Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 27. Al^{3+} Complexation to Monocarboxylic Acids

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In order to assess a general rule for the complexation of Al^{3+} to monocarboxylic acids, equilibria in the three systems H^+–Al^{3+}–cyclohexanecarboxylic acid, H^+–Al^{3+}–benzoic acid and H^+–Al^{3+}–3-hydroxybenzoic acid have been analyzed. The analysis was based on potentiometric (glass electrode) measurements in 0.6 M Na(Cl) at 25 °C, with data covering the metal concentrations 0.001–0.026 M and the ligand/metal ratios 0.2 to 5, and was performed using the least-squares computer program LETAGROPVRID. In all three systems, and in accordance with a previous investigation of Al^{3+} complexation to propionic and acetic acids, the species $Al_2(OH)_2L^{3+}$ was found to give the significantly best fit to the data. It was furthermore found that the stability of this species correlated strongly with the acidity constant of the monocarboxylic acid, and that a good estimation of its stability constant could therefore be obtained from the pK_a of the corresponding acid. With benzoic acid and 3-hydroxybenzoic acid, minor amounts of the binary species AlL^{2+} were also detected. Under the experimental conditions used, however, the proportion of this species never exceeded 7 % of the total aluminium concentration.

In computer modelling with the program SOLGASWATER, and with aluminium hydroxide as the solubility-limiting phase, it was shown that the complexing ability of monocarboxylate (benzoate) ions is too weak to explain the strong Al complexation possessed by natural humic material.

The past two decades have seen a burgeoning interest in the biological effects of aluminium.[1–3] From being regarded as a relatively innocuous element, aluminium is today regarded as one of the most serious threats to aquatic life in regions affected by acid deposition.[4] Also, with regard to man, the aluminium ion has been suggested to play a toxic role in Alzheimer's disease,[5] in dialysis encephalopathy/dementia,[6] in different bone disorders,[7] as well as in hematological disorders.[8]

Our contribution to this rapidly growing field of research is to supply hydrologists, toxicologists and physiologists with relevant thermodynamic data with regard to the interactions between substances of geo- and biochemical relevance and aluminium. The basic importance of such data is well recognized,[9] and their potential usefulness is well demonstrated in the first three articles[10–12] of a recent symposium. In these articles it was, however, also clearly pointed out that there is a direct dependence between the validity of the results obtained from thermodynamic modelling and the quality of the underlying thermodynamic database.

In Part 20 of this series[13] we investigated the interactions between Al^{3+} and two low-molecular-weight saturated fatty acids, acetic acid and propionic acid. In contrast to information available in the literature, we found that complexation in both systems was characterized by the formation of a dinuclear, mixed hydroxo species $Al_2(OH)_2L^{3+}$, and that the formation of simple, binary AlL_n^{3-n} complexes was more or less negligible.

The aim of the present study is to expand the work of Part 20 to comprise also cyclic and aromatic monocarboxylic acids and to evaluate whether or not the formation of this particular dinuclear species is a general feature for the interaction between Al^{3+} and monocarboxylic acids. As in the previous study, the interpretation of data will be based on precise potentiometric measurements covering concentration ranges that are as wide as possible, so that the formation of possible binary as well as ternary complexes can be examined.

Experimental

Chemicals and analysis. The cyclohexanecarboxylic acid sample used (Aldrich) was found to contain an acidic impurity (possibly benzoic acid) and therefore had to be purified. Since its aqueous solubility was found to be limited, the purification was made by allowing an amount corresponding to approximately twice its solubility to equilibrate with water under supersonic conditions. The resulting suspension was then filtered and the remaining solid was rinsed with ice-cold water and dried under vacuum at low temperature. The result of this purification

was tested by potentiometric titrations which now showed full agreement with the behaviour expected for a pure monoprotic acid.

Benzoic acid (Merck p.a.) and 3-hydroxybenzoic acid (Aldrich) were used as received after being dried at 80 °C. Stock solutions of the three ligands were prepared by dissolving the solids, together with appropriate amounts of NaCl, in boiled distilled water. The HL contents of these solutions were determined potentiometrically using the Gran extrapolation method[14] and showed good agreement with values expected from weighing. The preparation and analysis of other solutions are described in Ref. 15.

Apparatus. The automatic system for precise EMF titrations, the thermostat and the cell arrangement are fully described elsewhere.[15]

Temperature and medium. The present investigation was carried out at 25.00 ± 0.05 °C in a constant ionic medium of 0.6 M Na(Cl).

