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Kinetic and Thermodynamic Cyclic Voltammetric Parameters for Interaction of $MnSO_4$ with Amoxicillin and Their Effect on MnO_2 Deposition

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Abstract: In this work, the kinetic parameters for $MnSO_4$ were studied and evaluated by the use of cyclic voltammetry (CV) in the absence and the presence of Amoxicillin by using a glassy carbon electrode (GCE). Also, the stability constant and thermodynamic parameters were evaluated for the complex formed between Mn ions with Amoxicillin. In addition, the effect of scan rate on the kinetic and thermodynamic parameters in (absence /presence) of Amoxicillin was studied. The mechanism of redox behavior was proposed for $MnSO_4$ that forming MnO_2 deposited at the glassy carbon electrode. The results obtained were discussed by the use of the cyclic voltammetry method.

keywords: Kinetic Parameters, Thermodynamic parameters, $MnSO_4$, MnO_2, Cyclic Voltammetry, Amoxicillin.

1.Introduction

The stability constants for complexation of $MnSO_4$ with Amoxicillin can be explained using cyclic voltammetrically by measuring the shift anodic and cathodic peaks. The kinetic parameters necessary for the reduction of $MnSO_4$ which oxidized in 0.1M Na_2SO_4 forming MnO_2 deposited at the glassy carbon electrode were studied by the use of cyclic voltammetry. The voltammograms of $MnSO_4$ & MnO_2 using glassy carbon electrode (GCE) cycled between (1.5 and -1.0 V) vs Ag/AgCl/Saturated KCl at 0.1 v/s scan rate. The redox mechanisms and the stability constants for the complexes formed are discussed.

Manganese dioxides are used mainly for the manufacture of bacteria. MnO_2 are classified into three sorts, natural (NMDi), chemical (CMDi) and electro-chemical (ECMDi). The last one is deposited on an inert electrode as explained in equation (1):

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \quad (1)$$

The formed MnO_2 is reduced and deposited at the glassy carbon electrode [1, 2].

Experimental

1. Chemicals

The chemicals used in the experimental part such as $MnSO_4$ delivered from ADWIC Co, sodium sulphate is provided from Misr Chemical Co with high purity and used without purification to prevent damage to them, Amoxicillin was provided from E.I.P.C.O Co.

2. The instrument for cyclic voltammetry

The cell used is consists of three electrodes type connected to multichannel potentiostat DY 2000. Ag/AgCl filled with saturated KCl was used as the reference electrode, glassy carbon electrode (GCE) was polished with fine Al_2O_3 powder put above wool clean piece, and platinum wire (AE) used as an auxiliary electrode to prevent the destroying of glassy carbon electrode. N_2 flow was done to ensure measuring in an inert atmosphere. The electrodes were immersed in a cell containing 30 ml of 0.1 M of Na_2SO_4. The system was applied with 1.5 V to -1.0 V potential windows and (0.1 v/s) scan rate at 297.15K.

Results and Discussion

1. Redox reaction of $MnSO_4$ depositing MnO_2

The voltammogram exhibits two anodic peaks at about (0.8V and 0.3V) vs. Ag/AgCl/sat. KCl electrode resulting in the deposition of MnO_2 on a glassy carbon working electrode. The electro-reduction of the formed MnO_2 from the dissolution of $MnSO_4$ in 0.1M

Na_2SO_4 is represented in Figure (1). And the effect of concentration data for the first and second couple of waves was given in Tables (1-a, b).

As explained in the literature [1], studying the redox reaction of $MnSO_4$ in dilute H_2SO_4, also we reported two cathodic currents in cyclic voltammograms of MnO_2 in 0.1M Na_2SO_4. The layer MnO_2 deposited during the half-wave anodic part was not completely reduced, ratio $I_{p,a}/I_{p,c}$ is great through the half-wave cycles. It is evident that the concentration of Mn^{2+} ions influences the kinetics of the reaction.

