Ethanol Electro-Oxidation In Presence Of Surfactant Environment

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Abstract: Ethanol electro-oxidations on to platinum surface have been reported in surfactant environment. Analysis of the cyclicvoltammtry results shows that ethanol (EtOH) solution containing surfactants show a remarkable depression of all the peak current as compared to only ethanol solution. It is observed that in the presence of SDS (sodium dodecyl sulfate) the oxidation current of EtOH is reduced to a small extent but it is reduced to a large extent in the presence of CTAB (cetyl trimethyl ammonium bromide). Again, it is revealed from the study that both oxidation potential and the peak current are function of surfactant concentration.
**Keywords :** Ethanol-oxidation, Surfactant, Cyclic voltammetry, Diffusion coefficient, Deprotonation.

INTRODUCTION

Direct alcohol fuel cells (DAFCs) attract attention as power sources in numerous applications at low operating temperature [1]. Different types of alcohols can be used in DAFC. Electro-oxidation of long chain carbon atom alcohols involves more intermediates and products than that of methanol electro-oxidation and thus more efficient electro-catalysts are needed at low temperature. Platinum is the best choice as an electro-catalyst for alcohol fuel cell.

The electro-oxidation kinetics of organic molecules is of fundamental importance in electrocatalysis, and is also a vital factor in the application of the oxidation as anodic process in direct fuel cells. Mechanism of alcohol electro-oxidation on to platinum surface has been studied widely for long time. Many mechanisms for alcohol oxidation have been proposed form time to time [2-4]. Although a breakthrough in the understanding of the ethanol electro oxidation mechanism was obtained by techniques like in situ infrared reflectance spectroscopy, in situ IR reflection-absorption spectroscopy, in situ surface-enhanced IR absorption spectroscopy etc [5-6]. Among the published mechanisms the work of Lamy etal is interesting. They suggested that ethanol electro-oxidation involves parallel and consecutive reactions, as follows

$$C_2H_5OH \xrightarrow{\ H_2O\ } CH_3COOH + 4H^+ + 4e^-$$
…………………….. (1)

$$C_2H_5OH \longrightarrow CH_3CHO + 2H^+ + 2e^-$$
……………………(2)
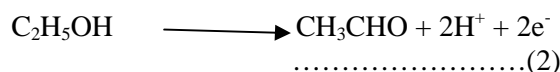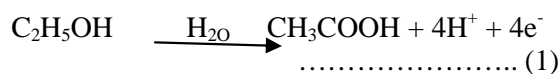
Reaction 1 occurs mainly at higher electrode potential and reaction 2 occurs at low electrode potential. It is seen that in both cases deprotonation occurs. Simulation study also shows that the formation of acetaldehyde through the oxidation of bulk ethanol is the rate determining step between 0.6 and 0.75 V vs. RHE. After 0.75 V vs. RHE, the formation of surface acetate through bulk ethanol becomes the rate determining step [4].

Since ethanol electro-oxidation occurs through different pathways on different catalytic surfaces, it is very difficult to elucidate the mechanism of ethanol electro-oxidation than methanol. In a recent study of ethanol electro-oxidation on Pt thin film

electrode using in-situ ATRSEIRAS, it is seen that most of adsorbed acetate comes from the direct oxidation of ethanol via a four electron pathway [6]. Thus it is seen that electro-oxidation of EtOH occurs via an initial adsorption onto the anode surface followed by deprotonation.

In the present study, we like to add more light on the proposed mechanism using cationic and anionic surfactant as probe molecules. It is expected that in surfactant medium the diffusion of alcohol molecules will be sluggish. Again cationic and anionic surfactants are expected to behave oppositely towards deprotonation step. It should be mentioned that electrode kinetic studies for large number reactions using surfactant have been reported earlier [7-9]. In almost all the cases it has been found that surfactants can markedly affect the redox reactions on the electrode surface. These may be due to i)changing the double layer structure ii) changing the rate of electron transfer by both acceleration or inhibition iii) changing the E1/2 value of an electro active species. It is expected that the present study will help understanding the mechanism of EtOH oxidation.

EXPERIMENTAL

Sulfuric acid (Merck), cetyl trimethyl ammonium bromide, CTAB (Aldrich) and sodium dodecyl sulfate, SDS (Himedia Lab.Limited, Mumbai) were used as supplied. EtOH (Bengal chemicals) was distilled under nitrogen atmosphere. A three electrode set up was constructed for this study,

where bare Pt foil was the working electrode, the counter electrode was the Pt foil, while a saturated calomel electrode (SCE) served as reference electrode .The supporting electrolyte was 1M H_2SO_4 solution. For surfactants, the concentration below and above CMC were investigated. The ethanol oxidation was measured by cyclic voltammetry in the potential window -0.2V to 1.2 V at different scan rates. All the experiments were carried out at room temperature, 25^oC. Electrochemical measurements were performed using a Potentiostat-galvanostat (VersaStat[TM] II, Princeton Applied Research).

