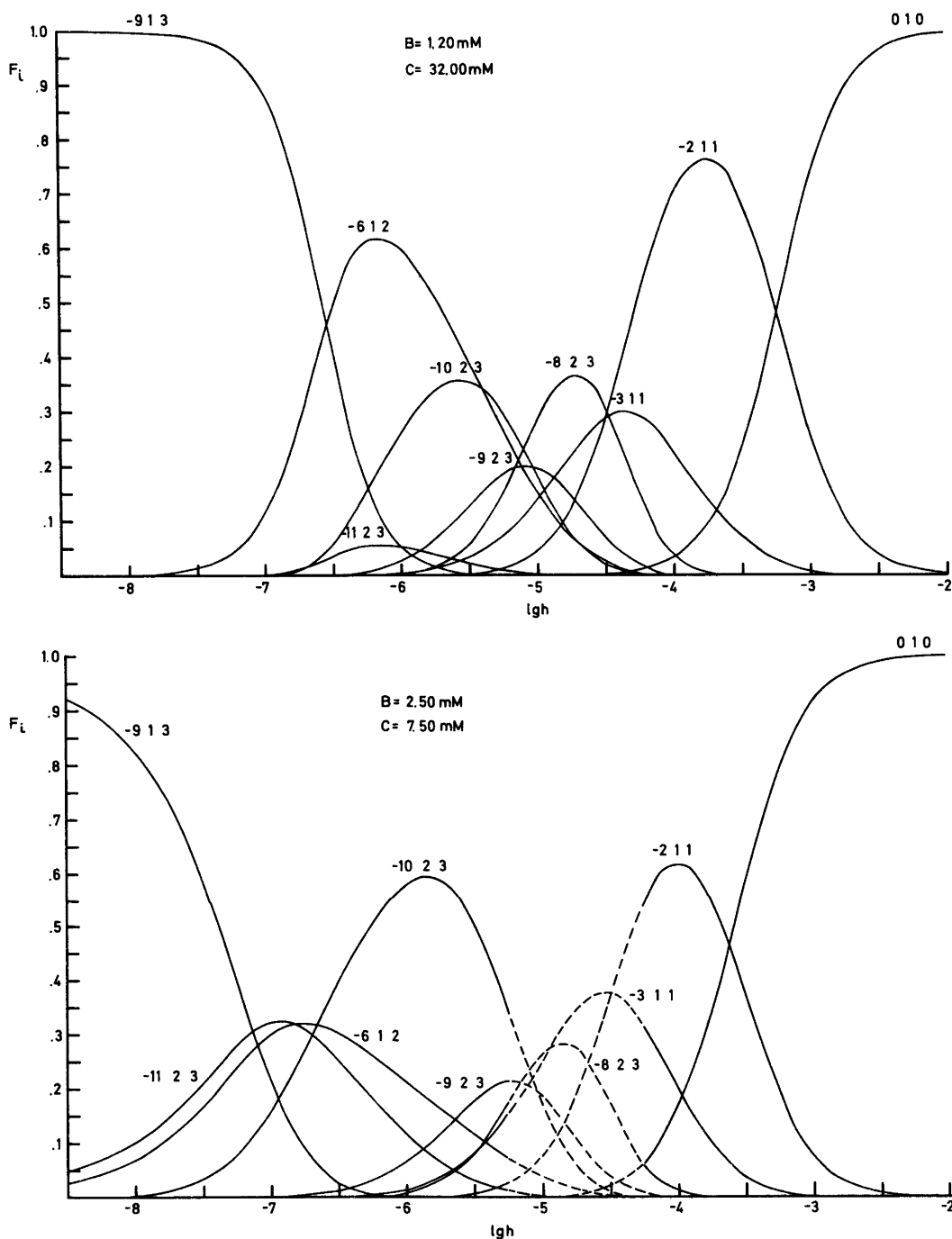
Fig. 6. Distribution diagrams $F_i(\lg h)_{B,C}$. F_i is defined as the ratio between aluminium(III) in a species and total aluminium(III). The calculations have been performed using the computer program SOLGASWATER with constants given in Table 2. Broken lines in Fig. 6b denote a range where no measurements have been performed due to precipitation.

These three pqr-analyses have clearly pointed out the existence of polynuclear complexes in the system. It is also clear that the existing polynuclear complexes are either purely dinuclear or a mixture of di- and tri-nuclear complexes. A number of alternatives were tested on the whole data material, comprising 25 titrations with 700 experimental points, and the result is given in Table 2. The best explanation of experimental data was obtained assuming the species $H_{-8}Al_2(H_3L)_3^{2-}$, $H_{-9}Al_2(H_3L)_3^{3-}$, $H_{-10}Al_2(H_3L)_3^{4-}$ and $H_{-11}Al_2(H_3L)_3^{5-}$ to be formed. The formation constants with standard deviations (3σ) are given in Table 2 and the analysis ended at $\sigma(Z_c)=0.005$, indicating a good fit.

