Research note

Cyclic Voltammetry of Cobalt Chloride with L-Carrageenan (LK) Using Glassy Carbon Electrode

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ABSTRACT

The redox behavior of cobalt chloride was studied voltammetrically in the presence and absence of L-Carrageenan (LK) as a natural polymer using glassy carbon electrodes in 0.1 M KCl supporting electrode. The interaction of $CoCl_2$ with L-Carrageenan (LK) has been studied using a cyclic voltammetry technique in the potential range of +1.5 to -1.0 V and at different scan rates in water at 292.15 K using KCl (0.1M) as a supporting medium and glassy carbon as a working electrode. The study is valuable for evaluating the thermodynamic properties [3-18]. The cobalt ions show two oxidation peaks at 0.02 and 0.06 V and two reduction peaks at 0 and -0.7 V. These two peaks correspond to the oxidation of cobalt zero-valent to monovalent, and then that of cobalt monovalent to divalent cobalt scan rates is studied for the redox behaviors of $CoCl_2$ alone or in the presence of L-Carrageenan (LK) natural polymer. Stability constants for the interaction of cobalt ions with L -Carrageenan (LK) natural polymer were evaluated.

1. Introduction

Carrageenan is a natural carbohydrate (polysaccharide) obtained from edible red seaweeds. The basic structure of carrageenan is a linear polysaccharide made up of a repeating dissacharide sequence of α-D-galactopyranose linked 1, 3 called A residue and β-D-galactopyranose residues linked through positions 1, 4 (B residues) [1].

Carrageenan or **carrageenins** are a family of linear sulphated polysaccharides extracted from red edible seaweeds. They are widely used in the food industry for their gelling, thickening, and stabilizing properties. Their main application lies in dairy and meat products due to their strong binding to food proteins. Carrageenans are used to suppress in-vivo and in-vitro immune responses via mechanisms believed to involve selective cytopathic effect on macrophages [2]. Non-gelling λ-carrageenan is used to induce inflammation and inflammatory pain in the rodent hindpaw or air pouch models. The basic unit for polymer lambda Carragenaan (L-Carragenaan) is seen in Fig. (1).

Cobalt salts have been used for centuries to produce brilliant and permanent blue colours in porcelain, glass, pottery, and tiles. Cobalt ions have been found to be effective in correcting a certain mineral deficiency

disease in animals. As an element in the diet of sheep, cobalt prevents a disease called swayback and improves the quality of the wool.

Cobalt chloride is used in commercial applications such as electroplating, catalyst preparation, painting on glass and porcelain, and vitamin B12 manufacturing. It is also used as an additive to fertilizer and feed.

In this work, the complexation of $CoCl_2$ with L-Carragenaan (LK) using the cyclic voltammetric technique at a glassy carbon electrode in 0.1 M of KCl as a supporting electrolyte in water at 292.15K was studied, from which the stability constant of the complex formed was estimated.
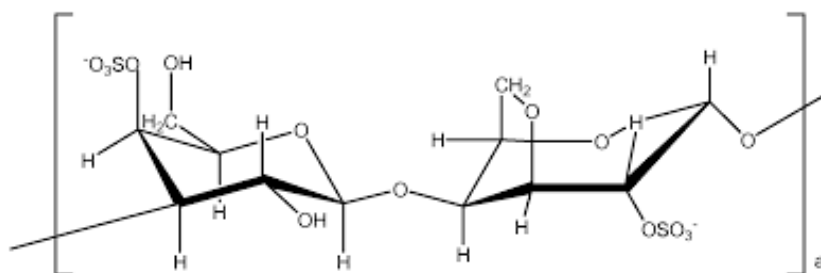

Figure 1. Basic unit of Lamda, L-Carrageenan (LK).

2. Experimental
2.1. Materials
Cobalt chloride and KCl provided from Al Nasr Chemicals Co. without purification, L-Carrageenan (LK) from Fluka, and double distilled water were all used.

