The difference between interfaces formed by mechanically renewed gold and silver electrodes with acetonitrile and aqueous solutions

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ABSTRACT

The impedance method and cycling voltammetry were used in studying the structure of interface between mechanically renewable electrodes of Au and Ag and solutions with different concentration of LiClO$_4$ in acetonitrile (AN). The obtained data allowed us to conclude that the considered systems are characterized by the wide potential regions in which these electrodes can be considered as ideally polarizable. These regions are: from -0.5 to 1.0 V for Au and from -1.7 to -0.2 V (vs. aqueous SCE) for Ag electrodes; the zero charge potentials of Au and Ag electrodes in these systems are: 0.62 and -0.37 V, respectively. It was shown that, in the above-noted potential regions, the experimental C vs. E curves can be well described by the classical model of Gouy–Chapman–Stern–Grahame. It was shown, as well, that the difference in experimental zero charge potentials of Au and Ag electrodes correlates with the difference in electron work functions of these metals. These data allow us to conclude that the interaction at the interface between renewable Au and Ag electrodes and AN solutions can be characterized as lyophobic, i.e., close to that observed for Hg/AN and mercury-like metals/AN systems. On the other hand, the interfaces of Au and Ag electrodes with aqueous solutions should be considered as hydrophilic systems being radically different from the interfaces of Hg and mercury-like metals with aqueous solutions. It was demonstrated that the specific features of the interface structure on Au and Ag electrodes in contact with aqueous and AN solutions can be well described on the qualitative level within the framework of phenomenological model of «two limiting states».

1. Introduction

The structure of the electric double layer (EDL) on interfaces of many metals with aqueous solutions was certainly studied very extensively. The electrochemical studies of the structure of interfaces between metals and solutions based on nonaqueous (first of all, aprotic) solvents are much fewer, despite the fact that this direction is of considerable interest both for fundamental science and practice. Acetonitrile (AN) is used very often in electrochemical investigations as the solvent. It is an aprotic solvent and the EDL structure at its interfaces with various metals was studied most thoroughly. Mention should be made of the studies carried out on liquid metal electrodes, including dropping electrodes of mercury and gallium-based binary alloys (e.g., see the data summarized in [1,2], the results by Bagotskaya, Damaskin, and Emets shown and analyzed in [3–7], and the references therein). Note that the electrochemical studies of liquid electrodes are highly advantageous because these electrodes have atomically smooth surface, which ensures their energy homogeneity. Moreover, the use of dropping electrodes (i.e., the procedure of regular renewal of the liquid

electrode surface immediately in electrolyte solution) makes it possible to lower down the requirements to the degree of purity of solutions, which is the burning problem when operating with nonaqueous solvents because of complications associated with their deep cleaning.

The EDL structure in AN solutions on solid electrodes was studied in much less detail. Among the systems studied, the interfaces of polycrystalline bismuth electrode and its individual faces with solutions based on this solvent deserve mention (e.g., see studies by Palm, Lust, et al. cited in [2]). By analyzing the correlations between zero charge potentials (and/or potentials at the equal high negative charges) of mercury-like metals and the electron work functions of these metals in vacuum, their weak interaction with this solvent was inferred.

Beyond the group of mercury-like metals, the capacitance curve of a polycrystalline gold electrode in AN solution of 2.5 mM LiPF$_6$ was measured and analyzed [8]. The authors of the latter study assumed the weak interaction of AN molecules with the gold surface (much similar to their interaction with electrodes of mercury-like metals). It should be noted that we failed to find any data for the silver electrode interface with AN-based solutions in the literature.

As regards their characteristics, the interfaces of Pt and Pd electrodes with AN solutions cardinally differ from interfaces of metals discussed above. This follows from, e.g., the capacitance curves obtained on mechanically renewed electrodes shown in [9,10]. Their authors showed that the shifts of zero-charge potentials with the transition from electrodes of mercury-like metals to those of Pt and Pd do not correlate with the difference in their work functions. The latter result apparently points to the considerable chemisorption of AN molecules on the surface of these electrodes. Later, the analogous conclusion was drawn in [11] based on the adsorption behavior of AN molecules in acidified solutions on electrodes of polycrystalline Pt electrode and different faces of Pt single crystal. The orientation of AN molecules on single-crystal Pt electrodes was studied by SNIFTIRS [12]. It was found that the potential of zero charge of the Pt electrode in the AN solution of a surface-inactive electrolyte is independent of the crystallographic orientation of the surface, which may be due to the strong chemisorption of AN molecules on different faces of Pt single-crystal.

Mention should be made of the procedure of electrochemical measurements on electrodes with the surface mechanically renewable *in situ* (i.e., without breaking the polarization circuit) which was proposed in [13]. This method solves the problem of acquiring reliable and well reproducible experimental results, which is very serious for solid polycrystalline electrodes. Indeed, the renewal produces the electrode surface free of oxides and other films which can appear upon the metal interaction with the solvent and also with uncontrolled impurities adsorbed from solution. This procedure was successfully used many times in our studies (e.g., see the latest studies [14–18] and references therein) of the interfaces formed by several metals (including Au and Ag) and alloys with aqueous solutions of surface-inactive electrolytes. As for the case on the dropping electrode of a liquid alloy, the procedure of mechanical renewal of the solid-electrode surface is especially promising when operating with nonaqueous solvents and was assumed to be suitable for carrying out capacitance measurements on Ag and Au electrode in AN solutions.

