VOLTAMMETRIC INVESTIGATIONS OF IODIDE CATALYSED REDUCTION OF IODATE AND PERIODATE IONS ON GLASSY CARBON ELECTRODES IN 0.5M HClO4 MEDIUM

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In 0.5M HClO4 medium, KI exhibits two oxidation voltammetric peaks around 0.50V and 1.00V vs SCE on glassy carbon (GC) electrodes. The first wave corresponding to $I^-/\frac{1}{2} I_2$ couple is highly reversible. The second wave corresponding to $\frac{1}{2} I_2/IO^-$ couple shows quasireversible behaviour. KIO3 shows an irreversible diffusion controlled wave on GC electrode around 0.16V in the first cathodic sweep. In the subsequent sweeps the reduction process commences at about 0.30V itself. The fact that this is due to the I^- catalysis of IO_3^- reduction is confirmed by studying the effect of KI addition on this process. Such type of I^- catalysis is even more pronounced in the case of IO_4^- reduction. In this case the catalytic shift is as much as 0.47V. Possible causes for such I^- catalysis is also discussed.

Key words: Voltammetry, glassy carbon electrode, iodate, periodate

INTRODUCTION

Electrochemical reduction of IO_3^- and IO_4^- oxyanions have been investigated widely on Hg [1-3], Pt [4,5], In [6] and a number of other metal electrodes [7]. The effect of solvent supporting electrolyte systems [8] and pH of the medium [9] have also recieved some attention. A brief note on the electrochemical behaviour on glassy carbon (GC) electrode is also available [10]. Electrochemical oxidation of I^- on Pt [11], pyrolytic graphite [12,13] and GC electrodes [14] have also been investigated. A comprehensive review that covers the voltammetric studies of all iodides and oxyiodides is also available [15]. However, no report on the catalysis of iodate or periodate by I^- is reported. The present work was undertaken to investigate the voltammetric behaviour of iodate and periodate ions on GC electrode in detail. However some unexpected voltammetric responses were noticed that could be ascribed to I^- catalysed reduction of iodate and periodate ions. In this paper, this catalytic aspect is highlighted with sufficient voltammetric evidence.

EXPERIMENTAL

5 mm diameter GC disk fixed in a glass tube using epoxy resin was used as the working electrode. The electrode was thoroughly polished and electrochemically cleaned by the method developed earlier in this laboratory [16]. The electrode reproducibility was evaluated by CV curve for ferricynaide system in KCl medium [16].

All the chemicals used were of Analar grade. Triple distilled water was used for making up the solution. Other details regarding the cell, deaeration system and instrumentation are all reported in the earlier paper [16]. The potentials reported are with respect to saturated calomel electrode (SCE). All the experiments were carried out at 25 ± 1°C in 0.5M HClO4 medium.

RESULTS AND DISCUSSION

Voltammetric behaviour of KI

The CV behaviour of KI in 0.5M HClO4 on GC electrode is presented in Fig. 1. The anodic peak appears around 0.50V (Table I).
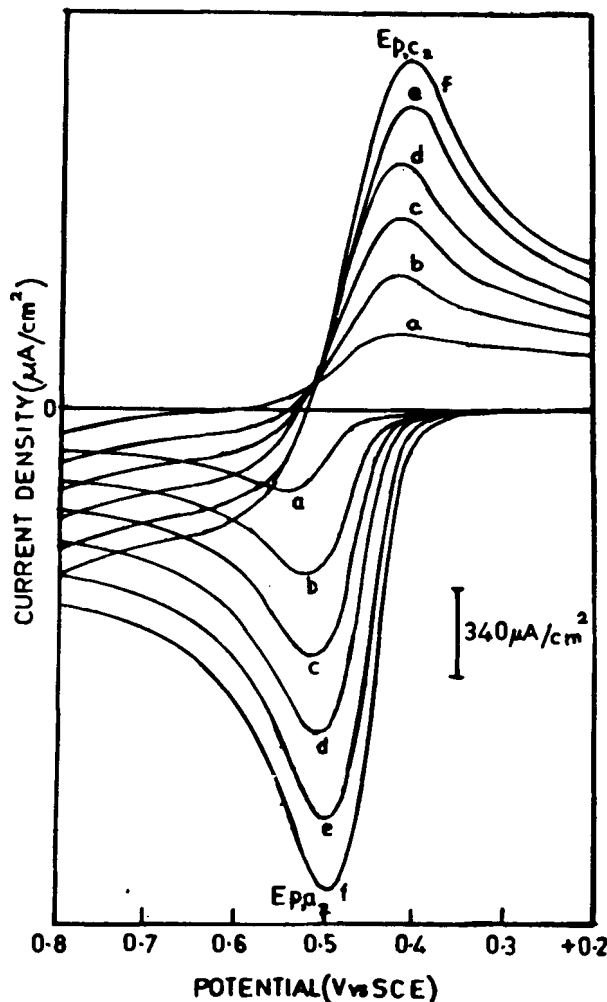

