

# Ascorbic acid oxidation in SDS micellar systems

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**Abstract** In this contribution the results of atmospheric and electrochemical oxidation of AA in the SDS micellar solutions and in the microemulsions pentanol/water stabilized by SDS are presented. The hydrophilic vitamin C readily dissolves in water and O/W microemulsions as well as undergoes the irreversible two-electron oxidation reaction. It was found that the atmospheric oxidation of AA is accelerated by the SDS up to the CMC and inhibited in the concentrated SDS solutions. We also found that the rate of atmospheric oxidation of ascorbic acid is higher in the water-in-oil (W/O) than in the oil-in-water (O/W) microemulsions and increases with the increasing oil content. The influence of the SDS on the electrochemical behavior of vitamin C was also studied. The general conclusion emerging from this investigation is that the increasing surfactant concentration shifts the ascorbic acid oxidation potential to higher values whereas the corresponding peak current values diminish. In the microemulsions the AA oxidation is slowed down by increasing the pentanol amount in the system.

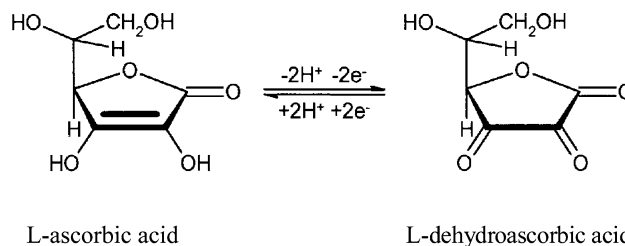
**Keywords** Ascorbic acid · Atmospheric oxidation · Electrochemical oxidation · Micellar solutions · Microemulsion

## 1 Introduction

There is considerable evidence that vitamin C (ascorbic acid, AA) plays an important role in prevention of a

large number of chronic diseases such as cancer, cerebral apoplexy, diabetes, atopic dermatitis, myocardial infarction and AIDS [1–3]. It is known that L-ascorbic acid scavenges active oxygen species and free radicals as a chain-breaking antioxidant [4]. These characteristic biological activities of AA result from its enediol structure which manifests strong electron-donating ability.

The reducing ability of AA is due to a two stage oxidation reaction. The first stage is readily reversible and yields dehydroascorbic acid, (DHAA), which still possesses reducing ability, especially in alkaline solution. DHAA degradative oxidation, for example, by molecular oxygen and hypiodite ion leads to L-threonic and oxalic acids. Alkaline hydrogen peroxide and acidic or alkaline permanganate also bring about oxidative cleavage, a number of different oxidation products being detectable in addition to the above mentioned acids. The rate of aerobic oxidation of ascorbic acid depends on the pH exhibiting maxima at pH 5 and 11.5. However, the reaction is much more rapid and the degradation more extensive in alkalia. Degradative oxidation also occurs, albeit slowly, under anaerobic conditions [4].



The oxidation reaction of L-ascorbic acid

The studies of AA atmospheric oxidation are often supplemented by electrochemical investigations [5–10]. Here

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the cyclic voltammetry method is most often used. Electrochemical oxidation of AA is a totally irreversible  $2e^-$  process [4] that gives hydrated dehydroascorbic acid ( $\text{DHAA} \cdot \text{H}_2\text{O}$ ) by way of the intermediate ascorbate free radical monodehydro-ascorbic acid (MDHA). The reduction of  $\text{DHAA} \cdot \text{H}_2\text{O}$  is not accomplished electrochemically and in acidic and neutral solutions only the oxidation peak in the positive potential scan is observed.

The activity of AA strongly depends on the character of the medium in which the oxidation process occurs. AA is a powerful reducing agent in aqueous solutions, this property being much less evident in non-aqueous media. Of special importance are micellar surfactant solutions and microemulsions characterized by extremely large oil/water interface. These systems are representative for many nutritional, pharmaceutical and cosmetic products and this is why the behaviour of AA in such systems is of scientific and practical interest. AA oxidation in various surfactant systems was investigated but these studies were fragmentary and mainly focused on microenvironment influence on electrochemical behaviour [5–8].

In this contribution we present systematic studies of atmospheric and electrochemical oxidation of AA in the SDS micellar solutions and in the microemulsions SDS/pentanol/water.

