

Effect of Various Parameters on Cyclic Voltammetry of Chromium in Choline Chloride Based Ionic Liquid

Md. Moynul Islam*

Department of Chemistry,
Bangladesh Army University of Engineering and
Technology, Qadirabad Cantonment,
Natore-6431, Bangladesh

M. Rostom Ali

Department of Applied Chemistry and
Chemical Engineering,
University of Rajshahi,
Rajshahi-6205, Bangladesh

Abstract:- Cyclic voltammetry (CV) experiments were used to explore the chromium interaction behavior from an ionic liquid dependent solution which includes chromium chloride ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) in choline chloride-ethylene glycol (EG). The interaction experiments were performed in variance of scan rate, cathodic sweeping potential, concentration of metal ions, temperature effects and also the effect of surfactants. The effects on cyclic voltammetry of different experimental conditions and other parameters were studied using a Potentiostat/Galvanostat fitted with a potential sweeper. The electrochemical activity of Cr(III) on platinum substrates was investigated at different scan rate values and different potential windows within the temperature range from room temperature to 80 °C. The method of cathodic reduction has received special attention. The cyclic voltammograms reported at different scan rate values showed that the reduction process for Cr(III) is mainly regulated by the diffusion of the electro-active species to the surface of the electrode. It was suggested that the chromium ion reduction mechanism occurs in a one-step cycle that transfers three electrons and is regulated by the diffusion of chromium ions in the ionic liquid.

Keywords:- Cyclic voltammetry; Chromium; Ethaline; Parameters; Effect.

I. INTRODUCTION

The most widely used technique for gaining qualitative information on electrochemical reactions is cyclic voltammetry. It provides a fast position of the electro active species' redox potentials. Diagnostic criteria can be established by correlating kinetic and experimental parameters, such that unknown structures can be identified by observing variations of peak current, half-peak potentials, or anodic peak currents ratio and cathodic peak currents as a function of voltage scanning rate. If the electron transmission reaction is irreversible, the peak to peak distance is wide while the peak to peak distance is short in the reversible system. The influence on the voltametric wave of a chemical reaction would depend on its rate, as comparison to the time taken to perform the experiment. In the kinetic parameter the ratio of the rate constant to the voltage scan rate occurs. This, in turn, allows these relationships to be used to define diagnostic criteria for investigating unfamiliar systems. The

authors investigated the reduction of Cr(III) in ethaline using cyclic voltammogram.

Chromium is being used widely for decorative, emulsifier, and anti-corrosion coating purposes. It is also used for mechanical precision part surface coatings, molds, surgical instruments, etc. Chromium is typically electrodeposited from hexavalent chromium (Cr(VI)) containing aqueous solutions [1]. Cr(VI) raises significant safety and environmental concerns: it is extremely irritating to nose and throat mucous membranes and is potentially carcinogenic.

There have been a variety of attempts to give successful trivalent chromium baths [2-7], however with minimal success owing to the complex Cr(III) ion chemistry [8]. A few suggestions were asked to explain the low Cr(0) deposition rate from Cr(III) baths which associated polymer formation [9,10]. Use of such ionic liquids could minimize the problems of baths with Cr(III) thus chosen to represent an effective choice for electrodeposition with chrome.

Ionic liquids possess a lot of distinct properties which make them highly fascinating electrodeposition solvents. Many organic and inorganic substances can be dissolved, with a wider electrochemical window and greater chemical stability than water, marginal vapor pressure and high thermal and chemical stability. A wide variety of metals, metal alloys and semiconductors, along with reactive metals such as magnesium, silicon, germanium and titanium, are electrodeposited from ionic liquid solutions, which cannot be extracted from aqueous solutions by electrodeposition [11-14]. These types of ionic liquids have been used only in few reports. Abbott et al . reported chromium deposition from Cr(III) solutions based on eutectic mixtures of choline chloride with a donor hydrogen bond species. The authors obtained an amorphous pale / gray crack-free deposit by using this electrolyte [15,16]. These liquids, also recognized as Deep Eutectic Solvents (DESSs), were used to deposit a variety of metal coating materials including Zn [17], Sn [18], Cu [19,20], Ni [21,22], and Ag [23,24] at good current efficiency and also for electropolishing type metal dissolution processes [25,26]. In many cases, the use of ionic liquid solvent overcomes the need for highly toxic salts (e.g., cyanide) and strong inorganic acids (e.g., HF, H_2SO_4 , H_3PO_4 , chromic acid).

