

CYCLIC VOLTAMMETRIC STUDY OF BENDROFLUAZIDE AT A CARBON PASTE ELECTRODE

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ABSTRACT:

Electrochemical oxidation of bendrofluazide was performed using cyclic voltammetry at a silicon oil impregnated carbon paste electrode (CPE) vs. Ag | AgCl reference electrode. Various qualitative parameters such as E_p , i_p , β_{nb} and D were determined in aqueous KCl, NaCl, NH_4Cl , KOH, NaOH, NH_4OH , HCl, CH_3COOH and H_2SO_4 systems. Bendrofluazide showed an irreversible electron transfer process with a CPE at 25, 35, and 45°C. The heterogeneous rate constant $K(E)$ was calculated to be 1.3×10^{-2} at 25°C. The shape of the CV wave was also drawn using simulation method. This obtained profiles similar to that of the experimental CV curves at different scan rates. Investigation through diagnostic tests confirmed the absence of adsorption (either weak or strong) of analyte on the surface of the test electrode. The present method provides quantification of analyte in the dilution range 10^{-4} to $10^{-5}M$.

INTRODUCTION

Bendrofluazide (2H-1,2,4-Benzothiadiazine-7-3,4-dihydro-3-(phenyl methyl)-6-1,1,dioxide) is a thiazide diuretic compound having similar action and uses compared to chlorothiazide. However, unlike chlorothiazide, it has been reported to be completely absorbed from the gastrointestinal tract, followed by its fairly extensive metabolism. The use of bendrofluazide in the treatment of hypertension showed a reduction in the rate of all strokes, while the myocardial infection and total mortality were found to be unaffected by the treatment. The above medical importance revealed this compound to be analyzed by different methods either in terms of in vivo/in vitro or in pharmaceutical studies. In this connection, bendrofluazide has been reported to be determined using conventional d.c. and differential pulse polarography. This work is reported to quality control assay of bendrofluazide alongwith other drugs such as bendrofluazide and dihydrazine sulphate. The reported method showed reproducible results compared to the limits of B.P or USP. Other methods like potentiometric titration, amperometry, and conductometry have also been reported in the literature for quantitative determination of this compound with 99.6% recovery. No work has been reported on the cyclic voltammetry of this compound at CPE. In this work, CV was performed at a CPE vs. Ag | AgCl reference electrode in the above said supporting electrolytes. Beside quantification of bendrofluazide, various parameters E_p , i_p , β_{nb} , D , $k(E)$, and adsorption were also determined at CPE.

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EXPERIMENTAL

Chemicals:

Supporting electrolytes such as H_2SO_4 (1-0.01M; B.D.H.), HCl (1-0.01M; B.D.H.), CH_3COOH (1-0.01M; B.D.H.), NaOH (0.1-0.001M; B.D.H.), KOH (0.1-0.001M; B.D.H.), NH_4OH (0.1-0.001M; B.D.H.), KCl , NaCl , and LiCl (each 0.1M; e. Merck) were used for the cyclic voltammetry of bendrofluazide. A stock solution of analyte in the above supporting electrolytes was prepared by dissolving 0.01g bendrofluazide (S.K. & F.; pharmaceutical grade) in a 1 litre volumetric flask. The analyte was diluted further to the required concentration. All reagents used were of analytical grade and were prepared in double distilled water.

Equipment:

CV-1B cyclic voltammogram, Bioanalytical system (BAS), USA, coupled with an XY-chart recorder was used for the cyclic voltammetric study. A carbon paste electrode (MF-2010, BAS) was packed with the carbon paste (CF-1010; BAS) accordingly. A three-electrode assembly consisting a carbon paste test electrode, an $\text{Ag} \mid \text{AgCl}$ reference electrode (MF-2020; BAS) and a platinum wire counter electrode were used for cyclic voltammetric study. Haake (model KT 33, Germany) thermostat was used to maintain constant temperature with an accuracy of $\pm 0.1^\circ\text{C}$ which was connected to the double wall (glass jacketed) cell assembly.

Procedure:

The cell vial was filled with the 10mL of supporting electrolyte or analyte solution prepared in one of these supporting electrolytes. The three-electrode assembly was set in to the cell. The packing/polishing surface renewal of the carbon paste test electrode was done as described in the instruction manual of (BAS). Nitrogen gas (99.99% pure) was flushed through the solution for 10 minutes to avoid oxygen interference. Cyclic voltammograms of these supporting electrolytes were recorded at different scan rates keeping temperature 25, 35, and 45°C . After taking base-lines, cyclic voltammograms of bendrofluazide were recorded in these supporting electrolytes. Effects of various parameters such as, voltage scan rate, concentration of analyte/supporting electrolytes and repeated scanning were also studied at these temperatures.

Determination of Base-lines:

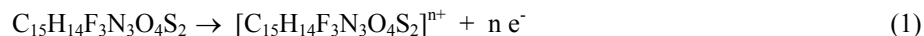
Cyclic voltammograms of pure supporting electrolytes were recorded at a carbon paste test electrode vs. $\text{Ag} \mid \text{AgCl}$ reference electrode at all temperatures and scan rates. The resulting base-lines were found to be horizontally straight with a larger anodic potential (+1.25V) compared to a small cathodic potential range (-0.70V) with all scan rates and temperatures.