## 2 Experimental

### 2.1 Materials

The materials used were: L-ascorbic acid, *n*-pentanol and SDS (sodium dodecylsulfate,  $\text{CMC} = 8 \times 10^{-3} \text{ M}$  (0.24 wt.%)), all Fluka Chemie and RdH Laborchemicalien production, and doubly distilled water. Microemulsion was prepared by adding water to the pentanol/SDS mixture of various weight ratios with vigorous mixing to obtain a clear and highly stable system. The microemulsions had a composition corresponding to one line of SDS concentration (6 wt.%) in the microemulsion region of the phase diagram. This line passes through the aqueous micellar solution, which forms the basis for the O/W microemulsion, a bicontinuous part and the inverse micellar solution, the basis for the W/O microemulsion [11, 12].

### 2.2 Methods

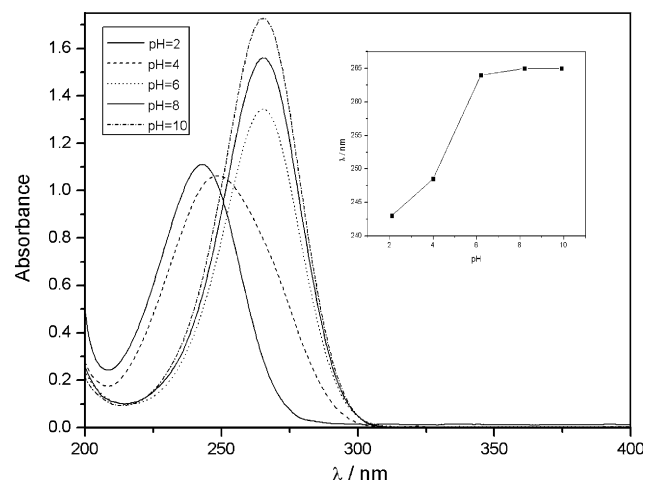
The kinetics of the ascorbic acid oxidation in micellar solutions being in contact with air was determined by ultraviolet spectroscopy using a Specord M-42 Carl Zeiss Jena, double-beam spectrophotometer. Stopped quartz cells with an optical path length of 1.00 cm were used. In the kinetic experiment the AA initial concentration was 0.002 wt.%. The

absorbance value of solution was around 1.2, i.e. stayed within the limits of spectrometer linearity of the concentration/absorbance relationship. The oxygen concentration changes in the experiment were not monitored.

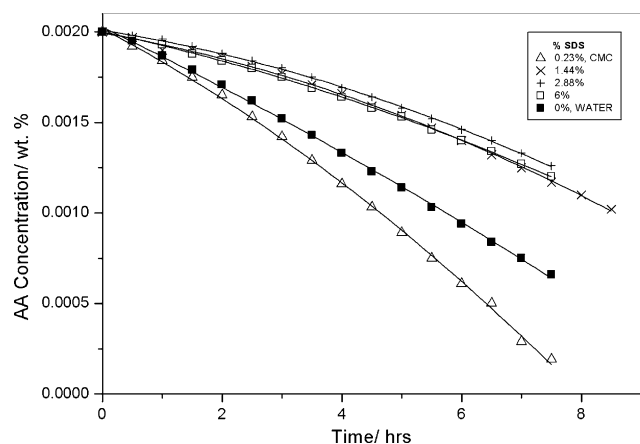
The electrochemistry studies of AA oxidation were performed with the cyclic voltammetry method (VC). Voltammetric measurements were carried out with an EG-20 function generator (Poland), a potentiostat EP-21 (Poland) and a recorder (former USSR). The working electrodes were made of glassy carbon (GCE,  $A = 0.00785 \text{ cm}^2$ ) and platinum (PtE,  $A = 1.12 \text{ cm}^2$ ). Prior to each measurement, the GCE was hand-polished for 30 s with  $\text{Al}_2\text{O}_3$  (0.3  $\mu\text{m}$ ) on the alumina polishing pad (Buehler) and cleaned ultrasonically in water for 30 s. The platinum electrode was cleaned by immersion in the concentrated sulphuric acid solution and heating over the Bunsen Burner. The saturated calomel (SCE) was used as the reference electrode, while the auxiliary one was a platinum wire-netting electrode. At the beginning, the surfactant solution or microemulsion was bubbled with purified nitrogen for 20 min. to remove oxygen from a voltammetry cell [13]. All data were taken at  $22 \pm 1 \text{ }^\circ\text{C}$ .