Fig. 1: CV behaviour of KI in 0.5M HClO4 on GC electrode at 40mV/sec. Concentrations in mM; (a-f) 1,2,3,4,5,6 respectively

No.	Compound	$E_{Pa,1}$	$E_{Pc,1}$	$E_{Pa,2}$	$E_{Pc,2}$	E_{Pcat}	$E_{Pc,3}$	$E_{Pc,4}$
1	KI	1.04	0.63	0.50	0.42	—	—	—
2	KIO₃	1.03	0.62	—	—	0.32	0.17	
3*	KIO₃+KI			—	—	0.29	0.16	
4	KIO₄	1.03	0.62	—	—	+0.07	—	0.40
5**	KIO₄+KI					+0.06		—0.41

TABLE-II: Peak potential characteristics of 2mM I⁻, IO₃⁻ and IO₄⁻ on glassy carbon electrode in 0.5M HClO₄ (volt vs SCE). Sweep rate = 20mV/sec

* Cathodic voltammograms from +0.35V as the starting point ** Cathodic voltammograms from 0.30V as the starting point

The peak current is found to increase linearly with concentration of KI and square root of sweep rate ($V^{1/2}$). The peak current constant value (iP/AC $\gamma^{1/2}$) is almost constant over a wide sweep rate and concentration range (Table II). On the reverse scan the

TABLE-II: Peak current characteristics of I⁻, IO₃⁻ and IO₄⁻ ions on glassy carbon electrode

| No	Ion	Wave	$I_P/CV^{1/2*}$
1	I⁻	$E_{Pa,1}$	280.0
2	I⁻	$E_{Pa,2}$	303.0
3	IO₃⁻	$E_{Pc,3}$	1308.0
4	IO₄⁻	$E_{Pc,4}$	769.0

* I_p in uA, C in mM,V in Volt/sec.

cathodic peak corresponding to this anodic peak is noticed around 0.42V. The peak separation value is around 100 mV.

All these observations agree with the view that this redox process corresponds to I⁻/I₂ redox couple.

$$\tfrac{1}{2} I_2 + e \rightleftharpoons I^- \qquad \ldots (1)$$

This is a quasireversible charge transfer process (Δ Ep is greater than 60 mV) and is diffusion controlled ultimately. The redox potential region also corresponds to the thermodynamic region suggested for this system.

If the cyclic voltammogram is recorded over a wider potential region a second oxidation wave is noticed for KI oxidation in the more anodic potential region (Fig. 2). This anodic wave (Ep, a) which occurs around 1 volt is also diffusion controlled and the peak current constant value again close to the value for the earlier oxidation wave. This oxidation process hence is obviously due to further oxidation of I₂ generated in the earlier process.

$$H^+ + HIO + e \rightleftharpoons 1/2\ I_2 + H_2O \qquad \ldots (2)$$
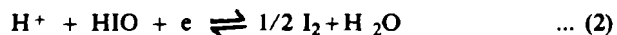
The HIO formed in this process is however more difficultly reduced on GC electrode. The peak potentials are separated by as much as 400 mV. This observation is in agreement with the general trend that oxyanions are more difficult to reduce with the increase in the number of oxygen coordination.

