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Electrochemical determination of antihypertensive drug irbesartan in pharmaceuticals

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ABSTRACT

A sensitive voltammetric method has been developed for the determination of irbesartan in a Britton–Robinson buffer medium. Irbesartan exhibited a well-defined cathodic peak over the entire pH range from 2.0 to 12.0. The mechanism of reduction was postulated on the basis of controlled potential electrolysis, coulometry, and spectral analysis. Under optimal conditions, a linear response of irbesartan was obtained in the range from 3.0×10^{-5} to 5.7×10^{-3} mol L^{-1} and with a limit of detection of 5.33×10^{-7} mol L^{-1}. The effect of cationic surfactant on the voltammetric reduction peak of irbesartan in Britton–Robinson buffer is also described.

Irbesartan is a potent, long-acting, nonpeptide angiotensin II receptor antagonist [1] having high selectivity for the AT1 subtype (angiotensin I). It is potentially safe and more tolerable than other classes of antihypertensive drugs. Irbesartan reduces the chances of cardiac failure, myocardial infarction, sudden death, and death from progressive systolic failure. Chemically, irbesartan is 2-butyl-3-{[2′-(1H-tetrazole-5-yl)(1,1′-biphenyl)-4-yl]methyl}-1,3-diaza spiro[4,4]non-1-en-4-one (Scheme 1) [2].

Irbesartan is officially listed in Martindale: The Extra Pharmacopoeia [3]. Its assay procedure in pure and dosage form is not reported in any pharmacopoeia; therefore, the development of an analytical procedure for the determination of irbesartan in pharmaceutical preparations is of great significance. A survey of the literature revealed that few methods have been reported for its determination such as high-performance thin layer chromatography (HPTLC)[1] [4], high-performance liquid chromatography (HPLC) [5], capillary zone electrophoresis (CZE) [6,7], and derivative spectrophotometry [8].

During the past decades, modern electrochemical techniques [9–46] have been widely used for the determination of pharmaceuticals and other analytes. Furthermore, determination of irbesartan using an electrochemical method is yet to be reported. The objective of current work was to develop a voltammetric method for the determination of irbesartan and to investigate its reductive properties in the presence of surfactant.

Additions of surface-active agents have proven to be an effective role in the electroanalysis of biologically active compounds and drugs. Aqueous micellar solutions and micro emulsions are surfactant-based self-organized systems [47] that can be used as less hazardous and versatile substitutes for organic solvents in voltammetry [48], HPLC separation [49], and catalysis [50]. The influence of surfactant aggregates at the electrode–electrolyte interface in micelle solutions has been indicated. The use of surfactants as drug carriers makes necessary the study of the interaction of drugs with micellar systems, implying the elucidation of the nature of these interactions. Solubilization of electroactive compounds in aqueous solutions containing surfactant micelles provides a new medium for electrochemical studies.

Materials and methods

Irbesartan (99% pure) was a gift from Sunpharma Pharmaceuticals (Mumbai, India). A tablet form containing irbesartan (Irovel, 300 mg) was obtained from commercial sources. A stock solution of irbesartan (2.8×10^{-3} mol L^{-1}) was prepared by direct dissolution in *N*,*N*′-dimethylformamide (DMF) and in

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[1] *Abbreviations used:* HPTLC, high-performance thin layer chromatography; HPLC, high-performance liquid chromatography; CZE, capillary zone electrophoresis; DMF, *N*,*N*′-dimethylformamide; CTAB, cetyltrimethylammonium bromide; DPP, differential pulse polarography; DME, dropping mercury electrode; SCE, saturated calomel electrode; CV, cyclic voltammetry; PAR, Princeton Applied Research; LOD, limit of detection; LOQ, limit of quantitation.

