

## The Effect of Surfactant Adsorption at a Glassy Carbon Electrode on Electrochemical Oxidation of Propyl Gallate

M. SZYMULA<sup>1,\*</sup> and J. NARKIEWICZ-MICHAŁEK<sup>2</sup>

<sup>1</sup>*Department of Radiochemistry & Colloid Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University, M. Curie-Skłodowska Sq. 3, 20-031, Lublin, Poland,*

<sup>2</sup>*Department of Theoretical Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University, M. Curie-Skłodowska Sq. 3, 20-031, Lublin, Poland,*

(\*author for correspondence, tel.: +48-81-537-5624; fax: +48-81-5332811; e-mail: szymu@hermes.umcs.lublin.pl)

Received 8 April 2005; accepted in revised form 1 November 2005

**Key words:** antioxidants, electrochemical oxidation, micellar solutions, microemulsions, propyl gallate

### Abstract

The electrochemical oxidation of propyl gallate (PG) in various surfactant solutions (AOT, Triton X-100 and CTAB) and microemulsions stabilised by the anionic surfactant SDS was investigated using cyclic voltammetry. This method has been widely applied to determine the role of microenvironment on antioxidative properties of natural and synthetic substances used to protect food and other products against oxidation. In general, the addition of surface-active agents to the system makes the oxidation of propyl gallate more difficult. The peak potential is shifted to more positive values due to the interaction of the electroactive substance with the surfactant structures at the electrode and with micelles in the bulk solution. In microemulsions the oxidation process is even more difficult than in the surfactant containing solutions. The oxidation potential increases significantly when the O/W microemulsion converts to W/O microemulsion through the bicontinuous phase.

### 1. Introduction

Scientists have come to appreciate the importance of oxygen in essential metabolic pathways for many forms of life. Although oxidation reactions are natural, it is critical to the food industry to inhibit these reactions through the use of antioxidants. The ultimate mission of the food product developer is to slow or stop the chemical oxidation reaction long enough for food to be eaten by the consumer before oxidation has rendered it inedible. Oxidation can transform food flavour into stale, fishy or cardboard, dull the colour to that of faded paint and change the nutritional value of lipids into toxic ketones and aldehydes.

In recent years the technological and economic requirements of the pharmaceutical and food industries have intensified the use of antioxidants. They are usually classified into two groups – natural antioxidants, such as vitamin C, vitamin E,  $\beta$ -carotene, and synthetic ones including propyl gallate (PG). The antioxidants are added to food and other commercial products to improve their stability and especially to prevent rancidity in the lipid or fat containing products [1].

The antioxidant activity of different species is closely related to their redox properties and, consequently, knowledge of their redox behaviour is a very important basis to obtain better explanations of their properties.

The electron-donating ability of antioxidants can be quantitatively assessed on the basis of their electrochemical characteristics. Among different electrochemical methods, cyclic voltammetry has been widely used to investigate the redox behaviour of different antioxidants in various media [2–7]. From these investigations it follows that the antioxidant activity is strongly dependent on the reaction environment. The surfactant solutions and microemulsions are chosen as electrochemical reaction media because they are the simplest chemical models of biological membranes and represent a major group of colloidal systems relevant to foods, cosmetics and pharmaceuticals.

Propyl gallate is a hydrophilic synthetic antioxidant widely used to stabilize commercial products. The objective of this work is to investigate its oxidative properties in surfactant solutions and microemulsions using cyclic voltammetry. Comparing the results with the earlier results by Gunckel et al. [2], who investigated the behaviour of PG in aqueous solutions, the influence of the microenvironment composition and structure on the electrode processes will be discussed.

Micellar effects may be of many kinds, including electrostatic and surface interactions, hydrophobic forces and antioxidant partition between the micelle and the water phase. Our studies are concerned with the influence of the surfactant on the oxidation potential

and current, charge transfer coefficient and diffusion coefficient.

Surfactant behaviour in solution, i.e., aggregation, as well as adsorption and organization on the electrode surface, influences the redox reaction of electroactive species, changing their redox potential  $E_{pa}$  and the corresponding peak current  $I_{pa}$  [2–7]. The significant shift of the oxidation potential and the change in the peak current may be associated with surfactant adsorption on the electrode surface. Adsorption may alter the over-voltage of the electrode process and influences the rate of electron transfer. In addition, the formation of micellar aggregates above the CMC may influence the mass transport of electroactive species to the electrode.

In order to choose the most suitable supporting electrolyte for voltammetric determination of propyl gallate, Ni et al. [8] tested various dilute 0.1 M acids. The following peak potentials vs. the Ag/AgCl reference electrode were found: hydrochloric acid  $E_{pa} = 598$  mV, sulfuric acid  $E_{pa} = 602$  mV, acetic acid  $E_{pa} = 541$  mV, chloroacetic  $E_{pa} = 578$  mV, tartaric acid  $E_{pa} = 568$  mV, oxalic acid  $E_{pa} = 598$  mV and perchloric acid  $E_{pa} = 560$  mV.

Agić and co-workers [9] oxidized PG at a cylindrical carbon fibre microelectrode (CFNEs) modified with poly(3-methylthiophene) (P3MT) coatings in a phosphate buffer solution at pH 2.0. They observed a well-defined oxidation peak at +0.45 V vs. the Ag/AgCl/KCl reference electrode.

