Aqueous Complexation for the Interaction of SeO2 with both Succinic acid and Dithizone in KCl Solution (Cyclic Voltammetry) Using Gold Working Electrode (GWE)

Yasmeen Y. Elfarhaty [1], Ali M. Elazly [1], Esam A. Gomaa [2]

[1] Nile Higher Institute for Engineering and Technology, Mansoura, Egypt.

[2] Chemistry Department, Faculty of Science, Mansoura University, 35516- Mansoura, Egypt.

Abstract

The electrochemical behavior was studied for SeO2 in the absence and presence of Succinic acid (SuA) and Dithizone (DT) separately in 0.1M KCl solution. The Gold electrode was prepared in our laboratory from gold wire 18K. The Gold wire was polished in Al2O3 piece put in woolen cloth and good washed. Gold electrode was used as working electrode for measuring the voltammograms of SeO2 in 0.1M KCl at 18°C. Stability constant and Gibbs free energy of interaction for SeO2 + Succinic acid and SeO2 + Succinic acid + Dithizone (DT) was done and their values were discussed.

Keywords: Voltammetric study, selenium oxide, electrochemical parameters, solvation parameters, stability constants and Gibbs free energy of complexation.

Introduction

By using cyclic voltammetry, the interaction between metal ions oxides, salts with organic active compounds can experimentally be followed [1]. The organic compounds used must have a functional active chelating group which can attract and withdraw the metal from solutions. The complex ability in solution can be followed by any change of peak heights, shift in both anodic and cathodic waves or appearance of new complex waves. The shift in half wave potentials also can be applied for studying the complex behavior in solutions [2-5]. Other important techniques can be used following the complex characters and behaviors in solutions, Conductometric titration, Potentiometry, UV spectroscopy, Visible spectroscopy, refraction index measurements and so on [2-5]. Here in our laboratory, we prepared new gold working electrode from gold wire 18K adhert with copper wire and isolated from solutions by quick fit heat shrink la polymer. Polishing the electrode with Al_2O_3 put in woolen piece of cloth, washed well and dried before practical use. Purified N_2 gas was passed in every solution for about 10 minutes to insure the removal of dissolved O_2 in the measured solutions.

Experimental:

SeO_2, KCl, Dithizone and Succinic acid are of the type Merck and used without any treatment to avoid changes in them. Gold wire was bought from a famous jewelry shop in downtown in Cairo, Egypt. DY 2000 potentiostate was used for developing the cyclic voltammograms at different scan rates. Three different electrodes were used for measuring the cyclic voltammograms put in the working cell. There are Ag/AgCl, reference standard electrode filled with saturated KCl solutions, The second electrode is platinum wire, auxiliary electrode and Gold electrode (GWE) as

working electrode. The last was prepared in our laboratory. De-ionized water of conductivity 2.7 micro Siemens was used in practical work. Cyclic voltammogram of SeO_2 in (absence/presence) of (Succinic acid + Dithizone) were obtained by immersing the three electrodes in a cell containing 30 ml of 0.1 M of KCl. The system was applied with 1.5 V to -1.5 V potential windows and (0.1 v/s) scan rate at (291.15K).

Results and Discussion:

The electrochemical redox reaction of SeO_2 (selenium dioxide) at Gold working electrode (GWE) was studied in the equilibrium conditions and temperature 18°C. The obtained cyclic voltammograms were analyzed by Eq. (1):

$$I_p= 0.4463 \, nF \, A \, C \, (nF \, U \, D/ \, RT) \qquad (1)$$

Where I_p is the measured current in Ampere, A is the surface electrode area ($0.031 cm^2$), D is the diffusion coefficient in cm^2/s, U is scan rate in volts/Sec and C is the concentration of SeO_2 in (Mol/cm^3). The voltammograms were done and developed by the use of Gold working electrode (GWE) from starting potential (1.5 to -1.5 v).The data are represented in Fig.(1) and their analysis date in Table 1-a.

Reaction mechanism:

The measured cyclic voltammograms results depend on SeO_2 movement and the transfer of electrons. The rate constant of forward reaction, k_f is characteristic of the cathodic reduction process. Rate constant, k_f is a function of E, if E increase, it will increase and vice versa as shown in equation (2):

$$k_f = k_f^{\circ} \exp \left(\frac{-\alpha nf}{RT}\right) (E - E^{\circ}) \qquad (2)$$

k_f is the forward electron rate constant, k_f° is the standard electron transfer rate constant for interaction. E is the reduction potential and α is the transfer coefficient [6], but k_f is a rate constant of forward reversible reactions depending on one step reaction mechanism [7], so we use the standard heterogeneous electron transfer rate constant k_s in cm/sec as SeO_2 show multi-reduction steps, was calculated by applying the following equation (3) [8-10]:

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

assuming that α coefficient is equal to 0.5, as explained in literature to give better results [9]. Hence, αna will be as the shown in

equation (4) [9,10]

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

Where $E_{pc/2}$ is the half wave potential for cathodic peak.

Then we evaluated the surface coverage Γ (surface concentration of the electro active species in Mol. cm^{-2}) by equation (5) [8,9]

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

The quantity of charge consumed during the reduction or adsorption of the adsorbed layer can be used to calculate the surface coverage [11] by eq. (6)
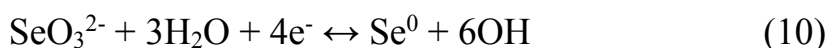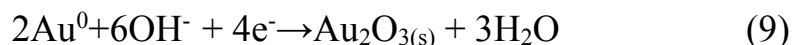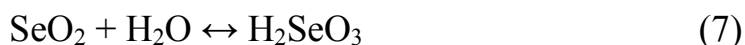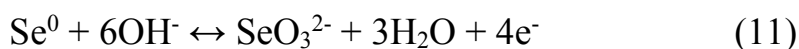
$$Q = n \, FA \, \Gamma \qquad (6)$$

All calculated data for different concentrations of SeO_2 are given in Table 1-a for the different three obtained peaks as an example. The general trend of the resulted data are increased by increasing SeO2 concentration indicating diffusion controlled reactions.

The electrochemical behavior of SeO₂ in the absence of ligands (Succinic acid + Dithizone):
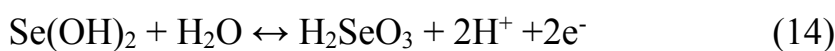
The cyclic voltammograms for selenium ions with different concentrations in 0.1M KCl supporting electrolyte using Gold electrode, were experimentally measured in (Fig.1) listed. At 18°C, we observed four reduction waves for selenium ions, and four oxidation peaks appeared. A blank solution of 0.1M KCl shows no specific wave other than the duck shape for the used gold working electrode (GWE).

The reaction of SeO_2 in aqueous media results in the formation of $H_3SeO_3^+$, $HSeO_3$, and SeO_3^{2-} species [13-15] eq. (7). There are 4 reduction peaks appear corresponding to 4 oxidation ones at inverted potential, the first reduction wave appears approximately at 0.6 V show the reduction to Au corresponding for inverted positive potential peak at 0.2 V which related to the reaction of Au via eq (8,9). Au can react with H_2SeO_3 and intermetallic (Au–Se) can take place on the gold electrode surface. The three reduction peaks for Se [16] appear from 0.1 to -0.08 V, the first cathodic peak appears at 0.1 V corresponding to the anodic peak at 0.73 V [17] express the pre-deposition of Se as single monolayer and reduction of Se to Se (0) by transfer $4e^-$ via a mechanism (10,11) respectively:

$$SeO_2 + H_2O \leftrightarrow H_2SeO_3 \tag{7}$$

$$AuO + 2H^+ + 2e^- \leftrightarrow Au + H_2O \tag{8}$$

$$2Au^0 + 6OH^- + 4e^- \rightarrow Au_2O_{3(s)} + 3H_2O \tag{9}$$

$$SeO_3^{2-} + 3H_2O + 4e^- \leftrightarrow Se^0 + 6OH \tag{10}$$

$$Se^0 + 6OH^- \leftrightarrow SeO_3{}^{2-} + 3H_2O + 4e^- \qquad (11)$$

There are also 2 cathodic reduction waves reported for the reduction of Se (0), one of them related to reduction of Se (0) to $Se^{2-}{}_{(ads)}$ which appear at -0.05 V [12] eq. (12), then evaluation of H_2Se appear at -0.08 V corresponding with anodic wave at 0.37 V via transfer of $2e^-$ eq (13), the Se^{2-} may react with remaining Se (0) and form $Se \cdot Se^{2-}$ on the surface of electrode [12].