The computer program SOLGASWATER[13] equipped with plotting procedures has been used to calculate distribution diagrams and predominance area diagrams in order to visualize the amounts of the different species (Figs. 6 and 7).

DISCUSSION

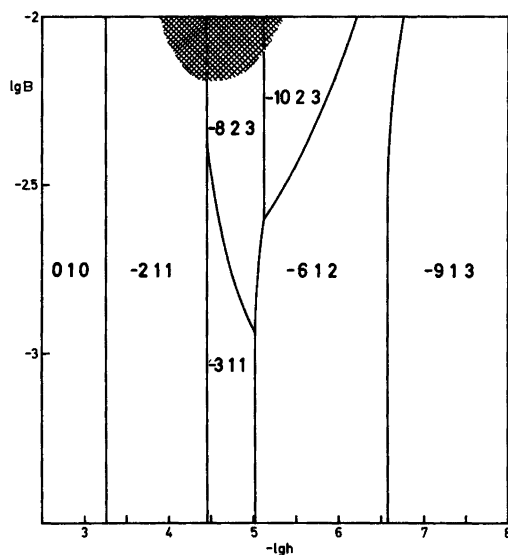In the present investigation equilibrium constants for the formation of binary H^+ – gallic acid as well

Fig. 7. Predominance area diagram for the different aluminium(III) gallic acid complexes. The calculation is performed at a total gallic acid concentration of 30 mM using the computer program SOLGASWATER. The shaded area at the diagram's top represents the approximate precipitation area.

as ternary H^+ – Al^{3+} – gallic acid complexes have been determined and, in all, 11 equilibrium constants have been evaluated. The fact that all complexes occur in great amounts (Fig. 6) and that the standard deviations of the equilibrium constants are low $(3\sigma(\lg \beta_{pqr}) \leq 0.07)$ (Table 2) makes it possible to regard the proposed complexes as well-determined. Since the free H^+-concentration was the only measured quantity it was found necessary to investigate as large concentration and quotient ranges as possible. The limits were set by: (i) systematic trends in β_n for gallic acid concentrations larger than ~ 0.035 M (probably due to medium effects) and (ii) the possibility of dissolving the amorphous precipitate produced at low quotients. The practical quotient range was thereby restricted to $3 \lesssim C/B \lesssim 25$. However, additional effects have been observed in the area $3 \lesssim -\lg h \lesssim 4$ at still lower quotients. This quotient range is now under investigation and the results will be given in a forthcoming paper.
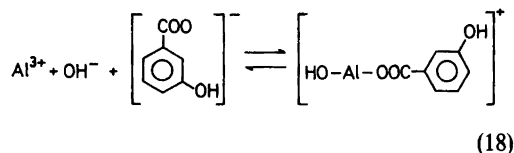
A computational problem in the evaluation of the three-component system has been the lack of a purely mononuclear curve. As is seen from Fig. 6, considerable amounts of dinuclear aluminium complexes are present even at the highest quotient titrated. This makes the behaviour described under "The H^+ – Al^{3+} – gallic acid system" absolutely necessary and is, from our point of view, a very good illustration of the possibilities to treat complicated equilibrium problems with the help of LETAGROPVRID and repeated pqr-searches.

Structural aspects. An equilibrium analysis of a system in solution gives no direct information on the structures of the different species formed. It is thus impossible to judge whether the "active site" in gallic acid comprises: two phenolic groups in ortho-position, one phenolic and one carboxylic group in meta-position or only one carboxylic group. The only way to distinguish between these possibilities is to compare the system with other systems where no doubts remain concerning the complex reactions.

Napoli and Liberti[14] have, in the system H^+ – Al^{3+} – benzoic acid (25 °C, 0.5 M $(NaClO_4)$), reported the reaction (17), with $\lg K = 12.1$.

