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Egypt. J. Chem. **Vol. 66,** No. 6 pp. 101 - 108 (2023)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Molecular Thermodynamics for the Redox Reaction of Sodium Tetrachloroaurate, NaAuCl₄ (Noble Material) with Giemsa Stain (GS) Dye in HNO₃ Solution Using Cyclic Voltammetry

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Abstract

The importance of this investigation is to try to form a complex between sodium tetrachloroaurate and Giemsa stain dye to help researchers in the field of ore dressing of gold in industry. The cyclic voltammetry of sodium tetrachloroaurate, NaAuCl₄, was studied in 0.1 M/L HNO₃ at 299.55K using a glassy carbon electrode. The effects of various scan rates were studied in this medium. Cyclic voltammetry was also done for sodium tetrachloroaurate in the presence of Giemsa Stain dye, and further scan rate effects were discussed. The molecular thermodynamics data like stability constants and Gibbs free energies of complexation resulting from the interaction of sodium tetrachloroaurate, NaAuCl₄ with Giemsa Stain (GS) dye were evaluated and found to be complexation reactions. All the Nicholson parameters for sodium tetrachloroaurate are increased by increase of Giemsa Stain concentration indicating the possibility for using this medium as leaching solution. The molecular Gibbs free energies for sodium tetrachloroaurate are increased by increase Giemsa Stain concentration till it reached -24.53 K.J using 2×10^{-3} M Giemsa Stain, The stability constants and Gibbs free energy of complexation of sodium tetrachloroaurate + Giemsa Stain are decreased by decrease of the scan rate till they reached 5.973 ,-34.258 K.J for log stability constant and Gibbs free energy of complexation using scan 0.01 V/Sec scan.

Keywords : electron transfer rate constant, stability constant, Gibbs free energy of complexation, charge transfer coefficient, diffusion coefficient

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1. Introduction

Ionic liquids like sodium tetrachloroaurate containing anion and cation forms are very important especially in Application in medicine. Also Au(I) and Au(III) oxidizing states are necessary for estimation, obtaining Nicholson parameters and electrochemical study which is our motivate aim and novel study, which many scientists are in need to them. Sodium tetrachloroaurate is the auric salt commonly used in chemistry [1]. Nitric acid is the auric leachate for metals. Hence, in this study, solutions of sodium tetrachloroaurate in HNO₃ were used to investigate reversible and redox reactions cyclically. A few studies have been carried out on the electrochemical reduction of auric solutions [2, 3]. The scanning tunneling microscope (STM), electrochemical study, and self-assembly process were all accomplished [4].

The cyclic voltammetry technique is generally used to study the electrochemical properties of the analyst in solutions [5-7].

Cyclic voltammetry is a method to get information about redox reactions of the ions by measuring the current generated versus the applied voltage applying

working electrode. Potential is measured between the working electrode and the counter electrode [8].

The redox reaction of sodium tetrachloroaurate, NaAuCl₄ is represented by the following reactions [9]:

$$AuCl_4^- + 2e^- \rightarrow AuCl_2^- + 2Cl^- \qquad (1)$$
$$AuCl_2^- + e^- \rightarrow Au(0) + 2\ Cl^- \qquad (2)$$
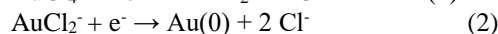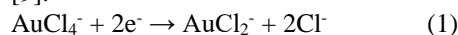
The objective of this work was to investigate the reaction process and mechanism of sodium tetrachloroaurate in HNO₃ medium cyclic voltammetrically. The redox reaction and half-cell reaction of gold III chloride in acidic medium are represented by reactions [10] of

$$AuCl_3 + HCl \rightarrow AuCl_4^- + H^+ \qquad (3)$$
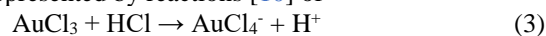
For half-cell reaction,

$$AuCl_3 + e^- \rightarrow AuCl_4^- \qquad (4)$$

7-(dimethylamino)-3H-phenothiazin-3-iminium chloride (Giemsa Stain dye) solution is used here for studying the complex ability with NaCl₄.

The Giemsa Stain is specific to the phosphate groups of DNA and attaches itself to where there are large amounts of adenine-thymine bonding.