$$Se + 2e^- \leftrightarrow Se^{2-}{}_{(ads)} \qquad (12)$$

$$Se + 2e^- + 2H^+ \leftrightarrow H_2Se \qquad (13)$$

$$Se(OH)_2 + H_2O \leftrightarrow H_2SeO_3 + 2H^+ + 2e^- \qquad (14)$$

$$H_2SeO_3 + H_2Se \leftrightarrow 3Se + 3H_2O \qquad (15)$$

Cyclic Voltammetric data for the effect of different concentrations of SeO_2 from (0.625 to 1.67) $\times 10^{-03}$M shown in Table (1-a) for three waves appear, given the increase in cathodic and anodic potentials.Figs.,2,3 represent the effect of succinic acid on the voltamogram of SeO_2 and the further effect of adding dithizone to the SeO_2+succinic acid solutions, respectively.

Effect of scan rates on final edition of SeO_2 in absence of Ligands (Succinic acid and Dithizone):

Cyclic Voltammogram of the final edition of SeO_2 in the absence of Ligands (Succinic acid + Dithizone) at different scan rates (0.1, 0.05, 0.02, 0.01 V/sec) at 291.15° K is represented in (Fig.4), and Table (2-a) represented the effect of different

scan on cathodic and anodic potentials with expressing different data corresponding to the three waves appeared. Figs. 5, 6 represent the scan rate effect for the effect of succinic acid and further effect of adding dithizone to selenium oxide solutions, respectively.

The plot of both anodic and cathodic peak current against the square root of scan rates (0.1, 0.05, 0.02, 0.01 V/sec) at temperature at 291.15° K are shown in (Figs. 7-9).

Electrochemical behavior of SeO$_2$ in presence of legends (Succinic acid + Dithizone) and thermodynamic parameters for complex:

For final addition of SeO$_2$ (1.67 X10^{-3}M), Succinic acid started to be added with different concentrations (from 1.369 to 1.429 x 10^{-3}M) forming 1:1 molar ratio complex, then adding (25, 33.33 x 10^{-3}M) respectively, leading formation of 2:1, 3:1 ligand to metal complex ratio as shown in (Fig.2). The formation of the complex results in decreasing in cathodic and anodic potential for (Se) three waves, the same for cathodic and anodic current also other cyclic calculation in Table (1-b).

After addition of (33.33 x 10^{-3}M) Succinic acid, which is 3:1 molar ratio ligand to metal, Dithizone started to add (from 0.001 to 0.004 M), (Fig.3) as given before shows that Dithizone affect obviously only the first wave which expected due to (Se) pre-deposited on the gold electrode surface, there is no other effect on the other 2 waves which may mean complete reaction between SeO$_2$ and Succinic acid.

The decreasing shift for cathodic and anodic potential of first wave indicated the formation of a complex between (Dithizone + Succinic acid + SeO_2), Table (3-a) show the effect of the addition of both ligands used on other cyclic voltammetry parameters.

Through thermodynamic parameters, we detected the formation of complexes (Succinic acid + SeO_2) and (Dithizone + Succinic acid + SeO_2), as 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 (Succinic acid + SeO_2) and (Dithizone + Succinic acid + SeO_2) complexes for each additions are calculated [3-5,18], by applying Eq. (16).

$$\Delta E° = E°_C - E°_M = 2.303 \ (RT/nF) * (\log \beta_{MX} + j \ \log s \ C_x) \qquad (16)$$

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

The formal potential E° can be found as the midway between the two cyclic Voltammetry peaks comprising the voltammograms by equation (17) [8-10]

$$E° = (Ep_a + Ep_c) \qquad (17)$$

Where both Ep_a and Ep_c are anodic peak potential and cathodic peak potential, respectively. The Gibbs free energy of interaction for Succinic acid and Dithizone with SeO_2 were calculated from stability constant (β_{MX}) using Eq. (18)

$$\Delta G = -2.303 \ RT \log \beta_{MX} \qquad (18)$$

The calculated values of E°, βMX, ΔG, are estimated and collected in Tables (2-c), (4-a).

Effect of different scan rates for (1:1) molar ratio complex between (Succinic acid + SeO₂):

Cyclic voltammograms of (1:1) molar ratio complex (Succinic acid + SeO₂) at 18°C for different scan rates (0.1, 0.05, 0.02, 0.01 V/Sec) shown in (Fig.5) as explained before, the effect of different scan rates on cyclic voltammetry parameters explaining the cathodic oxidation, anodic reduction potential and current for three waves represented in Table (2-b).

The plot of both anodic and cathodic peak current against the square root of scan rates (0.1, 0.05, 0.02, 0.01 V/sec) at temperature at 291.15° K are shown in (Figs. 10-12).

Effect of different scan rates on complex of (Dithizone + Succinic acid + SeO₂):

Studying the effect of different scan rates (0.1, 0.05, 0.02, 0.01 V/Sec) of complex Dithizone + (3:1) molar ratio complex (Succinic acid + SeO₂) as example at 291.15K shown in (Fig.6), and Table (4-b) gave the calculated cyclic Voltammetric data for the effect of different scan rates.

The plot of both anodic and cathodic peak current against the square root of scan rates (0.1, 0.05, 0.02, 0.01 V/Sec) at temperature at 291.15° K are shown in (Fig.13).

Short Review Communication:

Selenium is important collagen. It is directly used and applied in solar cells, fuel cells, electrocatalysis, batteries and metallic alloys. They attempt to explain

selenium and its uses in electrochemistry. Se is a group 6A member discovered by J. J. Berzelius [19]. Se is similar to sulphur. The coordination of Se atom and its compounds is two with a bond angle 105° [20]. Se and its compounds have some industrial applications like decolourizer in glass, constituent in pigments, additive in metallic alloys, photoreceptor in xerographic copies, semiconductor in electrical rectifiers and in photochemical and photovoltaic cells [21,22]. Se serves and used as a deoxidizer and grain refiner. First work on the photoconductive effect in the [24], also significant studies reported on the semiconducting propertied and light sensitivity of Se for electronic applications. More than two forms of light sensitive Sewere found with widely different electrical resistivity [23]. Compounds containing Se are extensively used as optoelectronic applications, advanced solar cells, infrared detectors, solid state lasers, fluorescent quantum dots [24]. Se is used and applied as a grain refiner in Pb-acid batteries [25]. Also, it is used cathode in Li-ion [26]. The Se is used as electrocatalyst extensively as an oxygen reduction catalyst in fuel cell cathodes [27]. Here an attempt on the electrochemistry and cyclic voltammetry of Se.

Most of voltammetry studies of Se give interpreted two step Se (IV) →Se (0) →Se (2II), where the reduction of Se (0) takes place at more negative potentials. The Se (IV) reduction takes place according to a four or six-electron. Formation of H_2Se often complicates the voltammograms. Chemical reaction of H_2Se with Se (IV) can occur rapidly in acidic and intermediate pH ranges, but slowly in alkaline solutions. [28]

$$H_2SeO_3 + H_2Se \leftrightarrow 3Se + 3H_2O \qquad (19)$$
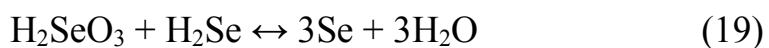
Quantum Chemical Calculations:

Quntum chemical calculations were done to explain the activity of SeO_2 in water using Hartree Fock method of calculation and 3-21G basis set for restricted atomic molecular orbitals in water calculated by using Gaussian 09 sets of evaluation.The evaluated date are explained and represented in Table (4) and Fig.(14).The selenium dioxide has no dipole moment but its activity of interaction is due to, the quadrupole moment (field independent basis) , traceless quadrupole moment,hexadecapole moment,different sums of electronic with zero point energies,thermal energies, thermal enthalpies, thermal energy (E), heat capacity at constant volume (CV) , entropies (S) and all the related partition functions (Q) [29].The activity of selenium dioxide in water can also be supported by the evaluation of energy gap which is the difference between LUMO and HOMO molecular orbitas and explained in Fig.(14) which gave the value of 0.33556 ev.

