

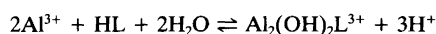
Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 20. Composition and Stability of Aluminium Complexes with Propionic Acid and Acetic Acid

Eva Marklund,* Lars-Olof Öhman and Staffan Sjöberg

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

Marklund, E., Öhman, L.-O. and Sjöberg, S., 1989. Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 20. Composition and Stability of Aluminium Complexes with Propionic Acid and Acetic Acid. – Acta Chem. Scand. 43: 641–646.

Equilibria in the title systems were studied in 0.6 M NaCl medium at 25 °C using potentiometric (glass electrode) measurements supplemented with quantitative ^{27}Al NMR measurements. All aluminium complexation data, covering the ligand/metal ratios 1/3 to 30 and metal concentrations 0.001–0.012 M can be explained on the basis of the single complex $\text{Al}_2(\text{OH})_2\text{L}^{3+}$. The corresponding equilibrium constants, defined according to the reaction



are $\log \beta_{-3,2,1} = -8.038 \pm 0.008$ and -7.979 ± 0.017 for propionic and acetic acid, respectively.

The ligand dissociation constants for the reaction $\text{HL} \rightleftharpoons \text{H}^+ + \text{L}^-$ were studied in separate titrations and were found to be $\log \beta_{-1,0,1} = -4.6058 \pm 0.0009$ and $\log \beta_{-1,0,1} = -4.4868 \pm 0.0007$ for propionic and acetic acid, respectively. All errors given are three times the standard deviations, $3\sigma(\log \beta_{p,q,r})$. Data were analysed using the least-squares computer program LETAGROPVRID.

The growing interest in the environmental chemistry of aluminium has focused our attention on the problem of speciation of aqueous Al(III). It is generally accepted that complexation affects both the distribution and toxicity of trace metals.^{1,2} Knowledge of the speciation of Al(III) in a natural water system is thus essential in order to be able to interpret its toxicity and understand its transport in soils, and in ground and fresh water.

In previous studies within the title series, speciation and equilibria have been determined in Al^{3+} systems with different ligand classes, e.g. hydroxy-substituted carboxylic acids (lactic acid,³ salicylic acid,⁴ citric acid^{5,6}) and dicarboxylic acids (oxalic acid,⁷ phthalic acid⁸). In these systems, mono- and polynuclear ternary $\text{Al}^{3+}-\text{L}-\text{OH}^-$ complexes have been frequently found.

The aim of the present study is to interpret complexation in Al(III) systems with saturated fatty acids. As propionic and acetic acid are the most water-soluble ones, and are also frequently found in natural waters, these were chosen as suitable representatives for this ligand class. In addition, acetic acid is commonly used as a buffer agent since it assumed to exhibit a negligible tendency to complexation towards metal ions.

Earlier interpretations of the equilibria involved in aqueous Al^{3+} -acetate solutions are based on two articles by the

same authors.^{9,10} In the first of these articles the existence of an AlL^{2+} complex ($\log K = 1.51$) was postulated. In the later article this result was revised, claiming the dominance of a mixed $\text{Al}(\text{OH})\text{L}^+$ complex. Considering the inconsistency in these interpretations, we found it urgent to perform an unbiased search for the stoichiometric composition of the complexes formed. Data (based on precise potentiometric titrations and ^{27}Al NMR measurements) covering as wide concentration ranges as possible have been collected, so that the formation of possible binary $\text{Al}^{3+}-\text{L}^-$ and/or ternary mono- and polynuclear $\text{Al}^{3+}-\text{L}^- - \text{OH}^-$ complexes can be examined.

Experimental

Chemicals and analysis. Propionic acid ($\text{CH}_3\text{CH}_2\text{COOH}$, HL) (Fluka *p.a.*) and acetic acid, glacial 100% (CH_3COOH , HL) (Merck *p.a.*) were used without further purification. Stock solutions were prepared in 0.6 M NaCl medium, and the HL content of these solutions was determined potentiometrically using the Gran extrapolation method.¹¹

All other solutions (NaCl, HCl, NaOH and Al^{3+}) were prepared and analysed as described elsewhere.³

*To whom correspondence should be addressed.

Apparatus. The automatic system for precise emf titrations, the thermostat and the electrodes have been described earlier.³ The ²⁷Al NMR spectra were recorded on a Bruker WM-250 spectrometer.

