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Effect of pH on the Electrochemical Redox Behavior of Co^{2+} in Acetate Buffer Solution

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Abstract

The electrochemical redox behavior of transition metal ion Co^{2+} at different pH in acetate buffer solution has been investigated using cyclic voltammetry and differential pulse voltammetry at glassy carbon electrode (GCE). In cyclic voltammograms (CVs), Co^{2+} shows a pair of cathodic and a pair of anodic peak. The peak potential separation and peak current ratio reveals that the redox process of the redox couples, Co^{2+}/Co^{+} and Co^{+}/Co followed a quasi-reversible behavior and are two step one-electron transfer processes. The electrochemical processes are diffusion controlled. The nature of CV of Co^{2+} has greatly influenced by the potential scan rate and solution pH. With increasing scan rate both cathodic peaks shifted towards negative potential and first cathodic peak was eventually diminished. In the reverse direction, unexpected behavior such as distinguishable second anodic peak, identical heights of two anodic peaks, three humps like peaks and finally domination of second anodic peak were noticed. However, in lower pH all the above mentioned behavior appeared with higher scan rate. While at higher pH of the solution the peculiar behavior was found at lower scan rate. Nevertheless, at pH 6.5, it demonstrated intense cathodic peaks and a very large anodic peak at all scan rates.

Keywords: Cyclic voltammetry, electrochemical processes, acetate buffer.

I. Introduction

Transition metals have great importance because of their functions in the living systems. Most of the first row transition metals are important for enzymes[1]. They have one or both of two important properties such as some readily change oxidation state and acting as critical redox couples. They are biologically important and can form complexes with different ligands. Transition metals are used as catalysts for the synthesis of carbon-carbon bonds in organic compounds. Palladium complexes are efficient catalyst in reactions involving nucleophilic substitutions on allylic acetates[2-9], Nickel complexes have also been used for the preparation of many organic compounds[10]. Simple cobalt salts of the type $Co^{II}X_2$ (X = Br, Cl) have been proved to be a very good and efficient catalyst precursors for the electrochemical and chemical synthesis of carbon-carbon bonds[11-16] and in the preparation of many organic compounds[17-19].

Electrodeposited cobalt is usually used as functional coatings because of its high temperature resistance and anti-oxidation properties, and cobalt alloy electrodeposits[20-22] and multilayer cobalt electrodeposits[23,24] have also attracted a great interest due to their advanced magnetic properties. Transition metal complexes are capable of catalyzing the reduction of protons to dihydrogen at low over potentials, an exciting challenge for coordination chemists. Cobaltocene, metalloporphyrins and certain macrocyclic complexes of cobalt, affect catalytic hydrogen evolution either the presence of sacrificial chemical reductants or electrocatalytically. However, more attention must be paid to the exploration of the electrochemical behavior and redox mechanism of the cobalt ions. To understand the insight of the electrocatalytic behavior of cobalt species, the details electrochemical behavior of Co^{2+} ion is essential. In this study the electrochemical redox behavior of Co^{2+} in acetate buffer solution at various pH (3.5, 4.0, 4.5, 5.0, 5.5, 6.0 and 6.5) has been presented. Cyclic voltammetry and differential pulse voltammetry have been chosen because of their potential ability in investigating the redox behavior of electroactive species.

II. Experimental

Material and methods

Analar grade cobalt(II) perchlorate hexahydrate have been purchased from Sigma Aldrich and used without further purification. Potassium chloride was purchased from BDH, England. For the preparation of acetate buffer solution, extra pure acetic acid (BDH, England) and sodium acetate (Merck, Germany) were used for maintaining the pH of the solution. All aqueous solutions were prepared in de-ionized water obtained from Milli-Q water purification system. The experiments were carried out at room temperature.

Equipments

A three electrode electrochemical system consists of glassy carbon electrode as working electrode, Ag/AgCl (satd. KCl) as reference electrode and platinum wire as counter electrode was used. Cyclic voltammetry and differential pulse voltammetry were performed using computerized electrochemical system, Model CHI 620D, Electrochemical

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Workstation by CHI Inc., USA. Solution pH was measured by pH meter-Metller Toledo, Germany.

