

Properties of an interfacial solution layer at gold electrode surface in perchlorate and chloride solutions: piezoelectric resonator and drag force study



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ABSTRACT

Piezoelectric resonator and drag force measurements show a decrease of interfacial viscosity of perchlorate and chloride aqueous solutions during polarization of gold electrode towards potential of zero charge. Though more noisy, drag force measurements have the advantage over piezoelectric technique as the former is insensitive to potential dependent adsorption, which causes distortion of data on liquid properties obtained from piezoelectric resonator measurements at more positive potentials. The shift in the potential of the viscosity minimum, obtained from drag force measurements follows the shift in the potential of zero charge (pzc) with a change in concentration. In addition, the Esin-Markov relation holds at these potentials: tenfold increase in concentration of specifically adsorbing chloride shifts the potential of viscosity minimum by -46 mV, whereas tenfold increase in concentration of weakly adsorbing perchlorate results only in the negligible shift of the potential of viscosity minimum (-4 mV).

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1. Introduction

The effect of an externally applied electric field on the viscosity of liquids is known for a long time [1–3]. Under the influence of an electric field of the order 10^5 – 10^6 V/m, the twofold and larger viscosity increase for polar liquids was reported [1,2]. However, there is still no agreement on the main mechanism among the numerous phenomena that might be the cause of the viscosity change. Another striking example of interaction between electric field and liquid is floating water bridge phenomenon, which is free standing connection of pure liquid water, formed under influence of electric field of approximately 10^6 V/m [4]. It is assumed that such bridges are stable by the action of electrohydrodynamic forces caused by electric field gradients counteracting gravity because X-ray measurements have shown no microscopic structural change in floating water [5]. On the other hand, ultrafast pump/probe measurements of the relaxation times of the OH-stretch vibration, which directly relates to the intermolecular bond strength, show that dynamically water in the bridge is different from bulk water [6].

At electrochemical interfaces, all the above and more phenomena can be manifested because the electric fields, which arise in the electric double layer at the charged electrode surface in aqueous solutions, are significantly higher, up to 10^8 – 10^9 V/m. Density functional theory calculations have shown that such electric field can break hydrogen bonds in water clusters and the linear, branched or net-like structures of water can be formed [7].

Potential polarization towards the pzc can operate the electrified interface to cause decreased ordering of the extended network of interfacial water molecules. That can shift the equilibrium in the direction of building smaller water clusters and make the layer near the surface (“transition” layer) less viscous and denser. A minimum of interfacial viscosity of NaF aqueous solution at the potential of zero charge of gold electrode (-0.05 V vs the SCE) was observed in electrochemical atomic force microscopy study of interfacial solution layer on gold electrode [8]. Piezoelectric resonator and drag force measurements show that there is a minimum of interfacial viscosity of sodium hexafluorophosphate aqueous solution at the potential of zero charge of gold electrode [9]. Disordering of the structure of interfacial water is in accord with the potential-dependent intensities of sum frequency generation (SFG) spectra measured for interfacial water on charged surfaces [10–12]. Although it has been shown that the two SFG spectra peaks at 3500 and 3250 cm^{-1} rise due to intramolecular vibrational coupling [13], consideration of their intensities as an indicator of the order of the interfacial water [10] was not argued. SFG studies of water

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structure at the metal–water interfaces in different aqueous solutions have shown that intensities for interfacial water molecules are diminishing near the potential of zero charge (pzc) [11,12].

In our previous paper [9], the electrode potential effect on interfacial viscosity was studied in sodium hexafluorophosphate solution. Hexafluorophosphate ion weakly adsorbs on gold surface in water solutions and its interaction with the adsorbed water molecules is also relatively weak. This anion was chosen in order to avoid or to decrease as much as possible the effect of mass loading due to adsorption of solution species on dual-resonator measurements. The purpose of present work is to measure and to analyse potential dependencies of interfacial liquid viscosity in more detail by using solutions of more common ions such as perchlorate and chloride, which exhibit stronger adsorbing properties.

2. Experimental

Analysis of frequency responses of gold coated dual-quartz resonator (two resonators with differently textured surfaces in a monolithic sensor) and of admittance behaviour of gold coated quartz resonator in contact with liquids have been performed as described previously [9]. Dual-resonator sensor and set-up were the same as earlier [9]. Fabrication of quartz supported electrodes for quartz resonator admittance measurements and instrumentation used are described previously [9].

Analysis of drag force on a gold coated sphere in a solution stream and the experimental set-up for measurement of electrode potential effect upon the drag force on gold sphere were as described previously [9]. In present work, the set-up was slightly modified. First, the gold coated bearing ball was joined with gold wire (0.1 mm diameter) by arc welding, not with copper wire. Second, laser and light detector were attached to the flow volume gauge (ETK-M with pulser, Zenner) in order measure the frequency of light reflection from the whirligig blades. That allowed to detect time for each 25 ml of liquid passed.