Method. The measurements were carried out as a series of potentiometric (glass electrode) titrations. The titration procedures, including a special procedure for calibrating the glass electrodes, have been described earlier in this series.[15,16] The reversibility of each equilibrium was tested by performing titrations in acidic as well as in alkaline directions. The dissociation constants for the monocarboxylic acids were determined in separate titrations within the concentration range 0.05–0.020 M and for $2.0 < -\log [H^+] < 6.4$. The three-component titrations were performed at a constant ratio between the total concentration of aluminium, B, and ligand, C. The upper $-\log [H^+]$ limits in these titrations were, for benzoic acid and 3-hydroxybenzoic acid, set by the appearence of sluggish homogeneous equilibria, most probably caused by the formation of polynuclear Al-hydrolysis products. For cyclohexanecarboxylic acid, the upper $-\log [H^+]$ limit was set by the formation of a thin, adhesive precipitate forming as a film on the surface of the solution.

Data treatment. The equilibria under consideration in the present study can be divided into three groups corresponding to: (1) the ionization of the monocarboxylic acid, (2) the hydrolysis of Al^{3+} and (3) the formation of three-component complexes of the general composition

$$HL \rightleftharpoons H^+ + L^-; \beta_{-1,0,1} \quad (1)$$

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

$$pH^+ + qAl^{3+} + rHL \rightleftharpoons H_pAl_q(HL)_r^{p+3q}; \beta_{p,q,r} \quad (3)$$

$H_pAl_q(HL)_r^{p+3q}$. The equilibrium constant corresponding to eqn. (1), in which HL represents cyclohexanecarboxylic acid, benzoic acid and 3-hydroxybenzoic acid, respectively, will be evaluated from separate titration experiments with $B = 0$.

For the hydrolytic equilibria of Al^{3+}, i.e. eqn. (2), the results obtained in earlier parts of this series[17–19] ($\log \beta_{-1,1,0} = -5.52$; $\log \beta_{-2,1,0} = -11.3$; $\log \beta_{-3,1,0} = -17.3$; $\log \beta_{-4,1,0} = -23.46$; $\log \beta_{-4,3,0} = -13.57$ and $\log \beta_{-32,13,0} = -109.2$) will be used.

In the mathematical treatment of three-component data, these binary complex models were considered as known, and all effects above that level were treated as being caused by the formation of ternary complexes [eqn. (3)].

Computer programs. The analysis of data was performed with the least-squares computer program LETAGROPVRID,[20] version ETITR.[21,22] The (p,q,r) triplets and corresponding equilibrium constants that best fit the experimental data were determined by minimizing the error-squares sum $U = \Sigma(H_{calcd} - H_{exptl})^2$, where H is the analytical proton concentration with H_2O, Al^{3+} and HL as zero level. The standard deviations $\sigma(H)$ and $3\sigma(\log \beta_{p,q,r})$ obtained in these calculations were defined and calculated according to Sillén.[23,24]

For the construction of distribution diagrams, the modelling computer program SOLGASWATER,[25] equipped with plotting procedures, was used. All computations were performed on a CD Cyber 850 computer.

Data, calculations and results

An initial stage of our data treatments always includes the construction of the standard graphical plots $Z_c(-\log [H^+])$ and $\bar{n}(\log [L^-])$. (Z_c is defined as the average number of hydroxide ions reacted per HL and $\bar{n}$ as the average number of L^- coordinated per Al^{3+}.) This was also done in the present systems; however, since the plots obtained in the three systems showed a very close resemblance, only the graphs valid for the H^+–Al^{3+}–3-hydroxybenzoic acid system have been illustrated (Figs. 1 and 2).

Graphical representations of this kind can be used to yield important information about the nature of the complexes that are formed. Thus, from the fact that $Z_c > 1$ in Fig. 1, it can directly be concluded that binary and/or ternary hydroxo complexes are formed in the system. Secondly, since each B/C combination results in a unique curve in the $\bar{n}(\log [L^-])$ graph (Fig. 2), and no coinciding range can be discerned, it can be concluded that binary AlL_n^{3-n} complexes are not the predominating complexes in the system. This implies that, in the present systems, unbiased searches for the stoichiometries and corresponding stabilities of appearing complexes must be undertaken.

