

# POLAROGRAPHIC INVESTIGATION OF THE COMPLEXONATES OF ALKALINE-EARTH METALS AND ALKALI METALS

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The effect of complex-formations on the polarographic waves of alkali and alkaline-earth metal ions has scarcely been studied. As the investigation of this matter is a very interesting one from theoretical, complex-chemical, practical and analytical point of view, I began investigations in this direction, at first using the Schwarzenbach's complexons.

After a few pre-experiments this method looked promising: to examine the formation of the polarographic waves of alkali and alkaline-earth metal ions as a function of pH in the presence of nitriloacetic acid (NTA i.e.  $H_3X$ ) and ethylenediaminetetraacetic acid (EDTA i.e.  $H_4Y$ ) as complexforming. According to Koryta and Kössler [1] between the stability constant of the complex ( $K_{MZ}$ ) and the height of the polarographic wave ( $i_1$ ) to be measured in solution with given pH the following expression exists:

$$K_{MZ} = \frac{(i_d - i_1) [H^+]}{i_1 \left[ c_s - c_M \left( 1 - \frac{i_1}{i_d} \right) \right] \cdot K_j}$$

where  $i_d$  is the height of the polarographic wave if there is no complex-formation  $c_s$  is the total (analytical) concentration of the complexforming,  $c_M$  is the total (analytical) concentration of the metal,  $K_j$  are the last dissociation constants of the NTA i.e. of the EDTA the values of them are according to Schwarzenbach and co-workers [2] in 0.1 n KCl solution for NTA:  $pK_3 = 9.73$ ; for EDTA:  $pK_3 = 6.16$  and  $pK_4 = 10.26$ .

This expression can be used for calculating stability constants, if the dissociation of the complex ion takes place rather slowly and the kinetic member from the dissociation of the complex ion does not increase the height of the diffusion wave corresponding to the concentration of free cations. In studying the NTA complex of the  $Cd^{2+}$  Koryta and Kössler used streaming mercury electrode to eliminate the kinetic member.

In our earlier investigations [3] we had shown that on streaming mercury electrode every alkali metal ion, further  $Ba^{2+}$ ,  $Sr^{2+}$ ,  $Ca^{2+}$  and  $Mg^{2+}$  gave excellent polarographic waves. So, using the streaming mercury electrode, it is possible to study the complexes of these ions polarographically.

### Experimental

The experiments were carried out with a modified streaming mercury electrode, described in a previous article [4], the polarograms were registered with Radiometer polarograph Type PO 3.

As supporting electrolyte recrystallized  $[\text{N}(\text{CH}_3)_4]\text{I}$  was used in 0.10 - 0.12 concentration. The pH of the solutions were adjusted with 0.1 HCl or  $[\text{N}(\text{CH}_3)_4]\text{OH}$  solution. The  $[\text{N}(\text{CH}_3)_4]\text{OH}$  solution was freed from carbonates with strongly basic anion exchange resin (Amberlite IRA-400). The investigated solutions contained the complexforming in 100-5g mg/25 ml concentration and the alkali or alkaline-earth metal ion in  $1.6 \cdot 10^{-3}$  concentration.

### Results and Discussion

From some pre-experiments it was clear, that the constant pH of the solutions could not be secured by employing buffer-systems, because then a disturbing kinetic hydrogen wave exhibited in the nearly neutral or slightly acidic solutions.

If buffer-system is not used, the experimentally examined pH-region is confined to acid side by the appearance of the hydrogen wave according to the hydroxonium ion reduction. In the presence of NTA this was about 4.8 - 4.9 pH, in the presence of EDTA about 4.5 pH, but this value depend on the concentration of the acid too. It is interesting that the EDTA gives about pH 5 a second wave too, which is probably in accordance with some non-ionized proton reduction (e.g. to the  $[\text{H}_2\text{Y}]^{2-} + e \rightarrow [\text{HY}]^{3-} + \text{H}$  electrode process) and in the environment of the cathode it has not any essential influence on the pH either.

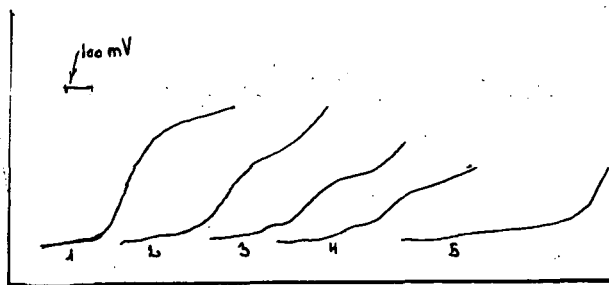


Fig. 1.

The variation of the strontium wave at various values of the pH in a solution containing NTA. Streaming mercury electrode; 0.1 m  $[\text{N}(\text{CH}_3)_4]\text{J}$ .

