Micellar effects on the oxidative electrochemistry of lipophilic vitamin C derivatives

Xiao-Lin Wen,[a] Jin Zhang, Zhong-Li Liu,*[,a] Zheng-Xu Han †[,b] and Anton Rieker[b]

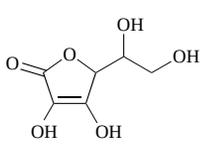
[a] *National Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, Gansu 730000, China*
[b] *Institute of Organic Chemistry, University of Tuebingen, Auf der Morgenstelle 18, D 72076 Tuebingen, Germany*

The anodic oxidation of ascorbic acid (VC) and its lipophilic derivatives ascorbyl-6-caprylate (VC-8),‡ 6-laurate (VC-12) and 6-palmitate (VC-16) have been studied by cyclic voltammetry at a glassy carbon electrode in the presence of cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) micelles. The peak potentials (E_{pa}) and peak currents (i_{pa}) have been found to be remarkably dependent on the lipophilicity of the VCs and on the character and concentration of the surfactant. Making VC lipophilic remarkably shifts its peak potential to negative values, the E_{pa} being 200, 70, −85 and −125 mV (*vs.* SCE) in aqueous solution at pH 6.8 for VC, VC-8, VC-12 and VC-16, respectively. In micellar solutions the E_{pa} and i_{pa} change abruptly around the critical micellar concentration (CMC) of the surfactants and reach a plateau above the CMC. The E_{pa} at the plateau is shifted to more positive values in SDS micelles. It is shifted to more negative values in CTAB micelles except in the case of VC-16, whose E_{pa} is shifted to the positive direction. The effectiveness of the micellar effect decreases in the order VC > VC-8 > VC-12 > VC-16. Sharp current maxima appeared in CTAB micellar solution below its CMC for VC-8, VC-12 and VC-16, demonstrating adsorption of these lipophilic VCs at the electrode surface and formation of premicellar aggregates. The electron-transfer rate constants and diffusion coefficients have been calculated from the cyclic voltammograms. From these data it is concluded that the hydrophobic/lipophilic interaction of the hydrocarbon tail and the electrostatic interaction of the ascorbate anion moiety of the VCs are the dominant factors controlling their electrochemical behaviour in micellar solutions.

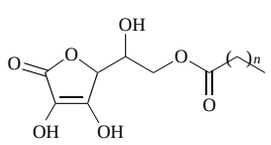
Introduction

There has been substantial interest in the electrochemistry in micellar systems in the past decade. Adsorption of surfactants on electrodes and solubilization of electrochemically active compounds in micellar aggregates might significantly change the redox potential, charge transfer coefficients and diffusion coefficients of the electrode processes, as well as change the stability of the electrogenerated intermediates.[1–5] For example, Rusling[1] has successfully used micelles and other surfactant microstructures to catalyze the electrochemical dehalogenation of organic halides. Kaifer and Bard[2] reported significant changes in the redox potential and peak current of methylviologen in the presence of the anionic micelle sodium dodecyl sulfate (SDS). Davidovic *et al.*[3] found that the rate of electrochemical reduction of *p*-nitrosodiphenylamine decreases in the presence of the cationic micelle cetyltrimethylammonium bromide (CTAB). In addition, micellar systems are considered to be primitive model systems for biological membranes.[6–8] Rusling and co-workers[5] have suggested that micelle-bound catalytic systems are attractive candidates for future design of surfactant assemblies that may mimic redox events in biological membranes.

Vitamin C (L-ascorbic acid) is a well-known bioactive reducing agent whose electrochemistry has been extensively studied.[9–15] However, only two reports have dealt with its electrochemistry in micellar systems. Ormonde and O'Neill[16] reported that the oxidation potential of vitamin C at a carbon paste electrode was shifted by 170 mV to more negative potentials in the presence of the non-ionic micelle Triton X-100, and we[17] found recently that the oxidation peak potential and current of vitamin C are significantly influenced by the cationic micelle CTAB and the anionic micelle SDS. These observations and our previous finding that the antioxidant activity of vitamin C is remarkably enhanced in micellar systems[18] and in erythrocytes[19] by making it lipophilic prompted us to see how micelles would influence the electrochemical behaviour of lipophilic vitamin C derivatives and its possible implication in biological applications. Here we describe a cyclic voltammetric study of the anodic oxidation of vitamin C (VC) and its lipophilic derivatives ascorbyl-6-caprylate (VC-8), ascorbyl-6-laurate (VC-12) and ascorbyl-6-palmitate (VC-16)‡ at a glassy carbon electrode in cationic CTAB and anionic SDS micellar systems.



