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Volumetric Study of Biologically Active Indole Derivatives in Aqueous and Micellar Media

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Abstract: Voltammetry study of some indole derivatives has been studied with particular reference to linear sweep voltammetry using pyrolytic graphite electrode in aqueous and micellar media. It was found that these types of compound i.e. 5-Hydroxy indoles can be determined in the concentration range 0 to 1.0 mM in aqueous medium. At higher concentration adsorption of these compound caused diminished peak current values. In presence of ionic and non-ionic surfactant i.e. Sodium Dodecyl Sulphate (SDS), Cetyl tri methyl ammonium bromide (CTAB) and Tween -40, the peak current values decreased and hence determination becomes difficult.

Keywords: Liner Sweep voltammetry, SDS, CTAB, Tween-40.

INTRODUCTION

Electro analytical techniques provide indispensable, versatile and significant potentialities to extend and deepen the understanding of physico-chemical aspects of biological changes undergoing in the living system. As all such biological system show redox reaction during metabolic transformations.
Some of the common features of biological electrochemical [1] reaction are:

a. The reaction occurs at same pH and temperature.
b. A specific orientation of the molecule is required for both type of processes to occur.

The electrochemical techniques have gained importance during recent years [2] Due to their pharmaceutical analysis i.e. quantitative and qualitative analysis of bio-organic compounds. An excellent review on application of voltammetry in pharmaceutical and toxicological analysis has also appeared in literature [3]. In view of these techniques, liner sweep voltammetry is used for the determination of indoles. In linear sweep voltammetry, when a stationary solid or liquid micro electrode is immersed in a quiet unstirred solution of electrospecies containing a large excess of supporting electrolyte, then a voltammogram can be obtained which would show a peak rather than a wave with a plateau.

The relation between peak current (ip) obtained in cyclic voltammograme and sweep rate [4, 5] can be given as-

$$ip = 2.687 \times 10^5 n^{3/2} AD^{1/2} CV^{1/2}$$

Where ip = Peak current (µA)
n= No. of electrons
A= Electrode Area (Cm^2)

C= Concentration of electroactive species (mili moles/ litre)

V= Scan Rate (volts/second)

Voltamogram is normally characterized by peak potential (Ep) and peak current (ip) for reversible electrode reaction:

For reduction reaction

$$Ep = E_{1/2} - \frac{0.0285}{n} \quad \text{(at 25° C)}$$

For oxidation reaction

$$Ep = E_{1/2} + \frac{0.0285}{n} \quad \text{(at 25° C)}$$

For irreversible electrode reaction

$$ip = 2.985 \times 10^5 n (\alpha n_a)^{1/2} AD^{1/2} CV^{1/2}$$

Where α = transfer coefficient

Then

$$Ep = E° - \frac{0.05915}{\alpha n a} [0.4565 + \log (\frac{\alpha\, na\, DV^{\frac{1}{2}}}{Ksh})]$$

Ksh = heterogeneous rate constant for electrode reaction is cm/sec.

Nicholson & shain [6] have solved theoretical equation for L.S.V. at stationary electrode under different condition of electrode reactions.

Indoles: Indoles, a six member heterocyclic compound found in biological system and play vital role in biological system. Indole derivatives represents many important classes of therapeutically agents in medicinal chemistry such as anticancer [7], antioxidant [8], antirheumatodial [9] and anti HIV [10, 11]. Some indole derivatives such as melatonin and serotonin, influence many important biological processes. They act as antioxidant and play an important role in immune system [12, 15]. Electrochemical behaviour of biologically

active indole was studied by Cigden Karaaslan and Sibel Suzen [16]. 5- Hydroxy indole indole are exacted in greatly enhanced quantities by the Patients with metastastasising characinoid tumours often in association characinoid tumours syndrome, which includes such features as diarroheacardiac vascular damage and fleshing attack of virus types. The syndrome has been found more marked when metastates are extensive [17]. A profile of oxidation chemistry of 5- Hydroxy indole under biometric condition was separated by Napolitano *et al* [18].

The present paper reports the voltammetry studies of 5-Hydroxy indole in aqueou micellear media by using linear sweep voltammetry.

