Significant Micellar Effect on the Oxidative Electrochemistry of Ascorbic Acid†

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The oxidation potential of L-ascorbic acid at a glassy carbon electrode shifts from 200 mV (*vs* SCE) in phosphate buffer at pH 6.8 to 10 mV in the presence of cetyltrimethylammonium bromide (CTAB) micelles, and to 460 mV in the presence of sodium dodecyl sulfate (SDS) micelles.

The selective electrochemical determination of ascorbic acid attracts much current interest, especially in bioelectrochemistry.[1,2] Micellar systems are considered to be a primitive, although simple, model system for biological membranes.[3] There have been a few reports on the electrochemistry in micellar systems.[4–7] Kaifer and Bard[4] have reported significant changes in the redox potential and peak current of methylviologen in the presence of an anionic micelle sodium dodecyl sulfate (SDS). Davidovic *et al.*[5] reported that the rate of electrochemical reduction of *p*-nitrosodiphenylamine decreased in the presence of the cationic micelle cetyltrimethylammonium bromide (CTAB). Ormonde and O'Neill[6] reported that the oxidation potential of ascorbic acid at a carbon paste electrode shifted 170 mV lower when treated with the non-ionic micelle Triton X-100. Rusling and co-workers[7] studied the micellar effects on the electrochemistry of cobalt complexes of bipyridyl derivatives and suggested that micelle-bound catalytic systems are attractive candidates for the future design of surfactant assemblies which may mimic redox events in biological membranes. Recent work from our laboratory[8] found that the antioxidant activity of ascorbic acid was enhanced over two orders of magnitude in the presence of a CTAB micelle, whilst it diminished in the presence of an SDS micelle. We were therefore motivated to find out if micelles can also influence the electrochemical behaviour of ascorbic acid and its possible implication in biological applications. Here we describe a cyclic voltammetric study on the anodic oxidation of L-ascorbic acid at a glassy carbon electrode in cationic CTAB and anionic SDS micelles.

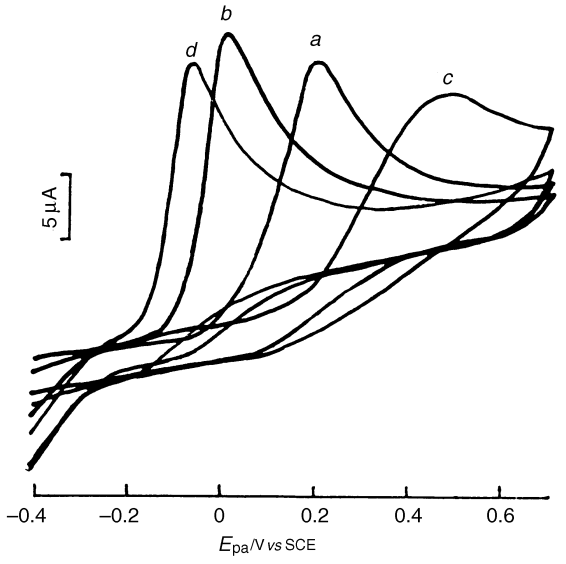

Fig. 1 Cyclic voltammograms recorded with a glassy carbon electrode of L-ascorbic acid (0.5 mmol dm^{-3}) in 0.1 mol dm^{-3} phosphate buffer: (*a*) aqueous solution, pH 6.8; (*b*) in 1.0 mmol dm^{-3} CTAB, pH 6.8; (*c*) in 5.0 mmol dm^{-3} SDS, pH 6.8; (*d*) in 1.0 mmol dm^{-3} CTAB, pH 9.4

