Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 29. A Potentiometric and ^{27}Al-NMR Study of the System H^+–Al^{3+}–L(+)-Ascorbic Acid

Lars-Olof Öhman* and Agneta Nordin

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

Öhman, L.-O. and Nordin, A., 1992. Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 29. A Potentiometric and ^{27}Al-NMR Study of the System H^+–Al^{3+}–L(+)-Ascorbic Acid. – Acta Chem. Scand. 46: 515–520.

Three-component equilibria between H^+, aluminium(III) and L-ascorbic acid (vitamin C, $C_6H_8O_6$, HL) were studied by means of potentiometric (glass electrode) titrations and quantitative ^{27}Al-NMR measurements at 25 °C in an ionic medium of 0.6 M Na(Cl). The total concentrations of aluminium, B, and ascorbic acid, C, were varied within the limits $1 \leq B/\text{mM} \leq 26$, $5 \leq C/\text{mM} \leq 21$, and $0.25 \leq C/B \leq 16$ within the range $1.8 \leq -\log [H^+] \leq 4.5$.

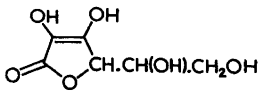
Data can best be explained with a weak binary species AlL^{2+} ($\log \beta_{-1,1,1} = -2.59 \pm 0.036$), together with two trinuclear mixed-hydroxo species $Al_3(OH)_4(H_{-1}L)^{3+}$ ($\log \beta_{-6,3,1} = -18.38 \pm 0.016$) and $Al_3(OH)_4(H_{-1}L)L_3^0$ ($\log \beta_{-9,3,4} = -24.19 \pm 0.083$). The formulae given are tentative. The acidity constant of ascorbic acid was studied in separate titrations and was found to be $\log \beta_{-1,0,1} = -3.966 \pm 0.001$. All equilibrium constants are defined according to the general reaction $pH^+ + qAl^{3+} + rHL \rightleftharpoons H_pAl_q(HL)_r^{p+3q}$, and the uncertainties reported are 3σ ($\log \beta_{p,q,r}$). Potentiometric data were analysed with the least-squares computer program LETAGROPVRID, and the quantitative ^{27}Al-NMR data were used to validate the speciation scheme.

In a series of model calculations, using gibbsite [$Al(OH)_3(s)$] as Al-solubility limiting phase, it is shown that the complexing ability of ascorbate ions is comparable to that of monocarboxylate ions.

The present great interest in the aquatic chemistry of aluminium(III) originates to a large extent from the extensive use of acidifying fossil fuels. Through this use, soil- and water-pH values have decreased in large areas with poorly buffering (silicate) bedrocks, and as a consequence a dramatically increased mobility of aluminium has resulted.[1]

Although aluminium was previously regarded as a relatively innocuous element, it has thereby been found that certain aquatic forms appear to be one of the most serious threats to aquatic life.[2] However, it has also been found that although the Al^{3+} ion and hydrolytic complexes thereof predominantly cause fish death[3] and root damage[4] at low concentrations, the toxic effects strongly diminish if the metal ion is bound to an organic ligand or an inorganic ligand other than the hydroxide ion.[3–5]

Through the increased mobility of aluminium in natural waters, its exposure to man has also increased during recent decades, and today it is believed that aluminium plays a toxic role in several human diseases and disorders.[6] Here also the chemical form in which aluminium is administered seems to be of utmost importance for its bioavailability.[7,8] In contrast to the findings made in aquatic systems, however, the chemical forms most susceptible to biouptake seem to be certain soluble, net-neutral organic complexes that are able to cross cell membranes via a passive diffusion mechanism.[9]



Scheme 1.

In several previous parts of this series[10–12] it has been shown that uncharged tris-complexes are formed in near-neutral solutions when the Al^{3+} ion is reacted with compounds carrying the '2-hydroxy-1-one' (cf. Scheme 1) binding site. Since ascorbic acid (Scheme 1) also contains such a binding site, and since its prevalent use as a food additive (an antioxidant, E300) potentially makes it highly relevant for aluminium biouptake, this study was undertaken.

