

VOLTAMMETRIC STUDY OF THE INTERACTIONS OF ALKALINE EARTH METAL IONS AND MELAMINE AT DIFFERENT pH

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Abstract

The electrochemical redox behavior of alkaline earth metal ions at different pH in acetate buffer solution has been investigated using cyclic voltammetric method at gold disk electrode (GDE). In the entire studied pH (3.68-6.23), metal ions show two cathodic and an anodic peak. The method has also been employed to observe the interaction of metal ions with melamine in acetate buffer solution. At all pH, a reasonably strong interaction occurs between metal ions and melamine at different metal ions/melamine molar ratio. However, maximum interaction takes place at 1:4 molar ratios of metal ions and melamine at pH 6.23. This is possibly the most suitable condition for alkaline earth metal-melamine interaction.

Key words: Melamine, acetate buffer, gold disk electrode, cyclic voltammetry, interaction

Introduction

Melamine (2,4,6-triamino-1,3,5-triazine, Mel) is a highly symmetrical ligand with six potential N-donor atoms to coordinate to transition metals (Nockemann and Meyer 2004). The ligand, Mel, has both hydrogen bonding acceptor and donor atoms which is analogous to nucleobases. Mel plays a role in a wide range of flame resistant materials as thermal liners, heat resistant gloves, and aprons to protect from splash back of hot substances. Mel derivatives of arsenical drugs are potentially important in the treatment of African trypanosomiasis (Lim *et al.* 1990). Standard tests such as the Kjeldahl and Dumas tests estimate protein levels by measuring the nitrogen content, so they can be misled by adding nitrogen-rich compounds such as Mel (Barrett and Gilbert 2006). As a fertilizer, Mel also showed economic benefit in agriculture.

The alkaline earth metals are a series of elements comprising Group 2 of the periodic table: beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra) (Royal Society of Chemistry 2012).

These highly reactive metals are present in nature and show common traits. Some of these elements are essential to life, and some are toxic, but all of them have important uses in modern manufacturing processes (Cox, 1989). Magnesium and calcium are critical to life. They play a vital role in the ion pumps that regulate cell behavior, and magnesium is the central atom in the chlorophyll molecule. Strontium has an important role in marine aquatic life, especially hard

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corals, which use strontium to build their exoskeletons. Other elements, including radium and beryllium, have no biological value and as such are toxic (Jakubke *et al.* 1994) to most organisms, including human.

Cyclic voltammetric method has been chosen for this present study because of its potential ability in investigating the redox behavior of electroactive species. The cyclic voltammetric study of various metal ions in presence of ligand has been investigated in our laboratory and reported in detail (Shaikh *et al.* 2005, 2006). We have therefore, started a wide ranging electrochemical studies of metal complexes of Mel using cyclic voltammetry. Here we report a study of cyclic voltammetric redox behavior of alkaline earth metal ions and their interaction with Mel in acetate buffer solution at different pH.

Materials and Methods

Analar grade $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ have been purchased from Merck Germany and used without further purification. Analytical grade Mel (BDH, UK) was used in this study. 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 procured and used without further treatment. Sodium hydroxide (Merck, Germany) was used as it is available for maintaining the pH of the solution. All aqueous solutions were prepared in doubly distilled water obtained from a Milli-Q water purification system. The experiments were carried out at room temperature.

Equipments: A three electrode electrochemical system consists of gold disk electrode (GDE) as the working electrode, Ag/AgCl (satd. KCl) as the reference electrode and platinum wire as the counter electrode was used. Cyclic voltammetric measurement was performed using Computerized Electrochemical System, Model HQ-2040 developed by Advanced Analytics, USA. Solution pH was measured by pH meter- Hanna instruments (model pH 211).

Preparation of acetate buffer solution: For the preparation of acetate buffer solution, 0.01 M $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ and 0.01 M CH_3COOH was prepared separately and the two solutions were then mixed together with same volume ratio. By adding 1.0 M CH_3COOH and 1.0 M NaOH, the desired pH (6.23, 4.72, 4.10 and 3.68) values were adjusted.

