

ON SOME ANOMALOUS FORMS OF POLARIZATION CURVES ON A DROPPING MERCURY ELECTRODE

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During studies of various electrical reduction reactions on a dropping mercury electrode, one often gets indications of some polarization curves with unusual forms. Some authors in noting this phenomenon, explain the distortion in the shape of the curve by polarographic maxima, although neither the potential region where the "maxima" are observed, nor the relation between the concentration and the nature of the supporting electrolyte indicates that one is dealing with the normal polarographic maxima here. During the polarographic determination of rhenium, Lingane [1], and Geyer [2], for example, observed complex polarograms with maxima which did not disappear on adding organic materials which normally suppress maxima of the first and second order quite efficiently. As Geyer points out, of all the materials tested by them, the maximum only disappeared on adding potassium iodide [2]. Distortion of the limiting current wave during reduction of ReO_4^- has also been observed by other authors [3].

Other authors do not give any explanation for the unusual forms of some polarograms, and only indicate that it is impossible to determine various materials polarographically. Unusual forms of polarograms have been obtained during a study of the reduction of niobium on a dropping mercury electrode [4], during the reduction of nickel and cobalt in a supporting electrolyte of potassium thiocyanate [5]. A sharp decrease in the limiting current in a certain potential range was observed by Filipovic et al. [6] during the reduction of V^{V} in various buffered solutions, by Bulovo $\check{\text{v}}$ a [7] while studying the reduction of indium in a supporting electrolyte of solutions with anions which can be deformed and which are not deformed, and by Souchay [8], and Jenšovský [9] who studied the conditions for the polarographic determination of IO_4^- . Filipovic and Bulovo $\check{\text{v}}$ a are of the opinion that the current drop on the $\text{I}-\varphi$ curve is possibly connected with the reduction of complex anions formed in solution.

As is evident even from this incomplete list of articles, in which there are indications of distortions of the $\text{I}-\varphi$ curves which apparently are not connected with polarographic maxima, polarization curves with unusual shapes crop up often.

In our opinion, the observed distortion of the shape of $\text{I}-\varphi$ curves, or the appearance of maxima which disappear on adding potassium iodide, can be explained in a number of instances by the fact that during the polarographic determination of some materials in a supporting electrolyte of an indifferent electrolyte at a concentration of 1 N and more, formation of complex anions is possible, these anions being then reduced on the dropping mercury electrode; the present authors relate the polarization curves thereby obtained, however, not to the reduction of the anions formed in solution, but to the reduction of the original materials taken for analysis.

A consideration of the experimental results given in the articles mentioned above confirms this explanation: the sharp drops in the current on the polarization curves for the reduction of rhenium, indium, etc., are observed at potentials approximating to the potential for the zero discharge of mercury, when there occurs a shift from a positively charged surface of the mercury to a negatively charged surface. At present, on the basis of a large amount of experimental data, it has been shown that the current drops observed in the region of negative charges on the electrode surface are characteristic for electrical reduction of at least two and more charged anions. The first current drop in $\text{I}-\varphi$ curves was observed by Kryukova during the reduction of $\text{S}_2\text{O}_8^{2-}$ on a dropping mercury electrode [10]. Subsequently, the slowing down of the reduction of anions was noted in a number of articles during the reduction of other anions [11].

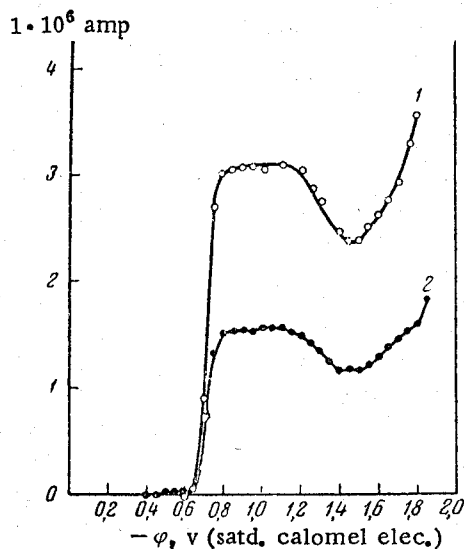


Fig. 1. $K_2Ni(SCN)_4$ in a solution of 1 N KSCN. Concentration of the complex: 1) 2×10^{-3} N; 2) 1×10^{-3} N.

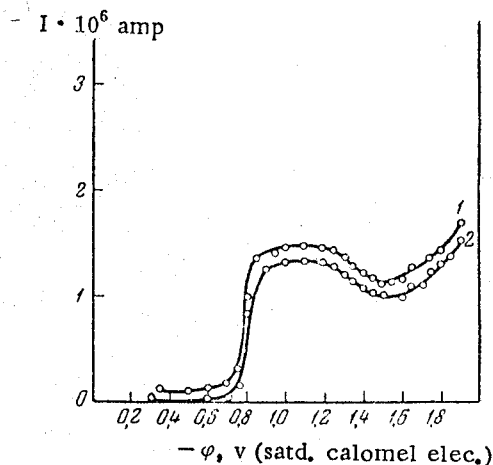


Fig. 2. 10^{-3} N $K_2Ni(SCN)_4$ in a solution of 1 N KSCN: Curves taken: 1) after 1 hour; 2) after 2 hours.