Experimental

Chemicals and analysis. L(+)-Ascorbic acid ($C_6H_8O_6$, HL) (Merck *p.a.*) was used without further purification. Solutions were prepared by dissolving weighed amounts of the solid, together with appropriate amounts of NaCl, in boiled distilled water. Since ascorbic acid is susceptible to

* To whom correspondence should be addressed.

oxidation, each experiment was started from a freshly prepared solution and the measurements were performed under an argon atmosphere. To keep an accurate control of the ligand concentration in each preparation, simultaneous titrations with and without Al^{3+} being added were undertaken in all cases. The ligand concentrations were determined using the Gran extrapolation method[13] and were consistently found to be 0.6 % lower than the values expected from weighing. This difference has been assumed to result from residual water in the solid chemical. Stock solutions of sodium chloride and aluminium chloride, and the dilute hydrochloric acid and sodium hydroxide solutions, were prepared and analysed as described earlier.[14]

Temperature and medium. The present study was carried out at 25 ± 0.05 °C in a constant ionic medium of 0.6 M Na(Cl).

Apparatus. The automatic system for precise EMF titrations, the thermostat and the electrodes have been described earlier.[14] The quantitative ^{27}Al NMR spectra were measured on a Bruker AC-250 spectrometer that was equipped with a 10 mm multinuclear probehead and operated in the absolute intensity mode.

Method. The potentiometric (glass electrode) data were collected via a series of titrations. The titration procedures, including a special procedure to calibrate the glass electrode on the proton concentration scale, have been described in earlier papers.[14,15] The reproducibility and reversibility of equilibria were tested by performing titrations in acidic as well as in alkaline directions. The acidity constant of ascorbic acid was determined from titrations in the absence of Al^{3+}.

The three-component titrations were performed at a constant ratio between the total concentration of aluminium (B) and ascorbic acid (C). The upper $-\log [H^+]$ limits in these titrations were set by the appearance of extremely sluggish equilibria (equilibration times exceeding 12 h). Based on these potentiometric measurements, suitable point solutions for Al-NMR characterization were prepared. Calibrated quantitative spectra were collected, and from each spectrum a quantitative measure of the free Al^{3+} concentration was evaluated. Owing to the high stability of the spectrometer and the quadropolar properties of ^{27}Al, resulting in relatively short aquisition times, these spectra were collected without having a D_2O lock on the instrument.

Data treatment. In order to visualize potentiometric results, the data sets Z_c vs. $-\log [H^+]$ were calculated, and some of them are presented in Fig. 1; Z_c is defined as the average number of OH^- reacted per ascorbic acid molecule, and is given by the relation $Z_c = (h - H - k_w h^{-1})/C$, where $h = [H^+]$ and H denotes the total, analytical concentration of protons calculated over the zero level H_2O, Al^{3+} and HL. The term $k_w h^{-1}$, where k_w is the ionic product of water in 0.6 M Na(Cl) medium, corresponds to the free concentration of hydroxide ions and is negligible is the present study. These curves reflect the total complexation behaviour of the system comprising binary [eqns. (1) and (2)] as well as ternary [eqn. (3)] equilibria.

