

Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 7. Redox, Hydrolysis and Complexation Equilibria in the System Al^{3+} -1,2-Naphthoquinone-4-sulfonate/1,2-Dihydroxy-naphthalene-4-sulfonate- OH^- . A Potentiometric Study in 0.6 M Na(Cl)

LARS-OLOF ÖHMAN, STAFFAN SJÖBERG and NILS INGRI

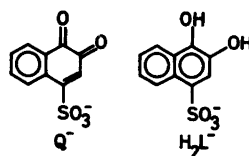
Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

Equilibria between aluminium(III) and 1,2-naphthoquinone-4-sulfonate (Q^-), aluminium(III), 1,2-dihydroxynaphthalene-4-sulfonate (H_2L^-) and OH^- as well as redox equilibria between the two organic substances were studied in 0.6 M Na(Cl) medium at 25 °C in the 1–10 mM, the 9.5–6.8 $-\lg\{e^-\}$ and the 1.5–9 $-\lg[\text{H}^+]$ ranges. The measurements were performed as emf titrations (glass and platinum electrodes) in which H_2L^- was generated coulometrically from Q^- by means of an integrating potentiostat. In the Al^{3+} - Q^- system no stable complexes were found. In the Al^{3+} - H_2L^- - OH^- system data could be explained with the complexes AlL_2^0 , $\text{Al}(\text{OH})\text{L}^-$, AlL_2^{3-} , $\text{Al}(\text{OH})\text{L}_2^{4-}$ and AlL_3^{6-} . Apart from these complexes, it was also possible to determine the stability constant for the aluminate ion, $\text{Al}(\text{OH})_4^-$. The redox reaction between Q^- and H_2L^- was found to be $\text{Q}^- + 2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2\text{L}^-$ for $-\lg[\text{H}^+] \leq 4.5$, while, at higher $-\lg[\text{H}^+]$, Q^- seems to decompose irreversibly. A full compilation of experimental results with equilibrium constants and corresponding standard deviations are given in Table 1. Data were analyzed with the least-squares computer program LETAGROPVRID.

In a current project at this department, the ability of Si(IV) and Al(III) to form aqueous complexes with ligand types occurring in natural waters, is being studied. In the Al^{3+} - OH^- -gallic acid system¹ it was found that strong complexes were

formed between Al^{3+} and two phenolic groups in *ortho*-position. In a natural water containing oxidizing agents, this type of ligand originating from lignin degradation, will always, at least partially, be oxidized to the corresponding *ortho*-diquinone. Indirect proofs have also been given that these types of organic compounds could act as ligands toward metal ions.² We have found it interesting to determine whether or not this is the case for Al(III). In the search for a suitable *o*-diphenolic/*o*-diquinonic redox couple³ it was found necessary to choose an *o*-dihydroxynaphthalenic/*o*-naphthoquinonic system as the quinonic state of the simple phenolics (e.g. pyrocatechol, gallic acid) is not stable but polymerizes irreversibly to some kind of synthetic humic acid.⁴

A suitable choice for the present investigation seems to be the compounds $\text{Q}^-/\text{H}_2\text{L}^-$ (structures given in Scheme 1), a couple whose redox and acid-base properties have been found to be reversible in earlier investigations.^{3,5}



Scheme 1.

EXPERIMENTAL

Chemicals and analysis. Potassium 1,2-naphthoquinone-4-sulfonate (KQ) was synthesized and purified according to Fieser⁶ from 1-amino-2-naphthol-4-sulfonic acid (Merck p.a.). As it was found that aqueous solutions of Q⁻ deteriorated on standing, fresh solutions prepared from the solid were always used in the measurements. The content of Q⁻ was determined potentiometrically using the Gran extrapolation method⁷ after reduction of Q⁻ to 1,2-dihydroxynaphthalene-4-sulfonate (H₂L⁻). The titrated amount was somewhat lower than that expected from the weighed amount (0.8 %) and was assumed to be correct.

Stock solution of sodium chloride and aluminium chloride as well as the dilute hydrochloric acid and sodium hydroxide solutions were prepared and standardized as described earlier.¹

Apparatus. The automatic system for precise emf titrations, the thermostat and the glass, hydrogen and Ag/AgCl electrodes were described in Ref. 1. The platinum electrodes were cleaned in boiling aqua regia, rinsed in distilled water and heated in an ethanol flame before use. The reduction of Q⁻ to H₂L⁻ was performed coulometrically at +240 mV vs. NHE with an integrating potentiostat, built at our department.