Preparation of metal ion and melamine solution: Metal ion solution of 0.1 mM Mg(II), Ca(II), Sr(II) and Ba(II) were prepared in 0.1M KCl and acetate buffer. For the complexation study, 0.2 mM, 0.4 mM, 0.6 mM and 0.8 mM Mel solution were also prepared in 0.1M KCl and acetate buffer solution.

Preparation of working electrode: GDE was polished with fine alumina powder of 0.3 micron on a wet polishing cloth. For doing so a part of the cloth was made wet with deionized water and alumina powder was sprinkled over it. The GDE was then polished on this surface by pressing softly the electrode against the polishing surface for about 40-50 minutes. A shiny golden mirror like electrode surface was then thoroughly washed with deionized water. First of all, the cell was

filled with desired volume of the experimental solution and the Teflon cap was placed on the cell. The purging glass tube together with reference electrode was inserted through the holes. Under computer controlled stirring, experimental solution was deaerated by purging for at least 10 minutes with 99.99% pure nitrogen gas. Thus traces of dissolved oxygen were removed from the solution.

Results and Discussion

Cyclic voltammetric investigation of the redox behavior of alkaline earth metal ions (Mg(II), Ca(II), Sr(II) and Ba(II)) in KCl and acetate buffer solution and their interaction with Mel at GDE in an identical voltammetric condition has been performed. The effect of pH (6.23, 4.72, 4.10, and 3.68) in KCl and acetate buffer was also examined in this study. The results are presented below:

Voltammetric response of metal ions in acetate buffer solution: Cyclic voltammetric response of 0.1 mM Mg(II), Ca(II), Sr(II) and Ba(II) in 0.01M KCl and acetate buffer solution at different pH values (pH 6.23, 4.72, 4.10 and 3.68) has been investigated at GDE within the potential window of -300 to +1500 mV. For all metal ions, two cathodic and an anodic peak was observed.

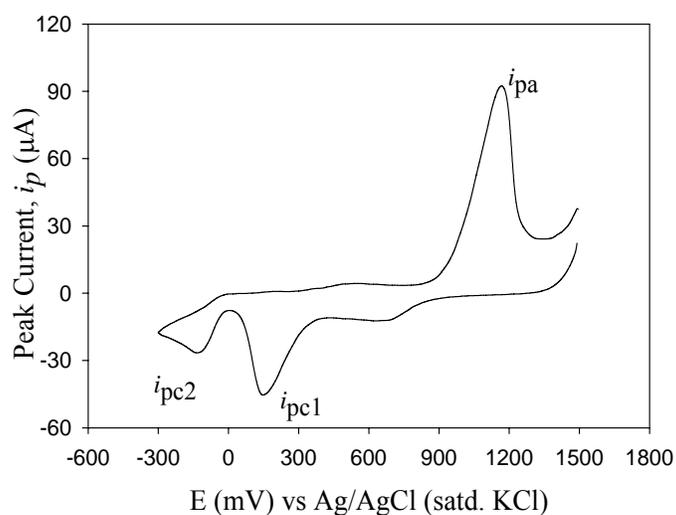
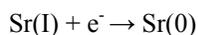
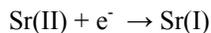


Fig. 1. Cyclic voltammogram of 0.1 mM Sr(II) in 0.01M KCl at GDE with scan rate of 50 mVs^{-1} at pH 6.23.

At more positive or negative potential values only solvent decomposition current was found. Fig. 1 shows a cyclic voltammogram of 0.1 mM Sr(II) in 0.01M KCl solution with scan rate of 50 mVs^{-1} at pH 6.23. In the forward scan two cathodic peak i_{pc1} and i_{pc2} at about +145.6 mV and -133.2 mV respectively and in the reverse scan an intense anodic peak i_{pa} at about +1166.4 mV was found. In the consecutive redox couple of Sr(II)/Sr(0), the cathodic peaks result from the reduction of Sr(II) to Sr(I) and Sr(I) to Sr(0), and the anodic peak is for the oxidation of Sr(0) to Sr(II).