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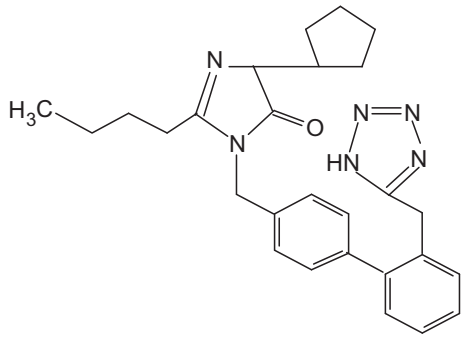

Scheme 1. Chemical structure of irbesartan.

cetyltrimethylammonium bromide (CTAB) solution. The solutions for recording voltammograms were prepared by mixing an appropriate volume of stock solutions and buffers of varying pH values. A series of Britton–Robinson buffers in the pH range of 2.0–12.0 were prepared in ultrapure deionized water. KCl solution (1.0 mol L^{-1}) was also prepared in distilled water and used as supporting electrolyte. All chemicals used were of analytical reagent-grade quality and were employed without further purification.

Instrumentation

The differential pulse polarography (DPP) measurements were carried out using an Elico Polarographic Analyzer CL 362. The drop time of 1 s was electronically controlled. The polarograms were recorded using a potential rate of 100 mV s^{-1}. The used electrodes were dropping mercury electrode (DME) as a working electrode, saturated calomel electrode (SCE) as a reference electrode, and platinum wire as an auxiliary electrode. The solutions were purged with pure nitrogen gas for 10 min and then polarographed at ambient temperature.

Cyclic voltammetry (CV) experiments were performed using EG&G PAR (Princeton Applied Research) 273 model, a potentiostat controlled by 270/250 Research Electrochemistry Software 4.30. A three-electrode system was composed of a glassy carbon as a working electrode (φ = 2 mm EG&G/PAR), Ag/AgCl as a reference electrode, and platinum wire as an auxiliary electrode. To provide a reproducible active surface and to improve the sensitivity and resolution of the voltammetric peaks, the working electrode was polished with 0.5-μm alumina powders on a polishing cloth prior to each electrochemical measurement. Then it was thoroughly rinsed with methanol and double distilled water and gently dried with a tissue paper. All measurements were carried out at room temperature (25 ± 0.1 °C). The pH metric studies were carried out on a Decibel DB 1011 digital pH meter fitted with a glass electrode and SCE as a reference, which was previously calibrated with buffer of known pH.

Procedure

Irbesartan determination was performed on commercially available tablet dosage form Irovel. The amount of irbesartan present in each tablet was 300 mg. Excipients such as microcrystalline cellulose, lactose, polyethylene glycol, and titanium dioxide were added to the dosage forms. Ten tablets were weighed accurately and crushed into a fine powder. A sufficient amount of powder for preparing a stock solution of 2.8×10^{-3} M was weighed and transferred into 50-ml standard flasks. After that, 40 ml of DMF and CTAB (2.97×10^{-4} mol L^{-1}) were added separately to each flask to dissolve the active material. The contents of the flasks were stirred magnetically for 30 min and then diluted to volume with the same solvent. After dilution, the solutions were centrifuged. An aliquot of the supernatant liquid was then transferred into a calibrated flask, and a series of dilutions were prepared with Britton–Robinson buffer in the pH range of 2.0–12.0 and mixed with 1.0 ml of potassium chloride as supporting electrolyte.

Results and discussion

The voltammetric behavior of irbesartan was examined in DMF and solubilized systems in the pH range of 2.0–12.0 employing DPP and CV techniques. Irbesartan exhibited a single, well-defined cathodic peak over this entire pH range. A typical differential pulse polarogram of irbesartan in DMF is depicted in Fig. 1. However, there was a peak following the first one due to the presence of Britton–Robinson buffer, and it is also observed in blank samples. But the analyte exhibited only one peak, which is shown in Figs. 1 and 5.

The peak shift to more negative potential as pH increases indicates the participation of protons during the electrode process [51,52]. The effect of pH on the polarogram of irbesartan leads to the conclusion that an acidic medium is suitable for analytical studies (Fig. 2). A sharp response and better peak shape with maximum current were observed at pH 2.2, so this pH value was chosen as the working pH for further studies. The influence of several electrolytes (phosphate and acetate buffer) on the analytical signal was also studied.