Preparation of stock solution

The buffer solution was prepared by mixing requisite volume of 0.1 M $CH_3COONa.3H_2O$ and 0.1 M CH_3COOH solution. 0.1 M $CH_3COONa.3H_2O$ and 0.1 M CH_3COOH solutions were prepared using 50% ethanol-water mixer individually. Stock solution of 0.8 mM Co^{2+} was prepared using analar grade Co(II) perchlorate hexahydrate salt and acetate buffer solution as solvent.

Preparation of working electrode

Electrode preparation includes the polishing and conditioning of the electrode. At the beginning of each experiment, the working electrode was polished with alumina slurry on the surface of water resistant polishing cloth. It was rinsed with plenty of de-ionized water and the whitish alumina was wiped off with a clean tissue paper.

III. Results and Discussion

Electrochemical redox behavior of Co^{2+} in acetate buffer solution was investigated at GCE with different scan rate. The effect of pH (3.5-6.5) in acetate buffer solution was also examined.

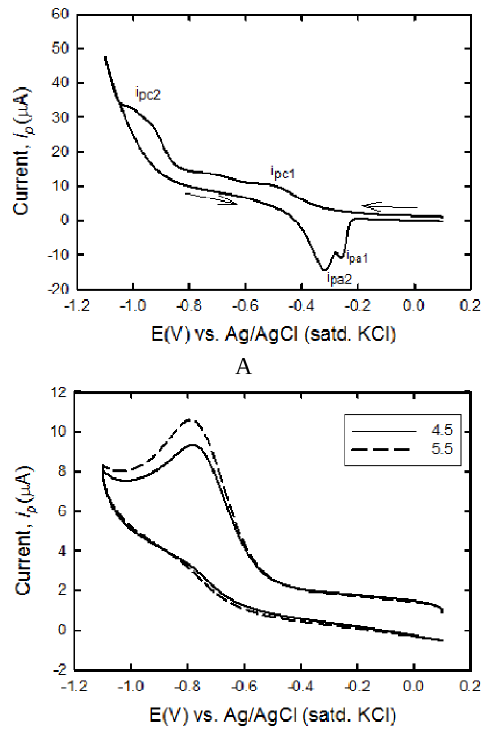
Cyclic voltammetric investigation of Co^{2+} in acetate buffer solution

Cyclic voltammetric study of 0.8 mM Co^{2+} in acetate buffer solution at different pH value (3.5, 4.0, 4.5, 5.0, 5.5, 6.0 and 6.5) was investigated at GCE within the potential window of +0.10 to -1.10 V. Fig. 1(A) shows a CV of 0.8 mM Co^{2+} in acetate buffer solution with scan rate of 100 mVs^{-1} at pH 4.5. In the forward scan two cathodic peaks, i_{pc1} and i_{pc2} and a hump like peak at about -0.518, -1.002 V and -0.750 V were found respectively. While in the reverse scan two anodic peaks, i_{pa1} and i_{pa2} at about -0.260 and -0.318 V were observed.

For identification of the hump like peak, CVs of acetate buffer solution has been recorded and CVs are shown in Fig. 1(B). The peak potential exactly matches with the position of hump like peak which is mentioned in the Fig. 1(A).

Effect of scan rate on the voltammetric response of Co^{2+}

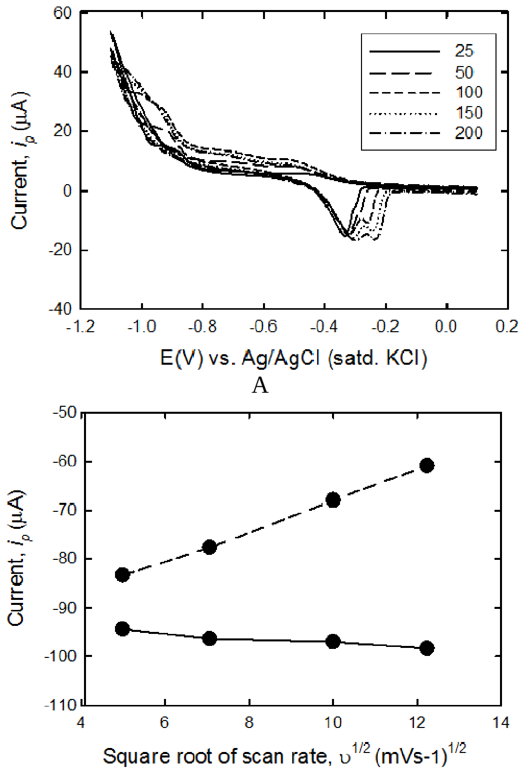
Effect of scan rate on the electrochemical response of Co^{2+} under the identical condition (0.8 mM Co^{2+} at pH 4.5) was examined by recording CVs of Co^{2+} with scan rate from 10 to 900 mVs^{-1}. The recorded voltammograms of scan rate 25, 50, 100, 150 and 200 mVs^{-1} is shown in Fig. 2(A). It was found that with the increase of scan rate, the cathodic and anodic peak current increased.



