Indian Journal of Chemistry
Vol. 64, June 2025, pp. 583-590
DOI: 10.56042/ijc.v64i6.15081

Voltammetric determination of the antimalarial drug hydroxychloroquine in synthetic urine sample

Pritimala Sahu[a,b], Nikita Raghuvanshi[a,b], Bhanushree Gupta*[b], Jahangir Ahmad Rather[c], Namrata Singh[d] & Kallol K Ghosh[a,b]

[a] School of Studies in Chemistry, Pt. Ravishankar Shukla University Raipur 492 010 (CG), India

[b] Center for Basic Sciences, Pt. Ravishankar Shukla University Raipur 492 010 (CG), India

[c] Department of Chemistry, Sri Pratap College, Cluster University, Srinagar 190 001, India

[d] Ramrao Adik Institute of Technology, D.Y. Patil University, Navi Mumbai 400 706, India

E-mail: bgupta1517@gmail.com

Received 14 November 2024; accepted (revised) 22 May 2025

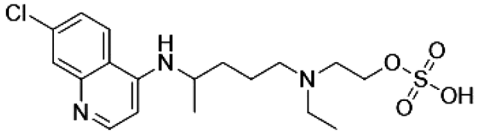
The present investigation reports a rapid electrochemical determination method for an antimalarial drug, hydroxychloroquine (HCQ), using a cationic surfactant. Different solubilized media including surfactants and organic solvents have been screened, and cetyltrimethylammonium bromide (CTAB) has been selected. Electrochemical techniques, namely, Cyclic Voltammetry (CV), Square Wave Voltammetry (SWV), and Differential Pulse Voltammetry (DPV) have been employed to determine the peak current of analyte solution. Adding CTAB to the HCQ solution results in the highest peak current among the studied solubilized systems. The current signal of HCQ observed due to its oxidation is found to be a function of drug concentration, *p*H of analyte solution and the type of additives. The DPV results are linear over the concentration range of 5-60 µg/mL with a limit of detection at 2.41 µg/mL. Excipients including important organic compounds and amino acids have been used to study their interference in HCQ quantification. The proposed method has been successfully applied to determine HCQ in spiked synthetic urine samples. The results reveal good recovery values in the range of 89-104% for different concentrations of HCQ. Thus, the proposed method shows potential applicability for *in vitro* determination of the drug in urine samples.

Keywords: Hydroxychloroquine, Solubilized system, Differential pulse voltammetry, Glassy carbon electrode, Synthetic urine

HCQ is an amino-4-quinoline derived from the quinolone nucleus of quinine, composed of two aromatic nuclei[1]. It is widely used in the treatment of malaria, erythematosus, rheumatoid, arthritis, and other inflammatory and skin diseases[2,3]. HCQ has been used worldwide for more than 70 years and is part of the World Health Organization (WHO) model list of essential medicines[4]. It is a cost-effective medicine with a clinical safety profile. Recently, HCQ has been permitted by several national and international organizations for the treatment of new coronavirus (COVID-19) infections.

Scheme 1 shows the chemical structures of HCQ. HCQ has three nitrogen atoms, responsible for pK_a values of 4.0, 8.3, and 9.7, out of which only two N-atoms with higher pK_a values are protonated under standard physiological conditions (shown in circles in Scheme 1)[5-8].

Several studies have been carried out for the determination of HCQ in pharmaceuticals and biological fluids by different HPLC methods[9] liquid chromatography-tandem mass spectrometry[10], X-ray diffraction[9] Scanning Electron Microscopy[11], spectrophotometric techniques[12], and fluorescence detection, but only a few voltammetric techniques have been employed for its detection. Cyclic Voltammetry (CV), Differential Pulse Voltammetry (DPV), Linear Sweep Voltammetry (LSV), and Square Wave Voltammetry (SWV) are among the commonly used electrochemical techniques for the development of an electrochemical sensing system[13]. The voltammetric studies are found to be simple, accurate, and rapid for the determination of HCQ in bulk form in the presence of surfactant[14].



Scheme 1 — Chemical structure of hydroxychloroquine

The applications of different electrochemical modes in the analysis of drugs and pharmaceuticals are available for quantification of drugs. Many studies have been reported to investigate the electrochemical behavior of different drugs using CV, SWV, and DPV[10,15,16].

The introduction of surfactants in the area of electroanalysis has added a novel approach to studying redox mechanisms of electroactive species and to improve the sensitivity and selectivity Being surface active, surfactants possess the property to adsorb at the interface between bulk phases electrode and solution of analyte and are well capable of controlling the properties of electrode surface[17-19]. These aims are based on the ability of surfactants to reduce interfacial tension and contact angle between solid particles and aqueous media, thus improving drug wettability and increasing surface availability for drug dissolution.

