Cyclic Voltammetric studies of Calcium acetate salt with Methylene blue Using Gold Electrode

Mohamed. M. El-Defrawy, Esam. A.Gomaa [✉], Shereen. E. Salem, Fatma.M. Abdel Razek

Chemistry Department, Faculty of Science, Mansoura University, 35516-Mansoura, Egypt

HIGHLIGHTS

- Detecting of calcium ions in form of acetate by cyclic voltammetry.
- Good detection of calcium ions at suitable potentials and not large potentials as usual.
- Complexation study with methylene blue which help in analytic determination of calcium ions.
- Determining the thermodynamic parameters for interaction of calcium ions with methylene blue.

GRAPHICAL ABSTRACT

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ABSTRACT

Cyclic Voltammetric studies of calcium acetate salt $[\text{Ca}(\text{CH}_3\text{COO})_2]$ in absence or presence of Methylene blue (MB) were performed to predict and analyze the behavior of complexation between the ligand and metal ion in aqueous solution. From these studies, the values of solvation and kinetic parameters $[E_p$ (peak potential), I_p (peak current), ΔE_p (peak potential difference), $E_{1/2}$ (half wave potential), D (Diffusion coefficient), K_s (electron transfer rate constant), Γ (surface coverage) and Q_a (quantity of electricity)] were evaluated. In addition, the effect of different concentration and a scan rate of above the calculated quantities were studied. In case of presence MB, the stability constants and Gibbs free energies were performed.

1. Introduction

Calcium acetate is used to decrease and prevent blood phosphate levels in patients suffering from dialysis due to kidney disease [1]. Hyperphosphatemia has a universal effect in patients with chronic disease [2]. Dialysis can remove some phosphate from the blood, but it is hard to remove enough to control the phosphate level [1, 2]. Decreasing on the blood phosphate levels help to keep

bones strong, prevent unsafe build up of minerals in the body and decrease the heart diseases. Calcium acetate is a natural mineral that works by extracting phosphate from the diet so that it passes out of the body [1].

Theoretical calculations, using equilibrium constants should be an effective phosphate binder [3]. In vitro experiments confirmed the theoretical binder [3]. In vivo

* Corresponding author: Tel: + 20222672163

E-mail: eahgomaa65@yahoo.com

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studies in normal subjects found calcium acetate to be more phosphorous binding than calcium carbonate[4].

Analytical determination of calcium acetate is therefore important to follow them in foods, environment and human bodies, which is our main target. Using cyclic voltammetry as electroanalytical tool for evaluation of calcium acetate is very important. Gold working electrode (GE) was prepared in our laboratory, facilitating the easy determination of calcium acetate in aqueous solutions. Calcium ions are well detected here using GE in opposite to that by using glassy carbon electrode which will appear at a high voltage area.

2. Experimental

2.1. Reagents and solutions

The chemicals used are calcium acetate salt $[\text{Ca}(\text{CH}_3\text{COO})_2]$, HCl and methylene blue from Sigma Aldrich Company (purity 98%). Pure water was used by distillation.

2.2. Instrumentation

The cyclic voltammetric studies were done by using a potentiostat of the type DY2000, delivered from USA. It was connected to a cell of three electrodes, Ag/AgCl, KCl_{sat} was used as reference electrode, gold electrode (GE) was used as working electrode and platinum wire, auxiliary electrode. GE was prepared in our laboratory from pure gold wire 18K bought from famous jewellery shop jointed with steel rod, isolated, covered with heat shrink polymer and polished good by woollen piece before using. Area of electrode is $7.853 \times 10^{-3} \text{ cm}^2$. The system was applied from 1.6 to -1.6 V potential windows and 0.1, 0.02, 0.01 v/s as scan rates at constant temperature 294.85 K. Flow of purified N_2 was done to ensure removal of O_2 and diffusion experiment.