The above result suggests that at pH 6.23, Sr(II) undergoes two electron transfer redox reaction. It agrees well with the previous study (Shaikh *et al.* 2011). The possible mechanism of the redox reaction is as follows:

For reduction reaction:



For oxidation:

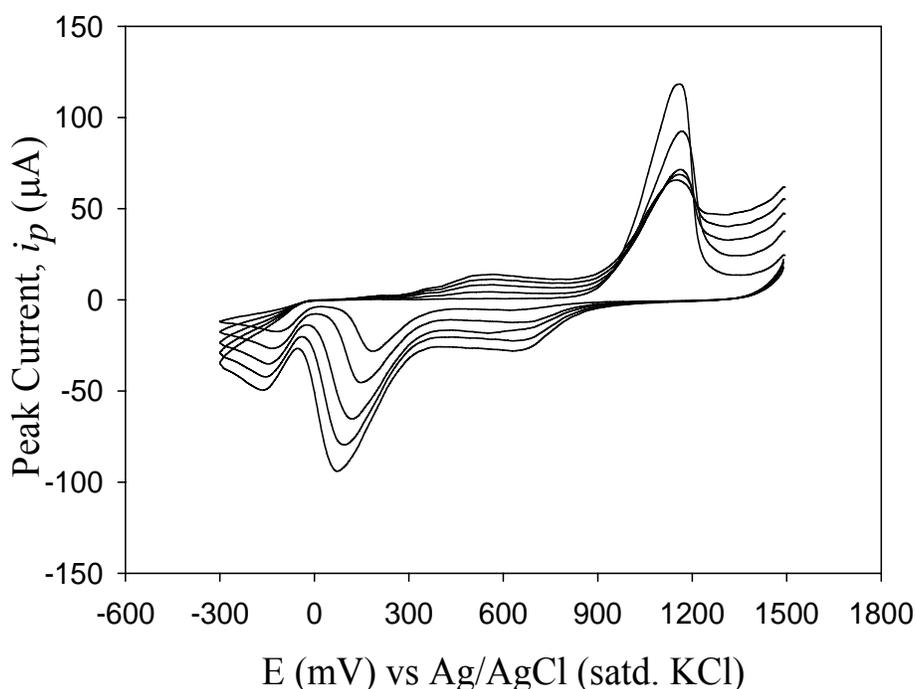


Fig. 2. Cyclic voltammograms of Sr(II) with different scan rate of 25, 50, 75, 100 and 125 mVs^{-1} at pH 6.23 at GDE.

Effect of scan rate: The effect of the scan rate on the electrochemical response of Mg(II), Ca(II), Sr(II) and Ba(II) at pH 6.23 is also examined by recording their cyclic voltammograms with scan rate of 25, 50, 75, 100 and 125 mVs^{-1} . The cyclic voltammograms of Sr(II) with scan rate of 25, 50, 75, 100 and 125 mVs^{-1} were recorded under identical condition (0.1 mM Sr(II) in 0.01 M KCl). The voltammograms obtained are shown in Fig. 2.

The recorded voltammograms are analyzed and various parameters such as anodic and cathodic peak current, peak potential separation and peak current ratio are recorded. It is found that with the increase of scan rate, both the cathodic and anodic peak current is increased (Fig. 2).

The peak potential separation and peak current ratio reveal that the redox process of Sr(II)/Sr(0) is quasi-reversible which is also characterized by the shape of the cathodic and anodic peaks (Quentel and Madec 1990). The peak potential separation (972.8-1079.2 mV) and peak current ratio (0.37- 4.20) also reveals that the redox process of Sr(II)/Sr(0) is quasi-reversible. It is observed that the cathodic peak is slightly shifted towards negative potential while the anodic peak is moved a little towards positive potential with the increase of scan rate. The shifting of the peak potential at various scan rates also indicates that the redox process is shifted from quasi-reversible to irreversible direction.

Fig. 3 apparently shows that the peak current for the redox system of Sr(II)/Sr(0) has a linear relationship with square root of scan rate and it passes through the origin. This observation is in favor of the fact that the electrode process is diffusion controlled rather than adsorption on the electrode surface. It is also in good agreement with the previous study (Akhtar *et al.* 2008).