Method

Potentiometric measurements. The present investigation was carried out as series of titrations at 25 °C in a constant ionic medium of 0.6 M NaCl. The titration procedures, including a special procedure for calibrating the glass electrode, have been described earlier in this series.³

The dissociation constants for propionic and acetic acid were determined in separate titrations within the concentration range 0.010–0.040 M and $2.8 \leq -\log [H^+] \leq 6.8$.

The three-component titrations were performed at a constant ratio between the total concentrations of aluminium, *B*, and ligand, *C*. In the Al-propionic acid system, *B* and *C* were varied within the limits $0.002 \text{ M} \leq B \leq 0.012 \text{ M}$; $0.004 \text{ M} \leq C \leq 0.020 \text{ M}$; $C/B = 0.33, 0.5, 1, 2, 5, 10$ and $1.9 \leq -\log [H^+] \leq 4.4$.

Corresponding data for the Al-acetic acid system are: $0.001 \text{ M} \leq B \leq 0.005 \text{ M}$; $0.005 \text{ M} \leq C \leq 0.030 \text{ M}$; $C/B = 1, 2, 4, 6, 10, 30$ and $2.2 \leq -\log [H^+] \leq 4.6$.

The upper $-\log [H^+]$ limits in these titrations were set by the appearance of extremely sluggish equilibria, most probably caused by the formation of polynuclear Al-hydrolysis products, viz. the species $Al_{13}O_4(OH)_{24}^{7+}$.

NMR measurements. The ²⁷Al NMR measurements were carried out at $295 \pm 1 \text{ K}$ using a Bruker WM-250 spectrometer equipped with a 10 mm multinuclear probe-head. The short spin-lattice relaxation times for the quadrupolar nucleus ²⁷Al and the high stability of the spectrometer made it possible to collect the data without D₂O lock of the instrument.

By calibrating the instrument versus a $10.00 \cdot 10^{-3} \text{ M}$ Al³⁺ solution at $-\log [H^+] = 2.00$ and operating it in the absolute intensity mode, quantitative information about the free concentration of Al³⁺ was obtained.

Data treatment. The equilibria under consideration in the present study can be divided into groups as follows: (1) ionization of propionic and acetic acid, (2) hydrolysis of Al³⁺ and (3) general establishment of three-component equilibria.

For eqn. (1), we make use of results obtained in separate potentiometric titration experiments.



In this equation, HL stands for propionic acid and acetic acid, respectively.

For the hydrolytic equilibria of Al³⁺ we use the results obtained in earlier papers of this series,^{12,13} showing the occurrence of Al(OH)²⁺ ($\log \beta_{-1,1,0} = -5.52$), Al₃(OH)⁵⁺ ($\log \beta_{-4,3,0} = -13.57$), Al₁₃O₄(OH)⁷⁺ ($\log \beta_{-32,13,0} =$

-109.2) and Al(OH)₄⁻ ($\log \beta_{-4,1,0} = -23.46$). For the formation of Al(OH)₂⁺ and Al(OH)₃, we have used values given by Dyrssen,¹⁴ recalculated to 0.6 M medium according to the equations given by Baes and Mesmer¹⁵ ($\log \beta_{-2,1,0} = -11.3$; $\log \beta_{-3,1,0} = -17.3$).



In the evaluation of three-component data, these binary complex models were considered as known and all effects above this level were treated as being caused by three-component species:



The mathematical analysis of data was performed with the least-squares computer program LETAGROPVRID¹⁶ (version ETITR).^{17,18} The *p, q, r* triplets and corresponding equilibrium constants that best fit the experimental data were determined by minimizing the error-squares sum, $U = \sum (H_{\text{calc}} - H_{\text{exp}})^2$, where H_{calc} and H_{exp} denote calculated and experimental values of the analytical H⁺ concentrations, respectively. The standard deviations $\sigma(H)$, $\sigma(\beta_{p,q,r})$ and $3\sigma(\log \beta_{p,q,r})$, obtained in the LETAGROP calculations, were defined and calculated according to Sillén.^{19,20} The computations were performed on a CD Cyber 850 computer.