A

B

Fig. 1. (A) CV of 0.8 mM Co^{2+} in acetate buffer solution at pH 4.5 with scan rate 100 mVs^{-1} at GCE and **(B)** CVs of acetate buffer solution at pH 4.5 (solid) and 5.5 (long dash) with scan rate 100 mVs^{-1} at GCE.



A

B

Fig. 2. (A) CVs of 0.8 mM Co^{2+} at pH 4.5 with scan rate of 25 (solid), 50 (long dash), 100 (short dash), 150 (dot) and 200 (dash dot) mVs^{-1} at GCE and **(B)** Anodic peak current, i_{pa} (solid) and cathodic peak current, i_{pc} (dash) as a function of square root of scan rate.

The observation suggests that the electrode process is diffusion controlled in acetate buffer medium. Moreover, cathodic peaks were slightly shifted towards negative potential, while the anodic peaks were moved a little towards positive potential with increasing scan rate. This observation indicates that there is a tendency of the redox process shifted from quasi-reversible to irreversible direction. The obtained voltammograms of Co^{2+} are analyzed and various parameters such as anodic and cathodic peak current (i_p), anodic and cathodic peak potential (E_p), peak potential separation (ΔE_p), peak current ratio (i_{pa}/i_{pc}) are tabulated in Table 1. The peak potential separation and peak current ratio reveals that the redox process of cobalt system is quasi-reversible. Moreover, the shifting of the peak potential at various scan rates indicates quasi-reversibility of the redox process, which is also characterized by the shape and separation of the cathodic and anodic peak.

Table 1. Data obtained from the CVs of 0.8 mM Co^{2+} in acetate buffer solution with different scan rate at pH 4.5.

Scan rate, v (mVs^{-1})	CPC, i_{pc2} (µA)	Anodic peak current (µA)		CPP, E_{pc2} (mV)	Anodic peak potential, (mV)		PCR i_{pa2}/i_{pc2}	$\Delta E_p = E_{pa2} - E_{pc2}$
		i_{pa1} (-)	i_{pa2} (-)		E_{pa1} (-)	E_{pa2} (-)		
25	4.732	17.49	3.925	892.2	334	299.7	3.590	592.5
50	5.931	15.27	6.227	935.1	323	285.9	2.574	649.4
100	10.80	14.09	12.361	1009.2	318	260.1	1.304	749.1
150	13.04	14.47	13.832	1028.2	310	237.7	1.061	790.5
200	-	14.74	20.205	-	299	234.4	-	-

CPC = Cathodic peak current, CPP = Cathodic peak potential, PCR = Peak current ratio

A plot of peak current versus square root of scan rate has been drawn and it is apparent (Fig. 2(B)) that the peak current for the electrochemical redox reaction of Co^{2+} in acetate buffer has linear relationship with square root of scan rates. This observation is again in favor of the fact that the electrode process is diffusion controlled. The ratio of the oxidation peak current with its corresponding reduction counterpart (i_{pa2}/ i_{pc2}) is about 1.061-3.590.