This can suitably be done in the form of a trial-and-error process in which the integer values of p,q and r for $H_pAl_q(HL)_r^{p+3q}$ [cf. eqn. (3)] are systematically varied. For each (p,q,r) combination, the "best possible" equilibrium constant, $\beta_{p,q,r}$, is determined using the LETAGROPVRID program, and the corresponding error-squares sum, $U = \Sigma(H_{calcd} - H_{exptl})^2$, is recorded. The search is then pro-

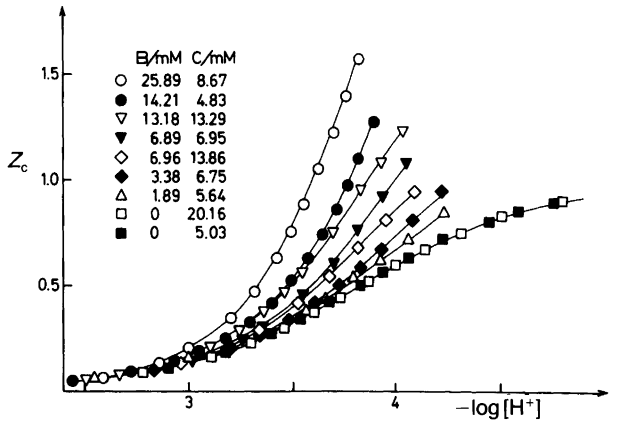

Fig. 1. Some of the experimental data in the system H^+–Al^{3+}–3-hydroxybenzoic acid plotted as curves showing $Z_c(-\log[H^+])$. The lines have been calculated using the set of proposed constants in Table 1.

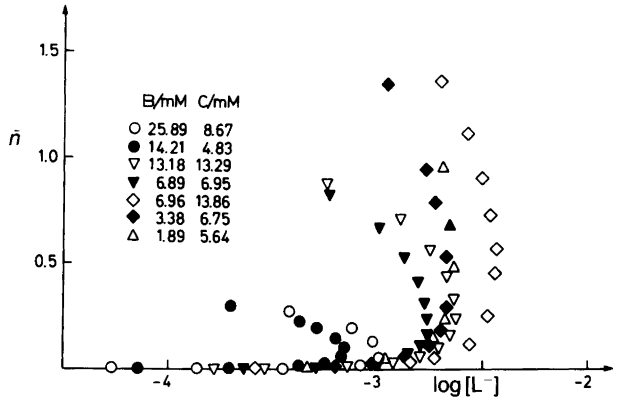

Fig. 2. Part of the experimental data in the system H^+–Al^{3+}–3-hydroxybenzoic acid plotted as curves showing $\bar{n}(\log[L^-])$.

ceeded until the "best" (p,q,r) triplet, i.e. the triplet giving the closest fit to experimental data, has been identified. This triplet may then be the true stoichiometry of a single species existing in solution, but it may also represent the best possible average of two or several coexisting complexes of different compositions. It is therefore essential to examine carefully the resulting $\Delta H(-\log[H^+], B, C, C/B)$ residuals to see whether these are within experimental uncertainties or whether systematic deviations between experimental data and the thermodynamic model still remain. In the latter case, the equilibrium analysis can proceed either by testing different complexes in addition to the species found or, in the more general case, by testing different pairs of complexes with an average composition close to the (p,q,r) composition found.

The system H^+–Al^{3+}–cyclohexanecarboxylic acid. Data used to evaluate the dissociation constant for cyclohexanecarboxylic acid were those for six titrations with 160 experimental data within the concentration range $0.005 \leq C \leq 0.020$ M and $2.9 \leq -\log[H^+] \leq 6.4$. The LETAGROP calculation using these data gave as a result $\log(\beta_{-1,0,1} \pm 3\sigma) = -4.641 \pm 0.003$, with $\sigma(H) = 0.03$ mM.

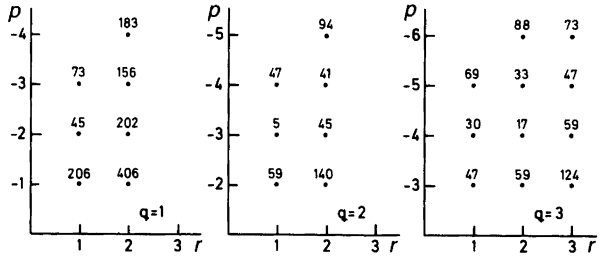

Fig. 3. Result of the (p,q,r) analysis on data in the H^+–Al^{3+}–cyclohexanecarboxylic acid system. The figures give error-squares sums 10 $U_H(pr)_q$ assuming one ternary complex with "best possible" equilibrium constant. The calculations are based on 264 points giving 10 $U_H(00)_0 = 695$.

Data in the three-component system consisted of 14 titrations with 264 experimental data. These covered the ranges $0.002 \leq B \leq 0.013$ M; $0.003 \leq C \leq 0.011$ M; $C/B = 0.33$, 0.5, 1, 2 and 4; $1.9 \leq -\log[H^+] \leq 4.2$.