## 3 Results and discussion

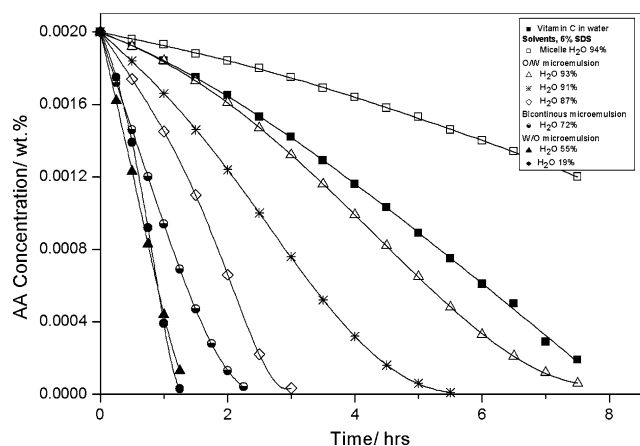
In Fig. 1 the UV spectra of L-ascorbic acid at different pH are shown. At pH 2.0 the UV spectrum reveals a  $\lambda_{\text{max}}$  of 243 nm ( $\epsilon = 11\,014 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ) which undergoes a red shift to 265 nm ( $\epsilon = 15\,600 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ) at pH 6.0–8.0 as a result of ionization of the C-3-OH proton. This result is in accordance with the earlier literature data [4, 14]. At the pH natural for the SDS solutions containing 0.002 wt.% of AA most of AA molecules are singly dissociated and absorb at 265 nm. Thus, the decay of the



**Fig. 1** Effect of pH on the absorption spectrum of 0.002% (about  $1 \times 10^{-4} \text{ mol dm}^{-3}$ ) ascorbic acid in the SDS aqueous solution at CMC



**Fig. 2** Kinetics of ascorbic acid atmospheric oxidation in the SDS aqueous solutions



**Fig. 3** Kinetics of ascorbic acid atmospheric oxidation in the pentanol/water microemulsion stabilized by SDS

absorbance at this wavelength was considered to find the AA concentration depletion.

In Figs. 2 and 3 the kinetics of AA atmospheric oxidation in the micellar solutions and in the microemulsions is shown. For SDS micellar solutions having natural pH between 4 and 5, an increase of the oxidation rate with the increasing surfactant concentration up to the CMC is observed. At the CMC the oxidation rate reaches its maximum value and then decreases gradually with the surfactant concentration. For the concentrated solutions (up to 6% of SDS) the oxidation process becomes even slower than in the pure aqueous solution.

The explanation of such behaviour is not straightforward. Below CMC the surfactant is present chiefly in the singly dispersed state. As the surfactant concentration increases the polarity of the medium decreases. Oxygen solubility in non-polar solvents is higher than in water [15]. Oh and co-workers [16] have found that AA stability in the aqueous buffer is higher than in the EtOH/H<sub>2</sub>O 1:1 (v/v) solution. Thus, one can expect that with the increasing

surfactant concentration more oxygen will be dissolved in the system causing acceleration of oxidation reaction.

At the CMC the micellization starts. The micelles and the aqueous intermicellar solution create two separate pseudo-phases. Oxygen may enter the micelles [17, 18] whereas a hydrophilic ascorbic acid molecule at pH 4–5 is negatively charged and its location in the hydrophobic core of the micelle can be excluded. Moreover, the repulsion between the ascorbic anions and the negatively charged micelles occurs, leading to separation of reagents and, thus, slowing down the reaction rate. It is also possible that the presence of negatively charged micelles affects the degree of dissociation of ascorbic acid molecules and/or the stability of the free radicals formed during the successive univalent reduction of dioxygen [16] and thus the rate of AA decomposition. The initial rates of atmospheric oxidation of AA in the SDS micellar solutions are given in Table 1. One can see that the rate of oxidation is the highest at the CMC.