In the present study, the effect of surfactant (anionic, non-ionic, and cationic) and organic solvent (DMF, ACN, and 1,4 Dioxane), its concentrations with the solution *p*H, deposition time, presence of excipients, and concentration of analyte on the voltammetric response of this drug has been studied. Thus, the main objective of the present work is to develop an electrochemical method for the determination of HCQ utilizing the enhancement effect of solubilized system. An assay is also developed to detect HCQ in synthetic urine for quality control purposes.

Experimental Section

Reagents and chemicals

Hydroxychloroquine sulfate commercially available from HCQS®-200, (98% purity) was used for carrying out the experiments. Ultrapure water, obtained from Mili-Q-purification system (Direct-Q® 3UV, Lot No. FONB25359), was used throughout the studies. Phosphate buffered saline (PBS) buffer solution was prepared by mixing 0.13 M sodium chloride (99.5%), 1.8 mM potassium dihydrogen orthophosphate anhydrous (99.5%), and 0.01 M disodium hydrogen orthophosphate anhydrous. Britton-Robinson buffer (BR buffer) was prepared by mixing equimolar (0.1 M) orthoboric acid, orthophosphoric acid, and acetic acid glacial along with an appropriate volume of 0.1 M sodium hydroxide and 0.1 M hydrochloric acid. To determine the role of excipients Glucose, dextrose, lactose, sucrose, citric acid, tartaric acid, ascorbic acid, sodium bicarbonate, potassium nitrate, dopamine, uric acid, glycine, threonine, asparagine, and aspartic acid concentration all the reagents were 1 mM. All chemicals of analytical grade (AR) were purchased from LOBA Chemie (India) and employed without further purification.

Preparation of standard and test solutions

Six tablets were weighed (314 mg/tablet) accurately and crushed using a mortar and pestle. Stock solution of HCQ (1 mM) was prepared in 1% dimethylformamide (DMF), 1% acetonitrile (ACN), 1% 1,4-dioxane, 1% cetyl trimethylammonium bromide (CTAB), 1% sodium dodecyl sulphate (SDS), and 1% Tween-20. Stock solutions of standard and sample were protected from light and stored in refrigerator. The solutions for recording the voltammograms were prepared by mixing appropriate volumes of BR buffer and the stock solution of HCQ.

Preparation of Synthetic Urine Samples

The synthetic urine was prepared according to methods reported in the literature[20-22]. 0.73 g of NaCl, 0.40 g of KCl, 0.28 g of $CaCl_2.2H_2O$, 0.56 g of Na_2SO_4, 0.35 g of KH_2PO_4, 0.25 g of NH_4Cl, and 6.25 g of urea (NH_2CONH_2) were added in a 250 mL volumetric flask, and the volume was completed with water.

Instrumentation

The voltammetric measurements were performed using a Potentiostat (Metrohm Autolab, AUT52250, PGSTAT204) controlled by the NOVA 2.1.4 software. A three-electrode system, composed of a glassy carbon electrode (GCE) as working electrode, an Ag/AgCl electrode as reference electrode, and a Platinum (Pt) wire as counter electrode, was utilized for the purpose. GCE was polished using alumina powder (particle size: 0.05μm) on a polishing cloth before each electrochemical measurement. *p*H of buffer systems was adjusted using a μ-digital *p*H meter (Systronics, 361) with a calomel electrode as the reference electrode.

Analytical procedure

0.01 M analyte solution of 50 mL was kept in an 80 mL electrochemical cell. The buffer solutions (BR and PBS buffer) were used as supporting electrolytes and an appropriate volume of the HCQ (1 mM) solution was added each time for different studies. The electrochemical techniques, CV, DPV, and SWV were employed for the determination of

HCQ with parameters. For CV the parameters were: upper vertex = -1.5 V; lower vertex = 2 V; start potential = 0 V; stop potential = 0 V; and scan rate = 0.05 V/s. For SWV, parameters were: start potential = 0 V; stop potential = 2V; step = 0.005V; frequency = 25 Hz; modulation amplitude = 0.02 V; interval time = 0.04 s; and deposition potential = -1.2 V. For DPV the Parameters were: start potential = 0.4 V; stop potential = 2.0 V; step = 0.005 V; modulation amplitude = 0.025V; modulation time = 0.05 s; interval time = 0.5 s; and deposition potential = -1.2 V.

