Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. Part 22.† A Potentiometric Study of Mono- and Poly-nuclear Aluminium(III) Tartrates

Eva Marklund * **and Lars-Olof Öhman**
Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

Equilibria between H^+, aluminium(III), and L-tartaric acid (2,3-dihydroxybutanedioic acid, H_2L) were studied in a 0.6 mol dm^{-3} Na(Cl) medium at 25 °C. The measurements were performed as e.m.f. titrations (glass electrode) within the limits $1.8 \leqslant -\log[H^+] \leqslant 6.7$; $0.000\,18 \leqslant B \leqslant 0.012$ mol dm^{-3}, $0.000\,18 \leqslant C \leqslant 0.042$ mol dm^{-3}, and $0.5 \leqslant C/B \leqslant 25$ [B and C stand for the total concentrations of aluminium(III) and tartaric acid, respectively]. All data can be explained with a mononuclear species $[AlL]^+$ ($\log \beta_{-2,1,1} = -3.44 \pm 0.047$) together with a series of binuclear complexes $[Al_2L(H_{-1}L)]^+$ ($\log \beta_{-5,2,2} = -6.30 \pm 0.040$), $[Al_2(H_{-1}L)_2]$ ($\log \beta_{-6,2,2} = -8.91 \pm 0.016$), $[Al_2(H_{-1}L)(H_{-2}L)]^-$ ($\log \beta_{-7,2,2} = -13.12 \pm 0.028$), and $[Al_2(H_{-2}L)_2]^{2-}$ ($\log \beta_{-8,2,2} = -18.95 \pm 0.19$). The formulae given are tentative. The acidity constants of tartaric acid were studied in separate titrations and were found to be $\log \beta_{-1,0,1} = -2.702 \pm 0.002$ and $\log \beta_{-2,0,1} = -6.401 \pm 0.002$. All equilibrium constants are defined according to the general reaction $pH^+ + qAl^{3+} + rH_2L \rightleftharpoons H_pAl_q(H_2L)_r{}^{p+3q}$ and the uncertainties reported are $3\sigma(\log \beta_{p,q,r})$. Data were analysed with the least-squares computer program LETAGROPVRID.

During the last 15 years it has been clearly established that certain soluble aluminium species exhibit severe toxic effects in the environment[1,2] but also that this element is involved in several human brain[3,4] and bone disorders.[5,6] The interest in the aqueous chemistry of this element has therefore been rapidly increasing during recent years as such information could provide a basis for a better understanding of its distribution, transport, and toxicity, in the environment as well as in man.

Within the title project, we are systematically investigating the ability of Al^{III} to form complexes with naturally occurring ligand classes. To produce data of relevance to modelling in natural systems, we spend much effort collecting and analysing data at low ligand/metal ratios and at near-neutral pH values where ternary mixed hydroxo complexes are most likely to form.

The aim of the present investigation is to interpret complexation in the system $H^+ - Al^{3+}$–tartaric acid. Tartaric acid is common not only in metabolic pathways of plants and animals but it is also used as an antioxidant and flavouring agent (E334) in food preparations. Tartaric acid in humans probably originates from food intake. Naturally occurring tartaric acid can be found in grape juice and wine. In experiments in which rabbits were exposed to repeated subcutaneous injections of aqueous aluminium tartrates, elevated brain levels of aluminium were recorded.[7] At high dosages the treatment also resulted in neurological disorders such as head tremor, ataxia, and general convulsions. Whether soluble aluminium tartrates parallel the behaviour of aluminium citrates,[8,9] *i.e.* that they can be directly absorbed from the gastrointestinal tract, has not been investigated.

Previous equilibrium studies of the present system have reached rather contradictory conclusions. Thus, in an investigation based on optical rotation measurements, Frei[10] postulated the existence of no less than 22 different mono- and binuclear complexes containing one or two tartrate ions. More recently, Motekaitis and Martell[11] reported, on the basis of potentiometric measurements, a model consisting of eight different monomeric species with one, two, and three L-tartrate ions co-ordinating the aluminium ion. In this latter investigation, however, the possible existence of polynuclear complexes was not taken into consideration. In the present study, data covering as wide metal/ligand quotient and concentration ranges as possible have been collected, so that the possible formation of not only binary mononuclear but also ternary mono- and poly-nuclear Al–OH–L complexes can be examined.