This paper presents an electrochemical study of the behavior of Cr(III) ions in an ionic liquid called ethaline, in the presence of surfactants, on platinum electrode at room temperature range up to 80 °C using cyclic voltammetric method. Eutectic mixtures of hydrogen bond donor and choline chloride such as ethylene glycol are the basis of the ionic liquid used as a solvent.

EXPERIMENTAL DETAILS

2.1 Chemicals

All the metal solution was provided in the range of 0.01 to 0.1 mol·L⁻¹ at a concentration of metal halides. Choline chloride (HOC₂H₄N⁺(CH₃)₃Cl⁻) ChCl (Aldrich 99%) was recrystallized, purified and vacuum-dried from absolute ethanol. As mentioned, ethylene glycol (EG) (HOCH₂CH₂OH) (Aldrich >99%) was used. The hexahydrate of chromium chloride (CrCl₃·6H₂O) (BDH 98%) was used as obtained.

As organic additives (surfactants), polyethylene glycol (HO(CH₂CH₂O)_nCH₂CH₂OH) (RDH 97%) and formic acid (HCOOH) (Merck 98%) were used in their original form. Additives at a concentration of 0.1 g·L⁻¹ polyethylene glycol and 40 mL·L⁻¹ formic acid were mixed in the electrolytic bath.

2.2 Preparation of ionic liquid

By mixing together the two components at 75 °C in the proportions specified, the eutectic mixture was created until a homogeneous, colorless liquid was created. For choline chloride (ChCl) with ethylene glycol (EG), the molar ratio was found to be 1:2 for the eutectic compounds. Before use, the ionic liquid was treated at 30 °C in a thermostatic oven.

2.3 Electrochemical measurements

All electrochemical studies such as potential step chronopotentiometry, chronoamperometry and cyclic voltammetry were performed using a potentially sweeper-equipped Hokudo Denko HAB-151 Potentiostat/Galvanostat, Tokyo, Japan. Using WinDaq software, data were recorded in a computer via a data acquisition system (USA). In all electrochemical studies, a three-electrode system consisting of a platinum (50 × 5 × 0.1 mm³) counter electrode, a platinum (50 × 5 × 0.1 mm³) working electrode and silver wire quasi-reference electrode were used. In 1.5 mol·L⁻¹ H₂SO₄-1.5 mol·L⁻¹ H₃PO₄ mixtures, the working and counter electrodes were electrochemically washed, then rinsed with deionized water and finally dried with acetone prior to use in all measurements. All voltammograms were obtained at 30 °C, with different scanning rates between 5 and 100 mV·s⁻¹. Throughout all electrochemical experiments, a silver wire (immersed throughout ethaline) quasi-reference electrode was used which has been shown to have robust reference potential in chloride dependent eutectics. With reference to this Ag|1:2 ChCl-EG reference electrode, which will be written as Ag|Ag(I), all the potential in this work is quoted. The overall instrumental cell set-up for the cyclic voltammetry experiment is shown in figure 1.



Fig. 1 The instrumental set-up of the three electrodes cell connected with the potentiostat/galvanostat via transducer with winDaq software installed computer system

RESULT AND DISCUSSION

3.1 Cyclic voltammetry of Cr(III) in ChCl:2EG (ethaline)

Fig.2 shows a cyclic voltammogram of 1:2:0.01 (mole ratio) ChCl:EG:CrCl₃·6H₂O ionic liquid measured on a platinum electrode at 30 °C with a scan rate of 10 mV·s⁻¹. The remaining rest potentials is +0.549 V. The negative path scan consists of the first reduction wave C₁ with the current beginning to increase to -0.144 V. With the current beginning to increase again at -0.677 V, additional reduction wave C₂ is observed. The reverse scan consists of the first oxidation peak P_{al} (-0.062 V). A further wave of oxidation is noted with the current initiating to raise again around +1.113 V. The reduction wave at -0.72 V corresponds to the reduction of cationic species (Cat⁺) in this ionic liquid relative to the voltammogram obtained in the absence of CrCl₃·6H₂O, while the oxidation wave appeared at +1.05 V for the oxidation of chloride ions (anions) to molecular/gaseous chlorine according to the following reaction.