VC



VC-8(n = 6); VC-12(n = 10); VC-16(n = 14)

Results

Cyclic voltammetric measurements on a 0.57 mmol dm^{-3} solution of vitamin C (VC) in 0.1 mol dm^{-3} aqueous phosphate buffer (pH 6.8) gave an irreversible cyclic voltammogram with the oxidation peak potential, E_{pa}, at 200 mV (*vs.* SCE).[16] Introducing a hydrocarbon tail into VC shifted the peak potential to

* FAX: +86 931 8885076; E-mail: liuzl@lzu.edu.cn
† Present address: Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600, USA.
‡ IUPAC name: 2-(3,4-dihydroxy-5-oxo-2,5-dihydrofuran-2-yl)-2-hydroxyethyl octanoate, VC-12 and VC-16 can be named similarly.

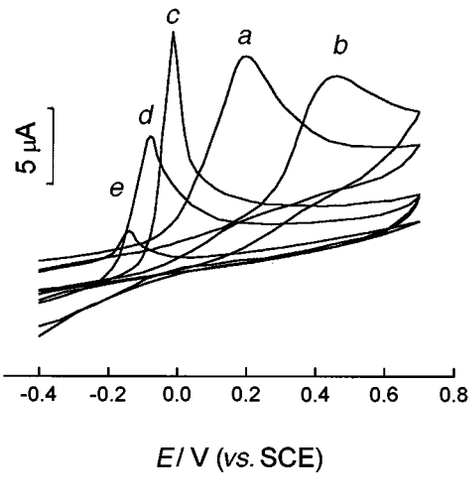


Fig. 1 Representative cyclic voltammograms of VCs recorded at a glassy carbon electrode in 0.1 mol dm^{-3} phosphate buffer at pH 6.8. (*a*) VC (0.57 mmol dm^{-3}) in aqueous solution; (*b*) VC (0.57 mmol dm^{-3}) in 1.0 mmol dm^{-3} SDS; (*c*) VC-8 (0.36 mmol dm^{-3}) in 0.3 mmol dm^{-3} CTAB; (*d*) VC-12 (0.28 mmol dm^{-3}) in 0.1 mmol dm^{-3} SDS; (*e*) VC-16 (0.15 mmol dm^{-3}) in aqueous solution.

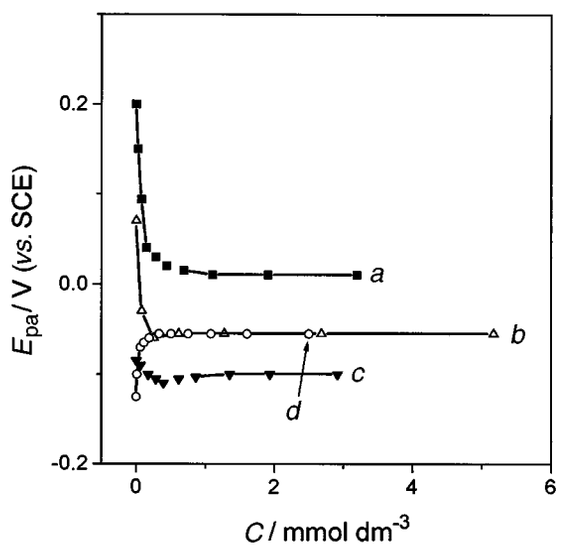


Fig. 2 Variation of the oxidation peak potential (E_{pa}) of VCs at a glassy carbon electrode *vs.* CTAB concentration (C) in 0.1 mol dm^{-3} phosphate buffer at pH 6.8. (*a*) VC; (*b*) VC-8; (*c*) VC-12; (*d*) VC-16.

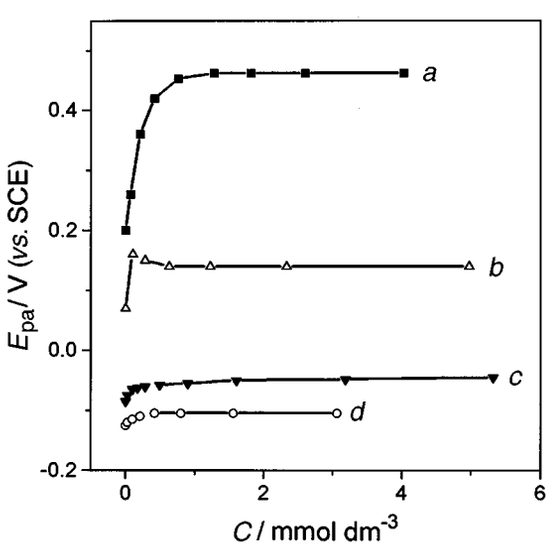


Fig. 3 Variation of the oxidation peak potential (E_{pa}) of VCs at a glassy carbon electrode *vs.* SDS concentration (C) in 0.1 mol dm^{-3} phosphate buffer at pH 6.8. (*a*) VC; (*b*) VC-8; (*c*) VC-12; (*d*) VC-16.