Each curve starts at -1.5 V.

|          |  |            |          |
|----------|--|------------|----------|
| Curve 1: | $0.8 \cdot 10^{-3}$ m $\text{Sr}^{2+}$ | 0 m NTA    |          |
| Curve 2: | $0.8 \cdot 10^{-3}$ m $\text{Sr}^{2+}$ | 2.09 m NTA | pH = 5.8 |
| Curve 3: | $0.8 \cdot 10^{-3}$ m $\text{Sr}^{2+}$ | 2.09 m NTA | pH = 6.6 |
| Curve 4: | $0.8 \cdot 10^{-3}$ m $\text{Sr}^{2+}$ | 2.09 m NTA | pH = 7.0 |
| Curve 5: | 0 m $\text{Sr}^{2+}$                   | 2.09 m NTA |          |

Figure 1, shows the changing of the  $\text{Sr}^{2+}$  wave at different pH in solution containing NTA.

Table I. shows the data obtained by the polarographic examination of the NTA and EDTA complexes of some alkaline-earth metal ions.

Table I

| Examined system        | Concentration of the complex-forming | pH   | $\frac{i_1}{i_d}$ | log $K_{MZ}$ measured | log $K_{MZ}$ in literature |
|------------------------|--------------------------------------|------|-------------------|-----------------------|----------------------------|
| $\text{Sr}^{2+}$ -NTA  | $2.09 \cdot 10^{-2}$                 | 5.0  | 0.843             | 5.68                  | 4.98                       |
|                        |                                      | 5.8  | 0.448             | 5.71                  |                            |
|                        |                                      | 6.6  | 0.256             | 5.28                  |                            |
|                        |                                      | 7.0  | 0.184             | 5.07                  |                            |
| $\text{Mg}^{2+}$ -EDTA | $6.85 \cdot 10^{-3}$                 | 4.15 | 0.442             | 10.46                 | 8.69                       |
|                        |                                      | 4.35 | 0.209             | 10.50                 |                            |
| $\text{Mg}^{2+}$ -NTA  | $2.09 \cdot 10^{-2}$                 | 4.95 | 0.50              | 6.47                  | 5.41                       |
| $\text{Ba}^{2+}$ -EDTA | $1.37 \cdot 10^{-2}$                 | 5.5  | 0.148             | 8.08                  | 7.76                       |

According to the data of the table the disturbing effect from the accidental unnegligible velocity of the complex-dissociation cannot be noticed, though we want to clear the latter factor by further examinations perhaps with dropping mercury electrode. So it will be possible to study the dissociation velocity constants [6] with polarographic measurements.

It is also remarkable that the appearance of the second wave according to the reduction of the complex ion could not be noticed in either of the cases examined. The explanation of this is that the  $\text{MeY}^{2-}$  i.e.  $\text{MeX}^-$  negative charged ions cannot be in contact with a cathode of strongly negative potential [7]

Among the alkali metals the  $\text{Li}^+$  ion forms the steadiest complex with NTA and EDTA. But polarographically in the latter experimental circumstances (using streaming mercury electrode in aqueous solution at  $10^{-2}$  m complexforming concentration) the lowering of the height of the  $\text{Li}^+$  wave could not be noticed up to pH = 10. This phenomenon can be explained by the fact that the  $\text{Li}^+$  complex dissociates with great velocity.

But if the composition of the medium is changed so that it should be favourable to the formation of a complex, the existence of alkali metal complex can be polarographically demonstrated. So in 50 % aqueous alcoholic solution of  $0.25 \text{ m } [\text{N}(\text{CH}_3)_4]\text{OH} + 0.25 \text{ m } (\text{N}(\text{CH}_3)_4)_2 \text{H}_2\text{Y}$  at  $4 \cdot 10^{-3}$  n  $\text{Na}^+$ -ion concentration an oscillopolarographic  $\frac{dV}{dt}$  - V curve could be made (Fig. 2.), on the cathode

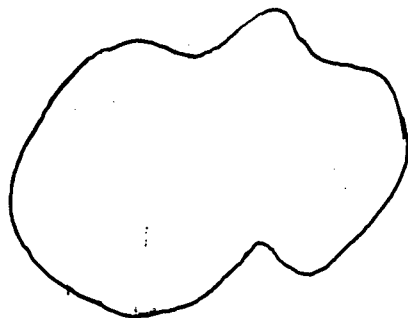


Fig. 2.

Oscillographic  $\frac{dV}{dt}$  - V curve of a solution containing  $\text{Na}^+$  and EDTA. The curve starts at  $-1,3$  V.

branch of which two cut-ins could be noticed.

From the  $-2,0$  V potential value belonging to the first cut-in it is probable, that it corresponds to the reduction of the free  $\text{Na}^+$  ions. The potential value belonging to the second cut-in is  $-2,4$  V; here the reduction of the Na-EDTA complex, i.e. at an anod process the solution of Na as a complex takes place.

The changing of the oscillogram in time is interesting, too. After preparing the solution, on the cathode branch only the first cut-in could be noticed, in a few minutes it became smaller and smaller and the second cut-in developed more and more. This observation shows the formation of the Na-EDTA complex in time.

### References

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