Procedure for the analysis of synthetic urine samples

5 mL of synthetic urine was added to 40 mL of BR buffer, followed by the addition of HCQ in different concentrations. Voltammograms were recorded with a deposition time of 140 seconds within the potential range of 0.4 to 2.0 V using DPV technique. Obtained current values were used to determine the recovery percentage of HCQ using the following Equation 1[23,24].

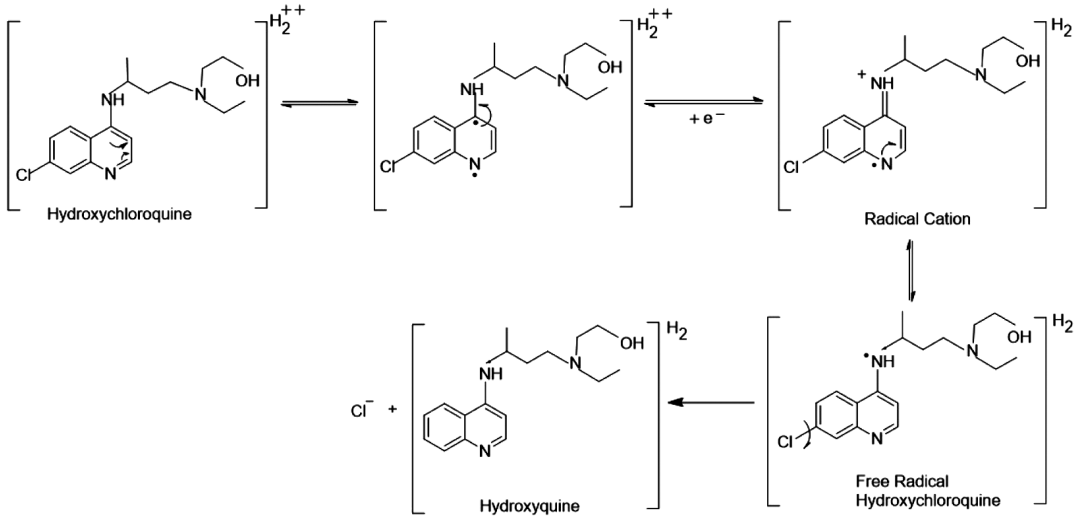
$$\text{Recovery (\%)} = \frac{\text{Found Concentration}}{\text{Added Concentration}} \times 100 \quad (1)$$

Results and Discussion

The plausible mechanism for HCQ oxidation on the surface of the GCE is shown in Scheme 2. The occurrence of anodic oxidation of HCQ at GCE in an electrolyte solution is a complicated process and is possibly related to the cleavage of the C-Cl bond. The first step shows the formation of a resonating free radical structure. The second step in acidic medium (*p*H 2-5) involves addition of an electron to the free radical forming a radical cation. This step possibly accounts for the appearance of a reduction peak during voltammetric investigation. The structure is stabilized by resonance and leads to the formation of a free radical of hydroxychloroquine. The last step of the mechanism is the removal of chloride ions to form hydroxyquine[1,14,25].

Optimization of operational parameters

Assay and electrochemical behavior of HCQ on glassy carbon electrode were determined by using DPV in the presence of the different solubilized systems. The effect of *p*H on the electrochemical behaviour of HCQ was studied in the presence of a supporting electrolyte (BR buffer) at various *p*H values ranging from 3 to 12. Due to their numerous advantages over other existing electrochemical techniques, DPV and SWV were employed in the present study. These techniques are faster, have single scan capability and provide sharp, well-defined peaks. Jain *et al.* have studied different solubilized systems by CV, SWV, and DPV techniques at modified electrodes. They observed that adding cationic surfactant to the analyte solution containing drug enhanced the peak current[26,27]. Jain *et al*. have studied electrochemical behavior of curcumin in different solubilized systems at multiwalled carbon nanotube glassy carbon electrode (MWCNT/GCE) by using SWV. In organic solvents (methanol, ethanol, DMF, and Dimethyl sulfoxide), curcumin was found to be unstable and exhibited rapid degradation. Also, electrochemical response did not increase linearly



Scheme 2 — Plausible mechanism for electrooxidation of hydroxychloroquine

with increasing concentration[28]. Based on these observations, surfactants (CTAB, SDS, and Tween-20) and organic solvents (DMF, ACN, and 1,4 Dioxane) were involved in the present investigation to study their effect on the electrochemical behavior of HCQ.