Voltammetric behaviour of KIO₃ with and without KI

Linear sweep voltammograms of KIO₃ in 0.5M HClO₄ are presented in Fig. 3. A single well defined voltammetric peak which
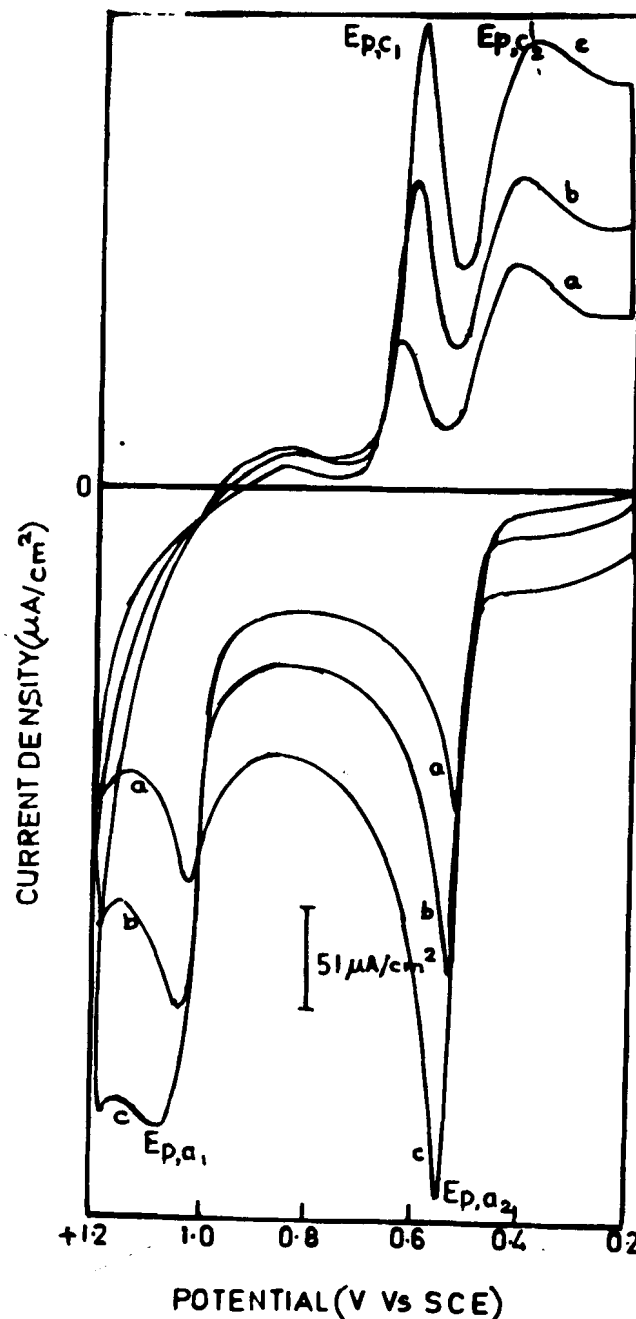

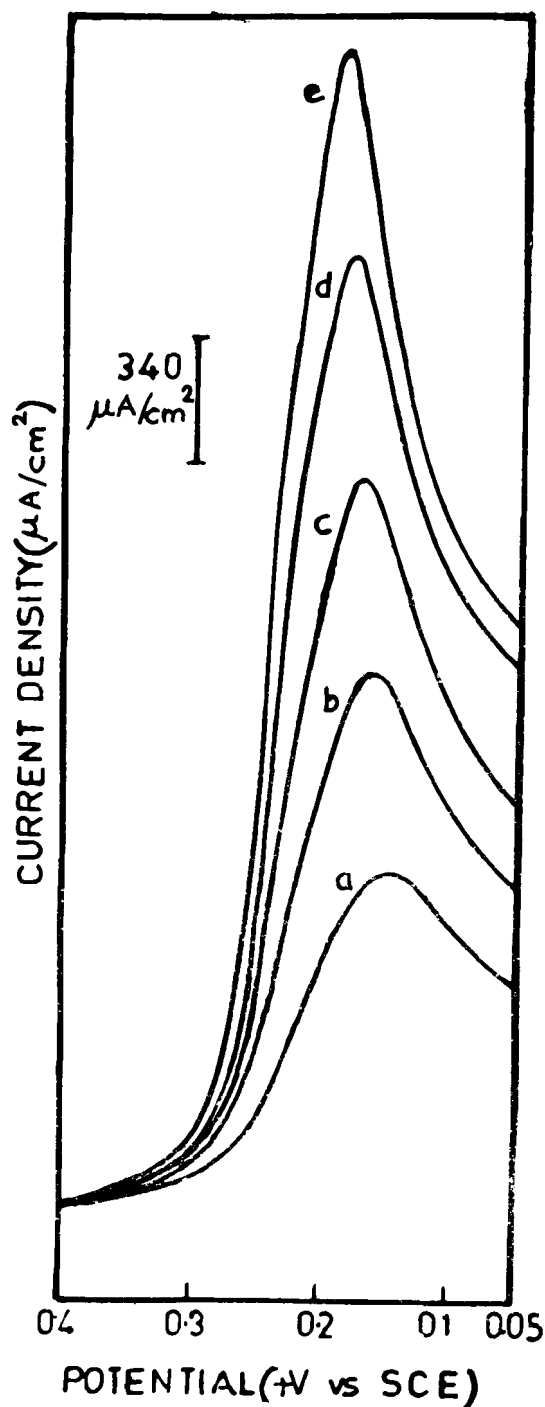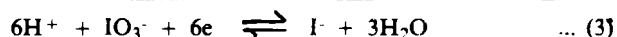Fig. 2: CV behaviour of 1mM KI in 0.5M HClO₄ on GC electrode sweep rates in mV/sec; (a) 20, (b) 40, (c) 80