3. Results and Discussion

3.1. Electrochemical behavior of Ca^{+2} ions in absence of ligand, MB at 294.85 K.

3.1.1. Solvation and kinetic parameters in absence of MB.

First, the cyclic voltammogram of 30 ml HCl (0.1 M) as a supporting electrolyte was measured from 1.6 to -1.6 V of potential window, the current is measured in Ampere unit, whereas the scan is 0.1 V/S (volt per second) at

294.85 K, (Fig.1). Then, the redox behavior of Ca^{+2} ions was examined in 0.1 M of HCl at 294.85 K. The Ca^{+2} ions solution is added step wisely from 0.2 ml ($6.62 \times 10^{-4} \text{ M}$) to reach until 1 ml ($3.23 \times 10^{-3} \text{ M}$) as shown in (Fig.2).

The electrochemical redox behavior of Ca^{+2} ions in absence of MB at the GE was studied at the steady state current, cyclic waves were obtained and explained using the following equation (1) [5-8]:

$$i_p = 0.4463 n F A C (n F D v / R T)^{1/2} \quad (1)$$

i_p is the current in Ampere, A is the surface area of working electrode in cm^2 , D is the diffusion coefficient in cm^2/Sec , v is the scan rate in volts/Sec and C is the concentration of the Ca^{+2} ions.

The peak potential difference, ΔE_p is calculated from equation (2):

$$\Delta E_p = E_{Pa} - E_{Pc} \quad (2)$$

If ΔE_p will close to $59/n \text{ mv}$ (at 25°C) the reaction is reversible where, n is the number of electrons in redox reactions.

Fig.1. Cyclic voltammogram of 30 ml HCl (0.1 M) as a supporting electrolyte at 294.85 K and scan rate 0.1 V/S.

Fig.2. Cyclic voltammogram of different Ca^{+2} ions concentrations in 30 ml HCl (0.1 M) and scan rate 0.1 V/S at 294.85 K.

The standard heterogeneous electron transfer rate constant k_s in cm/sec was calculated by applying the following equation (3) [9, 10]:

$$k_s = 2.18 * [D_c \alpha n_a F v / RT]^{1/2} * \exp [\alpha^2 n F \Delta E_p / RT] \quad (3)$$

Where, α is charge transfer coefficient and n_a is the numbers of electron transfer in the rate determining step. Assuming that α coefficient is equal to 0.5. Hence, αn_a will be as the shown in equation (4):

$$\alpha n_a = 1.857 RT / (E_{pc} - E_{pc/2}) F \quad (4)$$

Where $E_{pc/2}$ is the half wave potential for cathodic peak. Then the surface coverage Γ (surface concentration of the electroactive species in mol.cm⁻²) was evaluated by equation (5) [11, 12]:

$$\Gamma = i_p 4RT / n^2 F^2 A v \quad (5)$$

The quantity of charge consumed during the reduction or adsorption of the adsorbed layer can be used to calculate the surface coverage by eq. (6)[13]:

$$Q = n F A \Gamma \quad (6)$$

The different cyclic Voltammetry analysis data were calculated and the obtained data are E_p (anodic peak potential), E_c (cathodic peak potential), I_p (anodic peak current), I_c (cathodic peak current), ΔE_p (peak potential difference), $E_{1/2}$ (half wave potential), D_a (anodic diffusion coefficient), D_c (cathodic diffusion coefficient), K_s (electron transfer rate constant), Γ_a (anodic surface coverage), Γ_c (cathodic surface coverage), Q_a (anodic quantity of electricity) and Q_c (cathodic quantity of electricity) in Table 1.(a,b)[14-18].

Fig. 3 illustrates the relation between cathodic and anodic peak current I_p against different concentrations of Ca²⁺ ions in 0.1M HCl gives straight lines indicating the reversibility of the mechanisms.

All the kinetic parameters [D_a , D_c , K_s , Q_a , Q_c , Γ_a , Γ_c] for Ca²⁺ ions concentration are increased by increasing in the concentrations of calcium acetate favoring diffusion controlled reactions. Fig.3 gave a straight line relationship between current (i) and Ca²⁺ ion concentrations for both cathodic and anodic peaks supporting also the diffusion reaction.

