



Molecular Thermodynamic Interaction Parameters between Mercuric Chloride and Methyl Orange Cyclic voltammetry

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Abstract: The cyclic voltammetry measurement of mercuric chloride HgCl_2 was studied with 0.1M HNO_3 at 289.15 K using a glassy carbon electrode with a different scan rate applied in the medium. The cyclic voltammetry measurement applied against methyl orange dye (M.O.) at 289.15 K with the scan rate effect was studied. The complexation interaction between the mercury ions and M.O. dye occurs by measuring the stability constant and Gibbs free energy. It is seen that Gibbs free energy for molecular interaction between mercuric chloride and methyl orange increases with increased dye concentration and reach -12.1613 KJ/mol using 3.13×10^{-4} M of M.O. dye. In the complexation interaction between mercuric chloride HgCl_2 and M.O. dye, there is a decrease in Gibbs free energy and the stability constant with decreasing in the scan rate applied till it becomes -9.052 KJ/mol in the presence of 3.13×10^{-4} M M.O. dye. It is found that there is an increase in Nicholson parameters specific for mercuric chloride with the increase in the concentration of M.O dye that tells the possibility of this medium to work as a leaching solution.

keywords: Electron transfer rate constant, stability constant, Gibbs free energy of complexation, charge transfer coefficient, diffusion coefficient

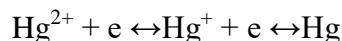
1.Introduction

Cyclic voltammetry (C.V.) is an electrochemical technique used to study redox reactions in solutions[1]. C.V. is also interested in studying the electrochemical properties of molecular species [1-3]. It is sensitive to metal ions, like mercury ions so enables us to detect this ion in an aqueous solution. Mercuric chloride (HgCl_2) is a compound that has been widely used due to its interesting redox properties [4]. Here is some reasons why the cyclic voltammetry of mercuric chloride is necessary. Firstly, redox behaviors can provide insights into stability and reactivity of the compound. Secondly cyclic voltammetry can be used for estimating important electrochemical parameters of mercuric chloride such as diffusion coefficient, electron transfer rate and charge transfer resistance. Thirdly, environmental monitoring, since mercuric chloride is a toxic compound that can have detrimental effects on human health. Cyclic voltammetry can be employed as a

sensitive analytical tool for detecting and quantifying mercuric chloride in environmental samples [5]. Fourthly, material science, since cyclic voltammetry can also be used to investigate the electrochemical behavior of materials containing or interacting with mercuric chloride such as electrodes or catalysts. It is a very toxic compound and its toxicity is not only due to mercury but also to its corrosion properties that lead to huge internal damage and is harmful to the environment [6].

Using a glassy carbon electrode as a working electrode and nitric acid occurs reduction to Hg^{2+} that is observed using rotating ring-disc voltammetry or linear sweep voltammetry. The reduction occurs for mercury in one step by a gain of two electrons. Linear sweep voltammetry shows that at a low sweep rate, the reduction for mercury ions occurs reversibly but with increasing the speed of the scan becomes irreversible [7]. When the

reduction occurs, there is an equilibrium between the oxidation state Hg^+ and the mercury ions. the obtained peak heights depend on the acid concentration [8].



Alternating-current inversion voltammetry is used to study the inversion voltammetric signal specific for Hg^{2+} redox reactions in the presence of a potentiated substance. this potential substance supports the redox reaction in the electrochemical process.

Dyes are considered one of the organic pollutants in the environment that is very toxic and used extensively in industries like plastic, food, paper pharmaceutical intermediate [9,10]. Usually dyes found in complex structures and have a synthetic nature. sometimes dyes degraded to give toxic and harmful chemical compounds [11, 12]. In recent years many works developed for the removal of dyes from water by adsorption mechanism [13,14]. Another important way to get rid of dyes is through degradation using the electro-oxidation technique.