Data, calculations and results

The H⁺-propionic acid system. Data used to evaluate the acidity constant for propionic acid were those for 5 titrations with 178 experimental points within the concentration range $0.010 \text{ M} \leq C \leq 0.020 \text{ M}$ and $3.0 \leq -\log [H^+] \leq 6.5$. A LETAGROP calculation using these data gave as result $\log(\beta_{-1,0,1} \pm 3\sigma) = -4.6058 \pm 0.0009$ with $\sigma(H) = 0.02 \text{ mM}$.

The H⁺-Al³⁺-propionic acid system. The data used were those for 7 titrations (166 experimental points) within the

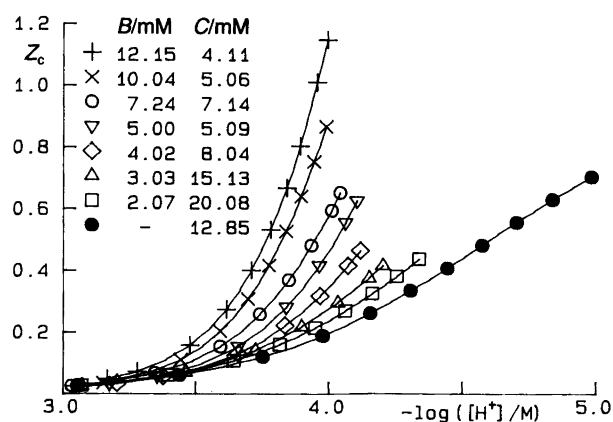


Fig. 1. Experimental data in the H⁺-Al³⁺-propionic acid system plotted as curves $Z_c(-\log [H^+])$. The drawn curves were calculated with the proposed constants.

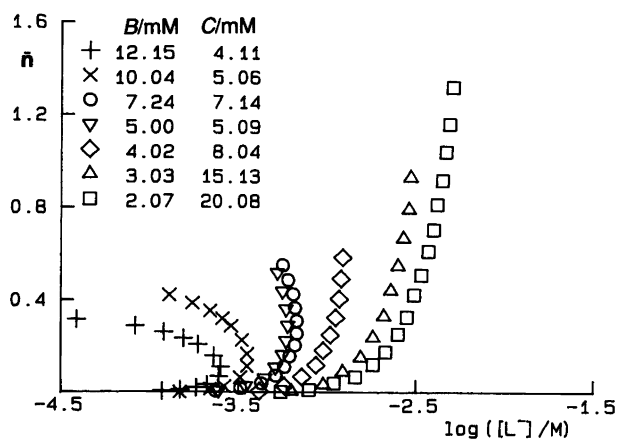


Fig. 2. Experimental data in the $H^+ - Al^{3+} - \text{propionic acid}$ system plotted as curves $\bar{n}(\log [L^-])$.

ranges $0.002 \leq B \leq 0.012 \text{ M}$, $0.004 \leq C \leq 0.020 \text{ M}$ and $1.9 \leq -\log [H^+] \leq 4.4$ covering the C/B ratios: 0.33, 0.5, 1, 2, 5 and 10.

The equilibrium analysis of the three-component system was started by plotting $Z_c(-\log [H^+])$ curves (cf. Fig. 1). Z_c is defined as the average number of OH^- reacted per HL , i.e. $Z_c = [H^+] - H - k_w/[H^+]^{-1}/C$. As can be seen, Z_c values greater than one are obtained close to the instability range at the lowest C/B ratios studied ($-\log [H^+] \approx 4$). This fact indicates that binary $Al^{3+} - OH^-$ and/or ternary $Al^{3+} - L^- - OH^-$ complexes are formed. To determine the composition and stability of possible $AlL_n^{(3-n)+}$ species, the average number of ligands bound per aluminium, \bar{n} , was calculated and plotted as curves $\bar{n}(\log [L^-])$ (Fig. 2). Coinciding \bar{n} curves are obtained if $AlL_n^{(3-n)+}$ complexes are formed predominantly. In the present system this is not the case, and \bar{n} is dependent of B as well as of the ratio C/B . This is a clear indication of the occurrence of binary and/or ternary hydroxo complexes in the system.