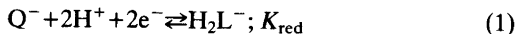
Special precautions. Since the system under study is extremely redox active it is necessary to perform the experiments in an inert environment. We have taken the same precautions as in Ref. 1 and in addition to these, performed the experiments in dark coloured vessels.

METHOD

The present study was carried out as a series of titrations at 25 °C in a constant ionic medium of 0.6 M NaCl. The free H⁺ concentration, *h*, and the (hypothetical) electron activity, {e⁻}, were determined by measuring the emf of the cell -RE// equilibrium solution/ME+, where ME denotes a glass or platinum electrode and RE=Ag, AgCl/0.6 M NaCl. -lg *h* is in this cell given by the expression -lg *h*=(*E*_{o,gl}+*E*_j-*E*_{gl})(59.157)⁻¹ where *E*_{o,gl} is a constant which was determined in each titration where complex formation could be neglected. -lg {e⁻} is defined as (*E*_H)(59.157)⁻¹ where *E*_H=*E*_{o,Pt}+*E*_j-*E*_{Pt}. *E*_{o,Pt} was determined separately by measuring the emf between the reference electrode and NHE(*E*_{NHE}≡0). *E*_{o,Pt} was found to be -250.5 mV, i.e. *E*_{RE}= +250.5 mV vs NHE. The liquid junction potential, *E*_j, could

in 0.6 M NaCl) be written⁸ *E*_j= -77*h*+42*k_w**h*⁻¹, where *k_w*=1.875 · 10⁻¹⁴ M² is the ionic product of water. According to the different types of equilibria which must be considered, the present study can be divided into parts as follows:

(i) redox and acid-base equilibria of Q⁻/H₂L⁻. The reduction of Q⁻ can be written

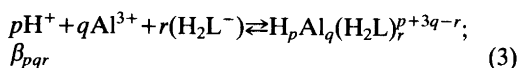


in acid solution. Knowing the total amount of Q⁻, generating a known amount of H₂L⁻ and measuring -lg *h* and -lg {e⁻} the equilibrium constant could be determined. 8 titrations with 64 experimental points within the ranges 0.001 M ≤ *C*+*D* ≤ 0.010 M; 0.025 ≤ *D*/*C* ≤ 20 were performed. (*C* and *D* stand for the total concentration of H₂L⁻ and Q⁻, respectively.) After complete reduction to H₂L⁻, -lg *h* was increased gradually by means of a coulometer in order to study the equilibrium



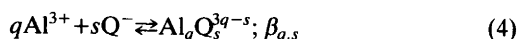
These experiments comprise 5 titrations with 103 experimental points within the concentration range 0.001–0.01 M. No attempts were made to evaluate the second acidity constant of H₂L⁻, as this would require such a high -lg *h* that the glass electrode would yield inaccurate values (-lg *k*₂~12.7).⁵ The redox behaviour at higher -lg *h* was studied by adding OH⁻ solution to Q⁻/H₂L⁻ buffers.

(ii) Three component equilibria in the system H⁺-Al³⁺-H₂L⁻ of the general form



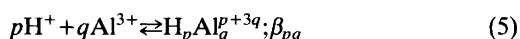
The system was investigated through 11 titrations with 504 experimental points where OH⁻ was generated coulometrically after complete reduction of Q⁻ to H₂L⁻. The ranges 1.5 ≤ -lg *h* ≤ 9; 0.0005 M ≤ *B* ≤ 0.004 M and 0.002 M ≤ *C* ≤ 0.009 M with the *C*/*B* ratios 15, 10, 7.5, 5, 2.5, 2.25 and 2 were covered. (*B* stands for the total concentration of Al³⁺.)

(iii) Two component equilibria in the system Al³⁺-Q⁻ of the general form



With knowledge of equilibria under (i) and (ii), it is possible to perform two types of potentiometric experiments in order to investigate this system: (I) By increasing $-\lg h$ with OH^- solution in an Al^{3+} , H_2L^- solution containing different amounts of Q^- . Two titrations ($B=0.001$ M; $C=0.005$ M; $D=0.005$ M and 0.02 M, respectively) were performed. (II) By studying changes in $-\lg \{e^-\}$ when Al^{3+} solution is added to a $\text{Q}^-/\text{H}_2\text{L}^-$ buffer at constant and low $-\lg h$ (no $\text{Al}-\text{H}_2\text{L}$ complexes present). One titration with $0 \leq B/D \leq 17$ was performed.

