

A POTENTIOMETRIC AND SPECTROPHOTOMETRIC STUDY OF THE SYSTEM H^+ - Al^{3+} -CHROME AZUROL S

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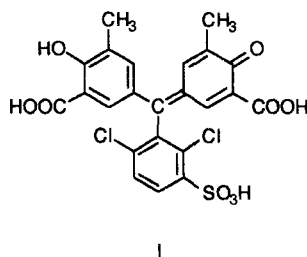
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Abstract—Equilibria in the Al^{3+} - H^+ -chrome azurol S (CAS) system ($pAl^{3+} + qH^+ + rL^{3-} \rightleftharpoons Al_pH_qL_r$) were studied in 0.10 M (and 0.60 M) KCl at 25°C. Proton-CAS equilibria were studied spectrophotometrically [$\log \beta_{0,-1,1} = -11.64$ (-11.24); $\log \beta_{0,2,1} = 6.93$ (6.56)] and potentiometrically [$\log \beta_{0,1,1} = 4.64$ (4.43)]. Potentiometric titrations ($p[H^+] = 2.5$ – 6.0) and fixed pH spectrophotometric titrations ($p[H^+] = 3.4$ and 5.0) were performed under excess ligand and excess metal conditions. The ligand displayed both 'salicylate' and '*p*-quinomethide-2-carboxylate' bonding. Results were interpreted in terms of a model containing five (six) species. These were a monomeric 1:1 complex $AlH_{-1}L$ [$\log \beta_{1,-1,1} = 2.01$ (1.80)] and, in excess ligand solutions, polymers with stoichiometries $Al_xH_{-x}L_{1+x}$ and $Al_xH_{1-x}L_{1+x}$, where $x = 4$ or 5 [for example, with $x = 4$, $\log \beta_{4,-4,5} = 26.57$ (24.72) and $\log \beta_{4,-3,5} = 31.35$ (28.56)], and in 0.6 M KCl $Al_xH_{-1-x}L_{1+x}$ ($\log \beta_{4,-5,5} = 19.53$). For solutions with excess metal additional species in the equilibrium model were $Al_3H_{-2}L_2$ (both ionic strengths), $Al_2H_{-1}L_2$ (0.1 M) and $Al_4H_{-4}L_2$ (0.6 M). Spectrophotometric titrations using malonate or oxalate as competitive ligands were performed to determine the polymer number x . Possible structures for the complexes are presented.

Aluminium chemistry has received attention in recent years due to Al^{3+} release into natural waters and soil solutions following acid deposition. Metallochromic dyes have often been used for colorimetric Al^{3+} analysis in environmental systems.¹⁻⁴ Some of these metallochromic dyes have the potential for multiple metal coordination. For example, chrome azurol S (3''-sulpho-2'',6''-dichloro-3,3'-dimethyl-4-hydroxyfuchson-5,5'-dicarboxylic acid; **1**; H_3CAS) undergoes interactions with a wide range of metal cations in aqueous solution.⁵ It has both salicylate and *p*-quinomethide-2-

carboxylic acid residues as potential coordination sites (sites A and B, respectively).



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Given this, and the propensity of Al^{3+} toward polymerization via hydroxy bridging, we decided

to investigate the Al^{3+} -CAS system. We were particularly interested in determining the stoichiometry of the interaction, and to identify the nature and extent of any polymerization. Experiments were carried out in 0.10 M and in 0.60 M KCl, to identify ionic strength effects. These effects are of interest due to the large size of the CAS ligand and the resulting metal complexes.

EXPERIMENTAL

Chemicals were analytical grade and used as supplied, except as indicated below. KOH solutions were prepared every 2–3 weeks in CO_2 -free H_2O from washed AnalaR pellets and standardized against Tris-HCl (Fluka, puriss). HCl solutions were standardized against this KOH. Al^{3+} solutions were prepared in dilute HCl from $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (ALFA, 99.9995%). The aluminium content was determined gravimetrically using 8-hydroxyquinoline; acidity was determined by Gran potentiometry. CAS (Aldrich) was purified by double recrystallization from 50 cm^3 of filtered 15% (w/w) aqueous solution by addition of an equal volume of concentrated HCl. The product was vacuum dried over NaOH then P_2O_5 at room temperature. Microanalysis gave C, 47.6; H, 3.70% (calculated for $\text{H}_3\text{CAS} \cdot 2\text{H}_2\text{O}$: C, 48.0; H, 3.50%). Experimental solutions (*ca* 1 g dm^{-3}) were filtered (0.025 μm) before use; significant insoluble residue was collected. Standardization by potentiometry gave >95% of the concentration by weight.