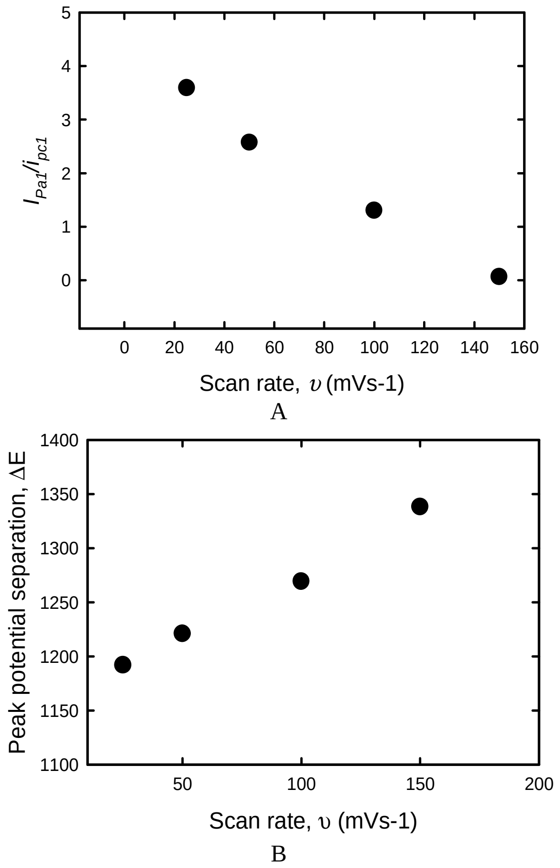


Fig. 3. (A) Peak current ratio (i_{pa}/i_{pc}) dependence on scan rate, and **(B)** Variation of peak potential separation with scan rate of 0.8 mM Co^{2+} at pH 4.5

It is found (Fig.3 (A)) that the peak current ratio is decreased with the increasing of scan rate. Also the peak potential separation (ΔE_p) is in between 592.5-790.5 mV. It is increased with the variation of scan rate (Fig. 3(B)). These observations suggest that the redox process is a quasi-reversible reaction rather than a reversible reaction.

In presence of chloride ion, Cl^-, the first electron transfer leads to a Co^+ species which was stable for scan rates above 10 mVs^{-1}. Under these conditions, the reduction of $CoCl_2$ is mono-electronic and the CV showed quasi-reversible behavior. Conversely, at lower scan rates, the electrogenerated Co^+ species undergoes disproportionation leading to solid Co(0) along with the release of half the starting $Co(II)Cl_2$. This phenomenon has a good agreement with the previous studies[25, 26].

The electrochemical redox mechanism can be written as follows:

$$Co(II)Cl_2 + e \leftrightarrow Co(I)Cl + Cl^-$$

$$Co(I)Cl \rightarrow \tfrac{1}{2}Co(s) + \tfrac{1}{2}Co(II)Cl_2$$

$$\tfrac{1}{2}Co(II)Cl_2 + \tfrac{1}{2}e \leftrightarrow \tfrac{1}{2}Co(I)Cl + \tfrac{1}{2}\,Cl^-$$

And overall reduction reaction observed at lower scan rate:

$$Co(II)Cl_2 + 2e \rightarrow Co(s) + 2Cl^-$$

If the scan rate was increased, the disproportionation reaction was progressively kinetically frozen and more and more Co^+ remains in the diffusion layer when its reduction potential was reached; the reduction of Co^+ also leads to solid Co(s).

Effect of pH on the cyclic voltammetric response of Co^{2+}

Cyclic voltammetric response of Co^{2+} in acetate buffer solution at pH 3.5

The effect of pH on the voltammetric behavior of the redox reaction of Co^{2+} in acetate buffer solution at pH 3.5 has been investigated at GCE. The recorded voltammograms at pH 3.5 (Fig. 4) demonstrates that at lower scan rate (10 mVs^{-1}), in the cathodic region a hump like peak and a distinguishable cathodic peak at about -0.665 and -0.974 V were found while a sharp anodic peak at about -0.291 V was visualized in the anodic region. However, at about 40 mVs^{-1} scan rate, two anodic peaks were found meanwhile both of the cathodic peaks showed lower peak heights. The two anodic peaks remained unchanged up to the scan rate of 68 mVs^{-1} while the cathodic peaks were diminished. After the scan rate of 75 mVs^{-1}, only one anodic peak was observed in the voltammograms.