Diego et al. [10] stated that the hydrophobicity of analytes is an important characteristic to be taken into account for the correct choice of electrode material. Furthermore, the hydrophobic character of the electrode surface seems to be more important than the working medium used. For example for PG at a graphite-poly(tetrafluoroethylene) composite electrode  $E_{pa} = +0.45$  V, at a carbon paste electrode  $E_{pa} = +0.58$  V vs. Ag/AgCl/3M KCl in 4:96 MeOH/ H<sub>2</sub>O.

Gunckel et al. [2] while studying the electron-donating ability of gallates, found that PG was easily oxidized in acid and neutral solutions. They also proposed the overall oxidation pathway of alkyl gallate derivatives, which is based on the well described route for the anodic oxidation of phenols, hydroquinone and derivatives [11, 12]. Electrochemical oxidation occurs via two electron-transfer steps, however for all gallate derivatives cyclic voltammetry on stationary electrodes showed only a single oxidation peak. Good resolution for the second peak was obtained only when the rotating disk electrode was used (differential pulse and hydrodynamic voltammetry). The oxidation process appears to be irreversible, diffusion controlled and pH-dependent. The same was stated by Diaz et al. [13] who studied the voltammetric behaviour of PG and other synthetic antioxidants at a glassy carbon electrode (static and rotating) using LS, sampled DC, DP and cyclic voltammetry in an acetonitrile-water medium at different pH values.

## 2. Experimental

### 2.1. Materials

The surfactants used were

- anionic surfactant – SDS (sodium dodecylsulfate), CMC in water  $8.0 \times 10^{-3}$  M [14],
  - anionic surfactant – AOT (bis(2-ethylhexyl) sulfosuccinate sodium salt), CMC in water  $5.0 \times 10^{-3}$  M [15],
  - nonionic surfactant – Triton X-100 (*t*-octyl phenoxy polyethoxyethanol), CMC in water  $3.0 \times 10^{-4}$  M [16],
  - cationic surfactant: CTAB – hexadecyltrimethylammonium bromide, CMC in water  $9.2 \times 10^{-4}$  M [14].
- All surfactants as well as propyl gallate and 1-pentanol were produced by Fluka Chemie Ag and RdH Laborchemicalien GmbH & Co. KG. In the experiments double distilled water was used.

### 2.2. Methods

Linear sweep voltammetry (CV) studies of a propyl gallate oxidation process were performed with a glassy carbon (GCE) working electrode,  $d = 1$  mm. A saturated calomel electrode (SCE) was used as reference, while the auxiliary electrode was a platinum wire-netting. The samples were measured and kept at  $22 \pm 1^\circ\text{C}$ . They were stored in glass vessels without stirring in daylight. In all the experiments the PG concentration was  $1 \times 10^{-3}$  M. The measurements were carried out in the potential ranges where the background currents of the supporting solutions were negligibly small (–200, +800 mV).

In the first experiment the measurements were carried out using surfactant solutions in phosphate buffer (pH 2 and 6.88). For each surfactant concentrations below and above CMC were investigated.

In the second experiment the electrochemical oxidation of PG was studied in the system whose composition corresponds 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 (SDS 6%, pentanol 5%, water 89%), a bicontinuous part (SDS 6%, pentanol 22%, water 72%), the inverse micellar solution, the basis for W/O microemulsion (SDS 6%, pentanol 39%, water 55%) [6, 17].

The microemulsion was prepared by titration of pentanol and sodium dodecyl sulfate mixtures of various weight ratios with water. This was vigorously mixed to obtain a clear and high stable microemulsion. Initially the supporting solution was bubbled with purified nitrogen for 20 min to remove oxygen [6, 7]. Then, the appropriate amount of solid PG was introduced to the solution. The measurements were carried out in the same potential range as in the first experiment.

The differential capacity of the electric double layer was measured using the *ac* impedance technique at a

frequency of 800 Hz with an AUTOLAB (Eco Chemie BI Holland) controlled by a computer. The reproducibility of the average capacity measurements was  $\pm 1\%$ .

### 3. Results and discussion

In order to determine how the surfactant changes the propyl gallate oxidation process we carried out measurements of oxidation potentials and peak currents in the buffered aqueous solutions containing various amounts of surfactant at pH 6.88 and 2. At both pH values propyl gallate gave irreversible voltammograms with a single oxidation peak (Figure 1).

To elucidate whether the electrode process is diffusion or electron transfer controlled, we measured peak potentials and peak currents at various values of the potential scan rate (from 10 to 100  $\text{mV s}^{-1}$ ). The dependence of the peak current ( $I_{\text{pa}}$ ) on the square root of the scan rate ( $v^{1/2}$ ) should be a straight line passing through the origin [18]. As an example, in Figures 2 and 3 such dependencies for various surfactant solutions with the concentration above the CMC and pH = 2 and 6.88 are presented.

For both pH values the dependencies  $I_{\text{pa}}$  vs.  $v^{1/2}$  are approximately straight lines going through the origin. Moreover, the peak potentials are shifted positively for higher scan rates (see Figure 4) though the changes are not so significant. According to Adams [18], for the irreversible two-electron oxidation reaction, the shift in  $E_{\text{pa}}$  at low values of  $v$  (as in our case) should be ca. 15 mV for each tenfold increase in the scan rate. Thus, Figs. 2-4 confirm that the PG oxidation in the surfactant solutions is a typical diffusion-controlled process. The results, which will be addressed in the forthcoming