To determine the composition and stability of the ternary complex(es) a LETAGROP analysis of data was therefore performed as an unbiased p, q, r analysis (systematic testing

of different p, q, r combinations) with the simple assumption that only one ternary complex $H_pAl_q(HL)_r^{+3q}$ was present. The criteria for "best fit" was thereby the magnitude of the error-squares sum $U = \sum (H_{\text{calc}} - H_{\text{exp}})^2$. The result of this analysis is given in Fig. 3, and it is seen that the lowest value of U was obtained for the complex $H_{-3}Al_2(HL)^{3+}$ with $\log(\beta_{-3,2,1} \pm 3\sigma) = -8.038 \pm 0.008$. This calculation ended at $\sigma(H) = 0.04 \text{ mM}$, indicating a good fit to all experimental data. With this species, no remaining systematic deviations could be seen (Fig. 4).

In order to visualize the amounts of different species in the system, the computer program SOLGASWATER²¹ equipped with plotting procedures was used to calculate some distribution diagrams. These are presented in Fig. 5.

An independent validation of this speciation model was also obtained from series of quantitative ²⁷Al NMR measurements of unbound Al^{3+} . Through these measurements, some of which are illustrated in fig. 5, it was shown that the measured free concentrations of Al^{3+} were in full agreement with those predicted by the potentiometric model. In these spectra, the position of the peak for $Al_2(OH)_2L^{3+}$ was not detectable, probably due to quadrupolar broadening.

The $H^+ - \text{acetic acid}$ system. For the evaluation of the binary system, data derived from 4 titrations with 152 experimental points within the limits $0.010 \leq C \leq 0.040 \text{ M}$ and $2.8 \leq -\log [H^+] \leq 6.8$ were used. A LETAGROP calculation on these data ended at $\sigma(H) = 0.03 \text{ mM}$, with $\log(\beta_{-1,0,1} \pm 3\sigma) = -4.4868 \pm 0.0007$.

The $H^+ - Al^{3+} - \text{acetic acid}$ system. Data used for the evaluation of the ternary system were those for 6 titrations with 153 experimental points within the limits $0.001 \leq B \leq 0.005 \text{ M}$; $0.005 \leq C \leq 0.030 \text{ M}$ and $2.2 \leq -\log [H^+] \leq 4.6$ covering the C/B ratios: 1, 2, 4, 6, 10 and 30. Calculated Z_c and \bar{n} plots (not illustrated) showed that the complexation behaviour in this system closely resembles that in the aluminium-propionic acid system described above.

The p, q, r search (Fig. 6) performed in the same way as for the Al-propionic acid system, showed that data could

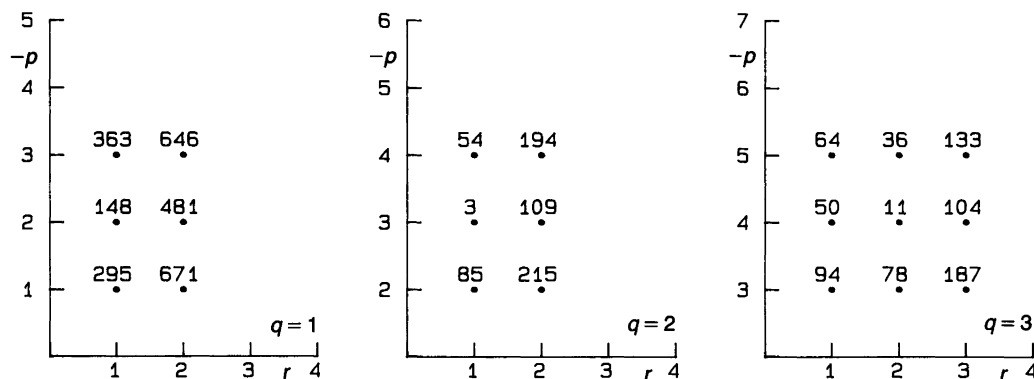


Fig. 3. Result of the p, q, r analysis on data in the $H^+ - Al^{3+} - \text{propionic acid}$ system. The figures give error-squares sums $U_H(p,r)_q \cdot 10$ assuming one ternary complex. The calculations are based on 166 points giving $U_H(00) \cdot 10 = 1013$.