Response enhancement effect of solubilized system

DPV response of HCQ in organic solvents (ACN, DMF, and 1,4-dioxane), and surfactants (CTAB, SDS, and Tween-20) was recorded. Results show substantial increase in peak current in cationic surfactant CTAB. While neutral and anionic surfactants showed an opposite effect[29]. An increase in voltammetric response was attributed to the adsorption of HCQ on the electrode surface, which leads to formation of self-micelle aggregates with the CTAB, which affects the mass transport[26,30]. The adsorption of amphiphilic species on the electrode surface may result in changing the overpotential of the electrochemical process and the rate of its corresponding charge transfer. Cathodic peak responses of HCQ in various solvents and surfactants are shown in Fig. 1.

Effect of cationic surfactant concentration

The effect of CTAB concentration on the square wave cathodic peak current of 1mM HCQ is shown in Fig. 2. The cathodic peak current increases steadily in the beginning with an increase in concentration of CTAB and reaches a maximum of 0.3 mM. It may be interpreted that the adsorption behavior of CTAB changes from monomer adsorption to monolayer adsorption with an increase in concentration of CTAB at the electrode surface. The CTAB concentration of 0.3 mM may have reached the critical micelle concentration (CMC), but the electrode process is cooperated by the adsorption and accumulation of CTAB[19,26]. Another reason for the increase in peak current may arise from the evidence given by Fuerstenau and co-workers of the occurrence of lateral interactions in the adsorbing species. These workers concluded that once the adsorbed ions reach a certain critical concentration at the interface; they begin to associate into two-dimensional patches of ions, which Fuerstenau *et al*. termed 'hemimicelles'[18]. However peak current decreases as further increases in CTAB concentration. It may be due to the micelle effect *i.e*., electron transfer between HCQ and

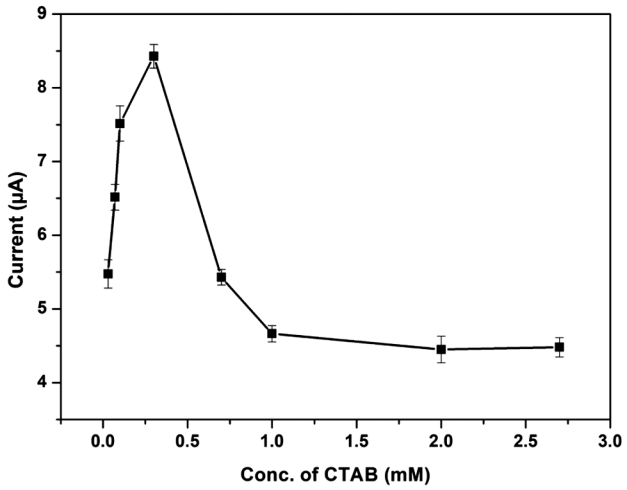


Fig. 2 — Effect of CTAB concentration on SWV peak current of 1 mM HCQ

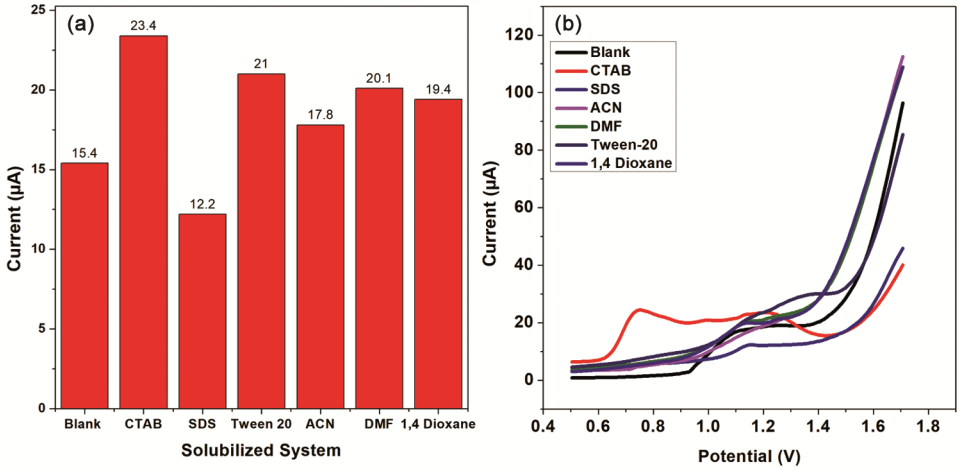


Fig. 1 — Comparison of cathodic peak current (A) response of HCQ (1mM) in different organic solvents (1% ACN, 1% DMF and 1% 1,4 Dioxane), and surfactants (1% CTAB, 1% SDS, and 1% Tween-20); (B) Inset picture represents overlapped differential pulse voltammograms of HCQ (1mM) in 1% surfactants, and 1% organic solvents

electrode surface would be inhibited by aggregates of micelles. Also, the increase of hydrophobicity of the possible CTAB micelles might decrease the electron transfer rate constant which results in the decline of peak current at a rather high CTAB concentration. Thus, CTAB concentration of 0.3 mM can further enhance the electrochemical to a maximum.

