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Effect of camphor on Cu(II) reduction kinetics in acid solutions

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ABSTRACT

Linear potential sweep (LPS) voltammetry and electrochemical impedance spectroscopy (EIS) was used for investigation of camphor effect on the stepwise Cu(II) reduction kinetics in 0.01 M Cu(II) solutions containing 0.6 M H_2SO_4 as supporting electrolyte. Polycrystalline Cu coatings deposited in acid $CuSO_4$ solution do not display the properties that were established for clean (oxygen-free) copper surfaces. Their surface activity seems to be suppressed by chemisorption of oxygen, which prevents the formation of two-dimensional condensed adsorption layers that are typical of other metals.

Addition of camphor (up to 6 mM) results in slight changes in impedance spectra and LPS voltammograms. Rather weak adsorption of camphor is enhanced by bromide anions, especially in the presence of Cu(II). Significant fall in double layer capacitance (down to ~5.4 μF cm^{-2}) and exchange current density (down to ~8 μA cm^{-2}) is accompanied by increase in cathodic charge transfer coefficient from 0.4 to 0.6. The model is suggested for synergistic adsorption of bromide and camphor, according to which specifically adsorbed halides act as species bridging the copper substrate with Cu(I)-camphor surface complexes.

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1. INTRODUCTION

Camphor is known as a surfactant that shows very high surface activity on a number of electrodes. Early studies of camphor adsorption behaviour carried out with liquid Hg [1–12] and some its amalgams [13,14] showed that camphor can form two-dimensional condensed adsorption layers, which are characterized by much more intense intermolecular interaction in the adsorption layer compared to simpler organic compounds. It was established that complete surface coverage is achieved even at very low (micromolar) bulk concentrations of camphor. Due to this, differential capacitance curves possess certain peculiarities consisting in the distortion of adsorption–desorption peaks [2,6,7,9]. It also follows from the data obtained [2,3,6,7] that the adsorption process on Hg electrode is slow; moreover, it is diffusion-controlled at certain potentials.

More recently, similar conclusions have also been drawn for some solid electrodes, such as Zn [15,16], Sn [17], Bi [18–25], Sb [26], Au [27–29]. Misshapen adsorption–desorption peaks of camphor were observed in the case of Zn, Sn, Bi electrodes. However, due to stronger adsorption of water on Zn, the adsorption energy of camphor on Zn was found to be significantly lower compared to that of Hg electrode [15]. Similar effects were observed in the case of Sn electrode and explained in the same way [17].

Bi electrode is also more hydrophilic than Hg and formation of condensed layer takes place at higher bulk concentrations of camphor [18–24]. Adsorption behaviour of camphor on negatively charged ($q < 0$) Bi is similar to that of Hg. Physically adsorbed camphor molecules were found to form a compact adsorption layer in this case. Certain differences arise at $q > 0$ where the loosening of adsorption layer was detected. Sharp splitted capacitance peaks were observed for positively charged Bi, and, again, this was attributed to strong chemisorption of water [18,25]. At the same time, the change in orientation of the surfactant was postulated [19,21]. Formation of stable adsorbate adlayer has been observed by *in situ* STM method at the positively charged electrode surface, where the weak co-adsorption of SO_4^{2-} anions and camphor molecules is possible. According to [24], heterogeneous adsorption and diffusion steps are the rate determining stages for camphor at the Bi(111) electrode. Similar data were obtained for Sb electrode at $q < 0$ [26], however, investigations at $q > 0$ failed due to the anodic dissolution of antimony.

Recently considerable attention has been focussed on nanostructured carbon of various morphologies (single-walled carbon nanotubes, filiform carbon, columnar structures, etc.) and interesting results were obtained [30–32]. It was found that the effect of

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camphor on differential capacitance is opposite for nanostructured electrodes (with highly developed surface) as compared to the smooth ones. In the presence of camphor, the differential capacitance increases (up to 3–5 times) in comparison with that of surfactant-free solutions. This experimental fact was explained by increase in the 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, leading to increase in differential capacitance.

In parallel with adsorption studies, some data concerning kinetics of electrode reactions in the presence of camphor have been obtained. Significant inhibition of different electrochemical processes was observed, e.g., reduction of periodate [28], nitrate and nitrite [31], $K_3[Fe(CN)_6]$ [29,31], persulphate [33] on different electrodes.

As noted above, according to some authors chemisorption of water prevents the formation of dense adsorption layers of camphor. In this regard, an extension of such investigations over more hydrophilic substances is of obvious interest. According to [34], the hydrophilicity of metals should increase in the series: Sb, Bi < Pb, Tl, Hg < Sn, Cd < Ga < Zn < Ag < Au < Cu < Fe. This succession is valid for polycrystalline surfaces of solid metals. It is obvious that copper can be chosen as sufficiently hydrophilic object. In particular, the formation of cyclic water hexamers has been confirmed on the close-packed Cu[111] surface using low-temperature scanning tunnelling microscopy and density functional theory calculations [35].