2.2. Measurements
Cyclic voltammetry in glass cell of 30 ml solution with three electrodes was used. Measurements were carried out using glassy carbon as a working electrode, platinum wire electrode as a counter electrode, and Ag/AgCl (satd. KCl) as the reference electrode [3-15]. The glassy carbon electrode was polished to a mirror-like surface with 0.5 and 0.02 µm alumina in doubly distilled water. Experimental solution was deaerated by purging for at least 10 minutes with 99.99 % pure nitrogen gas. Cyclic voltammetry experiments were carried out using different concentrations of L-Carragenaan (LK) and different $CoCl_2$ solutions in water at 292.15 °K. KCl (0.1M) as a supporting electrolyte

was used at different scan rates, and measurements were performed using a Potentiostat model DY2000, DY2000EN Multichannel.

3. Results and discussion
3.1. Electrochemical behavior of $CoCl_2$ in the absence of L-Carragenaan (LK)
The cobalt ions used show two oxidation peaks at 0.02 and 0.06 V and two reduction peaks at 0 and -0.7 V. The two oxidation peaks correspond to the oxidation of zero-valent to monovalent cobalts and then the oxidation of monovalent to divalent cobalts [16]. The very opposite for the reduction peaks is the reduction of divalent to monovalent cobalts, then the reduction of monovalent to zero valent cobalts. Each process consumes one electron. Effect of cobalt ion concentration was followed in the range from $3x10^{-4}$ to $2 x10^{-3}$ (2 mM) (See Fig. (2)).

3.2. Electrochemical behavior of $CoCl_2$ in the presence of L-Carrageenan (LK)

Adding different concentrations of L-Carrageenan in a 0.5 % solution by weight in water led to a decrease in reduction voltammogram height. Shift of the oxidation peaks was observed, as shown in Fig. (3).
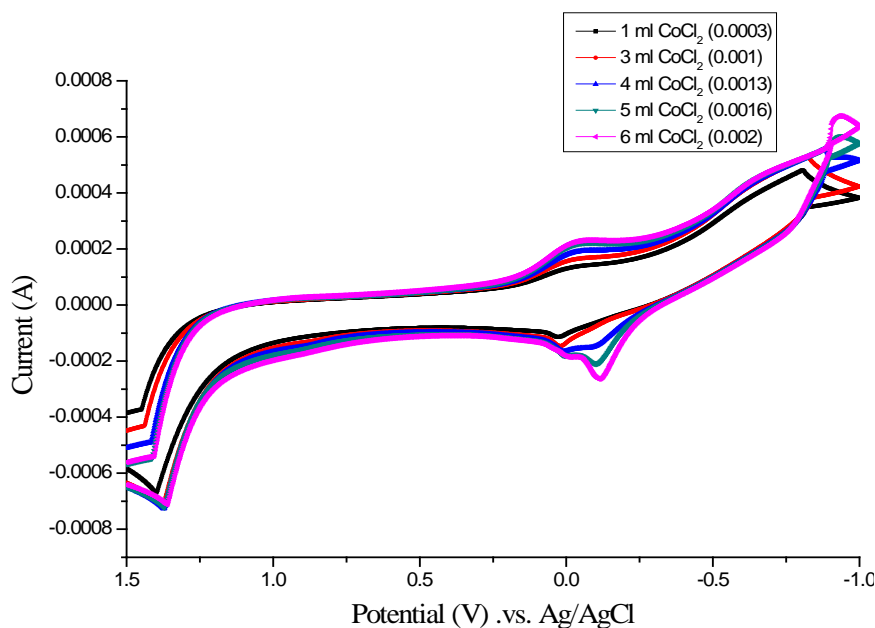