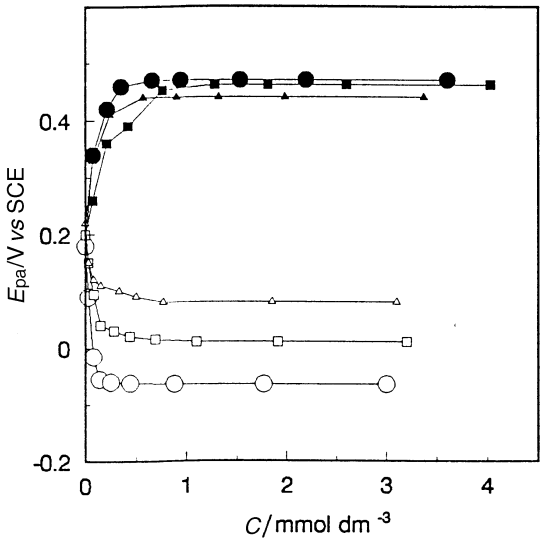

Fig. 2 Variation of oxidation potential (E_{pa}) of L-ascorbic acid at a glassy carbon electrode with surfactant concentrations (C) and pH: ● in SDS, pH 9.4; ○ in CTAB, pH 9.4; ■ in SDS, pH 6.8; □ in CTAB, pH 6.8; ▲ in SDS, pH 4.3; △ in CTAB, pH 4.3

Results and Discussion

Cyclic voltammetric determination of a 0.5 mmol dm^{-3} aqueous solution of L-ascorbic acid in 0.1 mol dm^{-3} phosphate buffer (pH 6.8) gave an irreversible cyclic voltammogram with the oxidation potential E_{pa} at 200 mV (*vs* SCE). Addition of cationic surfactant CTAB to the solution shifted the potential to negative, and increased the peak current I_{pa} (Fig. 1). This change of the voltammogram was found to be dependent on the CTAB concentration. At very low CTAB concentration the potential shift and the peak current increased abruptly with increasing surfactant concentration, whilst the potential and the current reached a plateau around a CTAB concentration of 0.2 mmol dm^{-3} (Figs. 2 and 3) which is close to the critical micellar concentration (CMC) of CTAB.[3] The oxidation potential at the plateau was 10 mV (Fig. 2), being 190 mV lower than that in water. In alkaline solution the potential shift was even more remarkable, *e.g.* from 180 mV in pH 9.4 aqueous buffer to −65 mV in CTAB micelle (Fig. 2). An anionic surfactant, SDS, influenced the cyclic voltammetric behaviour in a similar way, but in the opposite direction. It shifted the E_{pa} to positive and decreased I_{pa} (Figs. 1, 2 and 3). It can also be seen from Figs. 2 and 3 that the solution acidity influenced the E_{pa} and I_{pa} in a more complex fashion. In CTAB micelles the E_{pa} shifted to

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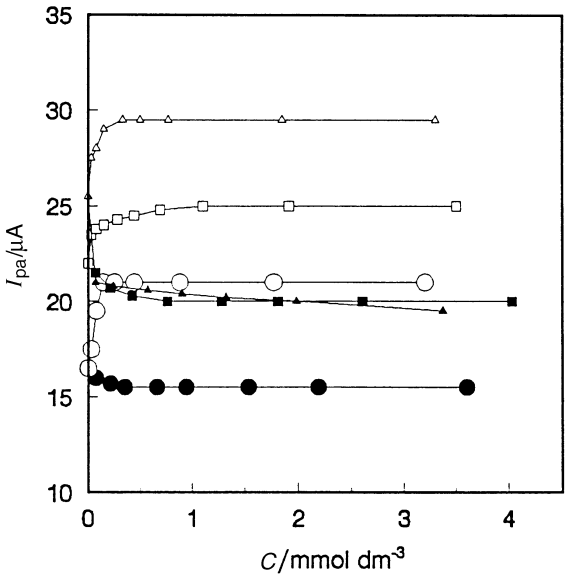

Fig. 3 Variation of peak current (I_{pa}) of L-ascorbic acid at a glassy carbon electrode with surfactant concentrations and pH: ● in SDS, pH 9.4; ○, in CTAB, pH 9.4; ■ in SDS, pH 6.8; □ in CTAB, pH 6.8; ▲ in SDS, pH 4.3; △ in CTAB, pH 4.3

more negative in alkaline solution, but the I_{pa} increased more pronouncedly in acidic solution. On the other hand, the solution acidity exerted a small effect on the E_{pa} and I_{pa} in SDS micelles.