(17)
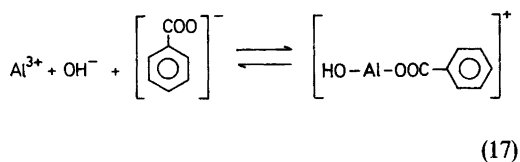
We have performed some preliminary measurements in the system $H^+ - Al^{3+} - $ [3-hydroxybenzoic acid] (25 °C, 0.6 M Na(Cl)). In addition to the carboxylate ion dissociation ($pK_a = 3.85$) we found clear evidence for the formation of a $(-2,1,1)$ complex. Written in the same form as above, eqn. 18, we found lg $K = 11.7$.

$$Al^{3+} + OH^- + \begin{bmatrix} \text{COO} \\ \text{OH} \end{bmatrix}^- \rightleftharpoons \begin{bmatrix} HO-Al-OOC-\text{OH} \end{bmatrix}^+$$

(18)

The formation constants of the $(-2,1,1)$ complexes are comparable in both systems, indicating that 3-hydroxybenzoic acid acts as a monodentate ligand towards Al^{3+}. Consequently, one phenolic and one carboxylic group in meta-position do not form a bidentate chelate with Al^{3+}. Two alternative ways in which gallic acid functions as a ligand thus remain.

If we rewrite the reaction giving $AlHL^+$ in the same form as above we obtain lg $K = 12.95$. As it is rather unreasonable that gallic acid would form a 20 times stronger hydroxo complex with Al^{3+} than 3-hydroxybenzoic acid, the only credible explanation that remains is that this complex is a chelate
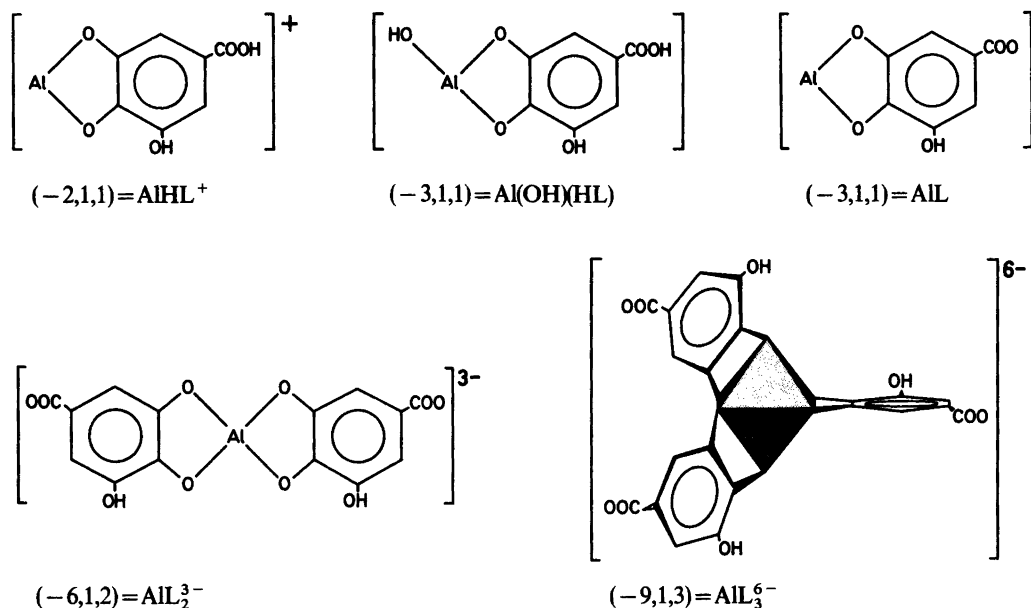
between Al^{3+} and two orthocoordinated phenolic groups.

According to this assumption, the tentative structures of the mononuclear complexes formed (with possible water molecules, sodium and chloride ions coordinated omitted) in this investigation would be as given in Scheme 1.
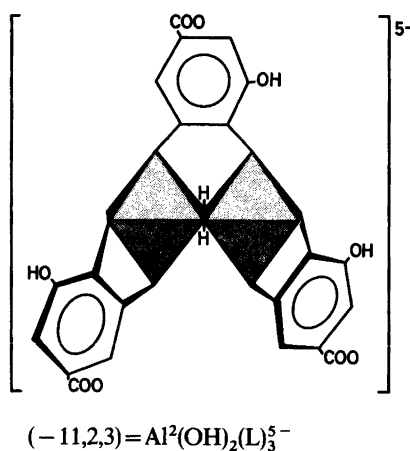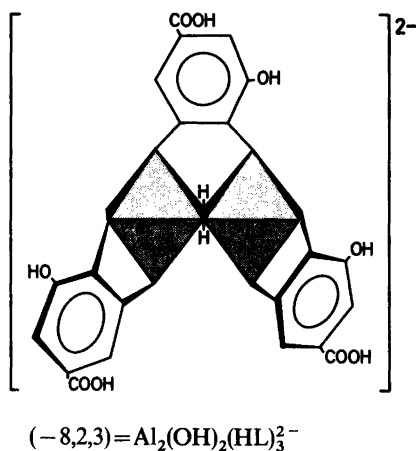
The structure of AlL_3^{6-} is also supported by the well-known tendency of Al^{3+} to coordinate oxygen octahedrally.