Apart from these equilibria, the hydrolysis of Al^{3+} :



have to be considered under (ii) and (iii). In Part 3 of this series,⁹ the complexes AlOH^{2+} ($\lg \beta_{-1,1} = -5.52$), $\text{Al}_3(\text{OH})_4^{5+}$ ($\lg \beta_{-4,3} = -13.57$) and $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ ($\lg \beta_{-32,13} = -109.2$) were found to explain the hydrolysis for $-\lg h \leq 4.2$. In neutral solution, small amounts of $\text{Al}(\text{OH})_2^+$ and eventually (*cf.* May *et. al.*¹⁰) $\text{Al}(\text{OH})_3^0$ occurs. Finally, in alkaline solution, the dominating species is $\text{Al}(\text{OH})_4^-$. Formation constants proposed by Baes and Mesmer¹¹ (recalculated to be valid in 0.6 M medium) are $\lg \beta_{-2,1} = -10.3$; $\lg \beta_{-3,1} = -16.1$ and $\lg \beta_{-4,1} = -23.7$, respectively.

Data treatment. In the evaluation of the experimental data, we have used standard graphical methods as well as least squares computer calculations (LETAGROPVRID,¹² version ETITR^{13,14}). As "best" model or models we will consider those giving the lowest error squares sum $U = \sum (H_{\text{calc}} - H_{\text{exp}})^2$. The LETAGROP calculations also give standard deviations $\sigma(H)$, $\sigma(\beta)$ and $3\sigma(\lg \beta)$, calculated and defined according to Sillén.^{15,16} The computations were performed on a CYBER 172 computer.

DATA, CALCULATIONS AND RESULTS

Redox and acid-base equilibria of $\text{Q}^-/\text{H}_2\text{L}^-$. Some of the data used to evaluate the redox equilibrium constant K_{red} (eqn. (1)) are illustrated in Fig. 1. A least-squares adjustment of the data gave $\lg(K_{\text{red}} \pm 3\sigma) = 21.27 \pm 0.09$ ($E^0 = 629 \pm 2.7$ mV).

The study of redox behaviour at higher $-\lg h$ showed that eqn. (1) could explain data for $-\lg$

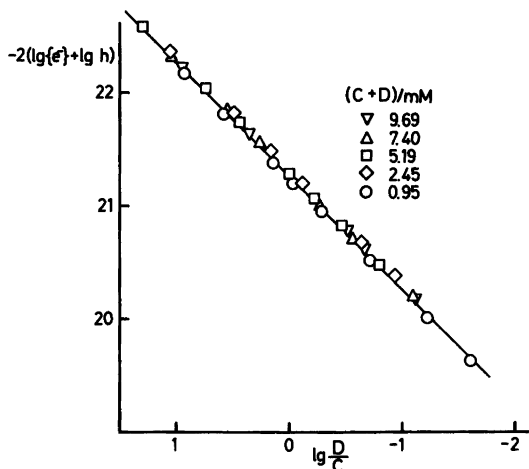


Fig. 1. A part of experimental data used to evaluate the redox equilibrium constant K_{red} . The figure visualizes the validity in the assumption of equilibrium reaction (eqn. (1)) as all the data points can be described by the expression $-2(\lg \{e^-\} + \lg h) = \lg K_{\text{red}} + \lg (D/C)$. The full curve has been calculated using the proposed constant $\lg K_{\text{red}} = 21.27$.

$h \leq 4.5$. At higher $-\lg h$, the colour of the solutions slowly changed from bright yellow to reddish-brown in connection with a release of protons. Even after 24 h no stable potential could be obtained and, upon standing, a precipitate was formed. This behaviour must be explained by a degradation of Q^- as the same result was obtained with a pure Q^- solution while a pure H_2L^- solution gave stable potentials in this range.

The evaluation of the first acidity constant of H_2L^- (eqn. (2)) was performed as a LETAGROP calculation. The analysis ended at $\sigma(H) = 0.02$ mM giving $\lg(k_1 \pm 3\sigma) = -7.798 \pm 0.002$.

These results will be considered as known in all the following calculations and no attempt will be made to adjust these equilibrium constants.

