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Studies of electrochemical behavior of composite electrode "[Co-(ortophenontroline)$_3$]$^{2+}$ + graphite" in aqueous and THF media

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ABSTRACT

In this research, we were interest to study the electrochemical behaviour of modified composite electrode" [Co-Ph$_3$]$^{2+}$, 2ClO$_4^-$complex" mixed with "graphite powder", at different per cent weights and pressures in aqueous and THF media. According to our results in aqueous solution, 0.1M NaClO$_4$, one irreversible system Co^{II}/Co^{I} ($\Delta E_p \cong 250$ mv) and in "THF + TBAP 0.1M, two irreversible systems Co^{II}/Co^{II} and Co^{II}/Co^{I}and appear and the later is more irreversible. The main idea is to verify electro-catalytic assisted behavior of this electrode.

Key words: composite electrode, cyclic voltammetry, 1,10-orthophenantroline-Co (II) complex and Tetrahydrofuran.

INTRODUCTION

Investigation of homogenous catalysis for oxydo-reduction reactions in liquid phase, by organometallic-transition has been developed widely like as industrial preparation of acetaldehyde from ethylene (Waker process)[1], industrial preparation of olefin by Rhodium complex (Wilkinson catalysis)[2]. In this regard, for oxydo-reduction reactions may be able to find some working electrode to have catalytic effect[3-9], the reason that in this work, our principle aim was to study electrochemical behaviour of composite electrode [Co-Ph$_3$]$^{2+}$ in different convenience media.

EXPERIMENTAL

All chemical were of analytical grade (Merck). Experiments were conducted at constant temperature (25°C ± 0.1). The cell was a three-electrode system consisting of an Ag/AgCl/KCl3M, platinum and "composite electrode" as reference, auxiliary and working electrode. Measurements were carried out with a Polarograph 746 VA Trace Analyzer and 747 VA stand (Metrohm, Swiss). In order to compare more exactly the obtained voltammograms, we pretreated "composite electrode" by pre-electrolysis at 250 mv for 120 s.

The preparation of [Co-Ph$_3$]$^{2+}$ complex was carried out by chemical method as below: we dissolved 3×10^{-4} mole of ligand and 1×10^{-4} mole of $CoCl_2$, $6H_2O$ in 20ml methyl alcohol, and then added 0.75 ml of $NaClO_4$ saturated solution. In this condition,[Co-Ph$_3$]$^{2+}$ complex precipitate. The deposit, after filtering and washing by ethyl alcohol was dried at 80°C for one hour (the yield was 93%). We prepared mixed and homogenous different "composite electrode" of complex, always 100 mg, (in 30, 50, 70% w/w of complex) at different pressures (2, 3.5 and 5 tons) in a netted platinum with 12 mm diameters as working electrode.

RESULTS AND DISCUSSION

a) Aqueous solution (0.1M $NaClO_4$)

In the present study, we study electrochemical behaviour by cyclic Voltametric method. According to our results, one irreversible system appears, Co^{II}/Co^{I} (Fig. 1).

In the present study, Table -1 shows some electrochemical characteristics of our results that show the system Co^{II}/Co^{I} will be more irreversible when "composite electrode" is more pressed, or contained more quantity of graphite.

We have focused our investigations, on composite electrode (50%, 2T) that presented more reproducible results, at scan rates between 0.1 to 1 mv/s (table 2), and we have observed the same results as previously (table 1). Also we have studied the variations of pick current, I_p, versus scan rate, v, according the relation , $I_p=\alpha v\beta$,and we obtained β=0.25and this value is influenced by relative "composition" more than "pressure". Finally, in this medium the reduction of solvent predominates.

b) Effect of pH- we have studied the effect of pH between 1 to 10, only for composite electrode (50%, 2T) at v=0.5 mv/s. The results are collected in table(3). These results demonstrate that system Co^{I}/Co^{II} is irreversible and "composite electrode" will be decay at elevated pH and color of medium changes to yellow.

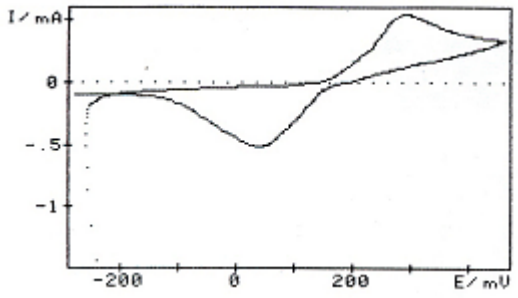

Fig. -1: Voltammogram of composite electrode (70%, 2T) at aqueous solution (0.1M $NaClO_4$), V=0.5 mv/s, $\Delta E_p \cong$ 225mv.