In Fig. 2 and Table 2 the results of AA atmospheric oxidation in the microemulsions are presented as a function of pentanol content in the system starting from oil-in-water microemulsion, through the bicontinuous phase to the water-in-oil system.

The literature data on AA stability in various media [9, 10, 19] show that its decomposition is accelerated by decrease in solvent polarity. Our results confirm this conclusion. With the increasing pentanol concentration in the system (decreasing polarity), the oxidation rate increases and reaches the maximum in the W/O microemulsion. Two sources of such behaviour can be considered. First, the pentanol molecules added to the system are built in the micelles lowering the micelle/solution interfacial tension and making the micelles grow in size. According to the model of a Laplace pressure acting across the micelle surface any process that serves to lower the interfacial tension at the micelle–water interface or causes the individual micelles to expand will lower the Laplace pressure and therefore will have the effect of increasing the micellar solubility of gases [20, 21]. Growing concentration of oxygen in the system increases the rate of AA oxidation.

Second, the pentanol molecules built in the SDS micelles not only suppress the interfacial tension but also reduce the charge density on the surface of a micelle. Decreasing repulsion between an AA anion and micellar surface facilitates a direct contact between reagents and accelerates the oxidation reaction (micellar catalysis).

The increasing pentanol content in the microemulsion also causes the increase of AA concentration in the water phase, the increase of oxygen content in the hydrophobic region of micelles and the growth of the interfacial contact area. All these circumstances are responsible for the acceleration of AA oxidation reaction (increasing value of AA oxidation initiation rate *R*).

**Table 1** Values of AA oxidation initiation rate  $R$ , calculated from the relation  $R = -n \, dc/dt$ , where  $n$ —AA stoichiometric factor equals 2. The derivative  $dc/dt$  was found from the linear regression of the experimental data dependence  $c = f(t)$ , where  $c$ —remainder of AA in the SDS solution

SDS conc. (wt.%)	0.00	0.23 (CMC)	1.44	2.88	6.00
$R = -2 \, (dc/dt / \text{wt.}\%/h)$	$0.00036 \pm 4.6 \times 10^{-6}$	$0.00050 \pm 1.1 \times 10^{-5}$	$0.00024 \pm 8.0 \times 10^{-6}$	$0.00020 \pm 7.0 \times 10^{-6}$	$0.00022 \pm 5.4 \times 10^{-6}$

**Table 2** Values of AA oxidation initiation rate  $R$ , calculated from the relation  $R = -n \, dc/dt$ , where  $n$ —AA stoichiometric factor equals 2. The derivative  $dc/dt$  was found from the linear regression of theexperimental data dependence  $c = f(t)$ , where  $c$ —remainder of AA in the SDS/pentanol/water microemulsion

	Aqueous solution	Conc. micellar solution	O/W	BC	W/O
Pentanol conc. (wt.%)	0.00 no SDS	0.00 6% SDS	5.00 6% SDS	22.00 6% SDS	75.00 6% SDS
$R = -2 \, (dc/dt / \text{wt.}\%/h)$	$0.00036 \pm 4.6 \times 10^{-6}$	$0.00022 \pm 5.4 \times 10^{-6}$	$0.00128 \pm 6.0 \times 10^{-5}$	$0.0018 \pm 8.0 \times 10^{-5}$	$0.0033 \pm 1.6 \times 10^{-4}$

The activity of antioxidants may be also evaluated on the basis of their redox parameters obtained using cyclic voltammetry with various electrodes and in various media [13]. The knowledge of oxidation potentials, electron transfer rate constants and diffusion coefficients of various antioxidants in the model systems may be useful for predicting their behavior in the systems of practical use.

In order to find out how the surfactant influences the ascorbic acid oxidation process the measurements of oxidation potentials and peak currents in aqueous solutions having different pH and containing different amounts of SDS were carried out. The results are shown in Fig. 4.

It is clearly seen that in the aqueous solution the AA oxidation potential,  $E_{pa}$ , strongly depends on the solution pH. The lower the pH, the higher the AA oxidation potential. It means that the electron transfer from the ascorbic anion to the electrode surface is easier than that from the neutral AA molecule.