Methyl orange one from organic dye that is considered azobenzene derivative. It used as pH indicator due to its unique and distinct color at different pH values. The chemical structure of methyl orange is the following:

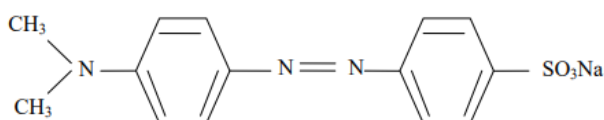


Fig 1: Chemical structure of methyl orange

2. Materials and methods

Chemicals

Dye is considered one of the organic pollutants in the environment that is very

The chemicals used, such as mercuric chloride and nitric acid, were obtained from Sigma-Aldrich Company. chloride methyl orange produced by Rankem Company.

Electrolytes

Cyclic voltammetry technique applied using 0.1M HNO_3 . preparation of 0.1 M mercuric chloride solution by dissolving 27.51 g HgCl_2 in 1000 ml distilled water. The M.O. dye solution was prepared by diluting 32.73 g of dye in 1 L of distilled water (0.1M).

Electrodes

Using a DY2000 potentiostat that includes three electrodes A glassy carbon electrode represents a working electrode. The auxiliary electrode used in measurement is platinum wire. The last electrode used is a saturated reference electrode that consists of an Ag/AgCl electrode filled with saturated KCl solution [15–18]. A four-neck vessel is used as a cell with a capacity of 0.01 L.

Results and Discussion

Equations used for cyclic voltammetry analysis:

Many equations [19, 20] can be applied for the estimation of the electrochemical parameter for the oxidation and reduction of the used mercuric chloride HgCl_2 in 0.1M HNO_3 at 289.15 K using a glassy carbon electrode.

Surface coverage Γ_c or Γ_a , which is included in the working electrode covered area by the active species in equation (1) [21, 22]:

$$\Gamma_c = I_{pc} 4RT/n^2 F^2 A v \quad (1)$$

Since Γ_c is the cathodic surface coverage the same for anodic surface coverage can be used on the use of cathodic peak current, n is the electron number consumed in redox reaction. F is Faraday's constant, A is the area of the electrode used as a working electrode, which is a glassy carbon electrode in HgCl_2 [23, 24]. the cathodic quantity of electricity Q_c can be calculated by the application of equation (2)

$$Q_c = nFA\Gamma_c \quad (2)$$

The cathodic and anodic diffusion coefficients can be calculated by applying an equation derived from the Randlessevcik equation[25, 26]

$$I_{p,a} = 0,4463 (n^3 F^3/RT) A.C.(D,v)^{0.5} \quad (3)$$

I_p is the peak current, number of electrons, F Farady,s constant, D is the diffusion coefficient in cm^2/s , A is t electrode surface area in cm^2 , C is the molar concentration and v is the scan rate in V.s .

Since $E_{p,c}$ is the cathodic peak potential, v is the scan rate and C is the metal ion concentration[26, 27].

The heterogenous electron transfer constant (K_s) we calculate by equation [25]:

$$k_s = 2.18 (D \alpha n_a F v/RT)^{1/2} \exp \{ \alpha^2 n F/RT$$

$$(E_{pc} - E_{pa}) \quad (4)$$

Since α is the charge transfer coefficient, n is the number of electrons consumed in the oxidation and reduction from equation [28] :

$$(E_{pc} - E_{pc} / 2) = (2.2 RT/nF) \dots\dots\dots(5)$$

Since E_{pc} is the cathodic peak potential.

All of the above parameters can be evaluated from the anodic and cathodic behavior for the redox peaks and the data is presented for each reaction after explaining the cyclic voltammograms

α , n_a , Γ_c , Γ_a , Q_c , Q_a can be calculated for each metal ion in absence and presence of the used ligand, and the redox mechanism was suggested and explained [29].

Redox behavior of HgCl₂ in 0.1M HNO₃ at 289.15 K:

The application of a glassy carbon electrode (GCE) for the redox reaction of HgCl₂ in 0.1M HNO₃ as a supporting electrolyte for cyclic voltammetry was examined here in this part. through oxidation happened after the reduction of HgCl₂ appeared at the electrode potential of +0.25 or +0.65 volts, involving one electron for the two oxidation processes [30]. Two wide waves were obtained for the reduction of HgCl₂, consuming one electron for each at 0.1 V and -0.3 V, which are the opposite of the oxidation peaks [31].

