THE REDUCTION OF COBALT (II) ION
IN THIOCYANATE MEDIA BY PULSE POLAROGRAPHY

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The electroreduction of cobalt(II) in aqueous thiocyanate solutions at the dropping mercury electrode depends on the thiocyanate concentration. At $[SCN^-] = 0.3$ mol/l the intermediate cobalt(I)–thiocyanate complex does exist electrokinetically and may be responsible for the appearance of a peaked catalytic wave. The predecessor species of this intermediate may be $CoSCN^+$ and $Co(SCN)_2$ in similarity to the behaviour of cobalt(II) with cyanide and azide ions.

The complex formation by cobalt(II) and thiocyanate ions has been mentioned in the literature[1,2]. Investigations using spectrophotometric methods have been made by several authors[3-5]. Our attention was directed to the electrometric methods and an extensive bibliography can be found in papers[6,7] dealing with the process of electroreduction of Co(II) in aqueous thiocyanate media on a mercury electrode. Taking into account all the arguments presented therein we tried to establish the nature of complex formation between thiocyanate and Co(II). Intending to elucidate the complex formation with SCN^- and Co(II) by potentiometric methods some preliminary studies were made using classical polarography. Just one wave was found, but further studies by pulse polarography showed two consecutive waves for the same working solution. This fact deserved a special attention and the experimental data obtained showed the possibility of existence of the Co(I) intermediate in the electroreduction of Co(II) in aqueous thiocyanate media. The present study deals with the results obtained to characterize the existence of this intermediate.

EXPERIMENTAL

Cobalt(II) perchlorate solutions were prepared by neutralizing cobalt(II) carbonate with perchlorate acid in excess just to maintain the pH around 3 to prevent the hydrolysis. The standardization of solutions was made both by the complexometric method with EDTA and by electrogravimetry. Water was bidistilled. All the other reagents used were analytical grade. The working solutions were deaerated by passing pure nitrogen previously freed from oxygen.

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The instrument used was a Pulse Polarograph Southern Analytical model A3100. The capillary characteristics, in open circuit, of the dropping mercury electrode were $m = 4.49 \cdot 10^{-4}$ g/s; $t = 2$ s. The potential of the DME was measured against a silver–silver iodide reference electrode. The temperature was 25°C in all experiments.

Co(II) solutions were made to a concentration of 10^{-4} mol/l, with varying concentrations of SCN$^-$, while the ionic strength was always kept at the 0·5 mol/l level by adding lithium perchlorate. Some experiments were made with varying concentrations of HClO$_4$ (0·5 to 5 · 10^{-3} mol/l) and the polarograms were recorded with a Metrohm Polarecord E506. Potentials were measured vs a normal calomel electrode.

RESULTS AND DISCUSSION

The normal pulse polarograms (NPP) of the working solutions are shown in Figs 1 and 2. The interpretation of these polarograms reveals that the electrode kinetic process is modified by the variation of thiocyanate concentration. In the absence of thiocyanate the wave is irreversible, involving two electrons simultaneously. As the concentration of thiocyanate increases an overvoltage decrease of 220 mV for the discharge of the cobalt ion was observed[8]. Only one wave is seen in Fig. 1a.
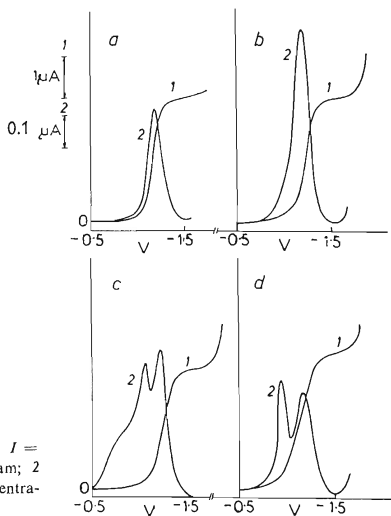

Fig. 1

Polarograms of 10^{-4} M cobalt(II); $I =$ $= 0.5$ M-(LiClO$_4$). 1 normal polarogram; 2 derivative polarogram. SNC$^-$ concentration (mol/l)- a 0; b 0·20; c 0·050; d 0·10

Increasing the thiocyanate concentration we observe the tendency to split into two waves and at 0·3M (Fig. 2b) there appear two consecutive and well defined waves of the same height, with $E_{1/2}$ equal to -0.88 V and -1.23 V, respectively. They correspond to a stepwise reduction of one electron each time. The sum of the two heights equals the height of the wave in perchlorate media, where two electrons are transferred simultaneously. With more concentrated thiocyanate solutions (1M, Fig. 2d) the two waves disappear rendering again just one wave discharge in a more anodic potential comparatively to perchlorate media.