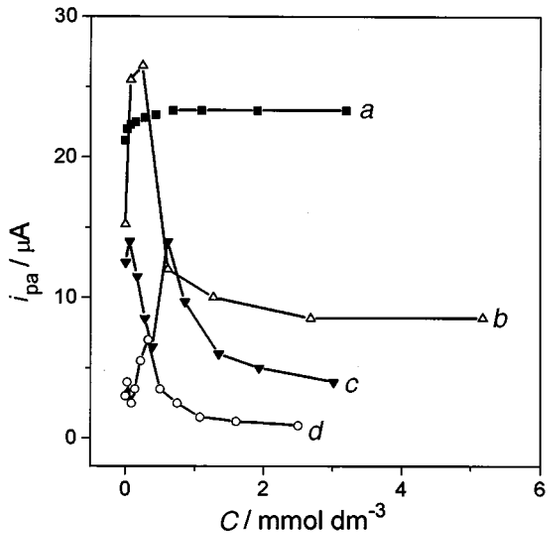


Fig. 4 Variation of the oxidation peak current (i_{pa}) of VCs at a glassy carbon electrode *vs.* CTAB concentration (C) in 0.1 mol dm^{-3} phosphate buffer at pH 6.8. (*a*) VC; (*b*) VC-8; (*c*) VC-12; (*d*) VC-16.

more negative values. The E_{pa} was 70, −85 and −125 mV for ascorbyl-6-caprylate (VC-8), ascorbyl-6-laurate (VC-12) and ascorbyl-6-palmitate (VC-16), respectively (Fig. 1 and Table 1).

Addition of the cationic surfactant cetyltrimethylammonium bromide (CTAB) to the solution shifted the E_{pa} of VC, VC-8 and VC-12 to more negative values, whilst it shifted the E_{pa} of VC-16 to more positive values. This change of the E_{pa} was found to be dependent on the CTAB concentration. At very low CTAB concentrations the potential shifted abruptly with increasing surfactant concentration, then it reached a plateau near the CTAB concentration of 0.5 mmol dm^{-3}. With VC-8 and VC-12, the potential moved to more negative values and then turned positive before reaching the plateau (Fig. 2 and Table 1).

The anionic surfactant sodium dodecyl sulfate (SDS) influenced the voltammetric behaviour in a similar way, but in the opposite direction. It shifted the E_{pa} to more positive potentials and reached a plateau near the SDS concentration of 2 mmol dm^{-3}. Fig. 3 shows that the surfactants exerted a more significant effect on VC than on the lipophilic VCs and that the effectiveness follows the sequence of VC > VC-8 > VC-12 > VC-16.

The anodic peak current, i_{pa}, of the VCs was also remarkably affected by the surfactants, but in a much more complex pattern (Figs. 4 and 5). The i_{pa} of VC increased in CTAB micelles whilst it decreased in SDS micelles, and both systems reached a plateau similar to the variation of E_{pa} *vs.* the surfactant concentrations (compare line *a* in Figs. 2 and 3 with that in Figs. 4 and 5). However, the i_{pa} of VC-8 in CTAB micelles steeply reached a maximum at a CTAB concentration of *ca.* 0.3 mmol dm^{-3} and then decreased to a lower plateau. VC-12 and VC-16 behaved similarly in CTAB micelles, but for VC-12 two current maxima appeared before reaching the plateau (line *c* in Fig. 4). On the other hand, the variation of i_{pa} in SDS micelles showed different patterns depending on the side-chain length. The i_{pa} of VC and VC-8 in SDS micelles decreased smoothly to a plateau with increasing SDS concentrations, whilst that of VC-12 reached a sharp maximum before reaching the plateau, similar to its behaviour in CTAB micelles. The i_{pa} of VC-16 increased a little and then came to a somewhat lower plateau with increasing SDS concentrations (Fig. 5).