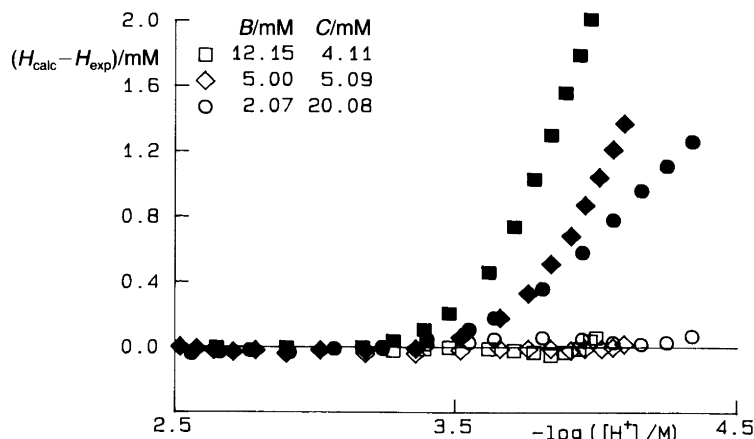


Fig. 4. Residual plot in the $H^+ - Al^{3+} -$ propionic acid system. The filled symbols show the initial residuals before the complex $Al_2(OH)_2L^{3+}$ is introduced into the model. The open symbols give residuals with the final model.

be explained with the same speciation model as for the Al-propionic acid system, i.e. with the single species $H_{-3}Al_2(HL)^{3+}$. In this system, the calculation ended at $\sigma(H) = 0.05$ mM and the equilibrium constant $\log(\beta_{-3,2,1} \pm 3\sigma) = -7.979 \pm 0.017$.

In a final attempt to allow for the formation of the

species AlL^{2+} in the two systems, calculations were performed in which the formation constant for this species was varied together with the constant for $H_{-3}Al_2(HL)^{3+}$. In the aluminium-propionate system it turned out that the species AlL^{2+} was rejected.

In the corresponding calculation on the Al-acetate data,

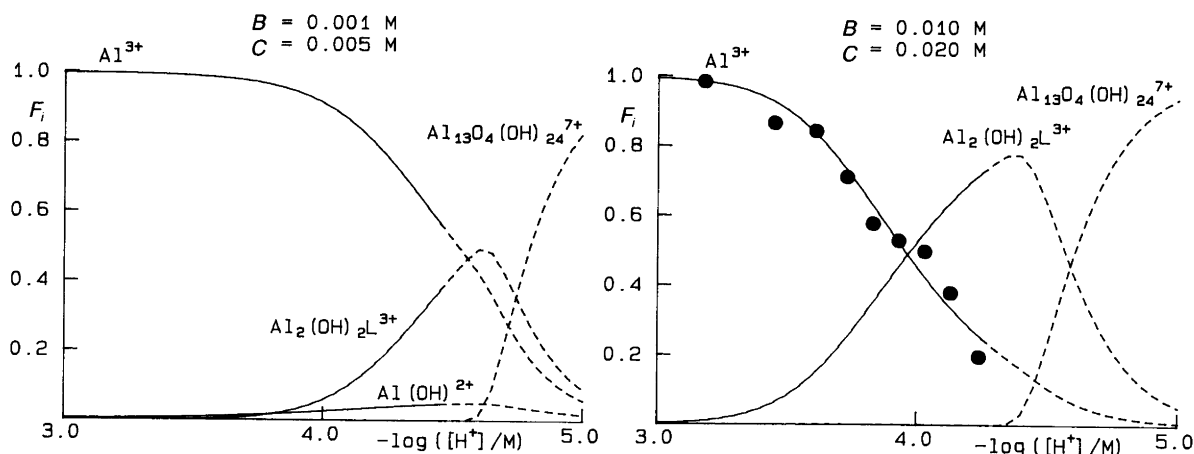


Fig. 5. Distribution diagrams $F_i(-\log[H^+])$ in the $H^+ - Al^{3+} -$ propionic acid system. F_i is defined as the fraction of total aluminium(III). The broken curves denote extrapolated values. Some of the ^{27}Al NMR measurements are included in the figure.