RESULTS AND DISCUSSION

The Qualitative Characteristics:

A cyclic voltammetric study of bendrofluazide performed in various aqueous systems based on its solubility (K., Florey, 1976, USP., 1975, The Merck Index 1976). The analytical applicability of CPE was investigated for the analyte in the supporting electrolytes such as KOH , NaOH , NH_4OH , HCl , CH_3COOH , LiCl , KCl , and NaCl . In the qualitative study, the first-scan cyclic voltammograms of bendrofluazide recorded with a carbon paste electrode vs. $\text{Ag} \mid \text{AgCl}$ reference electrode at 25°C are shown in Figure 1. The values of E_p , $E_{p/2}$, i_p , and D are enlisted in Table 1. The single anodic wave in the cyclic voltammograms of bendrofluazide appeared with a well defined current maxima in all these supporting electrolytes. The reverse wave (cathodic) did not

appear in the cyclic voltammogram profiles on the time scale of the experiment and temperatures. The shape of cycle voltammograms of bendrofluazide reveals that *the current* at the foot of the anodic wave is independent of the rate of potential scan (R. J. Klinger, 1980) which is shown in Figure I. This tendency justified the electron transfer from bendrofluazide is electrochemically unidirectional and termed as a totally irreversible process. Reinmuth (W.H, Reinmuth, 1960) was the first who reported this behaviour as totally irreversible. Equation 1 shows electrode reaction of bendrofluazide in these supporting electrolytes.



Work regarding stability of bendrofluazide on hydrolysis revealed the formation of formaldehydeK (Florey, 1976).

Quantitative Criteria for a Totally Irreversible System:

The shape of cyclic voltammograms of bendrofluazide in the above supporting electrolytes exhibited the current independence of sweep rates at the foot of the wave showing an intrinsically slow electron transfer process (see Figure I). To verify totally irreversible electron reaction, the reported diagnostic tests for such a system (R., Greef, 1985), was performed. Firstly, the value of r_p , in bendrofluazide is found to be proportional to the square root of scan rate (R., Greef, 1985, A., J., Bard, 1980, E., Gonzalez, 1990). This is illustrated in Figure 2. The anodic peak current i_{pa} increases linearly with the increase in sweep rate. A plot of $\log i_p$, vs. $\nu^{1/2}$ for each supporting electrolyte is given in Figure 3. Equations of the least square fitted lines for the dependence of i_{pa} on the square root of potential scan rate are given in Table II. Secondly, the anodic peak current is proportional to the concentration of bendrofluazide with in 3.4×10^{-5} - 10^{-6} M concentration range. This is shown in Figure 4. These criteria suggest diffusion as the rate limiting step (A.J. Bard., 1980, E. Gonzalez, 1990, R. S. Nicholson. 1964, A. M. Hartley. 1966). A test of electrochemical reversibility can be performed on the bases of different reported methods, such as the effect of sweep rate on the E_p and $E_{p/2}$ of CV wave, the consistency of the transfer coefficients β_n , calculated from various methods and the shape of the CV wave (R. J., Klinger, 1980, R. S. Nicholson, 1964 J. M., Saveant, 1978).

TRANSFER COEFFICIENTS β

Various reported methods like the magnitude of the slope in the plot of E_p or $E_{p/2}$, vs. $\log \nu$, E_p vs. $\log i_p$, and $E_p - E_{p/2}$ difference (which comes out from the width of a CV wave have been reported for the determination of transfer coefficients (R.J., Klinger, 1980, R. S. Nicholson, 1964 J.M. Saveant, 1978). These information are inferred from equations 2,3,4 and 5 respectively. For instance, the value of slope obtained from equations 2,3, and 4 ranges 0-30 mV per decade increase in scan rate represents a reversible reaction, whereas, higher slopes represent a totally irreversible process.

$$E_p = (2.3RT/2\beta_n F) \log \nu + B \quad (2)$$

$$E_p = (2.3 RT/2\beta_n F) \log \nu + B' \quad (3)$$

$$E_p = (2.3 RT/2\beta_n F) \log i_p + B'' \quad (4)$$

$$[E_p - E_{p/2}] = 1.857 (RT/(\beta_n F)) \quad (5)$$

where, B, B', and B'' are constants. The results for the evaluation of transfer coefficients from

above equations in the present work are given in Table-III which satisfy the criterion of a total irreversible electron transfer (R.J., Klingler, 1980). Moreover, the values of the slopes tabulated are 100 ± 40 mV from the above equations in the present work.

The Width of the CV Wave:

The difference $E_p - E_{p/2}$ from Table I is not constant and it varies from 40mV to 200 mV, which is against the established criterion for total irreversibility (A.J., Bard 1980 R.S. Nicholson 1964, H., Matsuda, 1955). The maximum value was obtained in case of acetic acid where bendrofluazide system behaved totally irreversible (Figure 1).