Giemsa Stain is is used to stain the blood cells of hematopoietic tissues. It can also be applied to all tissue sections in which the presence of microorganisms is suspected. This staining does not differentiate gram-positive and gram-negative bacteria (Fig. 1).Estimation of Giemsa stain by cyclic voltammetry alone or in conjunction with $CuCl_2$.

Fig. 1 Structure of Giemsa Stain (GS) Dye

Electrochemical, thermodynamic, kinetic study of redox reaction for sodium tetrachloroaurate, analytical treatment and detection of different Nicholson parameters for ions used is our novel study. Also the nobility of discussing the anion and cation liquid ions and doing solvation cycle is important also for industrial applications.

Experimental

Chemicals

Cyclic voltammetry measurements were performed using 100 mol/m^3 HNO_3, which was prepared by diluting 70% concentrated acid. The solution of gold ($AuCl_4^-$) salt was prepared by appropriate dilution from (0.5 M/L). The solution of Giemsa stain was prepared by appropriate dilution from (0.01 M/L) $AuCl_4^-$ and Giemsa stain dye were dissolved in de-ionized water.

Electrodes

The three electrode system was joined to the DY2000 potentiostat. A commercial glassy carbon electrode was used as the working electrode. The platinum wire auxiliary electrode was used and an Ag/AgCl electrode filled with saturated KCl was used as a saturated reference electrode [40]. The cell used is a four neck vessel with a capacity of 100 cm^3. The experimental design depends on the measurement of cyclic voltammetry using the DY 2000 apparatus provided by USA.

Results and Discussion

Cyclic voltammetry of $AuCl_4^-$

The cyclic voltammograms for different concentrations of sodium tetrachloroaurate, $NaAuCl_4$ were preceded by 0.331×10^{-3} M in 0.1 M HNO_3 at 299.55K. The resulting data is shown in Figs. 2 and 3 in the range of 0.3V to 1.3V on using different concentrations of sodium tetrachloroaurate, starting with 1.3V and demonstrating the reduction process first and then followed by the oxidation process. The range of

$AuCl_4^-$ concentrations used is from 3.31 to 31.25 mM/L. One reduction wave appears at ~ (0.60–0.72) V and one oxidation wave appears at ~ 1.18V. We noticed a big reduction wave corresponding to 3 electrons split into two waves at ~ 0.8 V and ~ 0.66 V. The reduction peaks correspond to the following mechanism of reduction [11]:
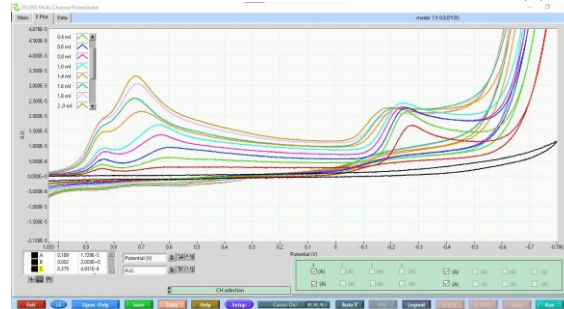
At ~ 0.66 V, $AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$ (4)

$3AuCl_4^- + 3e^- \leftrightarrow 2AuCl_2^- + Au + 4Cl_2 + 4Cl^-$ (5)

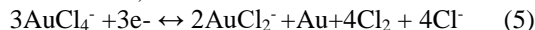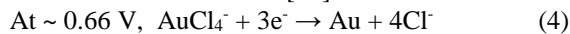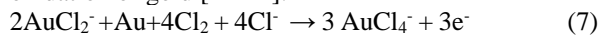$AuCl_2^- \leftrightarrow AuCl_2 + e^-$ (6)

Fig. 2 Measured cyclic voltammograms of different concentrations of $NaAuCl_4$.

We do analysis data for the last wave as the final state for gold chloride reduction to metal gold, consuming three electrons. The oxidation peak for $AuCl_4^-$ is one wave that appears at ~ 0.75 V, corresponding to the oxidation of gold [11-12].