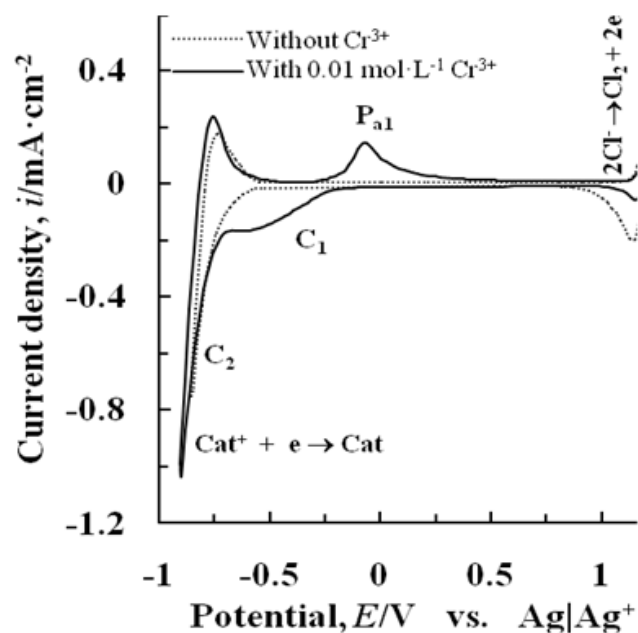


Fig. 2 Cyclic voltammograms recorded on a platinum electrode in ChCl:2EG ionic liquid containing 0.01 mol·L⁻¹ CrCl₃·6H₂O at 30 °C with a scan rate of 10 mV·s⁻¹.

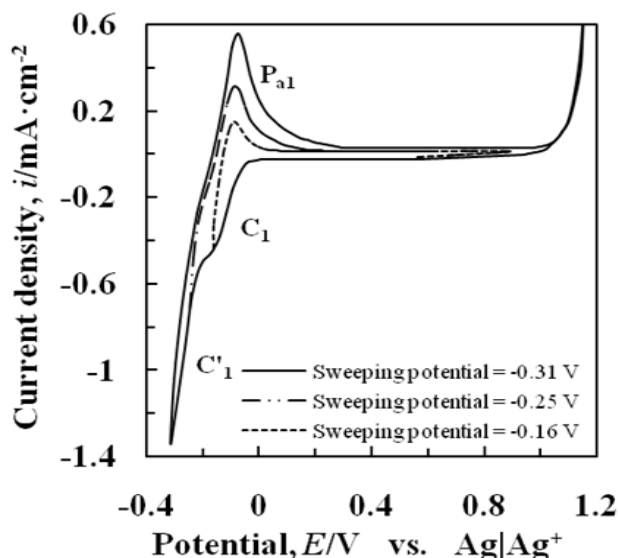
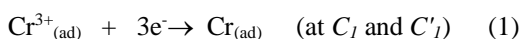


Fig. 3 Effect of cathodic sweeping potentials on the cyclic voltammograms recorded on a platinum electrode in 1:2:0.10 (mole ratio) ChCl:EG:CrCl₃ ILs with surfactant at 30 °C with a scan rate of 10 mV s⁻¹.

The effect of cathodic sweeping potential on the cyclic voltammograms documented on a platinum electrode in 1:2:0.10 (mole ratio) ChCl: EG: CrCl₃ ILs at 30 °C with a scanning rate of 10 mV s⁻¹ is shown in Fig. 3. From voltammograms it is clearly observed that the first reduction waves C₁ and C'₁ lead to the P_{a1} peaks of oxidation. The rise of the negative current in the first reduction waves (C₁ and C'₁) is definitely connected to the reduction of chromium ion to metallic state as per the following expression:



In ChCl:2EG IL only one stripping peak is observed at -0.74 V (P_{a1}) in the voltammogram. The voltammograms also show that the magnitude of the current densities in ChCl:2EG IL is much lower as a result of slow mass transport.

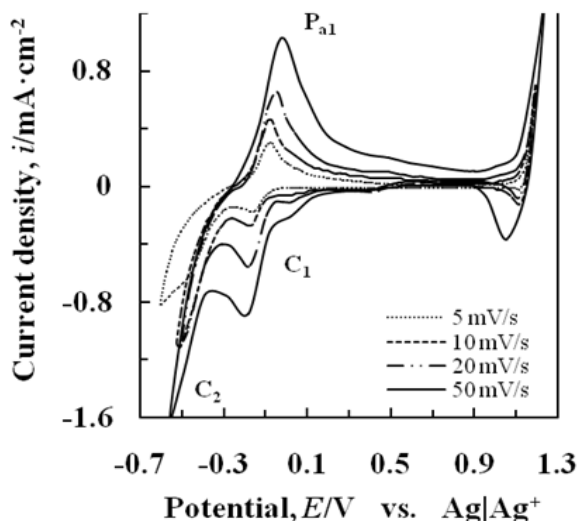


Fig. 4 Effect of scan rates on cyclic voltammograms recorded on a platinum electrode in ChCl:2EG:0.1 CrCl₃ ILs at 30 °C.

