

CYCLIC VOLTAMMETRY OF CHLOROaurIC ACID WITH GLASSY CARBON ELECTRODE IN ACETONITRILE

Sontara Konwar Boruah^{1*}, Hirendra Das², Arijit Bisharad¹

¹Dept. of Chemistry, Assam Don Bosco University, Guwahati-781017

²Department of Electronics and Communication Technology, Gauhati University, Guwahati-781014

*For correspondence. (sontara.boruah@dbuniversity.ac.in)

Abstract: The electrochemical behaviour of chloroauric acid in acetonitrile has been investigated over glassy carbon electrode. The reduction of $[\text{AuCl}_4]^-$ initially forms $[\text{AuCl}_2]^-$ before deposition on the electrode as Au(0). In the consecutive reduction steps chloride ions were released.

Keywords: Cyclic voltammetry; chloroauric acid; glassy carbon electrode; tetrabutyl ammonium perchlorate; acetonitrile.

PACS: XXXX, YYYY, ZZZZ

1. Introduction:

Chloroauric acid is also known as “gold chloride” and “gold chloride tetrahydrate”. Chloroauric acid is an orange-yellow solid composed in inorganic chemicals. The chemical formula is $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (Figure 1).

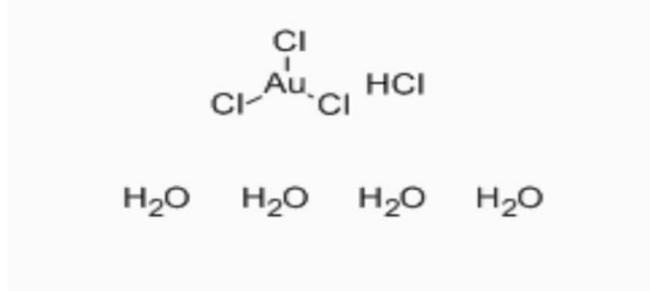


Figure 1: Structure of Hydrogen tetrachloroaurate(III)tetra hydrate $[\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}]$.

Chloroauric acid is a high molecular-weight monoprotic acid. The tetra-hydrate crystallizes as $[\text{H}_5\text{O}_2]^+[\text{AuCl}_4]^-$ and two water molecules [1]. The $[\text{AuCl}_4]^-$ anion has square planer molecular geometry. In solid form, chloroauric acid is a hydrophilic (ionic) protic solute. In addition, this acid is water soluble and as well as soluble in a number of oxygen-containing solvents such as ethers, esters, alcohol and ketones.

A precursor used in the electrolytic purification of gold is tetrachloroaurate(III) [2]. It is used for gold recovery, concentration, purification and analytical determination. Due to the improvements in nanotechnology gold nanoparticles with diameters ranging from 5nm to 400nm have been produced from chloroauric acid [2]. Chloroauric acid is used as a gold toner in photography, which is one of its most prevalent uses. Toning is a chemical process that changes the colour of the image. Gold compounds are well known for their biological and medicinal applications, for instance, in rheumatoid arthritis, anti-bacterial, anti-virus and anti-parasite activity as well as in alzheimer’s diseases. Osteoarthritis is the most frequent comorbidity with self-reported detrimental outcome in patients with systematic rheumatic disorders such as rheumatoid arthritis and other inflammatory arthritides that progressively affects joints [3,4,13]. The present study has been focused on the redox reactions of AuCl_4^- on glassy carbon electrode in acetonitrile using cyclic voltammetry technique [2-8,12].

2. Materials and Methods:

2.1. Chemicals:

Gold(III) chloride hydrate (HAuCl₄·4H₂O) 99.99% metal basis and tetrabutyl ammonium perchlorate were purchased from Sigma-Aldrich. Acetonitrile was purchased from AnalR was used.

2.2. Methods:

The cyclic voltammogram experiment was conducted in a 10 mL electrochemical cell with nitrogen purge system. The working electrode was a glassy carbon electrode (GCE), the auxiliary electrode was a platinum wire and the reference electrode was an Ag-AgCl electrode. The cyclic voltammogram was recorded with BAS 100A Electrochemical Analyzer, Bio-analytical Systems, USA.