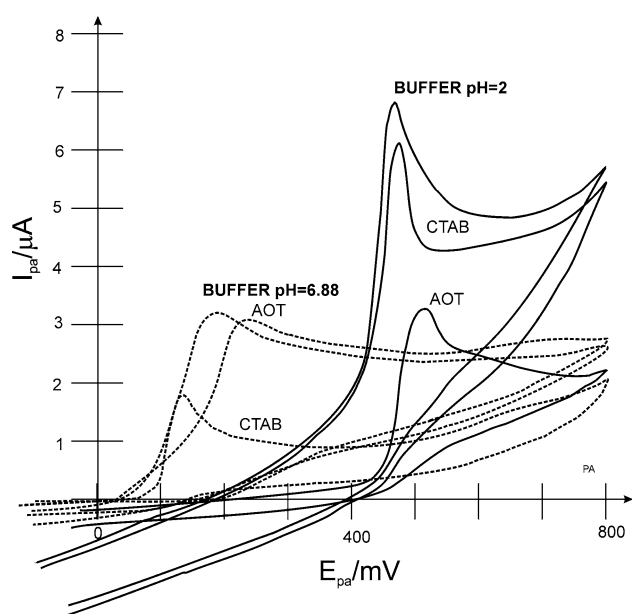


Fig. 1. Cyclic voltammograms of  $5 \times 10^{-3}$  M PG in the pure buffer and buffered surfactant solutions at the scan rate  $0.1 \text{ V s}^{-1}$ . Surfactant concentration was above the CMC.

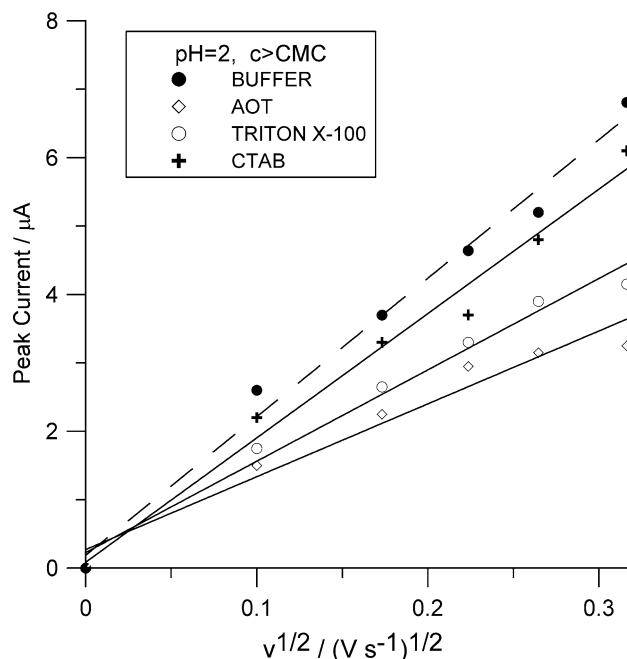


Fig. 2. The dependence of  $I_{\text{pa}}$  vs.  $v^{1/2}$  for PG oxidised in the acidic surfactant solutions, pH=2. The surfactant concentration was above the CMC.

discussion, were taken at  $v = 100 \text{ mV s}^{-1}$ . At this scan rate single well-shaped anodic peaks were observed in the all investigated systems.

From the voltammograms the apparent diffusion coefficient  $D/\text{cm}^2\text{s}^{-1}$  can be calculated using the following equation [6, 7, 19, 20]

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

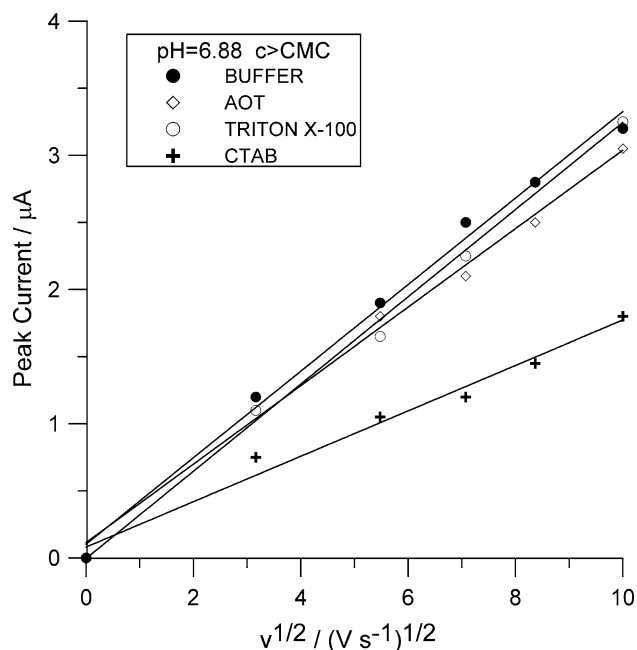


Fig. 3. The dependence of  $I_{\text{pa}}$  vs.  $v^{1/2}$  for PG oxidised in the neutral surfactant solutions, pH=6.88. The surfactant concentration was above the CMC.

Table 1. The values of the charge transfer coefficient  $\beta n_{\beta}$  and the apparent diffusion coefficient  $D$  for propyl gallate in 0.001 M surfactant solutions ( $c > \text{CMC}$ )

SOLUTION	pH = 6.88		pH = 2	
	$\beta n_{\beta}$	$D \times 10^6 \text{ cm}^2 \text{ s}^{-1}$	$\beta n_{\beta}$	$D \times 10^6 \text{ cm}^2 \text{ s}^{-1}$
Phosphate buffer	0.7	6.7	1.2	17.1
AOT	0.6	6.5	1.1	4.5
Triton X-100	0.7	6.9	1.2	6.4
CTAB	1.1	1.4	1.3	13.3

where  $I_{\text{pa}}$  is the anodic peak current/A;  $n$  is the number of electrons involved in the oxidation;  $A$  is the area of the electrode/ $\text{cm}^2$ ;  $v$  is the CV scan rate/ $\text{V s}^{-1}$ ;  $c^0$  is the concentration of the electroactive species in bulk solution/ $\text{mol cm}^{-3}$   $\beta n_{\beta}$  is the charge transfer coefficient which is given by the formula,

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

$E_{\text{pa}}$  is the oxidation peak potential and  $E_{\text{pa}/2}$  is the potential at which the current equals one half of the peak current (in V).