$2AuCl_2^- + Au + 4Cl_2 + 4Cl^- \rightarrow 3 AuCl_4^- + 3e^-$ (7)

The redox mechanism of the $AuCl_4^-$ ions:

The suggested redox mechanism of the redox reaction of $NaAuCl_4$ was proposed depending on the experimental cyclic voltammetry peaks and found to follow the $E_rC_iE_r$ mechanism, which is a reversible electron transfer (E_r)-irreversible chemical reaction (C_i)-reversible electron transfer (E_r) [12]. The suggested mechanism is explained in the following suggested cycle:

$3AuCl_4^- + 3e^- \leftrightarrow 3AuCl_2^- + 3/2\ Cl_2 + 3Cl^-$

$$\updownarrow \qquad\qquad \downarrow$$

$$3AuCl_2 + 3\ e^-$$
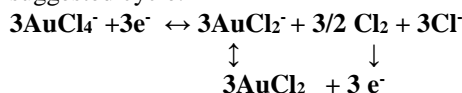
Cycle 1 : Redox cycle for tetrachloroaurate ions, $AuCl_4^-$

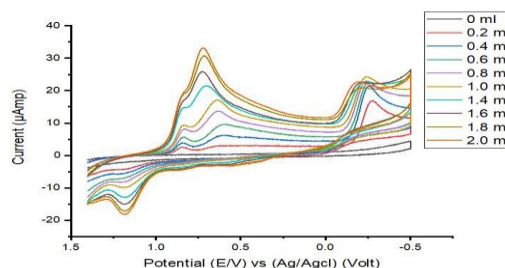**Fig. 3 Cyclic voltammetry of the addition of different amounts of $AuCl_4^-$ 0.5 mol/L to 3 x 10^{-2} HNO_3 0.1 mol/L, Scan rate 0.1 V. S^{-1} at 299.55K using a glassy carbon electrode.**

The redox reaction process occurs through mass transfer, electron transfer, and lastly reversible oxidation to reach the beginning $AuCl_4^-$ ion at potential of 0.85 V as given in Fig. (3), which supports the redox mechanism and electrochemical cycle 1.

We also noticed (Fig. 3), the catalytic appearance of the nitrate wave at ~ -0.3 V with a positive shift by increasing the concentration of $AuCl_4^-$ facilitating the catalytic oxidation reaction of the nitrate. The suggested nitrate mechanism as compared with electrode potential [13] is:
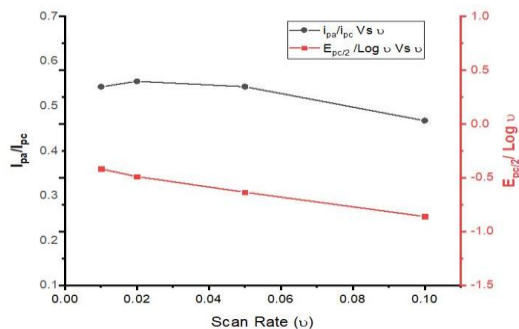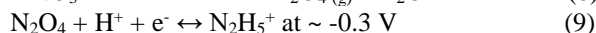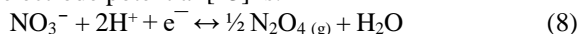
$$NO_3^- + 2H^+ + e^- \leftrightarrow \tfrac{1}{2} N_2O_4 {}_{(g)} + H_2O \qquad (8)$$
$$N_2O_4 + H^+ + e^- \leftrightarrow N_2H_5^+ \text{ at } \sim -0.3 \text{ V} \qquad (9)$$

Fig. 4 Relation (i_{pa}/i_{pc} and $E_{pc/2}/\log v$ Vs v) for $AuCl_4^-$ at final addition of Giemsa Stain dye at 299.55 K using glassy carbon electrode.

According to the relationships shown in this figure, Fig. 4 supports the above cyclic mechanism ErCiEr as explained by Mabbott [12].This support is elucidated by drawing the relations between i_{pa}/i_{pc} against scan rate and the relation between $\Delta E_{p/2} / \Delta \log v$ against scan rates, giving approximately constant value, which proved the named mechanism $E_rC_iE_r$. Cataytic effect of sodium tetrachloroaurate was observed for the used medium on appearing the nitrate wave which can be determined in other solutions analytically.