Experimental

Chemicals and Analysis.—L(+)-Tartaric acid (2,3-dihydroxybutanedioic acid, $C_4H_6O_6$, H_2L) (Merck *p.a.*) was used without further purification after drying. Stock solutions were prepared by dissolving $C_4H_6O_6$ in a 0.6 mol dm^{-3} Na(Cl) medium and the H_2L content determined potentiometrically using the Gran extrapolation method.[12] The titrated amount was found to be 0.3% lower than the value expected from weighing. Stock solutions of sodium chloride and aluminium chloride, as well as the dilute hydrochloric acid and sodium hydroxide solutions, were prepared and standardized as described earlier.[13]

Apparatus.—The automatic system for precise e.m.f. titrations, the thermostat, and the electrodes were described elsewhere.[13]

Method

The present investigation was carried out as a series of titrations at 25 °C in a constant ionic medium of 0.6 mol dm^{-3} Na(Cl). In the titrations, the free hydrogen-ion concentration, h, was varied by means of OH^- solutions and h was measured with a glass electrode. The titration procedures, calibrations, and the assumptions made in connection with the glass electrode were as described earlier.[13]

During the three-component titrations, the ratio between the total concentration of aluminium, B, and that of tartaric acid, C, was held constant. The measurements were performed within the limits $1.8 \leqslant -\log[H^+] \leqslant 6.7$, $0.000\,18 \leqslant B \leqslant 0.012$ mol

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† Part 21, L-O. Öhman, *Inorg. Chem.*, 1989, **28**, 3629.

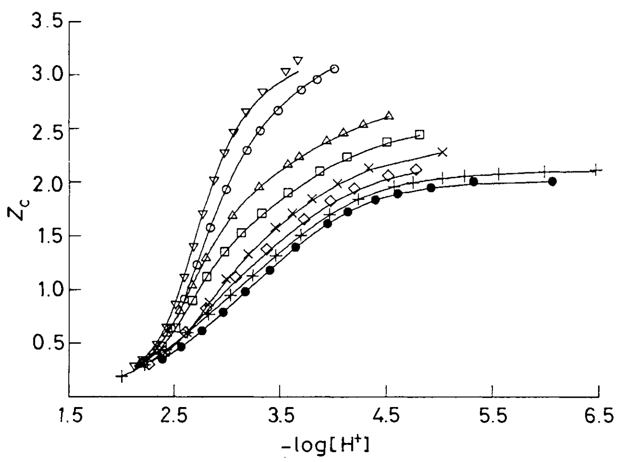

Figure 1. Part of the experimental data plotted as Z_c *vs.* $-\log[H^+]$ where $Z_c = (h - H - K_wh^{-1})/C$ and K_w is the ionic product of water in 0.6 mol dm^{-3} Na(Cl). All symbols represent initial concentrations. The full curves have been calculated using the set of constants in Table 2. Key (B,C/mmol dm^{-3}): 0, 11.48 (●); 2.07, 41.77 (+); 1.11, 10.10 (◇); 1.04, 5.04 (×); 3.01, 9.04 (□); 4.00, 8.01 (△); 4.40, 4.41 (○); 6.45, 3.23 (▽)

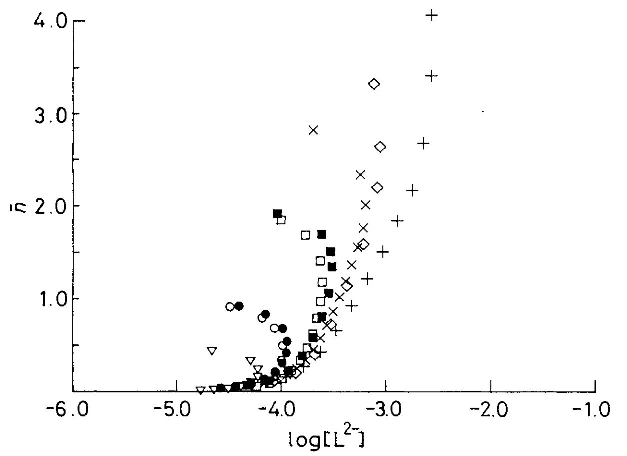

Figure 2. Experimental data plotted as $\bar{n}$ *vs.* $\log[L^{2-}]$. For C/B = 5 and 10:1, data with $\bar{n} > 4.0$ have been omitted. Key (B,C/mmol dm^{-3}): 1.11, 10.10 (+); 1.04, 5.04 (◇); 3.01, 9.04 (×); 3.03, 6.06 (□); 5.59, 11.19 (■); 3.15, 3.15 (○); 7.21, 7.21 (●); 6.45, 3.23 (▽)