The apparent diffusion coefficients of PG calculated from Equation (1) and the charge transfer coefficients given by Equation (2) in pure buffer solutions and in solutions containing different amounts of various surfactants are presented in Table 1. The word 'apparent' is included in recognition of the fact that the diffusion may be distorted due to the restricted molecular motion caused by interaction of PG molecules with micelles in solution and surfactant molecules adsorbed at the electrode surface. Thus, the diffusion coefficient,  $D$ , calculated from the CV data can be treated as an average of the actual values in the bulk solution, in micelles and in the surfactant film adsorbed on the

electrode surface and its value may provide some information concerning the effect of surfactant on PG transport to the electrode.

The peak potentials and peak currents of propyl gallate voltammetric oxidation in various surfactant solutions are shown in Figures 5a, b and 6a, b respectively. In the buffer solution, pH=2, the oxidation potential  $E_{\text{pa}}$  measured vs. SCE at  $100 \text{ mV s}^{-1}$  scan rate was 485 mV whereas it was only 185 mV in the buffer solution having pH=6.88. Such a difference indicates that the oxidation of PG is strongly pH dependent. The value of the peak current in acidic conditions is more than twice that in neutral pH ( $I_{\text{pa}} = 6.8 \mu\text{A}$  at pH=2 and  $I_{\text{pa}} = 3.2 \mu\text{A}$  at pH=6.88). It is noteworthy that the values of the peak current are correlated with the apparent diffusion coefficients i.e.,  $D$  at pH=2 is about three times as high as that at pH=6.88. This means that the transport of PG to the GC electrode in acidic solution is much faster than in neutral conditions.

As seen in Table 1, the value of  $\beta n_{\beta}$  generally depends on the total number of electrons exchanged in the oxidation process, the rate determining step of the oxidation reaction and on the stoichiometric reaction number (this number indicates how many times the rate determining step should take place in order to accomplish

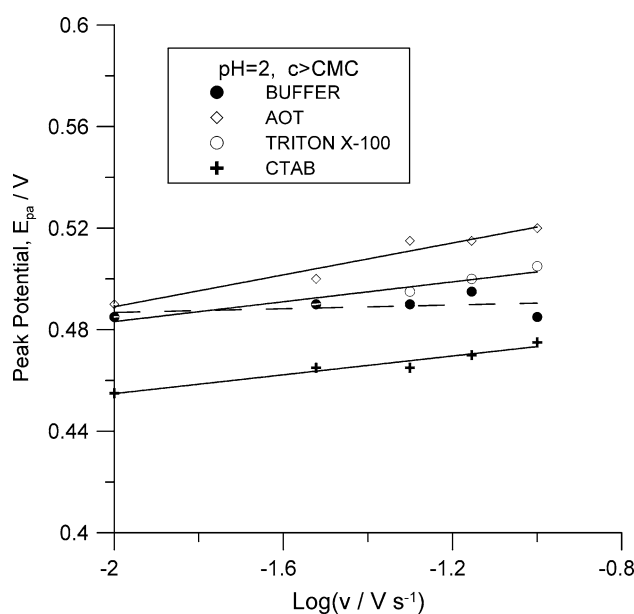


Fig. 4. The dependence of the PG oxidation peak potential vs. the logarithm of the scan rate in various surfactant solutions at pH=2. The surfactant concentration was above the CMC.

the oxidation reaction). The value of the effective charge transfer coefficient should be about 0.5 for a simple electrode reaction [18–20]. Values higher than 0.5 indicate that the mechanism is more complicated.

Table 1 shows that the charge transfer coefficients calculated from Equation (2) are pH dependent. At pH = 6.88  $\beta n_{\beta}$  equals 0.7 and at pH = 2  $\beta n_{\beta}$  exceeds 1.2. From this it can be concluded that the rate determining steps are different. In neutral conditions the second electron transfer determines the rate. In acidic conditions the first electron transfer is controlling. These results are consistent with those of Gunckel et al. [2] who obtained similar values of charge transfer coefficients for a series of alkyl gallates in acidic solution.

The addition of different surfactants to the system alters the PG oxidation potential and peak current. These changes are dependent on the surfactant type, its

concentration and the pH. In acidic conditions (Figure 5) nonionic Triton X-100 and anionic AOT exhibit similar behaviour. They increase the peak potential  $E_{pa}$  and decrease the peak current up to the CMC. Above the CMC both quantities remain approximately constant for Triton X-100. In the case of AOT, the abrupt increase in  $E_{pa}$  for the smallest surfactant concentration is observed. Then  $E_{pa}$  decreases with increasing surfactant concentration, but remains higher than in the pure buffer solution. The peak current decreases monotonically with AOT concentration. Probably, the adsorption of this surfactant on the electrode surface is faster than the transport of PG to the electrode and hence the oxidation of PG occurs at a more positive potential (the shift is +0.06 V for AOT and +0.03 V for Triton X-100). The presence of surfactant molecules in the vicinity of the electrode hinders the access of antioxidant