Estimation of the cyclic voltammetry data

The different equations applied to the redox reaction of $AuCl_4^-$ are the

$$i_p = 0.4463 \ n^{3/2} F^{3/2} D^{1/2} AC/CRT)^{1/2} v^{1/2} \qquad (10)$$
$$D^{1/2} = (\text{slope}, I_{PVS} v^{1/2}) \times (RT)^{1/2}/0.4465 \ n^{3/2} F^{1/2} AC \qquad (11)$$
$$\Delta E_p = E_{pa} - E_{pc} = 2.303 \ RT/nF \qquad (12)$$

Where α represents the charge transfer coefficient. k_s is the rate constant for electron transfer, v is the rate constant, D_c is the cathodic diffusion coefficient, and D_a is the anodic diffusion coefficient [14-25]. T is the absolute temperature. F is Faraday's constant, n is the electron number, and A is the surface area of the working electrode [26-30]. The heterogeneous electron rate constant from solution to working electrode material was evaluated by applying equations [31-35].

$$ks = 2.18* [Dc \ \alpha na \ F \ v/RT]^{1/2} .exp [\alpha^2 nF (Ep,c - Ep,a) /RT] \qquad (13)$$

The surface coverage of the working electrode was increased by an increase in metal ion concentration [36-38].

The cathodic quantity of electricity Q_a can be evaluated by the use of equations [39–41]:

$$Q_c = n \Gamma_c A F \qquad (14)$$
$$Q_a = n \Gamma_a A F \qquad (15)$$

The above parameters can be evaluated for the reduction peak at ~ 0.66 V and the oxidation peak at ~ 1.18 V [22,40], and the resultant values are presented in (Table 1).

We noticed the following from (Table 1):

1 – ΔE_P is a small amount.in the range of reversible processes.

2 – i_{pa} and i_{pc} are increased by an increase in $AuCl_4^-$ concentrations, indicating a large increase in the anodic process than the cathodic one, favoring the easier anodic process.

3: Increasing sodium tetrachloroaurate, $NaAuCl_4$ concentrations significantly increases the cathodic Dc and anodic Da diffusion coefficients, indicating a reversible reaction.

4 – Cathodic surface coverage Γ_c and anodic surface coverage Γ_a are increased by an increase in the concentration of $AuCl_4^-$ favoring more diffusion indicating the increase in the kinetic energy of the ions used.

5 – The cathodic quantity of electricity Q_c and the anodic quantity of electricity Q_a are largely increased by the increase in the sodium tetrachloroaurate concentrations, supporting also the diffusion mechanism of the reaction.

Effect of scan rate on $AuCl_4^-$

The effect of scan rate on $AuCl_4^-$ [31.25 mM/L] was investigated, and the data found in (Table 2) show that a decrease in scan rate resulted in an increase in the different solvation parameters, indicating a diffusion controlled reaction. (Fig. 5) also shows the effect of scan rate on the redox reaction of the final concentration used of $AuCl_4^-$ at 299.55K. 3.125 mM $NaAuCl_4$ was further studies in various scan rates and the voltammograms are seen in Fig. 5.

The number of electrons consumed in the both the reduction and oxidation of $NaAuCl_4$ gave different values on applying the equation for reversible reactions [36] giving a mean value of 2.908 for the data shown in Table 2 which is confirmed by thecyclic voltammograms in Figs. 3 and 5.This means that three electrons are consumed in both the reduction and oxidation of $NaAuCl_4$ in nitric acid supporting solutions using glassy carbon electrode as the working electrode, an Ag/AgCl reference electrode, and a platinum wire auxiliary electrode.

Table 1 The thermodynamic and kinetic properties sodium tetrachloroaurate, NaAuCl₄ at 299.55K and 0.1 scan rate

M x10⁻³ (M/L)	$E_{p,a}$ (Volt)	$E_{p,c}$ (Volt)	ΔE_p (Volt)	$I_{p,a}$ x10⁻⁵ (Amp)	$I_{p,c}$ x10⁻⁵ (Amp)	$E°$(V)	$E_{pc/2}$ (V)
0.331	1.180	0.602	0.578	0.177	0.165	0.891	0.697
0.658	1.181	0.615	0.566	0.237	0.433	0.898	0.704
0.980	1.182	0.615	0.567	0.336	0.701	0.899	0.704
1.299	1.183	0.645	0.537	0.405	0.977	0.914	0.734
1.613	1.183	0.647	0.537	0.510	1.235	0.915	0.734
2.229	1.184	0.711	0.473	0.672	1.737	0.947	0.833
2.532	1.185	0.724	0.461	0.830	2.096	0.955	0.856
2.830	1.186	0.725	0.461	1.059	2.528	0.956	0.858
3.125	1.186	0.726	0.460	1.296	2.773	0.956	0.859