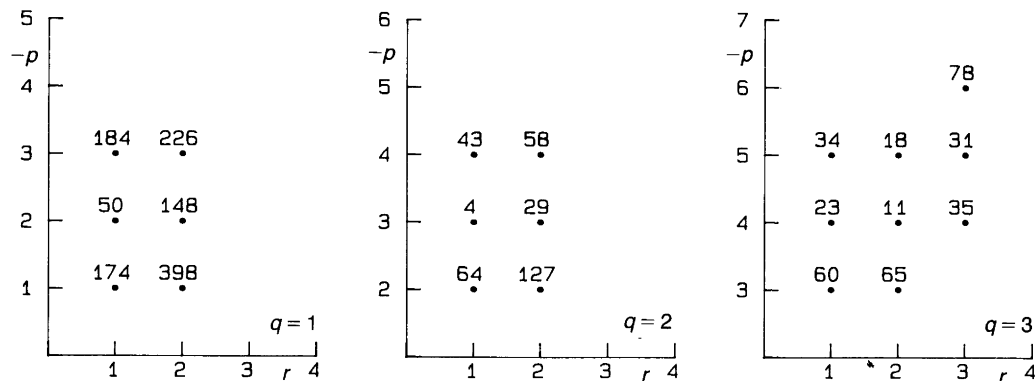


Fig. 6. Result of the p, q, r analysis on data in the $H^+ - Al^{3+} -$ acetic acid system. The figures give error squares sums $U_H(p, r)_q \cdot 10$ assuming one ternary complex. The calculations are based on 153 points giving $U_H(00) \cdot 10 = 542$.

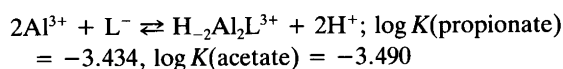
it turned out that the latter species was accepted ($\log(\beta_{-1,1,1} \pm 3\sigma) = -3.97 \pm 0.54$), but with no significant improvement of the fit to the data. Furthermore, when distribution diagrams were constructed using this stability constant, it turned out that the proportion of AlL^{2+} under our experimental conditions never exceeded 2% of the total aluminium concentration. For these reasons, together with the very distinct results of our equilibrium analysis, we find the existence of AlL^{2+} highly questionable.

Discussion

Speciation and equilibria. In striking contrast to information available in the literature, claiming that the Al^{3+} ion forms weak AlL^{2+} complexes with the propionate and acetate anions,⁹ the present study has clearly demonstrated the occurrence of a single dinuclear species, $\text{H}_3\text{Al}_2(\text{HL})^{3+}$, in dilute solutions.

A critical perusal of the paper from which the literature data originates does, however, reveal that these authors severely violated the rules of background medium replacement, postulated the composition AlL^{2+} in advance and, finally, neglected the systematic change in stability constant which occurred with change in solution composition. It may furthermore be noted that the same authors, in a later article,¹⁰ showed the dominant species in the Al–acetate system to actually be a mixed hydroxo complex. In neither of these papers, however, was any unbiased search for stoichiometric composition performed.

A direct comparison of $\log\beta_{-3,2,1}$ values obtained in the two systems reveals that, at a given value of $-\log[\text{H}^+]$, acetic acid is a somewhat stronger complex former for Al^{3+} than propionic acid. It can, however, also be seen that the acidity of propionic acid ($\text{p}K_a = 4.606$) is significantly lower than that of acetic acid ($\text{p}K_a = 4.487$). This difference is caused by the inductive effects of the longer carbon chain in propionic acid. This effect is also manifested in the stability of the Al species formed, by writing the formation reaction as:



it can be seen that the propionate ion actually has a somewhat stronger affinity for Al^{3+} than the acetate ion.

Concerning the structure of the species $\text{H}_3\text{Al}_2(\text{HL})^{3+}$, an investigation of this kind gives no direct information. As the number of ionizable protons in the ligand is exceeded it can, however, without doubt be described as the mixed hydroxo species $\text{Al}_2(\text{OH})_2\text{L}^{3+}$. It is interesting to note that a species of this composition also appears in the weakly coordinating Al–carbonate system.^{12,22} These species probably have the same structure, which might tentatively be described as a dihydroxo-bridged species with the ligand acting as a bridge between the two aluminium ions. This coordination around aluminium has been found in the minerals Dawsonite²³ $[\text{NaAlCO}_3(\text{OH})_2]$ and Dundasite²⁴

$[\text{PbAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot \text{H}_2\text{O}]$. As a comparison $\log\beta(2\text{Al}^{3+} + 2\text{H}_2\text{O} + \text{HCO}_3^- \rightleftharpoons \text{Al}_2(\text{OH})_2\text{CO}_3^{3+} + 3\text{H}^+) = -7.87$ was found for the carbonate system. This value is close to those $\log\beta_{3,2,1}$ values found for the present ligand systems. However, since the $\text{p}K_a$ value for the bicarbonate ion is significantly higher than those for propionic/acetic acid, the propionate/acetate complex will be formed at a lower value of $-\log[\text{H}^+]$.

