

# The Inhibiting or Accelerating Effect of Different Surfactants on Electroreduction of Zn<sup>2+</sup>

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## ABSTRACT

The course of differential capacity curves of the electric double layer at the mercury electrode/surfactant solution interface was described for three different surfactants from different groups. Using square-wave voltammetry (SWV) it was found that the surfactants had a varying effect on the kinetics of electroreduction of Zn<sup>2+</sup> ions. Simple relationships were presented between SWV peaks and the course of differential capacity curves in the presence of surfactants as compared with the curve of differential capacity for the basic electrolyte.

## KEYWORDS

Electroreduction, sodium 1-decanesulfonate, *N*-decanoyl-*N*-methyl-glucamine, octyltrimethylammonium bromide.

## 1. Introduction

Kinetic effects caused by adsorption phenomena at the electrode/electrolyte interface make it possible to control the rate of the electrode processes radically (including corrosion of metals) as well as the properties and structures of metal electrodeposits.<sup>1,2</sup> Transport of charge across membranes or layers, that separate two phases or solutions having different chemical compositions, plays a very important role in the functioning of such layers in biological systems and synthetic membranes which show technological promise.<sup>3</sup> That is why studies on the kinetics of electrochemical reactions taking place under adsorption of electrochemically inactive organic surfactants attract continuing interest despite the results already achieved.

The presence of adsorbed non-electroactive species can have a drastic influence on the rate of an electrode reaction, either in a decelerating or an accelerating sense. The catalytic influence of organic compounds on the electroreduction processes was discussed by Sykut *et al.*<sup>4–7</sup> The results of these studies made it possible to formulate the 'cap-pair' effect. This rule describes the conditions which must be fulfilled by the supporting electrolyte/depolarizer/organic compound system for the catalytic effect of the electrode process. The ability of an organic substance to form weak complexes with a depolarizer and location of the depolarizer reduction potential in the range of adsorption labile equilibrium of a given substance play a significant role in the catalytic effect.

Quasi-reversible electrode processes are most suitable for studies on the influence of organic compounds because they enable measurements of standard rate constants over a wide range of quantities. The Zn<sup>2+</sup> ions are such a model reactant. The electroreduction of Zn<sup>2+</sup> ions on the mercury electrode is a typical example of a reaction controlled both by diffusion and charge transfer.<sup>8</sup> The electroreduction process of this depolarizer in the presence of various organic substances according to the 'cap-pair' effect has already been described in the literature.<sup>9–26</sup> The surface catalytic substances adsorbed on the electrode surface decrease its area but increase its activity. The increase of its activity is connected with complex formation on the electrode

surface which facilitates electron transfer during the electrode process. Also multi-electron processes are widely discussed in the literature. The electroreduction of Bi<sup>3+</sup> ions on the mercury electrode is a multi-step process, which is catalyzed by methionine.<sup>27–29</sup> This acceleration effect of Bi<sup>3+</sup> electroreduction is connected with the formation of active complexes mediating in electron transfer, which are located inside the adsorbate layer.<sup>30</sup> Moreover, the catalytic influence of substituted thioureas: N-methyl-thiourea, N,N'-dimethylthiourea and N,N,N',N'-tetramethylthiourea, on Bi<sup>3+</sup> ion electroreduction has been shown.<sup>31</sup> Thiourea, N-methylthiourea, N,N'-dimethylthiourea and N-allylthiourea accelerate the electroreduction process of In<sup>3+</sup> in chlorates (VII).<sup>32</sup> The magnitude of the catalytic effect is determined by the equilibrium of the complexing reaction between a depolarizer and an accelerating substance on the electrode surface.

The electrochemical behaviour of europium at the dropping mercury electrode in different media was studied by Nemec.<sup>33</sup> Ikeda *et al.* showed that the influence of tetramethylurea and tetramethylthiourea on the reduction rate of Eu<sup>3+</sup> is in contrast to that on the reduction rate of Zn<sup>2+</sup> ions.<sup>34</sup> They suggest different locations for the formation of the activated complex: for Zn<sup>2+</sup> inside the adsorption layer and for Eu<sup>3+</sup> just outside the layer.