Discussion

The electrochemistry of VC has been studied at mercury electrodes,[9,10] platinum electrodes,[11,12] gold electrodes,[13] polymer-

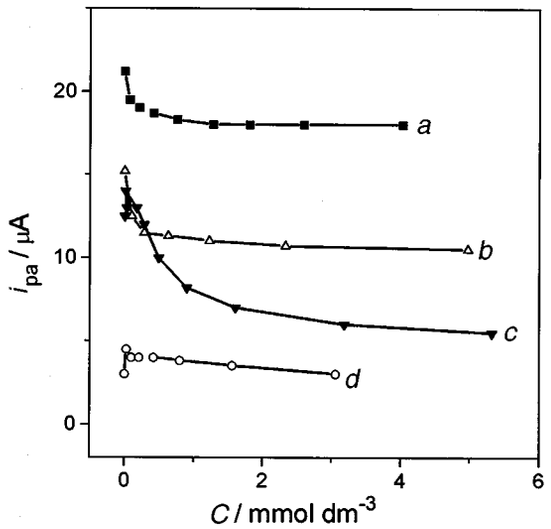


Fig. 5 Variation of the oxidation peak current (i_{pa}) of VCs at a glassy carbon electrode *vs.* SDS concentration (C) in 0.1 mol dm^{-3} phosphate buffer at pH 6.8. (*a*) VC; (*b*) VC-8; (*c*) VC-12; (*d*) VC-16.

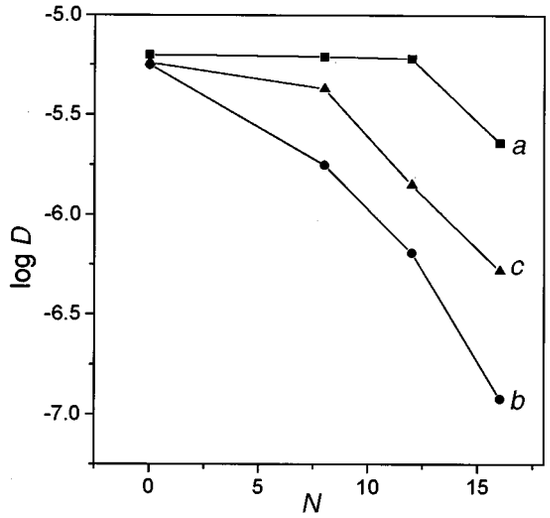


Fig. 6 Variation of the diffusion coefficient (D) of VCs at a glassy carbon electrode *vs.* the carbon number (N) of the side-chain of the VCs in 0.1 mol dm^{-3} phosphate buffer at pH 6.8. (*a*) in aqueous solution; (*b*) in 5 mmol dm^{-3} CTAB micellar solution; (*c*) in 5 mmol dm^{-3} SDS micellar solution.

coated electrodes[14] and glassy carbon electrodes.[15–17] The EC mechanism proposed by Ruiz[10] for the oxidation of VC at low pH is widely accepted; it 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.[14] Although the electrochemical reaction at mercury electrodes is reversible,[9,10] the large overpotential needed at carbon electrodes renders the oxidation of VC at carbon electrodes irreversible and the anodic potential is considerably higher than its standard oxidation potential. The anodic oxidation peak potential E_{pa} of VC at a carefully polished glassy carbon electrode in phosphate buffer (pH 6.8) was found to be 200 mV *vs.* SCE, which is close to that reported for an activated glassy carbon electrode obtained by vacuum heat treatment.[15] We found recently[17] that addition of CTAB and SDS significantly alters the E_{pa} and i_{pa} of VC, and concluded that adsorption of the surfactant on the electrode and electrostatic interaction between the surfactant and VC anion (ascorbate) were the predominant driving forces for the alteration. However, the electrochemistry of the lipophilic VCs is much more complex in micellar systems as shown in Figs. 2 and 3. Since the lipophilic VCs are themselves amphiphilic molecules, they are capable of adsorbing on the electrode surface and forming self-aggregates and/or mixed micelles with CTAB or SDS. Adsorption of amphiphilic molecules on electrodes may change the overpotential of the electrode and the rate of electron transfer,[16] and formation of micellar aggregates and/or premicellar aggregates may influence the mass transport of electroactive species to the electrode.[4,20] Therefore, it is necessary to analyze quantitatively micellar effects on the diffusion and electron transfer rates of the lipophilic VCs. This may help us to understand the electrochemistry of amphiphilic molecules in general.