Fig.3. The relation between peak current I_p ($i_{p,a}$ - $i_{p,c}$) against different concentrations of Ca²⁺ ions at 294.85 K and scan rate 0.1 V/S.

3.1.2. Effect of different scan rates

Effect of different scan rates for the redox behavior of Ca²⁺ ions in 0.1 M HCl was studied in the range 0.1, 0.02 and 0.01 (V.s⁻¹) at 294.85 K, (Fig.4). The solvation and kinetic parameters (E_p , I_p , ΔE_p , $E_{1/2}$, D , k_s , Γ and Q) of different scan rates of Ca²⁺ ions were presented in Table. 2 (a,b).

Randles Sevcik equation (10-17) was used to apply the relation between cathodic and anodic peak current I_p against the square root of scan rate in 0.1M HCl which gives straight lines indicating diffusion process as shown in Fig.5.

Fig.4. Cyclic voltammogram of different scan rates of 2.60×10^{-3} M Ca²⁺ ions in 0.1M HCl at 294.85 K.

Table.1 (a): The solvation and kinetic parameters [E_p , E_c , I_p , I_c , ΔE_p , $E_{1/2}$] of different concentrations of Ca^{+2} ions at scan rate 0.1 V/S and 294.85 K.

mL of M	[M] (mol.L ⁻¹)	E_p (V)	E_c (V)	$(-)I_p \times 10^{-6}$ (A)	$I_c \times 10^{-6}$ (A)	ΔE_p (V)	$E_{1/2}$ (V)
0.2	0.0006	0.246	0.105	0.824	0.618	0.142	0.175
0.4	0.0013	0.243	0.086	1.50	1.33	0.157	0.164
0.6	0.0019	0.245	0.079	2.02	3.17	0.166	0.162
0.8	0.0025	0.264	0.036	6.23	6.92	0.228	0.150
1	0.0032	0.278	0.006	8.44	9.00	0.272	0.142

Table.1 (b): The solvation and kinetic parameters [D_a , D_c , K_s , Γ_a , Γ_c , Q_a , Q_c] of different concentrations of Ca^{+2} ions at scan rate 0.1 V/S and 294.85 K.

mL of M	[M] (mol.L ⁻¹)	$D_a \times 10^{-12}$ (cm ² .s ⁻¹)	$D_c \times 10^{-12}$ (cm ² .s ⁻¹)	$K_s C \times 10^{-4}$ (cm.s ⁻¹)	$\Gamma_c \times 10^{-9}$ (mol/cm ²)	$(+) Q_c \times 10^{-6}$ (C)	$\Gamma_a \times 10^{-9}$ (mol/cm ²)	$(-) Q_a \times 10^{-6}$ (C)
0.2	0.0006	0.430	0.242	0.421	0.207	0.314	0.276	0.419
0.4	0.0013	0.360	0.284	0.629	0.446	0.676	0.502	0.761
0.6	0.0019	0.294	0.726	1.25	1.062	1.61	0.676	1.02
0.8	0.0025	1.60	1.97	5.50	2.321	3.52	2.089	3.16
1	0.0032	1.90	2.17	11.2	3.020	4.58	2.831	4.29

Table.2(a): The solvation and kinetic parameters (E_p , E_c , I_p , I_c , ΔE_p , $E_{1/2}$) of different scan rates of 2.60×10^{-3} M Ca^{+2} ions at 294.85 K.

v	E_p (v)	E_c (v)	$(-)I_{p,a}(A) \times 10^{-6}$	$I_{p,c}(A) \times 10^{-6}$	ΔE_p (v)	$E_{1/2}$ (v)
0.1	0.264	0.0361	6.23	6.92	0.228	0.150
0.02	0.232	0.112	1.35	1.49	0.121	0.172
0.01	0.231	0.114	1.61	1.61	0.116	0.173