dm^{-3}, and $0.000\,18 \leqslant C \leqslant 0.042$ mol dm^{-3}, covering the C/B ratios 0.5, 1, 2, 3, 4, 5, 8, 10, 20, and 25:1. The available $-\log[H^+]$ range was restricted to an upper limit due to the appearance of extremely sluggish equilibria, presumably caused by the formation of polynuclear hydrolytic species and/or aluminium hydroxide. To obtain more data points in the most interesting area (C/B = 1:1) some dilution experiments (titrations with pure medium) were also performed.

Data Treatment.—The equilibria to be considered in the present study can be divided into three groups. (*i*) The binary tartaric acid equilibria (1) and (2). These constants were

$$H_2L \rightleftharpoons HL^- + H^+;\ \beta_{-1,0,1} \qquad (1)$$

$$H_2L \rightleftharpoons L^{2-} + 2H^+;\ \beta_{-2,0,1} \qquad (2)$$

determined in separate titrations within the concentration range 0.005—0.020 mol dm^{-3}. No attempts were made to evaluate the hydroxylic acidity constants. (*ii*) The hydrolytic

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

equilibria (3) of Al^{3+}. For these equilibria, results evaluated earlier in this series[14] will be used. Dominating species and corresponding equilibrium constants, valid in 0.6 mol dm^{-3} Na(Cl), are given in Table 2. (*iii*) Three-component equilibria of the general form (4). In the evaluation of the three-component

$$pH^+ + qAl^{3+} + r(H_2L)_r \rightleftharpoons H_pAl_q(H_2L)_r^{p+3q};\ \beta_{p,q,r} \quad (4)$$

experimental data the binary complex models under (*i*) and (*ii*) were considered as known and all effects above this level were treated as being caused by ternary species. The mathematical analysis of data was performed with the least-squares computer program LETAGROPVRID[15] (version ETITR[16,17]). The p,q,r triplets and corresponding equilibrium constants that 'best' fit the experimental data were determined by minimizing the error squares sum $U = \Sigma(H_{calc.} - H_{exptl.})^2$. 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.[18,19] The computations were performed on a CD CYBER 850 computer.

Data, Calculations, and Results

Binary Proton–Tartaric Acid Equilibria.—Data used to determine the acidity constants of tartaric acid comprise 201 experimental points collected *via* five titrations within the ranges $0.005 \leqslant C \leqslant 0.020$ mol dm^{-3} and $2.1 \leqslant -\log[H^+] \leqslant 6.1$. The LETAGROP calculation ended at $\sigma(H) = 0.04$ mmol dm^{-3} and the following equilibrium constants were obtained: $\log \beta_{-1,0,1} = -2.702 \pm 0.002$ and $\log \beta_{-2,0,1} = -6.401 \pm 0.002$. The errors given are $3\sigma(\log \beta_{-n,0,1})$.

Ternary Proton–Aluminium(III)*–Tartaric Acid Equilibria.*—These data comprise 23 titrations with 657 experimental points within the ranges $0.000\,18 \leqslant B \leqslant 0.012$ mol dm^{-3}, $0.000\,18 \leqslant C \leqslant 0.042$ mol dm^{-3}, and $1.8 \leqslant -\log[H^+] \leqslant 6.7$. The following C/B ratios have been covered: 0.5, 1, 2, 3, 4, 5, 8, 10, 20, and 25:1. In order to visualize experimental data, Z_c *vs.* $-\log[H^+]$ curves were calculated and some of these data are given in Figure 1. This function gives the average number of OH$^-$ reacted per ligand. Some characteristic features of these curves may be pointed out. First, the fact that $Z_c > 2$ is direct evidence for the formation of binary $Al^{3+} - OH^-$, ternary $Al^{3+} - OH^- - L^{2-}$ and/or species where the hydroxy group(s) of tartaric acid is deprotonated. Secondly, the steepness of the curves at C/B = 1:1 indicate that polynuclear complex(es) are formed.

