Piezoelectric Resonator Study of the Viscosity of Interfacial Layers at Gold Electrode Surface in Perchloric Acid, Tetrafluoroborate and Sulphate Solutions

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Piezoelectric resonator measurements in perchloric acid, sodium tetrafluoroborate and sodium sulphate solutions and comparison with earlier reported measurements in hexafluorophosphate, perchlorate and chloride solutions show that a decrease of interfacial viscosity of anion solutions, when gold electrode is polarized towards potential of zero charge, is mostly governed by surface charge. At the potential of zero charge a decrease of interfacial viscosity of all solutions investigated was in the range from 0.5% to 0.8% of the bulk viscosity. Considering that interfacial viscosity is determined by averaging over the decay length scale of the damped shear wave radiated into the liquid by the resonator, model calculations show that the measured changes of average viscosity are caused by changes of the actual interfacial viscosity and the thickness of the layer, where the change of interfacial viscosity occurs.

1. INTRODUCTION

Most of the reported viscosity values were measured for nanoconfined water and differ by technique [1-4]. Simulations show that in comparison with the bulk the viscosity of water in the interfacial region at the polar, hydrophilic substrates is from 2 to 4 times larger [5]. The structure of interfacial water depends on the surface charge [3] and Guriyanova et al. have found a minimum of interfacial viscosity of 0.1 M NaF aqueous solution at the potential of zero charge of gold electrode, what corresponds to minimum strength of electric field [6].

Earlier we have used the piezoelectric resonator and drag force techniques, which allow the viscosity of interfacial water to be examined in the absence of confinement. In this way, we were able to show decrease of interfacial viscosity of hexafluorophosphate, perchlorate and chloride aqueous solutions during polarization of gold electrode towards potential of zero charge [7, 8]. The shift in the

potential of the viscosity minimum, obtained from drag force measurements, follows the shift in the potential of zero charge with a change in concentration according to the Esin-Markov relation. 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) [8]. However, whereas the largest decrease of interfacial viscosity obtained from drag force measurements has been equal to approximately 5% of the bulk viscosity, the dual-piezoelectric resonator measurements of gold electrode have shown a decrease of interfacial viscosity, which ranges from 0.5 to 0.8% of the bulk viscosity. Thus even in the absence of confinement the different techniques used can produce different interfacial viscosity values. After more thorough discussion it has been inferred [9] that the decrease in interfacial viscosity with positive potential scan, calculated from measured drag force data, is to some extent overestimated as the used empirical relationship between drag force coefficient and dynamic viscosity does not account for interdependence of frictional and pressure drags.

The purpose of present work is to further examine the generality of the character of interfacial liquid viscosity dependence on the potential by using greater variety of solutions like containing sodium sulphate, perchloric acid and sodium tetrafluoroborate. For this purpose, dual-quartz resonator (two resonators with differently textured surfaces in a monolithic sensor), quartz resonator admittance and EIS techniques are used. Also, the purpose is to discuss the change of viscosity with the distance from electrode surface by using results of present work and other published findings. It should be noted that piezoelectric resonator only probes the region close to the surface. The shear wave evanescently decays into liquid according to exponential law [10, 11]. Hence in piezoelectric resonator measurement interfacial properties are determined by averaging over the velocity decay length scale of the damped shear wave radiated into the liquid by the resonator [11]. This decay length $\delta = [2\eta/(\rho\omega)]^{1/2}$ [12] is 250 nm in water at $20^{\circ}C$ when f=5 MHz.