Effect of *p*H

The shape and characteristics of voltammograms were found to be dependent on supporting electrolyte and *p*H of the medium. For controlling *p*H, PBS and BR buffers were used. The best results with respect to sensitivity accompanied by better peak shape and stable response were obtained with BR buffer. The effect of *p*H on the peak current of HCQ was studied within the *p*H range 3–12. Peak current decreases as *p*H shifted to a higher value. Diprotonated form of HCQ exits in acidic medium, while the monoprotonated form is present in alkaline medium. At higher *p*H, lower solubility of the compound can be observed in both techniques. This electrodic process is affected by reduction of HCQ[1]. *p*H 3 was found suitable in terms of better peak shape and stable response. With the rise in *p*H the peak potential shifted towards more negative potential indicating the participation of protons in the electrode process[6,31].

Fig. 3 shows a plot of *p*H *vs* current obtained in the presence of BR buffer, recorded using SWV and DPV. According to the observed voltammograms, a change in *p*H from 3 to 12 significantly impacts the electro-oxidation of HCQ. The shift of peak current, on increasing the *p*H, indicates an influence of protonation on the electrodic process. The maximum peak current was observed at *p*H 3 in both cases.

System suitability evaluation

After optimization of the operational parameters of the proposed method, system suitability tests (SST) were performed. It was observed that cationic surfactants (0.3 mM) and *p*H 3 in BR buffer are highly effective in stabilizing the voltammetric response of analyte by protecting the electrode surface.

Effect of deposition time

Deposition time or pre-concentration is one of the most essential factors in the sensor's sensitivity and detection limit. Using DPV technique suitable deposition time was determined for the oxidation of 1mM HCQ at glassy carbon in BR buffer within the time range of 0 - 350 s. It was observed that peak current increased with an increase in deposition time up to 140 s indicating the enhancement of drug concentration at the electrode surface (Fig. 4). By 140 s, the electrocatalytic current intensity for the Q-OH donor group reaches its maximum value. Upon further increment in accumulation time, the electrode surface gets saturated with the oxidized HCQ molecules, thereby stabilizing the current[32].

Effect of Scan Rate

The CV study of HCQ in the presence of 0.3 mM CTAB showed a peculiar behavior in the BR buffer at 3 *p*H values. Fig. 4 shows the CV of HCQ at *p*H 3 in BR buffer at different scan rates (from 10 mV to 400 mV). It shows the well-defined anodic peaks at the glassy carbon electrode surface. As can be seen