On the basis of the electrochemical reduction of irbesartan, an analytical method was developed for the determination of the drug. A linear relationship between peak current and irbesartan concentration was observed in the concentration range of 5.7×10^{-3}–0.03×10^{-3} mol L^{-1} (Fig. 3). The linear regression equation is expressed as i_p (μA) = 4.7×10^3 C + 0.8671 A for the cathodic peak, where i_p is the peak current (in μA) and C is the concentration (in mol L^{-1}) with a good correlation (r^2 = 0.996). The peak height of both

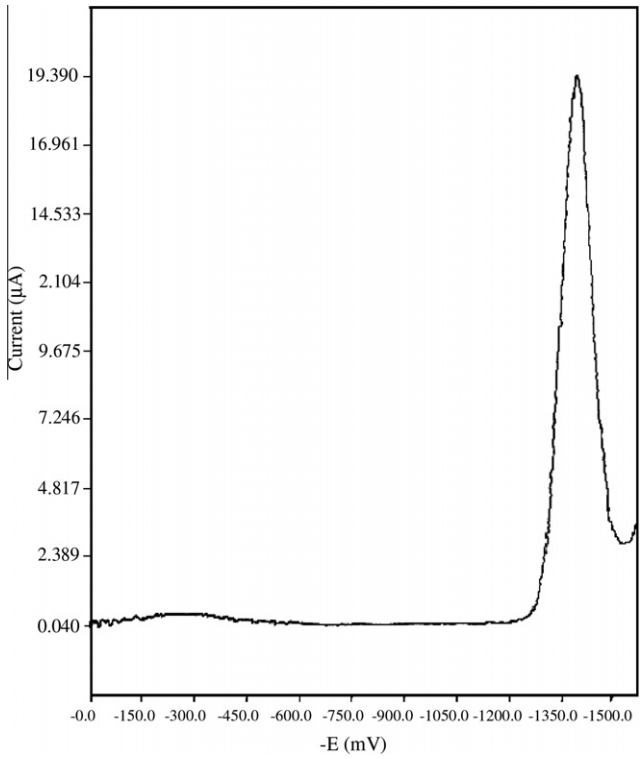

Fig.1. Differential pulse polarogram of 5.7×10^{-3} M irbesartan solution in Britton–Robinson buffer (pH 2.2) containing DMF with a pulse amplitude of 100 mV and a scan rate of 100 mV s^{-1}.

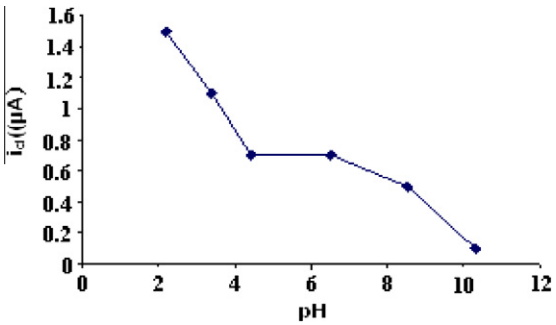

Fig.2. Plot of i_p (μA) versus pH for irbesartan (0.1×10^{-3} M) in Britton–Robinson buffer with a pulse amplitude of 100 mV and a scan rate of 100 mV s^{-1}.

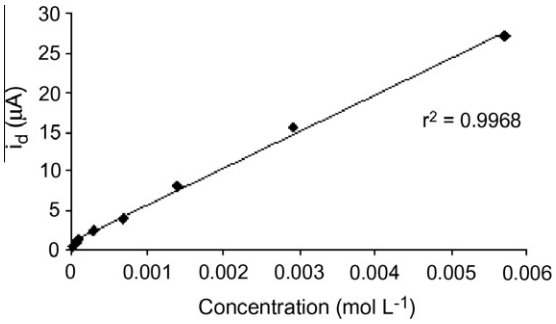

Fig.3. Plot of i_p (μA) versus concentration for irbesartan in Britton–Robinson buffer containing DMF with a pulse amplitude of 100 mV and a scan rate of 100 mV s^{-1}.

bulk and pharmaceutical formulation also increased linearly with pulse amplitude from 5 to 100 mV.