The $\text{H}^+ - \text{Al}^{3+} - \text{H}_2\text{L}^-$ system. In order to visualize the experimental results, data sets $Z_c(-\lg h)$ were calculated and some of them are given in Fig. 2. Z_c is defined as the average number of OH^- reacted per C and is given by the relation $Z_c = (h - H - k_w h^{-1})/C$ where H denotes the total concentration of protons calculated over

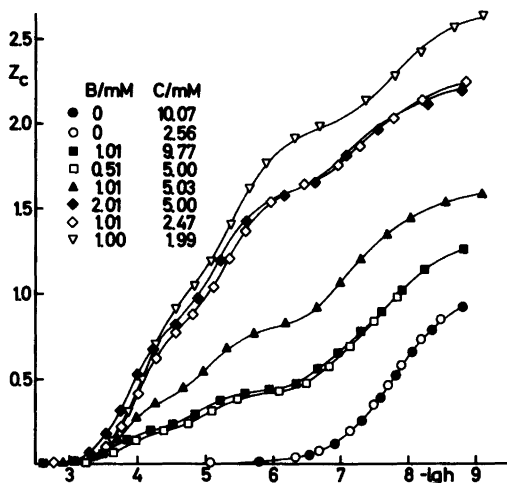


Fig. 2. A part of the experimental data in the system $H^+ - Al^{3+} - H_2L^-$ plotted as curves $Z_c(-\lg h)$ for C/B ratios 2, 2.5, 5, 10 and ∞ . The full curves have been calculated using the set of proposed constants in Table 1.

the zero level H_2O , Al^{3+} , H_2L^- . In addition, the Bjerrum plot $\bar{n}(\lg[L^{3-}])$, where \bar{n} denotes the average number of L^{3-} coordinated per Al^{3+} , was constructed (Fig. 3).

From this latter figure it could be concluded

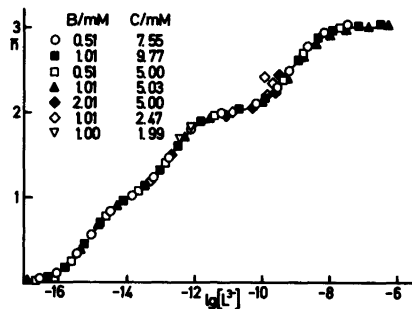


Fig. 3. Experimental data in the system $H^+ - Al^{3+} - H_2L^-$ plotted as curves $\bar{n}(\lg [L^{3-}])$ for C/B ratios 2, 2.5, 5, 10 and 15. In the calculation, the value $\lg k_2 = -12.66$, obtained for the second acidity constant of H_2L^- by Buffle and Martell,⁵ has been used. The chosen value affects the scale on the x-axis but not the shape of the \bar{n} curves. For ratio 2 and 2.5, the experimental data fulfilling the condition $Z_c > 2$ have not been possible to visualize with this function.

that the main complexes in the system are AlL^0 , AlL_2^{3-} and AlL_3^{6-} . There are, however, deviations and the fact that Z_c passes 2 at low C/B quotients (Fig. 2) makes it obvious that some hydrolytic ($Al(OH)_4^-$) or ternary hydroxo species are formed in appreciable amounts.

The assumption of three mononuclear complexes at high quotients (5–15) was confirmed by a LETAGROP calculation. The analysis ended at $\sigma(H) = 0.02$ mM giving $\lg \beta_{-2,1,1} = -5.34 \pm 0.01$; $\lg \beta_{-4,1,2} = -13.12 \pm 0.02$ and $\lg \beta_{-6,1,3} = -24.48 \pm 0.02$ (p, q, r notations according to eqn. (3)). Applying these species to the titrations at lower quotients (upper part of Fig. 4) showed that minor systematic deviations remained. (In this calculation, the Al^{3+} hydrolytic species with formation constants given earlier were included). As the deviations showed two well-separated broad peaks divided at $-\lg h \sim 6$, we decided to test the simple hypothesis that each peak could be explained by a single complex $H_p Al_q (H_2L)_r^{+3q-r}$. The search for composition and equilibrium constants for these complexes was performed as pqr -analyses (systematic testing of pqr combinations) using the LETAGROP-VRID program.

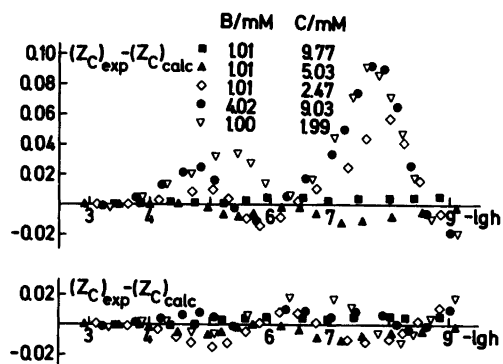


Fig. 4. Residual plots $\Delta Z_c(-\lg h)$ for the system $H^+ - Al^{3+} - H_2L^-$. The upper part of this figure shows the residuals obtained when aluminium(III) hydrolysis with equilibrium constants given under "METHOD" and the complexes $(-2,1,1)$: $\lg \beta_{-2,1,1} = -5.34$; $(-4,1,2)$: $\lg \beta_{-4,1,2} = -13.12$ and $(-6,1,3)$: $\lg \beta_{-6,1,3} = -24.48$ are applied. The lower part of the figure shows the same quantity when the final model with equilibrium constants given in Table 1 are applied.