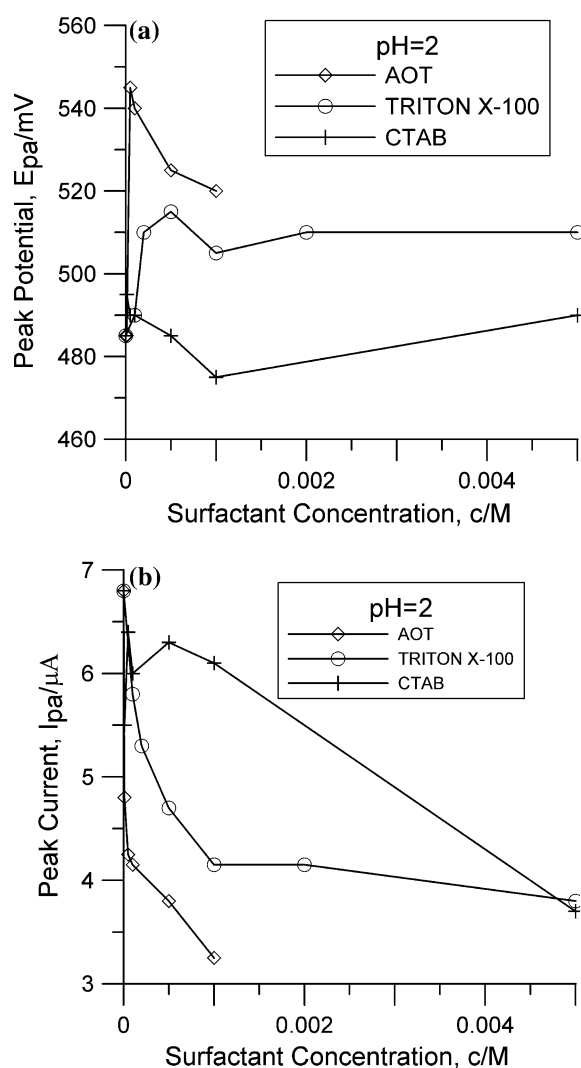


Fig. 5. (a) Variation of propyl gallate oxidation peak potential  $E_{pa}$  at the glassy carbon electrode in phosphate buffer (pH 2) with the surfactant concentration at the CV scan rate  $0.1 \text{ V s}^{-1}$ . (b) Variation of propyl gallate oxidation peak current  $I_{pa}$  at the glassy carbon electrode in phosphate buffer (pH 2) with the surfactant concentration at the CV scan rate  $0.1 \text{ V s}^{-1}$ .

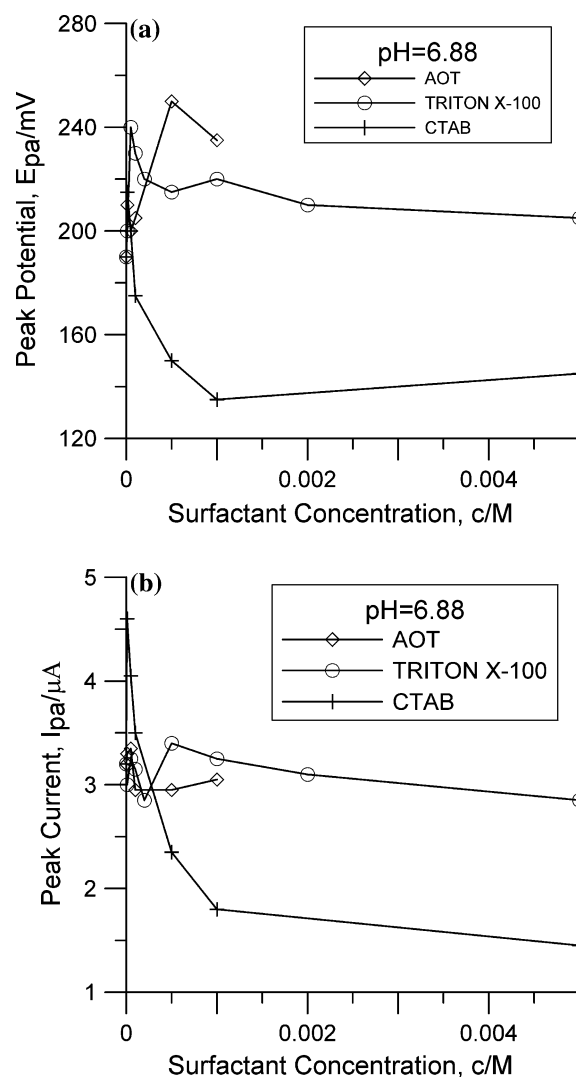


Fig. 6. (a) Variation of propyl gallate oxidation peak potential  $E_{pa}$  at the glassy carbon electrode in phosphate buffer (pH 6.88) with the surfactant concentration at the CV scan rate  $0.1 \text{ V s}^{-1}$ . (b) Variation of propyl gallate oxidation peak current  $I_{pa}$  at the glassy carbon electrode in phosphate buffer (pH 6.88) with the surfactant concentration at the CV scan rate  $0.1 \text{ V s}^{-1}$ .

molecules (the apparent diffusion coefficient and the peak current decrease in comparison with the pure buffer).