Since, as described above, the $\bar{n}(\log[L^-])$ plot had indicated that the formation of binary AlL_n^{3-n} species was of minor importance, an analysis of the data was directly performed as an unbiased (p,q,r) analysis. The result of this analysis is illustrated in Fig. 3 and shows that a species with the composition $H_{-3}Al_2(HL)^{3+}$ and with $\log(\beta_{-3,2,1}) = -8.04 \pm 0.011$ provides the closest fit to experimental data. The average remaining residual was $\sigma(H) = 0.04$ mM, and no signs of systematic behaviour were observed. To continue to allow for the formation of AlL^{2+}, a final LETAGROP calculation was performed in which the formation constants for $(-1,1,1)^{2+}$ and $(-3,2,1)^{3+}$ were co-varied on all three-component data. The result of this calculation was that, although the species was accepted with $\log(\beta_{-1,1,1} \pm 3\sigma) = -3.48 \pm 0.25$, no significant improvement in the fit to the experimental data was obtained. Some model calculations using this formation constant also showed that, in the concentration ranges studied, the proportion of AlL^{2+} never exceeded 2% of the total aluminium concentration.

The system H^+–Al^{3+}–benzoic acid. For the evaluation of the binary system, data derived from four titrations with 107 experimental data within the limits $0.004 \leq C \leq 0.019$ M and $1.9 < -\log[H^+] \leq 5.9$ were used. The LETAGROP calculation ended at $\sigma(H) = 0.04$ mM, with $\log(\beta_{-1,0,1} \pm 3\sigma) = -3.912 \pm 0.003$.

Data used for the evaluation of the three-component data were those for 14 titrations with 382 experimental data within the ranges $0.001 \leq B \leq 0.023$ M; $0.002 \leq C \leq 0.018$ M; $C/B = 0.2$, 0.4, 0.5, 0.7, 1.0, 1.5, 3 and 5 and $1.9 \leq -\log[H^+] \leq 4.4$.

The result of the unbiased (p,q,r) search is illustrated in Fig. 4 and shows that in this system also, the species $H_{-3}Al_2(HL)^{3+}$ $[\log(\beta_{-3,2,1} \pm 3\sigma) = -7.45 \pm 0.010]$ gave the closest fit to the experimental data. Compared to the

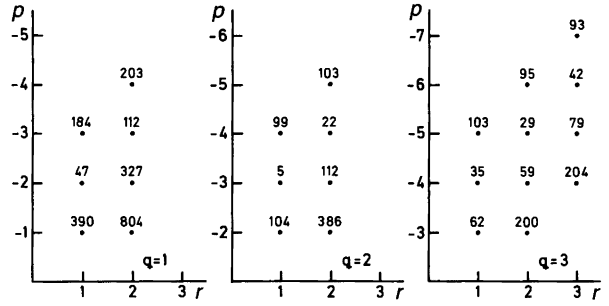

Fig. 4. Result of the (p,q,r) analysis on data in the H^+–Al^{3+}–benzoic acid system. The calculations are based on 382 data with $U_H(00)_0 = 892$, and error squares sums assuming one ternary complex are given.

cyclohexanecarboxylic acid data, however, the remaining average residual was considerable higher, $\sigma(H) = 0.12$ mM, and an inspection of them revealed that minor systematic deviations remained to be explained in the $-\log[H^+]$ range 2.5–3.5. The species AlL^{2+} was therefore added to the speciation scheme, and a LETAGROP calculation in which the equilibrium constants for $H_{-3}Al_2(HL)^{3+}$ and AlL^{2+} were simultaneously varied was performed. In this calculation the error-squares sum U decreased by a factor of two, and AlL^{2+} was accepted with a moderate uncertainty in its stability constant [$\log(\beta_{-1,1,1} \pm 3\sigma) = -2.67 \pm 0.069$; $\log(\beta_{-3,2,1} \pm 3\sigma) = -7.446 \pm 0.008$; $\sigma(H) = 0.08$ mM].

An inspection of the remaining residuals revealed that the systematic deviations previously seen had now vanished.

The system H^+–Al^{3+}–3-hydroxybenzoic acid. In Figs. 1 and 2 some of the experimental data collected in this system are presented. For evaluating the carboxylic dissociation constant of the ligand, five titrations (151 experimental data points) within the limits $0.005 \leq C \leq 0.020$ M; $2.8 \leq -\log[H^+] \leq 6.0$ were used. No attempts to evaluate the phenolic dissociation constant were made. The LETAGROP calculation on these data ended at $\sigma(H) = 0.02$ mM with $\log(\beta_{-1,0,1} \pm 3\sigma) = -3.837 \pm 0.001$.

