

POLAROGRAPHIC DETERMINATION OF LOW CONCENTRATIONS OF CERTAIN METAL IONS ON THE BASIS OF HYDROGEN CATALYTIC WAVES

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Translated from *Zhurnal Analiticheskoi Khimii*, Vol. 17, No. 3,
pp. 282 - 285, May-June, 1962

Original article submitted April 18, 1961

Heyrovsky and Babicka [1] were the first to discover the catalytic liberation of hydrogen from a dropping mercury electrode in protein solutions. Brdicka [2-4] made a detailed study of this phenomenon and showed that the catalytic effect becomes stronger in the presence of cobalt or nickel ions. Many research workers have developed the theory of the catalytic liberation of hydrogen [5-13]. It has been suggested that the following factors affect the mechanism of this process: the adsorbability of the organic compound, the charge of the proton donor, formation of active centers, (e.g. cobalt atoms) on the electrode surface, and the stability of the complexes of cobalt with a catalytically active organic compound. Catalytic waves of this type have found analytical application for the polarographic determination of small amounts of certain organic compounds, since the catalytic current is one or two orders higher than the diffusion current for the same concentration of the test material [1-3, 14, 15].

In principle it should also be possible to determine metal ions, above all cobalt and nickel. Thus Stromberg [6] has determined cobalt at concentrations down to 5×10^{-5} g.ion/liter on the basis of the catalytic action of dimethylglyoxime.

The aim of the work described here was to extend the possibilities of using the hydrogen catalytic wave for determining small amounts of a number of cations which form complex compounds with organic compounds possessing a catalytic effect. Cysteine was chosen as the catalytically active material [2-4].

Experimental work was carried out on a visual type polarographic setup with a dropping mercury electrode. The galvanometer sensitivity was 2×10^{-9} amp/mm/m. The capillary had the following characteristics $m^{2/3}t^{1/6} = 3.82 \text{ mg}^{2/3} \text{ sec}^{-1/2}$. A saturated calomel element was used as the reference electrode. Some measurements were made on a polarograph of the Heyrovsky LP-55 type.

The cysteine solutions were prepared immediately before taking polarograms. Their concentration was determined iodometrically. 10^{-3} M solutions of $\text{Ni}(\text{NO}_3)_2$ and CoCl_2 were prepared from the chemically pure preparations. Their concentrations were determined amperometrically. Solutions of $\text{Hg}(\text{NO}_3)_2$, $\text{Bi}(\text{NO}_3)_3$, SbCl_3 , SnCl_2 , CdCl_2 , $\text{Cu}(\text{NO}_3)_2$ were prepared by dissolving accurately weighed aliquots of the respective metals. In addition, solutions of lead and thallium nitrates, and zinc, manganese, and iron sulfates were prepared, the chemically pure preparations being used. The salt solutions were diluted by addition of the corresponding acid. The pH of the solutions was 1-2. Twice distilled water was used in all cases. Ammonia and ammonium chloride were used for preparing buffer solutions.

After carrying out a polarographic study of cysteine solutions at different pH values, we became convinced that cysteine does not exhibit a catalytic effect in alkaline media. On adding small amounts of cobalt or nickel salts to a weakly alkaline solution of cysteine (pH 9), catalytic hydrogen waves were detected on the polarograms (Fig. 1), these waves being proportional to the concentration of the metal ions. The relationship between the catalytic current and concentration of cobalt and nickel ions is shown in Fig. 2. It follows from these results that nickel and cobalt ions can be detected down to concentrations of 5×10^{-6} g.ion/liter in a 0.1 M ammoniacal buffer solution when the cysteine content is 2×10^{-3} M.