Cyclic voltammetric response of Co^{2+} in acetate buffer solution at pH 4.0 and 4.5

The voltammetric response of 0.8 mM Co^{2+} in acetate buffer solution at pH 4.0 and 4.5 were also carried out. The voltammograms obtained for 0.8 mM Co^{2+} in acetate buffer solution at scan rate of 100 mVs^{-1} at two different pH are shown in Fig. 5. For both the pH, the voltammograms showed two cathodic and two anodic peaks at a scan rate of 100 mVs^{-1}. However, at lower scan rate (10-30 mVs^{-1}) two cathodic and an intense anodic peak were observed in case of pH 4.0. While at pH 4.5, two cathodic peaks and one intense anodic peak was found at the scan rate of 10-25 mVs^{-1}. With the increase of scan rate the anodic peak height of peak, $i_{pa2}$was decreased and i_{pa1} was increased. Both the anodic peaks were identical heights at the scan rate of 210 mVs^{-1} for pH 4.0, and 180 mVs^{-1} for pH 4.5. Again with the increase of scan rate the reverse behavior was observed and at the very high scan rate (900 mVs^{-1}) peak, i_{pa2} was disappeared for both the pH and only i_{pa1} was existed.

Cyclic voltammetric response of Co^{2+} in acetate buffer solution at pH 5.0 and 5.5

Electrochemical study of 0.8 mM Co^{2+} in acetate buffer solution at pH 5.0 and 5.5 has also been performed. Both these media the CVs (Fig. 6) presented were almost identical in character, consists of two cathodic peaks, a distinguishable anodic peak, at lower scan rate. Additionally, in the forward direction (at lower scan rate) distinguishable cathodic peak, i_{pc2} was found but with the increase of scan rate it is shifted towards negative potential and eventually disappeared at higher scan rate.

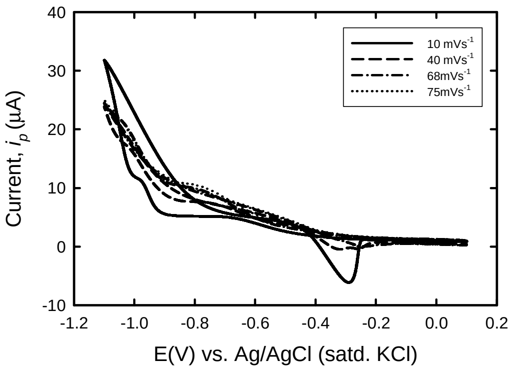


Fig. 4. CV of 0.8 mM Co^{2+} in acetate buffer solution at pH 3.5 with scan rate of 10 (solid), 40 (medium dash), 68 (dash dot) and 75 (dot) mVs^{-1} at GCE.

The appearance of second anodic peak, i_{pa1} was observed for both pH, and in different scan rate it was dominated. Table 2 shows the observed data obtained from the recorded voltammograms of the Co^{2+} species at pH 5.0 and 5.5. The overall electrochemical behavior of Co^{2+} is almost similar with those of at pH 4.0 and 4.5.

Cyclic voltammetric response of Co^{2+} in acetate buffer solution at pH 6.0

The voltammetric response of Co^{2+} in acetate buffer solution at pH 6.0 has also been recorded. The voltammogram obtained for 0.8 mM Co^{2+} in acetate buffer solution with scan rate 20 mVs^{-1} at pH 6.0 is shown in Fig. 7. The voltammogram showed two cathodic peaks, i_{pc1} and i_{pc2}, and two anodic peaks, i_{pa1} and i_{pa2} at the scan rate of 20 mVs^{-1}.

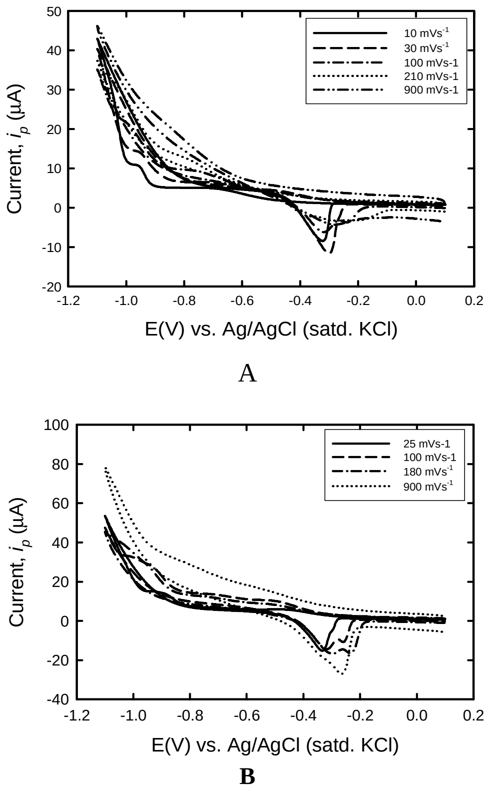
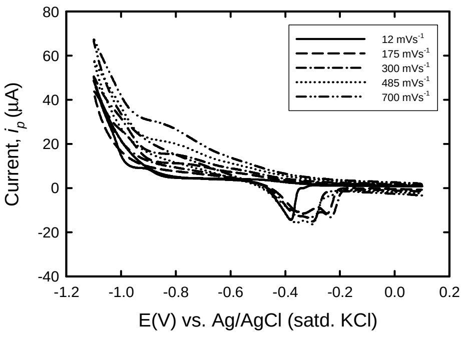


