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# Adsorption behaviour of camphor on copper electrode

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Electrochemical impedance spectroscopy was used for investigation of camphor surface activity on copper electrode in acid sulphate solutions. A large frequency dispersion of the differential capacitance is indicative of development of non-equilibrium adsorption layers involving slow relaxation processes. A rather weak adsorption of camphor is enhanced by bromide anions, especially in the presence of Cu(II). The respective orientation of adsorbed camphor dipoles results in the positive shift of the zero-charge potential. The model of the adsorption layer is suggested, according to which specifically adsorbed halides act as species bridging the copper substrate with Cu(I)-camphor surface complexes. Nevertheless, this does not lead to the exclusion of surface water and formation of two-dimensional condensed adsorption layers that are typical of less hydrophilic metals.

**Key words:** camphor, copper, adsorption, impedance

## INTRODUCTION

Camphor belongs to surfactants that show very high surface activity on a number of metals and on some carbon nanostructures [1–13]. A complete surface coverage is achieved even at very small (micromolar) bulk concentrations. Camphor can form two-dimensional condensed adsorption layers that are characterized by much more intense intermolecular interaction in the adsorption layer as compared with simpler organic compounds. Due to this, differential capacitance curves possess certain peculiarities consisting in the absence of adsorption-desorption peaks, as it takes place in the case of Hg electrode [2, 4, 5]. It also follows from the data obtained [2–5] that the adsorption process on Hg electrode is slow; besides, it is diffusion-controlled at certain potentials. These peculiarities gave rise to the modification of the quantitative analysis of capacitance data [3, 5, 14].

The adsorption behaviour of camphor on some other metals (Zn, Bi, Sb, Sn) is rather similar to that observed for mercury. Adsorption-desorption peaks of camphor are also degenerated in the case of Zn [6, 7] and Sn [8] electrodes. However, due to higher adsorption of water on Zn, the adsorption energy of camphor on Zn was found to be significantly lower as compared with that for Hg electrode [6]. Similar effects were established in the case of Sn electrode and explained in the same way [8].

Bi electrode is also more hydrophilic than Hg and the formation of a condensed layer takes place at higher bulk concentrations of camphor [9, 10]. The adsorption behaviour of camphor on negatively charged ($q < 0$) Bi and Hg is similar, but certain differences arise at $q > 0$. Sharp splitted capacitance peaks were observed for positively charged Bi, and, again, this was attributed to a high chemisorption of water at $q > 0$ [9]. At the same time, the change in orientation of the surfactant was postulated [10]. Similar data were obtained for Sb electrode at $q < 0$ [11], but the investigations at $q > 0$ failed due to the anodic dissolution of antimony.

Interesting results were obtained with some carbon nanostructures [12, 13]. It was found that the effect of camphor on differential capacitance is opposite for nanostructured electrodes (with highly developed surface) and smooth ones. In the presence of camphor, the differential capacitance increases (up to 3–5 times) as compared with surfactant-free solutions. This experimental fact was explained by the increase in an electrode surface area that prevails over the capacitance decrease caused by surfactant adsorption. It was assumed that, owing to high surface activity of camphor and other similar surfactants, the formation of adsorption layers is accompanied by at least partial disintegration of carbon nanoforms, resulting in the increase in the differential capacitance.

For the most part, the adsorption behaviour of camphor was characterized quantitatively for sufficiently hydrophobic electrodes. For this reason, an extension of such investigations over more hydrophilic substances is of obvious interest, since they could contribute to the comparative analysis of the results obtained. According to [15], the hydrophilicity of metals should increase in the series: Sb, Bi < Pb, Tl, Hg < Sn, Cd < Ga < Zn < Ag < Au < Cu < Fe. This series is valid for polycrystalline surfaces of solid metals. It is obvious that the copper electrodes can be chosen as significantly more hydrophilic objects.