The interpretation of these polarograms is based also on the corresponding differential pulse polarograms (DPP) of all solutions which are shown in Figs 1 and 2, where at 0·050M thiocyanate concentration (Fig. 1c) two peaks begin to appear in spite of the fact that the normal polarogram presents just one single wave, although
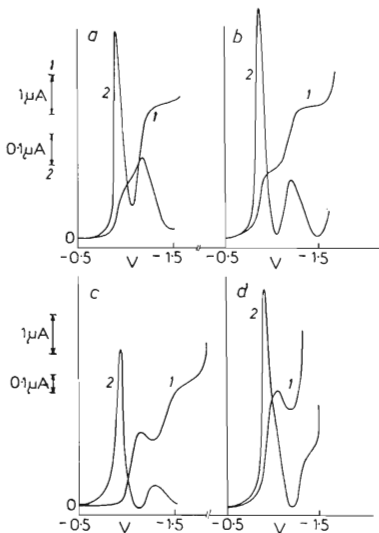

Fig. 2

As Fig. 1, but SCN$^-$ concentration (mol/l): a 0·20; b 0·30; c 0·50; d 1·0

with a slight distortion. Likewise, the two peaks in DPP improve in resolution with increasing thiocyanate concentrations until at a certain value the first peak becomes large and sharper, while the second one becomes smaller and flatter and finally disappears (Fig. 2d). This fact is a good evidence that the transfer of the first electron occurs faster, the first wave tending to reversibility, while the second electron transfers with more difficulty rendering its wave more irreversible. This behaviour of the electroreduction of cobalt(II) in thiocyanate media proves kinetically the existence of the cobalt(I) species.

Another series of polarograms made in the range of thiocyanate concentration 0·5 to 4·0 mol/l and $5 . 10^{-5}$ mol/l cobalt(II), that is, at a lower concentration of metal ion, showed still the two peaks in NPP and DPP, from 0·5 to 1·0 mol/l. Beyond this concentration and up to 4·0 mol/l the second wave disappears and the first one increases, and the single wave again involves two electrons simultaneously. As before the second electron transfer is slower than the first one. The global reduction of cobalt(II) in thiocyanate media, from 0 to 4·0 mol/l occurs gradually and the larger difference in the kinetics is found beyond $[SCN^-] = 0·5$ mol/l.

Thiocyanate, having a low ligand strength, cannot stabilize the cobalt(I) intermediate in aqueous solutions. The anion is a poor acceptor but, the cobalt complex may be adsorbed on the mercury surface by two reasons: a) SCN^- is strongly adsorbed at the mercury surface[9,10] and it can be expected that its complexes behave similarly; b) according to the molecular orbital theory and the crystal ligand field, when in the configuration of a metal ion the electrons fill the low-spin orbitals,
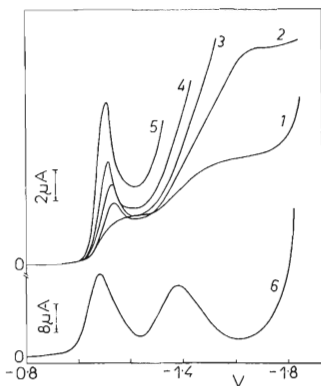

Fig. 3

Polarograms of 10^{-3}M cobalt(II), 0·30M-·SCN⁻; I: 0·5M-LiClO₄. 1 to 5 normal polarograms; 6 derivative polarogram of 1. Acid concentration (mmol/l): 1 0: 2 0·50; 3 1·0; 4 2·0; 5 5·0

paired or unpaired, the ion is prone to adsorption[11]. This is the case for nickel(II), and cobalt(I), having the same electronic configuration, can manifest some adsorption behaviour. This adsorption approach could throw some light on the mechanism of formation of cobalt(I). Thiocyanate is a good bridging ligand[12] and can be adsorbed on the mercury surface *via* the sulphur atom, bridging also the cobalt(II) ion or the complex of cobalt(II) thiocyanate *via* the nitrogen atom. The charge transfer can occur through a thiocyanate bridge by steps. At $[SCN^-] \geqq 0.3$ mol/l the delocalization of the first electron starts creating a kinetic barrier that hinders the transference of the second electron, allowing by this mechanism the existence of cobalt(I) alone.

The low state of cobalt(I) is not a stable chemical state but is the result of an electrokinetical difference in the reduction of both electrons at the DME that permits the existence of this ion for a short time, too short for detection by classical polarography, but not so for pulse polarography because of its inherently short sampling time. The differential polarograms evidence this fact.

The influence of the hydrogen ion concentration over the first wave can be seen in Fig. 3, where the catalytic wave described by Itabashi in acid solutions can be observed. The second discharge is due to the hydrogen ion as the thiocyanic acid is considered to be strong[13].

The main predecessor species of cobalt(I)thiocyanate complex seems to be Co.$NCS)^+$ and $Co(NCS)_2$ which predominate at $[SCN] = 0.3$ mol/l (ref.[14]) in similarity with the behaviour of cobalt(II) in cyanide and azide media.

This behaviour was also observed during the studies of catalytic currents involving the system azide–hydrazoic acid–cobalt(II) (ref.[15]). The formation of the cobalt(I)––azide intermediate complex occurred at an azide concentration, where the predecessor species CoN_3^+ and $Co(N_3)_2$ predominated[16].

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