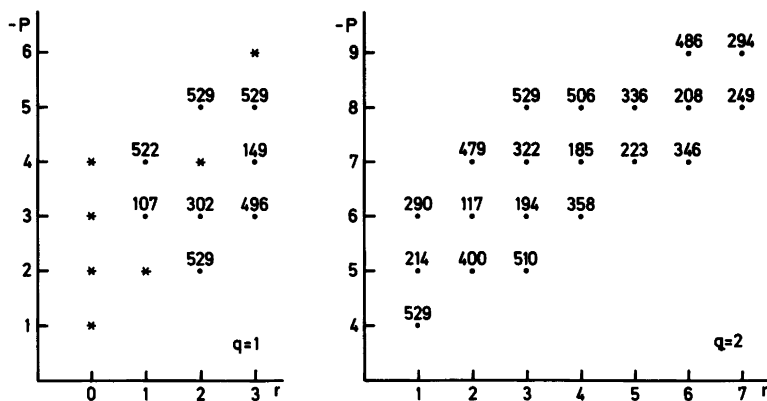


Fig. 5. Result of the first pqr -analysis concerning the acid ($-\lg h \leq 6$) peak in the system $H^+ - Al^{3+} - H_2L^-$. The diagrams give the error squares sums $U_H(pr)_q \cdot 10^3$ assuming one new complex. In the calculations, aluminium hydrolysis and $(-2,1,1)$, $(-4,1,2)$ and $(-6,1,3)$ (marked in the left diagram with asterisks) have been assumed to be known. The calculations are based on 117 points giving $U_H(00)_0 = 529 \cdot 10^{-3}$.

The result of the first analysis, performed on the acid peak, is given in Fig. 5 and it was found that the lowest value of U was obtained for the complex $H_{-3}Al(H_2L)^-$ with $\lg \beta_{-3,1,1} = -11.19 \pm 0.07$. The alkaline peak was, in the same manner, best explained with the complex $H_{-5}Al(H_2L)_2^{4-}$; $\lg \beta_{-5,1,2} = -21.12 \pm 0.08$ (Fig. 6).

Model calculations, performed with the computer program SOLGASWATER,¹⁷ had shown

that significant amounts of $Al(OH)_4^-$ were formed at the lowest quotients. In the final LETAGROP calculation on the whole data material, the formation constant for this species, as well as the equilibrium constants for all three component complexes found above, were refined. This calculation, which provides the final proposed model and corresponding equilibrium constants for the system, is presented in Table 1.

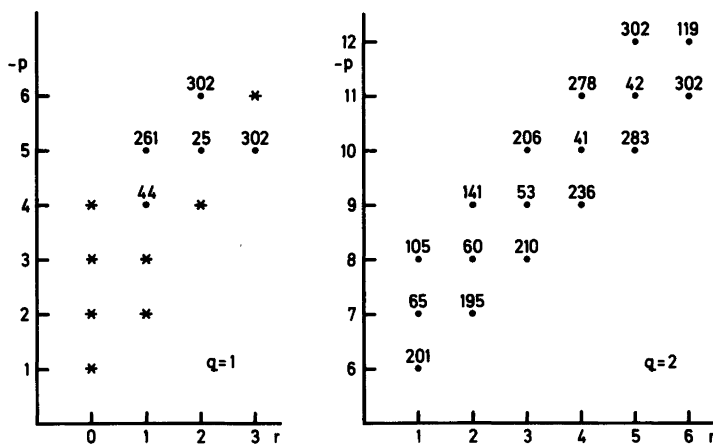


Fig. 6. Result of the second pqr -analysis on the alkaline ($-\lg h \geq 6$) peak in the system $H^+ - Al^{3+} - H_2L^-$. The complex $H_{-3}Al(H_2L)^-$ has, in addition to those complexes mentioned in the first pqr -analysis, been assumed to be known and the diagrams give $U_H(pr)_q \cdot 10^2$ assuming one new complex. The calculations are based on 49 points giving $U_H(00)_0 = 302 \cdot 10^{-2}$.

