Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 26. The Solubility of Aluminium Tris(tropolonate)

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Equilibria in the system H^+–Al^{3+}–tropolone (HL) were studied in a 0.6 M Na(Cl) medium (25 °C) by using potentiometric (glass electrode) and titrimetric (EDTA–Pb^{2+}) methods. The formation of aqueous complexes was found to be negligible (for $-\log[H^+] \geq 1.8$) and the system was characterized by the formation of a solid phase, $AlL_3(s)$. The equilibrium constant was $\log K$ ($Al^{3+} + 3HL \rightleftharpoons AlL_3(s) + 3H^+$) = 11.21 ± 0.05 (3σ), corresponding to $\log K_{s0} = -31.05$. In model calculations, this phase is shown to be more insoluble than $Al(OH)_3$ at all $-\log[H^+]$ but, most significantly, the low solubility is also maintained in strongly acidic solutions.

In part 12 of this series,[1] complexation in the H^+–$Si(OH)_4$–tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one, HL) system was studied, and it was found that a cationic, hexacoordinated tris complex, SiL_3^+, formed in acidic solutions. As the Al^{3+} ion also has a strong coordination tendency towards the "2-hydroxy-1-one" binding site, as shown in parts 18[2] and 19[3] of this series, and as it thus was believed that tropolone could be a suitable ligand for the study of a quaternary H^+–$Si(OH)_4$–Al^{3+}–ligand system, this investigation was initiated.

During the preparation of aluminium tropolonate solutions it was, however, found that these mixtures always yielded off-white amorphous precipitates, even if the solutions were prepared at such low pH values as 1. The original idea therefore had to be abandoned but, as tropolone is an abundant constituent in higher plants (e.g. as 4-isopropyltropolone, thujaplicine, in conifers),[4] and as it is well known that natural organic materials flocculate, i.e. precipitate, in the presence of aluminium, it was still found interesting to evaluate the stoichiometry and solubility of this solid phase.

Experimental

Solutions and analysis. Tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one, HL) (Aldrich, 98 %) was sublimed under vacuum before use. For the preparation of stock solutions, boiled distilled water was used. The content of HL, as well as its acidity constant, were determined by potentiometric titration, both being in good agreement with expected values. The preparation and analysis of other solutions is described in Ref. 5. The analyses of aqueous aluminium in suspensions were, after filtration, determined through in-direct titration with EDTA–$Pb(NO_3)_2$ using xylenol orange as indicator.

Temperature and medium. The present investigation was carried out at 25.0 ± 0.5 °C in a constant ionic medium of 0.6 M Na(Cl).

Apparatus. Solutions were prepared in Pyrex glass tubes which were then encapsuled with plastic caps. The solids formed were then kept in suspension for 20 h by means of a home-built end-rotating test-tube holder running at about 30 r.p.m. Resulting $-\log[H^+]$ values were determined using an Orion 8103 Ross combination electrode in conjunction to an Orion Research, model 601A, ionalyzer. The electrode was calibrated using a solution containing 5.00×10^{-3} M HCl in 0.6 M NaCl or, for alkaline determinations, 5.00×10^{-3} M NaOH in 0.6 M NaCl. In the latter case, the calibration solution was always freshly prepared from a stock solution before its use. Filtering of the suspensions were performed using Millipore, type VC, filters of 0.10 μm pore size coupled to Swinnex-47 filter holders.

Data treatment. The equilibria which must be considered in the present study are: (1) the hydrolysis of Al^{3+}, (2) the acid–base properties of tropolone and (3) the formation of three-component species according to the general reaction $pH^+ + qAl^{3+} + rHL \rightleftharpoons H_pAl_q(HL)_r^{p+3q}$. With regard to solid phases, this reaction might also include the participation of medium ions, i.e. Na^+ and/or Cl^-. The binary equilibria of H^+–Al^{3+}, as well as those of H^+–tropolone, have been studied in earlier papers of this series.[1,6-9] These constants are given in Table 1 and will, in the present study, be treated as known.

Table 1. Equilibria in the three-component system H^+–Al^{3+}–tropolone (HL). The equilibrium constants $(\beta_{p,q,r})$ are defined according to the formula $pH^+ + qAl^{3+} + rHL \rightleftharpoons H_pAl_q(HL)_r^{p+3q}$.