RESULTS AND DISCUSSION

Figure 1 represents the cyclic voltammograms of EtOH in 1M H_2SO_4 medium at 30 mVs^{-1} scan rate in the presence of different surfactants. Cyclicvoltammogram of pure ethanol solution shows that three oxidation peaks are observed at about 0.7V and at about 1.07V in the forward scan and in the cathodic sweep only one anodic peak (at about 0.4 V) is observed and this is attributed to renewed oxidation of the fuel. For the electro-oxidation of EtOH on Pt, the occurrence of two peaks on the anodic scan can be ascribed to the oxidation of the fuel by two kinds of chemisorbed oxygen species. In the region of first peak, a surface layer of Pt-OH is first formed on Pt and this is subsequently transformed in to a Pt-O layer at higher electrode potential.
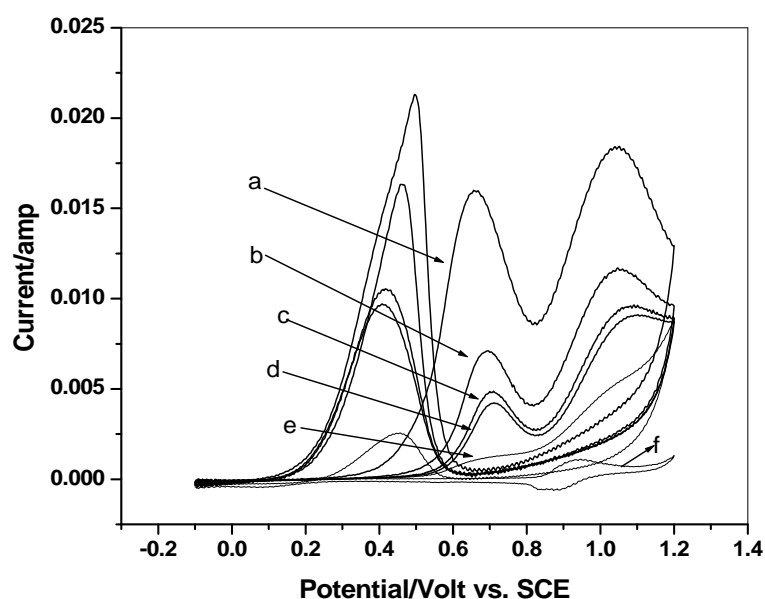

Figure 1. EtOH oxidation in surfactant environment (a) pure ethanol solution (b) in 3 mM SDS(c) in 8.1mM SDS (d) in 11mM SDS (e) in 0.2mM CTAB (f) in .95mM CTAB.

From the figure, it is seen that in the presence of SDS the oxidation current of EtOH i.e. Ip is reduced to a small extent but it is reduced to a large extent in the presence of CTAB (cationic surfactant) . But E_p values change to a small extent in both the surfactants. It is also observed that E_p (peak potential) and I_p(peak current) both are function of SDS concentration (figure 2 and figure 3) Above the CMC, the oxidation rate still decreases for the anionic surfactant systems, which was not observed for the cationic one and at high concentration of CTAB, the voltammograms are entirely changed and is due to the bromide oxidation.
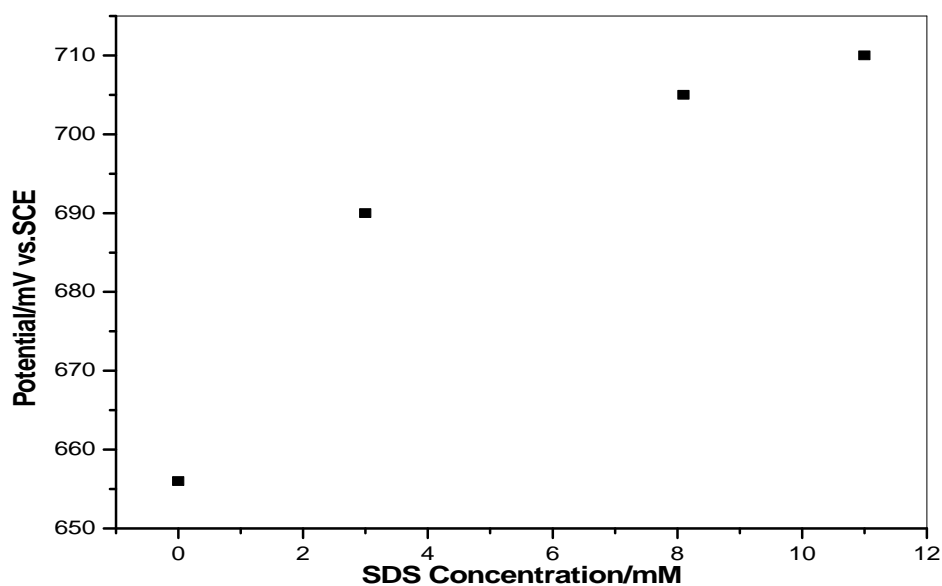