Potentiometry

Titrations were performed in an airtight, thermostatted 120 cm^3 reaction vessel held at $25 \pm 0.1^\circ\text{C}$ and flushed with O_2 -free N_2 . Titrations used a 2.5 cm^3 Radiometer ABU80 autoburette and were computer controlled to give constant pH increments. Base was added at the minimum rate (125 $\mu\text{l min}^{-1}$) to minimize the localized formation of polymeric Al^{3+} hydrolysis products. Solution pH was monitored at 150 s intervals after addition of each aliquot until the means of successive replicates (30 measurements) agreed within a present drift tolerance (0.003 pH). Potentiometric data were collected from a Radiometer PHM64 pH meter and Russell glass (SWR757) and calomel (CR5) electrodes. The system was calibrated as an $[\text{H}^+]$ probe before each titration. For ligand protonation titrations in 0.10 M KCl, a calibration method using $\text{p}[\text{H}^+]$ buffers generated by titration of phthalic acid was used, as described by Kennedy *et al.*⁶ Calibration for all other titrations was carried out by alkali titration of HCl to pH *ca* 11 in the appro-

priate ionic strength KCl electrolyte. Plotting pH (observed) against $\text{p}[\text{H}^+]$ (calc.) gave linear relationships ($r^2 \geq 0.995$) over the pH ranges 2.5–3.5 and 9.5–11.0. The subsequent titration data for CAS solutions were transformed using the overall linear least squares fit for the calibration data. This latter calibration approach removes reliance on the accuracy of standardization against a small number of NBS standard buffers, as required by the method used for the ligand-only titrations. It also removes errors associated with extrapolation of the acid-only region to higher pH, another commonly used calibration method.

Ligand-only titrations were carried out over the range 0.7– 1.6×10^{-3} M CAS. Calculation of K_2 (for protonation of the *p*-quinomethide-2-carboxylate group) used the non-linear least-squares program ORGLS.⁷ Total ligand concentration was fixed according to the mean equivalence volume for all ligand protonation titrations ($n = 5$).

Nine titrations of solutions containing Al^{3+} + CAS were carried out at six metal:ligand ratios between 0.48 and 3.22 at $[\text{Al}^{3+}] = 3.2$ – 7.45×10^{-4} M and $[\text{CAS}] = 2.40$ – 6.7×10^{-4} M, in 0.10 M KCl. In 0.60 M KCl, five titrations were carried out at metal:ligand ratios of 0.60 and 3.22 at $[\text{Al}^{3+}] = 3.6 \times 10^{-4}$ and 7.5×10^{-4} M. Excess acid was added to give a starting $\text{p}[\text{H}^+] \approx 2.5$. Data were analysed using the program SUPERQUAD⁸ to refine the relevant Al-CAS equilibrium constants. Al^{3+} hydrolysis constants were from studies in 0.1 M NaNO_3 ⁹ and 0.6 M NaCl.¹⁰ $\beta_{1,-4,0}$ for formation of $\text{Al}(\text{OH})_4^-$ was calculated by the method of Millero and Schreiber¹¹ from Palmer and Wesolowski's¹² determination of the thermodynamic constant [assuming $\gamma(\text{Al}(\text{OH})_4^-) = \gamma(\text{OH}^-)$].

Spectrophotometry

Titrations were carried out using a thermostatted cell as above. Titrant was added from a 2.5 cm^3 Gilmont micrometer syringe. Solutions were pumped through a 1 cm flow cell mounted in an adjacent Perkin-Elmer Lambda 2 spectrophotometer using a small peristaltic pump. Use of small-bore tubing (0.51 mm i.d.) and a 70 μl flow cell minimized dead volumes. Where appropriate the $\text{p}[\text{H}^+]$ was measured using instrumentation and calibration identical to that described above.

Ligand-only titrations were carried out at 6×10^{-5} M CAS. The 'salicylate' carboxylate group with $\log K_3 \approx 2$ was titrated with acid ($\text{p}[\text{H}^+] 2.0$ – 3.0) and absorbances recorded at 445, 520, 545 and 575 nm. The molar absorptivity of the protonated form was determined by addition of concentrated

HCl to $p[H^+] \approx 0.8$. The phenolic group ($pK_a \approx 12$) was titrated with base and absorbances recorded at 545, 570, 585, 595, 600 and 620 nm. The extinction coefficient of the conjugate base form was determined separately in 1 M KOH. The low ligand concentration allowed direct calculation of free $[OH^-]$ (or $[H^+]$) from the added concentration of alkali. Calculation of equilibrium constants used Ågren's¹³ graphical method.

Titrations of CAS with Al³⁺ at fixed $p[H^+]$ were carried out at 1.4×10^{-5} (0.10 M KCl) or 4.2×10^{-5} M CAS (0.10 and 0.60 M KCl) to establish the number and spectral characteristics of metal complexes. Al³⁺ was added in small volume increments to give a wide range of concentrations (2.2×10^{-6} – 7.3×10^{-5} M). The required value of $p[H^+]$ (3.40 or 5.00) was maintained by addition of small volumes of acid or base. Absorbance was scanned from 450 to 590 nm.

To establish the degree of polymerization in the complex, competitive ligand titrations were carried out at $p[H^+] = 5.00$. The choice of competing ligands [malonate (0.10 M KCl) or oxalate (0.60 M KCl)] was based on the availability of reliable stability constants.^{14,15} The competing ligand was titrated into solutions containing CAS and Al³⁺ at $p[H^+] = 5.00$. Concentrations were either 1.4×10^{-5} M CAS + 8.9×10^{-6} M Al³⁺ or 3.9×10^{-5} M CAS + 1.3×10^{-5} M Al³⁺ (malonate), and 3.6×10^{-5} M CAS + 2.2×10^{-5} M Al²⁺ or 5.7×10^{-5} M CAS + 4.3×10^{-5} M Al³⁺ (oxalate). The competing ligand was added in 10–40 μ M increments from 0 to 2.8×10^{-4} M.