D_a x10⁻⁹ (cm²/s)	D_c x10⁻⁹ (cm²/s)	α_{na}	k_s x10⁻³ (cm/s)	Γ_c x10⁻¹⁰ (mol/cm²)	(+) Q_c x10⁻⁶ (Coulomb)	Γ_a x10⁻¹⁰ (mol/cm²)	Q_a x10⁻⁶ (Coulomb)
1.496	1.295	0.506	2.167	0.624	0.567	0.671	0.610
0.679	2.266	0.537	2.103	1.640	1.490	0.898	0.816
0.614	2.676	0.541	2.343	2.655	2.414	1.273	1.157
0.508	2.961	0.544	1.031	3.701	3.363	1.532	1.393
0.523	3.065	0.550	1.040	4.676	4.250	1.931	1.755
0.475	3.175	0.394	0.142	6.578	5.979	2.544	2.313
0.562	3.583	0.364	0.101	7.936	7.213	3.142	2.856
0.732	4.172	0.361	0.109	9.572	8.700	4.009	3.644
0.900	4.118	0.358	0.107	10.501	9.545	4.909	4.462

Table 2 Cyclic voltammetry of sodium tetrachloroaurate, NaAuCl₄ [31.25 mM/L] at different scan rates in 299.55K

v V.S⁻¹	$E_{p,a}$ Volt	$E_{p,c}$ Volt	ΔE_p Volt	(-)$I_{p,a}$ x 10⁵ Amp	$I_{p,c}$ x10⁵ Amp	$I_{p,a}/I_{p,c}$	$E°$ Volt (V)	D_ax10¹⁰ cm².s⁻¹
0.100	1.186	0.726	0.460	1.296	2.773	0.467	0.956	8.999
0.050	1.170	0.748	0.422	0.916	1.686	0.543	0.959	8.981
0.020	1.147	0.775	0.372	0.519	0.934	0.555	0.961	7.202
0.010	1.137	0.786	0.351	0.347	0.639	0.543	0.962	6.457

D_c x10⁹ cm².s⁻¹	$E_{pc/2}$	αn_a	k_{sc} x10⁻³ (cm/s)	Γ_c x10⁻⁹ mol.cm⁻²	(+)Q_c x10⁻⁵ C(Coulomb)	Γ_a x10⁻⁹ mol.cm⁻²	(-) Q_a x10⁻⁵ C(Coulomb)	
4.118	0.859	0.358	106.520	1.050	0.954	0.491	0.446	
3.043	0.824	0.629	28.281	1.277	1.160	0.694	0.630	
2.337	0.829	0.877	4.326	1.769	1.608	0.982	0.893	
2.189	0.835	0.973	1.683	2.421	2.201	1.315	1.195	
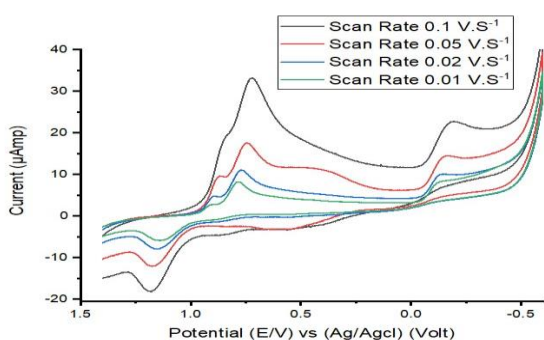
Fig. 5 Cyclic voltammetry of sodium tetrachloroaurate, NaAuCl₄ using different scan rates at 299.55K.

Effect of adding of Giemsa Stain (GS) dye

Different concentrations of Giemsa Stain dye were added to 31.25 mM AuCl₄⁻, within the (1.3 V to 0.1 V) potential range as shown in (Fig. 6), and the results are shown in (Table 3).

As shown in (Fig. 6), we noticed the appearance of sodium tetrachloroaurate, NaAuCl₄ reduction and oxidation waves plus new waves. The new appeared peaks are for Giemsa Stain compound. The new reduction peak at ~ 0 V and new oxidation peak at ~ 0.2 V was suggested [34] as corresponding to the redox reaction of Giemsa stain (GS) through the =NH₂⁺ group as:

=NH₂⁺ + 2e⁻   ↔   -- NH₂   (16)

This reduction mechanism for Giemsa stain (GS) is reversed in the oxidation side and the oxidation step is

divided into two steps consuming (two waves) one electron for each at ~ 0.2V and ~ 0.45V as shown in Fig 6. The waves of Giemsa stain are increased in their heights by more increasing of the Giemsa Stain dye concentration. This is due to the diffusion mechanism. Also, the cyclic voltammetry of Giemsa stain in this medium is clear in appearance indicting catalytic effect of $CuCl_2$ on the redox waves of Giemsa Stain. The reversibility of waves is necessary and found to be all reversible peaks.