The tentative structures of the dinuclear proton series can be deduced from crystal data. From the minerals dawsonite[15] [$NaAl(OH)_2CO_3$] and dundasite[16] [$PbAl_2(OH)_4(CO_3)_2$] it is known that aluminium can form chains through double hydroxo bridges and coordinated carbonate ions. The Al – Al distances are about 2.8 Å in these chains. In crystallized pyrocatechol[17] (1,2-dihydroxybenzene), it has been found that the O – O distance is 2.72 Å, a distance which must be very similar to that in gallic acid. It must therefore be considered very probable that gallic acid can form a bridge between two Al^{3+}-ions, held together by a double hydroxo bridge. The structures would then be as given in Scheme 2.

This assumption, leading to two unequal ligand sites, is in fact supported by the pK_a-values calculated from Table 2. While the values for

$(-2,1,1) = AlHL^+$

$(-3,1,1) = Al(OH)(HL)$

$(-3,1,1) = AlL$

$(-6,1,2) = AlL_2^{3-}$

$(-9,1,3) = AlL_3^{6-}$

Scheme 1.

$(-8,2,3) = Al_2(OH)_2(HL)_3^{2-}$ $(-11,2,3) = Al^2(OH)_2(L)_3^{5-}$

Scheme 2.

$(-8,2,3)$ and $(-9,2,3)$ are equal within experimental error (5.16 and 5.06, respectively) the pK_a for $(-10,2,3)$ is quite different (6.69) and should correspond to the ligand bridging the two octahedras.

According to the distribution and predominance area diagrams given in Figs. 6 and 7 it seems reasonable to assume that $Al_2(OH)_2(HL)_3^{2-}$ is formed according to the reaction:

$$2Al(OH)(HL) + H_3L \rightleftarrows (Al_2(OH)_2(HL)_2 + H_3L) \rightleftarrows$$
$$Al_2(OH)_2(HL)_3^{2-} + 2H^+ \quad \lg K = -3.794$$
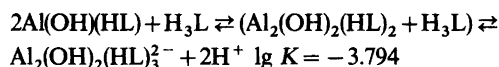
It must be mentioned that we have made several attempts to confirm these tentative structures by crystal growth experiments. The work has, however, been unsuccessful due to the extreme oxygen sensitivity of gallic acid under the conditions needed.

Application to conditions in natural waters. It has been claimed (*cf.* Sillén [18]) that the concentration of dissolved aluminium in natural waters is regulated by aluminosilicates. However, it is important to realize that the presence of organic ligands, *e.g.* humic and fulvic acids, may cause an increase in the solubility of Al-containing sediments.

The complexing ability of gallic acid is used to show the tendency of humic substances to form aluminium complexes in a natural water. Using an approximate value of the content of organic carbon and phenolic OH-groups in a reduced humus water, a total concentration of 30 μM *o*-diphenol is obtained (Gjessing [19]).

In a model calculation it has been shown (*cf.* Fig. 8) that with a total concentration of gallic acid equal to 30 μM, the solubility of kaolinite $[Al_2(OH)_4Si_2O_5]$ with respect to Al is increased by an average factor of 5 in the pH-region 5−9. According to Fig. 8 this increase is mainly due to the species AlL_n, ($n = 1,2,3$),
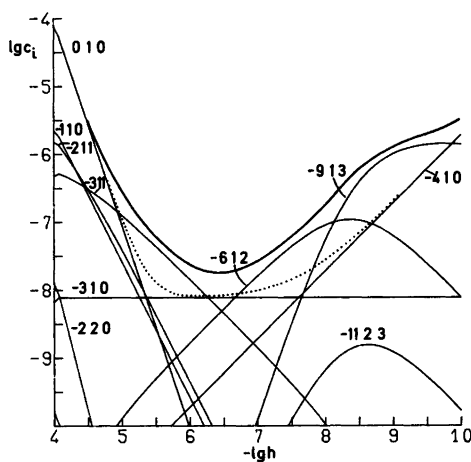

Fig. 8. Concentration (C_i) of binary and ternary complexes in a solution containing 30 μM gallic acid saturated with kaolinite $(Al_2(OH)_4Si_2O_5)$. The heavy full curve represents the total aqueous concentration of Al^{3+}. The heavy broken curve gives the same quantity in absence of gallic acid. The dissolution of kaolinite also yields small amounts of gibbsite, $Al(OH)_3$, within this pH-range. Formation constants for the solid phases are according to Helgeson.[20]

while the dinuclear complexes are of minor importance.

Thus it is of great importance that the complexing ability of ortho-diphenols like pyrocatechol, pyrogallol and gallic acid are considered when speciation and concentration of dissolved aluminium in a natural water are discussed.

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