It should be noted that the adsorption properties of copper electrodes are largely dependent on the method of preparation of their surface. Therefore, the literature data are often contradictory. It is believed that the main reason for this is a great tendency of copper to surface oxidation [36,37]. A typical example might be studies of zero charge potentials (E_{zc}). According to the earliest investigations [38–41], E_{zc} are close to 0 V vs. SHE and depend on adsorption of anions and on solution pH [42]. More negative values were estimated from the position of the adsorption–desorption peak at negative potentials of capacitance curves in the presence of tetrabutilamonium ions (TBA^+) [43].

Further experiments, which were performed with Cu electrodes maximal free from oxides, indicated rather negative E_{zc} values. Large differences were observed between open-circuit potentials obtained for freshly immersed metal surfaces and for metal surfaces renewed abrasively *in situ* in aqueous solutions. For Cu, the immersion potentials were ~600 mV more positive than the scrape potentials [44].This was also attributed to the presence of adsorbed oxygen that contributes a dipolar potential to copper. Rather negative E_{zc} (~ -0.7 V) were also determined for different faces of monocrystalline Cu electrodes in perchlorate solutions using impedance data [45]. The constant phase element (CPE) behaviour of the system was observed at frequencies from 1 to 100 Hz that caused a certain dispersion of impedance.

Adsorption of some corrosion inhibitors (benzotriazole and naphthalene [46,47]) as well as other surfactants (TBA^+, *n*-propanol, thiourea [43,48]) was investigated. Extensive experimental data on adsorption of polyethers are generalized in monograph [49]. These substances are widely used in the deposition of copper and its alloys. An interesting effect was established: weak adsorption of these substances can be significantly enhanced by micromolar amounts of halides. Similar conclusion also follows from our recent investigations performed with camphor [50]. In our opinion, further investigations are of obvious interest. In this communication, the main attention is focused on the kinetics of Cu(II) reduction on the camphor-modified copper electrode.

2. 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. Owing to the low solubility of camphor, its maximum concentration was 6 mmol dm^{-3}. Solutions were deaerated before experiments with an argon stream for over 0.5 h. To prepare the working electrodes, a platinum disc (1 cm^2, voltammetric measurements) or wire (0.36 cm^2, impedance measurements) were coated with 5–7 μm thick copper layer in the solution containing (g dm^{-3}): $Cu_2SO_4 \cdot 5H_2O$ – 250, H_2SO_4 – 50. A polycrystalline layer with well-exhibited crystallographic edges and faces was formed.

Linear potential sweep (LPS) voltammetry was performed using a potentiostat/galvanostat REF 600 from Gamry Instruments. LPS voltammograms were recorded at a potential sweep rate ranging from 0.01 to 0.2 V s^{-1}. In all cases, cathodic scans were applied, starting with the open-circuit potential.

Impedance measurements were carried out using 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 3×10^4 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, sufficiently low frequency $f = 19$ Hz was applied. Conventional electrochemical cell contained three electrodes. The working electrode was placed inside the ~10 cm^2 Pt cylinder, which was used for polarization. The electrode potential was measured in reference to the Ag|AgCl|KCl(sat) electrode and was converted to the standard hydrogen electrode scale. All experiments were performed at 20 °C.

Scanning probe microscopy (SPM) measurements were performed in the tapping mode using microscope Dimension 3100/ Nanoscope IVa (Digital Instruments, Inc./Veeco Metrology Group, USA). Randomly chosen two-dimensional surface areas of 10×10 μm size were analyzed and the following characteristics of surface morphology were obtained:

- arithmetic average of the absolute values of the surface height deviations measured from the mean plane $R_a = 100$–140 nm;
- the root mean square (RMS) average of height deviations taken from the mean data plane $R_q = 130$–180 nm;
- the difference between the image three-dimensional surface area and its two-dimensional, footprint area was 7–10%;
- the roughness factor, determined as the ratio between estimated and projected surface areas, was ~1.1;
- the maximum vertical distance between the highest and lowest datapoints in the image $R_{max} = 0.8$–1.2 μm.

When presenting the impedance values, no corrections for surface roughness were done.

3. RESULTS AND DISCUSSION

To characterize the surface of copper electrodes, cyclic voltammograms (CVA) and impedance spectra were measured in 0.6 M H_2SO_4 solutions (Fig. 1). Rather low current densities are characteristic of the double-layer region where CVA display no characteristic peaks. At the same time, significant dispersion of impedance is observed (inset in Fig. 1).

Between different reasons for impedance dispersion, copper oxidation has been discussed. First of all, surface oxides (Cu_2O and CuO) can be formed due to common copper corrosion. Besides, the interaction between Cu and Cu^{2+} ions produces intermediate Cu^+

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