3. Results and Discussions:

3.1 Redox behaviour of AuCl₄⁻ on glassy carbon electrode:

Figure 2 shows the cyclic voltammogram of 10⁻³ M solution of HAuCl₄ in acetonitrile on a glassy carbon electrode. The cyclic voltammogram was scanned towards positive potential from -1.5V to +1.5V with a scan rate of 50 Vs⁻¹, with sensitivity current of 100µA. Tetrabutyl ammonium perchlorate (0.1M) was added as supporting electrolyte.

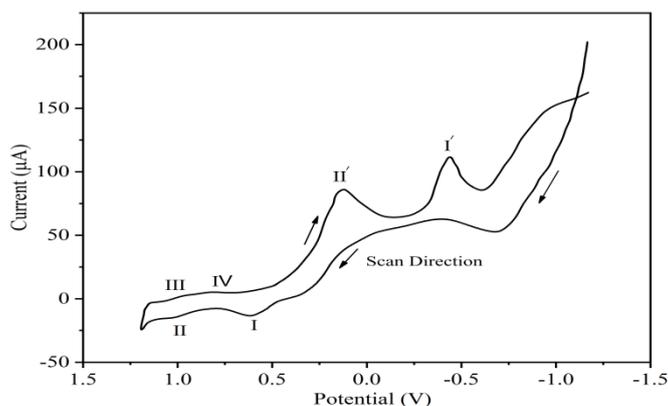
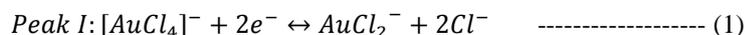
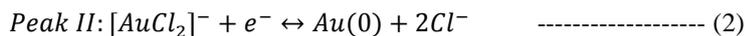


Figure 2: Cyclic Voltammogram of 10⁻³ M solution of HAuCl₄ in acetonitrile. Working electrode: Glassy Carbon electrode, Reference electrode: Ag-AgCl, Auxiliary electrode: Platinum wire, Supporting electrolyte: Tetrabutyl ammonium perchlorate. Scan rate 50Vs⁻¹, Sensitivity current 100µA.

In the voltammogram two cathodic peaks at ca. +0.600V (peak I) and +1.020V (peak II) with corresponding anodic peaks of ca. -0.436V (peak I') and +0.108V (peak II') in the reverse scan were observed. They were attributed to the consecutive reduction steps shown in equations (1) and (2) (i.e., the forward reactions of 1 and 2). In both processes, chloride ions were released into the solution. The first step is electroreduction of AuCl₄⁻ to AuCl₂⁻, and then the AuCl₂⁻ to Au(0) ad-atoms [4-9,12].



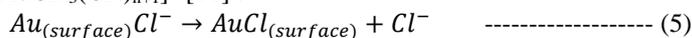
The reduction peak I at +0.600V corresponds to the two-electron reduction of AuCl₄⁻ to AuCl₂⁻ as shown in equation (1) [i.e., Au(III) to Au(I)]. The electrochemically formed AuCl₂⁻ by reduction undergoes disproportionation with the formation of active Au(0) ad-atoms monolayer on the glassy carbon electrode surface. Peak II corresponds to the one electron reduction of AuCl₂⁻ to Au(0).



The two anodic peaks at -0.436V (peak I') and +0.108V (peak II') respectively were for the backward reactions of (1) and (2) [9,11]. Initially, the reduction of Au(I) resulted in nucleation and deposition of Au(0) on the glassy carbon electrode at potential +1.020V. On reverse scan wave, two oxidation processes peak III (at ca. +1.0V) and peak IV (at ca. +0.797V) were observed. The peak III may be assigned to the two electron oxidations of chloride to trichloride [equation (3)], while peak IV is assigned to its subsequent one electron oxidation to chlorine [equation (4)].



