



Cyclic voltammetry of AuCl₄⁻ in absence and presence of KMnO₄ in 0.1 M HNO₃ at 297.15 K

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Received: 24/8/2020
Accepted: 23/9/2020

Abstract: In the present work, the cyclic voltammetry of sodium aurate was examined alone and with KMnO₄ in HNO₃ as supporting electrolyte using glassy carbon working electrode. The study is valuable for evaluating the thermodynamic properties. In absence of KMnO₄, adding different concentration of AuCl₄⁻ ions to HNO₃ gave redox waves. In the reduction effect, the nitrate was increased indicating catalytic peak. While in oxidation effect of Au⁰ to Au⁺³ gave broad peak. In presence of KMnO₄, all cyclic voltammetric data are greater in most parameters. The electron transfer rate constant resulting from the interaction of KMnO₄ on NaAuCl₄ were evaluated and their data were discussed.

keywords: Cyclic voltammetry, oxidation, gold chloride, potassium permanganate.

1. Introduction

The electrochemical behavior of AuCl₄⁻ ions was studied in HNO₃ as supporting electrolyte. The redox behavior of Au⁰/Au⁺³ was examined by some authors in acidic solutions by the use of different electrodes [1-3]. The effect of adding KMnO₄ to the sodium aurate on the redox waves is taken into account as it is a strong oxidizing agent [4-5]. Cyclic voltammetry measurements were carried out in a 30 ml glass cell. Cyclic voltammetry was achieved with computer controlled Auto lab DY2000 (USA). All runs were done with three electrode systems Pt wire counter electrode, standard electrode (Ag/AgCl), small glassy carbon (SGCE) was applied as a working electrode. The SGCE was carefully polished by aluminum oxide emery paper and rinsed with deionized water.

2. Experimental:

The chemicals used were sodium aurate (NaAuCl₄), potassium permanganate (KMnO₄) and HNO₃ which were collected from Sigma Aldrich Co. All these chemicals were employed without any purification to guarantee that there are no changes which may occur in their properties. Bi distilled water with a conductance of 2.5 micro Siemens, μ ohm⁻¹ was used. The employed glassware was left for one day in a chromic mixture, then washed by bidistilled water for various times and finally, they were

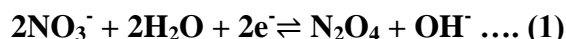
placed in electric oven and became dry. Cyclic voltammetry potentiostat of the type DY2000 was used for the measurements and after passing nitrogen gas for 10 minutes in each solution to remove the dissolved oxygen.

3. Results and discussion:

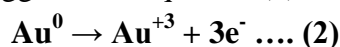
In absence of KMnO₄:

On adding different concentration of AuCl₄⁻ ions to the supporting electrolyte, nitrate wave was obtained at ~ - 0.85 V as maximum peak. On adding AuCl₄⁻ concentration, the nitrate was increased indicating that it is a catalytic cathodic peak [6].

The electrochemical mechanism for the reduction of nitrate was as explained in electrochemical series data is as follows [7]:



AuCl₄⁻ show two redox waves, the first one is the cathodic catalytic wave of nitrate ion and the second is the oxidation of peak corresponding to the oxidation of Au⁰ to Au⁺³ at ~ 1.0 V [8]. The oxidation mechanism is suggested as equation (2).



Three electrons are delivered by oxidation of zero monovalent gold. Broad peak (oxidation) is obtained because of consumption of 3 electrons in the oxidation process.

Evidence for catalytic nitrate wave:

The sharp at ~ -0.85 is catalytic nitrate wave and not belongs to gold because of:

- 1) Very high increasing of I_{pc} , cathodic peak potential.
- 2) Very small shift in E_{pc} , cathodic peak potential.
- 3) Sharp wave formed.
- 4) Closing the cyclic voltammogram at it.