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

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

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

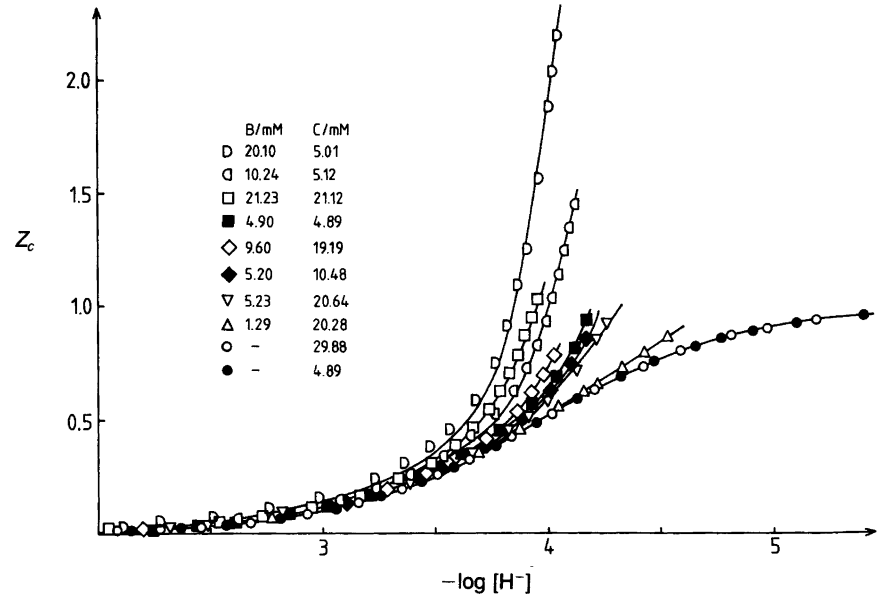


Fig. 1. Some of the experimental data plotted as curves $Z_c(-\log [H^+])$. All symbols represent initial concentrations and the lines have been calculated using the set of constants proposed in Table 1.

For the ionization constant of ascorbic acid [i.e. eqn. (1)], results from separate experiments at $B = 0$ were used, while for the hydrolytic equilibria of Al^{3+} [i.e. eqn. (2)], results obtained in earlier papers of this series[16-18] (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 $\beta_{-32,13,0} = -109.2$) were used.

These binary complex models were considered as known in the evaluation of three-component data, i.e. all effects above this level were treated as being caused by the formation of ternary [i.e. eqn. (3)] complexes. This evaluation was based on potentiometric data alone, and the ^{27}Al-NMR data were used to validate independently the resulting speciation model.

Computer programs. The mathematical analysis of EMF data was performed with the least-squares program LETAGROPVRID[19] (version ETITR).[20,21] 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_{calcd} and H_{exptl} denote calculated and experimental values of the analytical H^+ concentrations, respectively. The standard deviations $\sigma(H)$ and $3\sigma(\log \beta_{p,q,r})$ obtained in the LETAGROP calculations were defined and calculated according to Sillén and Warnqvist.[22,23] For the construction of distribution and solubility diagrams, the modelling program SOLGASWATER[24] was used. All computations were performed on a CD Cyber 850 computer.

Data, calculations and results

The H^+–ascorbic acid system. Data used to evaluate the acidity constant for ascorbic acid comprised six titrations with 189 experimental points within the concentration range $5 \leq C/\text{mM} \leq 40$ and $2.0 \leq -\log [H^+] \leq 5.6$. The LETAGROP calculation on these data gave as a result $\log (\beta_{-1,0,1} \pm 3\sigma) = -3.966 \pm 0.0010$ with $\sigma(H) = 0.04$ mM.

The system H^+–Al^{3+}–ascorbic acid. These data comprised 14 titrations (357 experimental points) within the ranges $1 \leq B/\text{mM} \leq 26$; $5 \leq C/\text{mM} \leq 21$ and $1.8 \leq -\log [H^+] \leq 4.5$. The following C/B ratios were covered: 0.25, 0.5, 1, 2, 4 and 16. Some of these data are presented in the form of Z_c vs. $-\log [H^+]$ curves in Fig. 1 and as $\bar{n}(\log [L^-])$ curves in Fig. 2. (Z_c denotes the average number of OH^- reacted per C and $\bar{n}$ the average number of L^- coordinated per B.)

In the presence of Al^{3+}, significantly more than one hydroxyl ion may be reacted per ascorbic acid molecule (cf. Fig. 1). This can be taken as a direct proof for the formation of species containing hydroxo ions and/or di-anionic ascorbate ions.