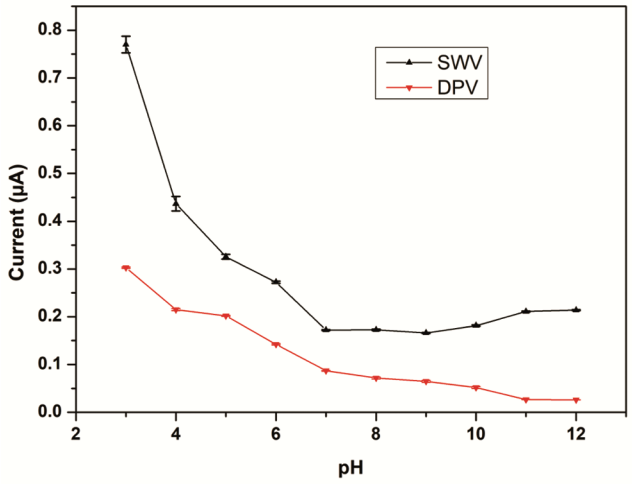


Fig. 3 — Plot of *p*H *vs* Current for HCQ (1 mM) using SWV and DPV in BR buffer

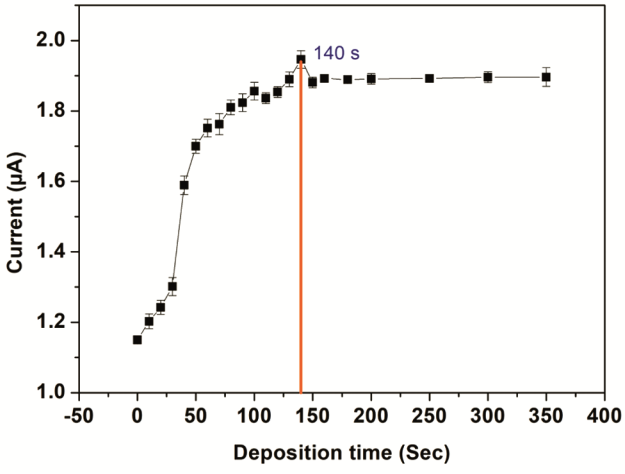


Fig. 4 — Effect of deposition time on oxidation peak current of 1 mM HCQ

(Fig. 5), the shift in the oxidation peak potential to more positive values as the scan rate increased, a behavior that is characteristic of irreversible processes[5,31]. Additionally, a linear regression relationship between the oxidation peak current and the square root of the scan rate (Randles - Seveik plot) was obtained, and the equation can be expressed as $Ip_a = 0.02(x)+0.07$, $R^2 = 0.966$ (Fig. 5B). According to this plot peak current is proportional with scan rate[33]. At higher scan rates the current was increased because the rate of diffusion is more than the rate of reaction and very few ions participate in the charge/electron transfer reaction. which is an indication that diffusion coupled with adsorption processes the electrocatalytic reaction process of HCQ on the surface of the electrode[11,34]. Fig. 5C shows the HCQ oxidation peak potential(E) with the logarithm of the scan rate (log v). the E(V) linearly with log v (mV/s) with a regression equation $Ep_a = 0.124(x) + 1.073$, $R^2 = 0.938$ which indicates the potential is sensitive to the electron transfer[35].

Calibration curve of HCQ

To develop a voltammetry method for determining HCQ quantitatively, a calibration curve is plotted between the concentration of HCQ and the current obtained using DPV techniques in the BR buffer. According to the obtained results, the oxidation peak current increases linearly with an increase in the concentration of HCQ, as shown in Fig. 6. The detection limit was calculated by equation LOD = 3 σ/m, where σ is standard deviation of the blank and m is slope of the regression line. LOD for a standard solution using DPV was found to be 2.41 µg/mL. A linear calibration curve is obtained for HCQ in the concentration range of 5-60 µg/mL following the equation $Ip_a = 0.31(x) + 18.30$; ($R^2 = 0.9797$).

Analytical application

Effect of excipients

A method's suitability for the possible analytical application can be evaluated by studying the effect of some common excipients used in pharmaceutical preparations. To evaluate the impact of interfering substances on 1mM of concentration of HCQ, some common excipients were added in the known concentration of 1mM HCQ by using DPV technique. The experimental results (Table 1) show that excess glucose, lactose, dextrose, sucrose, urea, citric acid, tartaric acid, ascorbic acid, calcium chloride, sodium bicarbonate, and potassium nitrate, dopamine, uric

Table 1 — Influence of potential excipients on the voltammetric response of 1 mM of HCQ

S. No.	Excipients (1.0mM) + HCQ (1.0mM)	Potential observed (V)	Signal change (%)
1	Only HCQ	1.08	0
2	Glucose + HCQ	1.06	+0.23
3	Citric acid + HCQ	1.06	+0.25
4	Lactose+ HCQ	1.06	+0.16
5	Dextrose+ HCQ	1.06	+0.20
6	Sucrose+ HCQ	1.05	+0.26
7	Tartaric acid+ HCQ	1.06	+0.23
8	Urea+ HCQ	1.07	+0.13
9	Ascorbic acid+ HCQ	1.07	+0.13
10	Calcium chloride+ HCQ	1.07	+0.13
11	Uric acid + HCQ	1.18	–0.90
12	Dopamine + HCQ	1.18	–0.90
13	Glycine + HCQ	1.19	–0.98
14	Asparagine+ HCQ	1.18	–0.95
15	Aspartic acid + HCQ	1.18	–0.93
16	Threonine+ HCQ	1.18	–0.93