Data interpretation: metal complexation equilibria

The structure of CAS (I) allows the possibility of polymer formation via coordination of bridging Al³⁺ at both sites A and B. If extended to a chain structure, excess ligand conditions are likely to lead to terminal CAS functionalities, whereas excess metal conditions will lead to terminal Al³⁺ moieties.

Analysis of the Al³⁺-CAS system established that for $p[H^+] 2.4$ – 6.0 polymerization is dominant under potentiometric conditions (millimolar concentrations) but not under spectrophotometric conditions (*ca* 10^{-5} M). Resolution of the equilibria for this complex system required an approach which involved combination of data from spectrophotometric (Al³⁺-CAS) titrations, competitive spectrophotometric titrations [Al³⁺-CAS-malonate (or oxalate)] and potentiometric titrations.

Competitive spectrophotometric titrations at $p[H^+] 5.0$ were used to establish the stability of the monomer (AlH₋₁L), which was assumed to dominate Al³⁺-CAS chemistry under conditions of

excess ligand (malonate, oxalate) in dilute solution. Spectrophotometric titrations at $p[H^+] 3.4$ confirmed the stoichiometry and stability of this monomeric species and its domination of speciation in dilute solution. Spectrophotometric titrations at $p[H^+] 5.0$, which involved a wide range of metal concentrations, established the existence of species with $M/L > 1.0$ in excess metal solutions.

Potentiometric end-point stoichiometry in 0.1 M KCl provided evidence for the existence of oligomers and/or polymers Al_xH_{-x}L_{x+1} under excess ligand conditions. Non-linear least-squares analysis of the potentiometric data yielded stability constants for oligomers with $x = 2$ and 3 and for polymers (and their conjugate bases) for a small range of possible values of x . Elucidation of the polymer number, x , was assisted by further analysis of the competitive spectrophotometric titration data under stoichiometric and excess metal conditions.

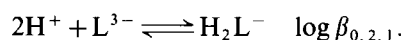
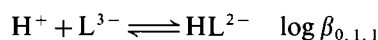
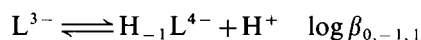
RESULTS

The zero proton level for CAS was chosen as L³⁻ to simplify discussion of metal coordination at the salicylate residue. The phenolic proton in such systems is normally very weakly acidic ($pK_a \approx 12$) but dissociates well into the acidic pH range upon metal coordination.

Ligand protonation equilibria

CAS has four potentially acidic groups in aqueous solution. The carboxylic and phenolic moieties on the salicylate residue (site A) were studied spectrophotometrically. The β -ketocarboxylic group (site B) was studied potentiometrically. Protonation of the strongly acidic sulphonate group was not studied.

Z functions ($Z_c =$ moles of protons bound per mole of ligand) for the potentiometric results are shown in Fig. 1. The data were fitted to the following model according to the definition $pAl^{3+} + qH^+ + rL^{3-}$:



Equilibrium constants are given in Table 1. They are in agreement with spectrophotometric literature values for 0.1 M KCl ($\log \beta_{0,-1,1} = -11.81$; $\log \beta_{0,1,1} = 4.71$; $\log \beta_{0,2,1} = 6.96$ ¹⁶) and for 0.1 M NaClO₄ ($\log \beta_{0,-1,1} = -11.75$; $\log \beta_{0,1,1} = 4.88$; $\log \beta_{0,2,1} = 7.13$ ¹⁷). The lower value for $\log \beta_{0,1,1}$ in the present work (4.64; 0.1 M KCl) may be due to

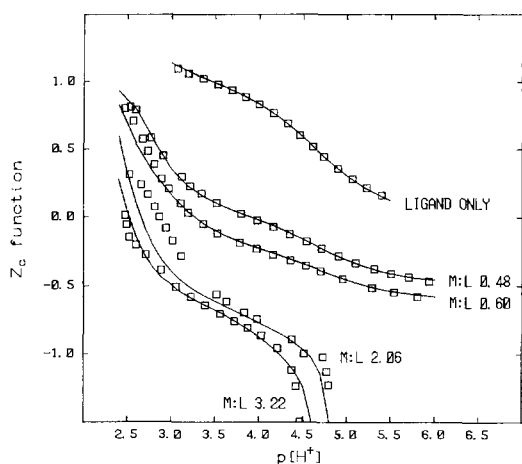


Fig. 1. A selection of the potentiometric results plotted as Z_c functions (moles H^+ released per mole of ligand) showing the fit of the final model at each indicated M:L ratio for 0.1 M KCl. For $[Al^{3+}]_{tot}$ and $[CAS]_{tot}$ see the text.

Table 1. Equilibrium constants $\beta_{p,q,r}$ for the system $pAl^{3+} + qH^+ + rL^{3-}$ at 25°C in KCl, determined from n titrations

Constant	l (M)	n	Value \pm s.d.	Method ^a
$\log \beta_{0,-1,1}$	0.10	3	-11.64 ± 0.03^b	S
	0.60	2	-11.24 ± 0.04^c	S
$\log \beta_{0,1,1}$	0.10	5	4.64 ± 0.02	P
	0.60	2	4.43 ± 0.01	P
$\log \beta_{0,2,1}$	0.10	4	6.93 ± 0.05	S
	0.60	3	6.56 ± 0.03	S
$\log \beta_{1,-1,1}$	0.10	4	2.01 ± 0.02	S
	0.60	3	1.80 ± 0.20	S
$\log \beta_{3,-2,2}$	0.10	3	12.29 ± 0.08	P
	0.60	2	11.99 ± 0.05	P
$\log \beta_{2,-1,2}$	0.10	3	12.92 ± 0.07	P
$\log \beta_{4,-4,2}$	0.60	2	7.45 ± 0.05	P

^a S = spectrophotometry; P = potentiometry.