In Fig. 2 coinciding curves are indicated at low $\bar{n}$-values. At higher values however, each B/C combination results in a unique curve. It can therefore be concluded that while AlL^{2+} is probably the first species formed, simple complexes of the form AlL_n^{3-n} are *not* the predominating species in the system.

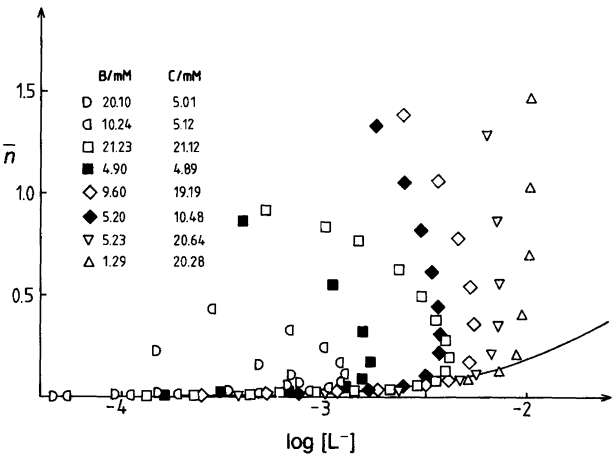


Fig. 2. Some of the experimental data plotted as curves $\bar{n}(\log [L^-])$. The full curve was calculated with log $\beta_{-1,1,1} = -2.59$.

Based on these graphical considerations, the first LETAGROP calculation was restricted to low $\bar{n}$ data ($-\log [H^+] \leqq 3.2$) on which the equilibrium constant for AlL^{2+} was determined as log $\beta_{-1,1,1} = -2.62 \pm 0.04$. This minor species was then included in the equilibrium model and an unbiassed *pqr*-search was performed on all data. This search was based on the simple assumption that only one three-component species $H_pAl_q(HL)_r^{p+3q}$ is formed and performed through a systematic variation in the integer values of p, q and r. For each (p,q,r) combination, the 'best possible' equilibrium constant, $\beta_{p,q,r}$, was determined using the LETAGROPVRID program, and the corresponding error-squares sum, $U = \Sigma(H_{calcd} - H_{exptl})^2$, recorded. The search was proceeded until the 'best' (p,q,r) triplet, i.e. the triplet resulting in the lowest error-squares sum, had been identified.

The result of this search is illustrated in Fig. 3, and, as seen, the closest fit to experimental data was obtained assuming a species $H_{-6}Al_3(HL)^{3+}$ (log $\beta_{-6,3,1} = -18.33 \pm 0.01$) to be formed.

When the resulting $\Delta H(-\log [H^+], B, C, C/B)$ residual was examined, it was however found that relatively small, but systematic, effects remained to be explained at the higher C/B-ratios. A renewed analysis was therefore performed in which the equilibrium constant for $H_{-6}Al_3(HL)^{3+}$ was co-varied with the equilibrium constant for an additional species of the composition (p',q',r'). In all these calculations, log $\beta_{-6,3,1}$ came out with a relatively invariant value, and the 'best' additional species was $H_{-9}Al_3(HL)_4$. It should be noted, however, that other triplets with $q \geq 2$ resulted in almost equally low error-squares sums, and that this species cannot therefore be considered as well established as the species $H_{-6}Al_3(HL)^{3+}$.