EXPERIMENTAL SECTION

Material and Methods: 5-Hydroxy indole were obtained from Sigma, USA and were used as received. Sodium dodecyl sulphate (SDS), Cetyl trimethyl bromide (CTAB) abd Tween-40 were obtained from Aldrich Chemical Company, USA. Phosphate buffer solutions were prepared by the method reported in literature [19]. Linear sweep voltammetry was carried out using a sweep generator attached with Omni scribed 2000 recorder. A three system electrode was employed using saturated calomel electrode (SCE) as reference, platinum as counter and poly graphite electrode (PGE) as working electrode.

Procedure for studies in aqueous medium: A stock solution of 5- Hydrorey indole (1mM) was prepared in double distilled water. The solution for recording linear sweep studies in aqueous medium were prepared by mixing 2.0 ml of the stock solution with 2.0 ml buffer solution (pH=7.0).So that the overall ionic strength of solution become 0.5M. Nitrogen was bubbled in the solution for 8-10 min before recording voltamograms. As the electrode surface was cleaned for each run. The peak current values showed a variation of ±10.1%. Hence for determining the peak current values an average of at least three runs was taken.

Procedure for studies in micellar medium: Same procedure was adopted for linear sweep studies in presence of ionic and non-ionic surfactant as above in aqueous medium. The stock solution of compound (1.0mM) was prepared in double distilled water. The solutions of ionic & non-ionic surfactant were prepared in phosphate buffers of desired pH. The stock solution (1 ml) was then mixed with 2.5 ml of buffer solution and appropriate surfactant volume of concentration. The linear sweep volommograms were then recorded at sweep rate of $20mvs^{-1}$

RESULT AND DISCUSSION

(A) Voltammetry behaviour of 5-Hydroxy indole in aqueous and micellar media: L.S.V of 5-Hydroxy indole in aqueous and different surfactants were carried out at sweep rate 20 mvs^{-1} using phosphate buffers (0.5M) of different pH. LSV of 5- Hydroxy indole exhibits one anodic peak in aqueous medium and was found to be dependent on pH. The dependence of peak current on pH can be given as-

$$Ep\ (pH\ 2.0\text{-}11.0) = [0.590\text{-}0.061pH]\ V\ vs.\ SCE$$

LSV of 5-HI in micellar medium also exhibit one anodic peak in all surfactant. The peak current was dependent on pH in each surfactant and shifted towards less positive potentials with increase in pH. The dependence of peak current on pH in Tween-40 can be given as-

Ep (pH 2.0-7.0) = [0.735 -0.047pH] V vs. SCE

Ep (pH 7.0-11.0) = [0.405 -0.007pH] V vs. SCE

Ep Vs. pH plot clearly shows a break around pH7.0, which indicate the pH of 5-HI in Tween-40 at pH 7.0. In CTAB medium, LSV of 5-HI exhibit one anodic peak Ia. The peak current was dependent on pH shifted to less positive potentials with increase in pH.

Ep (pH 2.0-7.0) = [0.660 -0.035pH] V vs. SCE

Ep (pH 7.0-11.0) = [0.535 -0.018pH] V vs. SCE

In SDS, the oxidation behaviour of 5-HI was slightly different. The peak current Ia was dependent on pH and the Ep Vs pH show was straight line (**Figure-1**)

Ep (pH 2.0-11.0) = [0.640 -0.033pH] V vs. SCE

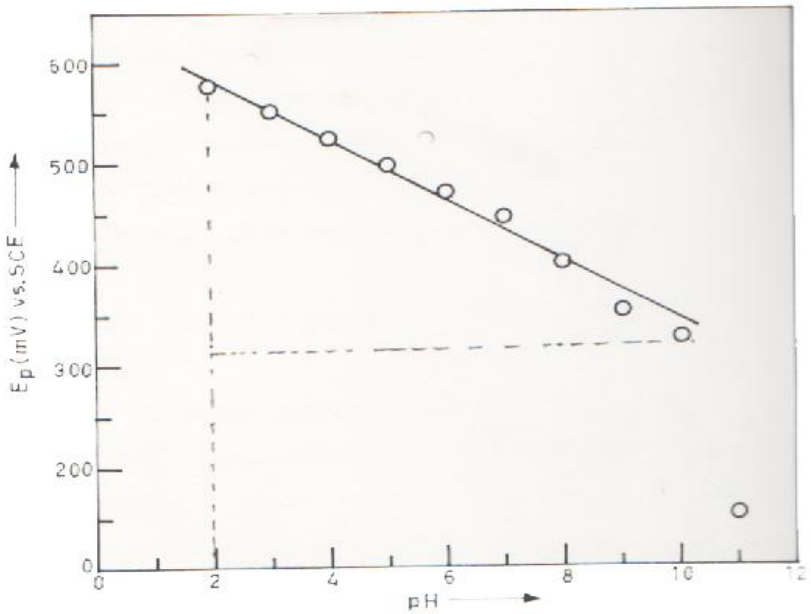

Figure 1: Dependence of E_p on pH for 5- Hydroxyindole in presence of SDS.