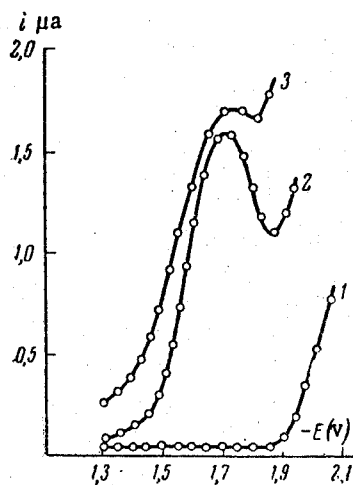


Fig. 1. Polarograms of solutions. 1) 2×10^{-3} M cysteine solution containing 0.1 M NH_4Cl and 0.1 M NH_4OH ; 2) the same solution in the presence of 10^{-5} g.ion Co^{2+} /liter. $S = 1/20$.

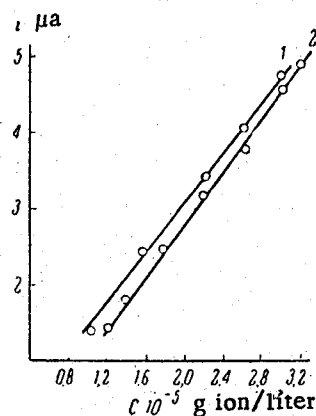


Fig. 2. Relation between the height of the catalytic wave and the concentration of nickel (1) and cobalt (2) ions.

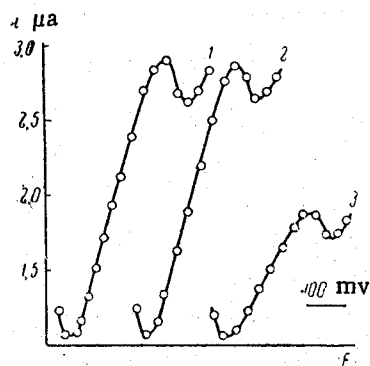


Fig. 3. Catalytic hydrogen waves caused by the cysteine complex of nickel. 1) 3×10^{-3} g.ion Ni^{2+} /liter, 6×10^{-6} M cysteine in a solution of 0.1 M $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$; 2) the same solution in the presence of 5×10^{-7} g.ion Zn^{2+} /liter; 3) the same solution in the presence of 5×10^{-7} g.ion Hg^{2+} /liter. Origin of the curves at -1.32 v (saturated calomel electrode). $S = 1/20$.

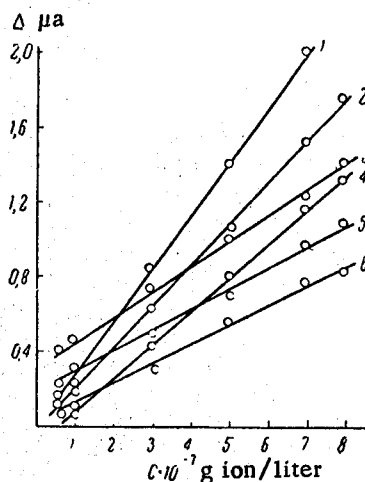
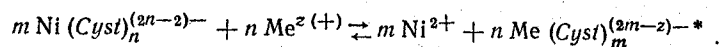


Fig. 4. The relation between the drop in the catalytic current (Δi) and the concentration of some ions. 1) Bi^{3+} ; 2) Tl^{3+} ; 3) Hg^{2+} ; 4) Cu^{2+} ; 5) Cd^{2+} ; 6) Sn^{2+} . Ni^{2+} concentration equal to 2×10^{-3} g.ion/liter; cysteine concentration 6×10^{-6} M, pH 9.

Next we examined the influence of a number of metal ions which form cysteinate complexes on the catalytic effect of cysteine. Mercury, cadmium, copper, lead, iron zinc, and manganese salts were added to a cysteine solution containing 0.1 M ammonia and ammonium chloride. Catalytic waves did not appear in one case.

The use of catalytic hydrogen waves for determining the ions of metals which form complexes with cysteine could be based on another principle. Cations which form more stable cysteinate complexes should expel cysteine

from nickel and cobalt complexes:



We used the cysteinate complexes of nickel.