Another useful graphical aid is the plotting of $\bar{n}$ *vs.* $\log[L^{2-}]$, where $\bar{n}$ denotes the average number of L^{2-} co-ordinated per Al^{3+} (Figure 2). From this a tendency to coinciding curves is observed, indicating the formation of binary $[AlL_n]^{3-2n}$ complexes for $\bar{n} < 0.2$. At higher $\bar{n}$ values the dependence of these curves on B and C is clear evidence for the formation of species containing a higher degree of deprotonation. (As $-\log[H^+]$ in these solutions is well below 3, the possible formation of binary Al^{3+}–OH^- complexes can be excluded.)

Therefore, a second Bjerrum plot assuming $H_{-1}L^{3-}$ as binding unit was constructed. In these calculations, a value of $\log K_3 = -14.3$ for the third acidity constant of tartaric acid was used.[20] The value chosen affects the scale on the x axis but not the shape of the $\bar{n}$ curves. The result of these calculations is illustrated in Figure 3 and shows that fairly coincident curves up to $\bar{n} = 0.8$ are obtained.

Thus, on the basis of these plots it can be concluded that tartaric acid acts as a diprotic as well as a triprotic ligand in its interaction with aluminium ions. From the width of the series

Table 1. Results of LETAGROP calculations for some different assumptions concerning the complexes formed at $\bar{n}(\log[H_{-1}L^{3-}]) < 0.8$.* The formation constants are related according to the equation $p\text{H}^+ + q\text{Al}^{3+} + r\text{H}_2\text{L} \rightleftharpoons \text{H}_p\text{Al}_q(\text{H}_2\text{L})_r^{p+3q}$ where H_2L stands for $C_4H_6O_6$. The errors given are $3\sigma(\log \beta_{p,q,r})$

No. of titrations, No. of points	p,q,r	$\log(\beta_{p,q,r} \pm 3\sigma)$	p,q,r	$\log(\beta_{p,q,r} \pm 3\sigma)$	U mmol² dm⁻⁶	$\sigma(H)$ mmol dm⁻³
23, 359	−2,1,1	−3.93 ±0.26	−3,1,1	−5.64 ±0.025	33.4	0.35
23, 359	−2,1,1	−3.19 ±0.024	−6,2,2	−8.79 ±0.015	4.38	0.13
23, 359	−2,1,1	−3.07 ±0.036	−9,3,3	−11.77 ±0.040	15.7	0.24

* The calculations are based on data giving $U_0 = 2\,783$ mmol² dm⁻⁶.

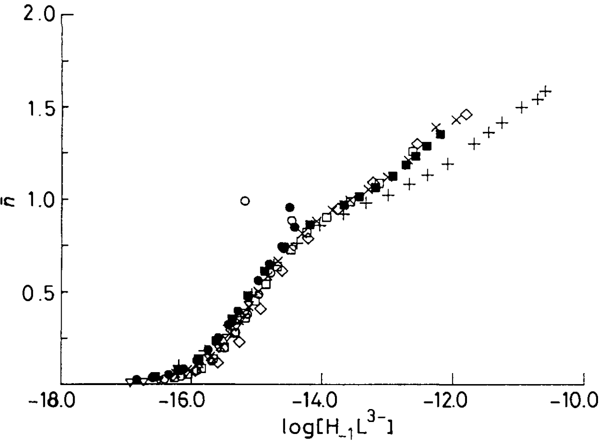

Figure 3. Experimental data plotted as $\bar{n}$ *vs.* $\log[H_{-1}L^{3-}]$. In the calculation a value for the first hydroxylic acidity constant of tartaric acid of $\log K_3 = -14.3$ was used.[21] The value chosen affects the scale on the x axis but not the shape of the $\bar{n}$ curves. Symbols as in Figure 2