Burgess et al. [21] investigated the structure of the layer formed by anionic surfactant SDS on a gold surface using electrochemical and neutron reflection methods. They found that the negatively charged surfactant did not adsorb at the electrode surface until it was very negatively charged. When the electrode potential increased the adsorption increased. By the neutron reflection method they found that at small or moderate absolute charge densities, the adsorbed SDS molecules aggregate into hemicylindrical stripe-like micelles. At large positive charge densities, the hemimicellar aggregates were found to melt to form a condensed film having a thickness of 20.5 Å, only 30% larger than that of the hemimicellar state. The properties of this condensed state are best explained by a model of an interdigitated film in which half of the sulfate groups are turned toward the metal and half toward the solution. Thus, it is highly probable that in the range of positive potentials investigated here the nonionic and anionic surfactants form hydrophilic films at the glassy carbon electrode with half of the polar head groups directed to the electrode surface and half into the bulk phase [21–23]. The negatively charged layer of AOT decreases the effective positive potential near the electrode and, thus, the oxidation of PG takes place at a more positive electrode potential than in the absence of anionic surfactant. Moreover, the adsorption of surfactants diminishes the area of the electrode available for the PG molecules and the growing thickness of the adsorption layer moves the plane of electron transfer away from the electrode surface. The diffusion of electrochemically active substance through the compact adsorbed layer of surfactant is much slower and this leads to the increase in the oxidation potential and the decrease in peak current.

At pH 6.88 and surfactant concentrations lower than the CMC the effect of Triton and AOT on  $E_{pa}$  is similar to that at pH = 2. The peak potential initially increases and then decreases with increasing surfactant concentration. For Triton X-100  $E_{pa}$  tends to a constant value above the CMC. Both surfactants, however, have no pronounced effect on the peak current. The explanation of this fact is not straightforward. We can only speculate that at neutral pH and higher surfactant concentrations the structure of the adsorbed layer is such that it does not affect the transport of PG molecules to the electrode (see Figure 1).

The cationic surfactant CTAB affects the electrochemical behaviour of propyl gallate in a somewhat different way. At pH = 2 it does not influence significantly the anodic peak potential,  $E_{pa}$ , and the peak current,  $I_{pa}$  (Figs. 1 and 5a, b). The charge transfer coefficient and the diffusion coefficient are almost the same as in the pure buffer solution (see Table 1). From this it can be deduced that cationic surfactant does not adsorb on the GC electrode at highly positive potentials. Above the CMC, the interaction of propyl gallate with

the cationic micelles in the bulk solution causes a decrease in peak current.

At pH 6.88 the situation is different. The addition of CTAB causes the decrease in peak potential and peak current (the smallest surfactant concentration is an exception). This means that in neutral conditions and at negative or moderately positive electrode potentials the adsorption of CTAB is significant. The adsorbed molecules block the electrode surface and thus hinder the access of PG molecules to the electrode. Due to this and the interactions of PG with bulk micelles the value of apparent diffusion coefficient is much lower than in pure buffer pH = 6.88. The value of charge transfer coefficient also differs from that in pure phosphate buffer indicating that the adsorption of cationic surfactant alters the mechanism of charge transfer. On the basis of the above results it can be concluded that the influence of the cationic surfactant CTAB on the voltammetric response of PG is more pronounced in neutral conditions.

To study the effect of CTAB in more detail we measured the differential capacity of the glassy carbon electrode immersed in the buffered CTAB solutions (pH = 6.88) as a function of electrode potential. The results are shown in Figure 7. For the surfactant concentration  $1 \times 10^{-5}$  M, the differential capacity curve (measured just after putting the electrode in the surfactant solution) lies below the curve characteristic of buffer solution. This means that in the whole range of electrode potentials surfactant adsorption takes place.

For concentrations higher than CMC and negative electrode potentials the capacity curve lies below that of the pure buffer. This can be explained by the strong adsorption of CTAB on the electrode. When the electrode potential increases the differential capacity increases and at moderately positive potentials it becomes higher than in pure buffer. This can be ascribed to partial desorption of adsorbed surfactant molecules and reorganisation of the adsorbed phase. At negative potentials the expected structures of the adsorbed surfactant are micelles, cylinders or a continuous bilayer with a part of the polar heads being in contact with the electrode surface. When the potential becomes positive the positively charged headgroups are repelled from the surface and reorganisation of the adsorbed phase leading to hemimicelles, hemicylinders or single layer of surfactant molecules with polar heads directed to the bulk solution takes place. These results suggest that the differential capacity depends not only on the adsorbed amount but also on the structure of the adsorbed layer. Recently, the differential capacity of a gold electrode immersed in the SDS solution was investigated by Lipkowski et al. [21]. Sharp peaks were observed for potentials where the adsorption/desorption of SDS took place as well as in the region where the reorganization of the adsorbed layer was assumed to occur. In our case we do not observe sharp peaks but a long increment in the differential capacity over the region of moderately positive potentials. This is characteristic of the gradual changes in the adsorbed layer structure.

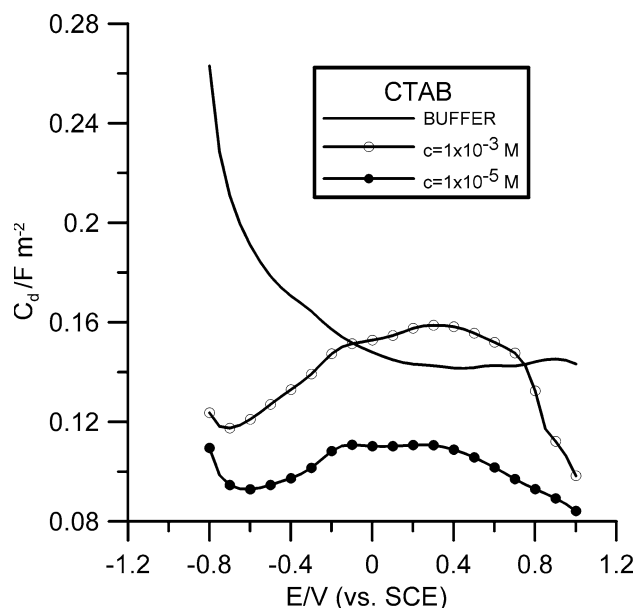


Fig. 7. Differential capacity curves recorded for GC electrode in the buffered CTAB solutions, pH = 6.88.