Table 1. A compilation of final results. Q^- stands for 1,2-dinaphthoquinone-4-sulfonate and H_2L^- stands for 1,2-dihydroxynaphthalene-4-sulfonate.

System	No. of titr./ No. of points	Equilibrium reaction	Tentative formula	$\lg(\beta \pm 3\sigma)$
$e^- - H^+ - Q^-$	8/64	$Q^- + 2H^+ + 2e^- \rightleftharpoons H_2L^-$ for $-\lg h \leq 4.5$ Q^- decomposes at $-\lg h \geq 4.5$		21.27 ± 0.09
$H^+ - Al^{3+} - H_2L^-$	5/103 11/504	$pH^+ + qAl^{3+} + r(H_2L^-) \rightleftharpoons H_pAl_q(H_2L)_r^{3q-r}$ $p, q, r: -1, 0, 1$ -4, 1, 0 -2, 1, 1 -3, 1, 1 -4, 1, 2 -5, 1, 2 -6, 1, 3	HL^{2-} $Al(OH)_4^-$ AlL^0 $Al(OH)L^-$ AlL_2^{3-} $Al(OH)L_2^{4-}$ AlL_3^{6-}	-7.798 ± 0.002 -23.46 ± 0.11 -5.343 ± 0.006 -11.24 ± 0.08 -13.115 ± 0.009 -21.15 ± 0.04 -24.47 ± 0.02
$Al^{3+} - Q^-$	3/41	$qAl^{3+} + sQ^- \rightleftharpoons Al_qQ_s^{3q-s}$ No stable complexes are formed		

The analysis ended at $\sigma(H) = 0.03$ mM, indicating a good fit, and from the lower part of Fig. 4 it is clear that no systematic deviations remain.

The $Al^{3+} - Q^-$ system. The two experimental procedures to investigate this system are described under "METHOD". In procedure I,

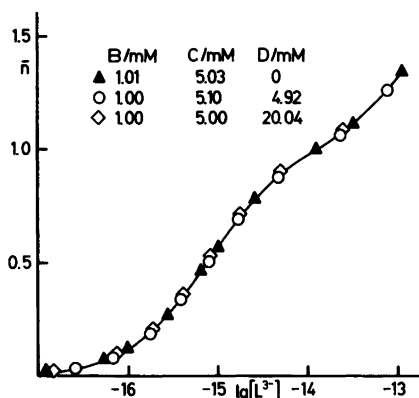


Fig. 7. $\bar{n}(\lg [L^{3-}])$ curves for the system $H^+ - Al^{3+} - H_2L^-$ in the presence of different amounts of Q^- . The full curve has been calculated with the set of proposed constants given in Table 1 and the figure indicates that the amount of Q^- is quite insignificant to the complex formation between Al^{3+} and H_2L^- . Thus the figure indicates that no complexes between Al^{3+} and Q^- are formed.

where Q^- competes with H_2L^- for Al^{3+} , the occurrence of a complex $Al_qQ_s^{3q-s}$ would lower \bar{n} (the average number of L^{3-} coordinated per Al^{3+}) at a given $-\lg [L^{3-}]$. The experimental results are shown in Fig. 7 and indicate no such tendencies. In procedure II, a complex $Al_qQ_s^{3q-s}$ would lower the free Q^- concentration and consequently (eqn. (1)) cause a decrease in $-\lg \{e^-\}$. As seen in Fig. 8, neither does this experiment indicate the existence of any complex between Al^{3+} and Q^- . (It could be mentioned that a satisfactory check of the validity of this latter procedure was obtained in procedure I, where H_2L^- was bound to Al^{3+} .)

On the basis of these two types of experiments, we find it credible to conclude that Al^{3+} does not form stable complexes with Q^- .

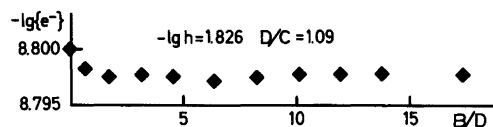


Fig. 8. The figure shows that $-\lg \{e^-\}$ is unaffected when aluminium(III) solution is added to a Q^-/H_2L^- buffer at low $-\lg h$ where no $Al^{3+} - H_2L^-$ complexes are formed (cf. Fig. 2), thus again indicating the absence of any complex $Al_qQ_s^{3q-s}$.