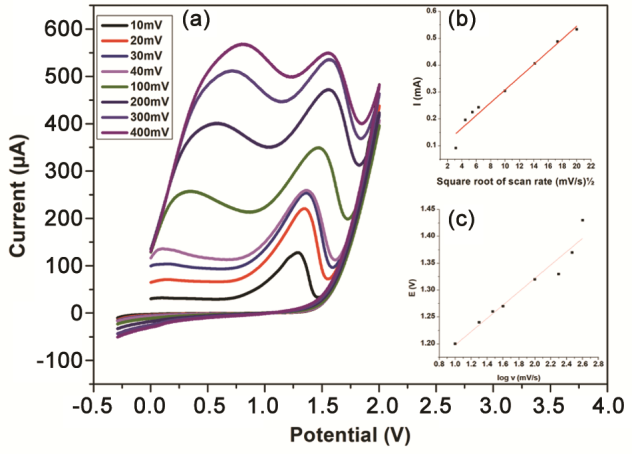


Fig. 5 — Cyclic voltammograms of 1 mM HCQ in 0.3 mM CTAB at different scan rates (10 mV/s to 400 mV/s)

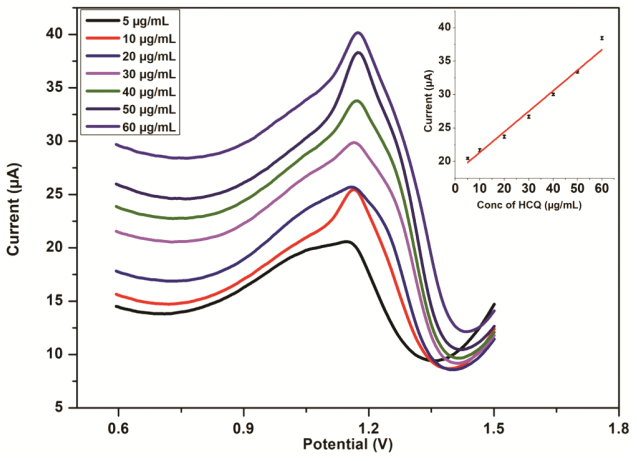


Fig. 6 — Plot of current against the different concentrations of HCQ (5-60µg/mL) DPV techniques

Table 2 — Recovery test of added samples 6, 7 and 25 µg/mL HCQ deposited in synthetic urine samples

Sample	Concentration of HCQ		
	Added (µg/mL)	Found (µg/mL)	Recovery (%)
Synthetic Urine + HCQ	6	6.26 ± 0.01	104
	7	6.72 ± 0.01	95
	25	22.28 ± 0.02	89

acid, and some amino acids such as glycine, threonine, asparagine, and aspartic acid did not interfere with the voltammetric signal of HCQ. Since the effect of excipients in terms of relative signal change (%) ranged from - 0.90 to + 0.26, an error of less than 5%, therefore they do not affect the determination of HCQ significantly[27,30,36]. Thus, the suggested method will be able to assay HCQ in the presence of excipients and be considered as specific.

Detection of HCQ in Synthetic Urine Sample

The developed DPV method for the HCQ determination was applied to synthetic urine samples. Drug-free urine was spiked with known concentrations of HCQ to determine the recoveries of drugs from urine at optimum conditions. The recovery rate was determined by the standard addition method[36]. The calibration graph was then used for the determination of spiked HCQ concentration in urine samples. The obtained results, shown in Table 2, indicate that there are no significant interferences for the samples when analyzed using the proposed DPV method[20-24].

Conclusion

Through the present study, we are able to investigate the electrochemical behavior of HCQ in surfactant and organic solvent media at various *p*H levels. The determination of HCQ in the presence of surfactants using DPV technique provides a new medium for studying the interaction of HCQ with surfactants. The proposed voltammetric procedure has been successfully applied for the evaluation of HCQ in urine samples. The influence of biologically important excipients like urea, uric acid, glucose, dopamine, aspartic acid, *etc*. was not found significant in the determination of HCQ. All studies were carried out on glassy carbon electrodes without any modification. The developed assay is found to be convenient, low-cost and reproducible due to its simple and less expensive preparation. Consequently, the proposed method has the potential to be a good analytical alternative for determining HCQ in urine and other pharmaceutical samples. It can be adopted for pharmacokinetic studies as well as for quality control across laboratories.

Acknowledgment

The authors are thankful to the Head of Department, School of Studies in Chemistry Pt. Ravishankar Shukla University, Raipur for providing the research facilities. The authors are also grateful to the Department of Science and Technology, Government of India for providing financial assistance (DST/INSPIRE Fellowship/2022/IF220056).