Consistency in the Values of Transfer Coefficients β_{nb} :

In general, the values of β_{nb} obtained using equations 2,3, and 4 are internally consistent. It has been a practice to regard the consistency of the values of β_{nb} obtained from equations 2,3,4 and 5 as an important criterion for a total irreversible electron transfer (R.I, Klingler, 1980). In the present work, as said earlier, equation 5 can not be normally used to evaluate β_{nb} as the difference $E_p - E_{p/2}$ is not constant over the range of potential scan rates (R.J., Klingler 1980). Since there is an internal consistency in the values of β_{nb} obtained from equation 2, 3, and 4, one feels encouraged to evaluate β_{nb} from equation 5 at each scan rate. This is in connection to provide a comparative view of the discrepancy that exists between the results from equation 5 and equations 2,3 and 4. The reason of this inconsistency is not known. It may be added here, that the surface of the carbon paste electrode was renewed before taking each CV run. Hence, aging of the electrode does not seem to be apparent. Similarly, the reported work has been performed at a mercury test electrode while determining β_{nb} values by the above equations for the diagnostic test. No information is available in the literature related to CV study at a carbon paste electrode. Neither, various effects have been reported at c.p.e. such as, the involvement of surface functional groups and interaction of impregnated material with the analyte which may contribute surface activity and alter the results from those criteria which are inferred from a diagnostic test when performed at Hg test electrode. However, this drawback of carbon paste electrode can be removed by improving the electrochemical response of the carbon paste electrode (R.C, Engstrom, 1984, W.J. Blaedel, 1974 G., Rivas, 1991, A., Duct, 1991, G. A., Rivas, 1994). The anodic oxidation of bendrofluazide does not seem to be a totally irreversible electron transfer process as given in equation 1. Another possibility is that the description of the reaction mechanism at the test electrode may not be simple, however, electrode reaction shown in equation I, may be chemically coupled one: followed by a fast chemical reaction (R., Greef, 1985). The present experimental conditions (the small cathodic potential and larger oxidation potential of bendrofluazide) do not allow to perform the diagnostic tests pertaining to coupled chemical reactions.

Effects of Successive Cyclic Scans:

The successive cycles of bendrofluazide in the solutions of KOH, NaOH, NH_4OH , HCl, CH_3COOH , LiCl, KCl, and NaCl recorded at a carbon paste electrode vs. Ag | AgCl reference electrode at 100mV/s scan rate are shown in Figure 5. A decrease in the peak current i_{pa} , as a result of successive cycling observed in these cyclic voltammograms. Earlier work correlated such behaviour to i) the depletion of an analyte at the CPE in an irreversible process causing such decrease (L.M. Santos, 1988), or ii) a chance of slow or weak adsorption or desorption of analyte at the surface of CPE (L.M., Santos 1988). The 1st reason is justifiable due to its unidirectional electron transfer process. Secondly, the detailed investigations were made pertaining to quantitative/qualitative adsorption of analyte at a carbon paste test electrode (LM. Santos, 1988).

Test for Adsorption of Analyte/Product at CPE:

To ensure adsorption effects, the diagnostic criteria of adsorption were taken into consideration (L. M., Santos, 1988, R. H., Wopschall, 1967) in bendrofluazide system. The shape of the single-scan or multi scan cyclic voltammograms as given in Figure 1 and 5 concludes no enhancement of peak current or an appearance of any pre-peak in addition to the anodic peak (Al, Bard, 1980, A.M., Hartely, 1996, W. Kemula, 1961). This shows that the adsorption of bendrofluazide or the product (may be a weak or strong) is not found at the carbon paste electrode. Tests regarding quantitative study of adsorption (R.H., Wopschall, 1976) were also confirmed like values of $i_p/C_0 \nu^{1/2}$ do not vary rapidly with the rate of potential scan. The value $i_p/C_0 \nu$ does not remain constant as the potential scan rate was increased. Similarly, in case of concentration dependence tests where the values of i_p/C_0 do not remain constant over the range of concentration. All these results are tabulated in Table IV. These findings showed strong evidence against the adsorption of analyte at the test electrode. However, the unidirectional electron transfer process has been reported to be the reason of such behaviour that is i_p decreases vs. rate of potential scan (L.M., Santos, 1988).

Dependence of Peak Currents on Square Root of Scan Rate:

The anodic current increases linearly with the square root of scan rate. A plot of i_{pa} vs. $\nu^{1/2}$ and $\log i_p$ vs. $\nu^{1/2}$ which is proportional in each supporting electrolyte with all scan rates at 25, 35 and 45°C are shown in Figure 3. Table V shows E_p shifts per decade increase in the scan rate for various supporting electrolytes (Martindle 1988, G. Sun, 1991, L. Chen, 1992).

E_p vs. $\log i_p$ and E_n vs. $\log \nu^{1/2}$

The CV profiles of bendrofluazide show a linear response between E_p and $\log i_p$. Similarly, the values of $E_{p/2}$ from the CV plotted vs. $\log \nu$ are also linear in nature. Figure 6 represents such behaviour for different supporting electrolytes.

Dependence of on Concentration and pH of Supporting Electrolyte:

The peak current increased by increasing pH of the supporting electrolytes at all scan rates and temperatures which is similar to the behaviour which has been reported earlier (J. Gardea, 1988, P., Hernarder 1987). The maximum response was found in KOH system while a minimum in CH_3COOH , suggesting that the solubility of the analyte plays a significant role in this regard.

Effect of Concentration of Supporting Electrolyte on E_p of CV Wave:

The peak potential decreased linearly as pH of the supporting electrolytes increased at all scan rates and temperatures. However, a maximum anodic potential was observed in case of low pH values in acetic acid (L.M., Santos, 1988). Such a trend suggests that the oxidation of bendrofluazide needs higher potentials due to its stability at low pH values (L.M., Santos, 1988). Figure 7 shows this response in various supporting electrolytes.