$$6H^+ + IO_3^- + 6e \rightleftharpoons I^- + 3H_2O \qquad ... (3)$$

Although this is a six electron reduction wave the peak current constant value is only 4 times that of I-oxidation wave to I_2 (Table II). This is probably due to the local acidity variation near the electrode surface since each equivalent of IO_3^- requires six equivalents of protons for the complete reduction. It is reported that 5.0 M $HClO_4$ acid medium is required for completely eliminating this acidity effect.

The most interesting aspect of this study is the CV curves and multi-sweep CV curves of KIO_3 reduction on GC electrode, which is presented in Fig. 4. In the cathodic sweep the
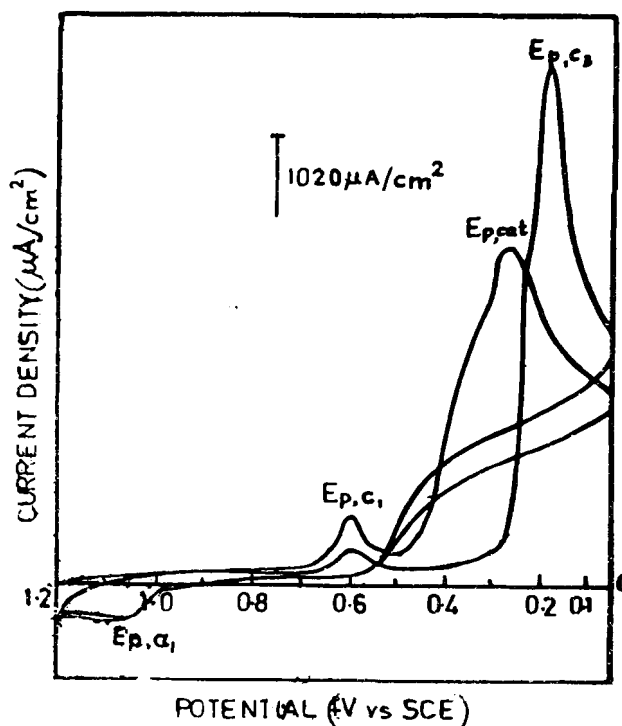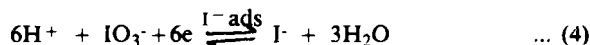

Fig. 4: Multisweep CV behaviour of 3mM KIO₃ in 0.5 M HClO₄ on GC electrode at 20 mV/sec

Fig.3: LSV behaviour of KIO₃ in 0.5M HClO₄ on G C electrode at 20mV/sec. Concentration in mM, (a) 1, (b) 1.5 (c) 2.0 (d) 2.5 (e) 3.0

IO_3^- reduction starts only at 0.17V whereas in the reverse sweep the IO_3^- reduction is noticed even upto 0.32V. In the second and all subsequent sweeps IO_3^- reduction starts around 0.32V itself. This multisweep experiment also indicates the presence of I^-/I_2 redox couple (see Epcl and Epal in Fig. 4) in the system on the reverse sweep and all subsequent sweeps. Linking up both these observations one may conclude that the presence of I^- ions on the electrode surface catalyses the reduction of IO_3^-.

is proportional to $C_{IO_3^-}$ and $V^{1/2}$ is again noticed. This reduction is due to the formation of I^- from IO_3^-.

$$6H^+ + IO_3^- + 6e \underset{\rightleftharpoons}{I^- \, ads} I^- + 3H_2O \qquad ... (4)$$

If adsorbed I^- is responsible for the catalytic behaviour observed above, external addition of small amount of KI along with