Table.2(a): The solvation and kinetic parameters (D_a , D_c , K_s , Γ_a , Γ_c , Q_a , Q_c) of different scan rates of 2.60×10^{-3} M Ca^{+2} ions at 294.85 K.

v	$D_a \times 10^{-12}$ (cm ² .s ⁻¹)	$D_c \times 10^{-12}$ (cm ² .s ⁻¹)	$K_s C \times 10^{-5}$ (cm.s ⁻¹)	$\Gamma_c \times 10^{-9}$ (mol/cm ²)	$(+) Q_c \times 10^{-6}$ (C)	$\Gamma_a \times 10^{-9}$ (mol/cm ²)	$(-) Q_a \times 10^{-6}$ (C)
0.1	1.60	1.97	0.550	2.32145	3.52	2.0893	3.16
0.02	0.377	0.457	2.06	2.49759	3.78	2.2705	3.44
0.01	1.06	1.06	1.97	5.38974	8.16	5.3897	8.16

The diffusion mechanism is also supported by scan rate effect which shows an increase in height of the waves by increasing scan rate.

Fig.5. The relation between peak current I_p ($i_{p,a}$ - $i_{p,c}$) against the square root of different scan rates for Ca^{+2} ions at 294.85 K.

3.2. Electrochemical behavior of Ca^{+2} ions in presence of ligand, MB at 294.85 K.

3.2.1 Effect of different MB concentrations.

3.2.1.1. Solvation and kinetic parameters in presence of MB.

The electrochemical behavior of the complexation between MB and Ca^{+2} ions in 0.1M HCl at 294.85 K with 1.6 V to -1.6 V potential windows and scan rate 0.1 V/S were shown in Fig.6.

The electrochemical redox behavior of Ca^{+2} ions in the presence of MB at the GE was studied at the steady state current, cyclic waves were obtained and explained using equations (1-6).

Fig.6. Cyclic voltammograms for the interaction of 3.2×10^{-3} M Ca^{2+} ions and different concentrations of MB at 294.85 K and scan rate 0.1 V/S.

The solvation and kinetic parameters (E_p , I_p , ΔE_p , $E_{1/2}$, D , k_s , Γ and Q) of interaction of 3.2×10^{-3} M Ca^{2+} ions and different concentrations of Methylene blue at 294.85 K and scan rate 0.1 V/S were presented in Table 3.(a,b).

Randles Sevcik equation (6-10) was used to apply the relation between cathodic and anodic peak current I_p against different concentrations of Ca ions in the presence of MB which gives straight lines indicating diffusion process as shown in Fig.7.

The gold wave at -1.0 volt is slightly affected by calcium acetate in the presence of MB due to the complexation reaction between metal ions (Ca^{2+}) and MB.

The calcium peaks illustrated before at 0.0 and 0.25 V are increasing in intensity, height by more adding MB to Ca ions, shifted to more negative values for the reduction peak and more positive values for the oxidation wave. All the results indicate complexation reaction between MB and Ca ions as calcium acetate.

Fig.7. The relation between peak current I_p ($i_{p,a} - i_{p,c}$) against Ca^{2+} ions concentrations in the presence of MB at 294.85 K and scan rate 0.1 V/S.

The kinetic parameters [D_a , D_c , K_s , Q_a , Q_c , Γ_a , Γ_c] for the interaction of MB with calcium acetate are smaller than that of calcium acetate solutions alone indicating complexation reaction between Ca ions and MB ligand.