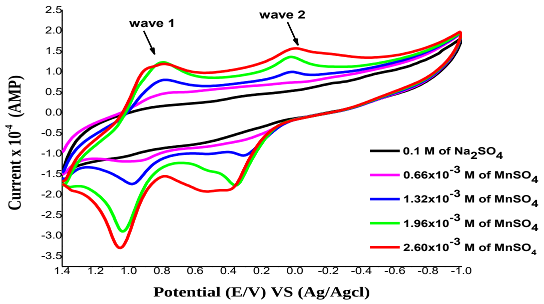

Fig. (1): Cyclic Voltammetry of $MnSO_4$ at 0.1 scan rate at 297.15 K **Analysis of the wave**

The following equations are used for complex analysis of the waves. The peak current is given by Randles-Sevcik equation [3-7]:

$$I_p = (2.69x10^5)\ n^{3/2}\ A\ C\ \nu^{1/2}\ D^{1/2} \quad (2)$$

Where I_p is the measured current in Ampere, A is the surface electrode area (cm^2), D is the diffusion coefficient in (cm^2/s), ν is scan rate in (volts/sec) and C is the molar concentration of metal ion (mol/cm^3).

Equation (3) was used for calculating the potential difference [8, 9]:

$$\Delta E_p = E_{p,a} - E_{p,c} \quad (3)$$

The charge transfer coefficient of electrons was calculated by applying equation (4) [10-13]:

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

The surface concentration of the redox ion in ($mol.cm^{-2}$) was evaluated by the use of equation (5) [14-18]:

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

The quantity of charge consumed during the redox reaction of MnO_2 adsorbed layer was evaluated by applying equation (6) [19]:

$$Q = n\ FA\ \Gamma \quad (6)$$

The heterogeneous charge transfer rate constant (k_s) can be calculated by the use of equation (7) [20-24]:

$$k_s = 2.18^*\ [D_c\ \alpha n_a\ F\ \nu/RT]^{1/2}\ {}^*\exp\ [\alpha^2\ nF\ (E_{p,c} - E_{p,a})\ /RT] \quad (7)$$

Most of the evaluated parameters, $E_{p,a}$, anodic wave potential, $I_{p,a}$ (anodic peak current), D_a (anodic diffusion coefficient), k_s (electron rate constant), anodic surface coverage Γ_a and anodic quantity of electricity Q_a for the anodic peaks are increase with increase of $MnSO_4$ concentration in 0.1M Na_2SO_4. Also the same for cathodic peak parameters and E°, standard are increase also by the increase of $MnSO_4$ concentration favoring diffusion processes. The diffusion mechanism was also supported by the increase in all peak currents by an increase in the concentration of $MnSO_4$.

2. Redox reaction of $MnSO_4$ in presence of Amoxicillin

The electrochemical interaction between $MnSO_4$ and Amoxicillin was studied cyclic voltammetrically in the range between (1.5 V to -1.0 V) vs. Ag/AgCl/Sat.KCl electrode. The electrochemical voltammograms presented in Figure (2) are similar for $MnSO_4$ in the absence of Amoxicillin and no new peaks were observed. All the current peak potentials for the obtained redox peaks in the presence of Amoxicillin are increased by increasing the ligand concentration favoring weaker bonds between the manganese ions and Amoxicillin than in the absence of it. Tables (3-a, b) explains the different analytical data obtained from the effect of Amoxicillin on $MnSO_4$ peaks.

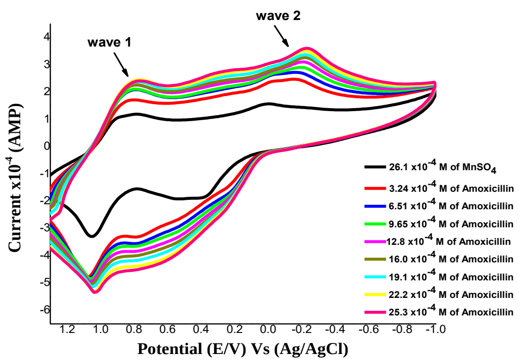

Fig. (2): Cyclic Voltammetry of Mn-Amoxicillin

Table (1-a): Cyclic voltammetric data of $MnSO_4$ at 297.15 K and 0.1 scan rate for wave 1