^b Calculated using $pK_w = 13.788$.

^c Calculated using $pK_w = 13.724$.

the sensitivity of potentiometry and spectrophotometry to different impurities.

Metal complexation equilibria, 0.10 M KCl

Spectrophotometric analysis. Spectrophotometry at $p[H^+] = 5.00$ (Fig. 2) showed an isosbestic point at 492 nm and $\lambda_{max} = 545$ nm ($\epsilon = 7.67 \times 10^4$) under excess ligand conditions. Excess Al^{3+} caused the isosbestic point to break down and reform at 560 nm. Absorbance at 545 nm decreased and a new

λ_{max} formed at 572 nm. At $p[H^+] = 3.40$, the excess ligand isosbestic point shifted to 508 nm, due to pH dependence of the ligand-only spectrum, but wavelengths for the maxima were unchanged. These results indicate formation of at least two complexes at $p[H^+] 3.4$ and 5.0.

A qualitative indication of linear polymer formation was obtained from spectrophotometric titration curves at $p[H^+] 5.00$. A plot of absorbance (corrected for uncomplexed ligand) against total $[Al^{3+}]$ contained two linear segments corresponding to excess ligand and excess metal conditions, respectively. The $[Al^{3+}]$ at the intersection of these segments provided a ligand:metal ratio, Y , for the terminal species arising under excess ligand conditions. Results from two titrations, which were carried out at different CAS concentrations, were $Y = 1.17$ and $1.07 (\pm 0.04)$. From this it was inferred that (i) polymerization to form chain polymers $Al_xH_{-x}L_{x+1}$ may be occurring, and (ii) ring polymers with $Y = 1.0$, $(AlH_{-1}L)_n$, are not significant contributors to speciation.

Results from spectrophotometric studies using malonate as a competitive ligand were used to determine $\log \beta_{1,-1,1}$. It was assumed that no polymer was present at the minimum concentration of CAS complex (i.e. at the highest amount of added malonate). [If it was assumed that only the monomer $AlH_{-1}L$ forms under all spectrophotometric conditions ($[CAS], [Al^{3+}] \sim 10^{-5}$ M), consistent constants ($\beta_{1,-1,1}$) were not obtained for different titration stoichiometries.] The concentration of Al-CAS complex was calculated after each titration

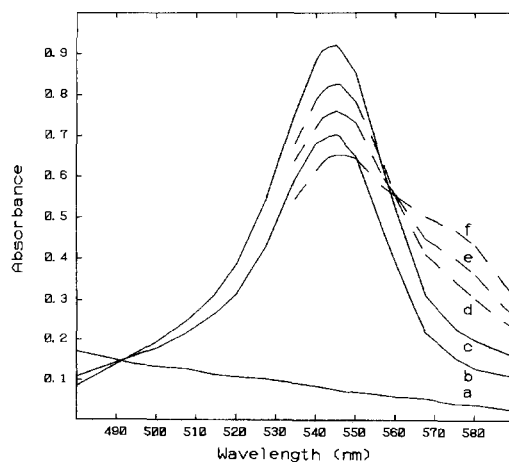


Fig. 2. Sample points from spectrophotometric titration of 1.39×10^{-5} M CAS with Al^{3+} at $p[H^+] = 5.00$ in 0.10 M KCl at 25°C. $[Al^{3+}]_{tot}$ for curves a-f was 0, 9.0, 15.9, 41, 55 and 74 μ M, respectively. Titration points falling outside the lower isosbestic point are omitted below 535 nm for clarity.

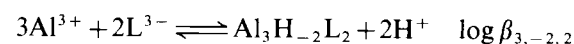
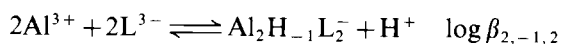
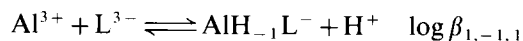
increment using absorbance data (A) at 540, 545 and 550 nm and the equation

$$[\text{complex}] = (A - \varepsilon(\text{CAS})[\text{CAS}]_t) / (\varepsilon(\text{complex}) - \varepsilon(\text{CAS})), \quad (1)$$