The phenomenon of the current drop was explained by electrostatic repulsion of the negatively charged anions by the negatively charged electrode surface, which leads to a drop in the concentration of the anions in the surface layer. On addition of an indifferent electrolyte, the drop in current during reduction of certain anions disappears. This could be explained by the fact that on increasing the concentrations of the cations of the supporting electrolyte, the electrical field of the negative charges of the electrode decreases. In some cases, on the other hand, addition of an indifferent electrolyte merely limits the region over which there is a drop in current, while the reaction is still slowed down.

As an example substantiating the explanations given above for the distortion of the polarization curves, we would like to give the experimental results we have obtained during the reduction of the thiocyanate complexes of nickel and cobalt on a dropping mercury electrode.

As pointed out already, polarographic curves of unusual shape which have been obtained during the reduction of Ni^{2+} in a supporting electrolyte of KSCN have been given in certain articles [5]. These distortions of the

$I-\phi$ curves could be explained on the grounds that, during the polarographic determination of nickel and cobalt in a supporting electrolyte of KSCN, reduction occurs, not of the cations Ni^{2+} and Co^{2+} , but of the complex anions of these metals which are formed in the electrolyte in the presence of KSCN, and during the reduction of which, there may be observed drops in the current in the area of the limiting current. In order to exclude the effect of other anions, we synthesized the complexes $K_2Ni(SCN)_4$ and $K_2Co(SCN)_4$, and studied their reduction on a dropping mercury electrode. All the potential values are quoted with respect to a saturated calomel electrode.

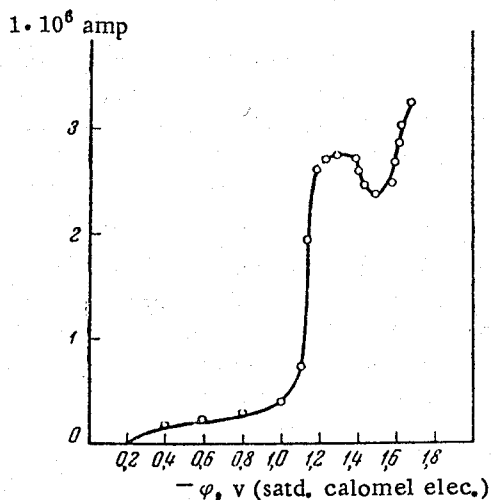


Fig. 3. 2×10^{-3} N $K_2Co(SCN)_4$ in a solution of 1 N KSCN.

In Fig. 1 are given the polarization curves for the reduction of $K_2Ni(SCN)_4$ in a supporting electrolyte of 1 N KSCN. Reduction starts at $\phi = -0.70$ v; the current increases and reaches the value of the limiting current. At $\phi = -1.2$ v, there is observed a current drop, and, after reaching some minimum current value, the reaction rate increases. In the region of the limiting current there is observed a proportionality between the values of I_d and the concentration of the complex. The

polarization curves for the reduction of $K_2Ni(SCN)_4$ in a supporting electrolyte of KSCN change with time, although the current drop does not disappear even after the solution has been allowed to stand for a long time in the cell (Fig. 2). A decrease in the concentration of KSCN leads to the disappearance of the wave, which is connected with the dissociation of the complex in the presence of low concentrations of potassium thiocyanate [12, 13].

The polarization curves for the reduction of $K_2Co(SCN)_4$ are shown in Fig. 3. In a supporting electrolyte of 1 N KSCN reduction of the complex starts at a potential of $\varphi = -1.15$ v. The value of the limiting current is proportional to the concentration of the complex. At a potential of $\varphi = -1.4$ v, the current starts to drop, and again increases at potentials which are more negative than $\varphi = -1.5$ v. The current drop in the case of the reduction of $K_2Co(SCN)_4$ is not so clearly marked as in the case of the reduction of $K_2Ni(SCN)_4$. By comparing the $I-\varphi$ curves for the reduction of these complexes, it is possible to understand why the diffusion current of cobalt is very unstable during the determination of cobalt in the presence of nickel in a supporting electrolyte of potassium thiocyanate [5]; reduction of $K_2Co(SCN)_4$ in a supporting electrolyte of 1 N KSCN starts at a potential of $\varphi = -0.15$ v, while the current drop on the reduction curve for 10^{-3} N $K_2Ni(SCN)_4 + 1$ N KSCN starts at $\varphi = -1.2$ volt, which is the reason for the instability of the limiting current for the reduction of cobalt.