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## EXPERIMENTAL

Solutions were prepared using deionised water, 0.01 M $CuSO_4 \cdot 5H_2O$ (Mallinckrodt, USA, chlorides less than 0.005%), and 0.6 M $H_2SO_4$ (high purity, Reakhim Russia) as a supporting electrolyte. Camphor (Fluka, >95% purity) was used as received. The solutions were deaerated before experiments with argon stream over 0.5 h. To prepare the working electrodes, a Pt wire of 0.36 $cm^2$ surface area was coated with 5–7 μm thick copper in the solution containing (g $dm^{-3}$): $Cu_2SO_4 \cdot 5\ H_2O$ – 250, $H_2SO_4$ – 50. A polycrystalline layer with well-exhibited crystallographic edges and faces was formed. Copper crystallites as large as 1–4 μm imparted a particular roughness of the surface.

Impedance measurements were carried out using an Electrochemistry PowerSuite (Princeton) PowerSine module. Nyquist plots (relations between the real ($Z^{/}$) and the imaginary ($Z^{//}$) components of the impedance) were obtained within the frequency ($f$) range from 0.1 to $3 \times 10^4$ Hz at the open-circuit potential. The amplitude of the imposed sinusoidal perturbation of the electrode potential was 5 mV. To obtain the capacitance vs electrode potential ($C$–$E$) plots, a sufficiently low frequency $f = 19$ Hz was applied.

The electrode potential was measured in reference to the Ag | AgCl | KCl(sat) electrode and was converted to the standard hydrogen scale. All experiments were performed at 20 °C.

## RESULTS AND DISCUSSION

An electrochemical impedance spectroscopy (EIS) is a powerful method that is widely applied in the investigations of electrochemical reactions involving adsorption steps. When adsorption layers are formed sufficiently fast and equilibrium in the double layer is achieved, the differential capacitance of the electrode does not depend on the frequency (the case of Hg electrode in the solutions of simple indifferent salts). Otherwise, the electrode impedance depends on $f$ to a significant extent and the so-called frequency dispersion is observed. The relaxation of the adsorbed species including the water molecules is among the reasons for such behaviour. The frequency dispersion is also typical of Cu electrodes making contact with the aqueous solutions. It is observed both in the absence and in the presence of surfactants. An example of such behaviour is presented in Fig. 1. Nyquist plots obtained for Cu(II)-free solutions present semicircles; in the absence of frequency dispersion, they should take the shape of vertical lines.

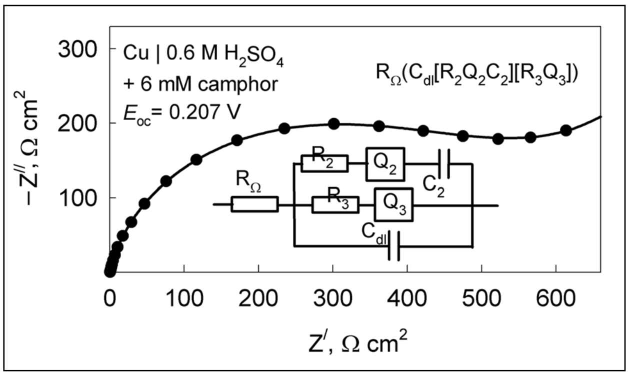

**Fig. 1.** Comparison of the experimental Nyquist plot (symbols) and that simulated for the given equivalent circuit (line). The EC parameters are given in the text

One simple model of the non-equilibrium adsorption layer has been suggested by Frumkin and Melik-Gaikazyan [16]. According to this research, electrochemical characteristics of the adsorption layer could be represented by two parallel subcircuits. One of them is a simple double-layer capacitance ($C_{dl}$). Another subcircuit contains three elements in series (resistance $R$, Warburg impedance $W$ and capacitance $C$) that account for the adsorption kinetics. The description code of such equivalent circuit could be ($C_{dl}$[$RWC$]). Here, elements in series are given in square brackets, and elements in parallel are enclosed in parentheses. In the case of inhomogeneous electrodes, some of the above elements may be replaced by the respective constant phase element (CPE) $Q$. Its admittance

$$Y = Y_0\ (j\omega)^n, \tag{1}$$

where $\omega = 2\pi f$ and $j = \sqrt{-1}$. At $n$ = 0, 0.5, 1 or –1, the CPE transforms into $R$, $W$, $C$ or inductance $L$, respectively.

