

# Polarography of aluminium(III) in the presence of complexing agents

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The work is comparing the polarographic behaviour of the aquoaluminium ion with that of other complexes of aluminium(III) in aqueous solution. Fluoride, tartrate, and citrate were used as complexing anions. The character of  $i-E$  curves, as well as the nature of polarographic limiting currents and half-wave potential changes dependent on the ligand concentration, complex concentration, and pH were followed.

The electrode reaction proper of aluminium(III) ion in aqueous solution is not in fact a reduction of Al(III) to metal but a reduction of three protons of the hexaquoaluminium ion [1]



Aluminium hydroxide which is formed as a product of this reaction influences catalytically the electrode process.

In the concentration range where the solubility product of aluminium hydroxide is reached, the electrode surface is covered by a compact film of precipitate which, on the other hand, has a hindering effect on the electrode process. These contradictory factors are considered to be the cause of differences between the reduction of protons of hexaquoaluminium ion and of weak acids [2]. The different behaviour is demonstrated by maxima in certain concentration ranges, the autocatalytic character of the wave (steep increase of current at the foot of the wave) and irregularities on the  $i-t$  curves.

The mentioned factors make the study of electroreduction of aluminium in aqueous solution as well as employing of the aluminium polarographic wave for analytical purposes difficult. In addition, an interference of protons occurs in solvents of low pH values while the increasing of pH values leads to hydrolysis of aluminium salts [3-6]. Therefore, very accurate experimental conditions must be kept at the polarographic analysis of aluminium.

The complexing agents form the corresponding complexes instead of aquo complex. The mechanism of the electrode process is different; maxima as well as the autocatalytic character of the wave disappear.

## Experimental

A Radelkis polarograph OH-102 was used for the registration of  $i-E$  curves. A Kaloušek vessel was applied as a working cell. All potentials are given *vs.* saturated calomel electrode at room temperature. In order to remove oxygen, purified nitrogen was passed through the cell for 5 minutes. The characteristics of the dropping mercury electrode (DME) were as follows: mercury reservoir height 50 cm, drop time 3.5 s, flow rate 2.4 mg s<sup>-1</sup>. The pH values were measured by an LP compensation pH meter PHK 1. The glass electrode was calibrated with phthalate and phosphate buffers (pH 4.0 and 6.64, respectively). The pH values were adjusted with 0.001 M analytical grade hydrochloric acid.

0.1 M-LiCl was used as a supporting electrolyte. Anal. grade commercial product had to be recrystallized from ethanol and carefully dried in an oven with gradually increasing temperature up to 120°C. Recrystallized KAl(SO<sub>4</sub>)<sub>2</sub> · 12H<sub>2</sub>O was used as aluminium salt. Complexing agents were treated as follows: sodium fluoride and sodium citrate were recrystallized from ethanol and water mixture 2 : 1 and potassium tartrate from the same mixture 1 : 1.

## Results

### *Polarographic behaviour of aquoaluminium ion*

The concentration dependence of the hexaquoaluminium ion was followed in the range 10<sup>-5</sup>–10<sup>-3</sup> M-Al(III). A measurable wave appears at a concentration of 4 × 10<sup>-5</sup> M-Al(III). With increasing depolarizer concentration the wave gets deformed by maxima and the Ilkovič equation for the diffusion controlled limiting current is not met in the whole concentration range. The first maximum appears at a concentration of 6 × 10<sup>-5</sup> M-Al(III), the second one (on the limiting current) at a concentration of 2 × 10<sup>-4</sup> M-Al(III). Both maxima disappear at a concentration of 10<sup>-3</sup> M-Al(III) and the wave shows its usual form. These phenomena make the wave height and the half-wave potential evaluation difficult in the mentioned concentration range.

In accordance with the earlier observations [2] the Al(III) wave shifts negatively with increasing depolarizer and protons concentration.

The limiting current intensity increases with decreasing pH value. Simultaneously, the maximum II is formed and gets higher as the current increases. In a solution, where no H<sup>+</sup> ions were added, the maximum appears only at much higher depolarizer concentrations.

With decreasing pH values the autocatalytic character of the wave diminishes. At the same time a new negative wave appears which shifts cathodically as the mercury reservoir height decreases.

### *Polarographic behaviour of aluminium(III) ion in the presence of complexing agents*

In the presence of anions forming with Al(III) more stable complexes than water, *e.g.* fluoride, citrate, and tartrate (further referred to as complexing agents) the autocatalytic character of the wave and maxima disappear and the wave obtains its usual shape (Fig. 1).