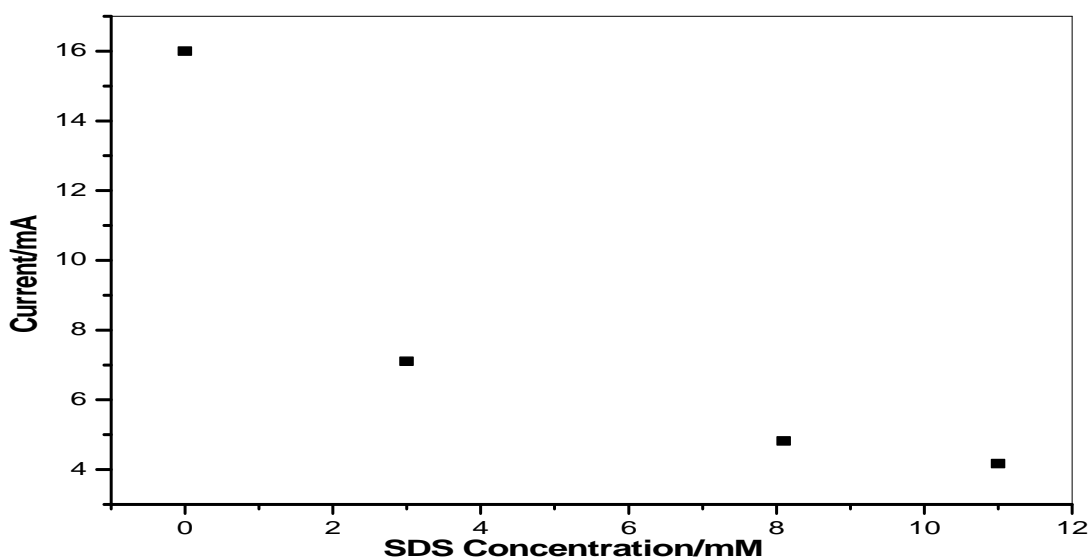**Figure 2. Variation of peak potential with SDS concentration.**

Figure 3. Variation of peak current with SDS concentration.

We assumed that the deportation step is the rate determining step. The cationic and anionic surfactants behave oppositely towards the de protonation step. SDS accelerates the deprotonation of ethanol but CTAB retards the deprotonation. The positively charged CTAB layer retards the deprotonation at the electrode surface via electrostatic repulsion. The negatively charged layers of SDS may favor the accumulation of H^+ ion near the electrode because of electrostatic interaction. The observed behaviors of two surfactants established the earlier proposed rate determining step of oxidation of ethanol. To understand the role of surfactant in the ethanol electro oxidation, we calculated the apparent diffusion coefficients for these systems. The apparent diffusion coefficient D has been calculated from the following equation [7-8]

$$Ip = 2.985*10^5 \, n \, (\, n\,)^{-1/2} \, A \, D^{1/2} \, C \, V^{1/2} \qquad (3)$$

Where Ip_a is the anodic peak current (mA), n is the number of electrons involved in the oxidation, A is the area of electrode (cm^2), V is the scan rate ($V.s^{-1}$), C is the concentration of the electro active species in bulk solution (mol cm^{-3}), and n have been calculated using the relation

$$n = 47.4/ (Ep_a - Ep_{a/2})$$

Above Ep_a is the oxidation peak potential (mV) and $Ep_{a/2}$ is the potential at which the current equals one half of the peak current.