Proposed formula	(p,q,r)	$\log (\beta_{p,q,r} \pm 3\sigma)$	Ref.
OH^-	$(-1,0,0)$	-13.727	10
$AlOH^{2+}$	$(-1,1,0)$	-5.52	6
$Al(OH)_2^+$	$(-2,1,0)$	-11.3	8
$Al(OH)_3$	$(-3,1,0)$	-17.3	8
$Al(OH)_4^-$	$(-4,1,0)$	-23.46	7
$Al_3(OH)_4^{5+}$	$(-4,3,0)$	-13.57	6
$Al_{13}O_4(OH)_{24}^{7+}$	$(-32,13,0)$	-109.2	6
H_2L^+	$(1,0,1)$	0.03	1
L^-	$(-1,0,1)$	-6.612	1
$Al(OH)_3(s)$	$(-3,1,0)$	-10.49	9
$AlL_3(s)$	$(-3,1,3)$	11.21 ± 0.05	This work

The computational problem is then to evaluate stoichiometries and corresponding equilibrium constants that best explain experimental data.

Data, calculations and results

To evaluate the stoichiometry of the solid formed, an experiment was performed in which a series of solutions containing a given amount of aluminium was mixed with variable amounts of tropolone solution. After 20 h equilibration, the $-\log[H^+]$ values of the suspensions were measured and then, after filtration, the resulting clear solutions were analyzed for aluminium content.

The result of this experiment is illustrated in Fig. 1 and shows that the precipitate formed has a tropolone to aluminium ratio of 3. From the amount of H^+ released into solution, it can also be concluded that each aluminium ion precipitated gives rise to the release of three H^+. Accordingly, this experiment has proved that the reaction between Al^{3+} and tropolone can be described by the formula $Al^{3+} + 3HL \rightleftharpoons AlL_3(s) + 3H^+$; $K^s_{-3,1,3}$. An independent
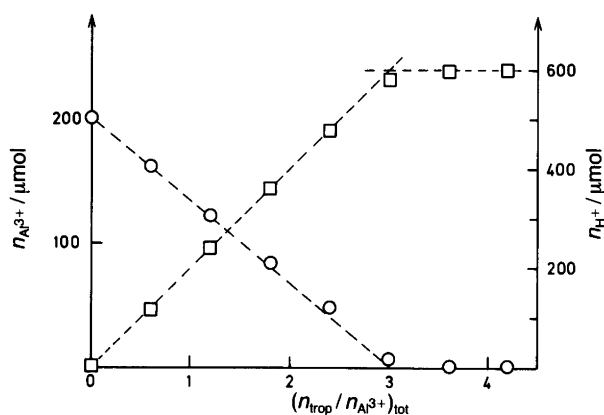

Fig. 1. Aqueous amounts of Al^{3+} (O) and H^+ (□) in an experiment in which 20×10^{-3} dm^3 of 10×10^{-3} M Al^{3+} solution was mixed with various volumes of 30×10^{-3} M tropolone solution.

confirmation of this stoichiometry was also given by the fact that the solid phase contained neither Na^+ (atomic emission) nor Cl^- (spot test with Ag^+).

Another very important piece of information from this experiment is that, although the measured $-\log[H^+]$ values are well below 2 in most of the solutions, the precipitate is formed in near-stoichiometric amounts. This implies that the formation of aqueous aluminium tropolonate species is negligible and, furthermore, that it will be very hard to evaluate the solubility product of $AlL_3(s)$ at the lower end of the $-\log[H^+]$ scale.

For this reason it was decided to raise the solubility of $AlL_3(s)$ not by adding acid but by lowering the free concentration of Al^{3+}. This can be achieved by adding hydroxide ions, as the aluminium speciation then will become dominated by the species $Al(OH)_4^-$ and the free Al^{3+} concentration will decrease by four orders of magnitude per $-\log[H^+]$ unit.

A series of 20 solutions at tropolone-to-aluminium ratios of 3.2, 4 and 5 and containing variable amounts of hydroxide ions $(10.9 \le -\log[H^+] \le 11.8)$ were therefore prepared. After 20 h equilibration, the resulting $-\log[H^+]$ values were determined using a glass electrode calibrated at $-\log[H^+] = 11.43$. As the five most alkaline preparations were free of precipitates, and as the recorded $-\log[H^+]$ values in these solutions were in full agreement with their stoichiometric compositions, taking the formation of $Al(OH)_4^-$, L^- and the ionic product of water into consideration, an internal validation of this calibration was obtained.

The precipitates from the remaining 15 solutions were then collected. As the IR spectra of these precipitates proved to be identical to the IR spectra of precipitates from acidic solutions, it was verified that the solid phase consisted of $AlL_3(s)$.