The analysis of three-component data (13 titrations; 292 experimental data; $0.003 \leq B \leq 0.026$ M; $0.005 \leq C \leq$ 0.014 M; $C/B = 0.3$, 0.5, 1, 2, and 3; $1.7 \leq -\log[H^+] \leq 4.2$) followed the same protocol as in the previous two systems.

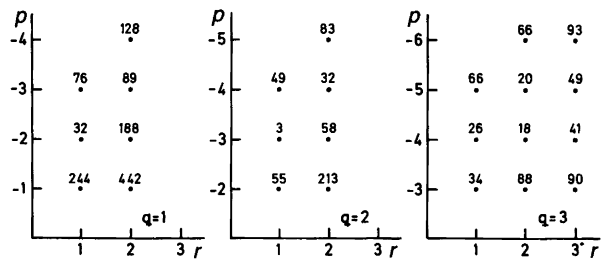

Fig. 5. Result of the (p,q,r) analysis on data in the H^+–Al^{3+}–3-hydroxybenzoic acid system. One ternary complex is assumed, and the figures give the error squares sum for each (p,q,r) composition. The calculations are based on 292 points giving $U_H(00)_0 = 443$.

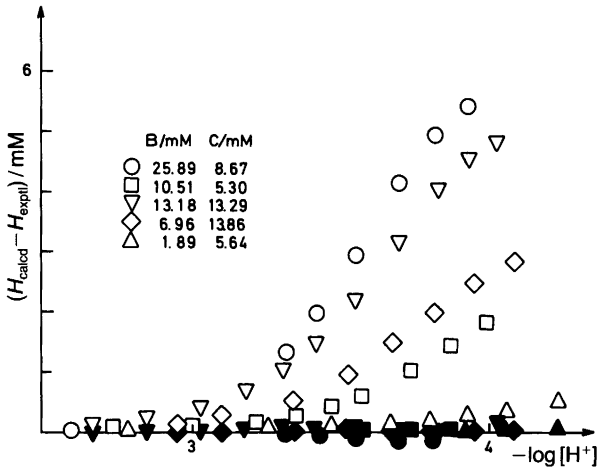

Fig. 6. Residual plot in the H^+–Al^{3+}–3-hydroxybenzoic acid system. Open symbols represent residuals between measured data and two-component model (i.e. Al hydrolysis and pK_a for the ligand), while filled symbols represent deviations between measurements and final model.

The (p,q,r) analysis is illustrated in Fig. 5, and once again the species $H_{-3}Al_2(HL)^{3+}$ [$\log(\beta_{-3,2,1} \pm 3\sigma) = -7.46 \pm 0.012$; $\sigma(H) = 0.10$ mM] was found to give the significantly best fit to the data. As in the case of benzoic acid, however, small systematic deviations were found at $2.5 \leq -\log[H^+] \leq 3.5$, and therefore the species AlL^{2+} was added to the model. In this case, the error-squares sum decreased by a factor of 3, and both species were accepted; $\log(\beta_{-1,1,1} \pm 3\sigma) = -2.59 \pm 0.056$; $\log(\beta_{-3,2,1} \pm 3\sigma) = -7.453 \pm 0.007$. The resulting average residual became 0.05 mM, and no remaining systematic deviations could be observed. This is illustrated in Fig. 6, in which the open symbols represent the residuals between measured effects and the two-component model (i.e. Al hydrolysis and acid/base behaviour of 3-hydroxybenzoic acid) and the filled symbols represent the corresponding residuals with the final model.

Discussion

Speciation and equilibria. In the present study, equilibria between Al^{3+} and three cyclic and aromatic monocarboxylic acids have been analyzed, and the results, together with the results previously reported for acetic acid and propionic acid,[13] are summarized in Table 1.

Common to all these ligands is thus the dominance of a species with the stoichiometric composition $H_{-3}Al_2(HL)^{3+}$. Since this stoichiometry implies that the number of ionizable protons in the ligands is exceeded, it can without doubt be described as a mixed hydroxo complex $Al_2(OH)_2L^{3+}$. A complex of this composition has also been found in the weakly coordinating Al-carbonate system,[17,26] and minerals containing dihydroxo-bridged aluminium

Table 1. Binary and ternary complexes in H^+–Al^{3+}–monocarboxylic acid systems. The (*p,q,r*) notations and formation constants are related to the reaction $pH^+ + qAl^{3+} + rHL \rightleftharpoons H_pAl_q(HL)_r^{p+3q}$.