The influence of the scan rates on the cyclic voltammograms observed in ChCl:2EG:0.1CrCl₃ ILs at 30 °C on a platinum electrode is shown in Fig. 4. The peak potential of E_p for a reversible device is independent of the scan rate (v) and the peak current density (i_p) is proportional to the square root of the scan rate (v^{1/2}).

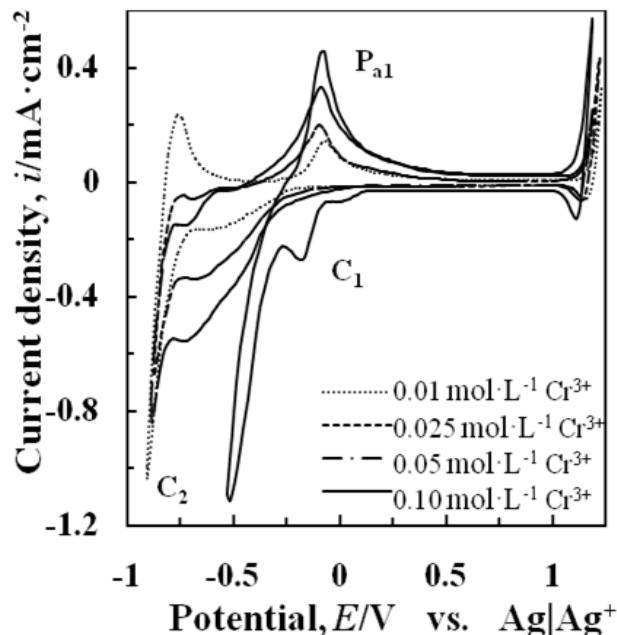


Fig. 5 Effect of CrCl₃·6H₂O concentrations at 30 °C with a scan rate of 10 mV·S⁻¹ on cyclic voltammograms recorded on a platinum electrode in ChCl:2EG ionic liquid.

Figure 5 displays the impact of CrCl₃·6H₂O concentrations with a scan rate of 10 mV·s⁻¹ on the cyclic voltammograms obtained on a platinum electrode in ChCl:2EG ionic fluid at 30 °C. From these voltammograms it is easily seen that magnitudes of current densities are enhanced with the increased concentrations of CrCl₃·6H₂O applied to the ionic liquids. The same abnormalities are also observed in Fig. 5 at the P_{a1} oxidation peak, which also indicates the magnitude of peak current densities is enhanced by introducing to the ionic liquid increased concentrations of CrCl₃·6H₂O. With the increase in concentrations of CrCl₃·6H₂O added to ionic liquids, the change in the magnitudes of decreasing current densities indicates the higher discharge levels of chromium ions at low overpotentials.

The effect of the ChCl:EG:CrCl₃·6H₂O ionic fluid temperature with a scan rate of 10 mV·s⁻¹ on cyclic voltammograms centered on a platinum electrode is shown in Figure 6. From the voltammograms it is readily seen that the onset potential of deposition and dissolution of chromium is unchanged with temperature increase. On the other hand, with the increase in temperature, the magnitudes of the current deposition and dissolution densities decrease. This implies inert metallic complex being formed to increase temperature.

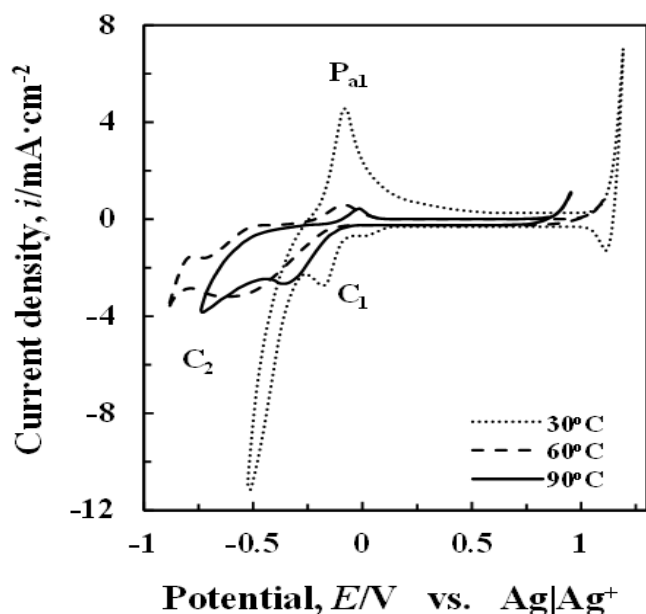


Fig. 6 Effect of temperature on the cyclic voltammograms recorded on a platinum electrode in ChCl:2EG ionic liquid containing $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ CrCl}_3\cdot 6\text{H}_2\text{O}$ with a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$.

