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Formation and Electrochemical Behaviour of 1,10-Orthophenanthroline-Co(II) Complex

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By studying cyclic voltammetry, it is established that Co^{2+} forms a complex with ligand 1,10-orthophenanthroline. The voltamogram of formed complex, $[Co(Ph)_3]^{2+}$, presents three quaisi-reversible systems. Coulometric studies at constant peak potentials show that n = 1 for every system.

Key Words: Voltammetry, 1,10-Orthophenanthroline-Co(II) complex, Coulometry.

INTRODUCTION

1,10-Orthophenanthroline ($C_{12}H_8N_2H_2O$) forms many complex with different cations[1,2]. Electrochemistry of Co^{2+} in the present of salen, bipyridine has been studied widely[3-16]. The kinetic studies of formation the complex $[Co(Ph)_3]^{2+}$ has also been carried out[17]. We were interested to study the formation of complex(s) Co^{2+} with 1,10-orthophenanthroline ligand at glassy carbon in acetonitrile by electrochemical methods and electrochemical behaviour of formed complex(s) have been carried out.

EXPERIMENTAL

Voltammetric experiments were carried out with polarecord 747 VA stand and 746 VA trace analyzer (Metrohm Swiss). The cell was a three-electrode system consisting of an Ag/AgCl/KCl 3M with double junction, glassy carbon and a platinum wire as reference, working and auxiliary electrode, respectively. All chemical were of analytical grade (Merck) and experiments were conducted at constant temperature (25 ºC ± 0.1). Glassy carbon electrode was, always, cleaned by alumina powder and concentration of tetrabutylammunium perchlorate (TBAP) as supporting electrolyte was 0.05 M. Stock solutions of $CoCl_2$, $6H_2O$ and 1,10-orthophenanthroline (Ph) used were 0.02 mM.

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RESULTS AND DISCUSSION

We have first studied voltammograms of Co^{2+} and Ph, separately. In the case of Co^{2+}, we obtained three peaks at potentials at + 0.03, -1.02 and -1.83 volt (Fig. 1), which proves Co^{2+} does not present a reversible system in this condition. In the case of 1,10-orthophenanthroline, two cathodic potential peaks at -2.09 and -2.28 volt were observed (Fig. 2) which means two irreversible systems. In order to examine the complex(s) formation of Co^{2+} with ligand Ph, we have studied cyclic voltammetry the different solutions, in relation $\frac{[Co^{2+}]}{[Ph]}$ in proportion of $\frac{1}{6}$ to $\frac{6}{1}$. The obtained voltammograms were complicated, unless in the relation of $\frac{[Co^{2+}]}{[Ph]} = \frac{1}{3}$, that corresponds to formation of complex $[Co(Ph)_3]^{2+}$ with yellow colour, (Fig. 3).

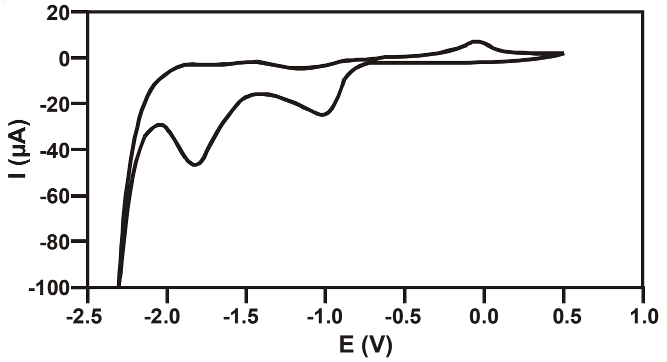

Fig. 1. Voltammogram of Co^{2+} 2 mM + TBAP 0.05 M in acetonitrile at glassy carbon electrode and V = 150 mv/s

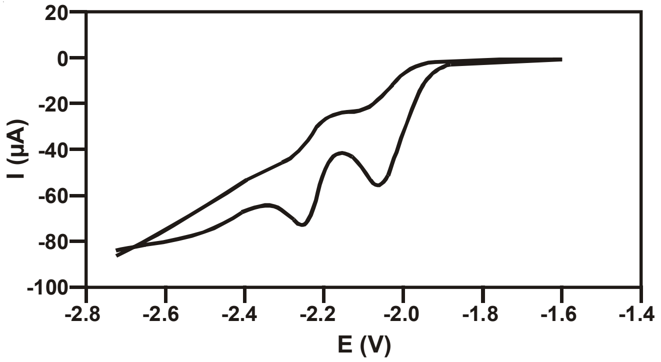

Fig. 2. Voltammogram of 1,10-orthophenanthroline 2 mM + TBAP 0.05 M in acetonitrile at glassy carbon electrode and V = 100 mv/s