(B) Determination on of 5-Hydroxy indole: LSV was used to determine the 5-HI at pyrolytic electrode in phosphate buffer medium (μ=0.5M) at pH 7.0. Initially voltamogram were recorded for different concentration of 5- HI at sweep rate of 20 mvs^{-1}. Each voltamogram exhibit a single well defined oxidation peak (Ia). The peak potential of oxidation peak varied in range 225-275 mv. The peak current vs. surfactant concentration Plot for 5-HI was found to be linear in concentration range 0.5 to 10 mM. A typical plot of 5-HI for various concentration of SDS is shown as- (**Figure 2** & **3A-3B**). It has been clearly seen that ip values decreased with increase in concentration of SDS. So miceller media play a significant role on peak current of 5-HI. For determining 5-HI in miceller media, It is essential that the concentration of SDS. Tween-40 or CTAB should be kept constant. The peak current vs. concentration of 5-HI is absence of surfactant is given as- (**Figure 4**).

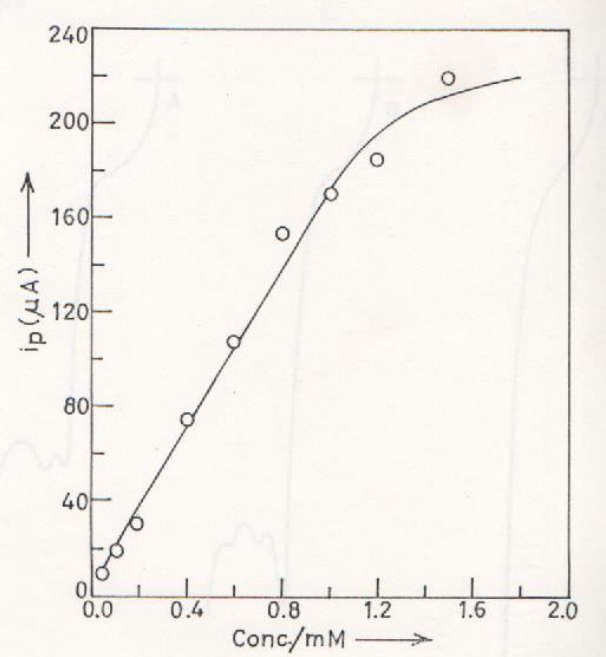

Figure 2: Peak current Vs concentration relation observed for 5- Hydroxyindole.