The negative shift to the cathodic potential of the first reduction wave by a greater increase

Table (1): Effect of different concentrations of HgCl₂ in 30 ml 0.1 M HNO₃ by using glassy carbon electrode at 289.15 K and scan at 0.1V.s⁻¹.

[M] x10 ³ mol.L ⁻¹	Ep,a Volt	-Ep,c Volt	ΔEp Volt	(-)Ip,a x10 ⁵ Amp	Ip,c x10 ⁵ Amp	Ip,a/Ip,c	E° Volt	Da x10 ⁵ cm ² .s ⁻¹	Dc x10 ⁷ cm ² .s ⁻¹	Epc/2	α _{inc}	k _s c	Γ _c x10 ¹⁰ mol.cm ⁻²	(+) Q _c x10 ⁶ C	Γ _a x10 ⁹ mol.cm ⁻²	Q _a x10 ⁶ C
0.66	0.30	0.09	0.387	1.36	0.50	2.706	0.106	0.718	9.82	-0.05	1.360	0.119	4.13	2.51	1.11	6.78
1.32	0.27	0.07	0.203	3.27	0.98	3.332	0.175	1.051	9.47	0.092	2.570	0.401	8.06	4.89	2.68	16.3
1.96	0.24	0.09	0.157	3.76	1.57	2.332	0.170	0.597	11	0.113	2.203	0.159	12.9	7.85	3.02	18.3
2.60	0.24	0.15	0.087	6.43	2.14	3.008	0.202	1.044	11.5	0.19	1.493	0.003	17.58	10.7	5.29	32.1
3.23	0.24	0.19	0.052	7.47	2.07	3.605	0.216	0.914	7.03	0.201	4.206	0.002	17.64	10.	6.14	37.2

Table (2): Effect of different scan rates of (3.23 x 10³ M) of HgCl₂ in 30 ml 0.1 M HNO₃ by using glassy carbon electrode at 289.15 K

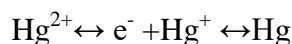
v V.S ⁻¹	Ep,a Volt	Ep,c Volt	ΔEp Volt	(-)Ip,a x10 ⁵ Amp.	Ip,c x10 ⁵ Amp.	Ip,a/Ip,c	E° V	Da x10 ⁶ cm ² .s ⁻¹	Dc. 10 ⁷ cm ² .s ⁻¹	Epc/2	α _n	ksc10 ² ×	Γ _c x10 ⁹ mol.cm ⁻²	(+) Q _c x10 ⁵ C	Γ _a x10 ⁹ mol.cm ⁻²	(-) Q _a x10 ⁵ C
0.10	0.24	0.19	0.05	7.47	2.07	3.61	0.202	9.11	7.1	0.20	4.19	2.14	1.70	1.03	6.12	3.71
0.05	0.23	0.2	0.04	4.98	1.17	4.24	0.217	8.13	4.51	0.21	5.78	1.01	1.93	1.17	8.20	4.97
0.02	0.22	0.21	0.01	3.03	0.73	4.18	0.216	7.54	4.32	0.22	5.14	0.37	2.99	1.81	12.5	7.56
0.01	0.21	0.21	0.002	2.21	0.99	2.22	0.210	7.97	16.1	0.22	6.61	0.48	8.17	4.94	18.2	11

in HgCl₂ concentration indicates a reversible and diffusion mechanism [32].

The cathodic surface coverage c , anodic surface coverage a , cathodic quantity of electricity Q_c , and anodic quantity of electricity Q_a are increased by an increase in HgCl₂ concentration, indicating a higher conduction result than the original glassy carbon [33].

From the result in Table 1, we found that I_{pa}/I_{pc} is very high indicating the oxidation process in the range of about three folds higher than the reduction one. The diffusion coefficient D_a and D_c have a great value, indicating the diffusion mechanism [34]

The following voltammetry response was shown for the system [30].



Metal ions were reduced directly in phase pollution; stabilisation of the Hg⁺ oxidation has happened, indicating the metal is re-oxidized, and wide range peaks were obtained [35].