Figure 2. Effects of different concentrations of CoCl$_2$ in 30 ml KCl (0.1M) on scan rate 0.1 (V/Sec), sens (A/V)= 1x10^{-3}, initial E (V)=1.5, high E (V)= 1.5 and low E (V)= -1.
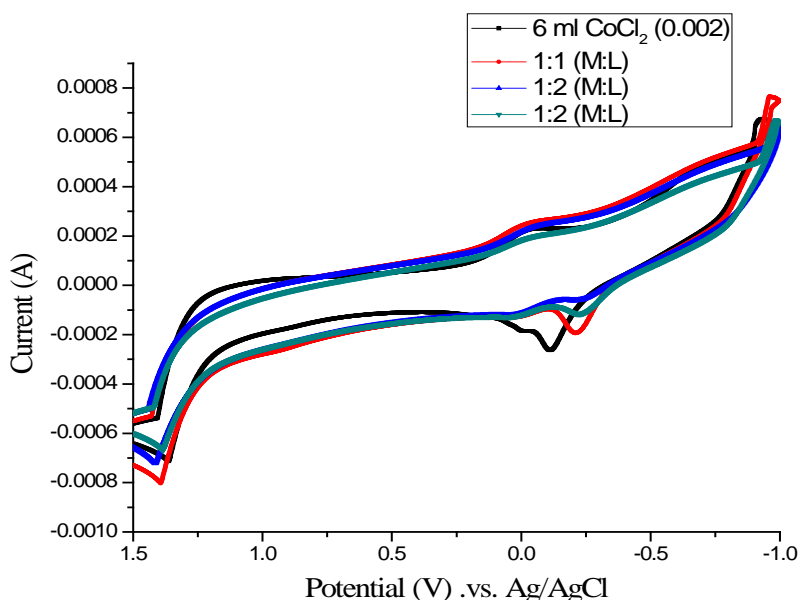

Figure 3. Effect of different concentrations of L-Carrageenan (LK) and CoCl$_2$ in 30 ml KCl (0.1M) on scan rate 0.1 (V/Sec), sens (A/V)= 1x10^{-3}, initial E (V)= 1.5, high E(V)= 1.5 and low E(V)= -1.

Based on Figure 3, it was observed that the complex is formed due to the decrease in anodic and cathodic peaks and potential shifts of their position to lower values.

A stability constant measures the strength of the interaction between the reagents that come

together to form the complex. The stability constant (β_{MX}) for CoCl$_2$ complexes with L-Carrageenan (LK) in 0.1 M KCl at (+1.5 to -1.0) V potential and scan rate 0.1V/S in water at temperature (292.15K) for each addition were calculated [13] by applying equation (1).

$$\left(E_p\right)_M + \left(E_P\right)_C = 2.303\frac{RT}{nF}Log\beta_{MX} + 2.303\frac{RT}{nF}LogC_X \qquad (1)$$

where $(E_p)_M$ is the peak potential of metal at the final addition in the absence of L-Carrageenan (LK), $(E_p)_C$ is the peak potential of metal complex, R is a gas constant (8.314 J.mol^{-1}.degree^{-1}), T is the absolute temperature, and C_x is the concentration of metal in the presence of L-Carrageenan (LK).

The Gibbs free energy of interaction for CoCl$_2$ with L-Carrageenan (LK) was calculated [16-44] from stability constant (β_{MX}) using equation (2).

$$\Delta G = -2.303RTLog\beta_{MX} \qquad (2)$$

The calculated values of (ΔE_p), (β_{MX}), and (ΔG) for CoCl$_2$ complexes in 0.1 M KCl at (+1.5 to -1.0) V potential, current 1A, and scan rate 0.1V/S in water at temperature (292.15K) were estimated, as shown in Tables 1 and 2.

Table 1

Cyclic voltammetric data for the interaction of CoCl$_2$ with L-Carrageenan (LK) in water at 292.15 K.