Plots of the anodic peak currents (considering only 1st peak) of ethanol oxidation (Ip) versus scan rates ($V^{1/2}$) ranging from 20 to 100 $mV.s^{-1}$ gave good straight lines in accordance with equation 1 (in figure 4), from which the apparent diffusion coefficients were calculated and plotted in figure 5.
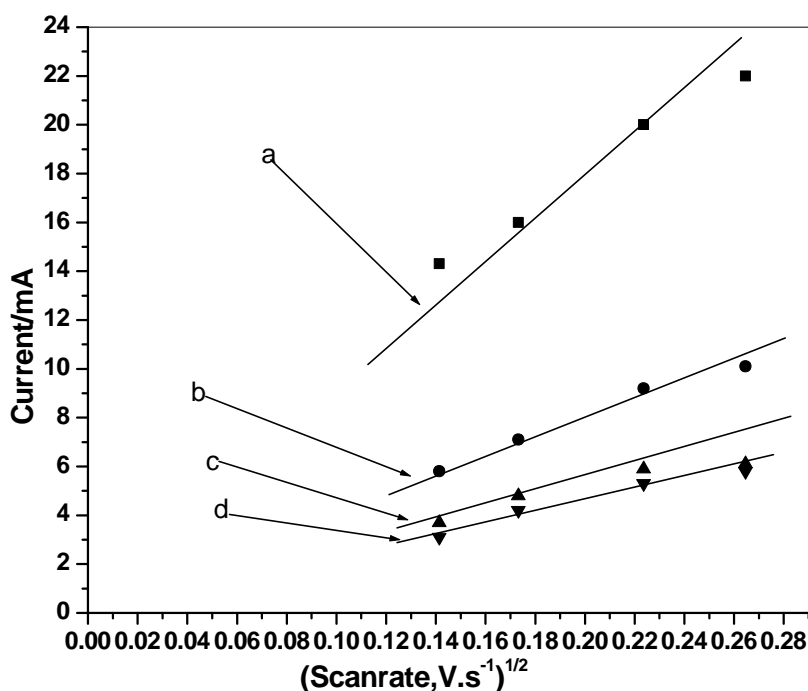

Figure 4. Scan rate dependence of the anodic peak current for (a) only EtOH (b) in 3mM SDS (c) in 8.1mM SDS (d) in 11 mM SDS solution.
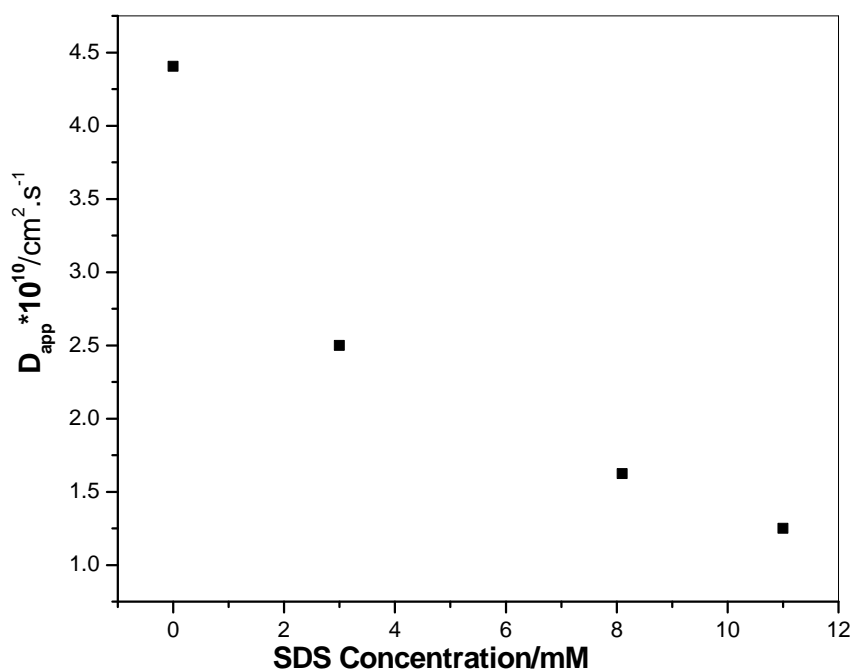
Figure 5. Variation of diffusion coefficient with SDS concentration.

The cyclic voltammograms of ethanol solution containing SDS show a remarkable depression of all the peak current as compared to only ethanol solution. These observations may be explained by changes of the diffusion coefficients (D) of the electro active species. The apparent diffusion coefficient value (D_{app}) value is a measurement of the charge transport rate within the liquid film near the electrode surface. In our case, the value of D_{app} is in the order of 10^{-10} $cm^2.s^{-1}$. The apparent diffusion coefficient decreases with the increase of surfactant concentration (figure 4). This may be due to the fact that the surfactant molecules are adsorbed on the electrode surface and simply serves as a wall to prevent the EtOH molecules for elctrodic reaction.

At the same time, the growing thickness of adsorption layer moves the plane of electron transfer away from the electrode surface. The diffusion of electroactive substance i.e, EtOH through the compact adsorbed layer of surfactant is much slower and this leads to the increase of the oxidation potential

CONCLUSION

A general conclusion emerging from our investigation is that the deprotonation is the vital step for the ethanol oxidation. It is also seen that the deprotonation of ethanol is much facile in SDS environment compared to CTAB. The positively charged CTAB layer retards the de protonation and the negatively charged layers of SDS may favor the accumulation of H^+. It is also observed from the study that the values of diffusion coefficients are gradually decreases with increasing SDS. Thus the surfactant molecules control the diffusion of ethanol molecules towards the electrode, which leads to decrease the rate of ethanol oxidation.

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