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On the Electroreduction of the Chromate Ion in Weakly-acid Solutions

Elektroredukcja jonu chromianowego w środowisku słabo kwaśnym

Электровосстановление иона хромата в слабокислой среде

Up to now, the chromates have been examined by means of polarographic methods mostly in solutions of high buffer capacity or at high acid alkaline concentrations, in view of the fact that the mechanism of reduction is strongly dependent on the pH value of the solution, and that the electrode reaction produces 14 OH^- ions per $\text{Cr}_2\text{O}_7^{2-}$ or neutralizes the same amount of H^+ ions. This large excess of OH^- ions in a narrow layer near electrode causes a local alkalinization which can easily reach several pH units. Colouring of phenolphthalein around the DME in neutral or weak-acid solutions can be detected visually [3]. In view of this situation, it would seem that adding small amounts of acids or bases to the neutral chromate solution should not influence markedly the polarographic curves.

However, experiments show that distinct changes on the DC curves are caused by the addition of acids or bases even below 10^{-4} mol \cdot dm $^{-3}$. These changes are particularly evident in the absence of any supporting electrolyte. Measurements were carried out using polarograph LP-60. The electrode system DME ($m = 1,31$ mg s $^{-1}$, $t = 3,2$ s) vs SCE was used.

Polarograms were recorded for chromate solutions containing H $_2$ SO $_4$ in a range of concentrations commensurate with that of the chromate ion (Fig. 1). The first maximum ends by a sharp step observed at potentials ranging from -0,5 to -0,8 V/SCE. With decreasing concentrations of H $_2$ SO $_4$ this maximum first rises (reaching its highest value ca 400 μ A at the concentration $5 \cdot 10^{-3}$ mol \cdot dm $^{-3}$ H $_2$ SO $_4$ and 10^{-3} mol \cdot dm $^{-3}$ CrO $_4^{2-}$) and then suddenly drops to a value of the order of 20 μ A (Fig. 2) inside a very narrow range of H $_2$ SO $_4$ concentrations ($1,7 - 1,8 \cdot 10^{-3}$ M).

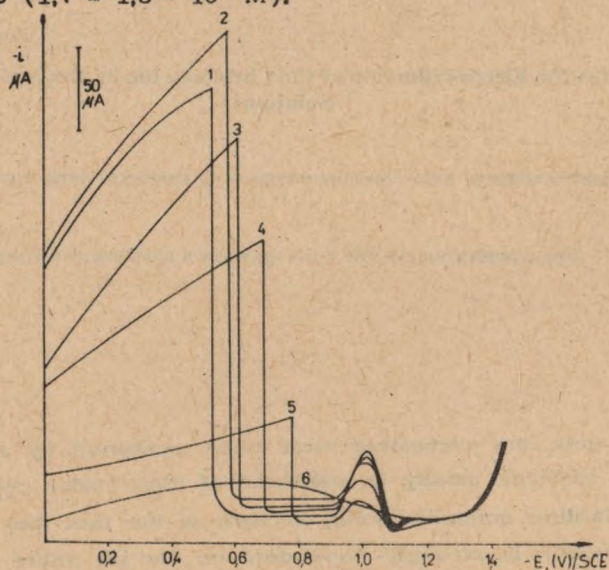


Fig. 1. Polarographic d.c. curves $1 \cdot 10^{-3}$ mol \cdot dm $^{-3}$ CrO $_4^{2-}$ in:

1. $1,7 \cdot 10^{-3}$ mol \cdot dm $^{-3}$ H $_2$ SO $_4$
2. $1,8 \cdot 10^{-3}$ mol \cdot dm $^{-3}$ H $_2$ SO $_4$
3. $2 \cdot 10^{-3}$ mol \cdot dm $^{-3}$ H $_2$ SO $_4$
4. $3 \cdot 10^{-3}$ mol \cdot dm $^{-3}$ H $_2$ SO $_4$
5. $5 \cdot 10^{-3}$ mol \cdot dm $^{-3}$ H $_2$ SO $_4$
6. $1 \cdot 10^{-2}$ mol \cdot dm $^{-3}$ H $_2$ SO $_4$