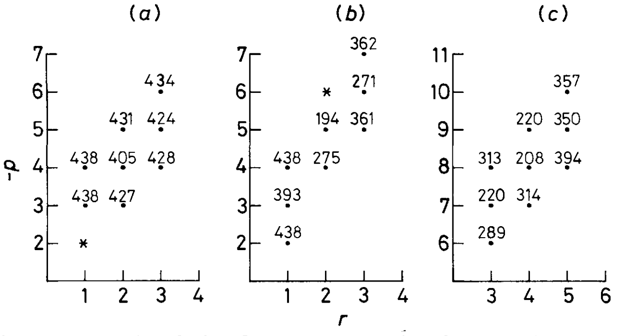

Figure 4. Result of the first p,q,r analysis of data with $\bar{n}(\log[H_{-1}L^{3-}]) < 0.8$. The diagrams give error-squares sums $10^2\ U_H(pr)_q$ assuming the presence of one additional complex. In the calculations the formation constants for the species (−2,1,1) and (−6,2,2) (*) were covaried together with that of the 'new' complex. The calculations are based on 359 points giving $10^2\ U_H(00)_0 = 438$ mmol² dm⁻⁶; $q = 1(a)$, $2(b)$, or $3(c)$

of curves in Figure 3, which clearly exceeds the precision of our titrations, it can however also be concluded that (−3,1,1), *i.e.* $[Al(H_{-1}L)]$, is probably not the major species formed. For this reason, a series of LETAGROP calculations was performed on data with $\bar{n}(\log[H_{-1}L^{3-}]) < 0.8$ in which the formation constant of (−2,1,1) was successively covaried with the formation constant for (−3,1,1), its dimer (−6,2,2), and its trimer (−9,3,3). The results of these calculations are given in Table 1 and show that the combination (−2,1,1) + (−6,2,2) gives the significantly best fit to data. However, some minor systematic deviations still remained, especially at $C/B = 1:1$. We therefore tried the simple hypothesis that an additional complex $H_pAl_q(H_2L)_r^{p+3q}$ was present together with (−2,1,1) and (−6,2,2).

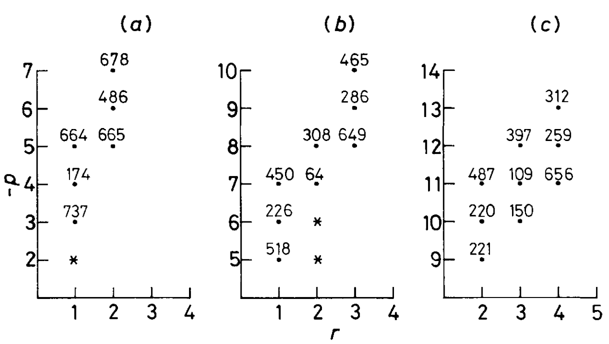

Figure 5. Result of the second p,q,r analysis on the whole data set. The complexes (−2,1,1), (−5,2,2), and (−6,2,2) (*) have been assumed. The diagrams give $10U_H(pr)_q$ assuming one new complex. The calculations are based on 657 points giving $10\ U_H(00)_0 = 743$ mmol² dm⁻⁶; $q = 1(a)$, $2(b)$, or $3(c)$

A trial-and-error procedure with the LETAGROP 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 p,q,r combinations have successively been tested one by one together with (−2,1,1) and (−6,2,2) and the complex giving the lowest error squares sum $U = \Sigma(H_{\text{calc.}} - H_{\text{exptl.}})^2$ was considered as the best explanation of data. The error squares sums U obtained for the tested combinations are given in Figure 4 and it is seen that the lowest value of U was obtained for the complex $H_{-5}Al_2(H_2L)_2^+$. The resulting stability constant for this species was $\log \beta_{-5,2,2} = -6.43 \pm 0.072$, giving $\sigma(H) = 0.08 \times 10^{-3}$ mol dm⁻³. Through this procedure, in which a large number of different complexes were matched against (−2,1,1) and (−6,2,2), also the existence of these two complexes was verified. Any complex giving a better fit to the data would have resulted in rejection of (−2,1,1) and/or (−6,2,2). In all these calculations, however, the stability constants for (−2,1,1) and (−6,2,2) always had small errors and relatively invariant values.