Nickel ions form two complexes with cysteine $[\text{Ni Cyst}]$ and $[\text{Ni(Cyst)}_2]^{2-}$. The indices of the total instability constants are: $\text{pK}_1 = 10.48$; $\text{pK}_2 = 19.77$ [16-17].

When nickel ions are taken in excess the height of the catalytic wave is proportional to the cysteine concentration. In the presence of ions of metals which form more stable cysteinate complexes than the nickel complex, there should be a drop in the catalytic current proportional to the concentration of these ions, under conditions where their amount is commensurable with the cysteine concentration.

We examined the following cations: Hg^{2+} , Fe^{3+} , Cu^{2+} , Cd^{2+} , Bi^{3+} , Sn^{2+} , Sb^{3+} , Tl^{3+} , Tl^+ , Pb^{2+} , Zn^{2+} , Fe^{2+} , Mn^{2+} . The instability constants of the cysteinate complexes of some of these are known [18].

The table contains experimental results on the effect of this series of cations, their concentration being the same (5×10^{-7} g.ion/liter), on the catalytic wave caused by the nickel cysteinate complex. The nickel ion concentration was 3×10^{-3} g.ion/liter while the cysteine concentration was 6×10^{-6} M. Some of these results are illustrated by the polarograms shown in Fig. 3.

Effect of Some Metal Ions on the Catalytic Wave Caused by the Nickel Cysteinate Complex

Metal ion	Drop in the height of the catalytic wave (Δi), μa	Stability of the cysteinate complexes		Metal ion	Drop in the height of the catalytic wave (Δi), μa	Stability of the cysteinate complexes	
		pK_1	pK_2			pK_1	pK_2
Hg^{2+}	1.00	19.2*	45.40	Tl^{III}	1.08	12.20	18.70
Fe^{3+}	0.80		32.10	Tl^+	0		
Cu^{2+}	0.80			Pb^{2+}	0		
Cd^{2+}	0.56			Zn^{2+}	0		
Bi^{3+}	1.40			Fe^{2+}	0		
Sn^{2+}	0.72			Mn^{2+}	0		
Sb^{III}	0.62					4.1	

* This value relates to the complex of univalent copper.

As the table shows, mercury, trivalent iron, copper ions which complex cysteine more stably than nickel, depress the catalytic wave. Bismuth, tin, and antimony which also, probably, form stable cysteinate complexes, show a similar effect. Trivalent thallium ions depress the catalytic wave, presumably, by oxidizing cysteine, while cadmium exhibits the same effect by forming a precipitate. At low concentrations Pb^{2+} , Zn^{2+} , Fe^{2+} , Mn^{2+} , and Tl^+ cations do not affect the catalytic wave. When, however, the content of lead and zinc ions is of the same order as that of nickel ions, since their cysteinate complexes have a similar stability to the nickel complexes, they should affect the value of the catalytic current. The effect of high concentrations of zinc ions was confirmed experimentally.

The drop in the catalytic current is proportional to the concentration of the metal ions (Fig. 4) which expel cysteine from the nickel cysteinate complexes. Under the conditions indicated, therefore, it is possible to determine mercury, trivalent iron, copper, cadmium, bismuth, tin, antimony, and trivalent thallium ions at concentrations down to 5×10^{-8} g.ion/liter.

The method is of interest for the analysis of some pure metals (aluminum, zinc, etc) and, in particular for the analysis of nonmetals (e.g. sulfur, selenium).

SUMMARY

It has been shown that it is possible to determine low concentrations of mercury, trivalent iron, copper, cadmium, bismuth, tin, antimony, and trivalent thallium ions on the basis of the drop in the height of the catalytic hydrogen wave caused by cysteine in the presence of nickel ions.

* $\text{Cyst} = -\text{SCH}_2\text{CH}(\text{NH}_2)\text{COO}^-$.

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