Proposed formula	(*p,q,r*) / log $\beta_{p,q,r}$	Cyclohexanecarboxylic acid	Benzoic acid	3-Hydroxybenzoic acid	Acetic acid[13]	Propionic acid[13]
L^-	(−1,0,1)	−4.641±0.003	−3.912±0.003	−3.837±0.001	−4.487±0.001	−4.606±0.001
AlL^{2+}	(−1,1,1)	−3.48±0.25	−2.67±0.07	−2.59±0.06	−3.97±0.54	–
$Al_2(OH)_2L^{3+}$	(−3,2,1)	−8.04±0.011	−7.446±0.008	−7.453±0.007	−7.98±0.017	−8.038±0.008

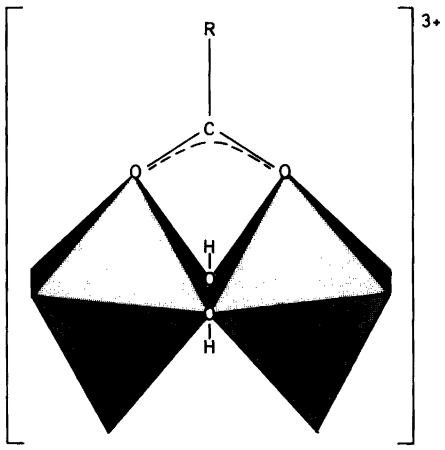

Fig. 7. Tentative structure for the species $Al_2(OH)_2L$ based on an assumed resemblance with the structure of Dawsonite.[27]

chains with carbonate ions acting as bridges between adjacent aluminium ions have been reported.[27,28] It is therefore tempting to assume that this complex $Al_2(OH)_2L^{3+}$ is the building block of these chains and that the structure, illustrated in Fig. 7, is a generally occurring structure for all dinuclear Al^{3+}-monocarboxylate complexes. To validate this assumption, work has now been started to grow single crystals of the different $Al_2(OH)_2L^{3+}$ complexes.

With benzoic acid and 3-hydroxybenzoic acid, the formation of a species AlL^2 was also indicated. The minor importance of this complex, as compared to that of $Al_2(OH)_2L^{3+}$, is illustrated in the distribution diagrams given in Fig. 8. It is interesting to note, however, that written in the form $Al^{3+} + L^- \rightleftharpoons AlL^{2+}$, the equilibrium constants for benzoate ($\log K = 1.24 \pm 0.07$), 3-hydroxybenzoate ($\log K = 1.25 \pm 0.06$), cyclohexanecarboxylate ($\log K = 1.16 \pm 0.25$) and acetate ($\log K = 0.52 \pm 0.54$) all fall within the same range.

Fig. 8 also shows that the species $Al_2(OH)_2L^{3+}$ is formed at a somewhat lower $-\log[H^+]$ with benzoic acid and 3-hydroxybenzoic acid than with cyclohexanecarboxylic acid. However, this does not directly imply that the benzoate and 3-hydroxybenzoate ions have a stronger affinity for the Al^{3+} ion. In fact, by rewriting the formation reaction as $2Al^{3+} + L^- \rightleftharpoons H_{-2}Al_2L^{3+} + 2H^+$ and recalculating the stability constants, data presented in Fig. 9 are obtained. From this plot it can thus be seen that the Al affinity increases with increasing pK_a, and also that there exists