Another systematic search was now performed on the whole data set assuming the complexes determined above as known. As can be seen from Figure 5 these calculations favoured the formation of a species with the composition (−7,2,2). The calculations resulted in $\log \beta_{-7,2,2} = -13.11 \pm 0.031$ with $\sigma(H) = 0.11 \times 10^{-3}$ mol dm⁻³. Now only minor deviations at high C/B ratios and at high $-\log[H^+]$ values remained. We therefore introduced yet another member of the protonation series, *i.e.* (−8,2,2), and performed a final calculation where the

Table 2. Binary and ternary complexes in the three-component system proton–aluminium(III)–tartaric acid. The constants $\beta_{p,q,r}$ are defined in Table 1 and the errors are $3\sigma(\log \beta_{p,q,r})$

No. of titrations, No. of points	*p,q,r*	Tentative structure	$\log(\beta_{p,q,r} \pm 3\sigma)$	Ref.
5, 201	−1, 0,1	HL^-	−2.702 ± 0.002	This work
	−2, 0,1	L^{2-}	−6.401 ± 0.002	This work
	−3, 0,1	$H_{-1}L^{3-}$	−20.7	21
	−1, 1,0	$[Al(OH)]^{2+}$	−5.52	14
	−2, 1,0	$[Al(OH)_2]^+$	−11.3	14
	−3, 1,0	$Al(OH)_3$	−17.3	14
	−4, 1,0	$[Al(OH)_4]^-$	−23.46	14
	−4, 3,0	$[Al_3(OH)_4]^{5+}$	−13.57	14
	−32,13,0	$[Al_{13}O_4(OH)_{24}]^{7+}$	−109.2	14
23, 657	−2, 1,1	$[AlL]^+$	−3.44 ± 0.047	This work
	−5, 2,2	$[Al_2L(H_{-1}L)]^+$	−6.30 ± 0.040	This work
	−6, 2,2	$[Al_2(H_{-1}L)_2]$	−8.91 ± 0.016	This work
	−7, 2,2	$[Al_2(H_{-1}L)(H_{-2}L)]^-$	−13.12 ± 0.028	This work
	−8, 2,2	$[Al_2(H_{-2}L)_2]^{2-}$	−18.95 ± 0.19	This work

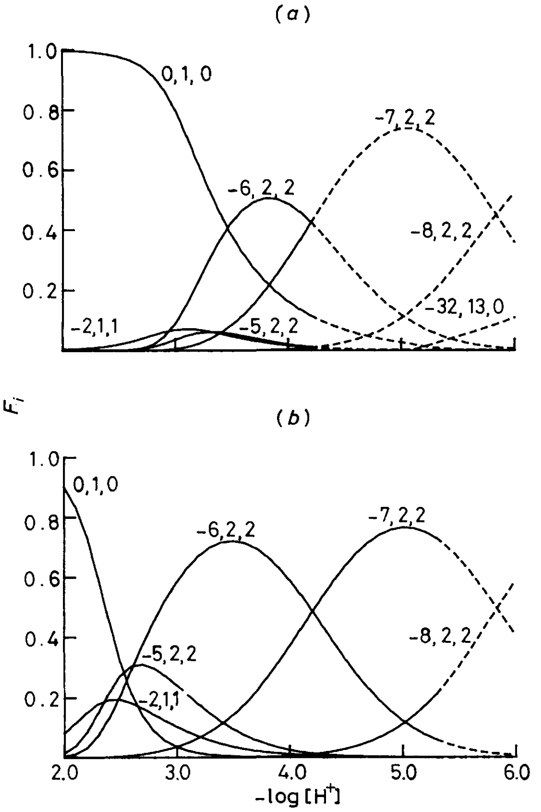

Figure 6. Distribution diagrams of F_i *vs.* $-\log[H^+]$ where F_i is defined as the ratio between aluminium(III) in a species and the total aluminium(III). The calculations have been performed using the computer program SOLGASWATER with constants given in Table 2. The broken curves denote extrapolated values. (*a*) $B = C = 0.001$; (*b*) $B = 0.003$, $C = 0.030$ mol dm^{-3}

equilibrium constants for all appearing ternary species were co-varied. The result of this calculation is given as our final model in Table 2. This calculation ended at $U = 5.7$ with $\sigma(H) = 0.09 \times 10^{-3}$ mol dm^{-3}, indicating a good fit to the data. With this final model, no systematic deviations could be observed.

In order to visualize the amounts of the different species, the computer program SOLGASWATER[21] equipped with plotting procedures has been used to calculate some distribution diagrams. These are presented in Figure 6.