The next step of our study was to investigate the voltammetric oxidation of PG in different microemulsion systems. For this purpose we took cyclic voltammograms of PG in the SDS/pentanol/water microemulsions of different compositions. The voltammograms are presented in Figure 8 and the peak potentials and peak currents as a function of microemulsion composition are plotted in Figure 9. The calculated apparent diffusion coefficients and charge transfer coefficients are given in Table 2.

Figure 9 shows that the microemulsion environment strongly affects the oxidation potential of PG, especially at low water content, i.e. in the W/O microemulsion. In this system the decrease in peak potential with increasing water content is very strong. At higher water contents, where the bicontinuous phase and O/W microemulsion exist, the decrease becomes somewhat slower.

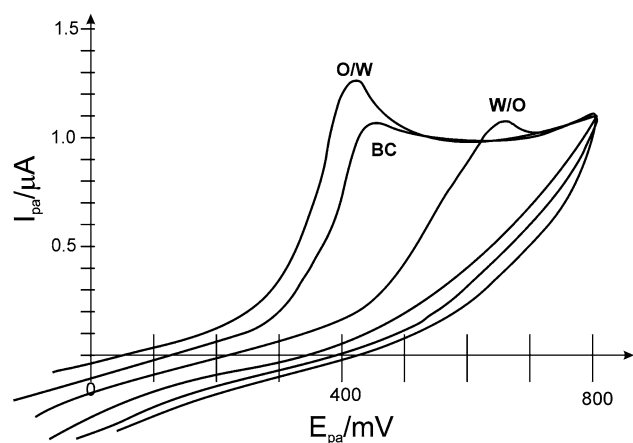


Fig. 8. Cyclic voltammograms of  $5 \times 10^{-3}$  M PG in various types of SDS/pentanol/water microemulsion at the scan rate  $0.1 \text{ V s}^{-1}$ .

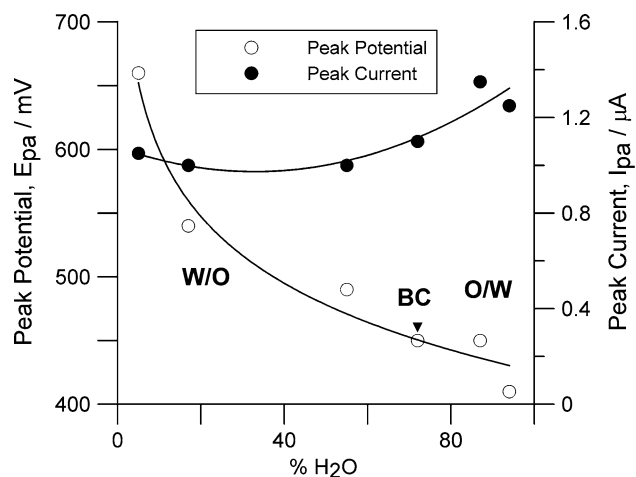


Fig. 9. Changes of the propyl gallate oxidation peak potential,  $E_{pa}$ , and peak current,  $I_{pa}$ , at the glassy carbon electrode in the SDS/pentanol/water microemulsion of different composition.

In contrast to the peak potential the peak current does not change much with composition, indicating that the effective rate of PG transport to the electrode is similar in all the systems. In the O/W microemulsion the apparent diffusion coefficient has a value close to that in the SDS/water micellar solution and it decreases slightly when the type of microemulsion changes from O/W to W/O.

In the region of positive electrode potential the SDS molecules adsorb on the electrode surface forming a compact layer. In the SDS/pentanol/water microemulsions this layer is additionally stabilized by pentanol molecules. The incorporation of pentanol molecules into the adsorbed surfactant layer reduces repulsion between the charged polar heads and makes the surface layer more compact. Due to this the penetration of PG molecules to the electrode is hindered. Electron transfer from the PG molecule to the surface, is also hindered.

The PG molecules are of hydrophilic character, i.e. they show higher affinity for water than for the oil phase. In consequence, in the W/O microemulsion all the propyl gallate is trapped in the aqueous interior of the reversed micelles. This is the reason why the electrochemical oxidation of PG in the W/O microemulsion is more difficult than in other microemulsion systems.

It was mentioned earlier that the PG oxidation is strongly pH dependent. In pure neutral buffer  $E_{pa}$  is 185 mV and in acidic buffer (pH = 2) it increases to 485 mV. The addition of anionic surfactant increases the oxidation potential and decreases the peak current, especially in acidic conditions. In the microemulsion systems investigated here, pH was not adjusted. It decreased in the vicinity of the electrode surface due to protons appearing as a product of oxidation reaction. As a result of pH changes the peak potential increased and, in the concentrated SDS solution, reached a value of 410 mV (close to that at pH = 2).