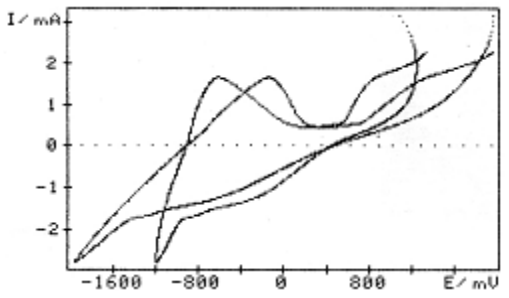

Fig. -2: Voltammogram of composite electrode (30%, 2T) at THF + TBAP 0.5M, v=0.5 mv/s

Table - 1: Electrochemical characteristics of composite electrodes: 30, 50, 70%, 2T and 50 %, 5T.

Composite electrode	Scan rate (mv/s)	E_{pa}	E_{pc} (mv)	ΔE_p	I_{pa}/I_{pc}	Q_a (mC)	Q_c	$\frac{Q_a}{Q_c}$
30%2T	0.5	271	30	241	0.93	194.1	195.0	0.99
30%2T	1	349	18	231	0.95	116.7	106.4	1.09
50%2T	0.5	276	40	236	0.98	83	91.7	0.90
50%2T	1	261	13	248	0.86	121	140	0.86
50%5T	0.5	285	46	239	0.92	57.4	60.4	0.95
50%5T	1	292	13	279	0.76	28.3	44.8	0.63
70%2T	0.5	284	41	243	0.75	68.8	116.6	0.59
70%2T	1	289	15	274	0.99			0.88

Table -2: Electrochemical characteristics of "composite electrode" 50%, 2T

scan rate(mv/s)	E_{pa}	E_{pc} (mv)	ΔE_p	I_{pa}/I_{pc}	Q_a (mc)	Q_c	Q_a Q_c
0.1	266	51	215	0.62	234.1	516.4	0.56
0.3	296	35	261	0.96	123.7	116.6	1.34
0.5	283	28	255	1.00	113.4	114.8	0.98
0.7	271	21	350	0.39	51.5	108.0	0.47
1.0	291	16	275	0.40	57.5	218.1	0.26
1.3	310	14	296	0.92	41.6	53.4	0.77
1.6	306	34	272	0.88	35.4	48.7	0.72
2	332	52	280	1.12	28.5	21.8	1.30

c) Organic medium (THF + TBAP 0.5M) – it must mention one difficult in these studies, is to find a medium that the complex is not soluble. THF is one convenience in this respect. According to our results two irreversible systems appears for composite electrode 30% and 70%, 2T. We obtained system Co^{II}/Co^{I} is more irreversible than Co^{III}/Co^{II} . As an example, we present the voltammogram of composite electrode (30%, 2T) in two consecutives cycle.

Table - 3: Effects of pH for composite electrode (50%, 2T) at v=0.5 mv/

pH	E_{pa}	E_{pc} (Mv)	ΔE_p
1	263	4	259
2	404	18	386
4	368	42	326
6	338	136	202
8	259	129	230
10	290	85	205

The voltammograms are not symmetric and Q_a/Q_c are very far from unity. we can present some electrochemical characteristic of systems Co^{III} / Co^{II} / Co^{I} in THF + TBAP 0.5M as below (table 4).

Conclusion

Composite electrode $[Co\text{-}Ph_3]^{2+}$,$2ClO_4^-$ in aqueous medium (0.1M $NaClO_4$ and pH between 1 to 10) presents only one irreversible system, whereas, in THF + TBAP 0.5 M, two irreversible systems: Co^{III}/Co^{II} and Co^{II}/Co^{I} appear, and the first is more irreversible than the second. Consequently, THF medium seems more convenience for electro-catalytic reactions if some oxydo-reduction steps assist in the desired reaction.

Table - 4: Electrochemical characteristics of some composite electrodes in THF + TBAP 0.5 M.

Composite	Co^{II} / Co^{I} E_{pa}	E_{pc} (mv)	ΔE_p	Co^{III} / Co^{II} E_{pa}	E_{pc} (mv)	ΔE_p
50 % , 2T	-774	-956	182	728	-234	962
50 % , 2T	-745	-915	170	890	-306	1196
50 % , 2T	-714	-896	185	809	-115	942
70 % , 2T	-657	-910	253	575	-23	552
70 % , 2T	-630	-840	257	604	-24	628

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