3.2.1.2. Electrochemical behavior of the complexation between MB and Ca ions.

From Fig.6, it is observed that the complex is formed as a result of decreasing in the anodic and cathodic peak beside the potential shifts to new values. Due to precipitating the complex during the process, no peak appeared. A stability constant is a measure of the strength of the interaction between the reagents that come together to form the complex. The stability constants (β_{MX}) for bulk and nano cadmium chloride complexes for each addition are calculated by applying Eq. (10) [5, 16]:

$$\Delta E^\circ = E^\circ_c - E^\circ_m = 2.303 (RT/nF) * (\log \beta_{MX} + j \log C_x) \quad (10)$$

Where E°_m is the formal peak potential of metal at finally adding in the absence of ligand, E°_c is the formal peak potential of metal complex after each addition of MB, R is a gas constant ($8.314 \text{ J.mol}^{-1}.\text{degree}^{-1}$), T is the absolute temperature, j is the coordination number of the Stoichiometric complex and C_x is the concentration of MB in the solution.

The formal potential E° can be found as the midway between the two cyclic voltammetric peaks comprising the voltammogram by equation (11):

$$E^\circ = (E_{pa} + E_{pc}) / 2 \quad (11)$$

Where both E_{pa} and E_{pc} are anodic peak potential and cathodic peak potential, respectively

The Gibbs free energy of interaction for Ca^{2+} ions with MB were calculated from stability constant (β_{MX}) using Eq. (12) [10-20]:

$$\Delta G = -2.303 RT \log \beta_{MX} \quad (12)$$

The calculated values of E° , β_{MX} and ΔG for Ca^{2+} ion complexes are estimated and collected in Table 4.

The thermodynamic parameters β_j and ΔG for the interaction of MB with calcium acetate are increased by increasing the concentration of MB in solutions indicating more complexation.

Table3.(a): The solvation and kinetic parameters (E_p , $E_{p,c}$, $I_{p,a}$, $I_{p,c}$, ΔE_p , $E_{1/2}$) of interaction of 3.2×10^{-3} M Ca^{+2} ions and different concentrations of MB at 294.85 K and scan rate 0.1 V/S.

mL of M	[M] $\times 10^{-3}$ (mol.L $^{-1}$)	ml of L	[L] $\times 10^{-6}$ (mol.L $^{-1}$)	$E_{p,a}$	$E_{p,c}$	(-) $I_{p,a} \times 10^{-6}$	$I_{p,c} \times 10^{-6}$	ΔE_p (v)	$E_{1/2}$ (v)
1	3.21	0.2	1.03	0.271	0.027	7.31	7.29	0.244	0.149
1	3.18	0.4	2.04	0.283	0.013	9.90	0.108	0.269	0.148
1	3.16	0.6	3.04	0.269	0.023	7.22	7.04	0.246	0.146
1	3.14	0.8	4.03	0.285	0.016	9.55	8.73	0.269	0.151
1	3.13	1	5.00	0.30	0.008	0.109	9.30	0.292	0.154

Table3(b): The solvation and kinetic parameters (D_a , D_c , K_s , Γ_a , Γ_c , Q_a , Q_c) of interaction of 3.2×10^{-3} M Ca^{+2} ions and different concentrations of MB at 294.85 K and scan rate 0.1 V/S.

mL of M	[M] $\times 10^{-3}$ (mol.L $^{-1}$)	ml of L	[L] $\times 10^{-6}$ (mol.L $^{-1}$)	$D_a \times 10^{-12}$ (cm 2 .s $^{-1}$)	$D_c \times 10^{-12}$ (cm 2 .s $^{-1}$)	$K_s \text{ C} \times 10^{-4}$ (cm.s $^{-1}$)	$\Gamma_c \times 10^{-9}$ (mol/cm 2)	(+) $Q_c \times 10^{-6}$ (C)	$\Gamma_a \times 10^{-9}$ (mol/cm 2)	(-) $Q_a \times 10^{-6}$ (C)
1	3.21	0.2	1.03	1.45	1.44	5.16	2.446	3.71	2.452	3.72
1	3.18	0.4	2.04	2.69	3.22	0.136	3.634	5.51	3.320	5.03
1	3.16	0.6	3.04	1.45	1.38	5.32	2.361	3.58	2.422	3.67
1	3.14	0.8	4.03	2.57	2.14	0.104	2.928	4.44	3.205	4.86
1	3.13	1	5.00	3.40	2.46	0.177	3.121	4.73	3.665	5.55