The results presented here are concerned with the effect of three different surfactants (anionic, non-ionic, and cationic) on the electroreduction of Zn<sup>2+</sup> ions at a mercury electrode. The surfactants were: sodium 1-decanesulfonate ( $C_{10}H_{21}SO_3Na$ ), *N*-decanoyl-*N*-methyl-glucamine ( $C_{17}H_{35}NO_6$ ) and octyltrimethylammonium bromide ( $C_{11}H_{26}NBr$ ). The chosen surfactant concentrations were lower than their critical micellar point (CMC).

## 2. Experimental

### 2.1. Instrumentation and Measurements

Voltammetric and impedance measurements were performed by employing an Autolab Fra 2 frequency-response analyzer (Eco Chemie BV, the Netherlands). The differential capacity of

the double layer ( $C$ ) was measured by using the AC impedance technique. The measurements were carried out at several frequencies in the range from 400 Hz to 2000 Hz, with an amplitude of 10 mV. The equilibrium capacities were obtained by extrapolation of the measured capacity *versus* square root of the frequency to zero frequency.

The studies on the electroreduction of  $Zn^{2+}$  ions were performed by means of square-wave voltammetry (SWV) and Faraday impedance techniques. In the SWV method the optimal experimental operating conditions were as follows: pulse amplitude 20 mV, frequency 120 Hz and step potential 2 mV. The Faradaic impedance data were collected at frequencies in the range from 15 Hz to 100 000 Hz for the formal potential.

The measurements were performed in a three-electrode cell with a dropping mercury electrode with a controlled increase in rate and a constant drop surface ( $0.013438 \text{ cm}^2$ ). A CGMDE was the working electrode (MTM Poland), Ag/AgCl was the reference electrode and a platinum spiral served as an auxiliary electrode. Measurements were carried out in thermostated cells at  $298 \pm 0.1 \text{ K}$ .

## 2.2. Reagents and Solutions

Analytical-grade chemicals from Fluka were used.

Optimal accuracy was achieved by maintaining the  $Zn^{2+}$  concentration around  $0.005 \text{ mol dm}^{-3}$ . A  $1 \text{ mol dm}^{-3} NaClO_4$  solution at pH 3 was used in those studies to prevent the hydrolysis of  $Zn^{2+}$  ions. The choice of  $NaClO_4$  as a supporting electrolyte results from the fact that  $ClO_4^-$  ions cause the strongest disruption in water structure<sup>35</sup> and have a low tendency to form complexes.

The surfactant solutions were prepared directly before the measurements. The concentration range of sodium 1-decanesulfonate was  $2.5 \times 10^{-4} - 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ , of N-decanoyl-N-methylglucamine  $4.0 \times 10^{-6} - 2.5 \times 10^{-4} \text{ mol dm}^{-3}$  and octyltrimethylammonium bromide  $1.0 \times 10^{-5} - 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ .

## 3. Results and Discussion

A qualitative evaluation of the interface state: mercury electrode/ $1 \text{ mol dm}^{-3} NaClO_4 +$  surfactant, can be performed based on the course of the differential capacity curves in comparison with the curve obtained for the supporting electrolyte  $1 \text{ mol dm}^{-3} NaClO_4$  (Fig. 1). A certain divergence of the applied concentrations of surfactants is connected with their visible effect on the height and position of SWV peaks for the reduction of  $Zn^{2+}$  ions.

All the examined surfactants were found to lower the differential capacity, but the potential area of this decrease depends on the kind of surfactant applied and increases in the order:  $C_{10}H_{21}SO_3Na < C_{17}H_{35}NO_6 < C_{11}H_{26}NBr$ . The effect obtained is undoubtedly the result of the presence or absence of electrostatic interaction between various ionic forms of the examined surfactants with the negatively charged electrode surface. In each of the investigated systems there are no clearly revealed adsorption peaks, whereas the desorption peaks appear on all curves. Their potentials practically do not depend on the concentration of anionic or non-ionic surfactants and are equal to, respectively:  $-0.9 \text{ V}$  and  $-1.2 \text{ V}$ .

In the case of the cationic surfactant the desorption peak potential is shifted with an increase of concentration towards more negative potentials to  $-1.4 \text{ V}$ . It should be emphasized here that at the concentration of  $2.5 \times 10^{-4} \text{ mol dm}^{-3}$  for each surfactant, the greatest decrease of differential capacity occurs for the non-ionic surfactant (Fig. 1B), whereas in the case of the remaining two surfactants this decrease is comparable.