Most orbitals calculated and explained in Fig. (14) gave similar configuration like LUMO+1 and HOMO-1.

This also is explained in Fig. (14) b which support the different contour lines for the HOMO orbitals.

Conclusion:

The main target is the easily estimation of selenium complexes using gold electrode in cyclic voltammetry. Also the analysis of the different peaks obtained for selenium ions are necessary.

The redox behavior for selenium dioxide was studied in the presence of KCl electrolyte solutions using gold electrode. The redox mechanism was explained in the absence and presence of the first ligand succinic acid and the second ligand

Dithizone. Selenium compounds form generally weak complexes directly but they form complexes through other ions. The stability constant and Gibbs free energies of complex formation were estimated and their values discussed. The thermodynamic parameters for interaction between SeO_2 and the two ligands indicated that the interaction in case of succinic acid is greater than that of dithizone on using mixed ligands. This is because the electrostatic interaction of the first ligand succinic acid leave little vacancies necessary for the solvation of the second ligand. The data given in this work can help for the estimation of selenium ions in solutions.

Table (1-a) : Solvation and Kinetic parameters (D, k_s, Γ and Q) of SeO_2 in the absence of (Succinic acid + Dithizone) at 291.15K, scan rate 0.1 V/Sec.

First wave

[M] x10^-03 mol/lit	Ep_a (volt)	Ep_c (volt)	ΔEp (volt)	Ip_a/Ip_c	$E°$ (volt)	Da x10^-13	Dc x10^-14	$Ep_{c/2}$ x10^-01 (volt)	αn_a	k_s x10^7	Γ_c x10^-11	(+) Q_c x10^-06	Γ_a x10^-11	(-) Q_a x10^-06
0.625	0.7218	-0.0089	0.7308	0.8762	0.3564	2.569	33.5	.0113	2.3018	1.71	8.992	4.36	7.879	3.82
0.909	0.7399	-0..0093	0.7492	1.219	0.3653	3.702	24.9	0.106	2.3391	3.1	11.29	5.47	13.76	6.67
1.18	0.7531	0.1001	0.6527	4.992	0.4266	2.415	0.969	1.05	9.0123	0.0256	2.881	1.40	14.38	6.97
1.43	0.75386	0.1024	0.6515	3.434	0.4281	1.679	1.42	1.11	5.3607	0.0228	4.239	2.06	14.56	7.06
1.67	0.7586	0.0956	0.6631	2.272	0.4271	1.485	2.88	1.06	4.4358	0.0467	7.023	3.41	15.97	7.75

Second wave

[M] x10^-03 mol/lit	Ep_a (volt)	Ep_c (Volt)	ΔEp (Volt)	Ip_a/Ip_c	$E°$ (volt)	Da x10^-14	Dc x10^-14	$Ep_{c/2}$ x10^-02 (volt)	αn_a	k_s x10^-01	Γ_c x10^-10	(+) Q_c x10^-05	Γ_a x10^-10	(-) Q_a x10^-05
0.625	0.5191	-0.0558	0.5749	0.3015	0.2316	0.1961	2.16	-04.45	4.133	1.23	1.6147	0.392	0.4868	0.118
0.909	0.5394	-0.07121	0.6106	0.5915	0.2341	0.4773	1.36	-05.95	3.995	1.96	1.8673	0.453	1.105	0.268
1.18	0.5636	-0.0198	0.5834	0.8254	0.2719	2.4602	3.61	-0.915	4.388	1.94	3.9317	0.953	3.245	0.787
1.43	0.5733	-0.0267	0.6001	0.8943	0.2733	4.2967	5.37	-1.158	3.081	2.77	5.8234	1.41	5.208	1.26
1.67	0.5928	-0.0329	0.6258	1.0601	0.2800	6.3775	5.67	1.06	2.837	4.55	6.9823	1.69	7.402	1.79

Third wave

[M] x10⁻⁰³ mol/lit	Epₐ (volt)	Epc (volt)	ΔEp (volt)	Ipₐ/Ipc	E° (volt)	Da x10⁻¹⁴	Dc x10⁻¹⁴	Epc/2 x10⁻⁰¹ (volt)	αnₐ	Kₛ x10⁻⁰³	Γc x10⁻¹⁰	(+) Qc x10⁻⁰⁶	Γₐ x10⁻¹⁰	(-) Qₐ x10⁻⁰⁶
0.625	0.3552	-0.1522	0.5075	1.2556	0.1014	0.9421	0.598	-1.43	5.198	1.89	0.8497	2.06	1.0668	2.59
0.909	0.3554	-0.1379	0.4933	1.2535	0.1087	1.571	1.00	-1.30	6.055	1.99	1.599	3.88	2.004	4.86
1.18	0.3595	-0.0886	0.44481	1.8818	0.1355	2.466	0.696	-0.803	5.661	0.653	1.727	4.19	3.248	7.88
1.43	0.3677	-0.1104	0.4781	1.3490	0.1286	4.186	2.30	-0.928	2.652	1.48	3.811	9.24	5.140	12.5
1.67	0.3706	-0.1295	0.5000	0.9900	0.1286	3.136	3.20	-1.02	1.724	2.18	5.243	12.7	5.191	12.6

Table (1-b): Solvation and Kinetic parameters (D, kₛ, Γ and Q) of SeO₂ in the presence of Succinic acid at 291.15K, scan rate 0.1 V/Sec.

First wave

[M] x10⁻⁰³ mol/lit	Epₐ (volt)	Epc (volt)	ΔEp (volt)	Ipₐ/Ipc	E° (volt)	Da x10⁻¹⁴	Dc x10⁻¹⁴	Epc/2 x10⁻⁰² (volt)	αnₐ	kₛ x10⁰⁶	Γc x10⁻¹¹	(+) Qc x10⁻⁰⁶	Γₐ x10⁻¹¹	(-) Qₐ x10⁻⁰⁶
1.3699	0.8075	0.0839	0.7236	0.8403	0.4457	6.529	9.25	9.39	4.6644	9.59	0.1260	6.11	10.59	5.14
2.7027	0.7924	0.0821	0.7103	0.8435	0.4373	6.192	8.7	9.25	4.4670	5.37	0.1223	5.93	10.31	5.00
5.2632	0.7865	0.0798	0.70663	0.8260	0.4331	4.567	6.69	9.09	4.2042	3.94	0.1072	5.20	8.858	4.30
7.6923	0.7807	0.0746	0.70604	0.7822	0.4277	3.767	6.16	8.42	4.8639	3.97	0.1029	4.99	8.046	3.90
10	0.7787	0.0737	0.7050	0.7250	0.4262	2.811	5.35	8.30	5.0464	3.62	9.586	4.65	6.950	3.37
14.2857	0.7711	0.0685	0.7026	0.3243	0.4198	0.367	3.49	8.03	3.9631	2.35	7.745	3.76	2.512	1.22
25	0.6638	0.0357	0.62815	3.8604	0.3498	17.13	1.15	4.26	6.7030	0.090	4.444	2.16	17.15	8.32
33.3333	0.6311	0.0306	0.6005	6.4730	0.3308	19.11	45.6	3.43	12.605	0.026	2.799	1.36	18.12	8.79
12.1951	0.7759	0.0718	0.7041	0.4195	0.4238	0.848	4.82	8.34	4.0156	2.95	9.102	4.41	3.818	1.85