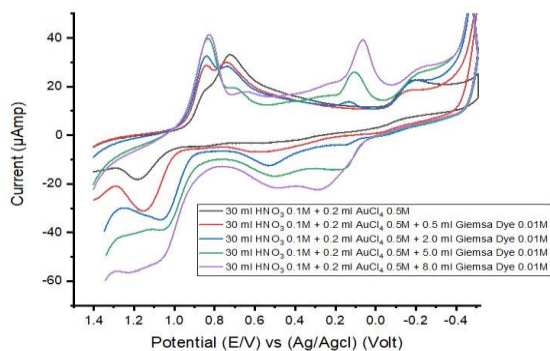**Effect of adding Giemsa Stain dye on i_{pc} for $AuCl_4^-$ and $AuCl_2^-$**

Fig. 6 Cyclic voltammetry of sodium tetrachloroaurate, NaAuCl₄ in presence of different concentrations of Giemsa Stain dye at 299.55K

The linear fit of i_{pc} for $AuCl_4^-$ and $AuCl_2^-$ in the presence of Giemsa stain dye was drowned, and we prove from them that the decrease of reduction current for the $AuCl_2^-$ wave by increasing the Giemsa stain concentration is due to the complexation behaviour between $AuCl_2^-$ and the Giemsa stain dye. The first two reduction waves, which are at 0.85V, correspond to the reaction of AuCl₂- AuCl2 +e-, as shown in Fig 6. This supports the redox cycle explained before for NaAuCl₄. The second reduction wave is the reduction of $AuCl_4^-$ ions, as explained before. Therefore, the first wave represents $AuCl_2^-$ ions and the second one indicates $AuCl_4^-$ ions. Both these reduction waves are decreased by adding more Giemsa Stain. We noticed complexation of $AuCl_4^-$ and $AuCl_2^-$ with Giemsa Stain dye (Fig. 7). Adding Giemsa stain increases the oxidation processes for NaAuCl₄ as shown in Fig 6 increase in I_p currents for voltammograms in the oxidation side. Because Giemsa Stain dye has a positive charge, it prefers to interact by complexation with the negatively charged ions $AuCl_4^-$ and $AuCl_2^-$ ions rather than the other neutral ones. The diffusion of sodium tetrachloroaurate ,redox states of gold ions and the Giemsa Stain as well as the complex formed from the intreraction between the metal ions and the ligand was considered to obey Fick,s law Convection and electrophoretic transport are not given.

The two straight lines given in Fig.7. can be easily used for the analytical estimation of the different two gold ions in the presence of leaching solution containing Giemsa Stain dye and nitric acid
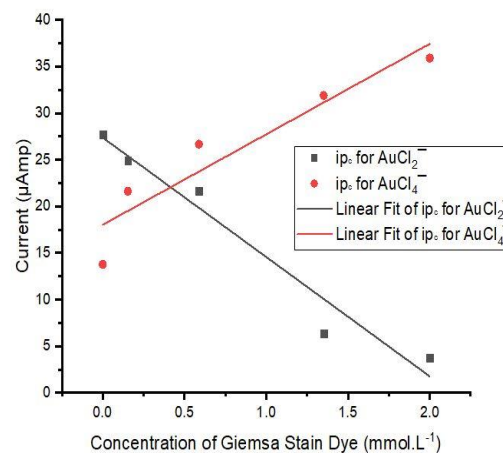

Fig. 7 Change of ip_c of $AuCl_4^-$ and $AuCl_2^-$ by increasing concentration of Giemsa Stain dye

We also noticed the following remarks from (Table 3):

1 - E_{pa}, E_{Pc} shift favors interaction between $AuCl_4^-$ and Giemsa Stain dye.

2 - ΔE_P is increased by an increase in Giemsa stain dye concentration, favoring complex reactions.

3 - i_{pc} decreases while i_{pa} increases in their values, compared to the absence of the dye, favoring interaction between the metal ions and the dye.

4 - D_c decreases while D_a increases in their values compared to that in the absence of Giemsa Stain dye, favoring complex reactions.