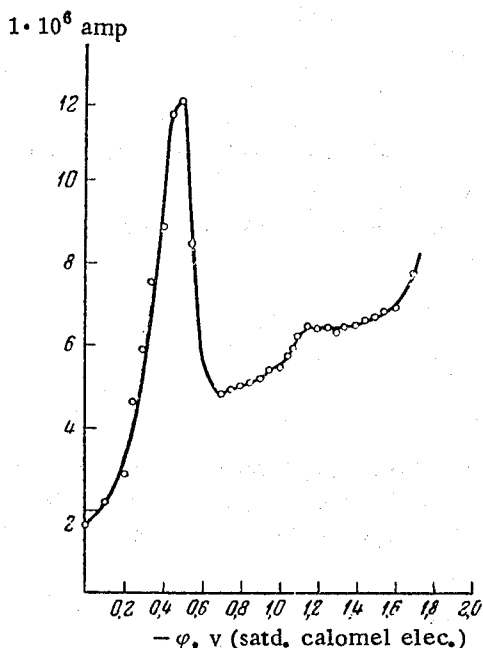


Fig. 4. 4×10^{-3} N $Pt(NH_3)_2(OH)_2Cl_2$.

on which there is a current drop in the region of the potential of zero charge. Addition of the iodide anion suppresses the reduction of the anions when there are positive charges on the electrode surface [2, 3], and the reduction potential of the complex anion shifts toward more negative potentials at which there is observed an increase in the current after the minimum.

Having mistakenly taken the increase in the reduction current of the anion, with its subsequent drop during overcharging of the electrode surface, for a polarographic maximum, the authors naturally could not explain why the maximum disappeared only on adding KI. It is impossible, of course, to affirm that unusual forms of the polarization curves which are observed during polarographic determinations are always connected with reductions of anions; however, we should like to bring attention to the possibility that this may be so. The form of the polarographic curves can also change as a result of exchange reactions between the complex anions and the anions of the supporting electrolyte [15].

The slowing down of electrical reduction reactions when the electrode surface is negatively charged is observed not only in the case of the reduction of complex anions, but also, as Kivalo and Laitinen [16] discovered recently, in the case of the reduction of neutral particles, for example, $cis-Pt(NH_3)_2Cl_2$. We have also observed a current drop during the reduction of the neutral complex $PT(NH_3)_2(OH)_2Cl_2$ (Fig. 4).

This phenomenon can be explained by the reduction of the complex anions which are formed during the hydrolysis of the original salt, or by the fact that although the particle as a whole is not charged, the atoms of chlorine which form part of it carry negative charges, and adsorption of these on the electrode surface becomes more difficult as the negative charge increases [17].

SUMMARY

The polarographic reduction of the thiocyanate complexes of nickel and cobalt have been studied on a dropping mercury electrode. It has been shown that the distortion of the polarographic curves which is observed in a number of cases can be explained by reduction of complex anions which are formed in solution.

LITERATURE CITED

- [1] J. Lingane, J. Amer. Chem. Soc. 64, 1001 (1942).
- [2] R. Geyer, Z. anorgan. Chem. 263, 47 (1950).
- [3] L. Rules and P. Elving, J. Amer. Chem. Soc. 73, 3284 (1951).
- [4] S. Dhar, Analyt. chim. acta 11, 289 (1954).
- [5] J. Kolthoff and G. Matsuyama, Industr. and Engng. Chem., Anal. Ed. 17, 615 (1945); J. Lingane and H. Kerlinger, Industr. and Engng. Chem., Anal. Ed. 15, 77 (1941).
- [6] J. Filipović, Z. Hahl, Z. Gasparal, and V. Klemenčic, J. Amer. Chem. Soc. 76, 2074 (1954).
- [7] M. Bulovová, Col. czech., chem. com. 19, 1123 (1954).
- [8] P. Součay, Analyt. chim. acta 2, 17 (1948).
- [9] L. Jenšovský, Chem. listy 50 (80), 1426 (1956).
- [10] T. A. Kryukova, Doklady Akad. Nauk SSSR 65, 517 (1949).
- [11] A. N. Frumkin and G. M. Florianovich, Doklady Akad. Nauk SSSR 80, 907 (1941); G. M. Florianovich and A. N. Frumkin, Zhur. Fiz. Khim. 29, 1827 (1955); A. N. Frumkin, Uspekhi Khim. 24, 933 (1955); A. N. Frumkin and N. V. Nikolaeva-Fedorovich, Vestnik Moskov (State) Univ. Ser. Mekh. Mat. Fiz. Khim. 169 (1957); A. N. Frumkin, Izvest. Akad. Nauk. SSSR, Ser. Khim. 1429 (1957).*
- [12] A. Rosenheim and R. Cohn, Z. anorgan. Chem. 27, 280 (1901); Walden, Z. anorgan. Chem. 23, 373 (1900).
- [13] A. K. Babko, Uspekhi Khim. 25, 872 (1956).
- [14] Drutse, Rhenium, (IL, Moscow, 1951).
- [15] N. V. Nikolaeva and V. N. Presnyakova, Doklady Akad. Nauk 87, 61 (1952).
- [16] P. Kovalo and H. Laitinen, J. Amer. Chem. Soc. 77, 5205 (1955).
- [17] A. N. Frumkin and N. V. Nikolaeva, J. Chem. Phys. 26, 1552 (1957).

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