Mx10^6 (mol/ cm^3)	Ep,a (volt)	Ep,c (volt)	ΔEp (volt)	-Ip,a x10^5 (Amp)	Ip,c x10^5 (Amp)	Ip,a/ Ipc (Amp)	E°	Dax10^5 (cm^2/s)	Dc x10^5 (cm^2/s)	αn_a	Ks (cm/sec)	Γcx10^9 (mol/ cm^2)	+Qc x10^5	Γax10^9 (mol/ cm^2)	- Qa x10^5
0.66	0.92	0.832	0.084	1.55	1.22	1.270	0.874	0.963	0.595	0.710	0.046	1.032	0.63	1.313	0.80
1.32	0.97	0.821	0.153	6.99	3.54	1.970	0.898	4.935	1.270	0.559	0.228	2.993	1.81	5.904	3.58
1.96	1.03	0.816	0.214	16.1	8.18	1.966	0.923	11.78	3.050	0.466	1.060	5.915	3.19	13.59	8.24
2.60	1.06	0.815	0.245	17.2	6.43	2.668	0.938	7.641	1.070	0.342	0.988	6.437	4.29	14.50	8.79

Table (1-b): Cyclic voltammetric data of $MnSO_4$ at 297.15 K and 0.1 scan rate for wave 2

Mx10^6 (mol/ cm^3)	Ep,a (volt)	Ep,c (volt)	ΔEp (volt)	-Ip,a x10^5 (Amp)	Ip,c x10^5 (Amp)	Ip,a/ Ipc (Amp)	E°	Dax10^5 (cm^2/s)	Dc x10^6 (cm^2/s)	αn_a	Ks (cm/sec)	Γcx10^9 (mol/ cm^2)	+Qc x10^5	Γax10^9 (mol/ cm^2)	- Qa x10^5
0.66	0.295	0.041	0.254	2.61	0.146	17.91	0.168	2.719	0.085	1.64	0.23	0.123	0.08	2.206	1.34
1.32	0.3	0.027	0.273	6.52	1.05	6.172	0.164	4.296	1.13	1.06	0.97	0.892	0.54	5.509	3.34
1.96	0.346	0.02	0.326	13.0	3.30	3.943	0.183	7.703	4.95	0.57	4.22	2.787	1.69	10.99	6.66
2.60	0.389	0.013	0.376	13.6	3.32	4.105	0.201	4.823	2.86	0.55	8.32	2.807	1.70	11.52	6.98

Table (2-a): Cyclic voltammetric data of $MnSO_4$ in the presence of Amoxicillin at 297.15 K for wave 1

M x10^6 (mol/cm^3)	L x10^6 (mol/ cm^3)	Ep,a (volt)	Ep,c (volt)	ΔEp (volt)	-Ip,a x10^5 (Amp)	Ip,c x10^5 (Amp)	Ip,a/ Ipc (Amp)	E°	Da x10^5 (cm^2/s)	Dc x10^6 (cm^2/s)	αn_a	Ks (cm/s)	Γc x10^9 (mol/ cm^2)	+Qc x10^5	Γa x10^9 (mol/ cm^2)	- Qa x10^5
2.59	0.32	1.07	0.85	0.218	14.8	8.77	1.69	0.96	5.73	2.16	0.72	1.16	7.41	4.49	12.5	7.58
2.58	0.65	1.04	0.84	0.199	12.5	9.06	1.38	0.94	4.11	2.01	0.76	0.85	7.66	4.64	10.6	6.40
2.57	0.97	1.03	0.84	0.194	11.8	7.57	1.56	0.93	3.67	1.52	0.76	0.64	6.40	3.88	9.96	6.03
2.56	1.28	1.02	0.83	0.187	10.7	6.85	1.56	0.93	3.05	1.25	0.87	0.55	5.79	3.51	9.05	5.48
2.56	1.60	1.01	0.83	0.184	9.46	5.44	1.74	0.92	2.40	0.79	0.85	0.41	4.60	2.79	8.01	4.85
2.55	1.91	1	0.82	0.178	8.69	5.46	1.59	0.91	2.04	0.80	0.82	0.36	4.62	2.80	7.34	4.45
2.54	2.22	0.99	0.82	0.172	8.57	4.80	1.79	0.90	2.00	0.62	0.78	0.27	4.05	2.46	7.25	4.39
2.53	2.53	0.98	0.82	0.165	6.98	4.16	1.68	0.89	1.33	0.47	0.85	0.22	3.52	2.13	5.90	3.37