5 - α_{na} is decreased by increase of Giemsa Stain dye concentration due to the attraction of dye with $AuCl_4^-$ following Nicholson parameters.

6 - Γ_c is decreased by increase in Giemsa Stain dye while Γ_a is increase favoring interaction between the dye and metal.

7 - Increase of Q_a while Q_c decrease for $AuCl_4^-$ and Giemsa Stain dye than sodium tetrachloroaurate alone.

Effect of different scan rates on $AuCl_4^-$ with Giemsa Stain dye complex at 299.55K

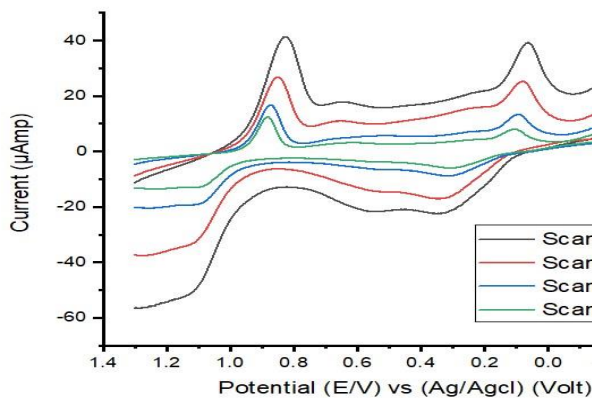The effects of different scan rates on the interaction of gold ($AuCl_4^-$) with Giemsa stain dye were investigated, and the results are shown in (Fig. 6). Most of the data given in (Table 4). It was noticed that the values increased with the decrease in scan rate, such as Γ_c, Γ_a, Q_c and Q_a. As shown in Fig.(8) the redox mechanism is approximately similar with the redox behavior of NaAuCl₄ alone.

Table 3: Kinetic and solvation parameters of AuCl₄⁻ in presence of Giemsa Stain dye at 299.55K and 0.1 (V/Sec) scan rate

$M \times 10^{-3}$ (M/L)	$L \times 10^{-3}$ (M/L)	$E_{p,a}$ (volt)	$E_{p,c}$ (volt)	ΔE_p (volt)	$I_{p,a} \times 10^{-5}$ (Amp)	$I_{p,c} \times 10^{-5}$ (Amp)	$E°$
3.077	0.154	1.155	0.742	0.413	2.412	2.492	0.948
2.941	0.588	1.122	0.735	0.387	2.523	2.165	0.928
2.703	1.351	1.115	0.693	0.423	2.625	0.637	0.904
2.500	2.000	1.107	0.654	0.453	2.734	0.377	0.880
$D_a \times 10^{-9}$ (cm²/s)	$D_c \times 10^{-9}$ (cm²/s)	α_{na}	k_s (cm/sec)	$\Gamma_c \times 10^{-10}$ (mol/cm²)	$(+) Q_c \times 10^{-6}$	$\Gamma_a \times 10^{-9}$ (mol/cm²)	$(-) Q_a \times 10^{-6}$
3.213	3.430	0.317	22.955	9.437	8.577	0.913	8.301
3.848	2.834	0.288	9.270	8.198	7.451	0.955	8.684
4.931	0.291	0.216	7.381	2.413	2.193	0.994	9.033
6.254	0.119	0.182	10.349	1.427	1.297	1.035	9.409

Table 4 Effect of different scan rates on AuCl₄⁻ with Giemsa Stain dye complex at 299.55K

υ (V/Sec)	$E_{p,a}$ (volt)	$E_{p,c}$ (volt)	ΔE_p (volt)	$(-)I_{p,a} \times 10^{-5}$ (Amp)	$I_{p,c} \times 10^{-6}$ (Amp)	$E°$	$E_{pc/2}$
0.100	1.107	0.654	0.453	2.734	3.769	0.880	0.917
0.050	1.104	0.661	0.443	1.913	2.427	0.883	0.927
0.020	1.039	0.667	0.372	1.003	1.079	0.853	0.935
0.010	1.026	0.683	0.343	0.641	0.547	0.852	0.951
$D_a \times 10^{-9}$ (cm²/s)	$D_c \times 10^{-10}$ (cm²/s)	αna	k_s (cm/sec)	$\Gamma_c \times 10^{-10}$ (mol/cm²)	$(+) Q_c \times 10^{-6}$	$\Gamma_a \times 10^{-9}$ (mol/cm²)	$(-) Q_a \times 10^{-5}$
6.254	1.188	0.182	10.3490	1.427	1.297	1.035	0.941
6.122	0.986	0.180	4.956	1.838	1.670	1.449	1.317
4.206	0.487	0.179	0.283	2.042	1.856	1.899	1.726
3.434	0.250	0.178	0.061	2.070	1.881	2.426	2.205