Table (1) explains the different cyclic voltammetric parameters for the redox reaction of $AuCl_4^-$ in 0.1 M parameters for the redox reaction of $AuCl_4^-$ in 0.1 M HNO_3 and at 297.15 K using glassy carbon electrode.

Surface coverage which is the electrode surface covered by electro active species is calculated using equation (3) [9-16].

$$\Gamma = I_p 4RT / n^2 F^2 A V \dots (3)$$

Where Γ is the surface coverage, R is the universal gas constant, F is Faraday constant 96485 C.mol^{-1} , A is the surface area of the electrode in cm^2 , n is the number of electrons in the redox reactions, V is the scan rate (V.S^{-1}), T is the absolute temperature, I_p is the current by ampere.

The quantity of electricity consumed during redox reaction can be calculated using equation (4) [17].

$Q = n F A \Gamma \dots$ (4) Diffusion coefficient was calculated by using Randles-Sevcik equation [18-19].

$$I_p = (2.69 \times 10^{-5}) n^{3/2} A D^{1/2} V^{1/2} C \dots (5)$$

Where I_p is the current in ampere unit, A is the surface area of the working electrode, D is the diffusion coefficient in cm^2/sec , V is the scan rate (V/S) and C is the concentration of $AuCl_4^-$.

ΔE_p is the difference between anodic and cathodic peak potentials.

$$\Delta E_p = E_{pa} - E_{pc} \dots (6)$$

The heterogeneous electron rate constant (k_s) can be calculated by applying equation [20-25].

$$k_s = 2.18 (D \alpha n_a F V / RT)^{1/2} \exp. \{ \alpha^2 n F / RT (E_{pc} - E_{pa}) \} \dots (7)$$

Where α is the charge transfer coefficient, n_a is the number of electrons involved in the

5) Very high electron transfer rate constant K_s .

6) High quantity of electricity for cathodic process Q_c was obtained which greater than that of the anodic process by four times.

7) Very high surface coverage data was obtained for the cathodic wave.

8) Decrease of D_c sharply

redox processes and αn_a can be calculated from the equation (8).

$$(E_{pc} - E_{pc} / 2) = (1.857 R T / \alpha n_a F) \dots (8)$$

Where $E_{pc}/2$ is the half peak potential and α equal 0.5 as approximation for quasi reversible system.

To explain the behavior of nitrate wave, we noticed in Fig (1) the relation between I_{pc} and $AuCl_4^-$ concentration than increase in the limiting current values very large with the increase in gold chloride concentration.

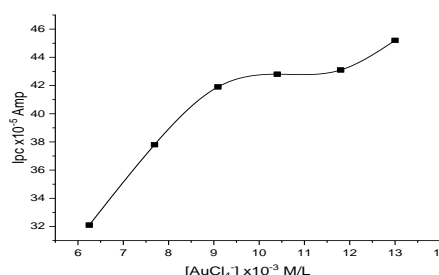


Fig 1. The relation between $AuCl_4^-$ concentration and I_{pc}

On increasing the $AuCl_4^-$ concentration the D_c decrease which indicate the evolution of nitrate wave which decrease the diffusion mechanism (Fig. 2)

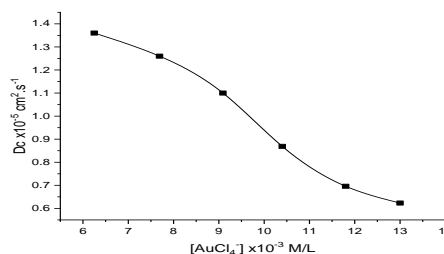


Fig 2. The relation between $AuCl_4^-$ concentration and D_c

By increasing $AuCl_4^-$ concentration the E_{pc} , cathodic peak potential is slightly decrease which is opposite to the normal trend, see Fig.(3).