The electrochemistry of ascorbic acid has been studied at a mercury electrode,[9] platinum electrode,[10] polymer-coated electrode[1] and glassy carbon electrode.[11] An EC mechanism proposed by Ruiz *et al.*[9] for the oxidation of ascorbic acid at low pH is widely accepted that involves two consecutive one-electron transfer processes to form dehydroascorbic acid immediately followed by an irreversible hydration to give the final product 2,3-diketogulonic acid. Although the electrochemical reaction at the mercury electrodes is reversible,[9] the large overvoltage needed at carbon electrodes renders the oxidation of ascorbic acid at carbon electrodes irreversible and the anodic potential considerably higher than its standard redox potential. The anodic oxidation potential E_{pa} of ascorbic acid determined at a glassy carbon electrode in phosphate buffer (pH 6.8) was 200 mV *vs.* SCE which is close to that reported previously on an activated glassy carbon electrode obtained by vacuum heat treatment.[11] The significant shift of the oxidation potential and change of the peak current upon addition of CTAB and SDS surfactants may be due to the adsorption of the surfactant at the electrode–solution interface which may alter the overvoltage of the electrode and influence the rate of electron transfer and the formation of micellar aggregates which may influence the mass transport of electroactive species to the electrode. It is well established that surfactants can be adsorbed on solid surfaces to form a surfactant film.[7,12] In the present case adsorption of CTAB at the electrode surface may form a positively charged hydrophilic film on the electrode with the polar head group directing to the bulk water phase. The adsorption of the hydrophobic surfactant tail on the electrode surface helps to release the oxidation product dehydroascorbic acid from the electrode surface, and hence the overvoltage is reduced. The positively charged hydrophilic layer enhances the concentration of ascorbate anion on the electrode surface via electrostatic interaction, and hence the electron transfer rate is increased. On the other hand, adsorption of anionic SDS excludes the ascorbate anion away from the electrode surface, and hence the reaction is retarded. The plateau that appeared in the plots of E_{pa} and I_{pa} *vs.* the surfactant concentration demonstrates the saturated adsorption of the surfactant at the electrode, because after complete coverage of the electrode by the surfactant the excess surfactant would form micelles in the bulk water and would no longer affect the electrode oxidation process. It has been well established that the saturated adsorption of surfactants on solid surfaces is generally coincident with the CMC of the surfactant[12] and cyclic voltammetry has been suggested as a method for estimating the CMC of surfactants.[4,13]

The influence of the solution acidity of micelles on electrochemical processes cannot be simply predicted[7,12] because the blocking of the electrode surface by the surfactant, the extraction of the ascorbic acid by the solution micelles, and the change of the dielectric constant at the interface can all influence the electrochemical behaviour. It can be seen from Figs. 2 and 3 that in aqueous solution the E_{pa} and I_{pa} decrease a little with increasing pH. The saturated E_{pa} and I_{pa} also decrease in micelles, but they are much more sensitive to pH in CTAB than in SDS micelles. The reason for this phenomenon is still unclear. Probably aggregation of ascorbate with CTAB micelle plays a role in controlling its diffusion rate, and the pH may influence the aggregation and the adsorption of the surfactants on the electrode surface.

Experimental

A conventional single-compartment, three-electrode cell thermostatted at 20 °C and kept under an argon atmosphere was used for all experiments. The electrochemical instrumentation consisted of a PAR model 173 potentiostat coupled with a PAR model 175 universal programmer, and a Houston Instruments model 2000 X-Y recorder. A glassy carbon electrode (3 mm in diameter) was employed as a working electrode which was carefully polished with 0.05 nm alumina slurry on a flat surface and sonicated immediately before use. A platinum wire was employed as an auxiliary electrode. All potentials were recorded with respect to a saturated calomel electrode (SCE) reference electrode.

All chemicals were reagent grade and used as received. The surfactants CTAB and SDS were recrystallized from ethanol. Ascorbic acid solutions were prepared immediately before use with triply distilled water and deaerated thoroughly with argon.

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