No changes can be observed in the wave when only half the equivalent of fluoride is added to the aquoaluminium ion. The wave height decreases moderately up to two equivalents of fluoride (Fig. 2). The maximum I is still clearly visible, but disappears at 4 equivalents of fluoride. From 3–6 equivalents of fluoride the wave height again

increases slowly. At 4 equivalents the autocatalytic character disappears, the wave becomes well defined and measurable.

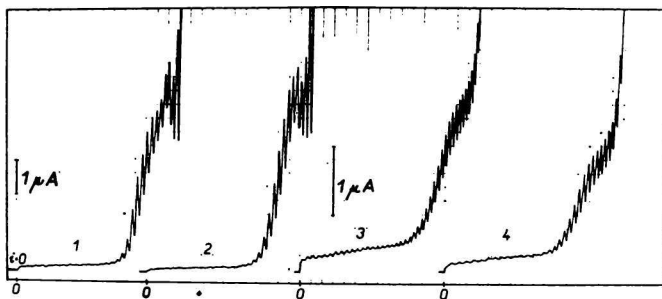


Fig. 1. The waves of aluminium ion reduction in the presence of complexing agents. 1. aquo complex; 2. fluoride complex 1 : 2; 3. tartrate complex 1 : 3; 4. citrate complex 1 : 3.

Sensitivity: 1. and 2.  $8 \times 10^{-8}$  A/div.; 3. and 4.  $4 \times 10^{-8}$  A/div.

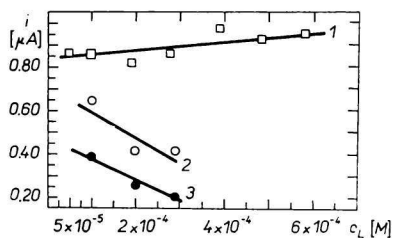
Concentration of Al(III):  $5 \times 10^{-4}$  M, supporting electrolyte 0.1 M-LiCl, 100 mV/absc.

When one equivalent of tartrate is added to the aquoaluminium ions, the maximum  $I$  cannot be observed but the autocatalysis still remains and disappears only by adding two equivalents of tartrate. However, at low Al(III) concentration ( $10^{-4}$  M) and aluminium to tartrate ratio 1 : 1 the wave is drawn out and poorly measurable. The limiting current merges with the cathodic reduction of the supporting electrolyte. The wave height decreases after adding one equivalent of tartrate approximately to three quarters of the wave height of aquo complex. If adding 2 and 3 equivalents it drops to one half (Fig. 2).

Fig. 2. The changes of the limiting current intensity values for various aluminium complexes with the complexing agents concentration.

1. fluoride; 2. tartrate; 3. citrate.

Concentration of Al(III):  $10^{-4}$  M.



The best defined wave in the presence of citrate appears after addition of equivalent amount of the complexing agent (for  $10^{-4}$  M-Al(III) concentration). Neither maximum nor autocatalytic character is present. With increasing concentration of citrate the wave becomes poorly evaluable for the same reasons as in the case of tartrate. The possibility of evaluation improves at higher concentrations of aluminium. The wave height decreases after addition of equivalent amount of citrate as much as to one half as compared with the wave height of aquo or fluoride complex.

Thus, with the complexing agent concentration increase in the case of tartrate and citrate the limiting current intensity decreases while in the case of fluoride it remains roughly unchanged.

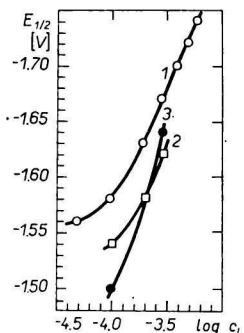


Fig. 3. The changes of the  $E_{1/2}$  values for various aluminium complexes with the complexing agents concentrations.

1. fluoride; 2. tartrate; 3. citrate.  
Concentration of Al(III):  $10^{-4}$  M.

The shifts of the half-wave potentials with increasing concentration of the complexing agents are shown in Fig. 3. The  $E_{1/2}$  value for the fluoride complex is shifted negatively by 180 mV at six equivalents of fluoride. The addition of one equivalent of tartrate causes a slightly positive shift (30 mV) in comparison with the aquo complex. However, further increase of tartrate concentration results in a negative shift of about 65 mV at three equivalents. As to the citrate complex reduction, the addition of one equivalent of complexing agent shifts the half-wave potential by as much as 60 mV positively compared with the potential of aquo complex. Again, by further increase of citrate concentration the wave shifts negatively by about 180 mV at three equivalents.