2. EXPERIMENTAL

2.1. Measurements and analysis of frequency responses and admittance of gold coated quartz resonators

Measurements and analysis of frequency responses of dual-quartz resonator has been performed as described previously [7, 8]. The dual-resonator set-up and the gold coated quartz resonators used were the same as used earlier [8]. By using AFM analysis and cyclic voltammetry in this work, the roughness of non-textured and textured surfaces of resonator electrodes was evaluated from the standpoint of their suitability for study of liquid properties. Interfacial viscosity and density values were calculated from measured frequency shifts of dual-quartz resonator via semi-empirical relations, which were first obtained by Martin et al. [13, 14]:

$$\Delta f_N = -c_{11}(\rho\eta)^{1/2} - c_{12}\rho \tag{1}$$

$$\Delta f_T = -c_{21}(\rho\eta)^{1/2} - c_{22}\rho \tag{2}$$

where Δf_N and Δf_N are the frequency shifts of the quartz resonator with non-textured surface and quartz resonator with textured surface upon their immersion, respectively;   are the empirical coefficients.

Quartz resonator admittance measurements and analysis of admittance data have been performed using non-textured resonator as described previously [7, 15]. In this analysis, the electrical equivalent of quartz resonator (Butterworth-Van-Dyke equivalent circuit) was used to calculate the changes of electrode mass and liquid properties (viscosity and density product). Roughness of non-textured gold surfaces of resonators used in admittance measurements 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 O_2 evolution, and from AFM data. It was obtained that the surface of gold layer on quartz resonator, which was also used in present admittance analysis, retained a weak roughness ($h/l << 1$, where h is the average rough height and l is the average lateral distance between the roughs) and the average roughness was well below 10 nm. It can be concluded that the obtained changes of electrode mass and liquid properties are not to a greater extent distorted by surface roughness as the impedance of the quarts resonator would be expected to respond to roughness of about 10 nm and above, ignoring most of the so-called atomic scale roughness [10]. Nevertheless, more thorough considerations had shown that there might be strong roughness but the size of surface defects, involved in strong roughness, should not exceed 10 nm [8].

2.2. Electrochemical impedance measurements

Electrochemical impedance spectroscopy (EIS) was used to determine potential dependence of the double layer capacitance of Au electrode (gold coated non-textured face of quartz resonator) in 0.1 M anion solutions, which were deaerated by bubbling prepurified nitrogen for one hour before measurements. Impedance was measured using AC amplitude 8 mV at frequencies from 1 to15000 Hz (10 points per decade) in 20 mV steps from -400 or -200 to 700 or 800 mV by using Gamry (USA) electrochemical instrument Reference 600 Potentiostat/Galvanostat/ZRA equipped with the Gamry Framework software version 5.30. Prior to impedance measurements, the surface of gold electrode was cleaned by cycling its potential from -150 to 1150 mV (v=200 mV/s, 50 cycles) in solutions investigated. In addition, potential cycles (v=200 mV/s, 3 cycles) of the same interval were applied to gold electrode at each potential stopped for subsequent measurement of impedance. The real surface area (0.84 cm^2) of the used gold electrode was calculated by integrating adsorbed oxygen reduction currents in the region of reduction peak of voltammogram where the charge associated with the formation or reduction of chemisorbed oxygen monolayer was assumed to be equal to 390 $\mu C/cm^2$ [16].

EIS data were analysed using the Gamry Echem Analyst software version 5.30. Potentials were measured and reported here against silver/silver chloride/(saturated NaCl) reference electrode, Ag/AgCl. Saturated NaCl solution was preferred as a filling solution because perchloric acid solution was among the studied solutions.

*2.3. Reagents and solutions*

0.1 M solutions of sodium sulphate (99%, Sigma-Aldrich), sodium tetrafluoroborate (98%, Sigma-Aldrich) and perchloric acid (70% solution, Sigma-Aldrich, ACS reagent) prepared in doubly distilled water were used. The solutions were de-aerated by bubbling Ar (99.999%) before measurements. In piezoelectric resonator experiments, solutions were poured into the cell and the system was left in a thermostat for at least half an hour before the measurements in order to ensure temperature change less than 0.02°C during the measurement.