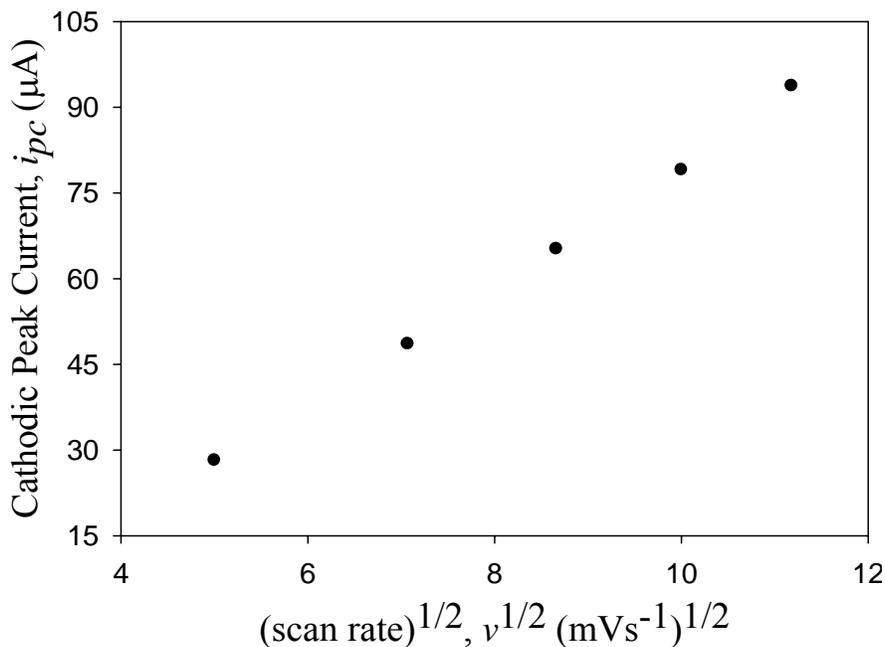


Fig. 3. Dependence of peak current with square root of scan rate for strontium system in 0.01 M KCl at pH 6.23.

The peak potential separation, ΔE_p is in between 972.8-1079.2 mV and it is increased with the increase of scan rate (Fig. 4). These observations suggest that the redox process is quasi-reversible reaction rather than a reversible process.

Effect of pH on the redox reaction of metal ions: The effect of pH on the electrochemical redox reaction of Mg(II), Ca(II), Sr(II) and Ba(II) at pH (6.23, 4.72, 4.10 and 3.68) has been investigated with GDE. A series of recorded voltammograms at different pH for Sr(II) are shown in Fig. 5. At lower pH (using acetate buffer) ranging from 3.68 to 4.72, one cathodic and an intense anodic peak were appeared. With the decrease of pH the anodic peak became sharper and

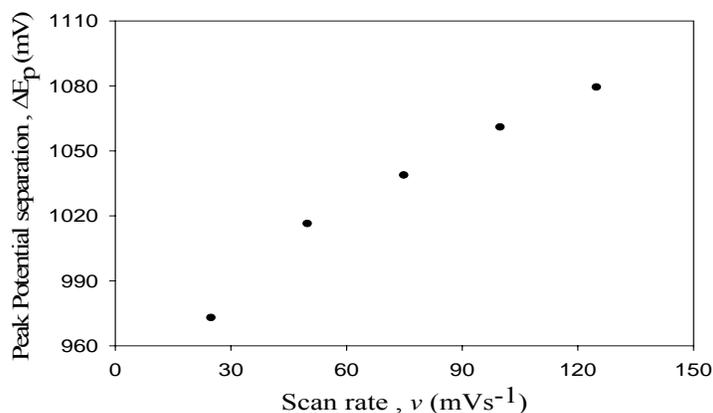


Fig. 4. Variation of peak potential separation with scan rate for 0.1 mM Sr(II) in 0.01M KCl solution at pH 6.23.