Second wave

[M] x10⁻⁰³ mol/lit	Epₐ (volt)	Epc (volt)	ΔEp (volt)	Ipₐ/Ipc	E° (volt)	Da x10⁻¹⁴	Dc x10⁻¹⁵	Epc/2 x10⁻⁰² (volt)	αnₐ	kₛ x10⁻⁰¹	Γc x10⁻¹⁰	(+) Qc x10⁻⁰⁶	Γₐ x10⁻¹⁰	(-) Qₐ x10⁻⁰⁶
1.3699	0.605	-0.0520	0.6566	6.232	0.276	21.43	5.19	-4.69	9.1070	4.56	2.111	5.12	13.16	31.9
2.7027	0.588	-0.0552	0.6428	12.55	0.266	16.31	1.04	-5.29	20.2773	2.31	0.9431	2.29	11.84	28.7
5.2632	0.578	-0.0561	0.6305	5.561	0.259	2.353	0.761	-5.42	24.3383	1.70	0.8085	1.96	4.496	10.9
7.6923	0.575	-0.0581	0.6364	14.24	0.260	5.777	0.285	-5.68	36.7661	1.44	0.4948	1.20	7.045	17.1
10	0.574	-0.0582	0.6326	10.92	0.258	2.353	0.197	-5.72	48.0647	1.27	0.4117	0.998	4.496	10.9
12.1951	0.567	-0.0635	0.6305	12.92	0.252	1.913	0.115	-6.28	64.6576	1.07	0.3138	0.761	4.054	9.83
14.2857	0.563	-0.0674	0.6305	11.14	0.248	0.972	0.078	-6.70	137.596	1.29	0.2593	0.629	2.890	7.01

Third wave

[M] x10⁻⁰³ mol/lit	Epₐ (volt)	Epc (volt)	ΔEp (volt)	Ipₐ/Ipc	E° (volt)	Da x10⁻¹⁴	Dc x10⁻¹⁴	Epc/2 x10⁻⁰¹ (volt)	αnₐ	ks x10⁻⁰²	Γc x10⁻¹⁰	(+) Qc x10⁻⁰⁵	Γₐ x10⁻¹⁰	(-) Qₐ x10⁻⁰⁵
1.3699	0.319	-0.1515	0.4705	1.311	0.084	1.983	1.15	-1.45	6.9929	1.46	3.1472	0.763	4.127	1.00
2.7027	0.317	-0.1578	0.4747	1.042	0.080	1.897	1.75	-1.48	5.0009	1.65	3.8738	0.939	4.037	0.98
5.2632	0.302	-0.1599	0.4624	0.793	0.071	1.551	2.46	-1.48	3.9073	1.36	4.6009	1.12	3.650	0.89
7.6923	0.301	-0.1627	0.4635	0.666	0.069	1.199	2.70	-1.51	4.1169	1.49	4.8178	1.17	3.210	0.78
10	0.302	-0.1647	0.4666	0.429	0.069	0.721	3.93	-1.40	1.8975	1.30	5.8074	1.41	2.489	0.60
12.1951	0.301	-0.1704	0.4709	0.374	0.065	0.637	4.55	-1.55	2.9939	1.91	6.2543	1.52	2.339	0.57
14.2857	0.298	-0.1760	0.3857	3.3061	0.0169	0.260	6.21	-1.58	2.6494	2.24	7.3033	1.77	1.494	0.36

Table (2-a): Solvation and Kinetic parameters (D, kₛ, Γ and Q) of effect of scan on final addition of SeO₂ in absence of (Succinic acid + Dithizone) at 291.15K.

v^(1/2)	Epₐ (volt)	Epc (volt)	ΔEp (volt)	Ipₐ/Ipc	E° (volt)	Da x10⁻¹²	Dc x10⁻¹³	Epc/2 x10⁻⁰¹ (volt)	αnₐ	kₛ	Γc x10⁻⁰⁹	(+) Qc x10⁻⁰⁵	Γₐ x10⁻⁰⁹	(-) Qₐ x10⁻⁰⁵
0.3162	0.7586	0.0956	0.6631	2.2718	0.4271	1.19	2.30	1.06	4.4358	2.41	0.2812	0.682	0.639	1.55
0.2236	0.5332	0.1193	0.4140	1.36	0.3263	0.768	4.14	1.3157	3.7934	56.5	0.678	0.341	0.924	1.12
0.1414	0.5218	0.1351	0.3868	1.43	0.3284	1.07	5.24	1.4648	4.0788	14.1	1.21	1.46	1.72	2.09
0.1	0.5185	0.1435	0.3760	2.09	0.3310	1.61	3.69	1.5234	5.2575	5.96	1.43	1.74	2.99	3.63

Second wave

v^(1/2)	Epₐ (volt)	Epc (volt)	ΔEp (volt)	Ipₐ/Ipc	E° (volt)	Da x10⁻¹¹	Dc x10⁻¹²	Epc/2 x10⁻⁰¹ (volt)	αnₐ	Ks C x10⁻⁰³	Γc x10⁻⁰⁹	(+) Qc x10⁻⁰⁵	Γₐ x10⁻⁰⁹	(-) Qₐ x10⁻⁰⁵
0.3162	0.5928	-0.0329	0.6258	1.0601	0.2800	0.0006	0.0567	-1.65	2.8374	455	0.6982	1.69	0.7402	1.79
0.2236	0.3144	-0.0063	0.3208	1.68	0.1540	1.07	3.7792	0.4974	4.1158	7.25	2.8971	0.423	4.8681	2.95
0.1414	0.3022	0.0245	0.2777	1.89	0.1633	0.890	2.4864	3.0127	8.2178	2.23	3.7165	2.25	7.0315	4.26
0.1	0.2923	0.0421	0.2502	1.21	0.1672	0.366	2.4938	4.6210	11.398	1.07	5.2624	3.19	6.3788	3.86

Third wave

v^(1/2)	Epₐ (volt)	Epc (volt)	ΔEp (volt)	Ipₐ/Ipc x10⁻⁰¹	E° (volt)	Da x10⁻¹²	Dc x10⁻¹²	Epc/2 x10⁻⁰¹ (volt)	αnₐ	ks x10⁻⁰³	Γc x10⁻⁰⁹	(+) Qc x10⁻⁰⁵	Γₐ x10⁻⁰⁹	(-) Qₐ x10⁻⁰⁵
0.3162	0.7991	-0.1295	0.9286	22.1	0.3348	0.1558	0.0320	-1.02	1.7237	1110	0.5243	1.27	1.1568	2.81
0.2236	0.1400	-0.0573	0.1855	29.7	0.0414	4.31	0.4873	-0.4910	5.7158	0.207	1.0403	0.318	3.0924	1.87
0.1414	0.1283	-0.0269	0.1518	10.1	0.0507	0.734	0.7161	-0.1951	6.2680	0.0849	1.9939	1.21	2.0191	1.22
0.1	0.1249	-0.0072	0.0072	9.18	0.0588	0.903	1.0719	-0.0268	10.369	0.0053	3.45	2.09	3.1664	1.92

Table (2-b): Solvation and Kinetic parameters (D, kₛ, Γ and Q) of effect of scan of addition of Succinic acid (0.0142 M) on SeO2 in absence of (Dithizone) at 291.15K.