Table(4): The values of (Formal potential E° , stability constant β_{MX} and Gibbs free energy ΔG) for Ca^{+2} ion complexes at 294.85 K and scan rate 0.1 V/S.

mL of M	[M] $\times 10^{-3}$ (mol.L $^{-1}$)	ml of L	[L] $\times 10^{-6}$ (mol.L $^{-1}$)	($E_{p,a}$)M (v)	($E_{p,a}$)C (v)	$j \times 10^{-4}$	Log[L]	Log β_j	β_j	ΔG (KJ/mol)
1	3.21	0.2	1.03	0.1418	0.1491	3.20	-5.989	0.251	1.781	-1.415
1	3.18	0.4	2.04	0.1418	0.1484	6.40	-5.691	0.231	1.700	-1.301
1	3.16	0.6	3.04	0.1418	0.1463	9.60	-5.517	0.158	1.440	-0.894
1	3.14	0.8	4.03	0.1418	0.1508	0.128	-5.395	0.316	2.072	-1.786
1	3.13	1	5.00	0.1418	0.1545	0.160	-5.301	0.441	2.762	-2.491

3.2.2. Effect of different scan rates

Effect of different scan rates on the interaction between Ca^{+2} ions and MB was studied in 0.1, 0.02 and 0.01 V.s $^{-1}$, (Fig. 8). The solvation and kinetic parameters (E_p , I_p , ΔE_p , $E_{1/2}$, D , K_s , Γ and Q) of different scan rates of Ca^{+2} ions in the presence of MB were presented in Table 5.(a,b). Randles Sevcik equation was used to apply the relation between cathodic and anodic peak current I_p against the square root of scan rate in 0.1M HCl which gives straight lines indicating diffusion process as shown in Fig.9. All scan rate parameters for interaction of MB with calcium acetate are smaller than that of the absence of ligand indicating also the complexation character (Fig.9). It indicates less slope obtained for the complex than the metal supported also the complexation behavior.

Fig.8. Cyclic voltammogram of different scan rate of 3.13×10^{-3} M Ca^{+2} ions with 5.00×10^{-6} MB at 294.85 K.

Table.5(a): The solvation and kinetic parameters (E_p , I_p , ΔE_p , $E_{1/2}$) of different scan rates of Ca^{+2} ion complexes at 294.85 K.

v	$[M] \times 10^{-3}$ (mol.L $^{-1}$)	$[L] \times 10^{-6}$ (mol.L $^{-1}$)	$E_{p,a}$	$E_{p,c}$	$(-)I_{p,a} \times 10^{-6}$	$I_{p,c} \times 10^{-6}$	ΔE_p (v)	$E_{1/2}$ (v)
0.1	3.13	5.00	0.300	0.009	0.109	9.30	0.292	0.154
0.02	3.13	5.00	0.252	0.094	3.99	3.81	0.159	0.173
0.01	3.13	5.00	0.243	0.100	3.46	1.96	0.143	0.171

Table.5(b): The solvation and kinetic parameters (D , k_s , Γ and Q) of different scan rates of Ca^{+2} ion complexes at 294.85 K.

v	$[M] \times 10^{-3}$ (mol.L $^{-1}$)	$[L] \times 10^{-6}$ (mol.L $^{-1}$)	$D_a \times 10^{-12}$ (cm 2 .s $^{-1}$)	$D_c \times 10^{-12}$ (cm 2 .s $^{-1}$)	$K_s C \times 10^{-5}$ (cm.s $^{-1}$)	$\Gamma_c \times 10^{-9}$ (mol/cm 2)	$(+)Q_c \times 10^{-6}$ (C)	$\Gamma_a \times 10^{-9}$ (mol/cm 2)	$(-)Q_a \times 10^{-5}$ (C)
0.1	3.13	5.00	3.4	2.463	0.0017	3.121	4.73	3.665	0.55
0.02	3.13	5.00	2.27	2.065	7.98	6.389	9.68	6.696	1.01
0.01	3.13	5.00	3.4	1.092	3.28	6.571	9.95	0.115	1.76

