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Effect of Gelatin on the Reduction of Cobalt(II) in Thiocyanate Solutions at Mercury Electrodes

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Synopsis. Reduction of cobalt(II) in thiocyanate solutions at mercury electrodes has been greatly accelerated in the presence of small amounts of gelatin. This accelerating effect results in an inhibition of the amalgamation of electrodeposited $Co(0)SCN^-$, which reacts chemically to yield CoS and CN^-. Both CoS and CN^- further stimulate the reduction of cobalt(II).

Recently, it has been shown that the reduction of cobalt(II) in thiocyanate solution at a hanging mercury drop electrode(HMDE) is accelerated by the reduction products of thiocyanate ions, cyanide and sulfide ions, produced by the chemical reduction of thiocyanate ion with the electroreduced metallic cobalt.[1] It is expected that the reduction rate of cobalt(II) in thiocyanate solution is further stimulated by the presence of surfactants, because the amalgamation of the electrodeposited cobalt is known to be inhibited by the presence of some surfactants.[2,3] It was indeed found that the reduction of cobalt(II) in thiocyanate solutions at dropping and stationary mercury electrodes was greatly accelerated in the presence of low concentrations of gelatin. This paper deals with the characteristics of the reduction wave of the above-mentioned system.

Experimental

The dropping mercury electrode(DME) had a flow rate of 0.95_6 mg s^{-1} at the controlled drop time of 4.95 s in deaerated 0.5 mol dm^{-3} $NaNO_3$ solution at -0.65 V *vs.* SCE for a mercury height of 60 cm. All the other experimental details were the same as previously described.[1] In Fig. 1, "current" means the maximum current observed just before the fall of the mercury drop.

Results and Discussion

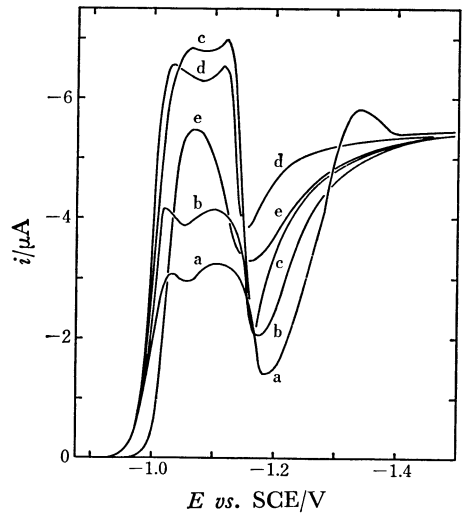

Fig. 1. Effect of concn of gelatin on the d.c. polarograms of 1 mmol dm^{-3} cobalt(II) in 0.01 mol dm^{-3} NaSCN and 0.49 mol dm^{-3} $NaClO_4$ at 25 °C. Gelatin concentration/%: (a), 0; (b), 1×10^{-3}; (c), 2×10^{-3}; (d), 5×10^{-3}; (e), 2×10^{-2}.

The influence of gelatin on the dc polarograms is shown in Fig. 1. Cobalt(II) in dilute thiocyanate solution gave a pre-wave which was produced at potentials more negative than those for the usual hydrated cobalt(II) reduction wave. This pre-wave increased in height with increase in thiocyanate concentration up to *ca.* 0.1 mol dm^{-3}. The present experiments, however, were performed with dilute thiocyanate solution, because the most significant effect of gelatin has been observed at a thiocyanate concentration below 0.03 mol dm^{-3}. Upon the addition of gelatin to the solution, the pre-wave increased in height with increase in concentration of gelatin up to *ca.* 5×10^{-3} %. With further addition of gelatin above 1×10^{-2} %, the opposite effect was observed. When trace amounts of gelatin was added, the maximum wave accompanying the hydrated cobalt(II) reduction wave observed at potentials more negative than -1.20 V was completely suppressed, and the hydrated cobalt(II) reduction wave shifted to somewhat less negative potentials. Such a shift of the reduction potential appears to be generally characteristic of the hydrated cobalt(II) reduction wave. There have been several investigations on the positive shift of the hydrated cobalt(II) reduction wave in the presence of low con-

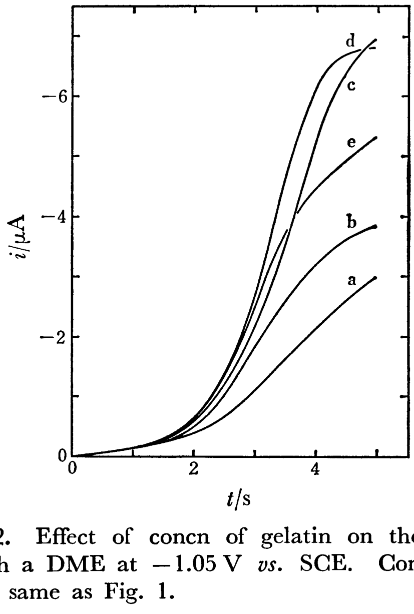

Fig. 2. Effect of concn of gelatin on the *i-t* curves with a DME at -1.05 V *vs.* SCE. Conditions are the same as Fig. 1.

centrations of some surfactants.[2,3]

The influence of gelatin on the current-time (*i*-*t*) curves for the pre-wave during the life of a mercury drop is shown in Fig. 2. The instantaneous current in a dilute thiocyanate solution in the absence of gelatin varies exponentially. This clearly indicates that the reaction mechanism of the pre-wave in dilute thiocyanate solution is autocatalytic in nature. The theoretical treatment of Laviron[4] predicts that the *i*-*t* curve varies exponentially for the catalytic polarographic wave involving a product of the electrode reaction. In the presence of gelatin, the *i*-*t* curves exhibit a sigmoid shape.

Figure 3 illustrates the influence of gelatin on the *i*-*t* curve obtained with a HMDE. In the potential region corresponding to the polarographic pre-wave, the *i*-*t* curves exhibited a maximum. With trace amounts of gelatin present, the diffusion-controlled current level is reached within several seconds. The falling portion after a maximum in the presence of gelatin follows an i-$t^{-1/2}$ relationship, indicating a diffusion-controlled mechanism.

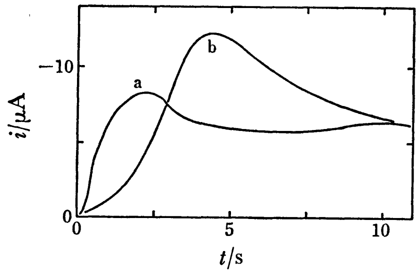

Fig. 3. *i*-*t* curves with a HMDE for the reduction of 1 mmol dm^{-3} cobalt(II) in 0.01 mol dm^{-3} NaSCN and 0.49 mol dm^{-3} $NaClO_4$ solutions in the absence (a) and presence (b) of 5×10^{-3}% gelatin. Electrode potential −1.05 V.

It has been recognized that the amalgamation of freshly deposited iron-group metals is inhibited by the presence of some surfactants.[2,3] The increase of the pre-wave height in the presence of small amounts of gelatin is accounted for by assuming an inhibition of the amalgamation of electrodeposited $Co(0)SCN^-$, which in part reacts chemically to yield CoS and CN^-. Cobalt sulfide as well as cyanide ion stimulates further reduction of cobalt(II). $Co(II)$–CN^- complex is more easily reduced at the mercury electrode than the $Co(II)$–SCN^- complex.[1] With large concentrations of gelatin present, the pre-wave becomes suppressed, gelatin then replacing the adsorbed thiocyanate ions from the surface of the electrode.

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