Figure 2 presents the square-wave voltammograms for the reduction of  $Zn^{2+}$  ions in the presence of different concentra-

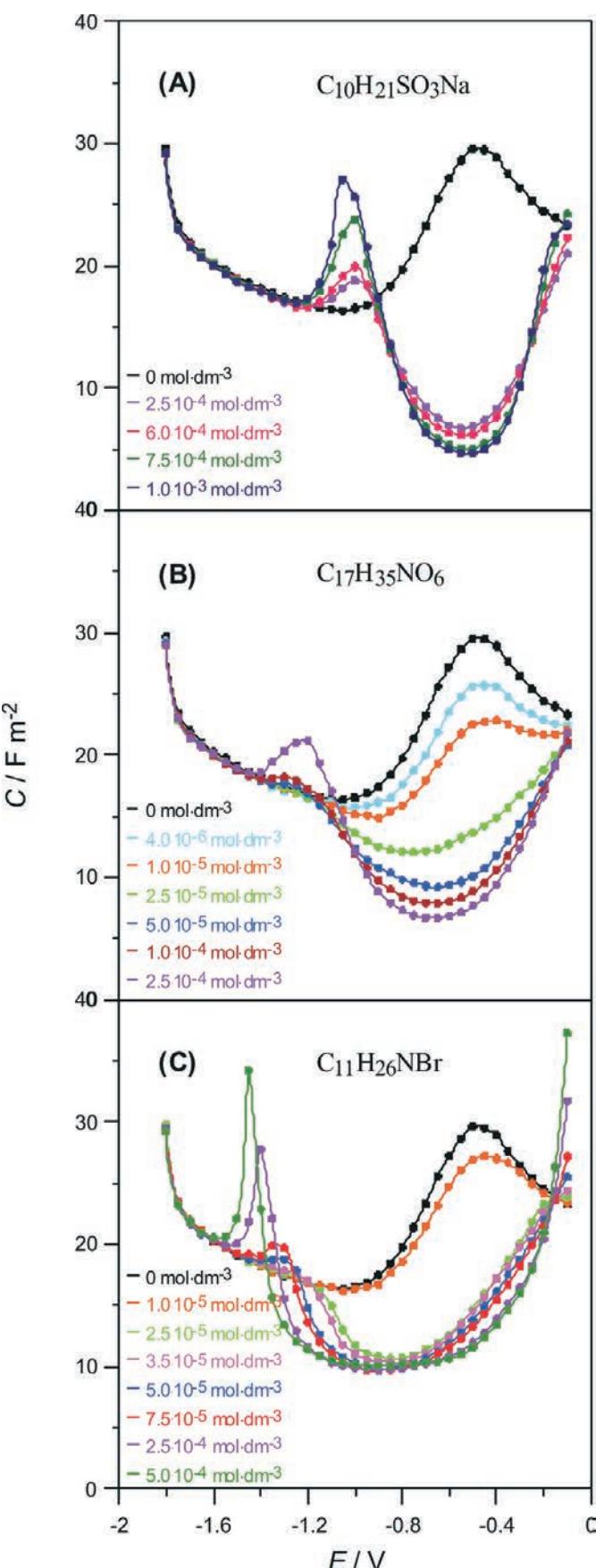


Figure 1. Differential capacity potential curves of: Hg/ $1 \text{ mol dm}^{-3} NaClO_4 + C_{10}H_{21}SO_3Na$  (A), the Hg/ $1 \text{ mol dm}^{-3} NaClO_4 + C_{17}H_{35}NO_6$  (B) and Hg/ $1 \text{ mol dm}^{-3} NaClO_4 + C_{11}H_{26}NBr$  (C).

tions of the examined surfactants. The changes in height and position of SWV peaks remain in simple relation with the values of the differential capacity in the area of the  $Zn^{2+}$  ion reduction potentials. The increase in concentration of the anionic surfactant results in an increased height of the SWV peak at a constant peak potential value,  $E_p = -0.946$  V (Fig. 2A). This increase of peak height is a qualitative measure of the increase of the rate of the electrode process as described earlier.<sup>23</sup> The catalytic activity of the anionic surfactant is also confirmed by the studies carried out by using the faraday impedance method. As can be seen from Fig. 3A the addition of  $C_{10}H_{21}SO_3Na$  to the solution of  $Zn^{2+}$  ions causes a decrease of the charge-transfer resistance values ( $R_a$ ) which indicates facilitation of  $Zn^{2+}$  ion electro-reduction in the presence of surfactant. In the systems containing an anionic surfactant, the  $Zn^{2+}$  ion reduction potentials are located in the area of increased differential capacity in comparison with the basic electrolyte (Fig. 1A). A similar relationship between acceleration of the electrode process and increased capacity was described earlier for the organic substance undergoing specific adsorption at a mercury electrode.<sup>6</sup>