The reversibility of the reduction process was studied at CV with glassy carbon as a working electrode, Ag/AgCl as a reference electrode, and platinum as an auxiliary electrode. Irbesartan exhibited a single cathodic peak in the pH range of 2.0–12.0, whereas no anodic peak was observed in reverse scan, indicating the irreversible nature of the electrode process [53]. Fig. 4 shows cyclic voltammograms of DMF solution at different scan rates. On subsequent scans, the reduction peak height decreased gradually and the peak moved to less negative potential.

As the scan rate is increased from 50 to 250 mV s^{-1} at a fixed concentration of irbesartan, (i) the peak potential shifts cathodically and (ii) the peak current function, $i_p/AC\upsilon^{1/2}$, exhibits almost constancy. A linear Randles–Sevcik plot (plot of i_p against $\upsilon^{1/2}$) with the linear regression equation [54,55] i_p (μA) = $0.4337 \times \upsilon^{1/2}$ (mV s^{-1}) + 0.5173 (r^2 = 0.991) was obtained, indicating that diffusion is the means of mass transport. This finding was further confirmed by plotting log i_p against log υ; a straight line was obtained and can be expressed by the equation log i_p (μA) = 0.0857 + 0.385 - log υ (V s^{-1}) (r^2 = 0.994) with a slope of 0.38, which is close to 0.5.

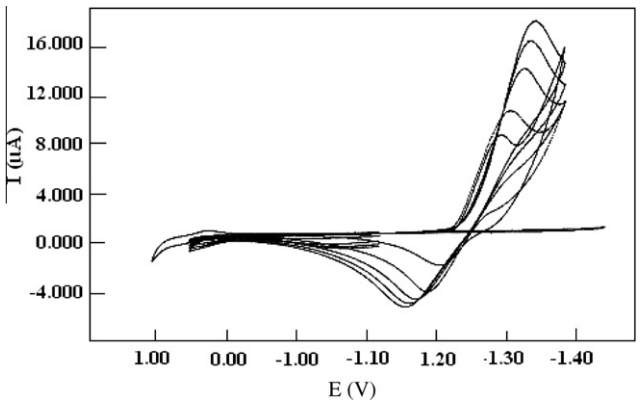

Fig.4. Cyclic voltammograms of 0.3×10^{-3} M irbesartan in DMF with different scan rates at pH 2.2.

A plot of reduction peak potential versus the square root of scan rate showed a linear relationship between 20 and 250 mV s^{-1} (r^2 = 0.90), confirming the diffusion-controlled nature of the electrode process. Furthermore, the diffusion-controlled and adsorption-free nature of the electrode process in the buffer system studied is evidence of the linear plot of I_m versus $t^{2/3}$, where I_m is the maximum current in DPV and t is the drop time. According to the equation $i_p = 4\upsilon^x$, the x values of 0.5 and 1 are expected for adsorption-controlled and diffusion-controlled reactions. The regression of i_p versus log $\upsilon^{1/2}$ gives a slope value of 0.991, indicating that the reduction current is diffusion controlled [56] in nature. A comparison of limiting current at various pH values indicates that the compound is reduced in the pH range of 2.0–12.0 by consuming an identical number of electrons. A shift in E_p with pH toward more negative potential was observed. This pH dependence of E_p suggests the participation of protons in the rate-determining step.

Validation of the proposed method

According to the International Conference on Harmonization (ICH) guidelines [57], the following expression is used to evaluate the limit of detection (LOD) and limit of quantitation (LOQ).

Sensitivity/detection limit

The LOD was calculated by the equation LOD = 3SD/b, where SD is the standard deviation of the intercept and b is the slope of the regression line. The calculated LOD for the standard solution was 5.3×10^{-7} mol L^{-1} or 0.22 μg ml^{-1}.

Quantitation limit

The LOQ was examined by the equation LOQ = 10SD/b. The lower limit of quantitation for the standard solution was found to be 1.77×10^{-6} mol L^{-1} or 0.75 μg ml^{-1}.

Specificity

Specificity is the ability of the method to measure the analytical response in the presence of all potential impurities. For the specificity test, voltammograms of the standard solutions of tablet excipients (starch, gelatin, lactose, and magnesium stearate) were recorded under selected conditions. The response of the analyte in this mixture was compared with the response of pure irbesartan. It was found that assay results were not changed.