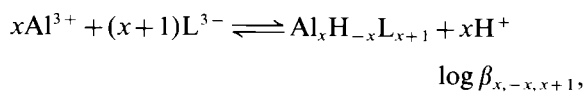
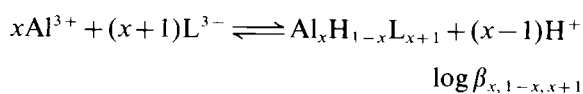
where $[\text{CAS}]_t$ = total CAS concentration. An iterative procedure was used to estimate the value for $\log \beta_{1,-1,1}$, which would account for the concentration of Al³⁺-CAS complex calculated using eq. (1). Composition of the resulting solutions changed from 0% (no added oxalate or malonate) to *ca* 85% aluminium malonate (95% aluminium oxalate) complex. Equation (1) assumes no ternary oxalate or malonate complexes. Visible spectra monitored during the experiments showed the expected isosbestic point and no unexpected features, which might have suggested ternary Al³⁺-CAS-malonate (or oxalate) complex formation. Extinction coefficients were from the present study. In 0.10 M KCl at $p[\text{H}^+] = 5.00$, $\varepsilon(\text{CAS}) = 5.40 \times 10^3$ (545 nm), 4.99×10^3 (550 nm); $\varepsilon(\text{complex}) = 7.67 \times 10^4$ (545 nm), 7.11×10^4 (550 nm). In 0.60 M KCl, $\varepsilon(\text{CAS}) = 3.97 \times 10^3$ (545 nm), 3.67×10^3 (550 nm); $\varepsilon(\text{complex}) = 7.28 \times 10^4$ (545 nm), 6.95×10^4 (550 nm). Uncertainties (\pm s.d.) were 250 for $\varepsilon(\text{CAS})$ and 1.5×10^3 for $\varepsilon(\text{complex})$.

Potentiometric analysis. Potentiometric end-point stoichiometry for excess ligand titrations in 0.1 M KCl was 0.98–1.06 H⁺/Al³⁺. This is consistent with the stoichiometry AlH₋₁L for a monomer or cyclic polymers, or with the stoichiometry Al_xH_{-x}L_{x+1} for linear polymers. The latter stoichiometry is supported by spectrophotometric titration curves and can arise if the non-coordinated donors in the terminal ligands correspond to one site A and one site B function.

The spectrophotometric value for $\log \beta_{1,-1,1}$ was incorporated as a fixed constant in refinements of potentiometric data. The data for 0.1 M KCl were fitted to the following model, for which results are given in Tables 1 and 2:



and the polymeric acid–base conjugate pairs



for which x was varied from 3 to 9. This procedure

found that $(\log \beta_{x,1-x,x+1} - \log \beta_{x,-x,x+1})$ ranged from 4.69 ($x = 3$) to 5.18 ($x = 9$).

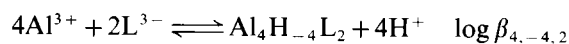
Potentiometrically derived constants for each assumed polymer chain length (Table 2) were then tested for their ability to predict observed Al–CAS complex concentrations for each datum point in the malonate titrations. Calculations used the speciation program SOLGASWATER.¹⁸ The relative errors for each datum point in the malonate titrations, $([\text{AlCAS}]_{\text{calc}} - [\text{AlCAS}]_{\text{obs}}) / [\text{AlCAS}]_{\text{calc}}$, gave R factors¹⁹ of 5.8–8.2% for $x = 3$ –9. Potentiometric refinement (Table 2) was acceptable over a wide range of chain lengths (to $x > 9$).

Metal complexation equilibria, 0.60 M KCl

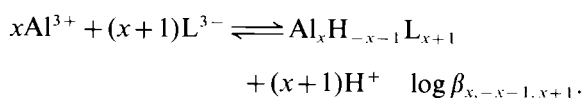
A spectrophotometric titration of CAS with Al³⁺ at $p[\text{H}^+] = 5.00$ gave a ligand:metal ratio of $Y = 1.16 \pm 0.04$ from the intersection of the excess metal and excess ligand segments of the absorbance vs concentration curve. This is similar to 0.1 M KCl results and is consistent with chain polymer rather than ring polymer formation. As for the 0.10 M KCl studies, results from spectrophotometric studies using a competitive ligand (oxalate) were used to estimate $\log \beta_{1,-1,1}$.

The potentiometric end-point stoichiometry for titrations under excess ligand conditions was 1.20–1.29 H⁺/Al³⁺ (mean = 1.23), significantly higher than the range of 0.98–1.06 H⁺/Al³⁺ for the 0.10 M KCl results. Inclusion of an additional polymer conjugate base species Al_xH_{-x-1}L_{x+1} was therefore necessary to match the end-point stoichiometry. This stoichiometry can arise if the non-coordinated donors in the terminal ligands are both site B functions.

The potentiometric titration data for 0.6 M KCl were fitted to a model similar to that for 0.1 M KCl but excluding Al₂H₋₁L₂ and including



and the polymer conjugate base



This procedure also established that $\log \beta_{x,1-x,x+1} - \log \beta_{x,-x,x+1}$ and $\log \beta_{x,-x,x+1} - \log \beta_{x,-x-1,x+1}$ are constant (at ≈ 3.9 and 4.6, respectively), regardless of empirical polymer chain length.

The potentiometric constants derived as a function of chain length (Table 2) were then tested for their ability to predict observed Al–CAS complex concentrations in the oxalate titrations. R factors (%) ranged from 9.4 to 10.1 for $x = 3$ to $x = 6$.