Fig. 5. CVs of 0.8 mM Co^{2+} in acetate buffer solution with scan rate of 10 (solid), 30 (medium dash), 100 (dash dot), 210 (dot), 900 (dash dot dot) mVs^{-1} at (A) pH 4.0 and 25 (solid), 100 (medium dash), 180 (dash dot), 900 (dot) mVs^{-1} at (B) pH 4.5.



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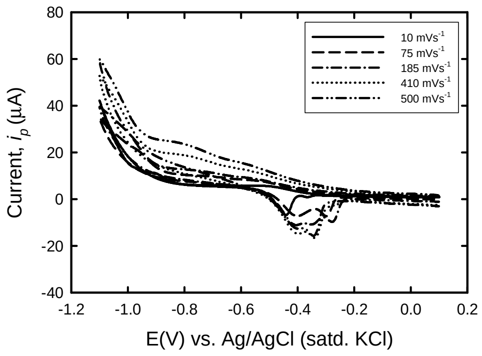


B

Fig. 6. CVs of 0.8 mM Co^{2+} in acetate buffer solution with scan rate of 12 (solid), 175 (medium dash), 300 (dot dash), 485 (dot), 700 (dash dot dot) mVs^{-1} at (A) pH 5.0 and 10 (solid), 75 (medium dash), 185 (dot-dash), 410 (dotted), 500 (dash-dot-dot) mVs^{-1} (B) pH 5.5.

Table 2. Effect of scan rate on CVs of 0.8 mM Co^{2+} at pH 5.0 and 5.5.

Pattern of the peaks	Scan rate (mVs^{-1}) at pH 5.0	Scan rate (mVs^{-1}) at pH 5.5
Distinguishable i_{pa1}	12	10
Almost identical i_{pa1} and i_{pa2}	175	75
Quasi state (three peaks appeared) of i_{pa1} and i_{pa2}	300	185
Again visibility of two anodic peak	485	410
Dominating i_{pa1}	700	500

However, at lower scan rate (10 mVs^{-1}) two cathodic peaks, and an intense anodic peak, i_{pa2} and hump like peak, i_{pa1} was observed. With the increase of scan rate the peak height of i_{pa2} was decreased and i_{pa1} was increased gradually, and both the anodic peaks were identical in heights at the scan rate 75 mVs^{-1}. However, with increasing scan rate three peaks were appeared at scan rate of 175 mVs^{-1}, and then at 410 mVs^{-1}, among them, i_{pa1} was dominating peak. Moreover, cathodic peak i_{pc2} was slightly shifted towards negative potential and eventually diminished, while the peak i_{pc1} is moved a little towards negative potential with scan rate.

Cyclic voltammetric response of Co^{2+} in acetate buffer solution at pH 6.5

Cyclic voltammetric behavior of Co^{2+} in acetate buffer solution at 6.5 has been carried out. Fig. 8(A) shows the CV of 0.8 mM Co^{2+} in acetate buffer solution in an identical condition. In the forward scan two cathodic peaks, i_{pc1} and i_{pc2} at about -0.548 and -0.897 V while in the reverse scan an intense broad anodic peak, i_{pa1} at about -0.372 V were observed. For the verification of the intense broad peak, differential pulse voltammetry (DPV) was performed and it was visualized that the broad peak consists of two peaks (Fig. 8(B)).