Table (2-b): Cyclic voltammetric data of $MnSO_4$ in the presence of Amoxicillin at 297.15 K for wave 2

M x10^6 (mol/cm^3)	L x10^6 (mol/cm^3)	Ep,a (volt)	Ep,c (volt)	ΔEp (volt)	-Ip,a x10^5 (Amp)	Ip,c x10^5 (Amp)	Ip,a/ Ipc (Amp)	E°	Da x10^5 (cm^2/s)	Dc x10^5 (cm^2/s)	αn_a	Ks (cm/s)	Γc x10^9 (mol/ cm^2)	+Qc x10^5	Γa x10^9 (mol/ cm^2)	- Qa x10^5
2.59	0.32	0.31	-0.13	0.447	12.7	1.64	7.75	0.09	4.24	0.07	0.49	15.7	1.39	0.84	10.8	6.53
2.58	0.65	0.33	-0.15	0.472	13.9	1.77	7.86	0.09	5.09	0.08	0.36	23.5	1.50	0.91	11.8	7.13
2.57	0.97	0.33	-0.17	0.502	15.8	2.56	6.16	0.08	6.57	0.17	0.91	98.1	2.16	1.31	13.3	8.07
2.56	1.28	0.35	-0.19	0.543	17.2	2.90	5.92	0.08	7.84	0.22	0.71	219	2.45	1.48	14.5	8.79
2.56	1.60	0.36	-0.20	0.563	18.3	4.06	4.50	0.08	8.95	0.44	0.64	432	3.43	2.08	15.5	9.36
2.55	1.91	0.39	-0.21	0.603	22.0	4.42	4.98	0.08	13.1	0.53	0.60	998	3.74	2.26	18.6	11.3
2.54	2.22	0.40	-0.22	0.621	24.9	4.62	5.40	0.09	16.9	0.58	0.65	1550	3.91	2.37	21.1	12.8
2.53	2.53	0.42	-0.24	0.658	26.3	5.01	5.25	0.09	18.9	0.69	0.57	3230	4.23	2.57	22.2	13.5

Table (3-a): Effect of different scan rate of $MnSO_4$ [2.60x10^{-6} M] at 297.15 K for wave1

υ	Ep,a (volt)	Ep,c (volt)	ΔEp (volt)	-Ip,a x10^5 (Amp)	Ip,c x10^5 (Amp)	Ip,a/Ipc (Amp)	E°	Da x10^5 (cm^2/s)	Dc x10^5 (cm^2/s)	αn_a	Ks (cm/s)	Γcx10^9 (mol/cm)	+Qc x10^5	Γa x10^9 (mol/cm)	- Qa x10^5
0.1	1.06	0.815	0.245	17.2	6.43	2.667	0.938	7.64	1.074	0.347	0.995	5.437	3.29	14.50	8.79
0.05	1.016	0.896	0.12	12.0	4.68	2.558	0.956	7.43	1.136	0.881	0.1	7.908	4.79	20.23	12.3
0.02	0.996	0.902	0.094	8.00	2.51	3.184	0.949	8.30	0.819	1.034	0.035	0.106	6.43	33.81	20.5
0.01	0.989	0.908	0.081	5.41	1.40	3.856	0.949	7.58	0.510	1.285	0.017	0.118	7.18	45.68	27.7

Table (3-b): Effect of different scan rate of $MnSO_4$ [2.60x10^{-6} M] at 297.15 K for wave 2