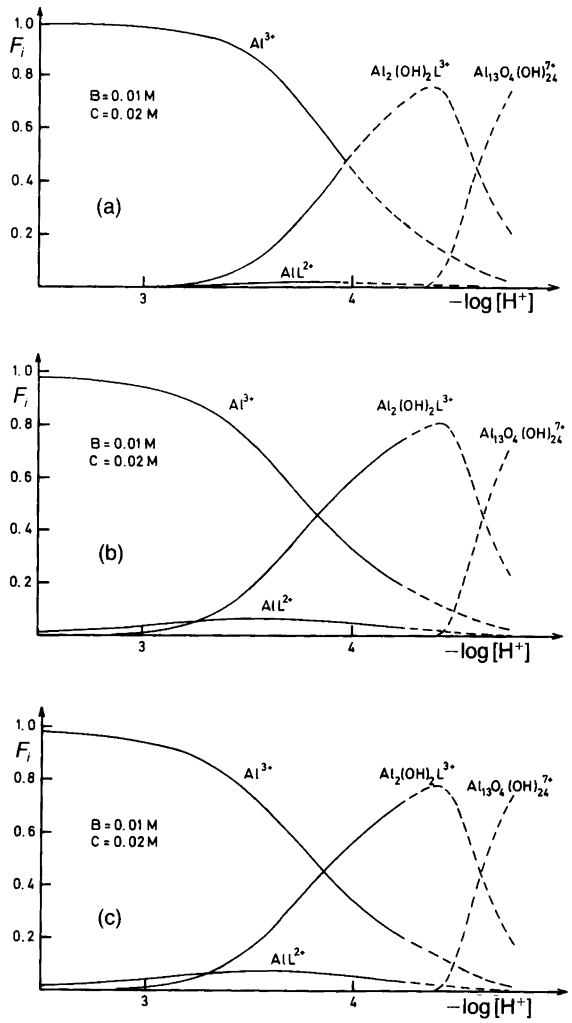

Fig. 8. Distribution diagrams $F_i(-\log[H^+])$ in (a) the H^+–Al^{3+}–cyclohexanecarboxylic acid system, (b) the H^+–Al^{3+}–benzoic acid system and (c) the H^+–Al^{3+}–3-hydroxybenzoic acid system. F_i is defined as the ratio between aluminium(III) in a species and total aluminium(III). The diagrams were constructed using the equilibrium models presented in Table 1, and broken curves denote an extrapolation beyond the measurement range.

an approximate linearity between these quantities. This plot can therefore be used to estimate the stability of $Al_2(OH)_2L^{3+}$ in other monocarboxylic acid systems in which the HL/L^- acidity constant is known.

It should, however, also be clearly pointed out that the formation of $Al_2(OH)_2L^{3+}$ might be more-or-less replaced

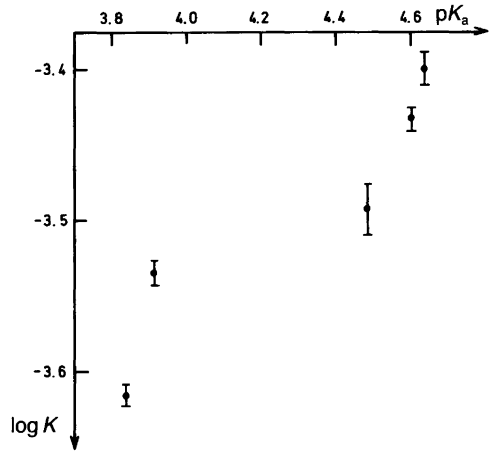

Fig. 9. Logarithm of the stability constant for the reaction $2Al^{3+}+2H_2O+L^- \rightleftharpoons Al_2(OH)_2L^{3+}+2H^+$ versus pK_a for HL. From left to right the ligands are 3-hydroxybenzoic acid, benzoic acid, acetic acid, propionic acid and cyclohexanecarboxylic acid.

by the formation of other species if the ligand contains other suitably placed Al-coordinating groups. Thus with α-hydroxypropionic acid, (lactic acid)[29] this complex was found as a minor species, while with 2-hydroxybenzoic acid (salicylic acid)[16] the speciation was found to be dominated by the bidentally bound complexes AlL^+ and AlL_2^-, whereas $Al_2(OH)_2L^{3+}$ was not identified at all. With 3,4,5-trihydroxybenzoic acid (gallic acid)[15] binding to the monocarboxylate group was totally over-ruled by the much stronger binding to the (3,4)-*o*-diphenolic site.

Modelling calculations. The benzoate binding site can probably be regarded as one of the most relevant sites in natural humic material.[30] It is therefore of interest to estimate the influence of this site on the chemistry of aluminium in natural waters. Since aluminium concentrations in nature are normally regulated by the presence of low-solubility phases such as aluminium hydroxide and/or aluminosilicates, the influence of a complexing ligand will be that of increasing the total aqueous aluminium concentration. This increase can suitably be illustrated in a solubility diagram showing the total aqueous solubility as a function of ligand concentration and $-\log[H^+]$ or, as illustrated in Fig. 10, as a distribution diagram showing the fraction of aluminium organically bound at various ligand concentrations and $-\log[H^+]$. From this figure it can be concluded that the benzoate site can be expected to have a significant influence on the chemistry of aqueous aluminium at concentrations exceeding ≈1–10 mM. Given, however,[32] that natural organics contain ≈5–10 μeqiv. of carboxylate groups per mg of organic carbon, and that a "normal" coloured stream water contains some 10–20 mg of dissolved organic carbon per dm^3, it is evident that this monodentate binding site is far too weak to explain the strong Al binding properties possessed by humic material.