[M] X10^3	[L] X10^3	$\gamma\pm$	$E_{p,\,c}$/V	$E_{p,\,a}$/V	$I_{p,\,a}$/A X10^4	$I_{p,\,c}$/A X10^4	ΔE_p	β	$-\Delta G$ in kJ	D_a	D_c
2	0.0278	0.9916	-0.098	-0.109	-1.494	1.395	-0.011	4.97X10^4	31.31	3.0527x10^{-12}	2.6616 x10^{-12}
2	0.083	0.9856	-0.082	-0.118	-1.832	1.473	-0.036	9.45x10^3	21.85	4.5903 x10^{-12}	3.0599 x10^{-11}
2.1	0.083	0.9856	-0.118	-0.144	-1.386	2.1	-0.026	1.73x10^5	28.79	2.6273 x10^{-12}	6.0315 x10^{-12}
2.1	0.165	0.9797	-0.13	-0.142	-1.283	1.2	0.012-	5.39x10^7	42.50	2.2513 x10^{-12}	1.9694 x10^{-12}
2.1	0.24	0.9756	-0.1	-0.161	-1.522	1	0.061-	7.63x10^3	21.34	3.1682 x10^{-12}	1.3677 x10^{-12}
2.1	0.33	0.9714	-0.1	-0.160	-1.713	0.98	-0.06	5.55x10^3	20.58	4.0133 x10^{-12}	1.3135 x10^{-12}
2.1	0.99	0.9510	0.09-	-0.186	-1.589	0.9	-0.096	1.14x10^3	16.8	3.4533 x10^{-12}	1.1078 x10^{-12}
2.1	2	0.9313	-0.08	-0.212	-1.291	0.8	-0.132	4.56x10^2	14.61	2.2795 x10^{-12}	8.7532 x10^{-13}
2.1	4	0.9041	-0.08	-0.25	-0. 7	0.78	-0.17	2.32x10^2	13.01	6.7017 x10^{-13}	8.3211 x10^{-13}
2.1	6	0.88373	-0.08	-0.23	-0.3	0.7	-0.15	1.52x10^2	12.01	1.2309 x10^{-13}	6.7017 x10^{-13}

3.3. Variation of the scan rate

Cyclic voltammogram of CoCl$_2$ in the absence and presence of L-Carrageenan (LK) in 0.1 M of KCl (+1.5 to -1.0) V potential and at different scan rates (0.1, 0.05, 0.02, and 0.01V/S) at absolute temperature 292.15 K.

is represented in Figures 4, 5. The peak current [20] for both of the anodic and cathodic peaks follows equation (3).

$$I_P = 2.69X10^5 n^{3/2} AC\sqrt{DV} \qquad (3)$$

I_p= peak current in ampere, n= number of

exchanged electrons, A= area of the electrons in mol/cm3, V= scan rate in volts/s. electrode in cm^2, D= diffusion coefficient in cm^2/s, and C= concentration of the species.
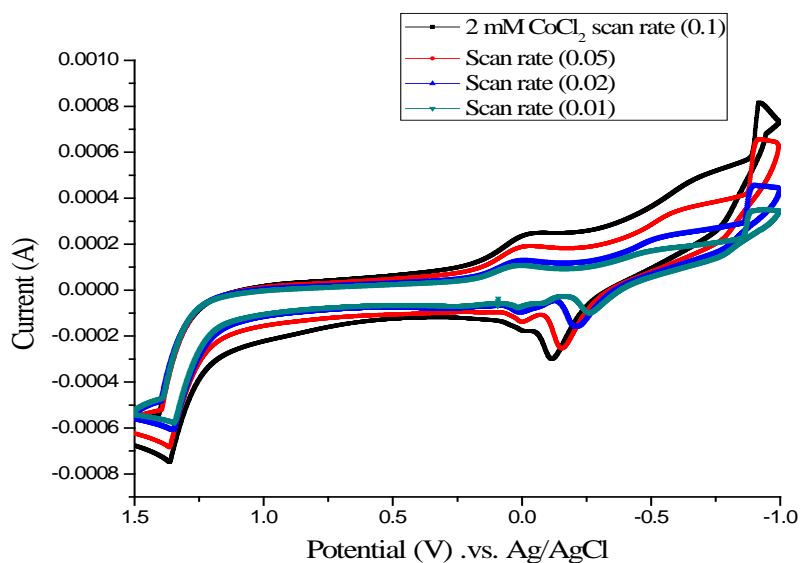