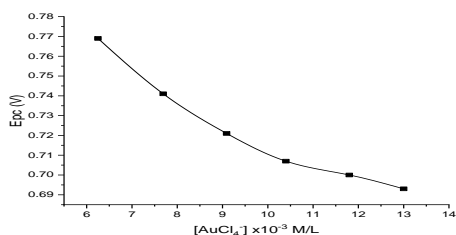


Fig 3. The relation between AuCl_4^- concentration and E_{Pc}

Fig (4) illustrate the increase in the cathodic quantity of electricity Q_c by more adding AuCl_4^- till constant value at 8×10^{-3} M/L

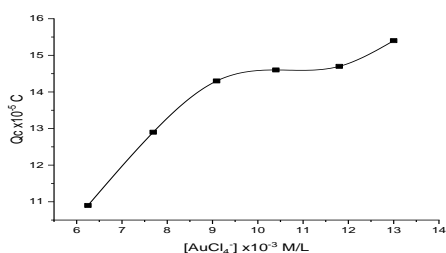


Fig 4. The relation between AuCl_4^- concentration and Q_c

Analysis of the anodic AuCl_4^-

On analyzing the oxidation peak of AuCl_4^- we noticed the following remarks: 1) The oxidation peak of AuCl_4^- is broad one because the three electrons consumed on the oxidation can happened one time of at intervals.

2) The peak is not sharp.

3) There are two small prewaves are given before that oxidation peak indicating bulk oxidation and not sharp one.

4) E_{Pa} is almost the same with slight difference indicating the irreversibility of the wave.

Analysis of the graphs

Fig (5) illustrate the relation between I_{Pa} and AuCl_4^- concentration with slight increase in I_{Pa} due to the diffusion mechanism.

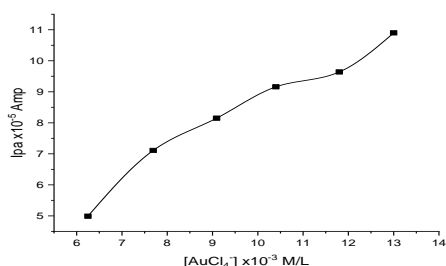


Fig 5. The relation between AuCl_4^- concentration and I_{Pa}

Fig (6) illustrate the relation between D_a , anodic diffusion coefficient and AuCl_4^- concentration which indicate that higher concentration decrease the diffusibility of sodium aurate due to the electrostatic coagulation and small ionic interactions.

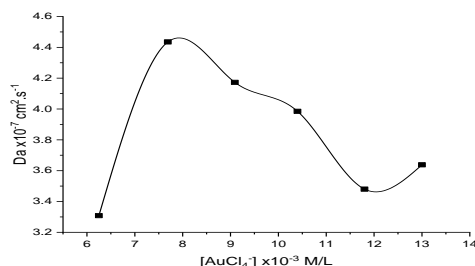


Fig 6. The relation between AuCl_4^- concentration and D_a

Fig (7) show the relation between Γ_a and AuCl_4^- concentration which increase gradually. The increase in anodic surface coverage Γ_a with AuCl_4^- concentration favour the decrease in D_a as a logic result.

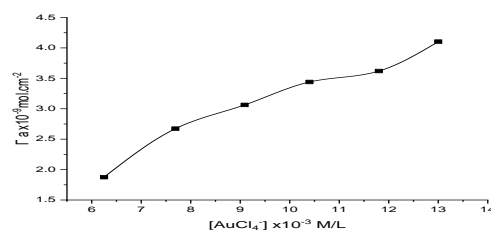


Fig 7. The relation between AuCl_4^- concentration and Γ_a

Fig (8) illustrate slight increase in anodic quantity of electricity Q_a with increase in AuCl_4^- concentration favouring high adsorption

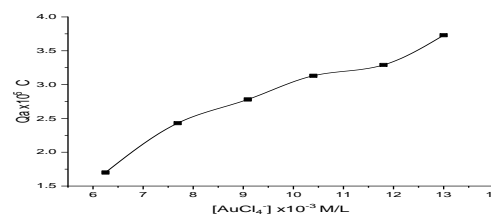


Fig 8. The relation between AuCl_4^- concentration and Q_a

Effect of KMnO_4 on AuCl_4^-

It is known that both KMnO_4^- and AuCl_4^- ions are oxidizing agents but MnO_4^- is stronger than the other.