KIO₃ should result in the appearance of IO₃⁻ reduction peak around 0.32V in the first cathodic sweep itself. This is indeed found to be the case as shown in Fig.5. Addition of 0.2 mM KI to
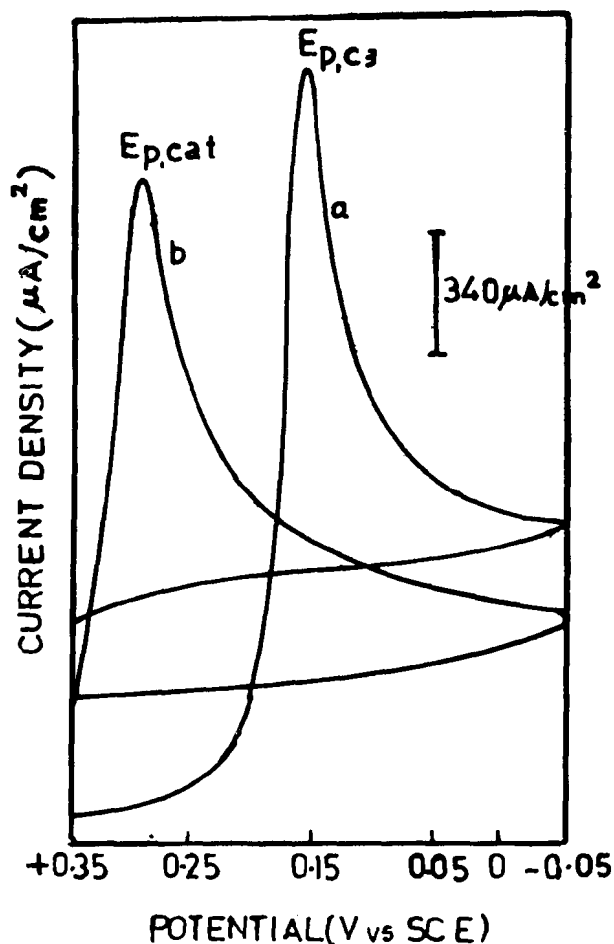

Fig.5: LSV behaviour of 2mM KIO₃ with and without KI in 0.5M HClO₄ acid on GC electrode at 20 mV/sec. Concentration of KI in mM (a) 0, (b) 0.2

KIO₃ itself results in the appearance of the catalytic shift in the IO₃⁻ reduction potential.

Voltammetric behaviour of KIO₄ with and without KI

The linear sweep voltammograms of 4mM KIO₄ at various sweep rates are presented in Fig. 6. The peak current is proportional to $V^{1/2}$ as well as the concentration of KIO₄. This reduction process may again be represented by the following expression:

$$8H^= + IO_4^- + 8e \rightleftharpoons I^- + 4H_2O \qquad ... (5)$$

The formation of I⁻ as the reaction product is again confirmed by the presence of I⁻/I₂ redox couple from the reverse sweep onwards (Fig. 7).
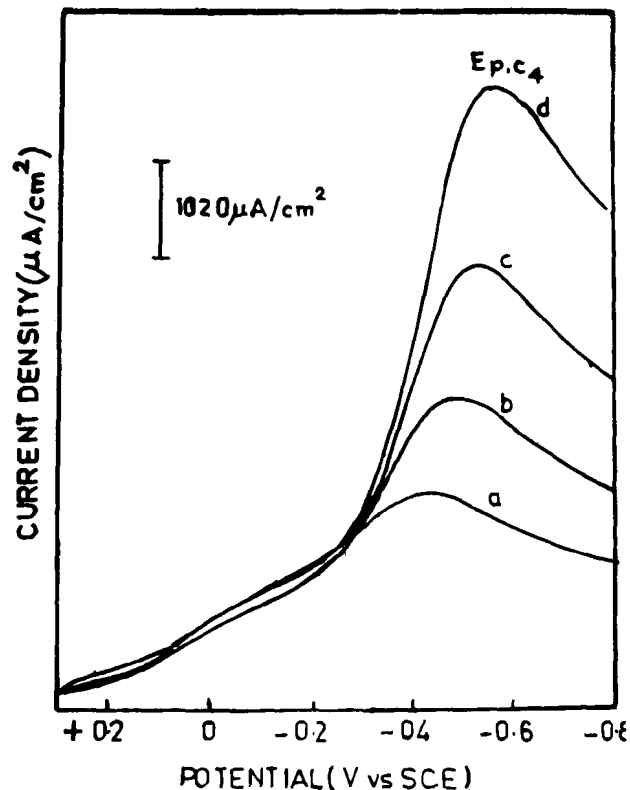