Determination of Heterogeneous Rate Constant:

The anodic oxidation of bendrofluazide exhibited a single wave as a totally irreversible electron transfer process which is purely an indication of the effect of electron transfer on the rate constant (W.H., Reinmuth, 1960). In a similar reported work, Klingler and Kochi (R.J., Klingler 1989), used the following equations to determine heterogeneous rate constant

$$K(E_p) = 2.18 [(D\beta_{nb} F v/RT)^{1/2}] \quad (6)$$

Where $k(E_p)$ and k_s are the rate constants for a heterogeneous electron transfer and rate constant at the CV peak potential respectively, while the value of k_s is

$$K_s = k(E_p) [\exp(-\beta_{nb} F/RT) (E-E_p)] \quad (7)$$

On combination, equation (6) and (7) yield equation (8)

$$K(E) = 2.18 [(D\beta F v/RT)^{1/2} \exp [(\beta_{nb} F/RT) (E-E_p)]]$$

which shows the dependence of rate constant of electron transfer process on potential in terms of CV parameters β and E_p (R.S. Nicholson, 1964). The values of $k(E)$ and k_s tabulated from above relations for CV study of bendrofluazide at a carbon paste test electrode are shown in Table VI.

Simulated CV Profiles of Bendrofluazide:

The absence of a reverse wave (cathodic wave) in the cyclic voltammograms of bendrofluazide in the above supporting electrolytes at different scan rates reveals that the concentration of electroactive species is not governed by the Nernst equation. In such a case, the use of transfer coefficients (β_{nb}) exhibits the entire shape of CV wave. Delahay (P. Delahay, 1993) was the first who pointed out this while correlating current dependence on the potentials. On the bases of equation 6 and diffusion laws, Nicholson and Shain (R.S. Nicholson, 1964) later reported this in an easy and general way by the equation 9.

$$i(t) = n FAC (\pi D b)^{1/2} (\chi bt) \quad (9)$$

where $b = (\beta_{nb} F v/RT)$. The current function (χbt) includes all the potential dependence when tabulated against different values of potentials for defining the entire shape of CV wave provided β_{nb} and rate of potential scan are to be known (A.J. Bard, 1980, R.S Nicholson, 1964). In case of bendrofluazide, the average value of β_{nb} was found to be 0.34 at 25°C when calculated by the above equations 2, 3 and 4. Because of the absence of a reverse wave for a totally irreversible process, it is not often to determine E° value which fixes the value of rate constant (R.S Nicholson, 1964). This makes an arduous task to evaluate the rate constants for such reactions. However, Klingler and Kochi (R.J. Klingler, 1984) have reported a simple method where, $(E-E_p)$ values have been used instead of $(E-E^\circ)$. The same method is applied in the present work and E_p was taken as 990, 1010, 1042, 1072, 1111, and 1146 mV vs. Ag | AgCl reference electrode. Figure 8 enlists the use of equation 9 in defining the entire shape of CV wave at different scan rates. The resultant simulated CV profiles (Figure 11) exactly match with the experimental cyclic voltarmnograms of bendrofluazide in the above supporting electrolytes (as shown in Figure 1 and 2). Such a comparison based on the excellent agreement between the experimental and calculated currents justifies that the rate expression for a totally irreversible electron transfer process which can be successfully applied to define the shape of the CV wave (even in case of a carbon paste test electrode).

Quantification of Bendrofluazide:

A liner dependence of peak current on the concentration of bendrofluazide found in the supporting electrolytes at all scan rates. Peak current is proportional to the concentration of bendrofluazide within $3.4 \times 10^{-4} - 1 \times 10^{-5} M$ which is shown in Figure 9. This linear behaviour reveals

that the diffusion is the rate limiting step in the electrode reaction (A.J., Bard, 1980, E., Gonzalez, 1990, A., Duct, 1991). The equations of least-square fitted lines (E. Gonzalez, 1990, G., Sun., 1991, L., Chen, 1992) for the dependence of i_{pa} on concentration of bendrofluazide are given in Table VII.

CONCLUSION

The present work comprises the cyclic voltammetry of bendrofluazide at a CPE vs. Ag | AgCl reference electrode in different aqueous systems. Various parameters like, E_p , $E_{p/2}$, β_{np} , and “ D ” were determined alongwith the heterogeneous rate constant $k(E)$ at 25°C. The shape of the CV wave was also drawn on the basis of reported simulation method. These calculated CV curves were almost superimposed on the experimental CV profiles in these supporting electrolytes. Quantitative study revealed that the present work provides a quantification method for bendrofluazide (3.4×10^{-4} to 10^{-5} M) concentration range.

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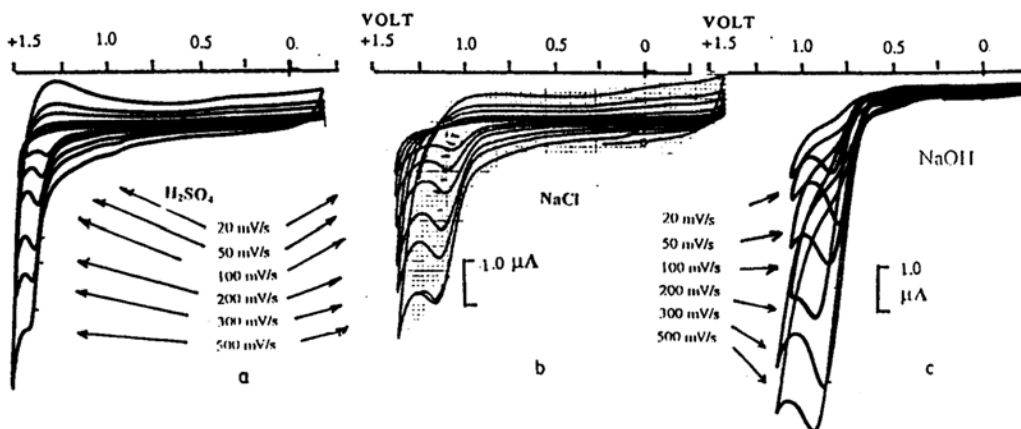