$v^{1/2}$	E_{pa} (volt)	E_{pc} (volt)	ΔE_p (volt)	I_{pa}/I_{pc}	$E°$ (volt)	D_a $\times 10^{-12}$	D_c $\times 10^{-12}$	$E_{pc/2}$ $\times 10^{-02}$ (volt)	αn_a	k_s $\times 10^6$	Γ_c $\times 10^{-09}$	$(+)Q_c$ $\times 10^{-05}$	Γ_a $\times 10^{-11}$	$(-)Q_a$ $\times 10^{-06}$
0.3162	0.7711	0.0685	0.7026	0.9329	0.3158	0.2431	0.2793	8.03	3.9631	6.65	0.3098	0.751	28.903	7.01
0.2236	0.7339	0.0923	0.6416	1.4535	0.4131	1.412	3.187	10.9180	2.7564	0.369	0.5949	0.721	0.0962	0.012
0.1414	0.7236	0.1103	0.6133	1.2994	0.4169	2.8125	1.666	12.9470	2.4279	0.162	2.151	2.61	0.1357	0.016
0.1	0.7235	0.1311	0.6400	0.9140	0.4511	1.3312	1.593	14.8630	2.6531	0.339	2.974	3.60	0.0934	0.011

Second wave

$v^{1/2}$	E_{pa} (volt)	E_{pc} (volt)	ΔE_p (volt)	I_{pa}/I_{pc}	$E°$ (volt)	D_a $\times 10^{-11}$	D_c $\times 10^{-14}$	$E_{pc/2}$ (volt)	αn_a	K_s $\times 10^{-01}$	Γ_c $\times 10^{-09}$	$(+)Q_c$ $\times 10^{-05}$	Γ_a $\times 10^{-10}$	$(-)Q_a$ $\times 10^{-06}$
0.3162	0.5631	-0.0674	0.6305	5.7616	0.1154	0.0003	0.0008	-0.0670	137.596	1.29	0.0259	0.0629	1.4944	3.62
0.2236	0.5431	0.0032	0.5399	5.8434	0.2731	3.989	36.226	0.0092	7.7434	2.43	0.8970	0.543	0.0723	0.044
0.1414	0.5186	0.0280	0.4906	3.0229	0.2733	2.3788	260.32	0.0329	9.4527	1.70	3.8018	2.30	0.0558	0.034
0.1	0.4971	0.0408	0.4563	3.6375	0.2689	2.3965	181.13	0.0444	12.6962	0.588	4.4848	2.72	0.0560	0.034

Third wave

$v^{1/2}$	E_{pa} (volt)	E_{pc} (volt)	ΔE_p (volt)	I_{pa}/I_{pc}	$E°$ (volt)	D_a $\times 10^{-12}$	D_c $\times 10^{-12}$	$E_{pc/2}$ $\times 10^{-01}$ (volt)	αn_a	K_s $\times 10^{-03}$	Γ_c $\times 10^{-09}$	$(+)Q_c$ $\times 10^{-05}$	Γ_a $\times 10^{-12}$	$(-)Q_a$ $\times 10^{-08}$
0.3162	0.2981	-0.1760	0.4741	3.3061	0.0169	0.6786	0.0621	-1.58	2.6494	3.84	0.730	1.77	0.0024	0.0059
0.2236	0.2722	-0.1178	0.3900	1.6335	0.0772	4.2548	0.3290	-1.0982	5.8413	10.1	0.8393	0509	2.3609	1.43
0.1414	0.2713	-0.0405	0.3118	1.0103	0.1154	0.9431	0.9240	-0.3680	12.453	3.30	2.265	1.37	1.1115	67.3
0.1	0.2686	-0.0224	0.2910	0.6215	0.1231	0.6353	1.6449	-0.1133	4.2100	1.20	4.2739	2.59	91.229	55.3

Table 2-c : Effect of different Scan rate on Metal

$[M] \times 10^{-03}$	$[L] \times 10^{-04}$	$(E°)M$ (volt)	$(E°)C$ (volt)	ΔE (volt)	$Log[L]$	ΔG (KJ/mol)	$Log \beta_{MX}$
8.22	6.85	0.4271	0.4457	-0.0181	-3.1644	5.6891	-1.0205
8.11	0.135	0.42712	0.4373	-0.0102	-2.8692	1.2523	-0.2246
7.89	0.263	0.42712	0.4331	-0.0060	-2.5798	-2.4686	0.4428
7.69	0.385	0.42712	0.4277	-0.0005	-2.4150	-6.5234	1.17018
7.50	0.500	0.42712	0.4262	0.0009	-2.30103	-8.8925	1.5952
7.32	0.610	0.42712	0.4238	0.0033	-2.2148	-11.5559	2.0729
7.14	0.714	0.42712	0.4198	0.0073	-2.1461	-14.7927	2.6535

[M] x10^{-03}	[L] x10^{-04}	(E°)M (volt)	(E°) C (volt)	ΔE (volt)	Log[L]	ΔG (KJ/mol)	Log β$_{MX}$
8.22	6.85	0.2800	0.2763	0.0037	-3.1644	-2.1823	0.3915
8.11	0.135	0.2800	0.2661	0.0138	-2.8692	-5.3323	0.9565
7.89	0.263	0.2800	0.2591	0.0208	-2.5798	-8.8160	1.5814
7.69	0.385	0.2800	0.2601	0.0199	-2.4150	-10.5639	1.8950
7.50	0.500	0.2800	0.2581	0.0219	-2.30103	-12.7740	2.2914
7.32	0.610	0.2800	0.2517	0.0283	-2.2148	-15.7428	2.8240
7.14	0.714	0.2800	0.2479	0.0321	-2.1461	-18.1540	3.2565

[M] x10^{-03}	[L] x10^{-04}	(E°)M (volt)	(E°) C (volt)	ΔE (volt)	Log[L]	ΔG (KJ/mol)	Log β$_{MX}$
8.22	6.85	0.1205555	0.084	0.037	-3.1644	-8.567	1.5368
8.11	0.135	0.1205555	0.080	0.041	-2.8692	-10.5686	1.896
7.89	0.263	0.1205555	0.071	0.049	-2.5798	-14.302	2.5656
7.69	0.385	0.1205555	0.069	0.052	-2.4150	-16.673	2.9908
7.32	0.610	0.1205555	0.065	0.055	-2.2148	-20.997	3.7665
7.14	0.714	0.1205555	0.061	0.059	-2.1461	-23.440	4.20478
7.50	0.500	0.1205555	0.069	0.052	-2.30103	-18.573	3.3316

Table 2-d: Effect of scan rate 1:1 Complex

υ	[M] x10^{-03}	[L] x10^{-03}	(E°)M (volt)	(E°) C (volt)	ΔE (volt)	Log[L]	ΔG (KJ/mol)	Log β$_{MX}$
0.1	7.14	7.14	0.4271	0.3158	0.1113	-2.1461	-54.918	9.8514
0.05	7.14	7.14	0.3263	0.4131	-0.0868	-2.1461	21.550	-3.8657
0.02	7.14	7.14	0.3284	0.4169	-0.0885	-2.1461	22.182	-3.9791
0.01	7.14	7.14	0.3310	0.4511	-0.1201	-2.1461	34.378	-6.1669

υ	[M] x10^{-03}	[L] x10^{-03}	(E°)M (volt)	(E°) C (volt)	ΔE (volt)	Log[L]	ΔG (KJ/mol)	Log β$_{MX}$
0.1	7.14	7.14	0.2800	0.1154	0.1646	-2.1461	-43.7220	7.8429
0.05	7.14	7.14	0.1540	0.2731	-0.1191	-2.1461	11.0187	-1.9766
0.02	7.14	7.14	0.1633	0.2733	-0.1100	-2.1461	9.2631	-1.6616
0.01	7.14	7.14	0.1672	0.2689	-0.1017	-2.1461	7.6667	-1.3753

υ	[M] $\times 10^{-03}$	[L] $\times 10^{-03}$	$(E°)M$ (volt)	$(E°) C$ (volt)	ΔE (volt)	Log[L]	ΔG (KJ/mol)	Log β_{MX}
0.1	7.14	7.14	0.3348	0.0169	0.3180	-2.1461	-73.3258	13.1533
0.05	7.14	7.14	0.0414	0.0772	-0.0358	-2.1461	-5.0519	0.9062
0.02	7.14	7.14	0.0507	0.1154	-0.0647	-2.1461	0.5228	-0.0938
0.01	7.14	7.14	0.0588	0.1231	-0.0643	-2.1461	0.4395	-0.0788

Table (3-a) : Solvation and Kinetic parameters (D, k_s, Γ and Q) of first wave of (SeO_2 + Succinic acid) in presence of Dithizone at 291.15K, scan rate 0.1 V/Sec.