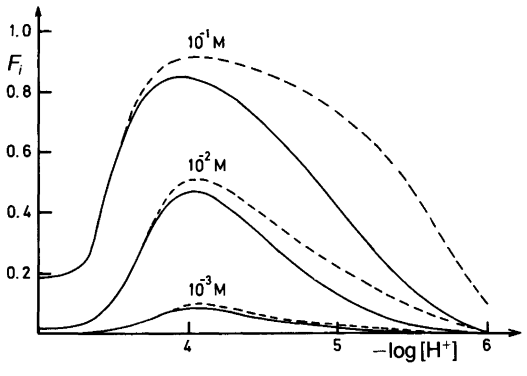

Fig. 10. Fraction of aluminium in the form of $Al_2(OH)_2(benzoate)^{3+}$ (curves) and sum of $Al_2(OH)_2(benzoate)^{3+}$ and $Al(benzoate)^{2+}$ (dashed lines) as a function of the total benzoic acid/benzoate concentration and $-\log[H^+]$. The aqueous aluminium(III) concentration is regulated by crystalline gibbsite ($\log {}^*K_{so} = 9.6$).[30]

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References

1. Sigel, H. and Sigel, A., Eds., *Metal Ions in Biological Systems,* Vol. 24, *Aluminium and its Role in Biology,* Marcel Dekker, New York 1988.
2. Gitelman, H. J., Ed., *Aluminium and Health,* Marcel Dekker, New York 1989.
3. Massey, R. C. and Taylor, D., Eds., *Aluminium in Food and the Environment,* Royal Society of Chemistry, London 1988.
4. Mason, J. and Seip, H. M. *Ambio 14* (1985) 45.
5. Crapper, D. R., Krishnan, S. S. and Quittkat, S. *Brain 99* (1976) 67.
6. Alfrey, A. C., Hegg, A. and Craswell, P. *Am. J. Clin. Nutr. 33* (1980) 1509.
7. Boyce, B. F., Elder, H. Y., Elliot, H. L., Fogelman, I., Fell, G. S., Junors, B. J., Beastall, G. and Boyle, I. T. *Lancet 2* (1982) 1009.
8. Wills, M. R. and Savory, J. *Lancet 2* (1983) 29.
9. Martin, R. B. *Metal Ions in Biological Systems 24* (1988) 1.
10. Clevette, D. J. and Orvig, C. *Polyhedron 9* (1990) 151.
11. Jackson, G. E. *Polyhedron 9* (1990) 163.
12. Martell, A. E., Motekaitis, R. J. and Smith, R. M. *Polyhedron 9* (1990) 171.
13. Marklund, E., Öhman, L.-O. and Sjöberg, S. *Acta Chem. Scand. 43* (1989) 641.
14. Gran, G. *Acta Chem. Scand. 4* (1950) 559.
15. Öhman, L.-O. and Sjöberg, S. *Acta Chem. Scand., Ser. A 35* (1981) 201.
16. Öhman, L.-O. and Sjöberg, S. *Acta Chem. Scand., Ser. A 37* (1983) 875.
17. Öhman, L.-O. and Forsling, W. *Acta Chem. Scand., Ser. A 35* (1981) 795.
18. Öhman, L.-O., Sjöberg, S. and Ingri, N. *Acta Chem. Scand., Ser. A 37* (1983) 561.
19. Öhman, L.-O. *Inorg. Chem. 27* (1988) 2565.
20. Ingri, N. and Sillén, L.-G. *Ark. Kemi 23* (1964) 97.
21. Arnek, R., Sillén, L.-G. and Wahlberg, O. *Ark. Kemi 31* (1969) 353.

22. Brauner, P., Sillén, L.-G. and Whiteker, R. *Ark. Kemi 31* (1969) 365.
23. Sillén, L.-G. *Acta Chem. Scand. 16* (1962) 159.
24. Sillén, L.-G. and Warnqvist, B. *Ark. Kemi 31* (1969) 341.
25. Eriksson, G. *Anal. Chim. Acta 112* (1979) 375.
26. Hedlund, T., Sjöberg, S. and Öhman, L.-O. *Acta Chem. Scand., Ser. A41* (1987) 197.
27. Frueh, A. I., Jr. and Godlightly, J. P. *Can. Miner. 9* (1967) 51.
28. Cocco, G., Fanfani, L., Nunzi, A. and Zanazzi, P. F. *Miner. Mag. 38* (1972) 564.
29. Marklund, E. and Öhman, L.-O. *Acta Chem. Scand. 44* (1990) 228.
30. Hayes, M. H. B., MacCarthy, P., Malcolm, R. L. and Swift, R. S., Eds., *Humic Substances II,* Wiley, New York 1989.
31. Baes, C. F. and Mesmer, R. E. *The Hydrolysis of Cations,* Wiley, New York 1976.
32. Thurman, E. M. *Organic Geochemistry of Natural Waters,* Martinus Nijhoff, Dordrecht 1985.

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