Table 2. Dependence of Al-CAS constants on polymer chain length, x , at 25°C in: (A) 0.10 M KCl, from four titrations, and (B) 0.60 M KCl, from three titrations, at $M:L < 1.0$

log constant	Value (\pm s.d.) ^a			
	$x = 3$	$x = 4$	$x = 5$	$x = 6$
A. 0.10 M KCl				
$\beta_{x,-x,x+1}$	19.92 (0.05)	26.57 (0.06)	33.27 (0.07)	39.99 (0.09)
$\beta_{x,1-x,x+1}$	24.61 (0.05)	31.35 (0.05)	38.14 (0.05)	44.93 (0.06)
B. 0.60 M KCl				
$\beta_{x,-1-x,x+1}$	13.16 (0.04)	19.53 (0.05)	25.92 (0.07)	32.33 (0.09)
$\beta_{x,-x,x+1}$	18.63 (0.02)	24.72 (0.04)	30.84 (0.05)	36.96 (0.08)
$\beta_{x,1-x,x+1}$	22.49 (0.02)	28.56 (0.03)	34.68 (0.05)	40.83 (0.06)

^as.d. of parameter calculated by SUPERQUAD.

DISCUSSION

The ligand stepwise protonation constants, $-\log \beta_{0,-1,1}$ and $\log K_3 (= \log \beta_{0,2,1}/\beta_{0,1,1})$ can be compared with the corresponding constants for salicylic acid, namely 13.6 and 2.80 (0.1 M KNO_3 ²⁰) and 2.724 (0.6 M NaCl ²¹). The effect of resonance between the phenolate ring and the quinomethide ring is to significantly increase the acidity of the phenolic group. The protonation constant K_2 ($\beta_{0,1,1}$) is ascribed to the β -ketocarboxyl group (site B); the numerical value is between those observed for aliphatic and aromatic carboxyl groups.

The formation of a dimeric ring system proposed for the Fe^{III} -CAS complex¹⁶ is clearly inconsistent with the present results at both ionic strengths. The postulated polymeric species account for potentiometric and spectrophotometric results over a wide range of complex concentrations. In the potentiometric titrations, complexed aluminium was between 2×10^{-4} and 5×10^{-4} M at $\text{p}[\text{H}^+] = 5.0$, depending on the titration. In the spectrophotometric competitive ligand titrations, complexed aluminium was between 1×10^{-6} and 2×10^{-5} M at $\text{p}[\text{H}^+] = 5.0$. The solubility of the larger polymers is remarkable, and is probably due to the presence of charge over the whole structure.

The species distribution diagram for 0.10 M KCl under excess ligand conditions (and assuming $x = 4$) is given in Fig. 3. At a fixed $\text{Al}^{3+} : \text{L}$ ratio (0.6), substantial speciation changes occur between concentrations typical of potentiometry and those used for spectrophotometric analysis. Under potentiometric conditions (Fig. 3; $[\text{Al}^{3+}] = 358 \mu\text{M}$), the AlH_{-1}L monomer is not a significant species. Formation of the dimer $\text{Al}_2\text{H}_{-1}\text{L}_2$ starts at $\text{p}[\text{H}^+] < 2.0$ and complexation of Al^{3+} by CAS is complete by $\text{p}[\text{H}^+] 3.5$. Formation of the tetramer $\text{Al}_4\text{H}_{-3}\text{L}_5$ starts at $\text{p}[\text{H}^+] 2.5$ and conversion to tetrameric species is complete by $\text{p}[\text{H}^+] 5.0$, where

the acid-base pair $\text{Al}_4\text{H}_{-3}\text{L}_5$ and $\text{Al}_4\text{H}_{-4}\text{L}_5$ are in approximately equal abundance.

Under dilute spectrophotometric conditions, where $[\text{Al}^{3+}]$ is two orders of magnitude lower, speciation is quite different. The monomer AlH_{-1}L is the dominant complex with maximum abundance at $\text{p}[\text{H}^+] 5.5$, although it is not significant until $\text{p}[\text{H}^+] > 3.5$. The dimer $\text{Al}_2\text{H}_{-1}\text{L}_2$ is a minor species with a maximum concentration (10%) at $\text{p}[\text{H}^+] 4.3$. Near the upper end of the concentration range employed for spectrophotometric analysis ($[\text{Al}^{3+}] = 35.8 \mu\text{M}$), the speciation pattern is intermediate. Between $\text{p}[\text{H}^+] 3.0$ and 4.2, the dimer $\text{Al}_2\text{H}_{-1}\text{L}_2$ is dominant. Polymer formation is significant at $\text{p}[\text{H}^+] > 3.5$. At $\text{p}[\text{H}^+] 5.0$, the pH where spectrophotometric analysis by CAS is normally

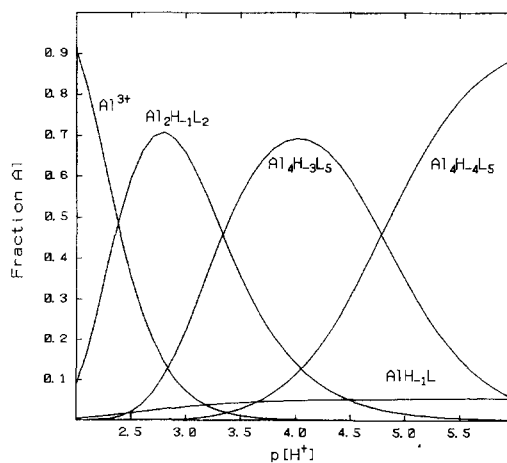


Fig. 3. Distribution diagram for the Al^{3+} - H^+ -CAS system at $\text{Al}^{3+} : \text{CAS} = 0.60$ (excess ligand), calculated¹⁸ for $[\text{Al}^{3+}]_{\text{tot}} = 3.58 \times 10^{-4}$ M and 0.10 M KCl at 25°C. This concentration corresponds to typical potentiometric conditions. Species with $< 5\%$ maximum abundance not shown. Calculations are for polymer chain length $x = 4$ (Tables 1 and 2A).