Figure 1: First-scan cyclic voltammograms of bendrofluazide (3.4×10^{-5} M) at a carbon paste electrode vs. Ag | AgCl reference electrode with different scan rates in various supporting electrolytes at 25°C.

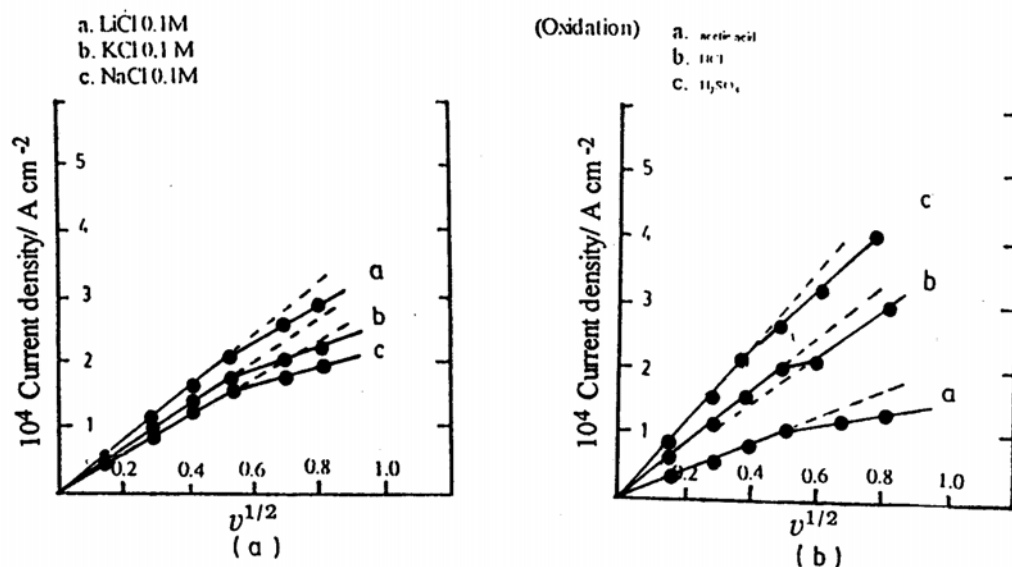


Figure 2: a) Variation of peak current i_p vs. square root of scan rate (a-d are LiCl, KCl and NaCl 0.1M).
b) Variation of log i_p vs. square root of scan rate (a-d are CH₃OOOH, HCl, and H₂SO₄ 0.01M) respectively.

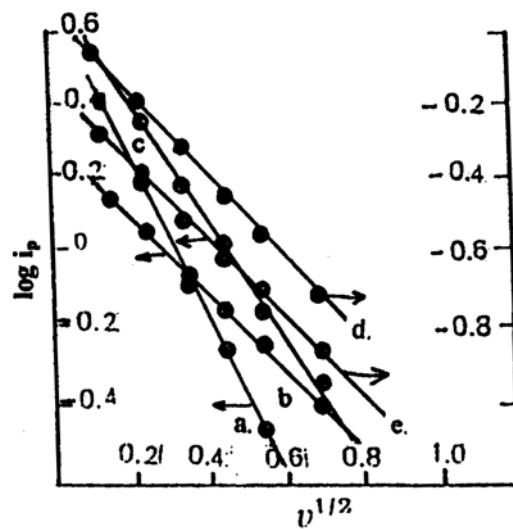


Figure 3: Variation of log i_p vs. square root of scan rate in a=NaCl, b=LiCl, c=H₂SO₄, d=NaOH and NH₄OH, e=KOH (0.01M each).

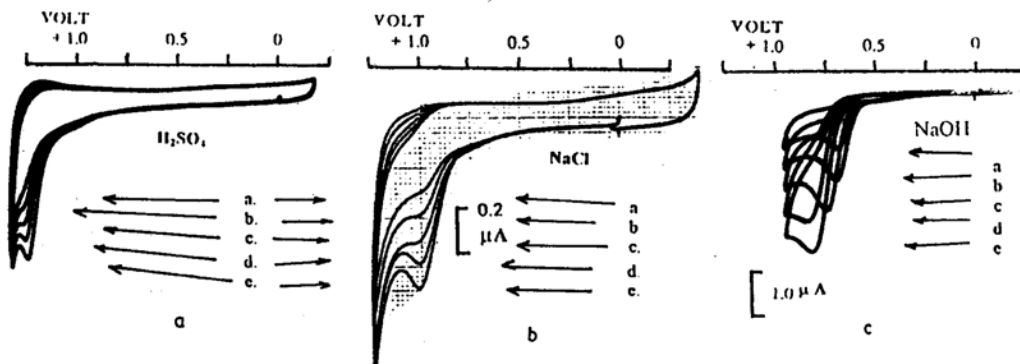


Figure 4: Variation of peak current vs. concentration of bendrofluazide $a=3.4 \times 10^{-5}\text{M}$ $b=0.8a$, $c=0.6a$, $d=0.4a$, $e=0.2a$ for calibration purpose at 100 mV/s at C.P.E.