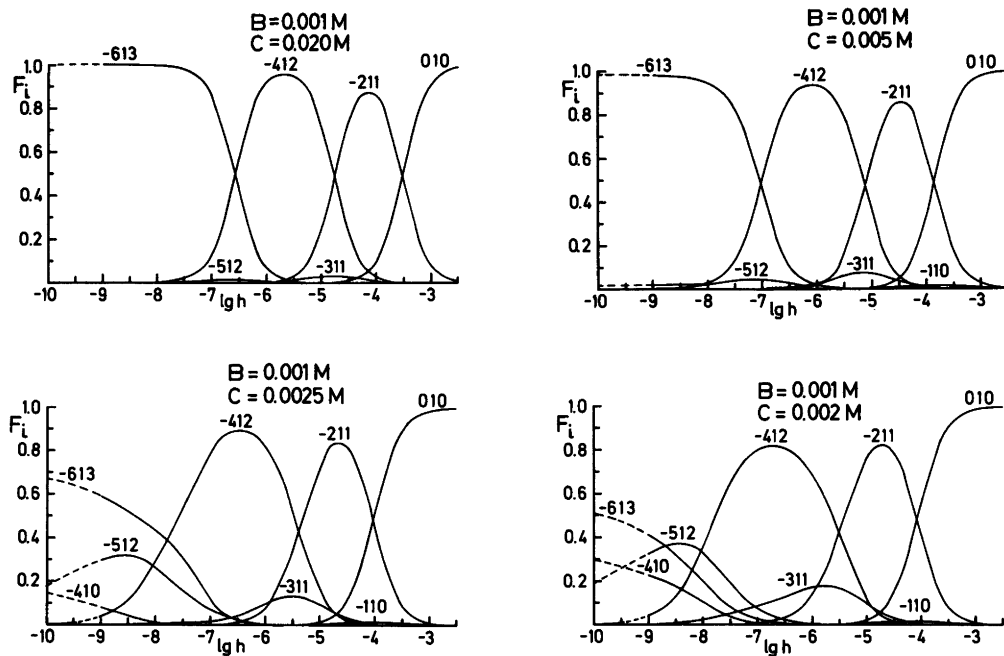


Fig. 9. Distribution diagrams $F_i(\lg h)_{B,C}$ in the system $H^+ - Al^{3+} - H_2L^-$. F_i is defined as the ratio between aluminium(III) in a species and total aluminium(III). The calculations have been performed using the computer program SOLGASWATER¹⁷ with constants given in Table 1. Broken lines in the figures denote ranges where no measurements have been performed.

DISCUSSION

The main purpose of the present study was to investigate whether complexes are formed between aluminium(III) and *o*-diquinones. As a model system, we chose the system $Al^{3+} - 1,2$ -naphthoquinone-4-sulfonate(Q^-) and found, on the basis of two independent types of potentiometric experiments, that no stable complexes were formed. We believe that this is a general observation and that it could be concluded that *o*-diquinones do not complexate aluminium(III) in any appreciable amount. Thinking in terms of soft and hard acids and bases,¹⁸ the result is in no way surprising, but our investigation has provided the experimental proof.

Concerning complex formation between Al^{3+} and the reduced state of the *o*-dinaphthoquinone, *i.e.* 1,2-dihydroxynaphthalene-4-sulfonate (H_2L^-), the study has given evidence for the formation of a main series of complexes $(-2,1,1)$, $(-4,1,2)^{3-}$, $(-6,1,3)^{6-}$ together with two hydrolyzed species $(-3,1,1)^-$ and

$(-5,1,2)^{4-}$. The amounts of the different species are illustrated in Fig. 9. It must be pointed out that although the species $(-3,1,1)^-$ gave the closest fit on the acid peak, an almost equal low error squares sum was obtained for the dimer of this complex, $(-6,2,2)^{2-}$. It is possible that these two species actually co-exist in solution, although we have no possibility to analyse this on the present data material. Regarding the other species, the fact that these are formed in great amounts (Fig. 9) and that the standard deviations of the equilibrium constants are low, (Table 1) makes it possible to consider these as well determined.

Although an emf investigation gives no structural information but merely gross compositions and formation constants of the species formed, we find it most credible that the species in the main series formed are chelates between Al^{3+} and the two orthocoordinated phenolic groups on the naphthalene and that these species could be written AlL_n^{3-3n} , $n=1,2,3$. As the ligand only

offers two hydrolyzable protons, we also conclude that the species $(-3,1,1)$ and $(-5,1,2)$ are hydroxo complexes and could be written $\text{Al}(\text{OH})\text{L}^-$ and $\text{Al}(\text{OH})\text{L}_2^{4-}$ respectively.