Stability

In this study, irbesartan stock solutions were kept in the dark at 4 °C for 1 month and were analyzed at different times (every day). It was seen that repeatable peak currents of irbesartan stock solution occurred up to 15 days, and after that the peak current decreased significantly. Therefore, the solutions were found to be stable for 15 days.

Voltammetric behavior of irbesartan in the presence of surfactant

The effect of CTAB concentrations was examined with irbesartan, and it was found that irbesartan with 2.97×10^{-4} mol L^{-1} cetrimide solution gave a single well-defined reduction peak (Fig. 5). The voltammetric response of irbesartan leads to the decrease in peak current in cetrimide. This may be explained on the basis of adsorption of the surfactant monomers on the electrode–solution interface. This is because on micelle formation,

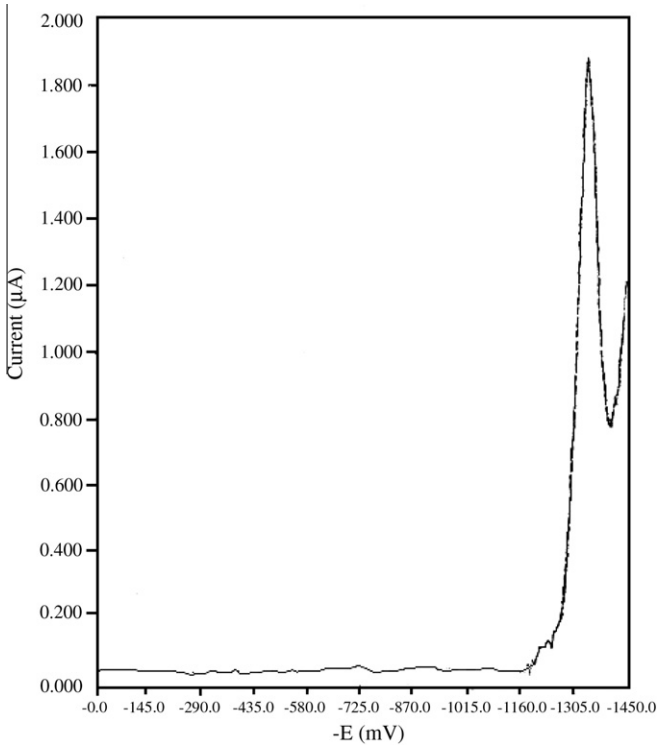

Fig.5. Differential pulse polarogram of 8.0×10^{-3} mol L^{-1} irbesartan in 2.9×10^{-3} mol L^{-1} CTAB with a pulse amplitude of 100 mV and a scan rate of 100 mV s^{-1}.

the drug is partitioned between the micelle and the aqueous phase; that is, it gets entrapped in the insulated hydrophobic environment of the micelle and then diffuses along with the micelle, leading to a drop in the peak current [58]. Table 1 lists the effect of CTAB concentration on the peak current (i_p) and the peak potential (E_p) of irbesartan. The peak current increases gradually with increasing CTAB concentrations. The appropriate CTAB concentration was found to be 2.9×10^{-3} mol L^{-1}. In addition, the peak potential shifted slightly toward positive potential with increasing CTAB concentrations. This also indicates the adsorption of irbesartan in the presence of CTAB [59]. Analytical parameters for voltammetric determination of irbesartan using DPP are tabulated in Table 2.

Controlled potential electrolysis and coulometry

By using controlled potential coulometry, the number of electrons (n) transferred was calculated from the charge consumed by the desired concentration of irbesartan during the electrode process. The charge consumed was determined in acidic medium.

Table 1
Effect of CTAB concentration on E_p and i_p for the reduction wave of 8.0×10^{-3} mol L^{-1} irbesartan.

	Concentration of CTAB ($C \times 10^{-3}$ mol L^{-1})			
	0.1	0.8	1.94	2.9
$-E_p$ (V)	−1.342	−1.339	−1.336	−1.334
i_p (μA)	0.37	0.62	1.26	1.90

Table 2
Analytical parameters for voltammetric determination of irbesartan.