Characteristics of the capillary: $1,31$ mg \cdot s $^{-1}$, drop time 3,2s-SCE

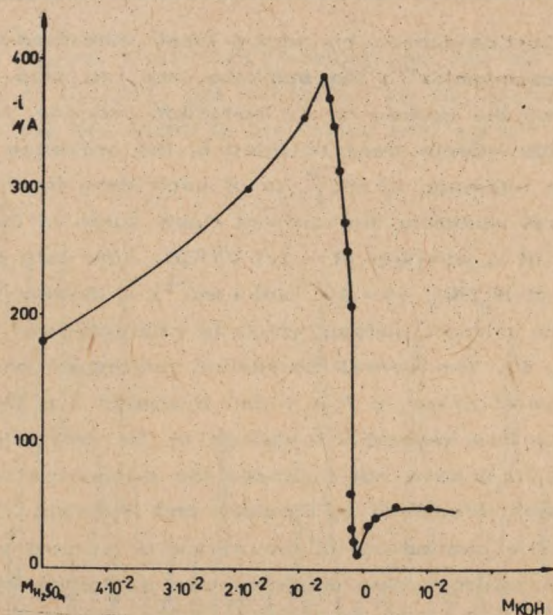


Fig. 2. The effect of the concentrations of H_2SO_4 or KOH on the current at the maximum in solution $10^{-3} \text{ mol} \cdot \text{dm}^{-3} \text{CrO}_4^{2-}$. Other conditions as in Fig. 1.

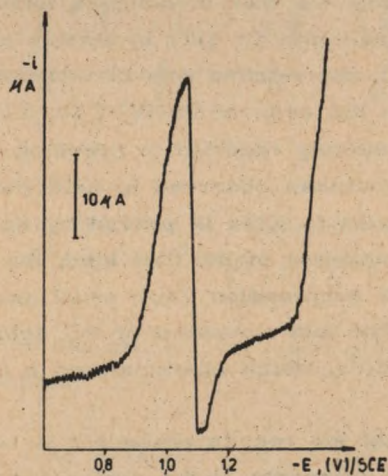


Fig. 3. d.c. polarogram of $10^{-3} \text{ mol} \cdot \text{dm}^{-3} \text{CrO}_4^{2-}$ in $5 \cdot 10^{-3} \text{ m} \cdot \text{dm}^{-3} \text{H}_2\text{SO}_4$. Other conditions as in Fig. 1

It is slightly better developed by adding small quantities of fluoride ions which can complex Cr^{3+} ; the sulphate ions can also complex the Cr^{3+} and influence the course of the reduction process, however the fact that similar effects were obtained in the presence of ClO_4^- indicates that the influence of SO_4^{2-} is of secondary importance.

After the first maximum, the current rises again in the form of a peak (Fig. 3) at a potential of $-1,0$ V/SCE. After this peak, and in the presence of H_2SO_4 ($5 \cdot 10^{-3}$ mol \cdot dm $^{-3}$) a distinct depression appears below the current plateau which is characterized by regular oscillations (Fig. 4). The overall oscillation pattern encompasses the period of several drops, a fact which indicates that the cause of their occurrence lies beyond the surface of the drop. Optical observations at $-1,05$ V have not indicated the occurrence of the "tubing" phenomenon described by Bockris and Parsons [1, 2] or Matysik [12]. The phenomena of occurrence of current oscillations in the range of a polarographic maximum was explained by a temporary depletion of reactant concentration in a zone wider than the diffusion layer (as a consequence of whirls in the solution during the maximum) and subsequent equalization of concentrations [9]. It is not out of considerations that Cr(II) formed at the electrode reacts with Cr(VI) diffusing from the bulk of solution: formation of Cr(II) at $-1,0$ V and its reaction with Cr(VI) in weakly acidic solutions has been described [8], the relative rate of these reactions may be changable as e.g. in the case of Te(IV) [10, 11]. Similar current oscillations have been already reported in previous papers [4-7].

