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THE ELECTRODE REACTION OF INDIUM(III) IN THE PRESENCE OF PENTAAMMINEIODO- AND PENTAAMMINEISOTHIOCYANATOCOBALT(III) COMPLEXES AT THE DROPPING MERCURY ELECTRODE

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Polarographic reduction waves of In(III) in the presence of pentaammineiodo- or pentaammineisothiocyanatocobalt(III) complexes have been investigated. The catalytic effect on the electrode process of In(III) by iodide or thiocyanate ions which were liberated from the cobalt(II) complexes reduced simultaneously at the electrode was confirmed experimentally. A marked difference was found in the acceleration process between thiocyanate and iodide ions of these electrode reactions.

It is well known that the reduction of indium(III) ions at the dropping mercury electrode is accelerated when iodide or thiocyanate ions are present in the solution$^{1)}$. This acceleration is explained as that an iodide or a thiocyanate ion which is adsorbed specifically on the surface of electrode becomes to be coordinated with In(III) ion to act as a bridge between the electrode and the In(III) ion and to accelerate the electron transfer. The mechanism is denoted CE$^{2)}$, where C and E mean the chemical and the electrochemical reaction, respectively. When iodo- or isothiocyanatoindium(III) species, which is surface active, is formed in the solution, the mechanism may be expressed as AE, where A means adsorption process. In addition, it is also known that many substitution-inert complexes are reduced at the electrode to substitution-labile complexes which dissociate immediately after the electron transfer takes place. These two phenomena suggested to the present authors that if the substitution-inert complex is reduced at less negative potentials than In(III) ion to a substitution-labile one which liberates immediately surface active ligands such as iodide or thiocyanate ions, the reduction of In(III) may be accelerated by the presence of such a substitution-inert complex. This kind of process may be denoted as ECAC'E' with several modifications such as AECC'E', ECC'AE' and AECDC'A'E', where D means desorption process. The existence of some of these processes has been confirmed experimentally by using pentaammineiodo- and pentaammineisothiocyanatocobalt(III) perchlorates as the substitution-inert complex and is presented in this communication.

Electrode Processes of In(III) in the Presence of Pentaamminejodocobalt(III) --- Polarograms of In(III) which were obtained in the presence of free iodide and pentaammineiodocobalt(III) ions are shown in Figs. 1 and 2, which indicate clearly that pentaammineiodocobalt(III) accelerates the reduction of In(III) as free iodide ions do, although the current accelerated by pentaammineiodocobalt(III) is much smaller than that by free iodide of the same concentration (See Table 1). The electrode processes of In(III) taking place in the presence of pentaammineiodocobalt(III) are expressed in the following:

$$[\mathrm{CoI(NH_3)_5}]^{2+} + e \rightleftharpoons [\mathrm{CoI(NH_3)_5}]^{+} \qquad (1)$$

$$[\mathrm{CoI(NH_3)_5}]^{+} + p\,\mathrm{H_2O} + (p-1)\mathrm{H}^{+} \rightleftharpoons [\mathrm{Co(H_2O)}_p\mathrm{(NH_3)}_{6-p}]^{2+} + \mathrm{I}^- + (p-1)\mathrm{NH_4}^{+} \qquad (2)$$

$$\mathrm{I}^- \rightleftharpoons \mathrm{I}^-_{\mathrm{ads}} \qquad (3)$$

$$\mathrm{I}^-_{\mathrm{ads}} + [\mathrm{In(H_2O)}_q]^{3+} \rightleftharpoons [\mathrm{InI_{ads}(H_2O)}_{q-1}]^{2+} + \mathrm{H_2O} \qquad (4)$$

$$[\mathrm{InI_{ads}(H_2O)}_{q-1}]^{2+} + 3e + \mathrm{Hg} \rightleftharpoons \mathrm{In(Hg)} + \mathrm{I}^-_{\mathrm{ads}} + (q-1)\mathrm{H_2O} \qquad (5)$$

These processes (1) to (5) may be denoted as ECAC'E'. The difference in accelerated current of In(III) obtained in the presence of free iodide and pentaammineiodocobalt(III) may be explained as follows: In the case of pentaammineiodocobalt(III), iodide ions which are liberated from the cobalt(II) complex formed electrochemically at the electrode surface diffuse back to the bulk of the solution because of the absence of free iodide ions in the solution. This and a smaller diffusion rate of the complex make the concentration of iodide ions at the electrode surface much smaller than that of the free iodide solution of the same concentration; the smaller concentration of iodide ions in turn gives a smaller accelerated current than that given by free iodide ions of the same concentration present in the solution.