υ	Ep,a (volt)	Ep,c (volt)	ΔEp (volt)	-Ip,a x10^5 (Amp)	Ip,c x10^5 (Amp)	Ip,a/Ipc (Amp)	E°	Da x10^5 (cm^2/s)	Dc x10^5 (cm^2/s)	αn_a	Ks (cm/s)	Γcx10^9 (mol/cm^2)	+Qc x10^5	Γa x10^9 (mol/cm^2)	- Qa x10^5
0.1	0.389	0.013	0.376	13.6	3.32	4.105	0.201	4.82	0.286	0.547	8.32	2.807	1.70	11.52	6.98
0.05	0.357	0.043	0.314	6.24	1.96	3.179	0.200	2.02	0.200	0.699	1.66	3.319	2.01	10.55	6.39
0.02	0.332	0.058	0.274	2.56	1.09	2.352	0.195	0.85	0.154	0.806	0.45	4.560	2.79	10.82	6.56
0.01	0.321	0.075	0.246	1.46	0.82	1.767	0.198	0.55	0.176	1.081	0.23	6.967	4.22	12.31	7.46

Table (4-a): Effect of different scan rate of Mn- Amoxicillin complex [2.53 x10^{-6} M] for wave1

υ	Ep,a (volt)	Ep,c (volt)	ΔEp (volt)	Ip,a x10^5 (Amp)	Ip,c x10^5 (Amp)	Ip,a/Ipc (Amp)	E°	Da x10^5 (cm^2/s)	Dc x10^5 (cm^2/s)	αn_a	Ks (cm/s)	Γcx10^9 (mol/cm^2)	+Qc x10^5	Γa x10^9 (mol/cm^2)	- Qa x10^5
0.1	0.98	0.815	0.165	6.98	4.16	1.678	0.898	1.331	0.472	0.849	0.22	3.515	2.13	5.899	3.57
0.05	1.04	0.873	0.167	14.0	3.94	3.548	0.957	10.69	0.849	1.486	0.28	6.664	4.04	23.64	14.3
0.02	1.03	0.891	0.139	11.6	2.00	5.765	0.961	18.24	0.549	1.486	0.08	8.472	5.13	48.84	29.6
0.01	1.01	0.899	0.111	8.30	1.28	6.499	0.955	18.81	0.445	1.321	0.03	10.79	6.54	70.13	42.5

Table (4-b): Effect of different scan rate of Mn- Amoxicillin complex [2.53 x10^{-6} M] for wave 2

υ	Ep,a (volt)	Ep,c (volt)	ΔEp (volt)	Ip,a x10^5 (Amp)	Ip,c x10^5 (Amp)	Ip,a/Ipc (Amp)	E°	Da x10^5 (cm^2/s)	Dc x10^5 (cm^2/s)	αn_a	Ks (cm/s)	Γcx10^9 (mol/cm^2)	+Qcx10^5	Γa x10^9 (mol/cm)	- Qa x10^5
0.1	0.421	-0.237	0.658	26.3	5.01	5.250	0.092	18.89	0.686	0.566	3230	4.234	2.57	22.22	13.5
0.05	0.41	-0.192	0.602	13.0	1.63	7.940	0.109	9.196	0.146	0.970	462	2.762	1.67	21.93	13.3
0.02	0.401	-0.172	0.573	6.45	0.888	7.267	0.115	5.683	0.108	1.160	156	3.751	2.27	27.26	16.5
0.01	0.396	-0.161	0.557	4.08	0.549	7.422	0.118	4.540	0.082	1.189	71.4	4.643	2.81	34.46	20.9

Table (5-a): Stability constant for $MnSO_4$ in presence of Amoxicillin at 297.15 K for wave 1

Mx10^6(mol/c^3)	Lx10^6(m)	E° M	E° C	ΔE (mv)	j	Log βj	ΔG (KJ/mol)
2.59	0.324	0.938	0.961	-0.024	0.125	0.014	-0.081
2.58	0.645	0.938	0.941	-0.003	0.250	1.446	-8.226
2.57	0.965	0.938	0.933	0.005	0.375	2.109	-13.62
2.56	1.28	0.938	0.927	0.011	0.500	3.319	-18.88
2.56	1.60	0.938	0.918	0.020	0.625	4.284	-24.38
2.55	1.91	0.938	0.911	0.027	0.750	5.185	-29.60
2.54	2.22	0.938	0.904	0.034	0.875	6.075	-34.80
2.53	2.53	0.938	0.898	0.040	1	6.939	-39.88

Table (5-b): Stability constant for $MnSO_4$ in presence of Amoxicillin at 297.15 K for wave 2