Electrochemical impedance spectroscopy (EIS) was used to determine potential dependence of the double layer capacitance of Au electrode (gold coated bearing ball) in sodium perchlorate solution, which was deaerated by bubbling prepurified nitrogen for one hour before measurements. Impedance was measured using AC amplitude 8 mV at frequencies from 4 to 3000 Hz (15 points per decade) in 10 mV steps from -100 to 760 mV by using Gamry (USA) electrochemical instrument Reference 600 Potentiostat/Galvanostat/ZRA equipped with the Gamry Framework software version 5.30. EIS data were analysed using the Gamry Echem Analyst software version 5.30.

Potentials were measured and reported here against silver/silver chloride/(saturated KCl) reference electrode, Ag/AgCl. Salt-bridge junction, filled with saturated NaCl solution, was used for measurements in sodium perchlorate solutions.

Sodium perchlorate (99,99%, Sigma-Aldrich) and sodium chloride (99%, Alfa Aesar) were used to prepare solutions. For piezoelectric resonator experiments and drag force measurements, doubly distilled water and mono distilled (first deionized) water was used, respectively.

3. Results and Discussion

3.1. Roughness of gold surfaces on quartz resonators used for measurements of the electrode potential effect on the properties of interfacial perchlorate and chloride aqueous solutions at a gold electrode

Liquid hydrodynamic behaviour near the surface of quartz supported electrode is crucially dependent on the surface roughness

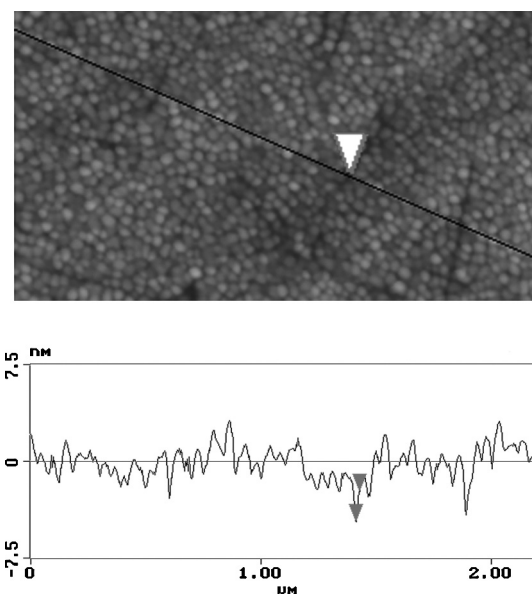


Fig. 1. AFM image and corresponding cross-sectional contour of a non-textured surface of resonator electrode, fabricated by gold vacuum deposition.

and its nature [14]. Roughness of the surfaces used in present work was approximately estimated from the roughness coefficient, calculated from the charge associated with the reduction of oxygen chemisorbed in a monoatomic layer on a gold electrode prior to O₂ evolution, and from AFM images.

For non-textured and textured gold electrodes of dual-resonator, the roughness factors were obtained to be equal to 1.31 and 1.30, respectively. The roughness factor of non-textured surface of gold layer on quartz resonator, which has been used for admittance measurements in present work, is equal to 1.61 as obtained from the charge associated with the reduction of oxygen chemisorbed on gold in 0.1 M HClO₄ aqueous solution. To get better insight into roughness character of the surface used for admittance measurements, AFM image and corresponding cross-sectional contour of a non-textured surface of resonator electrode is shown in Fig. 1, where contour is presented without filtering high frequency signals.

Analysis of the measured quartz resonator admittance data has been performed according to the Butterworth–Van Dyke equivalent circuit assuming that resonator surface, which is in contact with solution, is ideally smooth. That could be to some extent justified if the surface can be characterised as having weak roughness, $h/l \ll 1$, where h is the average of the surface heights measured from their lowest points and l is the average lateral distance between these heights, and the roughness is below 10 nm as the impedance of the quartz resonator would be expected to respond to roughness of about 10 nm and above [14]. Sectional contour of the non-textured surface of gold layer on quartz resonator (Fig. 1), which has been used for admittance measurements in present work, is typical for the surface. Roughness analysis of 4 square micrometers of the gold surface shown in Fig. 1 gives maximum vertical distance between the highest and lowest data points within the AFM image and root-mean-square average of deviations from the mean data plane equal to 13.44 and 1.149 nm, respectively. These data and the higher roughness factor (1.61), obtained from cyclic voltammetry data, lead to conclusion that this gold surface is rougher than that used in our previous work [9]. The higher roughness factor value, most probably, appears due to higher roughness density as shown in Fig. 1. Nevertheless, more detailed inspection of this

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