In Figs. 4 and 5 the shift of the half-wave potential with increasing concentration of complex is shown, *i.e.* Al(III) ion and complexing agents. The shift is most remarkable at the fluoride complex 1 : 6 (curve 1, Fig. 4). In the case of tartrate the shift occurs only at higher complex concentrations (curve 2, Fig. 5). At the tartrate complex 1 : 1 no shift of the wave can be found.

Comparison of the wave shift at various complexes with increasing depolarizer concentration (Figs. 4 and 5) shows the most remarkable shift at aquo complex. The shift gets smaller in the following sequence of complexes: aquo complex > fluoride complex > tartrate complex > citrate complex.

The half-wave potential values for fluoride and citrate complexes are independent of pH ( $-1.72$  and  $-1.66$  V, respectively). The  $E_{1/2}$  value of tartrate shifts slightly negatively with decreasing pH. (The change of pH from 4.4 to 3.4 causes a shift from approx.  $-1.54$  to  $-1.60$  V.)

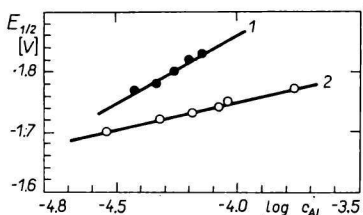


Fig. 4. The dependence of  $E_{1/2}$  values on the complex concentration for fluoride complex 1 : 6 (1); fluoride complex 1 : 3 (2).

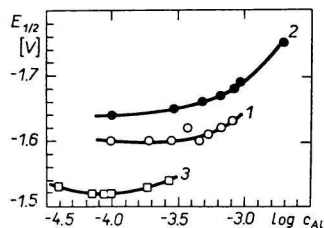


Fig. 5. The dependence of  $E_{1/2}$  values on the complex concentration for tartrate complex 1 : 2 (1); tartrate complex 1 : 3 (2); citrate complex 1 : 1 (3).

The limiting current intensity for various complexes as a function of the depolarizer concentration is demonstrated in Fig. 6. The plot in the followed concentration range is linear for all complexes. The highest limiting current is yielded by the fluoride complex. Since the wave is well measurable, it is suitable for analytical determination of low Al(III) concentrations.

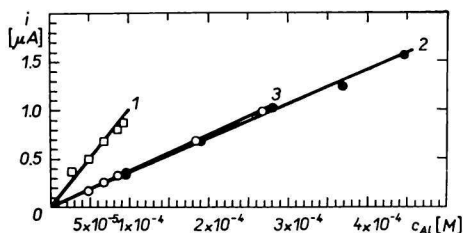


Fig. 6. The dependence of the limiting current intensity on the depolarizer concentration for various aluminium complexes.

1. fluoride complex 1 : 3; 2. tartrate complex 1 : 2; 3. citrate complex 1 : 1.

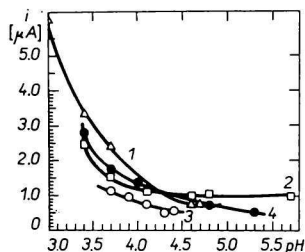


Fig. 7. The dependence of the limiting current intensity on pH for various aluminium complexes.

1. aquo complex; 2. fluoride complex 1 : 3; 3. tartrate complex 1 : 2; 4. citrate complex 1 : 2.

The wave height in the presence of complexing agents increases if the pH value decreases but more smoothly than in the case of aquo complex (Fig. 7). At the same time, the waves are more drawn out and poorly defined. The same effect is obtained by an increase of the mercury level.

Table 1

The exponents  $y$  of the limiting current dependence on the mercury height reservoir  $i = k \cdot h^y$  for aluminium complexes at various pH values

pH	$y$			
	Aquo complex	Fluoride complex 1 : 3	Tartrate complex 1 : 2	Citrate complex 1 : 2
5.7	—	0.46	—	—
5.3	—	—	—	0.49
4.8	0.74	0.38	—	0.40
4.7	0.55	—	—	—
4.6	0.60	0.37	—	—
4.4	—	—	0.36	—
4.3	—	—	0.37	—
4.1	—	0.34	0.32	—
4.0	—	—	—	0.32
3.9	—	—	0.23	—
3.7	0.69	0.31	0.34	0.26
3.4	0.66	0.29	0.23	0.25
3.0	0.60	—	—	—