In the case of a similar anionic surfactant: sodium dodecyl sulphate and  $Cd^{2+}$  ions, the increase of concentration of this surfactant results in inhibition of  $Cd^{2+}$  ion electroreduction, which is revealed by a decrease of the height of the DPP peaks.<sup>36</sup> This effect is related to a strong decrease of differential capacity in comparison with the basic electrolyte at  $Cd^{2+}$  ion reduction potentials, and thus to tight packing of the surface layer with the anionic form of the surfactant.

The introduction of a non-ionic surfactant to the solution of  $Zn^{2+}$  ions (Fig. 2B) results in a sharp decrease of the SWV peak height already at concentrations over tenfold smaller ( $2.5 \times 10^{-5}$  mol dm<sup>-3</sup>) than it was in the case of the anionic surfactant ( $2.5 \times 10^{-4}$  mol dm<sup>-3</sup>). For lower concentrations of non-ionic surfactant, the peak potential does not change and is equal to  $E_p = -0.950$  V, whereas for larger amounts of the surfactant circa  $\geq 2.5 \times 10^{-5}$  mol dm<sup>-3</sup> the peak height achieves a minimum and next increases. It is shifted towards more negative values and for the concentration of  $2.5 \times 10^{-4}$  mol dm<sup>-3</sup>,  $E_p = -1.1$  V. It should be emphasized that the range of reduction potentials for  $Zn^{2+}$  ions is situated in the area of decreased differential capacity. These changes are illustrated by the Faraday impedance measurements (Fig. 3B). The increase of  $C_{17}H_{35}NO_6$  concentration up to  $2.5 \times 10^{-5}$  mol dm<sup>-3</sup> results in the increase of the charge-transfer resistance values showing the inhibiting influence of the non-ionic surfactant. Next, a further increase of the surfactant concentration results in the slight decrease of  $R_a$  values which means a gradual increase of the electrode process rate.

A similar situation occurs in the case of the cationic surfactant (Figs 2C and 3C). However, the largest concentrations of this surfactant ( $\geq 2.5 \times 10^{-4}$  mol dm<sup>-3</sup>) cause not only a significant shift of the peak potential value from  $-0.950$  V down to  $-1.228$  V, but also an evident increase of the SWV peak height at those highly negative  $E_p$  values. Also in this case the height of the SWV peaks caused by the  $C_{11}H_{26}NBr$  concentration changes is reflected by the tendency of the impedance spectra to change (Fig. 3C). In  $5.0 \times 10^{-5}$  mol dm<sup>-3</sup> of cationic surfactant,  $R_a$  reaches the highest value which indicates the strongest inhibiting surfactant influence on the electrode process. Further increases of the surfactant concentration lead to a decrease in the  $R_a$  values and the evident increase of  $Zn^{2+}$  electroreduction rate.

The application of the  $Zn^{2+}$  ion as the pilot ion in the adsorption-desorption equilibrium allows one to obtain valuable information about the electrode/adsorbate solution interface.

