

CATALYTIC POLAROGRAPHIC DOUBLE WAVE OF CYSTEINE ON A HANGING MERCURY DROP ELECTRODE

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Solutions containing cysteine and cobalt(II) in an ammoniacal buffer were studied polarographically on a hanging mercury drop electrode. With concentrations of cysteine higher than $1 \cdot 10^{-5} \text{ M}$, a new peak of catalytic hydrogen evolution was found at a potential by 0.5 V more anodic than the catalytic polarographic maximum described by Brdička. A necessary condition for this phenomenon is electrodeposition of cobalt on the electrode at potentials more anodic than the catalytic peak.

Buffered solutions of organic low-molecular mass substances have attracted the attention of investigators thanks to the Brdička's discovery^{1,2} of catalytic hydrogen waves in the presence of organic SH derivatives and salts of cobalt or nickel. The catalytic effect of cysteine has been studied by many authors³⁻⁶. The hanging mercury drop electrode (HMDE) was used by Kalous⁷ in studying the Brdička catalytic effect in the presence of Co(III) and by Březina⁸ who studied the role of metallic cobalt in the catalytic reaction. In the present work, we investigated the conditions at which cysteine gives two catalytic waves on the HMDE.

EXPERIMENTAL

An equipment for the HMDE after Kemula (Radiometer, Copenhagen) was used in combination with an LP 60 type polarograph and EZ 2 type pen recorder (Laboratorní přístroje, Prague). The rate of increase of potential was 400 mV/min and the drop mass was 3.0 mg. Electrolyses were carried out in nitrogen atmosphere in a cell with a separated s.c.e. to which all potential values are referred. Cysteine hydrochloride (Výzkumný ústav sér a očkovacích látek, Prague), cobalt(II) chloride, ammonium chloride and ammonia (Lachema, Brno) were of reagent grade. Mercury for the electrode was labeled "for polarography" (Lachema, Brno). Stock solutions of 1M-NH₄Cl, 0.01M-CoCl₂ and 1M-NH₄OH were prepared, and from these a solution of 0.001M-CoCl₂ + 0.1M-NH₄OH + 0.1M-NH₄Cl was freshly prepared before every measurement.

RESULTS AND DISCUSSION

Cathodic polarographic curves corresponding to different concentrations of cysteine are shown in Fig. 1. With concentrations of cysteine equal to or larger than $2 \cdot 10^{-5} \text{ M}$ (curve 5), a new peak appears which increases with the concentration of cysteine. At a potential corresponding to this peak, bubbles of hydrogen are clearly visible

on the electrode by a microscope. Hence, catalytic evolution of hydrogen takes place at a potential by about 0.5 V more anodic than that of the second catalytic hydrogen wave (Brdička wave). Such a catalytic double wave of cysteine with markedly differing peak potentials has not yet been described in the literature. A not well-defined double wave of cysteine observed by Zuman and Kuik⁹ with the use

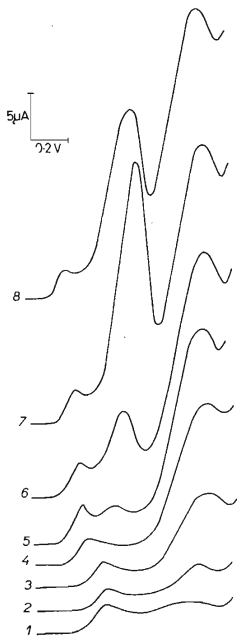


FIG. 1

Polarographic Curves of Cysteine in Cobalt(II) Solution on HMDE

$1 \cdot 10^{-3} \text{M-CoCl}_2 + 0.1 \text{M-NH}_4\text{OH} + 0.1 \text{M-NH}_4\text{Cl}$. Concentration of cysteine: 1 $0.5 \cdot 10^{-6}$; 2 $1 \cdot 10^{-6}$; 3 $5 \cdot 10^{-6}$; 4 $1 \cdot 10^{-5}$; 5 $2 \cdot 10^{-5}$; 6 $3 \cdot 10^{-5}$; 7 $5 \cdot 10^{-5}$; 8 $1 \cdot 10^{-4} \text{M}$. Beginning from -0.8V ; 400V/min .

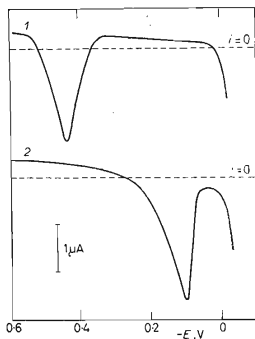


FIG. 2

Anodic Polarization Curve of $5 \cdot 10^{-5} \text{M}$ Cysteine in Cobalt(II) Solution

Pre-electrolysis 30 s at: 1 -1.35V ; 2 -1.0V . Beginning from -0.6V , 200mV/min .

of a dropping electrode is different in that the catalytic prewave appears at a potential by only 0.15 V more positive than the Brdička catalytic maximum. The shift of the catalytic cystine wave towards positive potentials by addition of a surface active substance¹⁰ can be discussed similarly. The new peak depends on previous polarization of the electrode. When the electrode was prepolarized on -0.9 V and the potential was then switched over to -1.35 V, no hydrogen bubbles were observed with a microscope; however, after preelectrolysis at -1.0 V a few bubbles appeared and after preelectrolysis at -1.1 or -1.2 V the evolution of hydrogen was considerable. When the electrode was polarized directly on -1.35 V, no hydrogen evolution was observed. Hence, in contrast to Brdička catalytic current, the new effect is conditioned by preelectrolysis of cobalt solution at potentials more anodic than the foot of the peak, whereby cobalt is deposited on the electrode. The deposit thus formed is different from that formed at the potential of the first catalytic wave, as follows from the study of its anodic dissolution (Fig. 2). The different nature of the deposited cobalt (possibly coordinated with cysteine¹⁰) is probably due to the existence of various cobalt(II) complexes in solution, which are reduced at different potentials by different mechanisms. Since preelectrolysis cannot be realized on a dropping mercury electrode, the described phenomenon has not been observed in classical polarography. Cysteamine and thioglycolic acid give similar effects as cysteine. The electrochemical properties of the cobalt deposit as well as the behaviour of other low-molecular mass thiols are the subject of a further study.

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