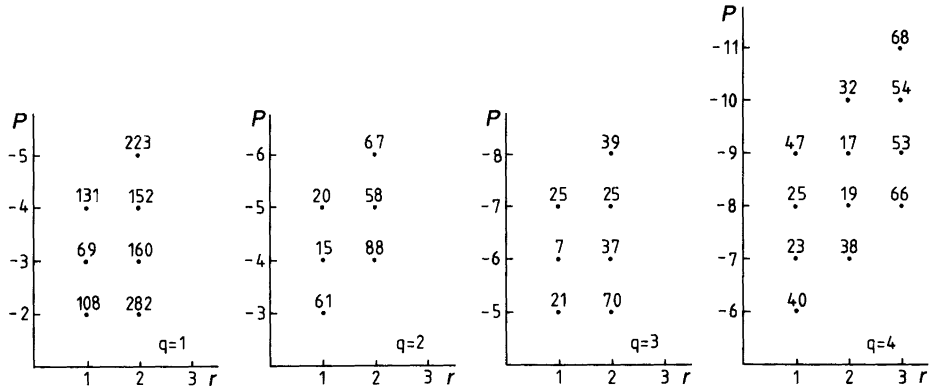


Fig. 3. Result of the first (p,q,r)-search. The figures give error-squares sums $U_H(pr)_q$ assuming one ternary complex with a 'best possible' equilibrium constant. The calculations are based on 357 points giving $U_H(00)_0 = 444$.

In a final LETAGROPVRID calculation, the equilibrium constants for AlL^{2+}, $H_{-6}Al_3(HL)^{3+}$ and $H_{-9}Al_3(HL)_4$ were simultaneously refined on all data. The result of this calculation, which ended at $\sigma(H) = 0.09$ mM and thus indicates a good fit to experimental data, is given as our final model for the system in Table 1. The fit of this model to potentiometric data is also illustrated by the solid calculated curves in Fig. 1.

The present model was also validated through a series of ^{27}Al-NMR measurements in which the fraction of unbound Al^{3+} was quantitatively determined. These measurements are illustrated together with a series of calculated distribution diagrams in Fig. 4 and, as seen, the predicted and measured fractions of Al^{3+} are in very good agreement.