In the case of the anionic surfactant the effect of acceleration

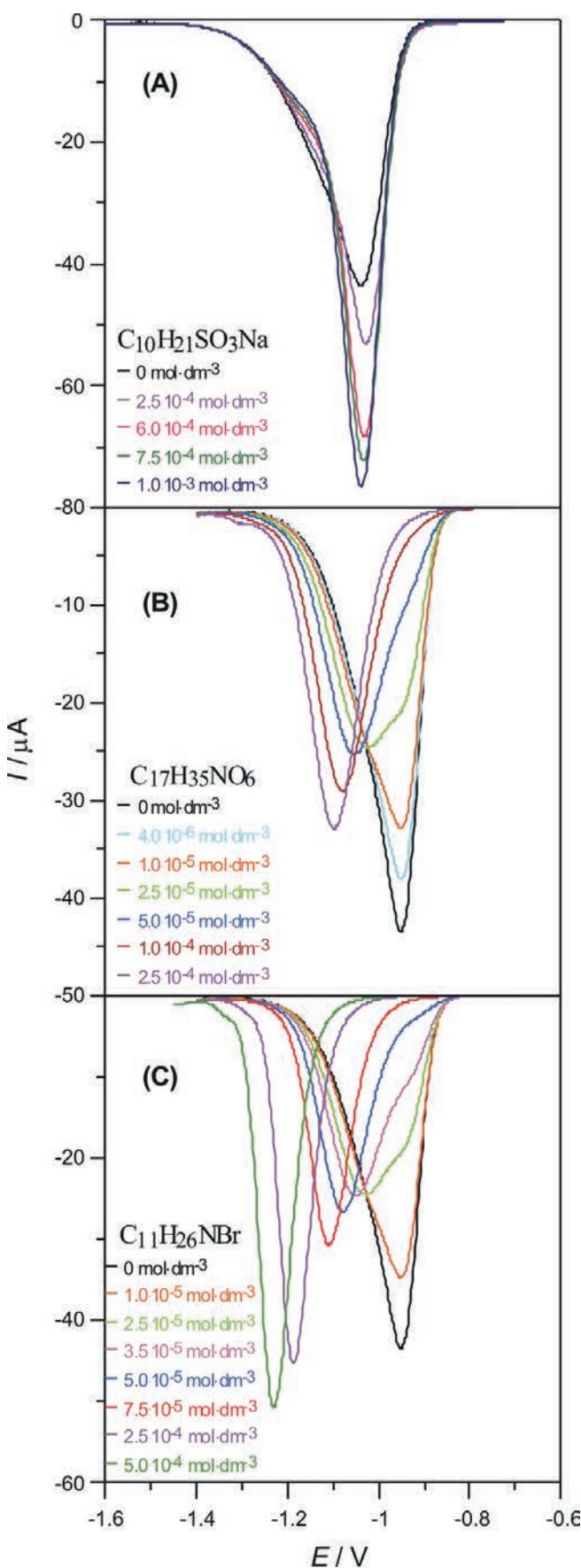
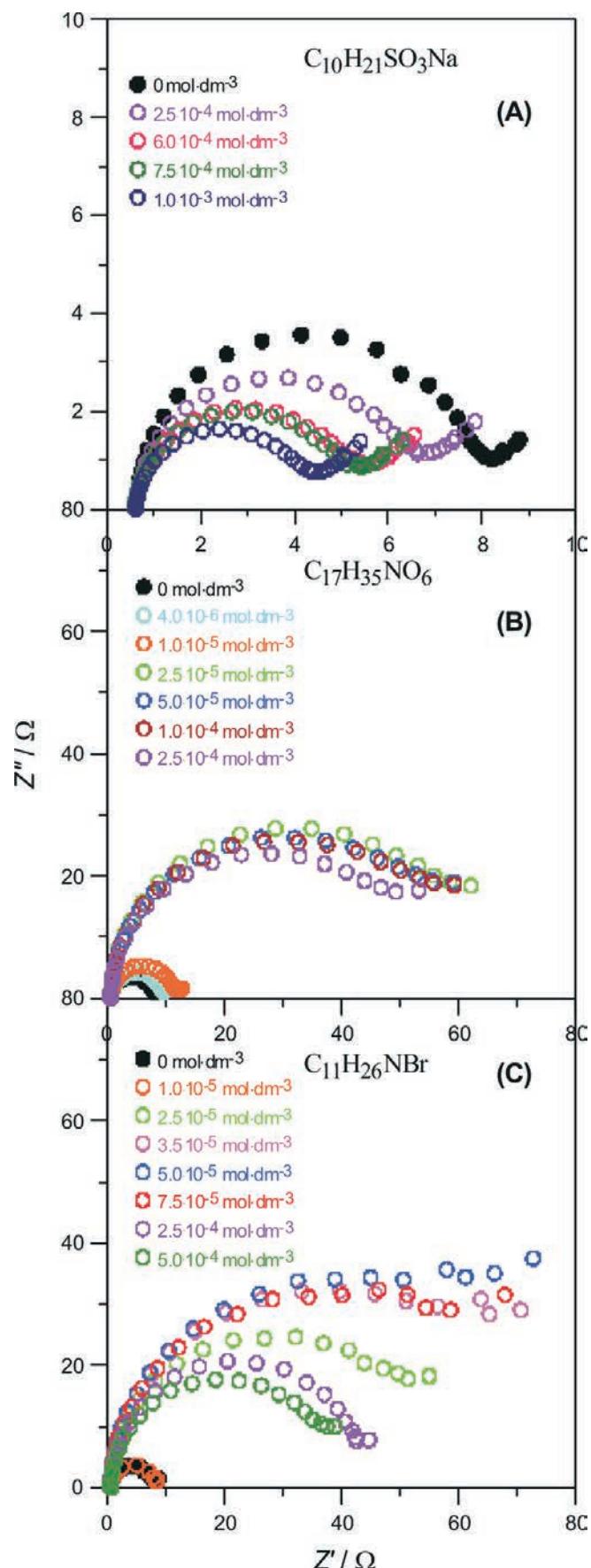