AuCl_4^- react with some nucleophiles in aqueous solutions [22].

Reduction process for KMnO_4^- ion can be follow the reaction:

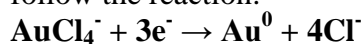


Table (1): Effect of different concentrations of gold chloride by using glassy carbon electrode at 297.15K and scan rate 0.1V.S⁻¹.

[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 ⁷ cm ² .s ⁻¹	Dcx10 ⁵ cm ² .s ⁻¹	αnac	Ksc	Γ c x10 ⁹ mol.cm ⁻²	(+) Qc x10 ⁵ C	Γ a x10 ⁹ mol.cm ⁻²	(-) Qa x10 ⁵ C
6.25	1.025	-0.769	1.795	4.99	32.1	0.156	0.128	3.308	1.36	0.685	8.93E+20	12.04	10.9	1.875	1.70
7.69	1.031	-0.741	1.772	7.11	37.8	0.188	0.145	4.435	1.26	0.620	4.23E+20	14.21	12.9	2.672	2.43
9.09	1.040	-0.721	1.761	8.15	41.9	0.194	0.160	4.173	1.10	0.567	2.72E+20	15.75	14.3	3.063	2.78
10.4	1.043	-0.707	1.751	9.16	42.8	0.214	0.168	3.985	0.869	0.621	1.86E+20	16.06	14.6	3.440	3.13
11.8	1.050	-0.700	1.750	9.64	43.1	0.224	0.175	3.480	0.696	0.567	1.56E+20	16.19	14.7	3.620	3.29
13.0	1.058	-0.693	1.750	10.9	45.2	0.242	0.182	3.638	0.623	0.567	1.49E+20	16.98	15.4	4.103	3.73

Table (2): Effect of different concentrations of KMnO₄ by using glassy carbon electrode at 297.15K and scan rate 0.1V.S⁻¹. (First wave)

[M] x10 ³ mol.L ⁻¹	[L] 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 ⁷ cm ² .s ⁻¹	Dc x10 ⁷ cm ² .s ⁻¹	αnac	Ksc	Γ c x10 ⁹ mol.cm ⁻²	(+) Qc x10 ⁵ C	Γ a x10 ⁹ mol.cm ⁻²	(-) Qa x10 ⁵ C
13.9	2.78	0.612	0.529	0.083	3.80	0.932	4.077	0.571	10.5	0.631	2.917	4.16E-03	3.15	0.955	12.85	3.89
13.5	5.41	0.606	0.523	0.083	3.21	1.25	2.563	0.565	7.90	1.20	2.678	5.49E-03	4.23	1.28	10.85	3.29
13.2	7.89	0.599	0.487	0.112	2.79	1.80	1.550	0.543	6.27	2.61	1.449	7.91E-03	6.07	1.84	9.42	2.85

Table (3): Effect of different concentrations of KMnO₄ by using glassy carbon electrode at 297.15K and scan rate 0.1V.S⁻¹. (Second wave)

[M] x10 ³ mol.L ⁻¹	[L] 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	Dax10 ⁷ cm ² .s ⁻¹	Dcx10 ⁷ cm ² .s ⁻¹	αnac	Ksc	Γ c x10 ⁹ mol.cm ⁻²	(+) Qc x10 ⁵ C	Γ a x10 ⁹ mol.cm ⁻²	(-) Qa x10 ⁵ C
13.9	2.78	0.293	0.048	0.245	4.43	3.25	1.362	0.170	14.2	7.67	0.590	3.17E-02	10.97	3.33	14.97	4.53
13.5	5.41	0.265	0.076	0.189	3.85	1.99	1.934	0.171	11.4	3.04	1.131	1.61E-02	6.74	2.04	13.03	3.95
13.2	7.89	0.266	0.083	0.182	3.65	1.67	2.180	0.175	10.8	2.26	1.833	1.64E-02	5.65	1.71	12.33	3.73