By writing the dissolution reaction of $AlL_3(s)$ in alkaline solutions as $AlL_3(s) + 4OH^- \rightleftharpoons Al(OH)_4^- + 3L^-$, it can be clearly seen that the $-\log[H^+]$ values in these suspensions will depend on the solubility of $AlL_3(s)$, as a higher solubility will correspond to a lower concentration of hydroxide ions and thus a lower value of $-\log[H^+]$. The computational task is therefore to find the numerical value of $K^s_{-3,1,3}$ which provides the closest fit between measured and calculated $-\log[H^+]$ values.

To do this, the computer modelling program SOLGAS-WATER,[11] supplied with the equilibrium model given in Table 1, was used to calculate theoretical $-\log[H^+]$ values for the suspensions at a series of values on $K^s_{-3,1,3}$. Thereafter, for each value of the equilibrium constant, the error squares sum $U = \Sigma[(-\log[H^+]_{calcd}) - (-\log[H^+]_{exptl})]^2$ was calculated and plotted against $K^s_{-3,1,3}$. From this plot, the "best" value of $\log K^s_{-3,1,3}$ was then determined to be 11.21 ± 0.05 (3σ) with $\sigma(-\log[H^+]) = 0.011$. The reported standard deviations were calculated as defined by Sillén.[12,13]

With this value for the equilibrium constant of $AlL_3(s)$, none of the solutions was calculated to be saturated with respect to aluminium hydroxide. Furthermore, with this
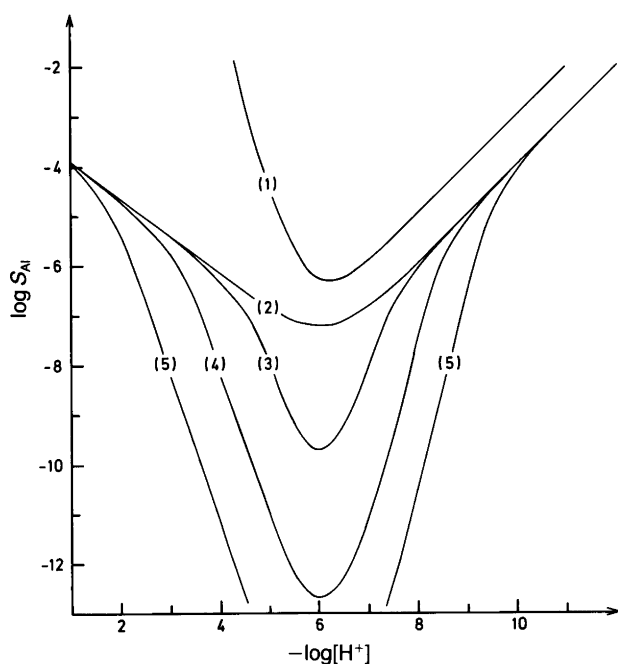
Fig. 2. Solubility diagram showing the solubility (as log S_{Al}) versus $-\log[H^+]$ for $Al(OH)_3(s)$ (1), $AlL_3(s)$ (2) and for $AlL_3(s)$ with 10^{-6} M (3), 10^{-5} M (4) and 10^{-4} M (5) excess of HL/L^-.

value of $K^s_{-3,1,3}$, the five clear solutions previously described were calculated to be undersaturated with respect to $AlL_3(s)$, i.e. in agreement with the experimental observations.

Discussion

To illustrate the low solubility of $AlL_3(s)$, Fig. 2 was constructed. This figure shows that AlL_3 is more insoluble than $Al(OH)_3$ at all $-\log[H^+]$ values, but, most significantly, that the low solubility of AlL_3 is also maintained in strongly acidic solutions. The second characteristic feature, which is seen from the lower curves in the figure, is that even a very minor access of tropolone will bring the permitted aluminium levels down to extremely low values in near-neutral solutions. In nature, however, a much more probable situation is that the access of aluminium will exceed the access of tropolone derivatives. Under such circum-

stances, the aqueous aluminium concentration will be regulated by aluminium hydroxide (and/or aluminosilicates) and, accordingly, result in very low tropolone concentrations in the aqueous phase. It is therefore most probable that tropolone derivatives, leached from decaying higher plants, are trapped in the uppermost part of the soil column.

An analytical application of the present system could be for the gravimetric determination of aluminium. The aluminium content of the solid corresponds to less than 10 % of its total weight, and, as shown, the precipitation is more or less quantitative over a wide range of $-\log[H^+]$. However, a major objection to this use of tropolone is probably the high price of the compound.

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