Calculation of apparent diffusion coefficients and electron-transfer rate constants

For irreversible anodic oxidations eqn. (1) is applicable for

$$i_{pa} = 2.985 \times 10^5 n[(1 - \alpha)n_a]^{1/2} AD^{1/2} Cv^{1/2} \quad (1)$$

calculation of the diffusion coefficient.[21] Here, i_{pa} is the anodic peak current (mA) at 25 °C, n is the number of electrons involved in the oxidation, α is the transfer coefficient, n_a is the number of electrons in the rate-limiting step, A is the area of the electrode (cm^2), D is the diffusion coefficient of the electroactive species (cm^2 s^{-1}), C is the concentration of the electroactive species in solution (mmol dm^{-3}) and v is the sweep rate (V s^{-1}).

The transfer coefficient for totally irreversible cyclic voltammograms can be calculated from eqn. (2), where E_{pa} (mV) is the

$$(1 - \alpha)n_a = 47.4/(E_{pa} - E_{pa/2}) \quad (2)$$

anodic peak potential and $E_{pa/2}$ is the potential at which the current equals one half of the peak current.[21]

Plots of the anodic peak currents of the VCs (i_{pa}) *versus* scan rates (v) ranging from 15 to 200 mV s^{-1} gave good straight lines in accordance with eqn. (1) (data not shown), from which the apparent diffusion coefficients (D) were calculated and are listed in Table 1. The apparent diffusion coefficient is an average of the actual values in the bulk solution, in micelles and in the surfactant film adsorbed on the electrode surface. Their relationships with the side-chain length of the VCs are depicted in Fig. 6.

The apparent heterogeneous rate constant, k^0 (cm s^{-1}), for irreversible anodic electrode reactions can be obtained from eqn. (3).[21] Here, $E^{0\prime}$ is the formal electrode potential and F is the

$$E_{pa} = E^{0\prime} + RT/([(1 - \alpha)n_a F]\{0.780 + 1/2 \ln [F(1 - \alpha)n_a Dv/RT]\}) - \ln k^0 \quad (3)$$

Faraday constant. The $E^{0\prime}$ value of VC was calculated to be −193 mV at pH 7.4,[16] which can be easily transferred to formal potentials at other pH conditions with eqn. (4).

$$E^{0\prime} = E^0 - (0.059/n)\text{pH} \quad (4)$$

Since the lipophilic VCs possess the same electroactive functional group as VC, it is reasonable to assume that they all have the same formal electrode potential. Therefore, the apparent electron transfer rate constants of the VCs were calculated from eqns. (3) and (4) and are listed in Table 1. Their relationships with the side-chain length of the VCs are depicted in Fig. 7. It should be pointed out that the validity of eqns. (1)–(4) may be influenced by adsorption phenomena. In any event, it seems justified to use these equations in a first order treatment, since a simulation including adsorption would be too complicated.

Electrochemistry of VCs in aqueous solution

It can be seen from Table 1 and Figs. 6 and 7 that in aqueous solutions the side-chain of VCs exerts a small effect on the apparent diffusion coefficient. VC-8 and VC-12 are fairly soluble in water because of the presence of three hydrophilic

Table 1 Electrochemical parameters of VCs determined at a glassy carbon electrode in 0.1 mmol dm^{-3} phosphate buffer at pH 6.8

Substrate[a]	Medium	E_{pa}/mV *vs.* SCE	i_{pa}/μA	α	$D/10^{-6}$ cm^2 s^{-1}	$k^0/10^{-6}$ cm s^{-1}
VC	H_2O	200	21.2	0.52	6.31	4.20
	SDS[b]	462	15.6	0.72	5.82	2.67
	CTAB[b]	10	23.0	0.36	5.60	52.0
VC-8	H_2O	70	15.2	0.39	6.19	20.4
	SDS[b]	140	10.5	0.56	4.22	17.1
	CTAB[b]	−55	8.5	0.32	1.79	130
VC-12	H_2O	−85	12.5	0.28	6.09	480
	SDS[b]	−45	5.8	0.34	1.42	96.8
	CTAB[c]	−100	4.1	0.29	0.65	228
VC-16	H_2O	−125	4.2	0.15	2.29	769
	SDS[b]	−105	2.2	0.10	0.52	167
	CTAB[c]	−55	1.0	0.13	0.12	14.5

[a] The concentrations were 0.57, 0.36, 0.28 and 0.15 mmol dm^{-3} for VC, VC-8, VC-12 and VC-16 respectively. [b] The surfactant concentration was 5 mmol dm^{-3}. [c] The surfactant concentration was 3 mmol dm^{-3}.