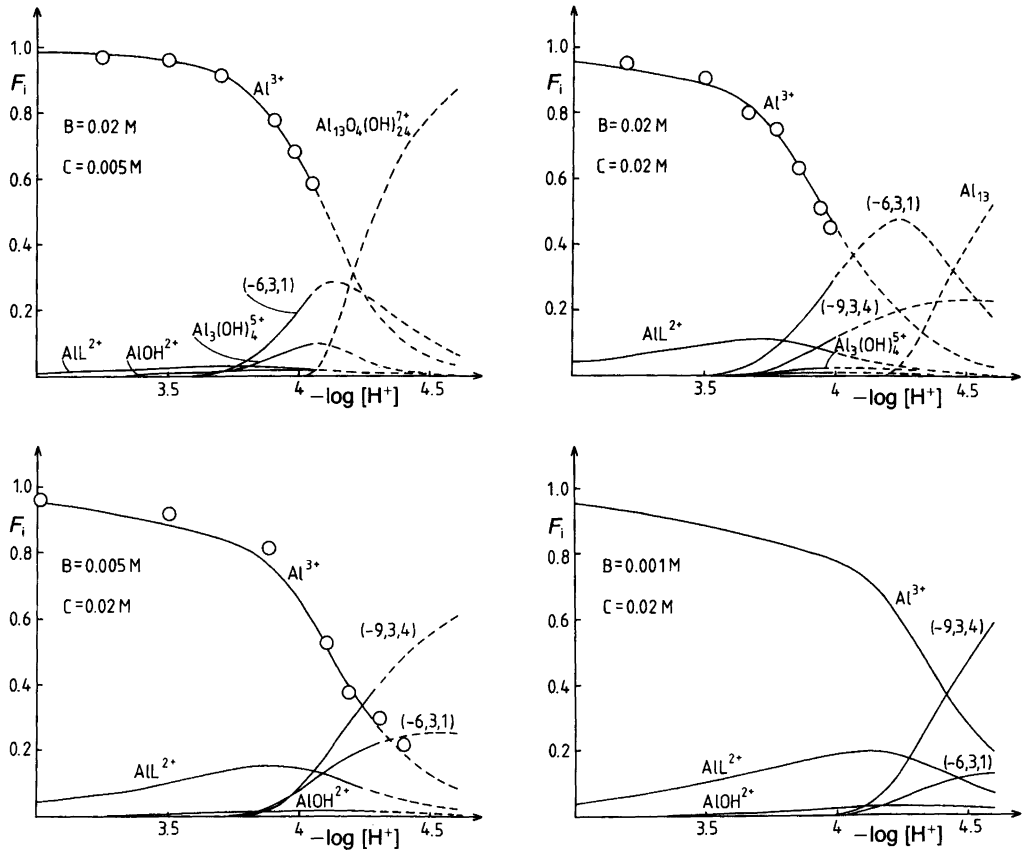


Fig. 4. Distribution diagrams $F_i(-\log [H^+])$. F_i is defined as the ratio between aluminium(III) in a species and the total aluminium(III). The calculations were performed with the computer program SOLGASWATER using the equilibrium constants given in Table 1, and dashed curves denote extrapolated values. Circles denote experimental fractions of Al^{3+} as determined by ^{27}Al-NMR measurements.

Table 1. Binary and ternary complexes in the system H^+–Al^{3+}–L(+)-ascorbic acid.[a]

No. of titrations/ No. of points	*p q r*	Tentative formula	log ($\beta_{pqr} \pm 3\sigma$)
6/189	−1 0 1	L^-	−3.966±0.001
14/357	−1 1 1	AlL^{2+}	−2.59 ±0.036
	−6 3 1	$Al_3(OH)_4(H_{-1}L)^{3+}$	−18.38 ±0.016
	−9 3 4	$Al_3(OH)_4(H_{-1}L)L_3$	−24.19 ±0.083

[a]The formation constants are related according to the reaction $pH^+ + qAl^{3+} + r(HL) \rightleftharpoons H_pAL_q(HL)_r^{p+3q}$, where HL stands for L(+)-ascorbic acid.

Discussion

In contrast to the expected behaviour (that ascorbic acid would form a series of stable AlL_n^{3-n} species with Al^{3+} via the '2-hydroxy-1-one' binding site), the present investigation has provided evidence of relatively weak interactions (Fig. 4). Only the first species in this series has been identified, and by writing the equilibrium reaction as $Al^{3+} + L^- \rightleftharpoons AlL^{2+}$; log k_1 = 1.38, the low stability of the ascorbate complex as compared to the corresponding maltolate complex[10] (log k_1 = 8.25) is evident.

The major reason for this low affinity of a 'normally' strong coordinating site for Al^{3+} is probably steric. Thus, while the oxygen–oxygen distances in maltol,[25] kojic acid[26] and tropolone[27] are all ca. 2.5 Å, the corresponding distance in ascorbic acid[28] is 2.98 Å. This probably implies that while the former substances can all replace two water molecules from the inner sphere of $Al(H_2O)_6^{3+}$ (O–O distance 2.66 Å),[29] the distance in ascorbic acid is too long to favour this substitution.

In less acidic solutions (−log [H^+] ≳ 3.6) the present study has given evidence for the formation of two polynuclear aluminium complexes, $H_{-6}Al_3(HL)^{3+}$ and $H_{-9}Al_3(HL)_4$. In this respect, ascorbic acid parallels the behaviour of several substances with weak Al-coordinating properties. The structures of these complexes are not known, but since they are formed close to the range at which the aluminium ion starts to be hydrolysed, and since the number of detatched protons they possess exceeds the number of ionizable ligand protons, it is tempting to assume that the two complexes bear a resemblance to the hydrolytic species $Al_3(OH)_4^{5+}$. A tentative formula for $H_{-6}Al_3(HL)^{3+}$ could therefore be $Al_3(OH)_4(H_{-1}L)^{3+}$, implying a species in which two hydroxyl groups of ascorbic acid are deprotonated and coordinated to $Al_3(OH)_4^{5+}$. Accordingly, the species $H_{-9}Al_3(HL)_4$, which appears at higher *C*/*B*-ratios, could be written as $Al_3(OH)_4(H_{-1}L)L_3$, thereby indicating $Al_3(OH)_4(H_{-1}L)^{3+}$ to be a 'core' to which additional ascorbate ions could coordinate at a ligand excess.