The formation constant for the aluminate ion, $\text{Al}(\text{OH})_4^-$, has hitherto mainly been determined indirectly, by measurements of the solubility of $\text{Al}(\text{OH})_3(\text{s})$ in alkaline solution. Baes and Mesmer¹¹ have discussed experimental difficulties and uncertainties with this method and estimate one standard deviation in the formation constant to be 0.3 logarithmic units. A revision of the constant with 0.24 log units therefore seems by no means unrealistic, especially since the complex is formed in considerable amounts in some of the experiments (Fig. 9). The fact that the resultant standard deviation is moderate ($3\sigma(\lg\beta)=0.11$), (Table 1) also gives support for this revision.

The reduction of Q^- to H_2L^- is a two-electron, two-proton transfer reaction. The relatively large standard deviation obtained in the equilibrium constant ($3\sigma(\lg K_{\text{red}})=0.09$) (Table 1) seems to depend upon a variation in $E_{\text{o,Pt}}$ between the titrations. It was found that the standard deviations were an order of magnitude lower within single titrations. As $E_{\text{o,Pt}}$ had to be determined separately and indirectly, the phenomenon is, however, beyond our control.

The results found in this acid area are in accordance with those found by Buffle *et al.*⁵ On the other hand, while we have found that Q^- decomposes irreversibly in neutral and alkaline solution, they claim that the reversibility holds to at least $-\lg h=10$ and that at higher $-\lg h$ a semiquinone is formed. We believe that this difference in results could be explained by the different experimental procedures used. As their experiments lasted only a few minutes it is most probable that they had a negligible decomposition of Q^- during that time.

As pointed out in Part I of this series, the occurrence of organic ligands in a natural water could change the speciation and significantly increase the solubility of Al-containing minerals. It was shown that with a total concentration of gallic acid equal to 30 μM , the solubility of the clay mineral kaolinite was increased by an average factor of 5 with respect to Al in the pH-region 5–9. (When we renewed this calculation, using the revised formation constant for $\text{Al}(\text{OH})_4^-$, the Part 3⁹ hydrolysis model and literature values for

$\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_3$, the average increase factor became 3.4.) In the present study we have confirmed the powerful complexing ability of two *ortho*-coordinated phenolic groups (an analogous calculation as above, ended at an average increase in Al-solubility of 4.8) and in addition, showed that the corresponding oxidized compounds, *i.e.* *o*-diquinones, do not form any stable complexes with Al(III).

Acknowledgements. The English of the present paper has been corrected by Dr. Michael Sharp. The work forms part of a program financially supported by the Swedish Natural Science Research Council.

REFERENCES

1. Öhman, L.-O. and Sjöberg, S. *Acta Chem. Scand. A* 35 (1981) 201.
2. Rashid, M. A. *Chem. Geol.* 9 (1972) 241.
3. Clark, W. M. *Oxidation-Reduction Potentials of Organic Systems*, Williams & Wilkins, Baltimore 1960, p. 373.
4. Gieseking, J. E., Ed., *Soil. Components, Vol. 1, Organic Components*, Springer, New York 1975.
5. Buffle, J. and Martell, A. E. *Inorg. Chem.* 16 (1977) 2221.
6. Fieser, L. F. *Org. Synth.* 21 (1941) 91.
7. Gran, C. *Acta Chem. Scand.* 4 (1950) 559.
8. Sjöberg, S., Nordin, A. and Ingri, N. *Mar. Chem.* 10 (1981) 521.
9. Öhman, L.-O. and Forsling, W. *Acta Chem. Scand. A* 35 (1981) 795.
10. May, H. M., Helmke, P. A. and Jackson, M. L. *Geochim. Cosmochim. Acta* 43 (1979) 861.
11. Baes, C. F. and Mesmer, R. E. *The Hydrolysis of Cations*, Wiley, New York 1976, p. 112.
12. Ingri, N. and Sillén, L. G. *Ark. Kemi* 23 (1964) 97.
13. Arnek, R., Sillén, L. G. and Wahlberg, O. *Ark. Kemi* 31 (1969) 353.
14. Brauner, P., Sillén, L. G. and Whiteker, R. *Ark. Kemi* 31 (1969) 365.
15. Sillén, L. G. *Acta Chem. Scand.* 16 (1962) 159.
16. Sillén, L. G. and Warnqvist, B. *Ark. Kemi* 31 (1969) 341.
17. Eriksson, G. *Anal. Chim. Acta* 112 (1979) 375.
18. Ahrland, S., Chatt, S. J. and Davis, W. R. *Quart. Rev.* 12 (1958) 265.

Received December 7, 1982.