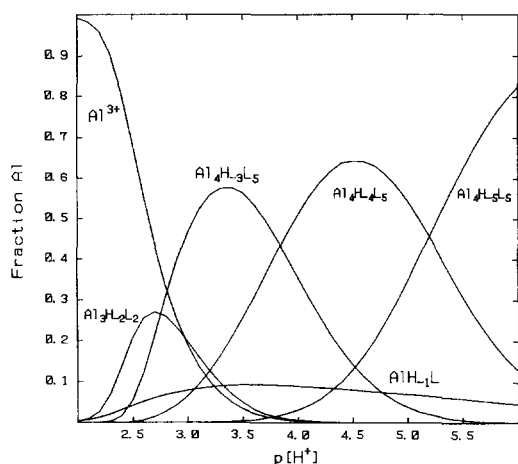
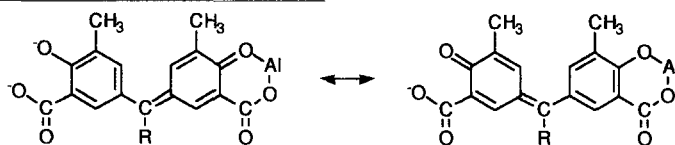


Fig. 4. Distribution diagram for the $Al^{3+} - H^+ - CAS$ system at $Al^{3+} : CAS = 0.60$ (excess ligand), calculated¹⁸ at $[Al^{3+}]_{tot} = 3.58 \times 10^{-4}$ M in 0.60 M KCl at 25°C. Species with < 5% maximum abundance not shown. Calculations are for polymer chain length $x = 4$ (Tables 1 and 2B).

carried out,²² the monomer $AlH_{-1}L$ represents 40% of complexed aluminium, polymers with a stoichiometry $L/Al^{3+} = 1.2$ account for some 50% of aluminium and dimers $Al_2H_{-1}L_2$ some 10%. Speciation (and the complex stoichiometry) therefore changes significantly over the range of $[Al^{3+}]$ likely to be used in spectrophotometric analysis.

Under excess metal conditions the dimer $Al_2H_{-1}L_2$ is again the most important complex



species at low pH, whereas the species $Al_3H_{-2}L_2$ is the dominant complex in the range $p[H^+] 3.7 - 5.0$. Unlike excess ligand conditions, where CAS totally suppresses Al^{3+} hydrolysis to $p[H^+] \geq 6$, the hydrolysis products $AlOH^{2+}$ and $Al_13(OH)_{32}^{7+}$ become significant above $p[H^+] 4.0$ and 4.7 respectively.

Increasing ionic strength to 0.60 M KCl effects significant changes to the model and hence the speciation. The tetrameric polymer sequence, which now includes two 'conjugate bases', dominates speciation under excess ligand potentiometric conditions (Fig. 4). The new dimer $Al_3H_{-2}L_2$ is only important at $p[H^+] < 3.5$ and is insignificant in diluted solutions. Consequently, the monomer $AlH_{-1}L$ is more important at the higher ionic

strength. Under dilute spectrophotometric conditions, $AlH_{-1}L$ is the only significant $Al - CAS$ complex, similar to 0.1 M KCl. Under excess metal conditions generation of the ' Al_{13} ' hydroxy polymer is suppressed and complexation is enhanced (relative to 0.1 M KCl results). This is especially noticeable at $p[H^+] > 4.0$ with the dominance of the excess metal species $Al_4H_{-4}L_2$. The inclusion of this species in the model reflects a substantially increased proton release under excess metal conditions in 0.6 M KCl.

It is unlikely that the ionic strength effects could be due to aluminium-electrolyte interactions. Chloride interactions with Al^{3+} are weak,²³ with no evidence for $Al^{3+} - Cl^-$ complex formation in 12 M HCl.²⁴ We know of no aqueous $Al^{3+} - Cl^-$ stability constant measurements. This low stability is borne out by calculations of activity coefficients¹¹ in KCl electrolyte. For La^{3+} , which has very weak chloride interactions ($\log K_1 = 0.29$,²⁵ $\gamma = 0.132$ (0.10 m) and 0.050 (0.61 m)). The values for Al^{3+} ($\gamma = 0.140$ and 0.063) indicate weaker $Al^{3+} - Cl^-$ interactions. This weakness renders formation of ternary $Al^{3+} - CAS - Cl^-$ complexes unlikely. However, all species in solution interact to a degree with the electrolyte. Stability constants are thus operationally defined as applying to the particular electrolyte, in the present case, KCl.

When Al^{3+} is coordinated to CAS to form the $AlH_{-1}L$ monomer, the two potential binding sites are rendered equal by resonance:

However, the greater charge neutralization resulting from 'salicylate' complexation suggests that this structure will be the more important contributor. A direct comparison between Al^{3+} binding by CAS and by salicylic acid can be made using the data of Öhman and Sjöberg.²¹ Their result for salicylate, when converted to the same ligand zero proton level as the present study, gives $\log \beta_{1,-1,1} (L^{3-} + Al^{3+} \rightleftharpoons AlH_{-1}L + H^+) = -0.33$ (0.6 M NaCl) compared with 1.80 for CAS (0.6 M KCl). This difference in Al^{3+} complex stabilities is consistent with the difference in acidities of the phenolic group [pK_a (salicylate) = 13.6;²⁰ pK_a (CAS) = 11.24]. The formation of dimers ($Al_2H_{-1}L_2$; $I = 0.1$ M KCl) and trimers ($Al_3H_{-3}L_2$; $I = 0.6$ M KCl) at $p[H^+] < 3$ implies strong coordination by both

donor sites. This factor promotes polymer formation.