However, the analysis shows that the impedance spectra obtained for Cu(II)-free solutions can be described with the frequency error ~1.5% by means of a more complicated equivalent circuit (Fig. 1) with $R_\Omega = 0.5\ \Omega\ cm^2$, $C_{dl} = 32.1\ \mu F\ cm^{-2}$, $R_2 = 78.4\ \Omega\ cm^2$, $Y_{02} = 0.00183\ \Omega^{-1}\ cm^{-2}\ s^{0.1345}$, $R_3 = 2.0\ \Omega\ cm^2$, $Y_{03} = 0.000147\ \Omega^{-1}\ cm^{-2}\ s^{0.804}$. Here, $R_\Omega$ is the ohmic resistance of the solution, and the rest EC part contains 3 subcircuits in parallel. The [$R_2Q_2C_2$] and [$R_3Q_3$] subcircuits could be treated as somewhat degenerated analogues of the above [$RWC$] subcircuit. They could be attributed to the relaxation of different species (e. g. camphor and water), but the physical sense of all their elements is not clear yet.

The differential capacitance in camphor-containing solutions depends to some extent on time and on direction of the potential sweep (Fig. 2). The best reproducibility is observed when the potential is swept from –0.3 V towards more positive values. The changes in the capacitance are low and comparable with the reproducibility; therefore, it can be stated that the effect of camphor in the Cu(II)-free solutions is rather weak. Since the halide-enhanced adsorption of polyethers was observed on copper electrode [17], we performed some experiments with addition of KBr. However, the effect of bromide is not strong (Fig. 2). Somewhat more perceptible changes in the capacitance arise in this case, and the $C$ maximum located at $E \approx -0.05$ V resembles a broad adsorption-desorption peak. Nevertheless, no effects indicative of the formation of two-dimensional condensed adsorption layers are observed in the Cu(II)-free solutions.

Similar experiments were carried out with solutions containing 0.01 M Cu(II). It should be noted that the faradaic process makes some contribution to the imaginary part of the impedance and the $C$ quantity ought to be treated as the pseudo-

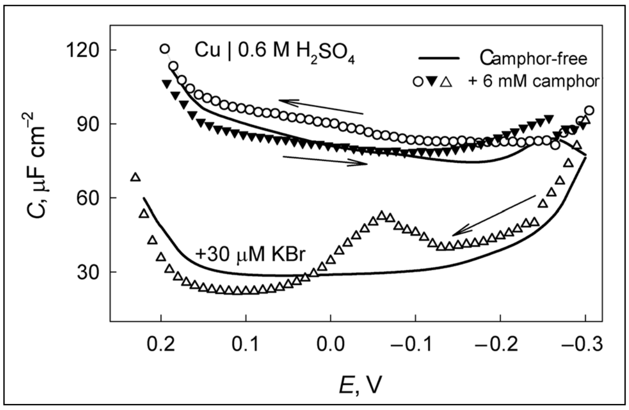

**Fig. 2.** Capacitance curves obtained for Cu(II)-free solutions containing supporting 0.6 M $H_2SO_4$ electrolyte (upper part) and that with the addition of 30 μM KBr (lower part). The data obtained in the presence of 6 mM camphor are shown by symbols as indicated