As mentioned in the experimental section, the present potentiometric measurements were interrupted when the equilibration times started to exceed 12 h. This was then taken as an indication of the onset of $Al_{13}O_4(OH)_{24}^{7+}$ formation; however, as shown in Fig. 4, this assumption seems to be valid only at the lowest *C*/*B*-ratio. It is therefore possible that additional complexes, with extremly slow formation kinetics, could exist at −log [H^+] ≳ 4–4.5. In this case the present system could resemble the Al^{3+} lactate system,[30] in which one ternary polynuclear species was not fully equilibrated within one month.

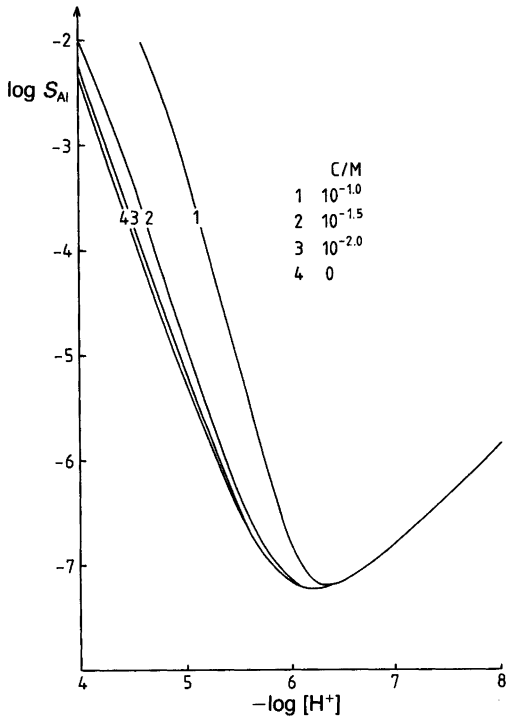


Fig. 5. Solubility of gibbsite (log $^*K_{so}$ = 9.6) expressed as log S_{Al} vs. −log [H^+] for different total concentrations of ascorbic acid, *C*.

To indicate the potential solubilization effects of ascorbate ions on aluminium hydroxide, Figs. 5 and 6 were constructed. Fig. 5 illustrates the total aqueous solubility of Al(III) in the presence of crystalline gibbsite (log $^*K_{so}$ =

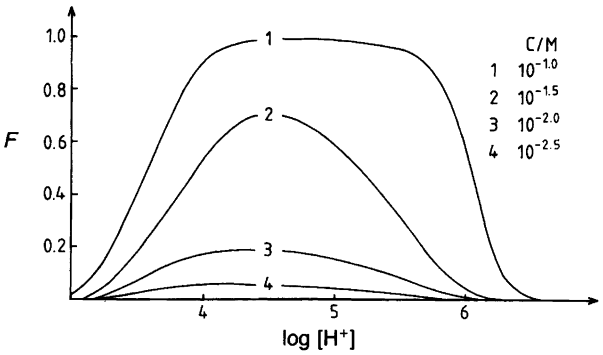


Fig. 6. The distribution coefficient for ascorbate-bound Al(III) as a function of total ligand concentration and −log [H^+]. The aqueous aluminium(III) concentration is regulated by crystalline gibbsite.

9.6)[31] and with various total concentrations of ascorbic acid/ascorbate ions; as expected, quite high ligand concentrations are needed to affect the solubility curve significantly. This information can also be gained from Fig. 6, which shows the fraction of ascorbate-bound aluminium as a function of the total ligand concentration and $-\log [H^+]$. It can thus be concluded that, in order to affect the aqueous aluminium chemistry significantly in a gibbsite suspension, the ascorbate concentration has to exceed $\approx 10^{-2}$ M. In this respect, the ascorbate ion shows its closest resemblance to the monocarboxylate ions.[32]

Acknowledgements. We are grateful to Prof. Staffan Sjöberg for valuable comments on the manuscript. This work forms part of a program financially supported by the Swedish Natural Science Research Council.