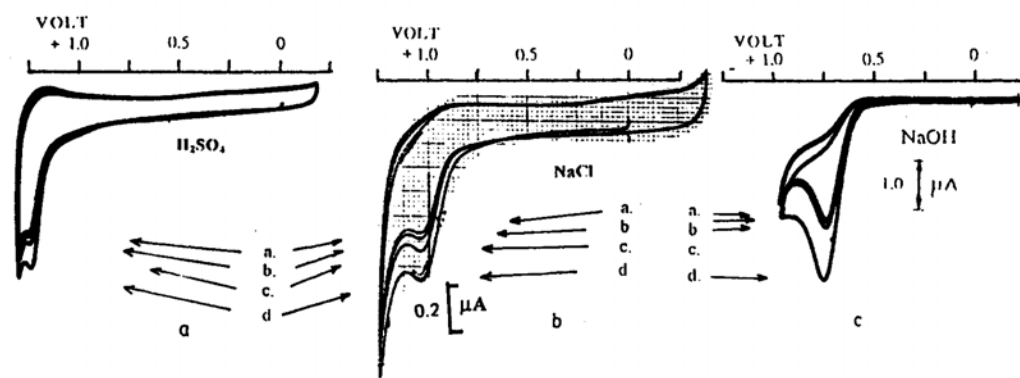


Figure 5: Repeated-scan cyclic voltammograms of bendrofluazide ($3.4 \times 10^{-5}\text{M}$) at a carbon paste electrode with 100 mV/s scan rates in various supporting electrolytes 25°C ($a=1^{\text{st}}$ cycle and $e=5^{\text{th}}$ cycle).

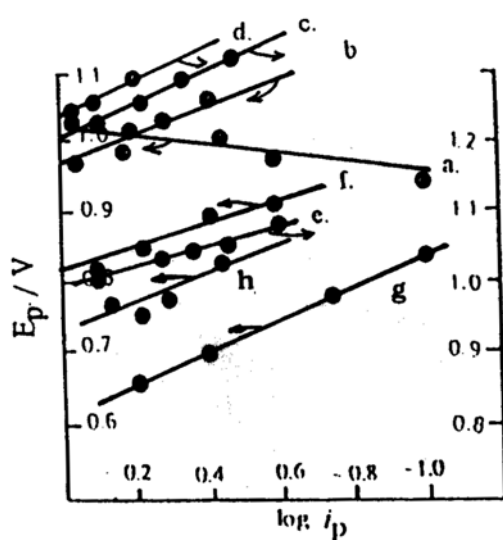


Fig. 6

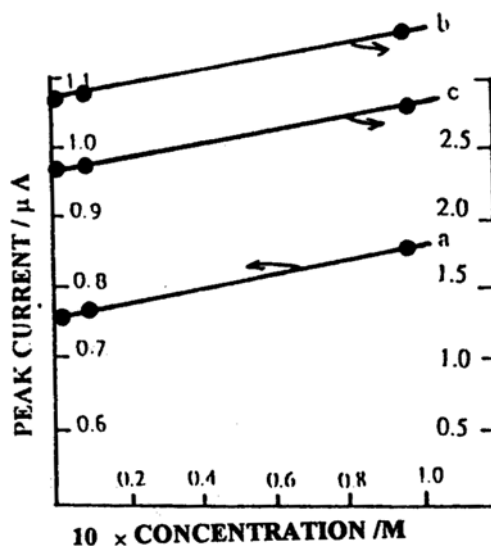


Fig. 7

Figure 6: a) The dependence of E_p on $\log i_p$ for the cyclic voltammograms of bendrofluazide ($3.4 \times 10^{-5} \text{ M}$) at a carbon paste electrode with 100 mV/s scan rates in various supporting electrolytes at 25°C (a=NaCl, b=LiCl, c=KCl, d= CH_3COOH and H_2SO_4 , e=HCl, f=NaOH and NH_4OH , g=KOH).

Figure 7: The dependence of peak current on the concentration of supporting electrolyte (a= CH_3COOH , b=NaOH, KOH, c= NH_4O).

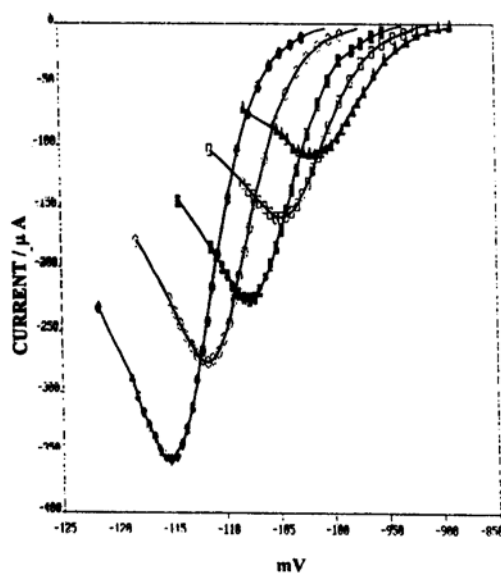


Figure 8: Calculated CV profiles for the bendrofluazide in 0.1M NaCl at a carbon paste electrode vs Ag | AgCl reference electrode at different scan rates keeping E_p at their experimental peak Potentials using Equation 9.