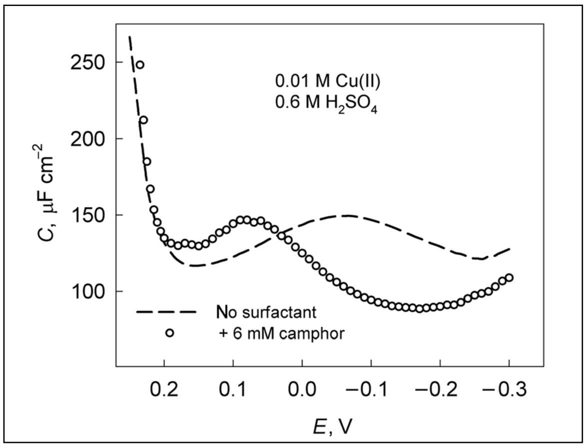

**Fig. 3.** Pseudo-capacitance curves obtained for surfactant-free (dotted line) and camphor-containing (symbols) 0.01 M Cu(II) solutions

capacitance in this case. However, as the electrode potential moves away from the equilibrium one (0.257 ± 0.002 V), this contribution rapidly falls due to the respective increase in the faradaic impedance. This keeping in mind, the changes in the pseudo-capacitance provide the basis for the estimation of adsorption ability of camphor in Cu(II) containing solutions.

In this case, camphor shows more noticeable surface activity over a wide potential range ($-0.3 < E < 0.2$ V) (Fig. 3). The main decrease in the capacitance is observed at $0 < E < 0.2$ V and the $C$ maximum located at $E \approx 0.03$ V seems to arise from adsorption-desorption processes. Addition of small amounts of bromide significantly enhances the surface activity of camphor (Fig. 4) and shifts the adsorption region to more positive potentials by ~0.1 V (Figs. 3, 4). At the same time, a pronounced cathodic adsorption-desorption peak arises at –0.05 V. In the region of maximum adsorption, the capacitance falls up to 20 μF cm$^{-2}$, what is a quite low value for copper electrode.

It is common knowledge that most organic compounds are adsorbed near the zero charge potential ($E_{zc}$), where the surface charge density is not too high. It can be seen from Fig. 4 that camphor is completely desorbed at –0.3 V since both capacitance curves coincide at this potential. Then, the surface charge density $q$ should be the same both in the presence and in the absence of camphor. This quantity can be obtained by the integration of the $C$–$E$ curve since

$$q = \int_{E_{zc}}^{E} C\,dE. \qquad (2)$$

Different $E_{zc}$ of copper electrode have been reported up to date. According to the results of the last investigations [18, 19], $E_{zc}$, determined for the bare, specially renewed Cu surface, falls between –0.6 and –0.7 V. More positive values (close to 0 V), that were reported earlier by Yegorov and Novoselskij [20, 21], are now attributed to the presence of adsorbed oxygen on copper. It is highly probable that most Cu electrodes, discussed herein, fall into the latter category. It follows from the capacitance measurements [21] that the $E_{zc}$ of copper electrode is equal to 0.09, 0.025, –0.01, –0.03 V in the presence of $F^-$, $ClO_4^-$, $SO_4^{2-}$ and $Cl^-$, respectively. When $Cl^-$ is replaced by $Br^-$, this region is shifted to more negative potentials by ~60 mV and even a more negative value is plausible for bromide-containing solutions [20]. Thus, having regard to low concentration of bromide in the solutions under investigation, it is reasonable to suggest that $E_{zc}$ takes the value of ca –0.05 V. In the case of camphor-free solutions, Eq. (2) yields $q = -40$ °C cm$^{-2}$ at –0.3 V. This $q$ value was used when the reverse integration was performed for camphor-containing solutions. The results obtained are shown in Fig. 5. Despite the rough estimation, it can be concluded that adsorption of camphor results in the positive shift of the zero-charge potential. This is attained when the positive charge of camphor dipole is directed towards the copper surface.

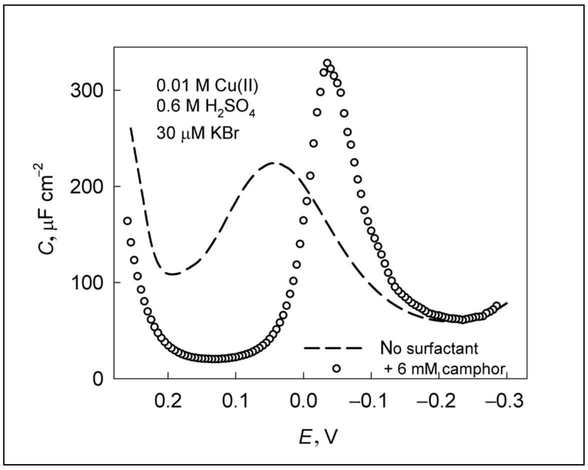

**Fig. 4.** Effect of bromide on pseudo-capacitance curves obtained for surfactant-free (dotted line) and camphor-containing (symbols) 0.01 M Cu(II) solutions