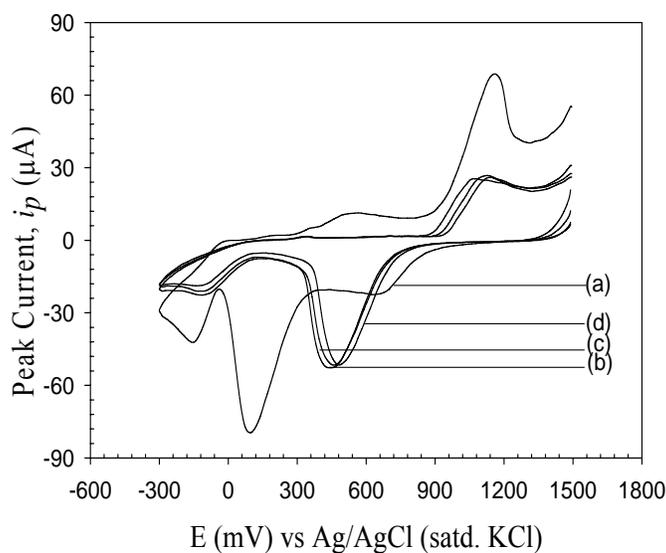


Fig. 5. Cyclic voltammograms of Sr(II) at (a) pH 6.23, (b) pH 4.72, (c) pH 4.10 and (d) pH 3.68 with scan rate of 100 mVs⁻¹.

cathodic peak shifted to more positive potential as given in Table 1. Although at lower pH one cathodic and one anodic peak were found, at higher pH (pH 6.23, solution prepared with 0.01 M KCl) two cathodic and one anodic peak were observed. At lower pH the disappearance of one of

the cathodic peaks is probably due to the presence of acetate buffer solution. In the case of pH 6.23, only KCl solution was used as a supporting electrolyte solution while in the other pH, acetate buffer was used as a supporting electrolyte.

Table 1. The data obtained for the voltammograms of Sr(II) system at different pH.

Solution pH	Anodic peak current		Cathodic peak current (μA)		Anodic peak potential (mV)		Cathodic peak potential (mV)		$\Delta E = E_{pa} - E_{pc}$	
	i_{pa1}	i_{pa2}	$i_{pc1}(-)$	$i_{pc2}(-)$	E_{pa1}	E_{pa2}	E_{pc1}	$E_{pc2}(-)$	ΔE_1	ΔE_2
6.23	68.99	-	79.63	42.14	1160.4	-	94	156	1066.4	-
4.72	25.58	-	51.24	-	1064.8	-	456.4	-	607.6	-
4.10	25.84	-	53.14	-	1116.8	-	442	-	674.8	-
3.68	26.15	-	51.81	-	1137.6	-	483	-	654.6	-