Figure 4. Effect of scan rate on CoCl$_2$ at concentration 2 mM. The scan rates were maintained at 0.1, 0.05, 0.02, 0.01 (V/Sec), Sens (A/V)= 1x10^{-3}, initial E (V)= 1.5, high E (V)= 1.5 and low E(V)= -1.
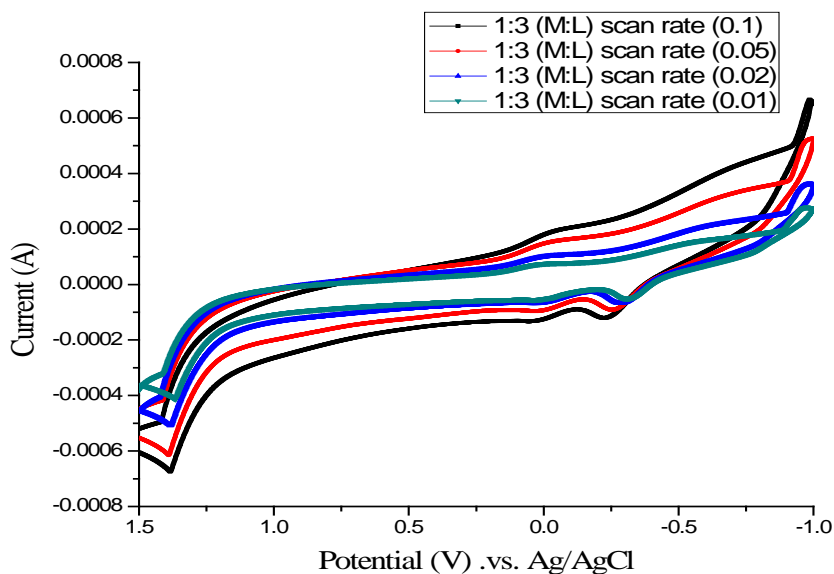

Figure 5. Effect of scan rate on CoCl$_2$ in the presence of L-Carrageenan (LK) (1:3) in 0.1 M of KCl at temperature (292.15 K). The scan rates were maintained at 0.1, 0.05, 0.02, 0.01 (V/Sec), Sens (A/V)= 1x10^{-3}, initial E (V)= 1.5, high E(V)= 1.5 and low E(V)= -1.

The plots of both of the anodic and cathodic peak currents against the scan rates (0.1, 0.05, 0.02, 0.01 (V/Sec)) at 292.15 K for CoCl$_2$ in the absence and presence of L-Carrageenan (LK) in 0.1 M of KCl at (+1.5 to -1.0) V potential are shown in Figs. 6 and 7, and the resulting data are listed in Tables 2,3 .
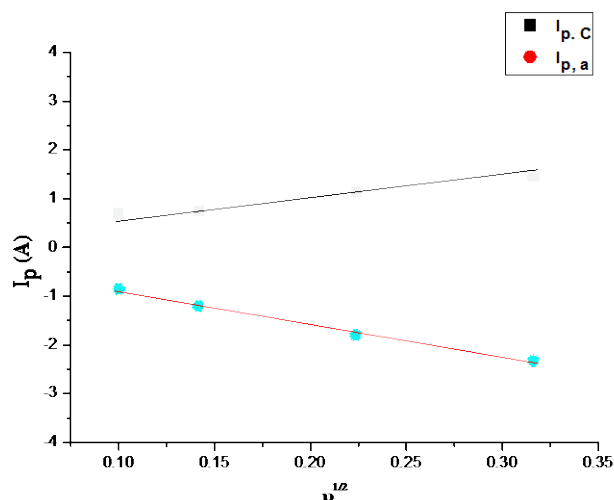
Figure 6. The relation between anodic and cathodic peak currents against the scan rates at 292.15 K for CoCl$_2$ in the absence of L-Carrageenan (LK).
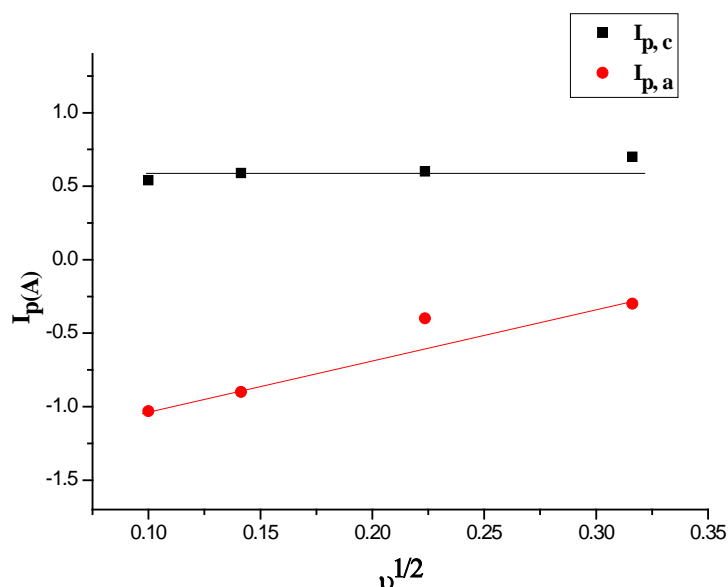