At each pH the oxidation potential increases with the increasing surfactant concentration, reaching a plateau above the CMC. The effect of SDS on the electrochemical

behaviour of ascorbic acid is due to the surfactant adsorption at the electrode surface and to the formation of micelles in the bulk solution. Ionic surfactants can form hydrophilic charged films at the glassy carbon electrode with the polar headgroups directed into the bulk phase. The negatively charged layer of SDS blocks the access of AA molecules to the electrode surface. With the increasing surfactant adsorption the free electrode surface diminishes. At the same time the growing thickness of adsorption layer moves the plane of electron transfer away from the electrode surface. In consequence, the increase of the oxidation potential and the decrease of the peak current are observed. In Table 3 the diffusion coefficients and the apparent heterogeneous rate constants calculated from the voltammograms are presented [22].

The apparent diffusion coefficient of AA was found from the formula:

$$D = \left( \frac{I_{pa}}{3 \times 10^5 n (\beta n_{\beta})^{1/2} A v^{1/2} C^0} \right) \quad (\text{cm}^2 \text{s}^{-1}) \quad (1)$$

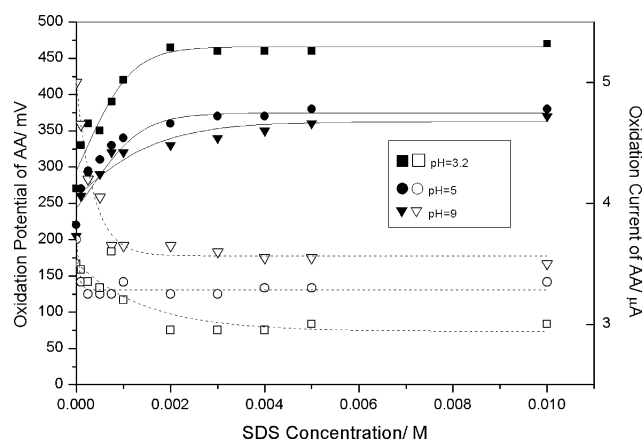
where  $I_{pa}$ —the peak current (A),  $v$ —the CV scan rate, ( $\text{V s}^{-1}$ ),  $C^0$ —the ascorbic acid concentration, ( $\text{mol cm}^{-3}$ ),  $n$ —the number of electrons involved in the oxidation process,  $\beta n_{\beta}$ —the charge transfer coefficient which can be estimated from the relation.

$$\beta n_{\beta} = \frac{0.048}{E_{pa} - E_{pa/2}} \quad (2)$$

where  $E_{pa}$ —the oxidation peak potential, (V),  $E_{pa/2}$ —the potential at which the current equals one half of the peak current, (V). The apparent heterogeneous rate constant  $k_s$  for irreversible anodic oxidation can be estimated from the anodic peak potential according to Eq. 3:

$$\log k_s = \frac{\beta n_{\beta}}{0.059} \left[ -(E_{pa} - E_f^0) \right] + \frac{1}{2} \log (D \beta n_{\beta} v) + 0.456 \quad (3)$$

where  $E_f^0$  is the formal oxidation potential (for ascorbic acid  $E_f^0 = -0.193 \text{ V}$  at  $\text{pH} = 7.4$  calculated from the literature electrochemical data, taking  $\text{p}K_1 = 4.10$  and

**Fig. 4** Variation of ascorbic acid oxidation peak potential  $E_{pa}$  and oxidation peak current  $I_{pa}$  with the SDS concentration at a GC electrode; CV scan rate  $3 \times 10^{-2} \text{ V s}^{-1}$

**Table 3** Electrochemical parameters of AA oxidation determined at a glassy carbon electrode at neutral pH = 7

Medium	$E_{pa} \times 10^3$ (V) vs. SCE	$I_{pa} \times 10^6$ (A)	$\beta n_{\beta}$	$D \times 10^6$ (cm <sup>2</sup> s <sup>-1</sup> )	$k_s \times 10^6$ (cm s <sup>-1</sup> )
H <sub>2</sub> O	200	4.75	0.40	2.1	1.26
SDS	330	3.75	0.32	1.6	0.66

The AA concentration was  $5 \times 10^{-3}$  mol cm<sup>-3</sup> and the SDS concentration was 0.001 mol dm<sup>-3</sup> (value higher than CMC in 0.1 M NaCl),  $\nu = 0.05$  V s<sup>-1</sup>

$pK_2 = 11.79$  [5, 23]).  $E_f^0$  can be easily transferred to the formal potential at other pH values using Eq. 4:

$$E_f^0 = E^0 - \frac{0.059}{n} \text{pH} \tag{4}$$

where  $E^0$  is the standard oxidation potential. Each value of the peak current and the peak potential used for  $D$  and  $k_s$  calculation was the mean of the three measurements.