Fig. 6: LSV behaviour of 4 mM KIO₄ in 0.5M HClO₄ on GC electrode Sweep rate in mV/sec; (a) 20, (b)40, (c) 80, (d) 160
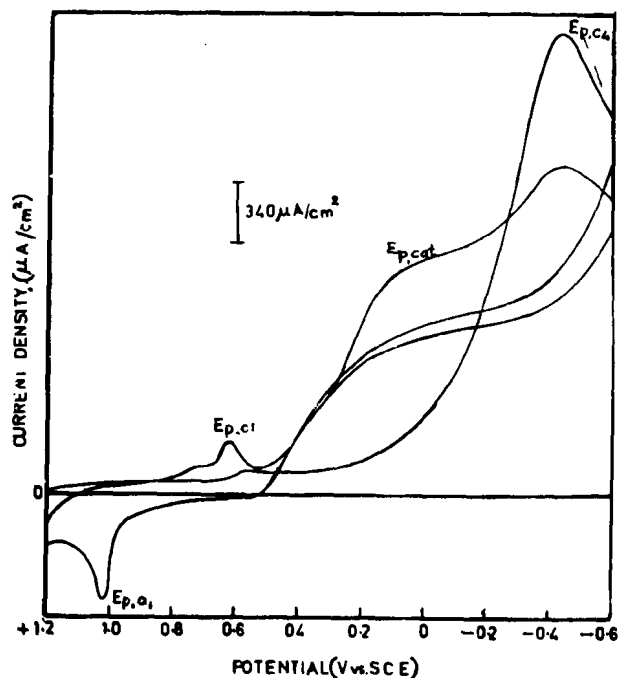

Fig. 7: Multisweep CV behaviour of 4mM KIO₄ in 0.5M HClO₄ on GC electrode at 20 mV/sec

The peak current constant value is again lower for an eight electron reduction process due to local acidity effects.

The multisweep experiment again indicates the catalysis of this process by I⁻ ions (Fig.7). The IO_4^- reduction starts at + 0.07 volt itself in the second and all subsequent cycles when compared to - 0.40V in the first sweep. This corresponds to a catalytic shift of 470mV.

The effect of addition of KI along with KIO_4 also had the same catalytic effect as shown in Fig.8. This again confirms that
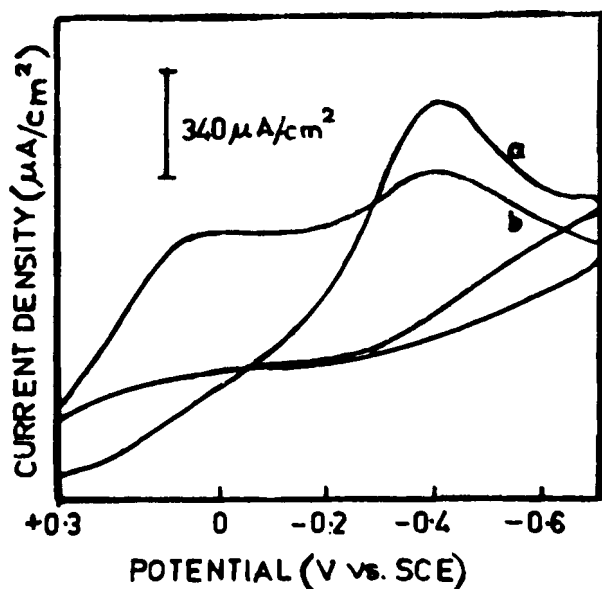

Fig. 8: LSV behaviour of 2mM KIO₄ with and without KI in 0.5 M HClO₄ on GC electrode at 20 mV/sec. Concentration of KI in mM (a) 0, (b) 0.2

adsorbed iodide catalyses the reduction of IO_4^- as well as IO_3^- ions. The catalytic effect is much more pronounced in the case of KIO_4 reduction.

CONCLUSIONS

The present voltammetric study clearly indicates the catalytic effect of I⁻ ions on the electroreduction of iodate as well as periodate ions. However it is really intriguing to notice a negatively charged ion catalysing the reduction of another negatively charged ion itself. Futher studies on the pH effects and other halide ion effects may throw some further light on this question. Further it may also be of interest to investigate whether this type of catalysis is specific to GC surfaces alone.

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