Fig. 8 Cyclic voltammetry of sodium tetrachloroaurate, NaAuCl₄ using different scan rates in presence of Giemsa Stain (GS) dye and at 299.55 K

    On drawing the relation between peak currents i_p and the square root of scan rate ($v^{1/2}$), straight lines were obtained as shown in (Fig. 9). The slopes of the two lines (nearly equal one) mainly support the diffusion reaction mechanism in the presence and absence of giemsa stain dye.
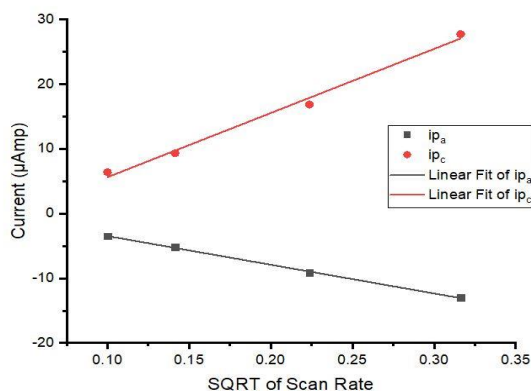
Fig. 9 : Relation (I_p Vs. $v^{1/2}$) for AuCl₄⁻ at final adding in different scan rates at 299.55 K

Using Fig .9 for the estimation of sodium tetrachloroaurate in nitric acid better at high square root of scan rate than that at low square scan rate.

Molecular Thermodynamic parameters for interaction of NaAuCl₄⁻ with Giemsa Stain dye.

The aim of this study is to determine the effect of Giemsa Stain on the molecular redox reaction of NaAuCl₄ and not the reversed action . We used the Langne equation as explained in previous work [16, 22] to calculate the stability constant and Gibbs free

energies of complexation for interaction between $AuCl_4^-$ with Giemsa Stain dye. The evaluated data was given in (Table 5) with the effect of the scan rate data shown also in (Table 6). Very large thermodynamic stability constants β and Gibbs free energy ΔG of complexation [23-41] were obtained, indicating complexation interaction is happening for the interaction between $NaAuCl_4$ and Giemsa Stain dye, forming very strong covalent bonds.

The factors affecting the electrode reaction of our system here are the mass transfer from bulk to electrode surface, electron transfer at the working electrode surface and chemical reactions following the electron transfer. All these factors are proved to form complex in liquid state between Giemsa Stain and sodium tetrachloroaurate

Table 5 Molecular Stability constants and Gibbs Free energies for $AuCl_4^-$ in presence of Giemsa Stain dye at 299.55 K and scan rate 0. 1V.S^{-1}

M x 10^{-3} (M/L)	(L) x 10^{-3} (mol/m^3)	$E°$ M (Volt)	$E°$ C (Volt)	ΔE (Volt)	log β_{MX}	ΔG (KJ/mol)
3.077	0.154	0.956	0.948	0.007	0.406	-2.327
2.941	0.588	0.956	0.928	0.028	1.516	-8.694
2.703	1.351	0.956	0.904	0.052	2.910	-16.689
2.500	2.000	0.956	0.880	0.076	4.277	-24.534

Table 6 : Molecular Thermodynamic parameters for different scan rates for interaction of $AuCl_4^-$ with Giemsa Stain dye complex at 299.55 K at different scan rates

υ (v/sec)	$E°$ M (Volt)	$E°$ C (Volt)	ΔE (Volt)	log β_{MX}	ΔG (KJ/mol)
0.1	0.956	0.880	0.076	4.277	-24.534
0.05	0.959	0.883	0.076	4.315	-24.747
0.02	0.961	0.853	0.108	5.899	-33.836
0.01	0.962	0.852	0.109	5.973	-34.258

Conclusion

As seen in (Tables 5 &6), the stability constants and Gibbs free energies of complexation are increased by the increase in Giemsa stain dye and decreased by the scan rate. (Table 6) shows that the thermodynamic parameters given are decreased by the decrease in scan rate, supporting the diffusion mechanism reaction also.

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