Table - II

The equations of the least-squares fitted lines for the dependence of peak currents on
i) the concentrations and ii) the square root of sweep rate (v)^{1/2} of
bendrofluazide with 100 mV/s sweep rate at 25°C

Supporting Electrolyte	pH	$y = mx + b$
KOH	12.6	$i_{pa} = (2.45 \pm 0.395) \times 10^{-2} C + (2.20 \pm 6.21) \times 10^{-7}$
KOH	11.7	$i_{pa} = (2.59 \pm 0.191) \times 10^{-2} C + (1.80 \pm 30.0) \times 10^{-8}$
KOH	10.7	$i_{pa} = (3.33 \pm 0.146) \times 10^{-2} C - (1.20 \pm 3.07) \times 10^{-7}$
NaOH	11.6	$i_{pa} = (2.72 \pm 30.351) \times 10^{-2} C + (1.04 \pm 2.76) \times 10^{-7}$
NaOH	10.5	$i_{pa} = (1.80 \pm 30.924) \times 10^{-2} C + (3.40 \pm 7.27) \times 10^{-7}$

Supporting Electrolyte	pH	$y = mx + b$
KOH	12.6	$i_p(\mu A) = (5.43 \pm 0.57) \times 10^{-1} v^{1/2} - (4.53 \pm 7.96) \times 10^{-1}$
KOH	11.7	$i_p(\mu A) = (4.38 \pm 0.495) \times 10^{-1} v^{1/2} + (4.21 \pm 6.91) \times 10^{-1}$
KOH	10.7	$i_p(\mu A) = (4.66 \pm 0.930) \times 10^{-1} v^{1/2} - (1.63 \pm 1.3) \times 10^{-1}$
NaOH	11.6	$i_p(\mu A) = (2.68 \pm 0.53) \times 10^{-1} v^{1/2} + (2.63 \pm 8.1) \times 10^{-1}$
NaOH	10.5	$i_p(\mu A) = (2.74 \pm 0.658) \times 10^{-1} v^{1/2} + (3.31 \pm 9.19) \times 10^{-1}$

Table-III
The values of β_{nb} by different methods for bendrofluazide [$2.37 \times 10^{-4} \text{M}$]
in KOH as supporting electrolyte at different pH and temperatures

Supporting Electrolyte	pH	Temp. °C	β_{nb} Values			
			$48(E_p - E_{p/2})^a$	E_p vs. $\log v^b$	$E_{p/2}$ vs. $\log v^c$	E_p vs. $\log ip^b$
KOH	12.6	25	0.57 ± 0.08	0.2 ± 0.01	0.27 ± 0.03	0.25 ± 0.02
KOH	11.7	25	0.56 ± 0.08	0.26 ± 0.03	0.33 ± 0.03	0.25 ± 0.01
KOH	10.7	25	0.60 ± 0.25	0.29 ± 0.02	0.29 ± 0.04	0.14 ± 0.02
NaOH	11.6	25	0.66 ± 0.26	0.29 ± 0.06	0.37 ± 0.06	0.25 ± 0.002
NaOH	10.5	25	0.73 ± 0.43	0.27 ± 0.01	0.74 ± 0.07	0.25 ± 0.03
NaOH	12.6	35	0.32 ± 0.05	0.13 ± 0.07	0.15 ± 0.03	0.09 ± 0.008
KOH	11.1	45	0.71 ± 0.34	0.27 ± 0.03	0.45 ± 0.09	0.32 ± 0.03
NaOH	11.0	45	0.52 ± 0.18	0.35 ± 0.05	0.42 ± 0.10	0.30 ± 0.05

a = Values obtained from equation (3.7)

b = Values obtained from equation (3.6)

c = Values obtained from equation (3.8)

d = Values obtained from equation (3.9)

Table - IV
The values of $i_p/(C_R \cdot v^{1/2})$, $i_p/(C_R \cdot v)$ from the cyclic voltammograms of bendro0uazide [$2.37 \times 10^{-4} \text{M}$] in KOH and NaOH as supporting electrolytes with different scan rates and pH at 25 and 35°C

Scan Rate mV/s	KOH at pH = 12.6 at 25°C		KOH at pH = 11.7 at 25°C	
	$i_p/C_R \cdot v^{1/2}$	$i_p/C_R \cdot v$	$i_p/C_R \cdot v^{1/2}$	$i_p/C_R \cdot v$
20	0.0537	0.38	0.067	0.46
50	0.064	0.287	0.064	0.286
100	0.057	0.206	0.058	0.21
200	0.072	0.16	0.065	0.15
300	0.070	0.13	0.062	0.11
500	0.068	0.096	0.060	0.08

Scan Rate mV/s	KOH at pH =10.7 at 25°C		NaOH at pH =12.1 at 35°C	
	$i_p/C_R \cdot v^{1/2}$	$i_p/C_R \cdot v$	$i_p/C_R \cdot v^{1/2}$	$i_p/C_R \cdot v$
20	0.095	0.675		
50	0.095	0.421		
100	0.077	0.278	0.0511	0.184
200	0.081	0.181	0.0589	0.132
300	0.076	0.139	0.059	0.109
500	0.069	0.098		