Figure 2 SWV peaks for the electroreduction of  $5 \times 10^{-3}$  mol dm<sup>-3</sup>  $Zn^{2+}$  in  $1 \text{ mol dm}^{-3} NaClO_4$  and in the presence of the surfactants:  $C_{10}H_{21}SO_3Na$  (A),  $C_{17}H_{35}NO_6$  (B) and  $C_{11}H_{26}NBr$  (C). The concentrations are shown in the figure.



**Figure 3** Impedance diagrams measured at the formal potential for the electroreduction of  $5 \times 10^{-3}$  mol dm $^{-3}$  Zn $^{2+}$  in 1 mol dm $^{-3}$  NaClO $_4$  and in the presence of the surfactants: C $_{10}$ H $_{21}$ SO $_3$ Na (A), C $_{17}$ H $_{35}$ NO $_6$  (B) and C $_{11}$ H $_{26}$ NBr (C). The concentrations are shown in the figure.

of Zn $^{2+}$  ion electroreduction results from the labile adsorption equilibrium of this surfactant in the area of the desorption peak potentials and also from the possibility of formation of the C $_{10}$ H $_{21}$ SO $_3^-$  – Zn $^{2+}$  active complex.

However, this acceleration effect is much weaker than the inhibition effect occurring in the systems containing the remaining two surfactants. This not very spectacular catalytic effect of anionic surfactant is probably caused by two factors: 1) on the electrode surface an insufficient amount of active complex is formed which makes the electron transfer between mercury and Zn $^{2+}$  ions easier due to low ligand excess (coming from the surfactant), 2) large surfactant molecules adsorbing on the mercury reduce Zn $^{2+}$  ion access to the electrode. In the case of the non-ionic surfactant the inhibition is due to the effect of blocking the electrode surface, which at high concentrations leads to an increase of overpotential. The presence of the cationic surfactant in solution at lower concentrations results in a similar blocking effect combined with electrostatic repulsion between the C $_{11}$ H $_{26}$ N $^+$  cation and Zn $^{2+}$  ions. The increase of the SWV peak height at the highest concentrations of the cationic surfactant may be due to a splitting of the adsorption layer as a result of repulsive interaction between the positively charged nitrogen atoms, directed towards the solution at the hydrophilic endings.

#### 4. Conclusions

The application of the Zn $^{2+}$  ion in 1 mol dm $^{-3}$  NaClO $_4$  solution allows the monitoring of adsorption equilibria for different surfactants at the mercury electrode by using SWV voltammetry. The results described have a qualitative character. However, they provide valuable information in view of the fact that at such negative electrode potentials at which reduction of Zn $^{2+}$  ions occurs, a thermodynamic description of adsorption is difficult to achieve. In addition, the knowledge of the course of the differential capacity curves can help to predict the effect of the adsorbate on the kinetics of the selected electrode process. Determination of the surfactant effect on the Zn $^{2+}$  electroreduction rate is possible from the kinetic parameters. They not only describe the kinetics qualitatively but also make it possible to study the mechanism of the electrode processes. The problems (e.g. temperature and supporting electrolyte concentration influence) have already been discussed.<sup>23–24,37</sup> It seems to be very interesting to investigate the influence of the molecular size of the organic compound which belongs to the same surfactant group, or the influence of the supporting electrolyte, on the mechanism and rate of Zn $^{2+}$  electroreduction. This should be the aim of further research.

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