The charge transfer coefficient has an approximate value of 0.5 in all microemulsion systems. This suggests

Table 2. The values of the apparent diffusion coefficient  $D$  for propyl gallate in various microemulsions

Solution composition	System	$\beta n_{\beta}$	$D \times 10^6 \text{ cm}^2 \text{ s}^{-1}$ ( $v = 100 \text{ mV s}^{-1}$ )
6% SDS, 94% water	micellar solution	0.48	1.46
6% SDS, 7% pentanol, 87% water	O/W	0.53	1.54
6% SDS, 22% pentanol, 72% water	bicontinuous	0.53	1.02
6% SDS, 39% pentanol, 55% water	W/O	0.44	1.03
6% SDS, 77% pentanol, 17% water	W/O	0.40	1.13
6% SDS, 89% pentanol, 5% water	W/O	0.32	0.88

that the first electron transfer determines the oxidation kinetics and that the kind of microemulsion does not play a decisive role. Modification of the electrode surface by the adsorbed species, which alters the transport of the electroactive substance to the electrode as well as the charge transfer mechanism, is of major significance.

#### 4. Conclusions

It can be concluded that

- The electrochemical oxidation of propyl gallate on a glassy carbon electrode is an irreversible and strongly pH dependent process.
- The addition of surfactants to the system influences both the oxidation potential and the peak current. The anionic and nonionic surfactant films formed at the electrode/solution interface hinder electron transfer. They also decrease the rate of transport of PG molecules to the electrode. The effect is more significant at lower pH values.
- In the case of cationic surfactant CTAB the peak potential and peak current changes are more noticeable in neutral conditions. This is because in acidic solution the range of potentials where PG oxidation occurs is shifted positively compared to neutral conditions. Adsorption of  $\text{CTA}^+$  ions at the positively charged electrode surface is inhibited and no essential changes in the peak potential and the peak current below the CMC are observed. For concentrations above the CMC changes are caused by the interaction of PG molecules with the bulk micelles.
- For all the surfactants the interactions of propyl gallate molecules with the micelles present in the solution above the CMC hinder their diffusion to the electrode and lead to lower peak currents.
- In the SDS/pentanol/water microemulsions a large increase in peak potential is observed with decreasing water content. At the same time the peak current does not change much. In these systems modification of the electrode surface by adsorbed surfactant is significant. The adsorbed surfactant layer alters the transport of the electroactive substance to the electrode as well as the charge transfer coefficient.

- More profound understanding of mechanism of antioxidant action of propyl gallate at a glassy carbon electrode in the presence of surface-active substances and microemulsion systems requires further investigation.

#### References

1. M. Castilho, L.E. Almeida, M. Tabak and L.H. Mazo, *Electrochim. Acta* **46** (2000) 67.
2. S. Gunckel, P. Santander, G. Cordano, J. Ferreira, S. Munoz, L.J. Nunez-Vergara and J.A. Squella, *Chem.-Biol. Interact.* **114** (1998) 45.
3. X.L. Wen, Z.X. Han, A. Rieker and Z.L. Liu, *J. Chem. Res. (S)* (1997) 108.
4. A.J. Downard and A.D. Roddick, *Electroanalysis* **7** (1995) 376.
5. Davidovic, I. Tabakovic, D. Davidovic and L.J. Duic, *Electroanal. Chem.* **280** (1990) 371.
6. M. Szymula, J. Szczypa and S.E. Friberg, *J. Dispersion Sci.* **23** (2002) 789.
7. M. Szymula and J. Narkiewicz-Michalek, *Prog. Colloid Polym. Sci.* **281** (2003) 1142.
8. Y. Ni, L. Wang and S. Kokot, *Analitica Chim. Acta* **412** (2000) 185.
9. L. Agüí, M.A. López-Huertas and P.J.M. Pingarron, *J. Electroanal. Chem.* **414** (1996) 141.
10. E. Diego, L. Agüí, A. Gonzalez-Cortés, P. Yanez-Sedano and J.M. Kauffman, *Electroanalysis* **10** (1998) 33.
11. O. Hammerich and B. Svensmark. Anodic oxidation of oxygen-containing compounds, in H. Lund and M. Baizer (eds), *Organic Electrochemistry*, (Marcel Dekker, New York, 1990), pp. 165.
12. V. Roginsky, *Arch. Biochem. Biophys.* **414** (2003) 261.
13. T.G. Diaz, A.G. Cabanillas, M.F.A. Franco, F. Salinas and J.C. Vire, *Electroanalysis* **10** (1998) 497.
14. P.C. Hiemenz and R. Rajagopalan, *Principles of Colloid and Surface Chemistry*, 3rd edn., (Marcel Dekker Inc., New York, Basel, Hong Kong, 1997).
15. L. Zheng, F. Li, J. Hao and G. Li, *Colloid Surface A: Physicochem. Eng. Aspects* **98** (1995) 11.
16. S. Paredes, M. Tribout, J. Ferreira and J. Leonis, *Colloid Polym. Sci.* **254** (1976) 637.
17. G. Guerin and A.M. Bellocq, *J. Phys. Chem.* **92** (1988) 2550.
18. R.N. Adams, *Electrochemistry at Solid Electrodes* (Marcel Dekker Inc., New York, 1969), pp. 142.
19. D.E. Ormonde and R.D. O'Neill, *J. Electroanal. Chem.* **279** (1990) 109.
20. Z. Galus, *Elektrochemiczne Metody Wyznaczania Stałych Elektrochemicznych* (PWN, Warszawa, 1979) in Polish.
21. Burgess, V. Zamylnny, G. Szymański, J. Lipowski, S. Satija and R. Ivkov, *Langmuir* **17** (2001) 3355.
22. S. Manne, J.P. Cleveland, H.E. Gaub, G.D. Stucky and P.K. Hansma, *Langmuir* **10** (1994) 4409.
23. Z. Kirally and G.H. Findenegg, *J. Phys. Chem.* **102** (1998) 1203.