Effect of film charge on the mid-point potential of encapsulated ferrocene

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Received 17 November 2003; revised 5 May 2004

Neutral surfactant film shifts cathodically the mid-point potential of ferrocene by 150 mV compared to organic solvent. Film with negative charge makes a further cathodic shift in mid-point potential of 50 mV. On the other hand, when the film has positive charge there is about 35 mV anodic shift in mid-point potential compared to neutral film. The nature of charge of the film can vary the mid-point potential of ferrocene over a range of 75 mV.

IPC Code: Int. Cl. C7, C25

Self Assembled Monolayer (SAM) films have gained a great deal of attention for their enormous potential in tailoring surface properties for a variety of technically important applications1. Such films have been used in the design of interfaces for chemical sensing applications, non-linear optical materials, photopatterning methodology, etc2,3. SAM also finds applications in a variety of interface studies4 such as interfacial electron transfer, electrochemistry, catalysis, biological membranes, etc. SAM formed on electrode surface has been found to control the reactivity of electrode surface so that it becomes selectively responsive to a given species5 and can be used for molecular recognition6.

Most of the SAM films on electrode are reported to be made of organo sulfur compounds on gold electrode1,5,7-12. There is report of SAM film formed by lipid13, hyperbranched polymer14, DNA-lipid complex15, tetradentate ligand systems16, etc on electrode. Bennett and co-workers reported SAM film of surfactant (11-ferrocenylandecyl)trimethylammonium bromide at platinum electrode17. Saji et al. reported formation of SAM film of different organic molecules by electrolys is of surfactants with ferrocenyl moiety18. Charged surfactant molecules have been employed for fine tuning of redox potential inside lipid SAM film13. Encapsulation of a probe (molecule or ion) inside a film on electrode surface requires proper tailoring of its mid-point potential in order to make it suitable for the target species. We feel one way to do this is to provide charge environment around the probe. The aim of this work is to investigate how an encapsulated molecule is effected by the charge environment on the electrode surface.

Surfactants have extensively been used as medium for electrochemical studies in aqueous micellar form19,22. The hydrophobicity and charge of the surfactant molecules were found to effect the electrochemical parameters of the species encapsulated inside it while in micellar form19,22. It is well established that surfactants can be adsorbed on solid surfaces to form a surfactant film23,24. The adsorption is through hydrophobic surfactant tail on the electrode surface with the polar head groups directing towards the bulk water phase25.

In this note we report the influence of charged surfactant molecules, in the form of film, on mid-point potential of ferrocene. Ferrocene has been chosen because of its ideal electrochemical behaviour.

Experimental

Cetyltrimethylammonium bromide (CTAB), sodium dodecylsulphate (SDS) and trishydroxyethylaminoethane (Tris-buffer) were from Merck. Ferrocene (bis(pentaheptacyclooctyladadienyl)iron) was from Fluka. Triton X-100 (TX-100) and tetrabutylammonium perchlorate (TBAP) were from Sigma. BAS 100W (Bioanalytical System) electrochemical analyzer with three electrode cell assembly with N₂ gas purging lines was used for electrochemical studies. Glassy carbon disc electrode (GCE) was used as working electrode with an Ag-AgCl electrode as reference. Cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) experiments were carried out to measure mid-point potential values. In the OSWV experiments the square wave amplitude was 25 mV, the frequency 15 Hz and potential for base staircase wave form 4 mV. Surfactant films were made as reported13 (using surfactant instead of lipid) from a solution of 0.2 g (1.07 mol) of ferrocene, 0.1 g of CTAB (or SDS or TX-100) and 0.01 g TBAP in 10 mL chloroform and by placing 20 µL by Hamilton microsyringe on the tip of the GC electrode. Electrochemical experiments were performed with
this electrode by immersing the tip into tris buffer solution at pH 7.14 and containing 0.1 M NaNO₃.

**Results and discussion**

The cyclic voltammetric (CV) response of the GC electrode covered with ferrocene encapsulated CTAB thin film at scan rate 150 mVs⁻¹ is shown in Fig. 1. The cyclic voltammogram is due to one electron ferrocene/ferrocenium couple. The mid-point potential value was found to be 350±5 mV vs. Ag-AgCl as reference electrode with the peak separation (ΔEp) of 96 mV (Fig. 1). CV response of GC electrode covered with ferrocene encapsulated SDS film at various scan rates were measured. The mid-point potential value was found to be 275±5 mV at scan rate 100 mVs⁻¹ and ΔEp value 76 mV. Ferrocene inside TX-100 film on GC electrode gives mid-point potential value 325±5 mV vs. Ag-AgCl (ΔEp=85) at scan rate 150 mVs⁻¹. The mid-point potential values are further confirmed by OSWV measurements. The plot of cathodic and anodic current versus square root of scan rate was found to be linear, which indicates that the ferrocene/ferrocenium couple is reversible inside the film.

In non aqueous medium such as dimethylformamide (DMF) mid-point potential of ferrocene was reported to be +0.473 V with a peak separation of 94 mV at scan rate 100 mVs⁻¹ vs. Ag-AgCl reference 26. Similar results have been found in other non aqueous solvents such as dichloromethane, acetonitrile and acetone 26. Thus, compared to organic solvent there is a cathodic shift of ca. 150 mV on the mid-point potential value of ferrocene when inside neutral surfactant film of TX-100. The trend is in agreement with the shift observed on mid-point potential value of ferrocene when encapsulated in TX-100 micelle 26. In CTAB film there is an anodic shift of ca. 25 mV compared to neutral TX-100 film. This is due to the fact that the positive ferrocenium ion is less stable compared to neutral ferrocene inside positive CTAB film. This makes the reduction of ferrocenium into ferrocene easier and hence the positive shift. Inside SDS film there is ca. 50 mV cathodic shift compared to neutral TX-100; this is because of the higher stability of positive ferrocenium ion inside negative SDS film making reduction relatively difficult.

A double potential step chrono coulometry (CC) experiment at GC electrode covered with ferrocene encapsulated CTAB thin film shows a sharp decrease in charge versus time (Fig. 2). The plot of charge versus square root of time (Inset, Fig. 2) yielded an inter-
cept of 4.25 μC and 5.90 μC for the forward and reverse step respectively. This result indicates considerable adsorption of ferrocene into the electrode surface. To verify the role of CTAB on adsorption of ferrocene on electrode surface, the GC electrode tip was immersed into a solution of ferrocene in chloroform without CTAB for 10 min and chloroform was then allowed to evaporate from the tip of the electrode. This electrode, however, did not show any response towards CV or CC confirming that CTAB helps adsorption of ferrocene into the electrode surface by the formation of thin film.

In summary, it is shown that the neutral surfactant film gives a cathodic shift in the mid-point potential of ferrocene to the tune of ca. 150 mV compared to that in organic solvent. Positive charge of film gives an anodic shift of ca. 25 mV and negative charge of film gives a further cathodic shift of ca. 50 mV compared to the neutral film. Thus, charges of film make it possible to tune ferrocene’s mid-point potential over a range of 75 mV (from 275 mV to 350 mV).

Acknowledgement
DKD thanks the UGC, New Delhi for a Major Research Project (No. 12-6/2003(SR)). DST, New Delhi, for fund under FIST and Prof. O K Medhi for useful discussions.

References