References

1. Sposito, G., Ed., *The Environmental Chemistry of Aluminium,* CRC Press, Boca Raton, FL 1989.
2. Mason, J. and Seip, H. M. *Ambio 14* (1985) 45.
3. Dobbs, A. J., French, P., Gunn, A. M., Hunt, D. T. E. and Winnard, D. A. In: Lewis, T. E., Ed., *Environmental Chemistry and Toxicology of Aluminium,* Lewis Publishers, Chelsea 1989, p. 209.
4. Hue, N. V., Craddock, G. R. and Adams, F. *Soil Sci. Soc. Am. J. 50* (1986) 28.
5. Asp, H. *Influence of Aluminium on Mineral Uptake by Beech and Spruce Roots,* Thesis, University of Lund, Sweden 1991.
6. Gitelman, H. J., Ed., *Aluminium and Health,* Marcel Dekker, New York 1989.
7. Partridge, N. A., Regnier, F. E., White, J. L. and Hem, S. L. *Kidn. Int. 35* (1989) 1413.
8. Fulton, B. and Jeffrey, E. H. *Fundam. Appl. Toxicol. 14* (1990) 788.
9. Martin, R. B. *Clin. Chem. 32* (1986) 1797.
10. Hedlund, T. and Öhman, L.-O. *Acta Chem. Scand., Ser. A 42* (1988) 702.
11. Clevette, D. J., Nelson, W. O., Nordin, A., Orvig, C. and Sjöberg, S. *Inorg. Chem. 28* (1989) 2079.
12. Öhman, L.-O. *Acta Chem. Scand. 44* (1990) 793.
13. Gran, G. *Acta Chem. Scand. 4* (1950) 559.
14. Öhman, L.-O. and Sjöberg, S. *Acta Chem. Scand., Ser. A 35* (1981) 202.
15. Öhman, L.-O. and Sjöberg, S. *Acta Chem. Scand., Ser. A 37* (1983) 875.
16. Öhman, L.-O. and Forsling, W. *Acta Chem. Scand., Ser. A 35* (1981) 795.
17. Öhman, L.-O., Sjöberg, S. and Ingri, N. *Acta Chem. Scand., Ser. A 37* (1983) 561.
18. Öhman, L.-O. *Inorg. Chem. 27* (1988) 2565.
19. Ingri, N. and Sillén, L. G. *Ark. Kemi 23* (1964) 97.
20. Arnek, R., Sillén, L. G. and Wahlberg, O. *Ark. Kemi 31* (1969) 353.
21. Brauer, P., Sillén, L. G. and Whiteker, R. *Ark. Kemi 31* (1969) 365.
22. Sillén, L. G. *Acta Chem. Scand. 16* (1962) 159.
23. Sillén, L. G. and Warnqvist, B. *Ark. Kemi 31* (1969) 341.
24. Eriksson, G. *Anal. Chim. Acta 112* (1979) 375.
25. Finnegan, M. M., Rettig, S. J. and Orvig, C. *J. Am. Chem. Soc. 108* (1986) 5033.
26. McKinstry, H. A., Eiland, P. F. and Pepinsky, R. *Acta Crystallogr. 5* (1952) 285.
27. Muetterties, E. L. and Guggenberger, L. J. *J. Am. Chem. Soc. 94* (1972) 8046.
28. Hvoslef, J. *Acta Crystallogr., Sect. B 24* (1968) 23.
29. Buchanan, D. R. and Harris, P. M. *Acta Crystallogr., Sect. B 24* (1968) 954.
30. Marklund, E. and Öhman, L.-O. *Acta Chem. Scand. 44* (1990) 228.
31. Baes, C. F. and Mesmer, R. E. *The Hydrolysis of Cations,* Krieger, Malabar, Florida 1986.
32. Öhman, L.-O. *Acta Chem. Scand. 45* (1991) 258.

Received October 28, 1991.