Effect of scan rate on redox reaction of HgCl₂ in 0.1M HNO₃:

Different scan rates 0.01, 0.02, 0.05, and 0.1 v/s were applied for studying its effect on 3.23 mM HgCl₂ in 0.1 M HNO₃ and their cyclic voltammograms are seen in Fig 3.

We noticed that by the decrease in scan rate, the reduction peaks of Hg²⁺ become less pronounced than that at higher scans.

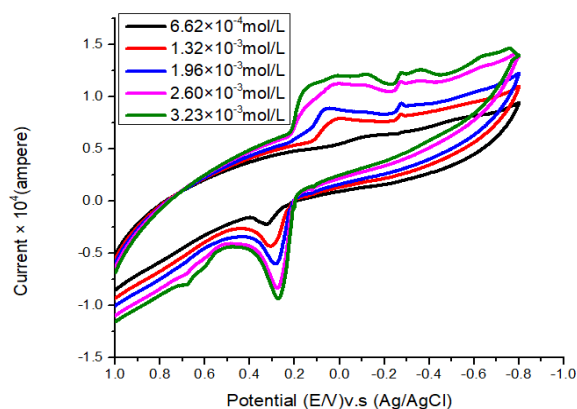


Fig. (2): Effect of different concentrations of HgCl_2 in 30 ml 0.1 M HNO_3 by using glassy carbon electrode at 289.15 K and scan rate $0.1 \text{ V} \cdot \text{s}^{-1}$.

Fig.(2) illustrates the appearance of two main peaks one for the reduction and other for oxidation at approximately +0.1 and +0.25V respectively. The appearance of plateau at range corresponding to the reduction of mercuric ions to mercurous ones and the two will precipitated at the working electrode. The main redox peaks are used for further study here.

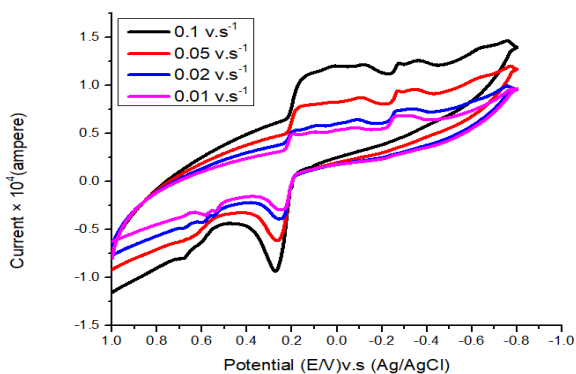


Fig.3. Effect of different scan rates of ($3.23 \times 10^{-3} \text{ M}$) of HgCl_2 in 30 ml 0.1 M HNO_3 utilizing glassy carbon electrode at 289.15 K

We observed from Table 2 that:

Increasing cathodic and anodic surface coverage by decreasing of scan rate is

Table (3): Effect of different concentrations of M.O. dye in 1 ml HgCl_2 0.1 M in 30 ml 0.1 M HNO_3 by using glassy carbon electrode at 289.15 K and scan rate $0.1 \text{ V} \cdot \text{s}^{-1}$.

[M] $\times 10^5 \text{ mol} \cdot \text{L}^{-1}$	[L] $\times 10^5 \text{ mol} \cdot \text{L}^{-1}$	$E_{p,a} \text{ V}$	$E_{p,c} \text{ V}$	$\Delta E_p \text{ V}$	(-) $I_{p,a} \times 10^5 \text{ Amp}$	$I_{p,c} \times 10^5 \text{ Amp}$	$I_{p,a} / I_{p,c}$	$E^\circ \text{ V}$	$D_a \times 10^6 \text{ cm}^2 \cdot \text{s}^{-1}$	$D_c \times 10^6 \text{ cm}^2 \cdot \text{s}^{-1}$	$E_{pc}/2$	$\alpha_{an,c}$	kc	$\Gamma_c \times 10^9 \text{ mol} \cdot \text{cm}^{-2}$	(+) $Q_c \times 10^5 \text{ C}$	$\Gamma_a \times 10^9 \text{ mol} \cdot \text{cm}^{-2}$	(-) $Q_a \times 10^5 \text{ C}$
3.21	6.41	0.23	0.09	0.14	6.05	2.84	2.12	0.16	6.07	1.34	0.11	2.20	0.12	2.34	1.42	4.97	3.01
3.18	12.7	0.23	0.08	0.15	4.96	0.41	11.9	0.15	4.13	0.02	0.09	5.78	0.00	0.34	0.21	4.08	2.47
3.16	19	0.23	0.07	0.16	4.98	2.75	1.81	0.14	4.21	1.29	0.1	1.32	0.14	2.27	1.37	4.09	2.48
3.14	25.2	0.23	0.06	0.17	4.56	2.28	2.00	0.14	3.58	0.89	0.09	1.59	0.15	1.87	1.13	3.75	2.27
3.13	31.3	0.23	0.05	0.17	4.53	2.47	1.84	0.14	3.58	1.06	0.09	1.28	0.16	2.03	1.23	3.72	2.26