Mx10^6(mo^3)	Lx10^6(mol/c^3)	E° M	E° C	ΔE(mv)	j	Log βj	ΔG (KJ/mol)
2.59	0.324	0.201	0.091	0.111	0.125	4.559	-25.94
2.58	0.645	0.201	0.091	0.110	0.250	5.278	-30.03
2.57	0.965	0.201	0.080	0.121	0.375	6.380	-36.09
2.56	1.28	0.201	0.083	0.119	0.500	6.965	-39.62
2.56	1.60	0.201	0.079	0.122	0.625	7.744	-44.06
2.55	1.91	0.201	0.089	0.113	0.750	8.092	-46.19
2.54	2.22	0.201	0.091	0.111	0.875	8.670	-49.66
2.53	2.53	0.201	0.092	0.109	1	9.257	-53.20

Table (6-a): Effect of scan rate on Stability constant of Mn-Amoxicillin complex [2.53 x10^{-6} M] for wave 1

υ	E° M	E° C	ΔE (mv)	j	log βj	ΔG (KJ/mol)
0.10	0.938	0.8975	0.040	1	6.95	-39.56
0.05	0.956	0.9565	-0.001	1	5.58	-31.75
0.02	0.949	0.9605	-0.012	1	5.21	-29.62
0.01	0.949	0.9545	-0.006	1	5.39	-30.68

Table (6-b): Effect of scan rate on Stability constant of Mn-Amoxicillin complex [2.53 x10^{-6} M] for wave 2

υ	E° M	E° C	ΔE (mv)	j	log βj	ΔG (KJ/mol)
0.10	0.201	0.092	0.109	1	9.29	-52.88
0.05	0.200	0.109	0.091	1	8.68	-49.41
0.02	0.195	0.1145	0.0805	1	8.33	-47.38
0.01	0.198	0.1175	0.0805	1	8.33	-47.38

The relation between Ip versus square root of scan rate presented in Figures (5, 6) has straight lines for both cathodic and anodic manganese waves in the absence and presence of Amoxicillin indicating diffusion-controlled reactions

.The complexation stability constant (βc) for interaction of $MnSO_4$ and Amoxicillin is calculated by applying equation (8) [25]:

$$(E_{1/2})_C - (E_{1/2})_M = 2.303\ (RT/nF) * 2.303\ (RT/nF) \log C_L \qquad (8)$$

Since $(E_{1/2})_M$ is half-wave potential for manganese in absence of Amoxicillin, $(E_{1/2})_C$ is the half-wave potential of complex formed, C_L is the concentration of ligand.

The complexation Gibbs free energy of interaction between $MnSO_4$ and Amoxicillin is calculated by use of equation (9) [26]:

$$\Delta G = -2.303\ RT \log \beta_c \qquad (9)$$

Figures (3, 4) represent the effect of scan rate on the cyclic voltammograms $MnSO_4$ in the absence and presence of Amoxicillin. Tables (3-a, b) and (4-a, b) illustrated the effect of scan rate on the anodic and cathodic currents for both a couple of peaks.

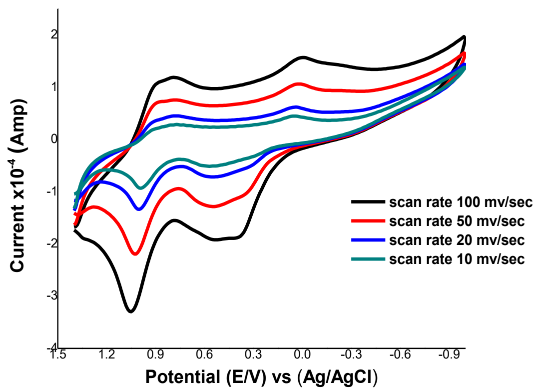

Fig. (3): Effect the different scan rates of $MnSO_4$ at 297.15 K

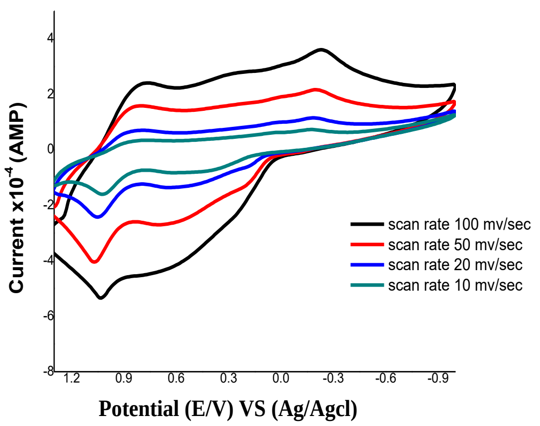

Fig. (4): Effect the different scan rates on Amoxicillin with $MnSO_4$ at 297.15 **K**