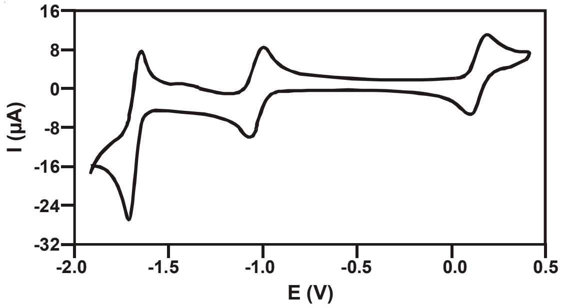

Fig. 3. Voltammogram of solution having $\frac{[Co^{2+}]}{[Ph]} = \frac{1}{3}$ + TBAP 0.05 M in acetonitrile, at glassy carbon electrode and V = 200 mv/s

In conformation of this result, we, have examined, first, polarographic behaviour of this solution by DC and DPP (Fig. 4a-b) and then by coulometry at peak potentials for the solution initial concentrations of $[Co–(Ph)_3]^{2+}$ 2 mM + TBAP 0.05 M in acetonitrile. The present quantitative coulometric measurements proved that n = 1 in three cases. The current investigations also proved the diffusion regime is established for every system, because of I_p varies linear *vs.* $v^{½}$ (Fig. 5) from 200 to 1000 mV/s.

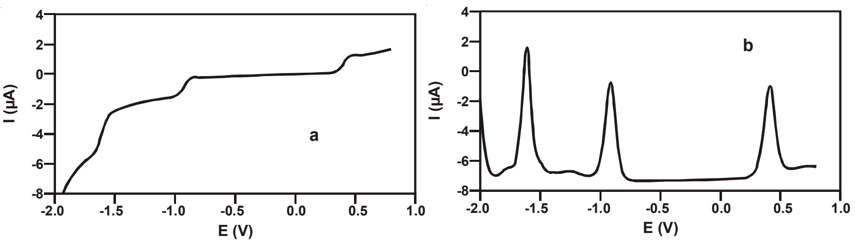

Fig. 4. Polarographic studies of solution $[Co(Ph)_3]^{2+}$ 2 mM at glassy carbon electrode: a) DC (V = 7.5 mv/s) and b) DPP

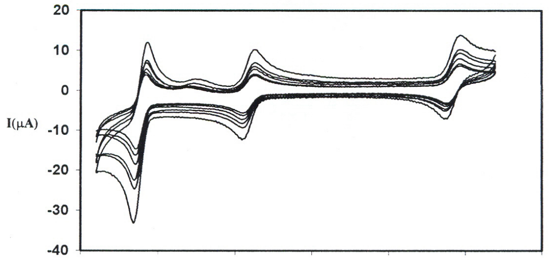

Fig. 5. Voltammograms of solution $[Co(Ph)_3]^{2+}$ 2 mM + TBAP 0.05 M in acetonitrile at glassy carbon electrode and V = 100, 300, 400, 500, 600, 1000 mv/s

Conclusion

Our results demonstrate that Co^{2+} and Ph ligand, in acetonitrile + TBAP solution, forms $[Co(Ph)_3]^{2+}$ complex and this complex presents three quasi - reversible system with characteristic as below:

System	E_{pa}/V	E_{pc}/V	ΔE_p/V	I_{pa}/I_{pc}
$[Co(Ph)_3]^{3+} / [Co(Ph)_3]^{2+}$	0.45	0.35	0.10	$\simeq$ 1.00
$[Co(Ph)_3]^{2+} / [Co(Ph)_3]^{+}$	-0.88	-0.97	0.09	= 1.00
$[Co(Ph)_3]^{+} / [Co + 3(Ph)]$	-1.60	-1.79	0.19	0.56

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