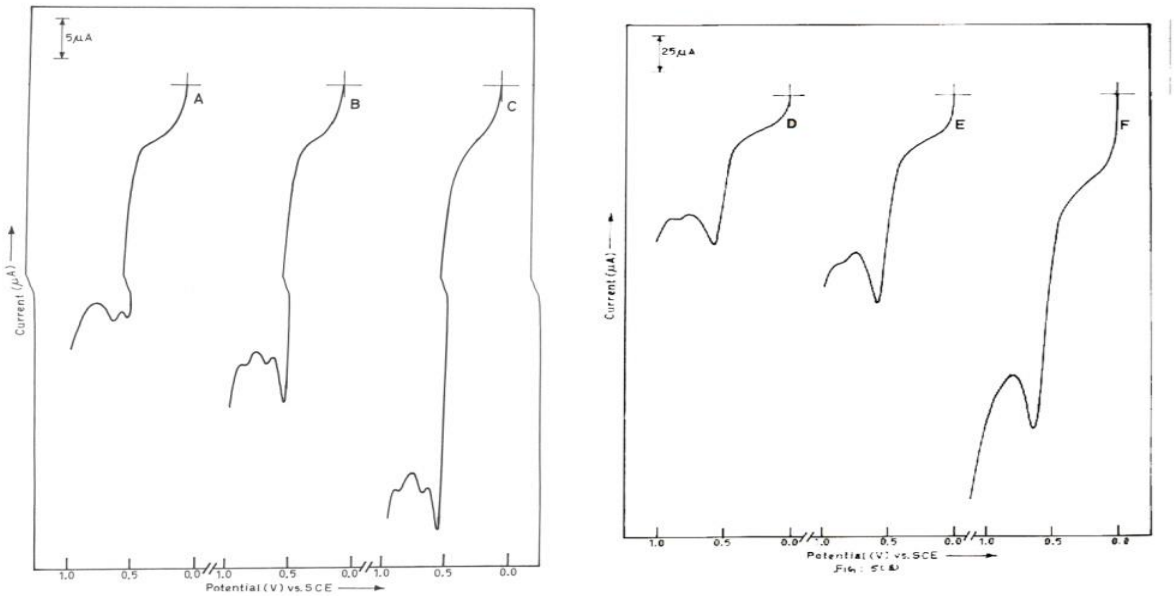

Figure 3: (A & B) linear sweep voltammograms for 5 Hydroxyindole in 2mM SDS. Curves A to F are recorded at 10, 20, 50, 100, 200 and 400 mVs^{-1} sweep rate.

The behaviour of plot suggests that 5-HI is absorbed at electrode surface and hence the determination of 5-HI is possible only up to 1.0mM. An attempt was also done that the studies were carried out at different sweep rates in various surfactants to moniter the nature of oxidation peak. It was observed that E_P and i_P value change significantly with increase in sweep rate. The results of sweep rates studies in different surfactant are given in **Table-1**.

S. No.	S.R. (mVs^{-1})	Aqueous		SDS		CTAB		Tween-40	
		E_p(mV)	i_p(µA)	E_p(mV)	i_p(µA)	E_p(mV)	i_p(µA)	E_p(mV)	i_p(µA)
1.	10	325	27	175	36.1	250	16	225	10.2
2.	20	350	37	200	72.6	275	46	225	11.3
3.	50	375	68	225	81	375	35	300	154
4.	100	400	116	250	81	225	55.8	300	41
5.	200	425	181	275	137	250	82.5	350	39
6.	400	475	152	285	154	250	106	375	50
7.	600	500	307	315	208	325	97	375	58
8.	800	525	395	350	208	350	141	375	116

At pH = 7.0, µ = 0.25 M, S.R. effect in aqueous medium and all three Surfactant (2 mM) of compound 5-Hydroxy indole (0.5 mM)

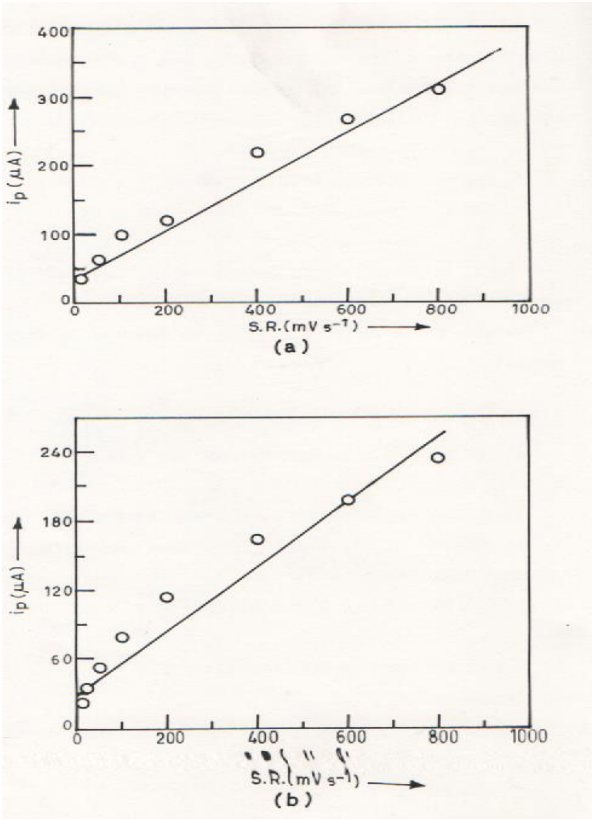

Figure 4: A comparison of i_p and sweep rate relation for 5- Hy droxyindole in aqueous (A) and 2 mM CTAB medium (b).

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