Parameter	DPP	
	Solvent	Surfactant (cetrimide)
Concentration range (mol L^{-1})	5.7×10^{-3}–3.0×10^{-5}	11.0×10^{-3}–1.0×10^{-5}
Measured potential (mV)	−1410	−1328
LOD (μg/ml)	0.22	0.49
LOQ (μg/ml)	0.75	1.65
Correlation coefficient (r^2)	0.996	0.996
Intercept (μA)	0.8671	0.1465
Slope (μA/μg ml)	4.7×10^3	3.6×10^2
Recovery (%)	98.7	96.8
Applications	Tablets	Tablets

Note. LOD, limit of detection; LOQ, limit of quantitation.

For this purpose, 2 ml of 5.0×10^{-3} M solution of the electroactive species was placed in the cell and electrolysis was carried out. During the electrolysis, solutions were continuously stirred and purged with nitrogen. The number of electrons (n) was calculated using the equation $Q = nFN$, where Q is the charge in coulombs, F is the Faraday constant, and N is the number of moles of substrate. Millicoulometry was also employed to find the number of electrons involved in the electrode process using the method of De Vries and Kroon and was found to be 2 for –N=N grouping for irbesartan.

Reaction mechanism

On the basis of DC, DPP, CV, coulometry, and spectral studies, the following mechanism may be postulated for the reduction of irbesartan:

$$-N{=}N- \overset{2e^-\ 2H^+}{\rightarrow} -NH-NH-.$$

Analysis of drug in pharmaceutical formulation

The applicability of the proposed voltammetric method for the sample dosage forms was examined by analyzing Irovel (300-mg tablet form). The amount of the compound in the tablets was

Table 3
Statistics and performance characteristics of analytical method from calibration data set.

Standard				Tablet			
I (μA)	$(x-\bar{x})^2$	E (mV)	$(x-\bar{x})^2$	I (μA)	$(x-\bar{x})^2$	E (mV)	$(x-\bar{x})^2$
28.50	0.04	−1420	12.96	28.12	0.0001	−1410	1
28.98	0.08	−1428	19.36	28.08	0.0025	−1405	16
28.84	0.02	−1426	5.76	28.16	0.0009	−1407	4
28.53	0.03	−1420	12.96	28.17	0.0016	−1413	16
28.66	0.01	−1424	0.16	28.12	0.0001	−1410	1
$\sum x$	$\sum (x-x)^2$	$\sum x$	$\sum (x-x)^2$	$\sum x$	$\sum (x-x)^2$	$\sum x$	$\sum (x-x)^2$
143.51	0.18	7118	51.2	140.6	0.0052	7045	38.00
RSD = 0.21		RSD = 3.57		RSD = 0.03		RSD = 3.08	
CV = 0.73		CV = 0.25		CV = 0.12		CV = 0.21	

Note. RSD, relative standard deviation; CV, coefficient of variation.

calculated by the standard addition method [60]. The percentage recovery obtained in this manner was 98.7% for the reduction peak of irbesartan. The effect of excipients (starch, gelatin, lactose, and magnesium stearate) on the voltammetric response of irbesartan was studied using the above process, and it was found that they do not interfere with the assay. Thus, the proposed method is simple, sensitive, precise, reproducible, and accurate; hence, it can be used for the determination of irbesartan in both bulk and pharmaceutical preparations. The performance data of the proposed method are tabulated in Table 3.

Conclusions

The electrochemical behavior of irbesartan at DME and glassy carbon electrode has been established and studied for the first time. The proposed study also provides a sensitive and selective method of irbesartan analysis in solubilized systems. The analytical results obtained by DPP and CV are adequately accurate and precise and are in good agreement with those obtained by other researchers using different techniques [4,5,8]. As low as 3.86×10^{-6} mol L^{-1} irbesartan was measured by the proposed method with sufficiently good accuracy and precision.

Furthermore, the other main advantage of this new method is the use of surfactant media in place of hazardous organic solvents. Consequently, the proposed method has high potential for being a good analytical alternative for determining irbesartan in pharmaceutical formulation.

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