Table 6: The solvation and kinetic parameters (E_p , I_p , ΔE_p , $E_{1/2}$, D , k_s , Γ and Q) of 0.1M HCl, 3.13×10^{-3} M Ca^{+2} ions and 5.00×10^{-6} MB at 294.85 K and scan rate 0.1 V/S.

mL of M	$[M]$ (mol.L $^{-1}$)	mL of L	$[L]$ (mol.L $^{-1}$)	$E_{p,a}$	$E_{p,c}$	ΔE_p	$(-)I_{p,a} \times 10^{-5}$	$I_{p,c} \times 10^{-6}$	E°
0	0	0	0	1.16	1.162	0.767	0.431	6.30	0.965
1	3.23×10^{-3}	0	0	1.15	1.146	0.596	1.29	6.27	0.871
1	3.13×10^{-3}	1	5.00×10^{-6}	1.13	1.128	0.584	1.13	6.51	0.856

D_a (cm 2 .s $^{-1}$)	D_c (cm 2 .s $^{-1}$)	$E_{p,c}/2$	$K_s C$ (cm.s $^{-1}$)	$\Gamma_c \times 10^{-9}$	$(+)Q_c \times 10^{-6}$ (C)	$\Gamma_a \times 10^{-9}$	$(-)Q_a \times 10^{-6}$ (C)
0	0	0.826	0.000	2.111	3.20	1.445	2.19
4.46×10^{-12}	1.05×10^{-12}	0.704	0.149	2.104	3.19	4.337	6.57
3.62×10^{-12}	1.21×10^{-12}	0.700	0.134	2.183	3.31	3.784	5.73

3.3. Effect of HCl (0.1) M as a supporting electrolyte.

From Fig.10, it was observed that HCl (0.1) M as a supporting electrolyte show a cathodic peak which disappear by adding Ca^{+2} ions and MB due to complexation.

Fig.9. The relation between peak current I_p ($i_{p,a}$ - $i_{p,c}$) against different scan rates of Ca^{+2} ions with MB at 294.85 K. **Fig.10.** Cyclic voltammogram of 0.1M HCl, 3.13×10^{-3} M Ca^{+2} ions and 5.00×10^{-6} MB at 294.85 K and scan rate 0.1 V/S.

4. Conclusion

The cyclic voltammetry of the supporting electrolyte (0.1M HCl) was obtained by using Gold electrode (GE). One reduction wave was obtained at ~ -1 V corresponding to the reduction of gold chloride to gold metal. By adding different concentrations from calcium acetate appearance of two new waves happened, one reduction peak at ~ 0.0 V and one oxidation peak at ~ 0.25 V corresponding to the reduction and oxidation of calcium ions. All the kinetic parameters [anodic diffusion coefficient D_a , cathodic diffusion coefficient D_c , electron rate constant K_s , anodic quantity of electricity Q_a , cathodic quantity of electricity Q_c , anodic and cathodic surface coverage, Γ_a , Γ_c] for calcium acetate concentrations are increased by increasing in the concentrations of calcium acetate favoring diffusion controlled reactions. The calcium peaks were increased in intensity by adding methylene blue (MB) to calcium ions, the potential of reduction peak was shifted to more negative and the potential of oxidation peak was shifted to more positive values. All the results, indicate that the solvation and kinetic parameters [K_s , Q_a , Q_c , Γ_a , Γ_c] of the complexation reaction between MB ligand and Ca^{+2} ions are smaller than that for Ca^{+2} ion in HCl solution as supporting electrolyte. The thermodynamic parameters [stability constant, β_j and Gibbs free energies of complexation, ΔG] for the interaction of MB with Ca^{+2} ions are increased by increasing the concentration of MB in solutions indicating more complexation.

5. References

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