happening increasing in the conduction due to precipitation on glassy carbon electrode (GCE).

The decrease of heights for both the oxidation and reduction wave by decrease in the scan rate was clear in Table 2 and Fig 3 indicating a diffusion-controlled reaction.

The rate constant for electron transfer is decreased by the decrease in scan rate, indicating a kinetic reaction.

The limiting current from the anodic wave to the cathodic one is in the range of 3–4 folds, indicating diffusion-controlled reactions and the oxidation process are easily possible.

The number of electrons was evaluated from the data given in Table 2 ($E_p = 0.059/n$) and found to be one.

All other kinetic parameters are increased by decreasing the scan rate, referring to kinetic and diffusion processes.

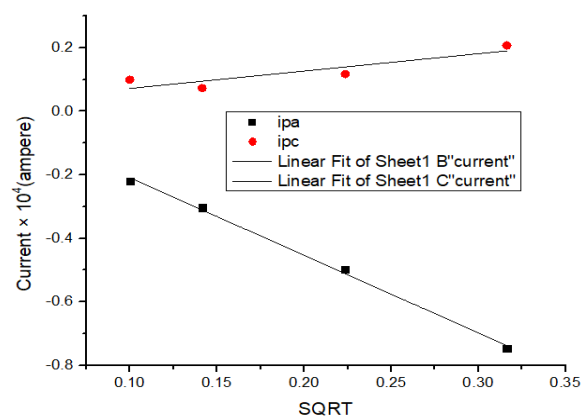


Fig (4): The relation between peak current and SQRT of scan rate of final addition of HgCl_2 . From the slope of the two straight in Fig 4, we found that the slope of oxidation process used is bigger than the reduction indicating more faster and more diffusion of the oxidation than the reduction.

The second reduction peak for Hg^{2+} appears at -0.3V indicating the reduction of mercury ion to mercury metal precipitated at the glassy carbon electrode.

Table (4): Effect of different scan rates of (31.3×10^5 M) of M.O. dye in 1 ml HgCl_2 0.1 M in 30 ml 0.1 M HNO_3 by using glassy carbon electrode at 299.55K and scan rate 0.1 V.s^{-1} .

$v \text{ V.s}^{-1}$	$E_{p,a} \text{ V}$	$E_{p,c} \text{ V}$	$\Delta E_p \text{ V}$	$(-)I_{p,a} \times 10^5 \text{ Amp}$	$I_{p,c} \times 10^6 \text{ Amp}$	$I_{p,a} / I_{p,c}$	$E^\circ \text{ V}$	$D_a \times 10^6 \text{ cm}^2 \text{ s}^{-1}$	$D_c \times 10^6 \text{ cm}^2 \text{ s}^{-1}$	$E_{pc/2}$	u_{na}	$k_{sc} \times 10^3$	$\Gamma_c \times 10^9 \text{ mol.cm}^{-2}$	$(+)Q_c \times 10^5 \text{ C}$	$\Gamma_a \times 10^9 \text{ mol.cm}^{-2}$	$(-)Q_a \times 10^5 \text{ C}$
0.10	0.227	0.054	0.173	4.53	24.7	1.837	0.1405	3.578	1.061	0.090	1.285	164	2.028	1.23	3.725	2.26
0.05	0.218	0.072	0.146	2.72	19.3	1.406	0.145	2.583	1.306	0.111	1.186	72	3.182	1.93	4.476	2.71
0.02	0.211	0.188	0.023	2.06	6.49	3.166	0.1995	3.685	0.368	0.198	4.627	4.04	2.670	1.62	8.452	5.12
0.01	0.205	0.202	0.003	1.47	5.55	2.653	0.2035	3.784	0.537	0.206	11.567	3.66	4.565	2.77	12.11	7.34