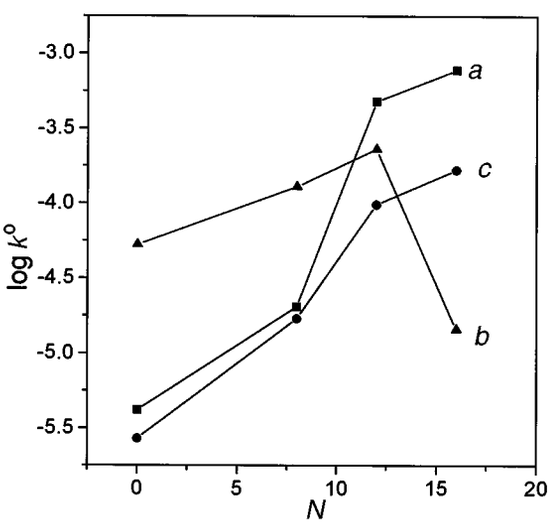


Fig. 7 Variation of the electron transfer rate constant (k^0) of VCs at a glassy carbon electrode *vs.* the carbon number (N) of the side-chain of the VCs in 0.1 mol dm^{-3} phosphate buffer at pH 6.8. (*a*) in aqueous solution; (*b*) in 5 mmol dm^{-3} CTAB micellar solution; (*c*) in 5 mmol dm^{-3} SDS micellar solution.

hydroxy groups. VC-16 is less soluble in water owing to formation of micellar and/or premicellar aggregates as indicated by its significantly diminished diffusion coefficient (see Fig. 6 and Table 1).

It was reported previously that VC-16 forms micelles with the critical micellar concentration (CMC) of 2.6×10^{-4} mol dm^{-3}.[22] On the other hand, the side-chain exhibits a remarkable effect on the apparent electron transfer rate. The k^0 increases with increasing side-chain length of VCs and over two orders of magnitude of rate enhancement is achieved from VC (4.2×10^{-6} cm s^{-1}) to VC-16 (7.7×10^{-4} cm s^{-1}). This strongly suggests that the substantial negative shift of E_{pa} of VCs with increasing side-chain length in aqueous solution (from 200 mV for VC to −125 mV for VC-16, *vide supra*) stems from increase of the apparent electron transfer rate. The rate enhancement of the lipophilic VCs is most likely due to their adsorption on the electrode surface. It has been well established that amphiphilic molecules tend to adsorb at water–electrode interfaces to form a monolayer, bilayer, multilayer and/or hemimicelle film.[1,5,7] In the present case adsorption of the lipophilic VCs on the electrode should increase their local concentration at the electrode surface and thus increase the apparent rate constant. It can be seen from Table 1 and eqn. (3) that this is the predominant factor that decreases the peak potential.

Electrochemistry of VCs in micellar solutions

Addition of CTAB or SDS surfactants significantly alters the E_{pa} and i_{pa} in a concentration-dependent manner, and the variation reaches a plateau over a definite surfactant concentration (Figs. 2–5). As pointed out previously,[17] the plateau demonstrates saturation of adsorption of the surfactant on 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 recognized that saturated adsorption of surfactants on solid surfaces generally coincides with the critical micellar concentration (CMC) of the surfactant,[7] and cyclic voltammetry has been suggested as a method for estimating the CMC of surfactants.[2,4]

The diminished apparent diffusion coefficients of the lipophilic VCs and the correlation of the diffusion coefficient with the side-chain length (Table 1 and Fig. 6) in CTAB and SDS micelles clearly indicate an aggregation of the lipophilic VCs with the micelles to form mixed micelles, which should slow down the transport of the VCs in the micellar solution. Obviously, the longer the side-chain, the stronger the aggregation with the micelle, hence the slower VCs diffusion should be. Fig. 6 also shows that CTAB is more effective than SDS in decreasing the apparent diffusion coefficient. This is due to the fact that the lipophilic VCs possess negatively charged ascorbate head groups, hence both hydrophobic and electrostatic interactions facilitate them aggregating with CTAB micelles. In the case of SDS, only the hydrophobic interaction makes a contribution to the aggregation and the electrostatic force works in the opposite direction. This causes the lipophilic VCs to form stronger aggregates with CTAB micelles than with SDS micelles. It was reported previously[23] that the movement of a molecule in micelles depends not only on its chain length but also on its binding ability with the micelles. The longer hydrocarbon tail of CTAB (16 carbons) compared to SDS (12 carbons) might also make it more lipophilic and exert stronger micellar effects than the latter.