Dash (-) indicate no significant values

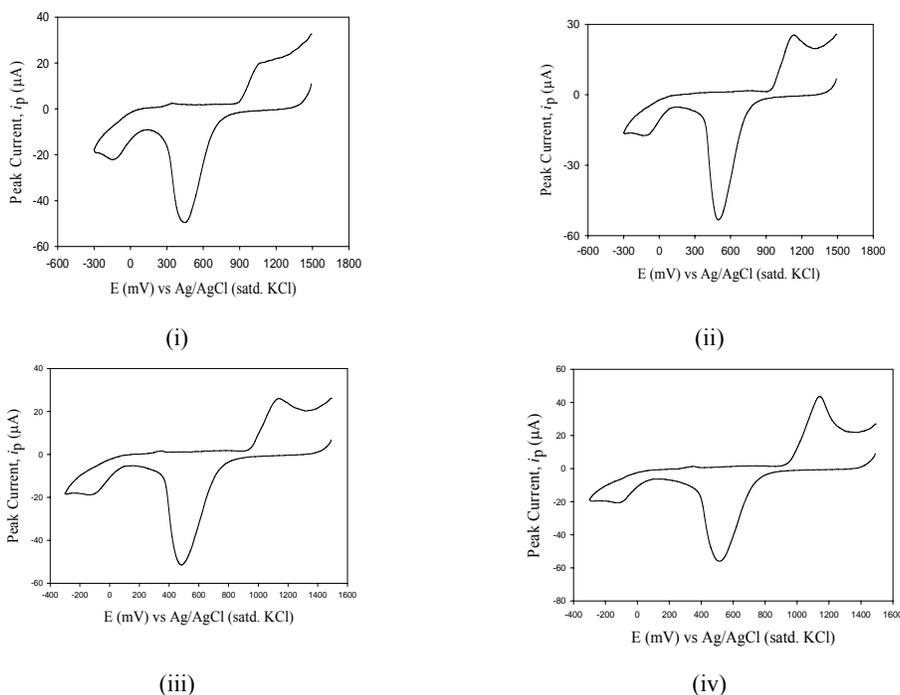


Fig. 6. Cyclic voltammograms of 1.0 mM (i) Mg(II), (ii) Ca(II), (iii) Sr(II), (iv) Ba(II) at pH 4.72 with scan rate of 100 mVs^{-1} at GDE.

Comparative studies of the voltammetric behavior of different members of alkaline earth metal ions, cyclic voltammograms were recorded for all metal ions at pH 4.72 and they are shown in Fig. 6. From the figures it is found that at studied pH all the metal ions show the identical behavior.

Voltammetric response of metal ions in presence of melamine in acetate buffer solution: The voltammograms of Mg(II), Ca(II), Sr(II) and Ba(II) in presence of Mel at various metal/Mel molar ratio (1:1, 1:2, 1:3 and 1:4) at different pH (6.23, 4.72, 4.10 and 3.68) in acetate buffer (except pH 6.23) have been recorded at GDE within the identical potential window. Fig. 7 shows the recorded voltammograms of Sr(II), and Sr(II) in presence of Mel with different molar concentration at pH 6.23. A dramatic change of the shape of voltammograms is observed. The anodic peak is completely disappeared especially at higher molar concentration of Mel, and both cathodic and anodic peak current drastically decreased than that of solely Sr(II) for each molar ratio of Sr(II) and Mel.

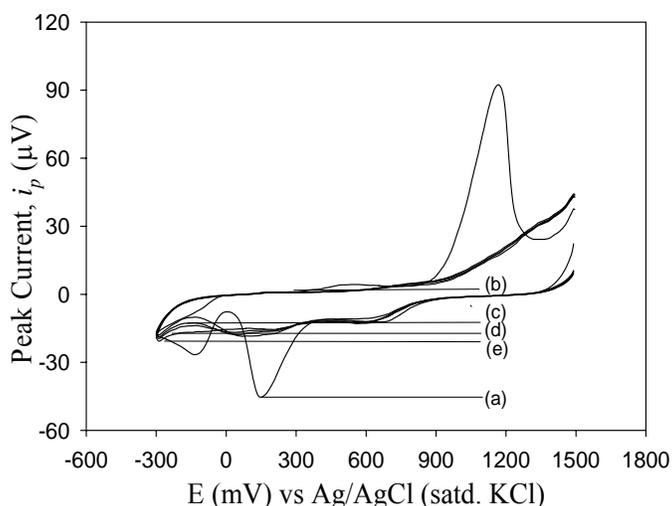


Fig. 7. Cyclic voltammograms of 0.1mM (a) Sr(II), (b) 1:1, (c) 1:2, (d) 1:3 and (e) 1:4 ratio of Sr(II) and Mel at GDE with scan rate of 50 mVs^{-1} at pH 6.23.

In presence of Mel the cathodic peak potentials also shifted slightly towards negative direction. Furthermore, the heights of the peaks are apparently inconsistent with respect to Mel concentration. Since the lowest peak current (Table 2) is found for 1:4 molar ratio of Sr(II) and Mel, the maximum interaction is indeed, occurred with this molar ratio at this pH medium. It is noted that the voltammogram of Mel in identical condition exhibits no anodic or cathodic peak within the studied potential window.

Again, the voltammograms of Sr(II) at various Sr(II)/Mel molar ratio (1:1, 1:2, 1:3 and 1:4) at pH 4.72 (in acetate buffer) have also been examined. At this pH, the anodic peak is almost disappeared but more intense cathodic peak is obtained. The peak currents are relatively lower and the peak potentials are also shifted than that of Sr(II) alone (Fig. 8). The lowest peak current is again found at 1:4 molar ratio of Sr(II) and Mel and thus the maximum interaction occurs at this composition.