Table 2

The exponents  $y$  of the limiting current dependence on the mercury height reservoir  $i = k \cdot h^y$  of aluminium complexes at various Al(III) to L ratios  
Concentration of Al(III) =  $10^{-4}$  M

Al(III) L	$y$		
	Fluoride complex	Tartrate complex	Citrate complex
1 : 0.5	0.48	—	—
1 1	0.49	0.36	0.47
1 2	0.52	0.36	0.49
1 3	0.46	0.39	0.51
1 : 4	0.44	—	—
1 : 5	0.41	—	—
1 6	0.30	—	—

At the fluoride complex, there appears a new, more positive wave at about pH 4.1 the height of which increases as the pH value decreases. At pH 3.4 again only a single wave can be observed. On the limiting current of the wave there appears a current minimum getting deeper with the mercury reservoir decrease. The formation of the minimum at the low pH values can also be observed at pH 3.4 for tartrate complex (1 2), the dependence on the mercury reservoir height being the same.

The exponents  $y$  of the limiting current dependence on the mercury height reservoir  $i = k \cdot h^y$  are shown in Table 1 for various aluminium complexes and pH values. In Table 2, the  $y$  values are listed for various aluminium complexes and Al(III) to ligand ratios.

The logarithmic analysis of  $i-E$  curves of various complexes shows that the reduction proceeds in all cases irreversibly. The obtained  $n\alpha$  values are as follows

aquo complex	0.381
fluoride	0.437
tartrate	0.391
citrate	0.419

## Discussion

The differences in the polarographic behaviour of aquo complex and other investigated complexes of aluminium show that in the presence of agents, forming with aluminium more stable complexes than water, no protons are reduced; but some of the complexes taking part in the series of complex equilibria are reduced directly. The evidences are the following.

— Different shape of  $i-E$  curves (Fig. 1). In the presence of complexing agents the maxima and autocatalytic effects are absent.

— Independence of half-wave potentials of complex ions reduction of pH (with the exception of tartrate at low pH values) contrary to the aquo complex.

— Differences in the  $y$  values of the limiting current intensity dependence on the mercury height reservoir [7]. While at aquo complex the adsorption of product,  $\text{Al}(\text{OH})_3$ , is affecting the overall character of the process, at fluoride and citrate the current is diffusion controlled. With decreasing pH values it becomes kinetic. Limiting current of the tartrate complex is partially kinetic in the whole pH range.

— With increasing depolarizer concentration the  $E_{1/2}$  value of aquo complex shifts much more negatively than is the case with other aluminium complexes. The fluoride complex 1-6 shows the maximum negative shift which is still nearly one half smaller than the shift of aquo complex.

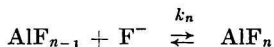
The negative shift of  $E_{1/2}$  values with increasing depolarizer concentration at aquo complex is explained by *Heyrovský* [2] as being caused by the suppression of the complex dissociation. It is necessary to provide more energy for the release of proton in the course of the reduction. The adsorption of the product contributes also to the shift of  $E_{1/2}$  values with increasing depolarizer concentration.

It is well known that at pH values higher than 4.1 the hydrolysis of the aquoaluminium salts occur and consequently irreducible particles  $\text{Al}(\text{H}_2\text{O})_{6-n}(\text{OH})_n$  are formed in the solution [8]. This is the reason of limiting current increase with decreasing pH values. At low pH values ( $\text{pH} < 3.4$ ) a separate hydrogen wave is formed. This wave can be observed at fluoride complex at low pH values as well. The interference of hydrogen wave is most likely the cause of an abrupt rise of the limiting current at aluminium complexes (Fig. 7) contrary to the smooth increase of the limiting current of aquo complex. This is caused by continuous suppression of hydrolysis with increasing proton concentration in the solution.

The autocatalytic character of the aquo complex wave decreases with a decrease of pH values. This is obviously the consequence of the equilibrium shift in such a way that  $\text{Al}(\text{OH})_3$  formation supporting the release of proton from the aquo complex and thus influencing catalytically the electrode process is inhibited.

### *Fluoride complex*

The consecutive stability constants of fluoride with Al(III) were established [9]. For the reaction



the values of  $k_n$  for  $\mu = 0.1$  and  $25^\circ\text{C}$  are the following:

$$\begin{array}{ll} \log k_1 = 6.45 \pm 0.01; & \log k_3 = 3.71 \pm 0.01; \\ \log k_2 = 5.21 \pm 0.01; & \log k_4 = 3.18 \pm 0.02. \end{array}$$

The dissociation constant of hydrofluoric acid under the same conditions is  $\text{p}K_{\text{HF}} = 3.02$ .