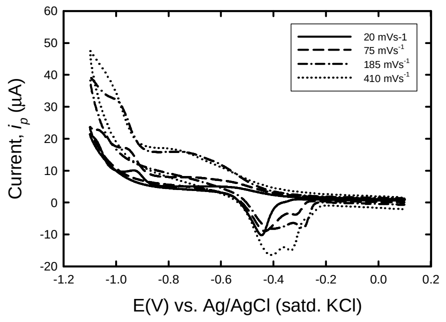
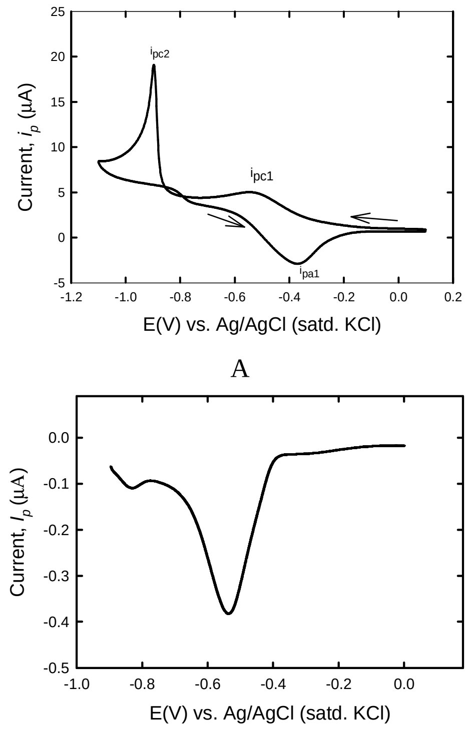


Fig. 7. CV of 0.8 mM Co^{2+} in acetate buffer solution with scan rate of 20 (solid), 75 (medium dash), 185 (dot dash), and 410 (dot) mVs^{-1} at pH 6.0.



B

Fig. 8.(A) CV of 0.8 mM Co^{2+} in acetate buffer solution at pH 6.5 with scan rate 10 mVs^{-1}, (B) Differential pulse voltammograms of Co^{2+} in identical condition.

The voltammetric behavior of Co^{2+} has also been carried out with various scan rate at pH 6.5. With increasing scan rate it is found that both the cathodic peaks were shifted significantly towards negative direction. Among all the pH, the sharp and well defined peaks were observed in the pH 6.5. This condition may be useful for the determination of cobalt species in various environmental samples as needed.

Several reports[27,28] explained that during the electrochemical reduction of Co^{2+} from aqueous solution, the hydrogen evolution reaction takes place more readily because of its position in the emf series. This may lead to formation of OH$^-$ ions causing local pH increase in the diffusion layer. It was reported[29] that a mechanism of cobalt deposition occur for the formation of CoOH$^+$ and Co(OH)$_2$. Variation of the pH in the vicinity of the cathode and deposition of cobalt through hydroxide mechanism can be shown by the following ways:

$$2H_3O^+ + 2e \rightarrow H_2 + 2H_2O$$
$$2H_2O + 2e \rightarrow H_2 + 2OH^-$$

At lower pH, the cathodic surface is covered by the hydrogen and the reaction proceeded as follows:

$$Co(II) + OH^- \rightarrow CoOH^+$$
$$H^+ + e \rightarrow H_{ads}$$
$$CoOH^+ + H_{ads} + 2e \rightarrow Co(s) + OH^- + H_{ads}$$

At higher pH, the reactions proceeded as follows:

$$Co(II) + 2OH^- \rightarrow Co(OH)_2$$
$$Co(OH)_2 + e \rightarrow Co(OH)_{ads} + OH^-$$
$$Co(OH)_{ads} + e \rightarrow Co(s) + OH^-$$

IV. Conclusion

Cyclic voltammetric investigations of Co^{2+} show a pair of cathodic and a pair of anodic peaks. The peak potential separation and peak current ratio reveals that Co^{2+}undergoes redox processes which are two steps one-electron transfer processes. The results further indicated that the redox processes were quasi-reversible in nature and diffusion controlled. Solution pH and scan rate has a great influence on the CV of Co^{2+}. In forward direction, with increasing scan rate both cathodic peaks shifted towards negative potential and first cathodic peak was eventually diminished. In the reverse direction, unexpected behaviors such as distinguishable second anodic peak, identical heights of two anodic peaks, three humps like peaks and finally domination of second anodic peak were found. However, all the above mentioned behaviors were appeared in lower pH at higher scan rate. While at higher pH of the solution the peculiar behavior was found at lower scan rate. Nevertheless, it demonstrated intense cathodic peaks and a very large anodic peak around the neutral pH (6.5) at all scan rates.

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