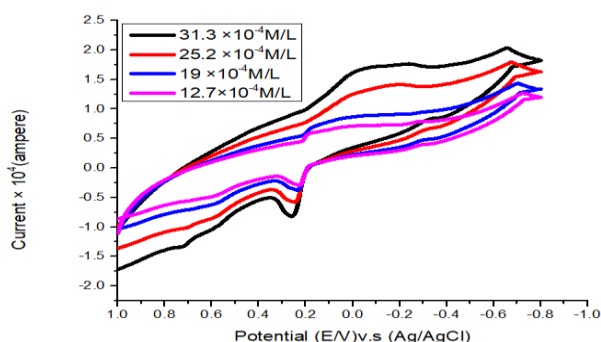


Fig .(5): Effect of different concentrations of M.O. dye in 1 ml HgCl_2 0.1 M in 30 ml 0.1 M HNO_3 by using glassy carbon electrode at 289.15 K and scan rate 0.1 V.s^{-1}

Effect of methyl orange on the redox process of HgCl_2 :

Different concentration of M.O. was added to $3.13 \times 10^{-3} \text{ M/L}$ HgCl_2 in 0.1 M HNO_3 and at 289.15 K as shown in Fig 5.

We noticed from Fig 5 a decrease in both cathodic and anodic peak currents for HgCl_2 negative shift for the cathodic potential for the cathodic wave and positive shift for the anodic peak potential for the anodic wave.

The experimental data are presented in Table 4 and Fig 5 with the decrease in most parameters by adding more M.O. indicating a complex reaction.

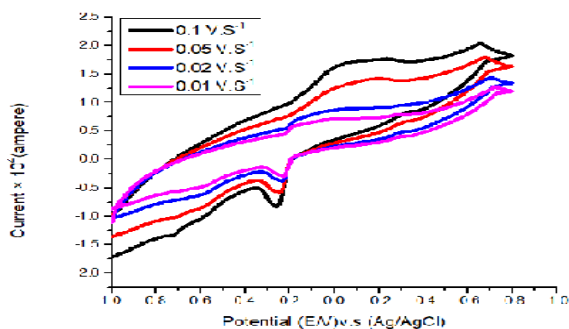


Fig (6): Effect of different scan rates of (31.3×10^5 M) of M.O. dye in 1 ml HgCl_2 0.1 M in 30 ml 0.1 M HNO_3 by using glassy carbon electrode at 289.15K and scan rate 0.1 V.s^{-1}

The effect of scan rate on the interaction between HgCl_2 and M.O.:

The cyclic voltammograms are presented in Fig 6 showing that the effect of M.O. on 3.13 mM HgCl_2 is decreased in scan rate proving the diffusion mechanism.

Most data given in Table 5 like Γ_c , Γ_a , Q_c , and Q_a are increased by a decrease in the scan rate supporting the diffusion mechanism.

The kinetic parameters, scan rate constant, D_c cathodic diffusion coefficient, and D_a anodic diffusion coefficient are decreased by a decrease in the scan rate indicating a kinetic reaction.