The first current increase observed in acid medium has the nature of convective maximum. This is proved by its typical shape which is the one of a maximum of the first kind, the abnormally high current and its complete suppression when small amounts of galein (0,005 %) are added. The fast movement of the solution around the drop is directed downwards, which characterizes a maximum of the positive type.

The interpretation of the results presented is based on the hypothesis that tangential movements at the surface of the electrode can be hindered by the compact layer of products ($\text{Cr}(\text{OH})_3$ and alkaline chromium chromates) which are formed during the process of reduction of CrO_4^{2-} :

The significative role of the layer in the electrode reaction and especially in limiting of the polarographic current was postulated in

numerous papers. Miller [13] established that the different hindering properties of $\text{Cr}(\text{OH})_3$ are depending on the thickness, structure and charge of the film which is connected with the pH value of the solution.

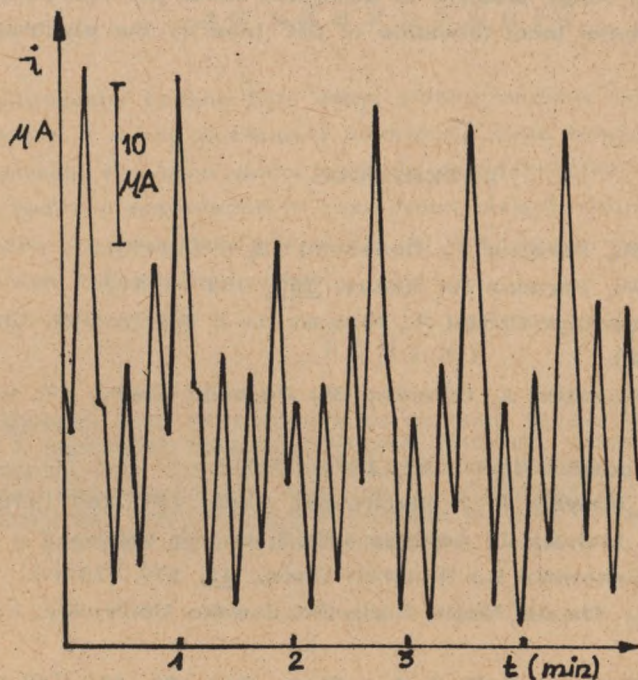
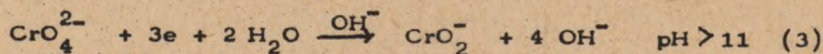
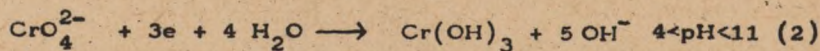
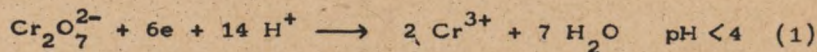


Fig. 4. Current oscillations in a solution $1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3} \text{ CrO}_4^{2-}$ and $5 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$. Other conditions as in Fig. 1

Depending on the pH, the reduction process involves the following stoichiometries:



In the second case, $\text{Cr}(\text{OH})_3$ may form a compact film on the electrode surface and have suppressing effect on the polarographic maximum. Thus in pH range from ca 4 to 11, the maximum does not occur since this is the range where chromium hydroxide is insoluble. As a matter of fact, the actual range extends to somewhat lower pH values, in view of the additional local formation of OH^- ions by the electrode reaction.

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S T R E S Z C Z E N I E

Chromiany badane były dotąd polarograficznie najczęściej w roztworach o dużej pojemności buforowej, silnie kwaśnych lub silnie zasadowych. Przeprowadzono badania doświadczalne i dyskusje wyników redukcji chromianów w roztworach niebuforowanych, w których zachodzą znaczne zmiany wartości pH wpływające na szybkość i mechanizm reakcji elektrodowej.

Р Е З Ю М Е

Хроматы были исследованы до сих пор полярографически и очень часто в растворах большой буферной емкости, сильнокислых или сильнощелочных. Проведено опытные исследования и обсуждено результаты восстановления хроматов в небуферных растворах, в которых выступают значительные изменения величин pH влияющие на скорость и механизм электродной реакции.

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