Table (4): Effect of different concentrations of KMnO₄ by using glassy carbon electrode at 297.15K and scan rate 0.1V.S⁻¹. (Third wave)

[M] x10 ³ mol.L ⁻¹	[L] x10 ³ mol.L ⁻¹	Ep,a Volt	Ep,c Volt	ΔEp Volt	(-)Ip,ax10 ⁵ Amp	(-)Ip,cx10 ⁵ Amp	Ip,a/Ip,c	E° Volt	Dax10 ⁷ cm ² .s ⁻¹	Dcx10 ⁷ cm ² .s ⁻¹	αnac	Ksc	Γ c x10 ⁹ mol.cm ⁻²	(+) Qc x10 ⁵ C	Γ a x10 ⁹ mol.cm ⁻²	(-) Qa x10 ⁵ C
13.9	2.78	0.059	0.419	0.360	6.33	1.43	4.431	0.239	29.1	1.48	1.177	6.01E-02	4.83	1.46	21.40	6.48
13.5	5.41	0.099	0.425	0.326	6.55	2.06	3.182	0.262	32.9	3.25	1.154	6.38E-02	6.96	2.11	22.14	6.71
13.2	7.89	0.154	0.452	0.298	7.23	2.35	3.071	0.303	42.2	4.48	1.017	5.36E-02	7.96	2.41	24.43	7.40

Which gave the three redox peaks illustrated in Fig. (9)

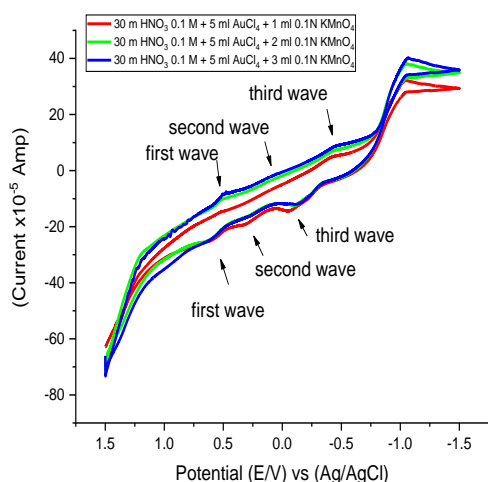
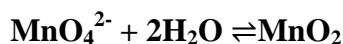
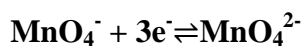


Fig 9. Effect of different concentrations of KMnO₄ by using glassy carbon electrode at 297.15K and scan rate 0.1V.S⁻¹

The concentration of AuCl₄⁻ is double than that of MnO₄⁻ giving illustrating the waves of the first metal ion.

Permanganate ion facilitate the redox reaction of AuCl₄⁻ by providing the reaction medium with more 3 electrons as:



It was observed from Fig (9) and Table (2) that on adding MnO₄⁻ to AuCl₄⁻ ion the three different couple of peaks can be examined. All cyclic voltammetric data are greater for the third couple of waves and follow the order:

Third couple of waves > Second couple of waves > first couple of waves

In most all parameters.

We can use that for analytical estimation of gold ion different concentrations.

The K_s , electron transfer rate constant are small in comparison to that in absence of MnO_4^- ions. Also it is observed from data that analyzing the oxidation peaks gave more valuable results than the reduction peaks because of their clearness.

Conclusion:

Cyclic voltammetry of $KMnO_4$ was done and the redox peaks were explained. Oxidation of $NaAuCl_4$ by $KMnO_4$ was illustrated and examined. The mechanism of redox reaction for the interaction between $NaAuCl_4$ and potassium permanganate was suggested. Formation of complex after oxidation was observed for the oxidation of sodium aurate with $KMnO_4$.

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