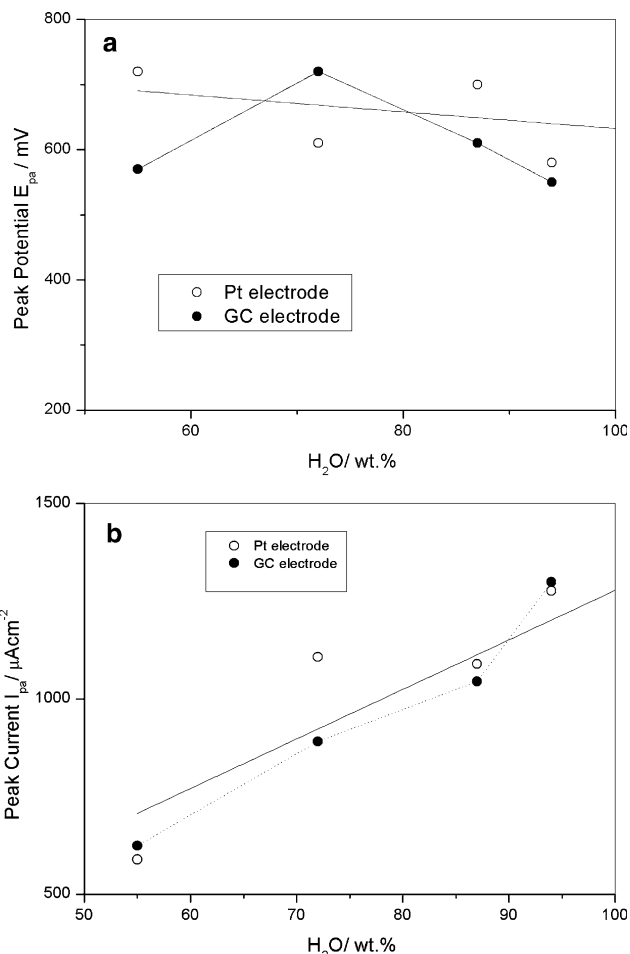
From Table 3 one can see that the diffusion of AA to the electrode surface is more difficult in the presence of SDS. The apparent diffusion coefficient is an average of the actual values in the bulk solution, in the micelles and in the surfactant film adsorbed on the electrode. In the SDS solution the interaction of AA anions with the bulk micelles is weak and the main effect comes from the adsorbed surfactant film, i.e. from electrostatic repulsion between the negatively charged surfactant headgroups and the AA anions. The apparent electron transfer rate constant  $k_s$  is lower in the presence of SDS micelles, approximately twice in comparison with the pure aqueous solution.

For both systems the  $k_s$  values satisfy approximately the condition for totally irreversible behaviour  $k_s \leq 2 \times 10^{-5} \nu^{1/2}$  cm s<sup>-1</sup> [22].

The next step of our study was to investigate the influence of the microemulsion composition on the AA electrooxidation. For this purpose we took cyclic voltammograms of AA at the Pt and GC electrodes. The results are shown in Fig. 5. In addition, the apparent diffusion coefficients and the charge transfer coefficients are presented in Table 4.

Looking into Fig. 5 one can see that the microemulsion environment affects the oxidation potential of AA. At both electrodes the  $E_{pa}$  increases with the decreasing water content.