[M] M/L $\times 10^{-03}$	[L] M/L	Ep_a (volt)	Ep_c (volt)	ΔEp (volt) $\times 10^{03}$	Ip_a/Ip_c	$E°$ (volt)	Da $\times 10^{-14}$	Dc $\times 10^{-14}$	$Ep_{c/2}$ (volt) $\times 10^{-02}$	αn_a	k_s $\times 10^3$	Γ_c $\times 10^{-10}$	(+) Q_c $\times 10^{-05}$	Γ_a $\times 10^{-10}$	(-) Q_a $\times 10^{-05}$
8.33	0.0014	0.5789	0.0534	0.5255	0.7616	0.3161	0.2522	0.435	6.86	3.0539	0.628	1.367	0.663	1.041	0.505
8.33	0.0027	0.5927	0.0592	0.5335	1.2090	0.3260	1.759	1.20	7.92	2.3348	1.26	2.274	1.10	2.749	1.33
8.33E	0.004	0.6042	0.0512	0.5530	2.8342	0.3277	2.8015	0.349	6.60	3.1626	1.71	1.224	0.594	3.469	1.68

Table (3-b): Solvation and Kinetic parameters (D, k_s, Γ and Q) of effect of scan of addition of

(0.004 M of Dithizone) on (Succinic acid 0.033 M + SeO2) at 291.15K.

$v^{(1/2)}$	Ep_a (volt)	Ep_c (volt)	ΔEp (volt)	Ip_a/Ip_c	$E°$ (volt)	Da $\times 10^{-12}$	Dc $\times 10^{-12}$	$Ep_{c/2}$ (volt)	αn_a	k_s $\times 10^{02}$	Γ_c $\times 10^{-09}$	(+) Q_c $\times 10^{-05}$	Γ_a $\times 10^{-12}$	(-) Qa $\times 10^{-08}$
0.3162	0.6042	0.0512	0.5530	2.8342	0.3277	3.47	0.224	0.0686	0.0029	4.15	0.352	0.427	1.51	1.83
0.2236	0.5714	0.0711	0.5003	0.9017	0.3212	2.65	0.235	0.1029	1.4638	8.28	0.511	0.619	1.32	1.60
0.1414	0.5292	0.1110	0.4182	1.4321	0.3201	2.29	1.12	0.1283	2.6923	0.586	1.76	2.14	1.23	1.49
0.1	0.5022	0.1087	0.3934	0.9916	0.3055	1.16	1.18	0.1273	2.5062	0.153	2.55	3.10	0.870	1.05

Table 4-a : Effect of different Scan rate on Metal with dithizone

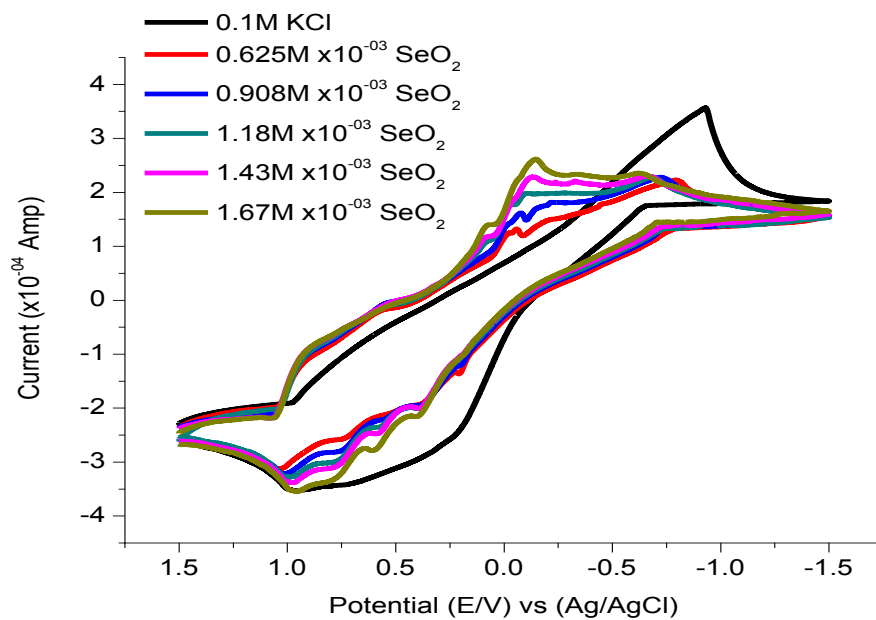| [M] $\times 10^{-02}$	[L] $\times 10^{-03}$	$(E°)M$ (volt)	$(E°)_D$ (volt)	$(E°)_c$ (volt)	ΔE (volt)	Log[L]	ΔG (KJ/mol)	Log β_{MX}
1.86	0.515	0.3211	-0.005	0.3161	0.005	-3.2878	-2.4399	0.4377
1.84	1.02	0.3211	0.0048	0.3260	-0.0048	-2.9912	0.9410	-0.1688
1.82	1.52	0.3211	0.0066	0.3277	-0.0066	-2.8195	1.2319	-0.2210

Fig. 1: Cyclic Voltammograms of Effect of concentration of SeO$_2$ at 291.15K, scan.1 V/Sec
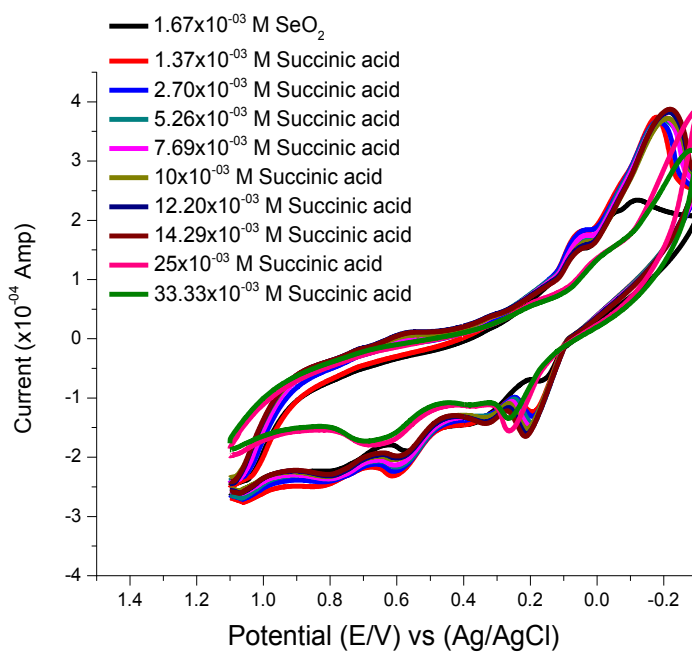
Fig. 2: Cyclic Voltammograms of Effect of concentration of Succinic acid on SeO₂ at 291.15K, scan rate 0.1 V/Sec.
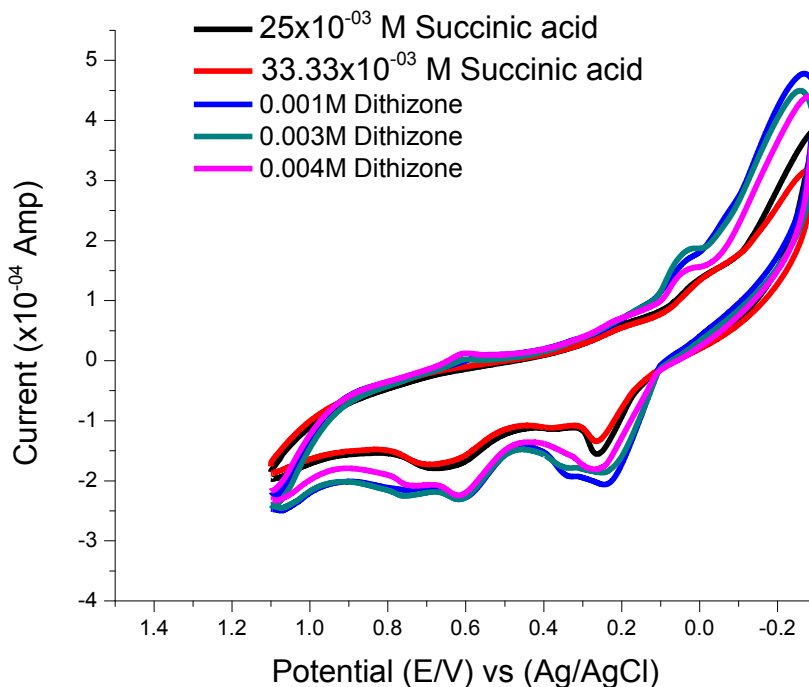