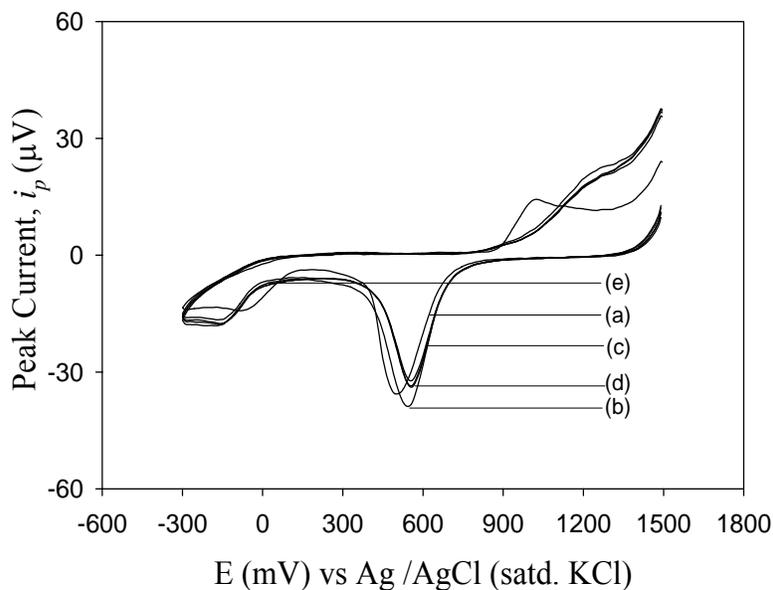


Fig. 8. Cyclic voltammograms of 0.1 mM (a) Sr(II), and Sr(II) and Mel with different ratio (b) 1:1, (c) 1:2, (d) 1:3 and (e) 1:4 at pH 4.72 with scan rate of 50 mVs⁻¹.

In presence of Mel, Sr(II) displays almost identical electrochemical behavior at pH 4.10 and at 3.69. The voltammograms recorded at pH 4.10 and at 3.69 are shown in Figs. 9 and 10 respectively. It is needed to be mentioned here that at these pH the cathodic peak has shifted slight more positive direction than those of other pH.

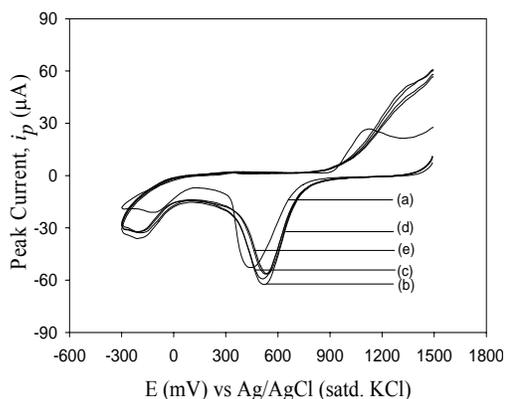


Fig. 9. Cyclic voltammograms of 0.1mM (a) Sr(II), Sr(II) and Mel with different ratio (b) 1:1, (c) 1:2, (d) 1:3 and (e) 1:4 at pH 4.10 with scan rate 100 mVs⁻¹.

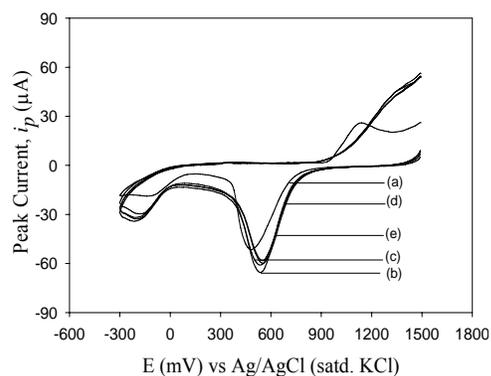


Fig. 10. Cyclic voltammograms of 0.1 mM (a) Sr(II), Sr(II) and Mel with different ratio (b) 1:1, (c) 1:2, (d) 1:3 and (e) 1:4 at pH 3.68 with scan rate 100 mVs⁻¹.