As shown in Fig. 7, the apparent rate constant k^0 increases in CTAB and SDS micellar solutions with increasing side-chain length of the VCs, except in the case of VC-16 in CTAB micelles. But the side-chain effect is less pronounced in micellar solutions than in aqueous solution. It is also seen from Figs. 2 and 3 that the micellar effect on E_{pa} follows the sequence of VC > VC-8 > VC-12 > VC-16. Differences of E_{pa} between CTAB and SDS micelles above their CMC are *ca.* 450, 200, 55 and 50 mV for VC, VC-8, VC-12 and VC-16, respectively. This suggests a competition between adsorption of the lipophilic VCs on the electrode surface and their aggregation with the surfactant micelles. In the case of hydrophilic VCs, no such competition should occur. Hence, the electrochemical behavior of VC is simply governed by adsorption of the surfactant at the electrode surface and the electrostatic interaction of ascorbate anion with the surfactant film adsorbed on the electrode as discussed previously.[17] This results in its E_{pa} decreasing in CTAB and increasing in SDS micellar solutions. In other words, the surfactant film adsorbed on the electrode surface

simply serves as an 'electrostatic wall' to help or prevent the electrode reaction. In the case of the lipophilic VCs, however, the amphiphilic character of the molecules allows them to adsorb on the electrode surface and/or join the surfactant film adsorbed at the electrode surface, leading to enhancement of the electron-transfer rate (see Table 1 and Fig. 7) and decrease of the E_{pa}. In addition, aggregation of the VCs with the surfactant micelles decreases the diffusion coefficient of the VCs which also decreases the E_{pa} according to eqn. (3).

In CTAB micellar solution both hydrophobic and electrostatic interactions facilitate the adsorption of the lipophilic VCs at the CTAB film adsorbed on the electrode surface and the E_{pa} shifts to a more negative potential than that in aqueous solution except in the case of VC-16. On the other hand, in SDS micellar solution the hydrophobic interaction partly compensates the electrostatic repulsion between adsorbed SDS film and the negatively charged VCs; hence the E_{pa} shifts to a less positive potential than in aqueous solution. Altogether, the E_{pa} difference between CTAB and SDS micelles decreases with increasing side-chain length of the VCs, demonstrating that lipophilic/hydrophobic interactions play a predominant role in controlling the electrochemistry of the lipophilic VCs, especially in the case of VC-12 and VC-16. It should be pointed out in this context that the E_{pa} of VC-16 increases appreciably in CTAB micellar solution (line *d* in Fig. 2), presumably due to the formation of VC-16–CTAB mixed micelles. It is known that cationic and anionic surfactants can form large mixed micelles with aggregation numbers up to hundreds.[24–26] Such large aggregates diffuse slowly in solution, hence slowing down the electrode reaction. Indeed, the apparent diffusion coefficient and the apparent electron transfer rate constant of VC-16 are remarkably decreased in CTAB micelles (Figs. 6 and 7).

Adsorption and formation of premicellar aggregates of lipophilic VCs

The variation of i_{pa} *vs.* surfactant concentrations (Figs. 3 and 4) reveals the substantial difference of VC from its lipophilic analogs in their electrochemical behavior. The smooth increase and decrease of i_{pa} of VC in CTAB and SDS micelles, respectively, can be readily rationalized by the electrostatic interaction of ascorbate anion with the surfactant film adsorbed at the electrode surface as discussed previously.[17] On the other hand, the i_{pa} of the lipophilic VCs decreases to a very low plateau above the CMC of the micelle both in CTAB and in SDS micellar solutions, and it decreases with increase of the side-chain length and diminishes more in CTAB than in SDS micellar solution. This strongly suggests aggregation of these lipophilic VCs with the micelles which leads to appreciable decrease of their apparent diffusion coefficients in the micellar solutions (Fig. 6).