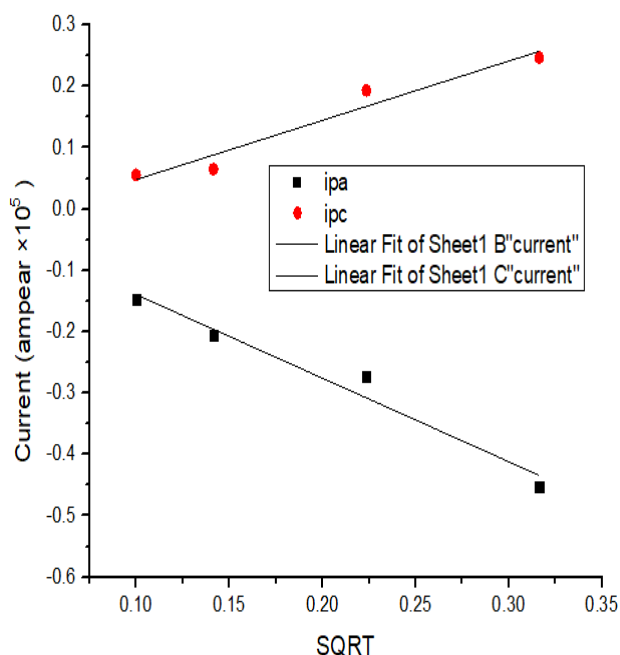


Fig (7): The relation between peak current and SQRT of scan rate of complex

The slopes for the anodic and cathodic peaks are almost the same with a slightly increased value for the anodic one for the interaction of HgCl_2 with M.O. Actually the cyclic voltammetry of mercuric ions is important for further following of this toxic material [44-46].

Table (5): Cyclic voltammetric data of HgCl₂ complex with M.O. in 30 ml 0.1M HNO₃ utilizing glassy carbon electrode at 289.15K and scan rate 0.1 V.s⁻¹, (n = 2).

Mlof L	[L] x10 ⁴ mol.L ⁻¹	(Ep,a) M	(Ep,a) C	ΔE m.v	j	Log[L]	Log βj	ΔG(kJ/mol)
0.2	0.641	0.216	0.1615	-0.0545	0.02	-7.193	8.924	-11.8855
0.4	1.27	0.216	0.153	-0.0630	0.04	-6.895	8.745	-11.6395
0.6	1.90	0.216	0.1465	-0.0695	0.06	-6.721	8.294	-11.0393
0.8	2.52	0.216	0.1435	-0.0725	0.08	-6.599	9.041	-12.0335
1	3.13	0.216	0.1405	-0.30755	0.1	-6.505	10.67	-12.1613

Table (6): Stability constant for different scan rates of (31.3x10⁵ M) of M.O. dye in 1 ml HgCl₂ 0.1 M in 30 ml 0.1 M HNO₃ utilizing glassy carbon electrode at 289.15 K (n=2)

v	(Ep,a) M	(Ep,a) C	ΔE m.v	j	Log[L]	Log βj	ΔG (kJ/mol)
0.100	0.216	0.1405	-0.0755	1	-6.505	10.67	-12.1686
0.050	0.2165	0.1450	0.0715	1	-6.505	8.997	-11.9750
0.020	0.216	0.1995	0.0165	1	-6.505	7.080	-9.4234
0.010	0.212	0.2035	0.0085	1	-6.505	6.801	-9.0521

The stability constant and Gibbs free energy of complexation for the interaction of HgCl₂ with M.O. which are the molecular thermodynamic functions are slightly increased by an increase in methyl orange M.O. concentration indicating complexation as explained in previous works [33, 36-43] proving interaction by physical attraction.

On decreasing the scan rate the thermodynamic functions for HgCl₂ and M.O are decreased supporting the diffusion-controlled reaction.

4. Conclusions:

The appearance of two main peaks, one for reduction and the other for oxidation, at approximately +0.1 and +0.25 V, respectively, for HgCl₂ in HNO₃-supporting electrolyte, which increase in their currents by increasing mercuric chloride concentration, The appearance of a plateau at the range corresponds to the reduction of mercuric ions to mercurous ones, and the two will precipitate at the working electrode. The molecular thermodynamic parameters, stability constants, and Gibbs free energies of interaction were estimated for the interaction of HgCl₂ with methyl orange and found to increase with increased concentration of methyl orange proving electrostatic attraction.

The molecular thermodynamic parameters for the reaction of HgCl₂ with methyl orange are decreased by the decrease in scan rate indicating a diffusion-controlled reaction.

5. Conflict of Interest:

We, the researchers, testify in this scientific

paper that we have no scientific or material enmity regarding this research with anyone in the local or international environment.

6. References

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