Fig. 3: Cyclic Voltammograms of Effect of concentration of Dithizone and Succinic acid on first wave SeO₂ at 291.15K, scan rate 0.1 V/Sec.
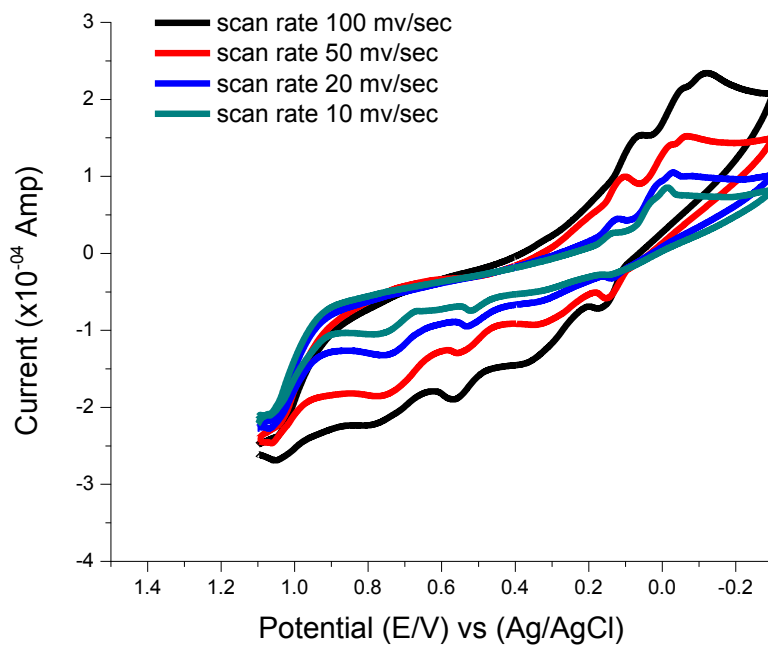
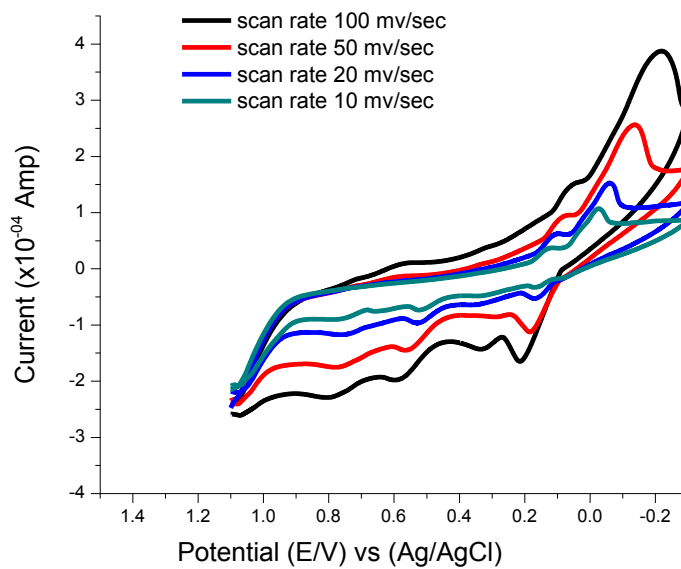**Fig. 4: Cyclic Voltammograms of different scan rates on SeO₂ at 291.15 K.**