References

1 Arguelho M L P M, Andrade J F & Stradiotto N R, *J Pharm Biomed Anal*, 32 (2003) 269.
2 Pikkel J, Chassid O, Sharabi-Nov A & Beiran I, *Graefe's Archive Clin Exp Ophthalmol*, 251 (2013) 1687.
3 Stelton C R, Connors D B, Walia S S & Walia H S, *Clin Rheumat*, 32 (2013) 895.
4 Liu J, Cao R, Xu M, Wang X, Zhang H, Hu H, Li Y, Hu Z, Zhong W & Wang M, *Cell Disc*, 6 (2020) 16.
5 Zhang H, Cheng L, Shang H, Zhang W & Zhang A, *Russian J Electrochem*, 57 (2021) 872.
6 Nate Z, Gill A A S & Chauhan R, *Microchem J*, 160 (2021) 105709.
7 Armstrong N, Richez M, Raoult D & Chabriere E, *J Chromat B*, 1060 (2017) 166.
8 Derendorf H, *Int J Antimicrobial Agents*, 55 (2020) 106007. .
9 Henrique J M M, Monteiro M K S, Cardozo J C, Martínez-Huitle C A, Silva D R D & Santos E V D, *J Electroanal Chem*, 876 (2020) 114734.
10 Bouabi Y E L, Farahi A, Labjar N S, Hajjaji E l, Bakasse M & Mhammedi M A E l, *Mat Sci Eng C*, 58 (2016) 70.
11 Zoubir J, Bakas I, Qourzal S, Tamimi M & Assabbane A, *J App Electrochem*, 53 (2023) 1279.
12 Monteiro M, Silva D D, Quiroz M, Vilar V, Martínez-Huitle C & Dos S E, *Materials*, 14 (2020) 37.
13 Thapliyal N, Chiwunze T E, Karpoormath R, Goyal R N, Patel H & Cherukupalli S, *RSC Adv,* 6 (2016) 57580.
14 Nate Z, Gill A A S, Chauhan R & Karpoormath R, *Results Chem*, 4 (2022) 100494.
15 Bensalah N, Midassi S, Ahmad M I & Bedoui A, *Chem Eng J*, 402 (2020).
16 Zhang H, Cheng L, Shang H, Zhang W & Zhang A, *Russian J Electrochem*, 57 (2021) 872.
17 Jain R, Jadon N & Radhapyari K, *Talanta,* 70 (2006) 383.
18 Jain R, Dwivedi A & Mishra R, *J Coll Int Sci*, 318 (2008) 296.
19 Jain R, Radhapyari K & Jadon N, *J Electrochem Soc*, 155 (2008) F104.

20 Laube N, Mohr B & Hesse A, *J Crystal Growth*, 233 (2001) 367.
21 Oliveira J de, Silva S, Sant'Anna M V S, Gevaerd A, Lima J B S, Monteiro M D S, Carvalho S W M M & Midori S E, *Electroanal*, 33 (2021) 2152.
22 Ribeiro C de L, de Souza J R, Pereira□da□Silva M A & Paterno L G, *Electroanal,* 33 (2021) 609.
23 Oliveira J de, Silva S, Sant'Anna M V S, Gevaerd A, Lima J B S, Monteiro M D S, Carvalho S W M M & Midori S E, *Electroanal*, 33 (2021) 2152.
24 Deroco P B, Vicentini F C, Oliveira G G, Rocha-Filho R C & Fatibello-Filho O, *J Electroanal Chem,* 719 (2014) 19.
25 Atta N, Darwish S, Khalil S & Galal A, *Talanta,* 72 (2007) 1438.
26 Jain R & Rather J A, *Coll Surf A: Physicochem Eng Asp*, 378 (2011) 27.
27 Jain R, Rather J A & Dwivedi A, *Mat Sci Eng C*, 31 (2011) 230.
28 Jain R, Haque A & Verma A, *J Mol Liq*, 230 (2017) 600.
29 Jain R & Vikas, *Coll Surf B: Bioint*, 88 (2011) 729.
30 Jain R & Rather J A, *Coll Surf A: Physicochem Eng Asp*, 378 (2011) 27.
31 Araújo D M D, Da S M, Paiva S, Henrique J M M, Martínez-Huitle C A & Dos S E V, *Materials,* 14 (2021) 4990.
32 Zoubir J, Bakas I, Qourzal S, Tamimi M & Assabbane A, *J App Electrochem*, 53 (2023) 1279.
33 Aoki K J, Chen J, Liu Y & Jia B, J *Electroanal Chem*, 856 (2020) 113609.
34 Li C, *Colloids Surfaces Biointer*, 55 (2007) 77.
35 Zoubir J, Bougdour N, Radaa C, Idlahcen A, Bakas I & Assabbane A, *Sens Int*, 3 (2022) 100160.
36 Gowda J I & Nandibewoor S T, *Asian J Pharm Sci*, 9 (2014) 42.