Discussion

In the present investigation equilibrium constants for the formation of binary proton–tartaric acid as well as ternary proton–aluminium(III)–tartaric acid complexes have been determined and, in all, seven equilibrium constants have been evaluated. A computational problem in the evaluation of the three-component system has been the lack of a 'mononuclear' curve. As is seen in Figure 6, the binuclear aluminium complexes are predominant over the whole area investigated. The present study can therefore be regarded as a good illustration of the possibilities for treating complicated equilibrium problems with the help of LETAGROPVRID and repeated *p,q,r* searches.

In 1984 this system was investigated by Motekaitis and Martell[11] with quite divergent results. When we tried to adapt their complexation model to our data the resulting error squares sum with 'best possible' values on the equilibrium constants became 360 with $\sigma(H) = 0.75 \times 10^{-3}$ mol dm^{-3}, *i.e.* an error squares sum exceeding our value by a factor of over 60. We are therefore fully confident that the model presented by us gives the correct speciation for the system. A question which, however, might be raised is whether the binuclear complexes determined by us at the mmol dm^{-3} level have their corresponding mononuclear counterparts at very low concentrations. In our data analysis we have therefore repeatedly tried to insert the species (−3,1,1) into the equilibrium model. Thus, in a final covariation on the whole data set it was found that although this species was accepted, the resulting equilibrium constant ($\log \beta_{-3,1,1} = -7.8 \pm 0.6$) indicates it to be of very minor importance. From the calculated dimerization constant [$2(-3,1,1) \rightleftharpoons (-6,2,2)$; $\log K = 6.7$] it can be concluded that the dimeric species is predominant even at micromolar concentrations.

Through previous investigations within the present series, the common occurrence of binuclear aluminium–ligand complexes has been demonstrated (*e.g.* refs. 22—25). As these complexes have all been formed at $-\log[H^+] \geqslant 4$, they have been proposed to consist of an $Al_2(OH)_2$ core surrounded by one or several ligands. In the present system, however, the binuclear species start to form at $-\log[H^+] \leqslant 2.5$, *cf.* Figure 6. At such high acidities the formation of mixed hydroxo complexes seems highly improbable. Therefore, the present series of binuclear complexes are likely to have quite a different structure with the hydroxy groups of tartaric acid being deprotonated and coordinated in the complexes formed. As these hydroxyl acidity constants have not been determined in the present study, it will not be possible to recalculate our stability constants to 'normal'

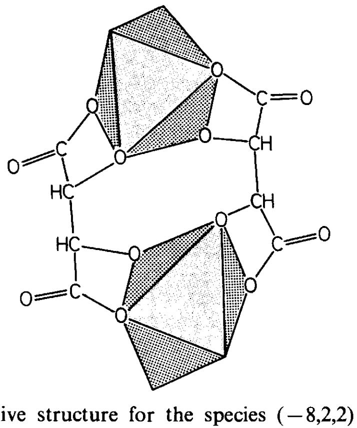

Figure 7. Tentative structure for the species (–8,2,2) based on an assumed resemblance with copper(II) tartrates[27]

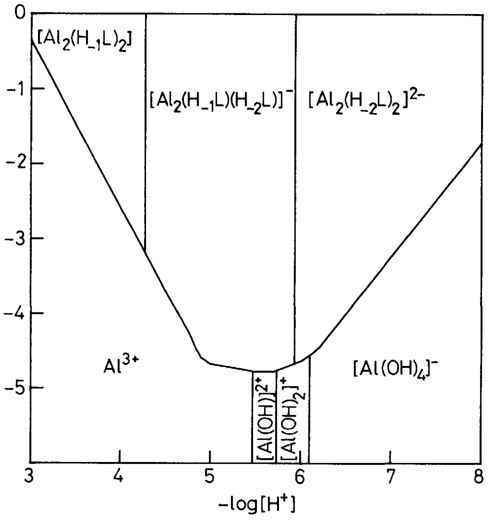

Figure 8. Predominance area diagram showing dominating aqueous aluminium species in equilibrium with gibbsite (log $^*K_{s0}$ = 9.6 where $^*K_{s0}$ = $[Al^{3+}]/[H^+]^3$ (C. F. Baes and R. E. Mesmer, 'The Hydrolysis of Cations,' Wiley, New York, 1976, p. 121) as a function of log C and $-\log[H^+]$

