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Didodecyldimethylammonium Bromide Films Containing Cobalt Phthalocyanine Tetrasulfonate for Electrochemical Catalysis

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Abstract: Electrochemistry of didodecyldimethylammonium bromide (DDAB) films containing cobalt phthalocyanine tetrasulfonate ($CoPcTS^{4-}$) was examined. $CoPcTS^{4-}$-DDAB film electrode showed stable cyclic voltammetric responses in buffers and could catalyze reductions of trichloro-acetic acid.

Keywords: Cobalt phthalocyanine tetrasulfonate; didodecyldimethylammonium bromide; electrochemical catalysis.

Films of water-insoluble surfactants can be prepared by casting their solution onto solid surface and evaporating the organic solvent, forming ordered multiple bilayer structure. These surfactant films provide a unique micro environment for electrode reaction and may improve the electrochemical properties for some incorporated species and have various potential uses in analytical chemistry[1,2].

Didodecyldimethylammonium bromide (DDAB) was from Eastman Kodak. Cobalt phthalocyanine tetrasulfonate ($CoPcTS^{4-}$) was a gift from Dr. De-Ling Zhou of University of Connecticut, USA. Cyclic voltammetry was done with a model 173 potentiostat (PARC, USA). DDAB films were prepared by casting 10 μL of 0.1 mol L^{-1} DDAB chloroform solution onto a pyrolytic graphite (PG) electrode. Chloroform was then evaporated overnight. All potentials reported are *vs.* SCE.

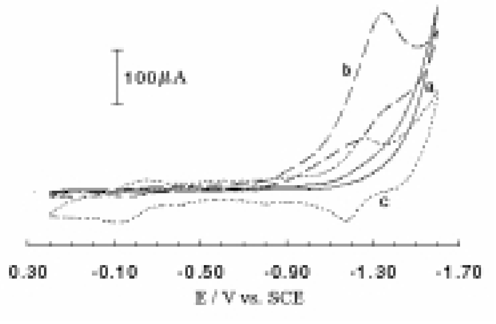
When a DDAB film electrode was placed into $CoPcTS^{4-}$ solution, two pairs of well-defined and near reversible peaks appeared at around -0.23 V and -1.24 V, respectively, and grew with soaking time, indicating anionic $CoPcTS^{4-}$ could enter into positively charged DDAB films by Coulombic attraction. The steady state CV was achieved after 9-10 hours of soaking. These two sets of CV redox peaks might be attributed to reductions of Co (II) $PcTS^{4-}$ to Co (I) $PcTS^{5-}$, and Co (I) $PcTS^{5-}$ to Co (I) $PcTS^{6-}$, respectively[3]. When the DDAB films fully loaded with $CoPcTS^{4-}$ were removed from its solution and transferred into buffers without $CoPcTS^{4-}$, the CV remained the same as in $CoPcTS^{4-}$ solutions and showed very good stability for at least 4-5 days (**Figure 1c**). Thus, hydrophobic interaction between $CoPcTS^{4-}$ and DDAB might contribute to the stability more significantly. For the first pair of peaks of $CoPcTS^{4-}$-DDAB films, the cathodic peak current (i_{pc1}) at -0.28 V showed linear relationship with scan rate (v) at $v < 0.02$ V s^{-1}, suggesting typical thin-layer behaviour[4]. While at $v > 0.05$ V s^{-1}, i_{pc1} was proportional to

$v^{1/2}$, indicating diffusion-like behaviour[4] even in this very thin film. The transformation of the system from diffusion controlled to thin-layer controlled with increasing scan rate is characteristic of film modified electrodes[5].

According to the slope of i_{pc1}-$v^{1/2}$ straight line at faster scan rates, charge transport diffusion coefficient, D_{ct}, for the film system was estimated to be 2.2×10^{-7} cm^2 s^{-1} by Randles-Sevick equation[4]. The potential difference between cathodic and anodic peaks, ΔE_p, was used to estimate the apparent heterogeneous electron transfer rate constant, $k^{o\prime}$, by Nicholson's method[6]. The average of $k^{o\prime}$ was 7.4×10^{-4} cm s^{-1}.

When a CoPcTS^{4-}-DDAB film electrode was placed in buffers containing trichloroacetic acid (TCA) , a large increase in cathodic current at the potential of the second reduction peak of the film was observed (**Figure 1b**). The anodic peak seen in the absence of TCA (**Figue 1c**) was not observed in its presence. These results are consistent with the reaction of reduced Co (I) PcTS^{6-} with TCA in a catalytic cycle. The catalytic peak arose at about -0.9 V, more positive than its direct reduction at bare DDAB films which begins at -1.3 V (**Figure 1a**). The catalytic current increased with the concentration of TCA in the range of 4.0×10^{-5} - 1.0×10^{-3} mol L^{-1} (r=0.9965) suggesting the possibility of analytical application of CoPcTS^{4-}-DDAB films as sensors to monitor the environmental pollutants such as TCA.

Figure 1. Cyclic voltammograms in pH 7.0 buffers containing 0.1 mol/L KBr at 0.1 V s^{-1}. a, DDAB in 1.0×10^{-2} mol/L TCA; b, CoPcTS^{4-}-DDAB in 1.0×10^{-2} mol/L TCA; c, CoPcTS^{4-}-DDAB in blank buffers.



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