Most interestingly, the i_{pa} of VC-8 in CTAB micellar solution exhibits a very sharp peak near a CTAB concentration of 0.3 mmol dm^{-3}, which is below the CMC of the surfactant (Fig. 1*c* and line *b* in Fig. 4). Kaifer and Bard,[20] and others[27] have reported similar large parabolic peak currents in the electroreduction of methylviologen in SDS micelles below its CMC and suggested that aggregation of the methylviologen radical cation with the SDS film adsorbed at the electrode surface and/or formation of premicellar aggregates are responsible for the enhancement of the peak current. In the present case, both the hydrophobic side-chain and the negatively charged head group of VC-8 should facilitate VC-8 joining the CTAB assemblies adsorbed at the electrode surface, increase its local concentration at the electrode surface and hence enhance the peak current. When the concentration of CTAB is increased above 0.5 mmol dm^{-3}, the anodic peak loses sharpness and the current decreases gradually to its diffusion controlled value. This strongly suggests that VC-8 prefers to aggregate with CTAB micelles rather than with the CTAB film adsorbed at the electrode surface. As soon as the concentration of CTAB reaches its CMC and forms micelles, VC-8 is solubilized into the micelle and desorbed from the electrode surface, which causes disappearance of the adsorption pattern. This mechanism is reinforced by the fact that no such adsorption pattern appeared in SDS micellar solution for VC-8, but it appears both in CTAB and SDS micellar solutions for VC-12 and VC-16 because the hydrophobic force of VC-12 and VC-16 prevails over the electrostatic repulsion force with the SDS film adsorbed at the electrode surface, whilst that of VC-8 is not enough to compensate the electrostatic repulsion. Similar parabolic peaks also appear in the potential lines of VC-8 and VC-12 (Figs. 2 and 3).

A more amazing observation is the appearance of two current maxima in the case of VC-12 and VC-16 in CTAB micellar solutions below its CMC (lines *c* and *d* in Fig. 4). The first maximum appears at very low concentrations of CTAB (*ca.* 0.1 and 0.05 mmol dm^{-3} for VC-12 and VC-16, respectively). Increasing the surfactant concentration makes the current decrease to a minimum and then increase to the second maximum. In addition, it was found that the appearance of the second current maximum accompanied turbidity of the solution and, when the surfactant concentration was further increased, the current decreased to its diffusion controlled value and the solution became clear again. This demonstrates in a convincing way the involvement of a kind of mixed premicellar aggregate of CTAB and VC-12 or VC-16 with the latter being the main component. The formation of such premicellar aggregates should solubilize the adsorbed lipophilic VC from the electrode surface and should decrease the current. This is similar to the formation of micelles described above, but the CTAB concentration at which the current reaches a minimum (*ca.* 0.4 and 0.1 mmol dm^{-3} for VC-12 and VC-16 respectively) is appreciably lower than the CMC of CTAB. Continuing increase of the concentration of CTAB would progressively neutralize the negative charges of the lipophilic VC and finally destroy its premicellar aggregates, which in turn would release the lipophilic VC and make it go back to the electrode surface, hence increasing the current to the second maximum. The turbidity of the solution at the second current maximum supports this mechanism because at this point the unstable organic salt CTA^+ $VC\text{-}12^-$ or CTA^+ $VC\text{-}16^-$ precipitated from the solution. Formation of similar micelle-like organic salt aggregates composed of cationic and anionic surfactants have been reported previously.[24–26] For instance, Kato *et al.*[25] reported that octyltrimethylammonium bromide and SDS formed a mixed micelle-like aggregate at the total concentration of the surfactants of 0.8 mmol dm^{-3}. This kind of aggregate was unstable at low concentration, and phase separation occurred, leading to turbidity of the solution. Further increase of the CTAB concentration causes formation of CTAB micelles and solubilizes the lipophilic VC into the micelles, hence decreasing the current to its diffusion controlled value.

Conclusions

The electrochemistry of lipophilic vitamin C derivatives (VCs) in micellar solutions is significantly different from that of their hydrophilic parent molecule. The amphiphilic character of the lipophilic VCs allows them to adsorb onto the electrode surface, to form premicellar and/or micellar aggregates, to solubilize into the surfactant micelles forming mixed micelles, and to interact electrostatically with the surfactant molecules. These effects remarkably shift the anodic peak potential and change the peak current, due to the change of the electron-transfer rate and, to a lesser extent, due to the change of the diffusion coefficient. The electrochemical behavior of the VCs is determined predominantly by the hydrophobic/lipophilic interaction of the hydrocarbon side-chain and the electrostatic interaction of the head group of the VCs with the surfactant. These two effects work cooperatively in CTAB micelles, while they compensate each other in SDS micelles due to the negatively

charged ascorbate anion. Therefore, the electrochemical process of the VCs, and other electroactive species in general, can be controlled by changing their lipophilicity and changing the microenvironment of the reaction medium. The information obtained from this investigation may also have general implication for understanding electron-transfer processes in biomembranes and for design of antioxidant medicines.

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 (4.5 mm in diameter) employed as a working electrode 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 relative to a saturated calomel electrode (SCE) reference electrode.

All chemicals were reagent grade and used as received. The lipophilic VCs were synthesized by esterifying the corresponding carboxylic acid with VC as described previously.[26] 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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