Gold undergoes the halide-catalyzed dissolution in acetonitrile solvent [11]. The dissolution was initiated by the presence of Cl^- formed by the reduction of $[AuCl_4]^-$ as shown in equation (1). In this case, it was assumed that complete monolayer of electrostatically adsorbed Cl^- was responsible for the dissolution of gold. In acetonitrile solvent the dissolution mechanism was thought to be initiated by the formation of an $AuCl$ surface layer [equation (5)] followed by dissolution of the gold in the form of $[AuCl(CH_3CN)_n]$ with the subsequent catalytic regeneration of Cl^- , ultimately yielding solutions of $[AuCH_3(CN)_{n+1}]^+$ [11].



4. Conclusions

The redox reaction of $AuCl_4^-$ in CH_3CN has been studied using a cyclic voltammetry technique. Voltammetric reduction of $AuCl_4^-$ took place through a two-step reduction of $AuCl_4^-$ to $AuCl_2^-$ and further reduction of $AuCl_2^-$ to Au . In both steps, Cl^- ions were released into the solution. In CH_3CN solvent, electrostatically adsorbed $Au_{(surface)}Cl^-$ undergoes dissolution of gold in the form $[AuCl(CH_3CN)_n]$ with the subsequent catalytic regeneration of Cl^- , ultimately yielding solutions of $[AuCH_3(CN)_{n+1}]^+$.

Acknowledgement:

The authors gratefully acknowledge the Department of Chemistry, Gauhati University for providing sophisticated analytical instrument facilities.

References:

- [1] J. M. Williams, S. W. Peterson, J. Am. Chem. Soc., 91, 776-777. DOI:10.1021/ja01031a062, ISSN 0002-7863.
- [2] www.geeksforgeeks.org
- [3] M. Koperuncholan, International Journal of Phytopharmacy, 5, 72-80, (2015) .ISSN: 2277-2928 (Online), DOI:10.7439/ijpp
- [4] Orazio De Lucia, Antonella Murgo, Francesca Pregolato, Irene Pontikaki, Mirian De Souza, Alessandro Sinelli, Rolando Cimaz and Roberto Caporali, Adv. Ther. 37, 1347-1359, 2020.
- [5] M. B. Hariri, A. Dolati and R. S. Moakhar, J. Electrochem. Soc., 13, 2688-2700, 2021.
- [6] Leigh Aldous, Debbie S. Silvester, Constanza Villagrán, William R. Pitner, Richard G. Compton, M. Cristina Lagunas and Christopher Hardacre, New Journal of Chemistry, 30, 1576-1583, 2006.
- [7] Andrey Korshunov, Bohdan Josypcuk, Michael Heyrovský, Collection of Czechoslovak Chemical Communications, 76, 929-936.
- [8] Afolabi Ayeni, Shafiq Alam, Georges Kipouros, Journal of Materials Science and Engineering, 6, 80-89, 2018.
- [9] Mohiedin Bagheri Hariri, Roozbeh Siavash Moakhar, Payman Sharifi Abdar, Hossein Zargarnezhad, Matthew Shone, Seyyed Alireza Rahmani, Nasrin Moradi, Vahid Niksefat, Kasra Shayar Bahadori, Abolghasem Dolati, Analytical Methods, 13, 2688-2700, 2021.
- [10] X. -H Xu, C.L. Hussey, J. Electrochem. Soc., 139, 3103, 1992.
- [11] R. Kissner, J. Electroanal. Chem., 385, 71, 1995.
- [12] Md. Mahbubur Rahman, Xiao-Bo Li, Nasrin Siraj Lopa, Jae-Joon Lee, Bull:Korean Chem. Soc., 35, 2014. DOI: 10.5012/bkcs. June 2014.35.7. XXX
- [13] Custódia Fonseca and Manuel Aureliano, BioChem Vol. 2, 145-159, 2022. [http:// doi.org/10.3390/biochem2020010](http://doi.org/10.3390/biochem2020010).