On its certain stage, the development of theoretical concepts on the structure of the EDL dense part under the conditions of absence of specific adsorption of ions passed from the models which took into account only the contribution caused by different orientation and polarization of solvent molecule dipoles on the electrode/solution interface to the models which also considered the electronic structure of metals [19]. Based on these theoretical concepts, we proposed [20] the phenomenological model of «two limiting states», which allowed the double-layer properties of electrodes, particularly, those made of mercury, gallium, and platinum-group metals at their interface with solutions of different nature to be interpreted from a unified viewpoint.

Bearing in mind everything aforesaid, in the present study, we formulated the following objectives:

1. In addition to the literature data including those obtained in our earlier studies for interfaces of mechanically renewable Au and Ag electrodes with aqueous solutions of surface-inactive electrolytes, to obtain new data on the EDL structure on the latter electrodes in AN solutions of surface-inactive electrolytes.

2. Based on the obtained dependences and the reference data, to analyze the role of the solvent nature in the formation of interface upon the transition from aqueous to AN solutions within the framework of the model of «two limiting states».

2. Experimental

The working electrodes were prepared from gold and silver samples containing 99.999 at.% of the main component. The original samples were drawn through hard-alloy dies to obtain wires with the diameter of 0.8 mm, which were later subjected to homogenizing annealing in pure argon atmosphere at 800°C for 20 days. To carry out measurements on the renewable electrodes, the wire segments with the length

of ~2 cm were pressed into Teflon tubes. The working surface (the wire end) was renewed by cutting off a thin metal layer (~10 μm) with a sapphire tool immediately in electrolyte solution.[1] The description of the special cell equipped with the system for renewing electrodes of individual metals and alloys can be found, e.g., in [13] or in our studies [14–18].

For solutions, we used AN (Sigma Aldrich, HPLC grade, water content below 0.01% according to Fischer test) and $LiClO_4$ (Sigma Aldrich, battery grade). Solutions were prepared in atmosphere of purified argon and deaerated by bubbling argon during the measurements.

Saturated aqueous calomel electrode (SCE) was used as the reference electrode. All the potentials in this work are referred to SCE. The experimental dependences of electrode impedance components $1/C\omega$ and R (where C is the differential capacitance, $\omega = 2\pi f$ is the angular frequency, f is the ac frequency in Hz, R is the resistance) on the potential E and also the current vs. potential dependences were measured by means of setup AUTOLAB PGSTAT 100 involving the FRA (Frequency Response Analyzer) system.

The analysis of impedance diagrams measured on the renewed gold and silver electrodes in 0.1 M $LiClO_4$ has shown that in the ac frequency range from 100 to 2500 Hz, the frequency dispersion of C values does not exceed 7–10% in potential regions from −0.70 to 1.00 V and from −1.75 to 0 V on the Au and Ag electrodes, respectively. The quantitative analysis of experimental impedance spectra was carried out with the use of "ZVIEW2" program [23]. The slight frequency dispersion of C observed in the mentioned intervals was probably associated with a certain field asymmetry between the working and the counter electrodes and also with the roughness of the electrodes studied. Hence, the aforementioned potential intervals can be considered with good approximation as the regions of ideal polarizability for these electrodes. This conclusion adequately agrees with the data of cyclic voltammetry (for the potential intervals mentioned, the current density did not exceed several μA/cm^2 for the potential scan rate of 100 mV/s). In the majority of cases, the EDL capacitance was measured at the ac frequency of 370 Hz chosen based on the analysis of impedance spectra at different potentials. Below, we show the differential capacitance values recalculated to the true electrode surface. The recalculation was carried out with regard to the roughness coefficients determined by the Parsons-Zobel method [24].

3. Results and discussion

3.1. Capacitance measurements on mechanically renewed Au and Ag electrodes in AN solutions of $LiClO_4$

Figs. 1 and 2 show dependences of the differential capacitance on the potential measured on renewable Au and Ag electrodes in AN solutions of $LiClO_4$ of different concentration. It is seen that in dilute solutions the dependences have a well pronounced capacitance minimum at potentials in the range from 0.60 to 0.65 V on the Au electrode and from −0.4 to −0.35 V on the Ag electrode, which deepen with the decrease in $LiClO_4$ concentration. Both for gold and for silver electrodes, the potential of the capacitance minimum is virtually independent of the supporting electrolyte concentration. This makes it possible to associate the minimums with the maximum diffusivity of the EDL at the zero-charge potentials. Note that according to the literature data [25–28] and also to our results [29–31], in aqueous solutions the potentials of such capacitance minimums are 0.00 ± 0.05 and $−0.98 \pm 0.05$ V on polycrystalline gold and silver electrodes, respectively. Hence, the difference between the potentials of minimums

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[1] From our viewpoint, the renewal of surface by cutting can be very effective procedure to avoid possible contamination of the electrode surface with platinum atoms. The substantial influence of ultra-low platinum coverages on the electrochemical behavior of gold electrodes was mentioned in [21,22].