The data for the different voltammograms recorded for Sr (II)/Mel molar ratio of 1:4 at various pH is gathered in Table 2.

Table 2. The data for the voltammograms recorded for 1:4 molar ratio of Sr(II)/Mel at different pH with scan rate of 100 mVs⁻¹.

Solution pH	Peak current, μA		Peak potential, mV		Peak current ratio (i_{pa}/i_{pc})	Peak potential separation, ΔE_p
	i_{pc} (-)	i_{pa}	E_{pc} (-)	E_{pa}		
6.23	-	-	-	-	-	-
4.72	32.22	-	553.6	-	-	-
4.10	56.18	-	529.2	-	-	-
3.68	56.10	-	550.4	-	-	-

Dash (-) indicate no significant values

Like Sr(II), other alkaline earth metals (Mg(II), Ca(II) and Ba(II)) show identical behavior in acetate buffer solution at different pH, and their interaction with Mel at GDE. Fig. 11 shows the recorded voltammograms of Ca(II), and Ca(II) in presence of Mel with different molar concentration at pH 4.10.

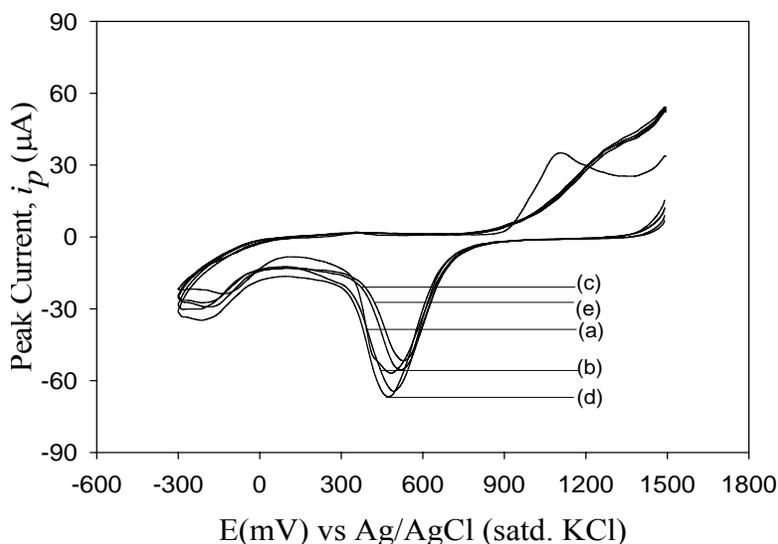


Fig. 11. Cyclic voltammograms of 0.1mM (a) Ca(II), and Ca(II) and Mel with different molar ratio (b)1:1, (c) 1:2, (d) 1:3 and (e) 1:4 in acetate buffer at pH 4.10 with scan rate 100 mVs⁻¹.

Conclusion

The electrochemical redox behavior of alkaline earth metal ions (Mg(II), Ca(II), Sr(II) and Ba(II)) in 0.01 M KCl and acetate buffer has been studied at different pH (6.23, 4.72, 4.10 and 3.68). At

pH 6.23 (in 0.01 M KCl), the voltammograms of the studied systems show two cathodic and an anodic peak. While at pH (4.72, 4.10 and 3.68) in acetate buffer medium one anodic and one cathodic peak is observed. The peak potential separation, and peak current ratio of the systems Mg(II)/Mg(0), Ca(II)/Ca(0), Sr(II)/Sr(0) and Ba(II)/Ba(0) reveal that the redox processes are quasi-reversible. The linear behavior of peak current vs. square root of scan rate plot suggests that electrode processes are diffusion controlled. In presence of Mel, in acetate buffer medium at pH (4.72, 4.10 and 3.68), the anodic peak is completely disappeared while cathodic peak intensity slightly increases. Moreover, cathodic peaks are shifted towards positive direction. Nevertheless, at pH 6.23, both of the cathodic and the anodic peak are almost disappeared. This observation indicates that the strong interaction occurs between metal ions and Mel at pH 6.23 in 0.01 M KCl at a molar ratio of 1:4.

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