All H^+ -CAS and H^+ -CAS- Al^{3+} equilibrium constants decreased with increasing ionic strength. The possible exception to this involves $\log \beta_{3,-2,2}$. An alternative, simpler stoichiometry ($Al_2H_{-1}L$) fitted the potentiometric data equally well. However, the ionic strength dependence of $\log \beta_{2,-1,1}$ gave unacceptable activity coefficient ratios. Since other species in the model followed expected ionic strength patterns, alternatives to $Al_2H_{-1}L$ were sought which gave a decreased $\log \beta$ at 0.6 M KCl. The simplest of these was $Al_3H_{-2}L_2$, which may be considered as the combination of $Al_2H_{-1}L + AlH_{-1}L$. This process, where ionic strength dependence is used as a criterion for model development, is quite novel. It constitutes a strong argument for collecting equilibrium data over a range of ionic strengths.

Ionic strength arguments were also used in postulating the probable polymer chain length. Fitting statistics (χ^2 , σ ; not shown) for the 0.1 M KCl model (Table 2A) favoured a higher polymer number, x , under excess ligand potentiometric conditions. Under similar conditions, statistics for the 0.6 M KCl model (Table 2B) favoured a smaller polymer. Similarly, R factors for the malonate (0.1 M) and oxalate (0.6 M) spectrophotometric titrations favoured smaller polymers. These apparently disparate results were resolved by using the end-point stoichiometry for the 0.6 M potentiometric titrations ($H^+/Al^{3+} = 1.23$), a stoichiometry which is consistent with a tetramer or pentamer only. Applying a principle of parsimony, that the same polymer chain lengths are likely to form at both ionic strengths, we assumed that $x = 4$ or 5 (or both). R factors and fitting statistics were acceptable at both ionic strengths.

The protonation constants for the polymers can be compared with those for the free ligand at each ionic strength. At 0.1 M KCl, the dissociation of $Al_4H_{-3}L_5$ to $Al_4H_{-4}L_5$ gives $\log K$ ranging from -4.78 ($x = 3$) to -5.2 ($x = 9$), values which are in qualitative agreement with dissociation of the *p*-quinomethide-2-carboxylic acid group ($\log K = -4.64$ for the free ligand). The small decrease in acidity of this terminal group in the polymer complex is consistent with the electron donating effect of the phenolate group at site A (coordinated to Al^{3+}). At 0.6 M KCl, two polymer deprotonation reactions must be considered. Further, to account for the end-point stoichiometries, it is necessary that the polymer has terminal functional groups which are both site B at 0.6 M (compared with one site A and one site B at 0.1 M). $\log K$ for dissociation of $Al_4H_{-4}L_5$ to $Al_4H_{-5}L_5$ is -5.2 ($x = 4$)

or -4.9 ($x = 5$), which is in qualitative agreement with dissociation from the *p*-quinomethide-2-carboxylic acid group (-4.43). The $\log K$ value for dissociation of $Al_4H_{-3}L_5$ to $Al_4H_{-4}L_5$ (-3.84 ; $x = 4$) is indicative of a different reaction. It is postulated that this reaction involves two concerted processes, the interchange of binding sites at one terminal ligand (from quinomethide-2-carboxylate coordination to salicylate coordination) coupled with the deprotonation of the phenolate group, which is then coordinated.

The decrease in the ligand protonation constants ($\log \beta_{0,n,1}$) with ionic strength (Table 1) can be compared with calculated values for simple inorganic acids, assuming that the K^+ interaction is the same for all conjugate bases of the same charge. The appropriate deprotonation constants of H_2SO_4 , H_3PO_4 and H_3AsO_4 for 0.10 m and 0.61 m KCl were calculated using the individual ion form of the Pitzer equation.¹¹ The comparison gave good agreement for the dissociation of HSO_4^- ($\Delta = 0.13$; *cf* 0.16 ± 0.08 for $\log K_3$) and $H_2PO_4^-$ ($\Delta = 0.10$), but poor agreement for $H_2AsO_4^-$ ($\Delta = 0.03$). Deprotonation data of HPO_4^{2-} ($\Delta = 0.25$) and $HAsO_4^{2-}$ ($\Delta = 0.26$) gave good agreement with $\log K_2$ ($\Delta = 0.21 \pm 0.03$), and were lower than the value for $\log K_1$ ($\Delta = 0.40 \pm 0.07$). The latter deprotonation involves a tetravalent conjugate base.

The values of Δ for CAS increase with successive deprotonations and are generally similar to those for the above simple inorganic acids. Despite the size of the CAS molecule leading to significant spatial separation of the charged groups, this appears not to mask coulombic interactions with other ions (accounted for by the Debye-Hückel term of the Pitzer equation). According to the Pitzer model,²⁶ these interactions are still very important at the ionic strengths used in the present study.

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