The calculation thermodynamic parameters β_c and ΔG for the interaction of $MnSO_4$ with Amoxicillin are given in Tables (5-a, b) and (6-a, b). It is concluded that for 1:1 stoichiometric complex that the thermodynamic parameter, stability and Gibbs free energies of complexation increase by the increase in the Amoxicillin concentration indicating more complexation

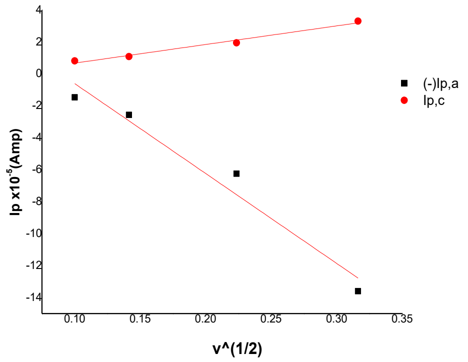

Fig. (5): v^1/2 *vs* Ip for of $MnSO_4$ at 297.15 K

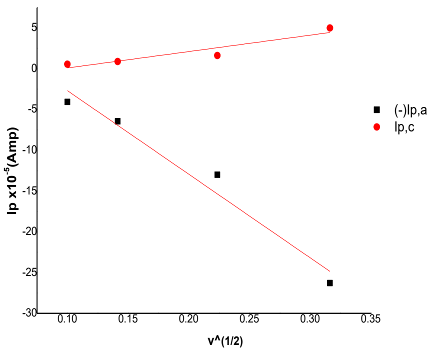

Fig. (6): v^1/2 *vs* Ip of complex ($MnSO_4$ with Amoxicillin) at 297.15 K

Redox Mechanism

The redox mechanism for $MnSO_4$ in 0.1M Na_2SO_4 at the GCE the suggested given process including two electrons in each step

During preparation, some of the manganese sulfate (Mn^{2+}) ions oxidize to Mn^{+4} as MnO_2 as reported in the literature [1]:

$$MnSO_4 + 2H_2O \leftrightarrow MnO_2 + 4H^+ + 2e^- \quad (10)$$

At first, the reduction and oxidation of manganese (IV) to manganese (II) on GCE appear in ≈ 0.8V and ≈ 0.9V respectively and the mechanism suggested by the following process:

$$MnO_4 + 4\ H^+ + 2e \leftrightarrow Mn^{2+} + 2H_2O \ (11)$$

Second, the reduction and oxidation of manganese (II) to manganese (0) on GCE appears in ≈ 0 V and about ≈ 0.3V respectively and the mechanism suggested by the following process:

$$Mn^{2+} + 2e \leftrightarrow Mn \quad (12)$$

Unlikely reaction (1) took place by one step because it mainly takes two electrons transferred through one step. Also, the formation of MnO_2 oxidation of water molecules must occur. It prefers that the reaction (1) occurs in simple reaction steps. The working electrode changed black due to the electrodeposition of MnO_2.

The reaction is diffusion one as explained before because if the peaks correspond to reversible reactions, it must be separated by 30 mV nearly and the peak potentials change with scan rates. This fact applied for our voltammograms supports the reversibility of the waves studied.

Conclusion

A Scheme is explained for the oxidation, reduction of $MnSO_4$ forming MnO_2 based on cyclic voltammetry. Also, diffusion and reversible reactions are proved. First, it involves oxidation Mn ions from (II) to (IV) on interaction with water molecules. Then begin the cyclic voltammetry of MnO_2. Complexation between manganese ions and Amoxicillin was proved from the different thermodynamic parameters obtained.

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