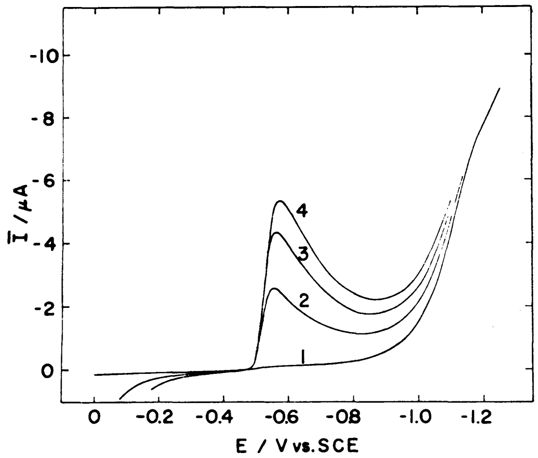

Fig. 1 Polarograms of 1 mM $In(ClO_4)_3$ obtained in the solutions containing 0.1 M $HClO_4$ and 0.9 M $NaClO_4$ (1) in the absence and in the presence of (2) 0.36, (3) 0.67 and (4) 0.92 mM iodide ions.

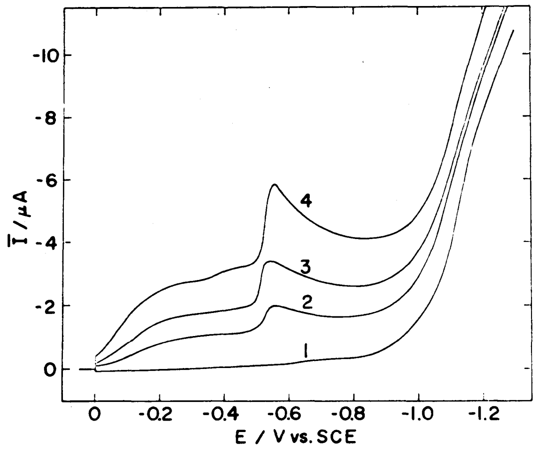

Fig. 2 Polarograms of 1 mM $In(ClO_4)_3$ obtained in the solutions containing 0.1 M $HClO_4$ and 0.9 M $NaClO_4$ (1) in the absence and in the presence of (2) 0.35, (3) 0.63 and (4) 0.99 mM pentaammineiodocobalt(III).

Table 1 Polarographic reduction currents of 1 mM In(III) at -0.700 V vs. SCE obtained at 25°C in the solutions containing 0.1 M $HClO_4$ and 0.9 M $NaClO_4$ in the presence of free iodide or pentaammineiodocobalt(III).

Conc. of I^- or $[CoI(NH_3)_5]^{2+}$ mM	$\bar{I}_{In}$/μA obtained in the presence of	
	I^-	$[CoI(NH_3)_5]^{2+}$
0.33	-1.12	-0.58
0.57	-2.05	-0.81
0.90	-3.22	-1.15
1.00	-3.66	-1.28

Table 2 Polarographic reduction currents of 1 mM In(III) at -0.700 V vs. SCE obtained at 25°C in the solutions containing 0.1 M $HClO_4$ in the presence of free thiocyanate or pentaammineisothiocyanatocobalt(III).

Conc. of SCN^- or $[CoNCS(NH_3)_5]^{2+}$ mM	$\bar{I}_{In}$/μA obtained in the presence of	
	SCN^-	$[CoNCS(NH_3)_5]^{2+}$
0.33	-1.06	-0.77
0.57	-1.83	-1.60
0.75	-2.33	-2.40
1.00	-3.03	-3.63

Electrode Processes of In(III) in the Presence of Pentaammineisothiocyanatocobalt(III) --- Pentaammineisothiocyanatocobalt(III) also accelerated the polarographic reduction of In(III), as was observed with free thiocyanate ions. The currents of In(III) obtained in both of the cases are given in Table 2. In contrast with the case of pentaammineiodocobalt(III), the acceleration by pentaammineisothiocyanatocobalt(III) was found to become greater than that by free thiocyanate ions, when the concentrations of the complex and thiocyanate ions were increased. This tendency may be explained by considering a greater ability of thiocyanate ion to coordinate with In(III). In(III) coordinated with thiocyanate ion near the electrode was first adsorbed on the electrode surface and then reduced; the electrode reaction of In(III) in the presence of pentaammineisothiocyanatocobalt(III) seems to proceed by the ECC'AE' mechanism. In addition, the processes of the AECC'E' and the AECDC'AE' mechanism also seem to proceed. The supply of thiocyanate at and/or near the electrode is nearly equal in both solutions which contain pentaammineisothiocyanatocobalt-(III) or free thiocyanate ions by the same concentration, because most of thiocyanate ions in the solution are coordinated with In(III) under the experimental conditions. Moreover, in the solution of pentaammineisothiocyanatocobalt(III), most of thiocyanate ions which diffuse from the electrode surface to the bulk of the solution may be coordinated with In(III) in the vicinity of the electrode surface to form isothiocyanatoindium(III) which diffuses back to the electrode again. This process may not be effective in the solution of free thiocyanate, because In(III) is already coordinated with thiocyanate ion and the second stability constant (K_2) is not so large as the first one (K_1).

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