The equilibrium restoration is slow especially when forming lower aluminium(III) fluoride complexes [10]. This fact, together with the above-mentioned stability and dissociation constants and experimental results listed in Table 2 lead to the conclusion that the particles taking part in the electrode reaction are some of the lower, relatively stable aluminium fluoride complexes  $\text{AlF}_2^{2+}$  or  $\text{AlF}_2^+$ . (Note: the coordination sphere is completed by water molecules, just to make it simple they are not recorded.)

The exponents of the limiting current dependence on the mercury reservoir height in Table 2 decrease for aluminium fluoride complexes with increasing concentration of ligand. Thus, the current becomes partially kinetic [7]. The complexes with higher  $n$  values prevail in the solution at a higher ligand concentration. The complexes with  $n = 1$  or  $2$  are formed only by repeated equilibrium restoration in the reaction layer. The rate of equilibrium restoration is comparable with the rate of diffusion. This is the cause of the current being only partially kinetic controlled.

Further experimental results also lead to the same conclusions. Maximum and auto-catalytic character of the wave observed at aquo complex disappear after the addition of four equivalents of fluoride (related to the Al(III) concentration), the wave height remaining constant. Supposing the reducible particle were one of the higher complexes, the limiting current height would decrease and the polarographic behaviour of aquo complex would still prevail.

The conclusion may be made that the substitution of only one or two water molecules in the coordination sphere of aquo complex by fluoride results in a different electrode mechanism. The particle is losing its high symmetry and the central ion is more easily accessible to the direct reduction. The reduction of protons from the rest of the water molecules in the complex does not take place [11].

### *Tartrate and citrate complex*

The dissociation constants value of tartaric acid to the first and second steps ( $pK_I = 3.07$  and  $pK_{II} = 4.35$ , respectively) suggest that under given experimental conditions the concentration of twice dissociated tartaric acid anion in the solution is low and obviously decreases with decreasing pH value. In the whole pH range the character of the limiting current is kinetic (Table 1). With decreasing pH value the coefficient  $y$  decreases. Thus, the influence of the chemical reaction upon the electrode process is strengthened. This is in agreement with the slightly negative shift of  $E_{1/2}$  values with decreasing pH. The slowest and therefore rate-determining step is apparently the dissociation of the second hydrogen of tartaric acid. However, there is no possibility to establish in which stage of the process it takes place.

The differences between the reduction of tartrate and citrate complexes are reflected in different values of  $y$  exponents in Tables 1 and 2 as well as in the small, but still existing half-wave potential dependence of the tartrate complex reduction on pH and depolarizer concentration (Fig. 5).

In Table 2 it can be seen that the limiting current of the citrate complex is diffusion controlled and becomes kinetic only at low pH values (Table 1). This means that the reducible particle is sufficiently concentrated in the bulk of the solution. The dissociation constants of the citric acid are as follows:  $pK_I = 3.07$  to the first step,  $pK_{II} = 4.77$  to the second step, and  $pK_{III} = 6.40$  to the third step. Thus the concentration of the citric acid anion dissociated to the first step is under given experimental conditions maximum. This anion obviously forms a reducible complex with Al(III). The same conclusion can be derived from the different limiting current intensities of various Al(III) complexes (see Fig. 2). The differences are caused by various diffusion coefficients of the reducing particles. While the size of the fluoride anion is comparable to that of water molecules, in the case of tartrate and citrate complexes there exist bulky particles. Their diffusion to the electrode is much slower and, in consequence, the limiting current is lower. In addition, in the case of tartrate the kinetic factor contributes to the limiting current decrease.

A small positive shift of the half-wave potential values is observed when adding equivalent amount of tartrate or citrate to the aquoaluminium ion. This means that the reduction of the complex ions occur more readily and reversibly than that of the aquo ion [11]. This is well in agreement with the results of the  $i-E$  curves logarithmic analysis for various complexes. All are reduced irreversibly but the reduction of aquo ion attains the highest degree of irreversibility.

The general insufficiency of the complexing agents in the solution causes a very in-



tensive negative shift of the aluminium complexes half-wave potential with an increasing complexing agent concentration. The consequence is their depletion in the vicinity of the electrode. Under such experimental conditions it is impossible to calculate from the polarographic data directly the number of ligands or the stability constants of complexes.

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