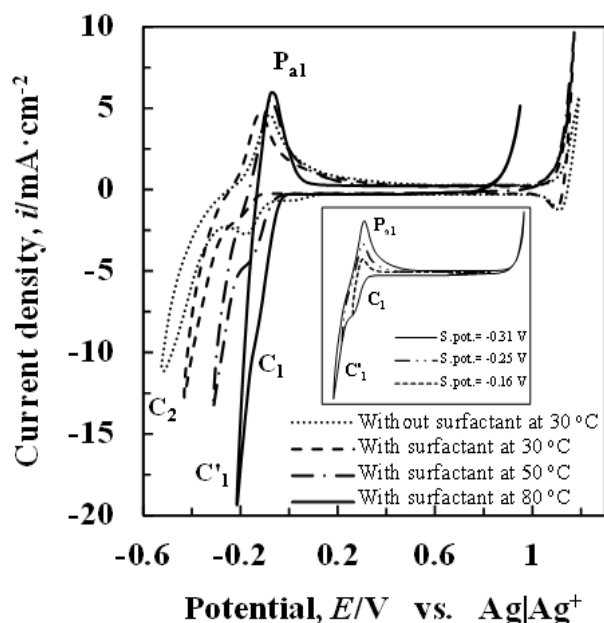


Fig. 7 Effect of surfactant and temperature on the cyclic voltammograms recorded on a platinum electrode in ChCl:2EG ionic liquids containing $0.10 \text{ mol}\cdot\text{L}^{-1} \text{ CrCl}_3\cdot 6\text{H}_2\text{O}$.

Fig. 7 shows the effect of surfactant ($0.10 \text{ g}\cdot\text{L}^{-1}$ polyethylene glycol and $40 \text{ mL}\cdot\text{L}^{-1}$ formic acid mixture) and temperature on cyclic voltammograms recorded on a platinum electrode at 1:2:0.1 mole ratio of ChCl:EG:CrCl₃·6H₂O ionic fluid with a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$. The onset potential of chromium deposition and dissolution is easily seen from the voltammograms to the anodic and cathodic range, with the addition of $0.10 \text{ g}\cdot\text{L}^{-1}$ polyethylene glycol and $40 \text{ mL}\cdot\text{L}^{-1}$ formic acid mixture as surfactant and temperature rise, respectively. The difference between the starting voltage of chromium deposition and dissolution is

0.137 V (0.280 V without surfactant), showing the quasi-reversible changes that occur when surfactant is applied at $80 \text{ }^\circ\text{C}$ in the reversible existence of chromium deposition in this ionic liquid. The reasoning behind this can be due in this ionic liquid to the high temperature shift of the metallic complexes. On the other hand, the magnitudes of the oxidation-reduction current densities are also rising with the addition of surfactant and the increase in temperature. Cathodic potential sweeping experiments on cyclic voltammograms (in Fig. 7) show that the first (C_1) and second (C'_1) reduction waves lead to the first (P_{a1}) oxidation peak. With the use of $0.10 \text{ g}\cdot\text{L}^{-1}$ polyethylene glycol and $40 \text{ mL}\cdot\text{L}^{-1}$ formic acid mixture as a surfactant at temperatures above $45 \text{ }^\circ\text{C}$, pure chromium was extracted from this ionic liquid containing CrCl₃·6H₂O by constant potential and constant current methods.

CONCLUSIONS

This study shows that ionic fluid, based on eutectic formulations of choline chloride and hydrogen bond donors such as ethylene glycol, could be used as electrochemical solvents. With the increased concentrations of CrCl₃·6H₂O added to the ionic liquids show the higher discharge levels of chromium ions at low overpotentials. Inert metallic compound is formed on temperature rises. The quasi-reversible nature of chromium deposition changes to reversible in nature when surfactants are added at $80 \text{ }^\circ\text{C}$ due to the alteration of metallic complexes in this ionic liquid at high temperatures. As the surfactant is applied and the temperature increases, the magnitudes of the present reduction and oxidation densities are also raised.

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