Modelling calculation. Acetic acid has generally been regarded as a very weak complex-forming substance towards metal ions, e.g. aluminium. It has therefore often been used as a non-complexing buffer agent in the pH range 4.0–6.5. For instance, May *et al.*²⁵ used 0.001 M acetic acid/acetate as a buffer in their determination of solubility curves for synthetic and natural gibbsite (0.01 M NaNO_3 ; 25°C). The authors stated that at the concentrations used, acetate ions cannot significantly complex Al^{3+} ions.

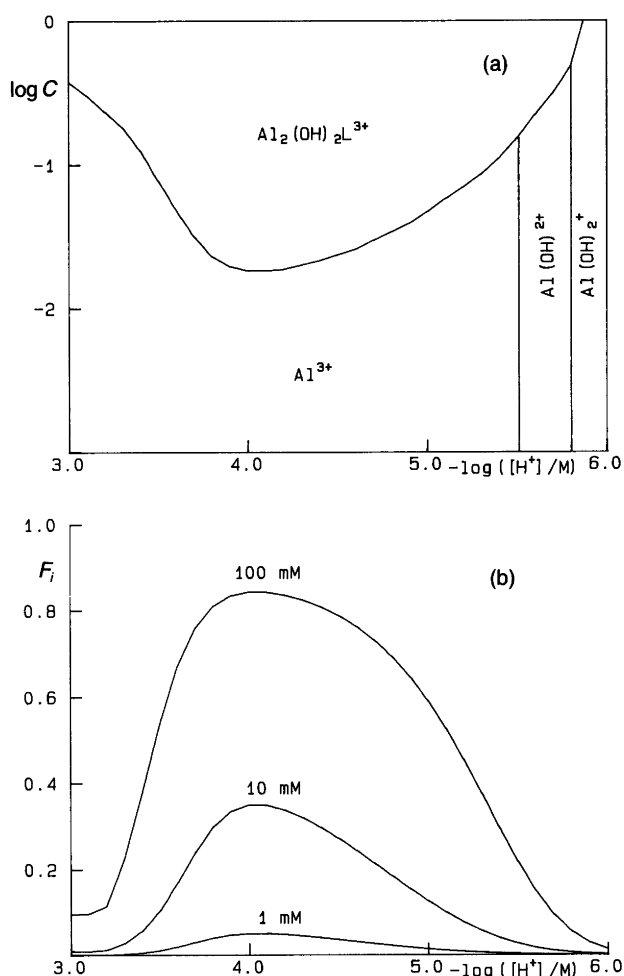


Fig. 7. (a) Predominance area diagram in the $\text{H}^+ - \text{Al}^{3+} - \text{acetic acid}$ system showing dominant aqueous Al(III) species in equilibrium with gibbsite as a function of $\log C$ and $-\log[\text{H}^+]$. (b) The distribution coefficient for $\text{Al}_2(\text{OH})_2(\text{acetate})^{3+}$ as a function of total ligand concentration and $-\log[\text{H}^+]$. The aqueous aluminium(III) concentration is regulated by crystalline gibbsite.

To check this statement, we performed a SOLGAS-WATER modelling calculation in which the solubility of gibbsite $[\text{Al}(\text{OH})_3]$; $\log^*K_{s0} = 9.60$ in 0.6 M NaCl¹⁵ was calculated as a function of acetic acid concentration and pH. In Fig. 7 the results of these calculations are presented in the form of predominance area and distribution diagrams.

Thus, with an acetic acid/acetate concentration of 0.001 M, the solubility of gibbsite might increase by a maximum of 5% at pH = 4.0. However, if the acetic acid concentration is raised to 0.010 M, the solubility increase might be as large as 35%. We can therefore conclude that in the presence of a gibbsite phase, an acetic acid/acetate buffer concentration of 0.001 M is an approximate upper limit if the complexation of the buffer is to be neglected.

In the presence of an amorphous aluminium hydroxide phase, the situation becomes more complicated. Under such conditions the available buffer concentration range is even more restricted. Model calculations at relevant values of \log^*K_{s0} , buffer concentration and pH are needed to quantify the complexation influence of the buffer.

Acknowledgement. This work forms part of a program supported financially by The Swedish Natural Science Research Council.

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Received November 28, 1988.