Fig. 5: Cyclic Voltammograms of different scan rates on Succinic acid with SeO₂ at 291.15 K
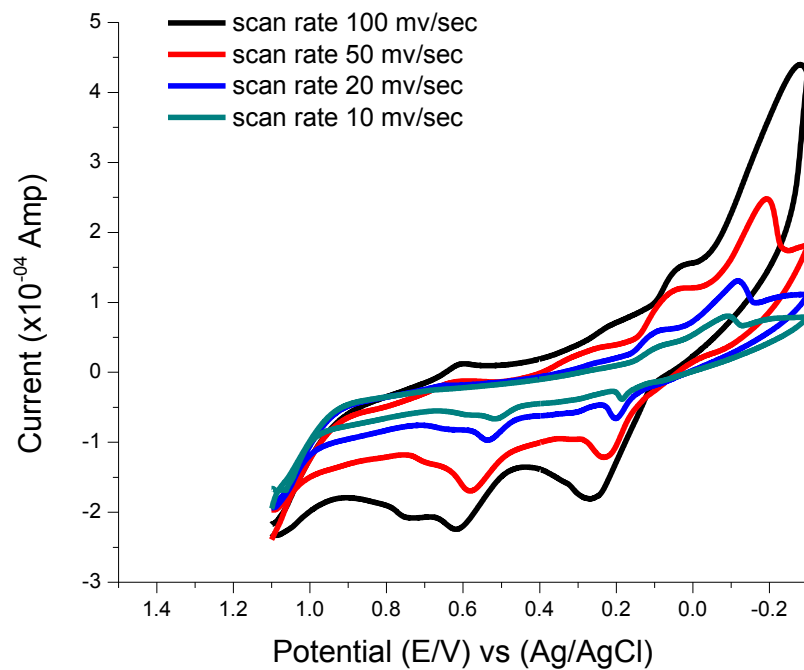
Fig. 6: Cyclic Voltammograms of different scan rates on Dithizone plus Succinic acid and SeO$_2$ at 291.15 K.
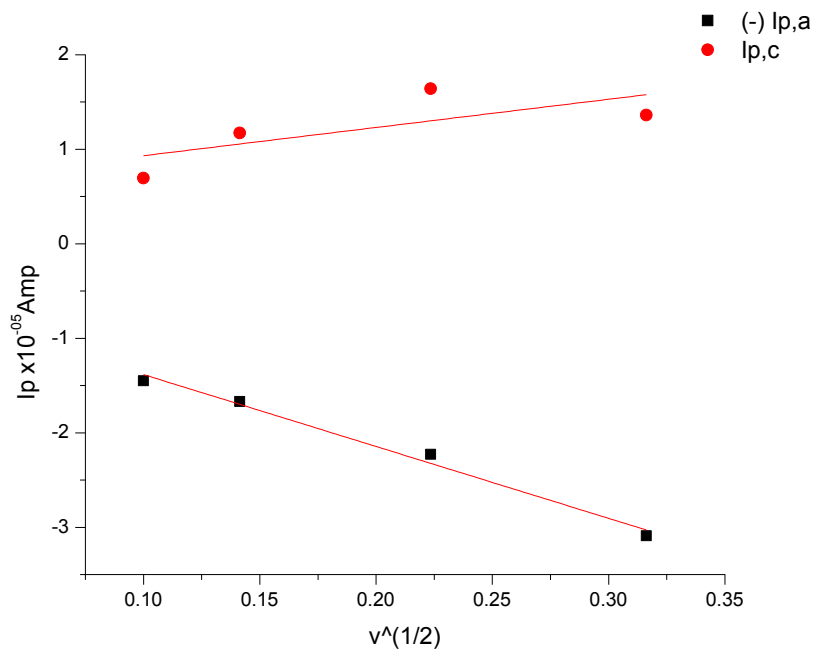
Fig. 7: v^1/2 vs. Ip for first wave of SeO₂ at 291.15°K
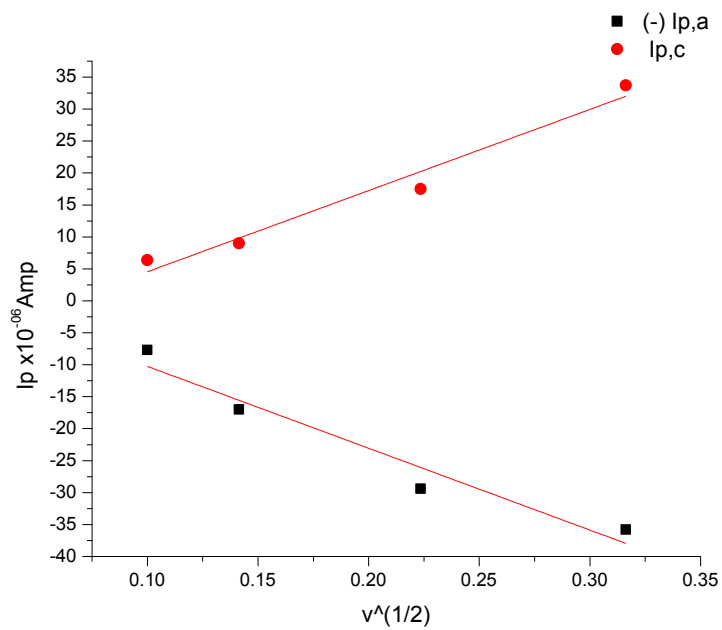
Fig. 8: v^1/2 vs. Ip for second wave of SeO₂ at 291.15°K
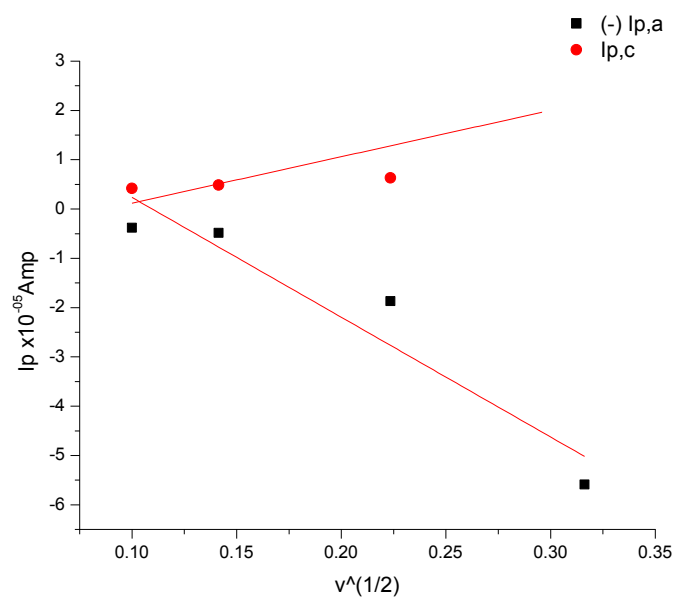
Fig. 9: v^1/2 vs. Ip for third wave of SeO₂ at 291.15°K
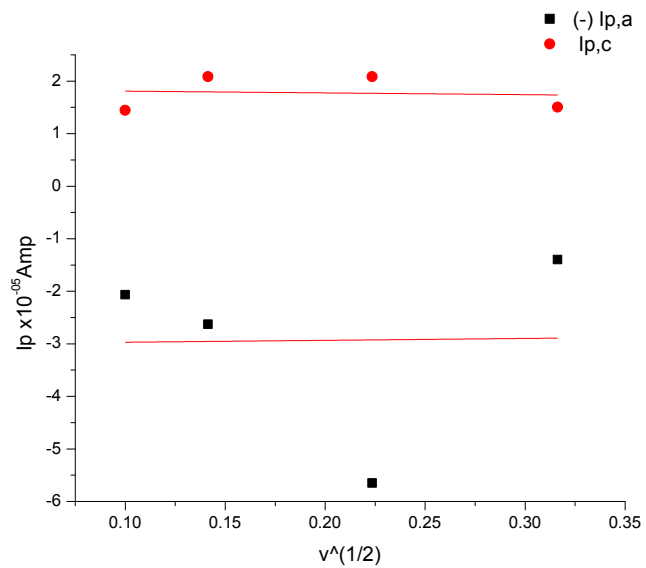
Fig. 10: v^1/2 vs. Ip for effect of Succinic acid on first wave of SeO₂ at 291.15°K.
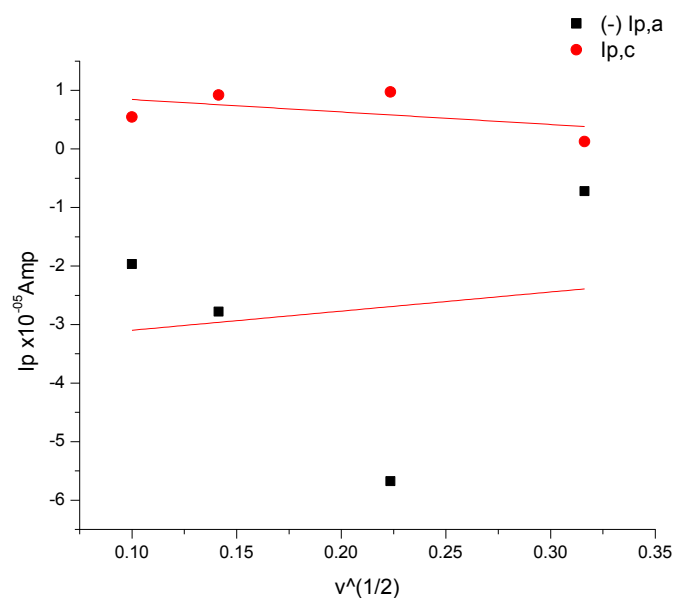
Fig. 11: v^1/2 vs. Ip for effect of Succinic acid on second wave of SeO$_2$ at 291.15°K.
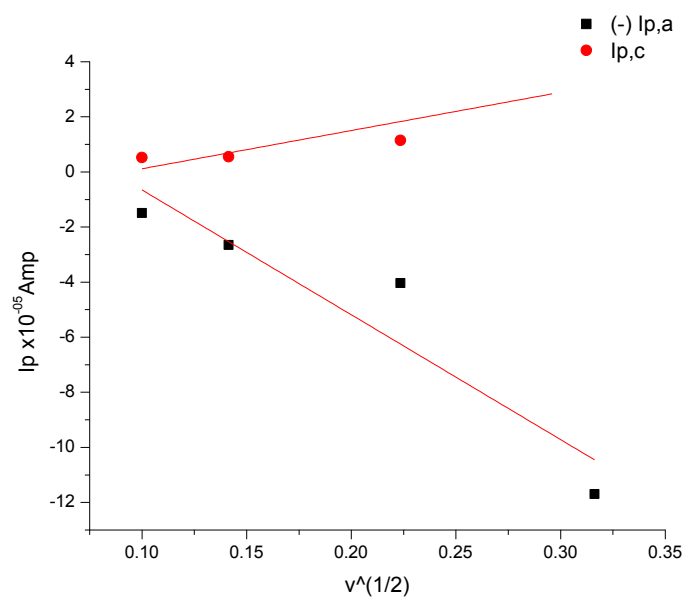
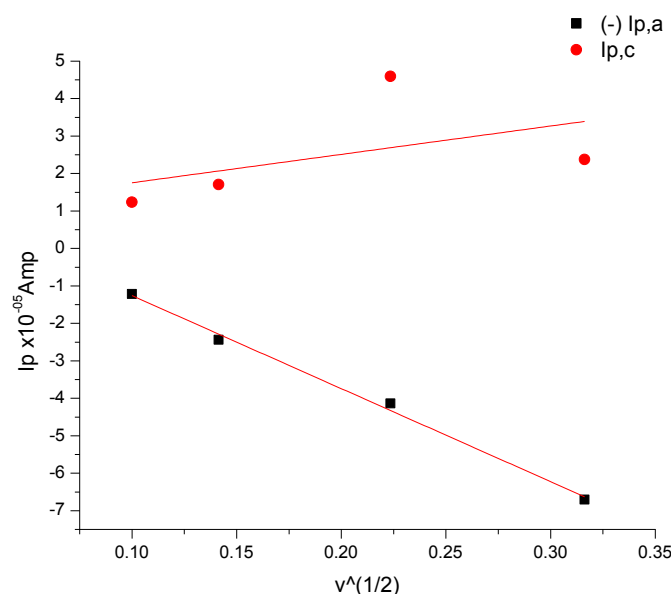**Fig. 12: v^1/2 vs. Ip for effect of Succinic acid on third wave of SeO$_2$ at 291.15°K.**

Fig. 13: v^1/2 vs. Ip for effect of Dithizone on first wave of SeO$_2$ at 291.15°K.

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