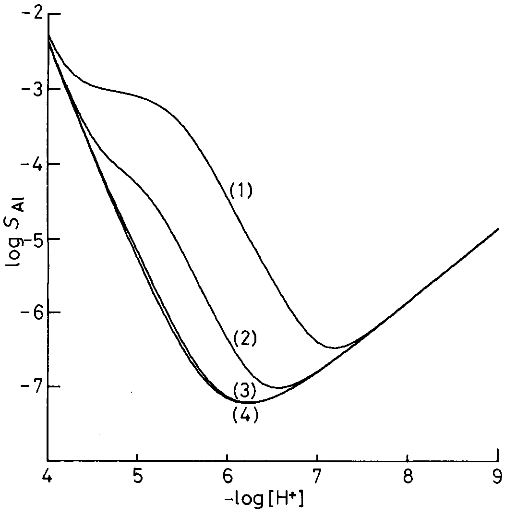

Figure 9. Solubility of gibbsite expressed as log S_{Al} *versus* $-\log[H^+]$ for different total concentrations of tartaric acid, C: 10^{-3} (1), 10^{-4} (2), 10^{-5} (3), and 0 mol dm^{-3} (4)

stability constants in which the deprotonated ligands are used as binding units.

The ability of tartaric acid to form binuclear bis(ligand) complexes with metal ions being bridged by two quadridentate (4–) ligands has previously been reported, in solid phases[26,27] as well as in solution.[28,29] According to Tapscott, *et al.*[30] the most favourable co-ordinations for a L(+)-tartrate dimer are those resulting in a trigonal bipyramidal or octahedral geometry around the metal ions. As the normal oxygen co-ordination around the aluminium ion either is octahedral or tetrahedral, the trigonal bipyramidal alternative seem highly unlikely in the present case. For these reasons, we suggest that the species (–8,2,2) actually should be written $[Al_2(H_{-2}L)_2]^{2-}$ with a structure as given in Figure 7. For the preceding proton series (–5,2,2) to (–7,2,2), it is then logical to assume a gradual protonation of the hydroxy groups, *i.e.* that these species should be written $[Al_2L(H_{-1}L)]^+$, $[Al_2(H_{-1}L)_2]$, and $[Al_2(H_{-1}L)(H_{-2}L)]^-$ respectively.

In an attempt to validate these assumptions, attempts have also been made to prepare a single crystal of the complex (–6,2,2). Highly concentrated solutions of this composition can be prepared by dissolving appropriate amounts of aluminium metal in a tartaric acid solution. However, on evaporation this solution turned into a transparent glass without yielding any signs of crystalline material. On the other hand, it was also found that the solubility of this complex drastically decreased through the addition of methanol, ethanol, or acetone. For this reason, slow vapour-diffusion experiments employing these solvents were carried out. In all of these experiments a white precipitate formed but in none of the cases did the procedure yield single crystals suitable for structure determination. At the present time, crystallization experiments at other neutralization degrees as well as in other solvents are in progress. Furthermore, the precipitate reported above will be the subject of an investigation employing modern spectroscopic techniques.

Modelling Calculations.—In an attempt to indicate the significance of different aluminium tartrates in a natural water, model calculations were performed in which crystalline gibbsite, $Al(OH)_3$, was equilibrated with solutions of different tartrate contents. In Figure 8 a predominance area diagram shows that $[Al_2(H_{-1}L)_2]$, $[Al_2(H_{-1}L)(H_{-2}L)]^-$, and $[Al_2(H_{-2}L)_2]^{2-}$ predominate within a broad $-\log[H^+]$ range. This implies that the solubility of gibbsite increases in the presence of tartrate ions. The magnitude of this increase is shown in Figure 9 for different values of C. Compared to other substances previously investigated within this series, the complexation ability of tartrate ions shows their closest resemblance with salicylate ions.[31]

In human bio-uptake considerations, also the charges of the species are of vital importance, as neutral complexes of low enough molecular weight (⩽650) can cross cell membranes *via* a passive diffusion mechanism.[32] According to Martin,[33] the appearance of such a species in the aluminium citrate system can explain why for instance a concomitant digestion of antacids and lemon juice causes increased blood concentrations of aluminium in man.[34] In the present system, an even higher predominance of a water-soluble, neutral species, $[Al_2(H_{-1}L)_2]$, is present in the range pH 3—5 (*cf.* Figure 6). It would therefore be most probable that tartrate ions might also cause an increased absorption of aluminium into the body from the gastrointestinal tract.

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