Table - V
The values of E_p shift per decade increase in scan rate for bendrofluazide
in different supporting electrolytes with different scan rates at 25°C

Scan Rate mV/s	KOH at pH =12.6		KOH at pH III =11.7	
	E _p /mV	E _p /mV shift ^a	E _p /mV	E _p /mV shift ^a
20	640 ± 10	140 ± 14.1	730 ± 10	100±14.1
50	700 ± 10		770 ± 10	
200	780 ± 10	140 ± 14.1	8340 ± 10	180±14.1
500	840 ± 10		950 ± 10	

Scan Rate mV/s	KOH at pH =10.7		KOH at pH =11.6	
	E _p /mV	E _p /mV shift ^a	E _p /mV	E _p /mV shift ^a
20	780 ± 10	120 ± 14.1	800 ± 10	110 ± 14.1
50	810 ± 10		850 ± 10	
200	900 ± 10	220 ± 14.1	910 ± 10	
500	1120 ± 10			

a = E_p shift per decade increase in scan rate.

Table – VI

The determination of heterogeneous rate constant ^a for electron transfer process of the oxidation of bendrofluzide in different supporting electrolytes with a carbon paste electrode at 25°C

Scan Rate mV/s	NaOH 0.01M			NH ₄ OH 0.01M		
	E _(P) /mV	k (E _P) x10 ³	k _(E) at E=700 mV	E _(P) /mV	k (E _P) ^b	k _(E) at E=700 mV
20	830	3.57	1.09x10 ⁻⁴	805	3.44 x10 ⁻³	2.51 x10 ⁻⁴
50	840	6.08	7.76 x10 ⁻⁵	775	5.44 x10 ⁻³	8.37 x10 ⁻⁵
100	850	7.99	1.42 x10 ⁻⁴	843	6.31 x10 ⁻³	5.75 x10 ⁻⁴
200	910	9.90	1.30 x10 ⁻⁴	886	9.23 x10 ⁻³	3.67 x10 ⁻⁴
300	980	10.1	1.79 x10 ⁻⁴	925	1.0 x10 ⁻²	4.27 x10 ⁻⁴
500	1030	12.5	1.59 x10 ⁻⁴	963	1.25 x10 ⁻²	3.86 x10 ⁻⁴

Scan Rate mV/s	KOH 0.01M			LiCl 0.1M		
	E _(P) /mV	k (E _P) ^b x10 ³	k _(E) at E=700 mV	E _(P) /mV	k (E _P) ^b	k _(E) at E=700 mV
20	825	3.57	1.24x10 ⁻⁴	1040	3.75 x10 ⁻³	6.31 x10 ⁻⁵
50	875	5.44	6.94 x10 ⁻⁵	1080	5.09 x10 ⁻³	1.12 x10 ⁻⁴
100	863	7.45	1.65 x10 ⁻⁴	1100	7.39 x10 ⁻³	8.37 x10 ⁻⁵
200	913	8.82	2.71 x10 ⁻⁴	1110	1.04 x10 ⁻²	8.14 x10 ⁻⁵
300	988	10.7	1.07 x10 ⁻⁴	1140	1.19 x10 ⁻²	1.05 x10 ⁻⁴
500	1010	13.1	1.50 x10 ⁻⁴	1170	1.54 x10 ⁻²	7.21 x10 ⁻⁵

Scan Rate mV/s	NaCl 0.1M			KCl 0.1M		
	E _(P) /mV	k (E _P) ^b x10 ³	k _(E) at E=900 mV	E _(P) /mV	k (E _P) ^b	k _(E) at E=1000 mV
20	1000	4.21	1.00x10 ⁻⁴	1110	3.07 x10 ⁻³	3.29 x10 ⁻⁴
50	1020	6.52	1.06 x10 ⁻⁴	1150	4.17 x10 ⁻³	2.85 x10 ⁻⁴
100	1050	8.39	9.90 x10 ⁻⁵	1160	6.94 x10 ⁻³	2.72 x10 ⁻⁴
200	1080	10.9	1.39 x10 ⁻⁴	1180	1.09 x10 ⁻²	1.39 x10 ⁻⁴
300	1090	12.0	2.41 x10 ⁻⁴	1200	1.25 x10 ⁻²	1.59 x10 ⁻⁴
500	1130	13.4	4.41 x10 ⁻⁴	1250	1.33 x10 ⁻²	3.28 x10 ⁻⁴

Scan Rate mV/s	CH ₃ COOH 0.01M			HCl 0.01M		
	E _(P) /mV	k (E _P) x10 ³	k _(E) at E=700 mV	E _(P) /mV	k (E _P)x10 ³	k _(E) at E=700 mV
20	1180	4.49	6.97x10 ⁻⁷	1180	5.04	4.44 x10 ⁻⁷
50	1200	7.04	2.08 x10 ⁻⁶	1230	6.66	1.48 x10 ⁻⁶
100	1210	9.72	2.32 x10 ⁻⁶	1250	8.60	3.92 x10 ⁻⁶
200	1240	14.9	2.01 x10 ⁻⁷	1260	14.1	2.45 x10 ⁻⁷
300	1260	14.9	4.52 x10 ⁻⁶	1290	14.6	2.68 x10 ⁻⁶
500	1280	21.7	3.21 x10 ⁻⁷	1300	20.1	7.73 x10 ⁻⁷

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