Contrary to the peak potential, the peak current and the apparent diffusion coefficient of AA decrease when the water content in the system decreases. As the AA molecules do not interact with SDS micelles, the current lowering is feasibly due to the adsorption layer formed by SDS on the electrode surface in the region of positive potentials. This layer is additionally stabilized by pentanol molecules. Their incorporation into the adsorbed phase reduces repulsion between the charged polar heads and makes the surface layer more compact. Due to this, the penetration of AA molecules to the electrode is harder. The



**Fig. 5** **a** Variation of AA oxidation peak potential,  $E_{pa}$ , with the microemulsion composition at the Pt and GC electrodes and CV scan rate  $0.1$  V s<sup>-1</sup> (lines are drawn to help the eye). **b** Variation of oxidation peak current,  $I_{pa}$ , with the microemulsion composition at the Pt and GC electrodes and CV scan rate  $0.1$  V s<sup>-1</sup> (lines are drawn to help the eye)

electron transfer from the AA molecule to the surface is also more difficult. In Tables 3 and 4 the charge transfer coefficients calculated from the peak width according to the formula (2) are reported. Their values distinctly lower than 0.5 indicate that the oxidation process is under the kinetic control of slow electron transfer (ET) and that the actual oxidation potentials are much more positive than the standard potential of the rate determining ET step.



**Table 4** The apparent diffusion coefficients  $D$ , charge transfer coefficients  $\beta n_{\beta}$  and the apparent heterogeneous rate constants  $k_s$  of ascorbic acid in various microemulsion systems at the glassy carbon and platinum electrodes calculated from CV experimental data

Solution composition		Glassy carbon electrode				Platinum electrode			
		$\beta n_{\beta}$	$E_{pa}$ (V)	$D \times 10^6$ ( $\text{cm}^2 \text{s}^{-1}$ )	$k_s \times 10^6$ ( $\text{cm s}^{-1}$ )	$\beta n_{\beta}$	$E_{pa}$ (V)	$D \times 10^6$ ( $\text{cm}^2 \text{s}^{-1}$ )	$k_s \times 10^6$ z( $\text{cm s}^{-1}$ )
0.1 M NaCl (GCE) or 0.1 M KCl (PtE), pH = 4	Aqueous solution	0.4	0.32	6.2	1.9	0.15	0.67	10.0	11.8
SDS 6%									
94% water	Micellar solution	0.24	0.55	7.8	2.6	0.22	0.58	8.30	3.56
7% pentanol, 87% water	O/W	0.24	0.61	5.1	1.2	0.15	0.70	8.79	9.32
22% pentanol, 72% water	BC	0.20	0.72	4.4	1.4	0.18	0.61	7.38	6.11
39% pentanol, 55% water	W/O	0.25	0.57	1.7	0.8				

Scan rate:  $v = 0.1 \text{ V s}^{-1}$ 

#### 4 Conclusions

The aim of this work was to investigate the influence of micellar and microemulsion systems on the oxidative properties of ascorbic acid. The results of our work can be summarized as follows.

- SDS accelerates the atmospheric oxidation of AA at the concentrations up to the CMC whereas in the concentrated solutions inhibiting effect occurs.
- Atmospheric oxidation of AA in the microemulsion SDS/pentanol/water is faster in the pentanol rich systems.
- The electrochemical oxidation of AA on the glassy carbon electrode is an irreversible and strongly pH dependent process.
- The addition of SDS to the system increases the oxidation potential and decreases the peak current.
- In the SDS/pentanol/water microemulsions the increase of the peak potential is observed with the decreasing water content. At the same time the peak current decreases.
- In the SDS solutions and microemulsions the modification of the electrode surface by the adsorbed surfactant seems to be the most important factor affecting the oxidation process. The adsorbed surfactant layer moves the electron transfer plane away from the electrode surface and alters the oxidation potential and the charge transfer rate.
- The presence of SDS and pentanol in the system influences the rate of chemical and electrochemical oxidation of AA. However, the reasons for these changes are different. The effects of SDS and pentanol on chemical oxidation of AA are due to the fact that AA and oxygen molecules are located in the different phases of the system (polar and apolar). This reduces the probability of contact between the reacting

molecules. Also the oxygen concentration changes with the system composition. In the case of electrochemical oxidation, the changes of AA oxidation parameters are mainly due to the formation of surfactant adsorption layer at the electrode surface.

More profound understanding of mechanism of antioxidant action of AA in the presence of surface-active substances and in microemulsion systems requires further investigations.

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