The results obtained show that the surface activity of camphor on copper electrode in the acid sulphate media

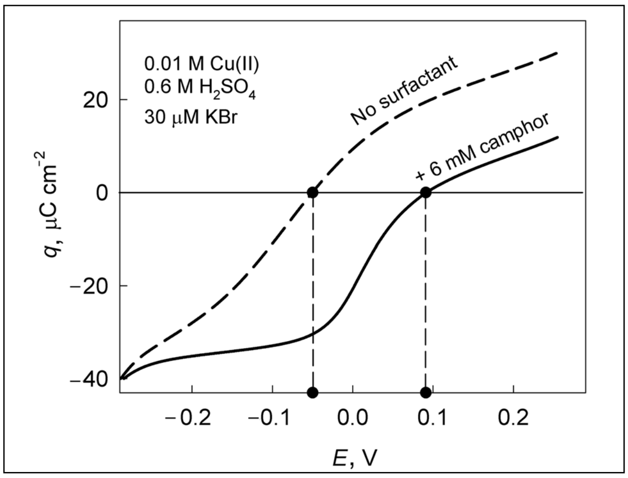

**Fig. 5.** Estimation of surface charge density performed by integration of capacitance curves

is rather weak. Bromide enhances camphor adsorption to a certain extent, especially in the presence of Cu(II). Similar phenomena have been found to occur in the Cu(II) solutions containing different polyethers [17]. It was concluded that specifically adsorbed halides can act as species bridging the copper substrate with polyether complexes containing intermediate $Cu^+$ ions. A similar model seems to be acceptable for Cu|Cu(II), camphor system. Nevertheless, enhanced adsorption does not lead to the complete exclusion of water and formation of two-dimensional condensed adsorption layers that are typical of less hydrophilic metals.

## CONCLUSIONS

1. Camphor shows a rather weak adsorption on copper electrode in acid sulphate solutions. A large frequency dispersion of the differential capacitance is indicative of development of non-equilibrium adsorption layers involving slow relaxation processes.

2. Bromide enhances camphor adsorption, especially in the presence of Cu(II). The respective orientation of adsorbed camphor dipoles results in the positive shift of the zero-charge potential.

3. The model of the adsorption layer is suggested, according to which specifically adsorbed halides act as species bridging the copper substrate with Cu(I)-camphor surface complexes. Nevertheless, this does not lead to the exclusion of surface water and formation of two-dimensional condensed adsorption layers that are typical of less hydrophilic metals.

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## KAMPARO ADSORBCINĖ ELGSENA ANT VARIO ELEKTRODO

*Santrauka*

Elektrocheminės impedanso spektroskopijos metodu ištirtas kamparo adsorbcinis aktyvumas ant vario elektrodo rūgščiuose sulfatų tirpaluose. Žymi diferencinės talpos dažnio dispersija parodo, kad susidaro nepusiausvyriniai absorbcijos sluoksniai, kuriuose vyksta lėti relaksacijos procesai. Silpną kamparo adsorbciją sustiprina bromido anijonai, ypač jei tirpale yra Cu(II). Atitinkama adsorbuoto kamparo dipolių orientacija sąlygoja teigiamą nulinio krūvio potencialo poslinkį. Pasiūlytas adsorbcijos sluoksnio modelis, numatantis, kad specifiškai adsorbuoti halogenidai gali surišti vario paviršių su Cu(I) – kamparo kompleksais. Tačiau dviejų dimensijų kondensuoti adsorbcijos sluoksniai, būdingi mažiau hidrofiliškiems metalams, nesusidaro.