Figure 7. The relation between anodic and cathodic peak currents against the scan rates at 292.15 K for CoCl$_2$ in the presence of L-Carrageenan (LK) (1:3).

Table 2
Cyclic voltammetric data of CoCl$_2$ in the absence of L-Carrageenan (LK) in 0.1 M of KCl at (+1.5 to -1.0) V potential and different scans (0.1, 0.05, 0.02, 0.01 (V/Sec)) at 292.15 K.

[M] x10^{-3}	v	v$^{1/2}$	I$_{p,a}$ x10^4/A	I$_{p,c}$ x10^4/A	D$_a$/cm^2.s^{-1}	D$_c$/cm^2.s^{-1}
2	0.1	0.3162	-1.39	1.47	2.6275 x 10^{-12}	2.9556 x 10^{-12}
2	0.05	0.2236	-1.80	1.16	8.8982 x 10^{-12}	3.6492 x 10^{-12}
2	0.15	0.1414	-1.21	0.763	1.0013 x 10^{-11}	3.9803 x 10^{-12}
2	0.2	0.1	-0.855	1.08	9.9989 x 10^{-12}	1.5953 x 10^{-11}

Table 3

Cyclic voltammetric data of $CoCl_2$ in the presence of L-Carragenaan (1:3) in 0.1 M of KCl at at (+1.5 to -1.0) V potential and different scan rates (0.1, 0.05, 0.02, 0.01 (V/Sec)) at 292.15 K.

[M] x10^{-3}	V	v$^{1/2}$	$I_{p, a}$ x10^4/A	$I_{p, c}$ x10^4/A	D_a/cm^2.s^{-1}	D_c/cm^2.s^{-1}
2	0.1	0.3162	-5.360	3.215	3.9296 x 10^{-11}	1.4137 x 10^{-11}
2	0.05	0.2236	-5.20	2	7.397 x 10^{-11}	1.0942x 10^{-11}
2	0.15	0.1414	-4.38	2.15	1.312 x 10^{-10}	3.1613 x 10^{-11}
2	0.2	0.1	-3.408	1.806	1.586 x 10^{-10}	4.4612x 10^{-11}

Based on Fig. 7, it is observed that the scan rate of the complex mixtures increases the corresponding current, and the slopes are in 0.5 range; therefore, the electrochemical processes are diffusion controlled in case of anodic peak which can be confirmed from the graph of ip vs v$^{1/2}$, as shown in Figures 6, 7. However, in case of cathodic peak, the slope is greater than 0.5; therefore, the electrochemical process is catalytic.

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