3. RESULTS AND DISCUSSION

3.1. Dual-quartz resonator measurements of the electrode potential effect on viscosity of perchloric acid, tetrafluoroborate and sulphate aqueous solutions at a gold electrode

During potential scan into positive direction the resonant frequencies of non-textured and textured resonators were recorded at 12 mV increments. Every scan was repeated five times. The resonant frequency value, measured before immersion, was subtracted from every recorded frequency value. Measured resonant frequency shifts Δf_N and Δf_T were recalculated into viscosity values via semi-empirical equations (1) and (2) where coefficients c_{ij} were determined in advance from Δf_N and Δf_T measured upon immersion into different liquids of known viscosities and densities [7]: $c_{11} = 632.5 \, \text{kg}^{-1}\text{m}^2\text{s}^{-1/2}$, $c_{12} = 0.671 \, \text{kg}^{-1}\text{m}^3\text{s}^{-1}$, $c_{21} = 742.5 \, \text{kg}^{-1}\text{m}^2\text{s}^{-1/2}$, $c_{22} = 3.528 \, \text{kg}^{-1}\text{m}^3\text{s}^{-1}$. In this way, five sets of calculated values of the viscosity change (function) with potential (independent variable) were obtained. Then these sets where joined into one and the LOESS procedure (local smoothing technique with tri-cube weighting and polynomial regression) was used to smooth the viscosity change data as a function of the potential. LOESS fits (sampling proportion and polynomial degree equal to 0.15 and 1, respectively) for gold coated sphere drag versus potential of gold electrode in 0.1 M perchloric acid, sodium tetrafluoroborate and sodium sulphate solutions are shown as curves 1 in Figs. 1A, 2A and 3A. The minimum and maximum values of viscosity change were used to draw experimental error ranges, which a shown as dashed curves enveloping curves 1 in Figs. 1A - 3A.

In introduction, it was mentioned that piezoelectric resonator and drag force measurements have shown a decrease of interfacial viscosity of hexafluorophosphate, perchlorate and chloride aqueous solutions during polarization of gold electrode towards potential of zero charge [7, 8]. In present work, the question of the correlation between the pzc of gold electrode and the position interfacial viscosity minimum is pursued further.
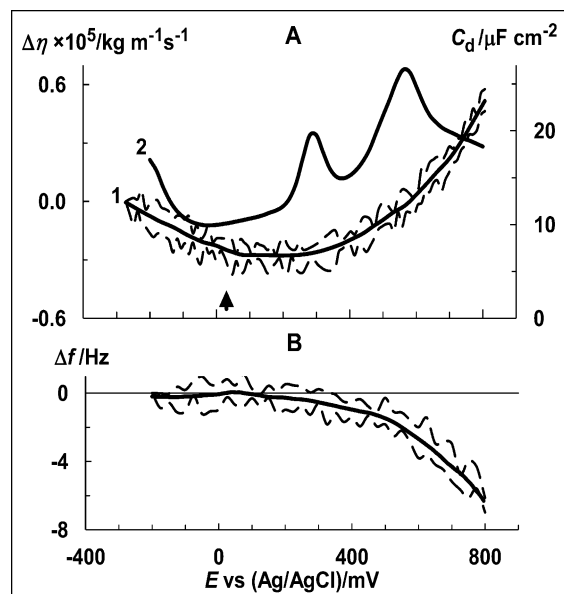
Figure 1. (A) Interfacial viscosity change (1), calculated from dual-resonator data, with its error ranges (dashed curves) vs potential of gold electrode in 0.1 M HClO$_4$ aqueous solution (dE/dt=100 mV/s, θ=21.82±0.02°C) and dependence of double layer capacitance (2) on the potential for Au electrode (gold coated non-textured face of quartz resonator) in aqueous 0.1 M HClO$_4$ solution; arrow shows the approximate position of the *pzc*. (B) resonant frequency change due to mass change, calculated from admittance data, with its error ranges (dashed curves) vs potential of gold electrode in 0.1 M HClO$_4$ aqueous solution, θ=19.50±0.03°C.
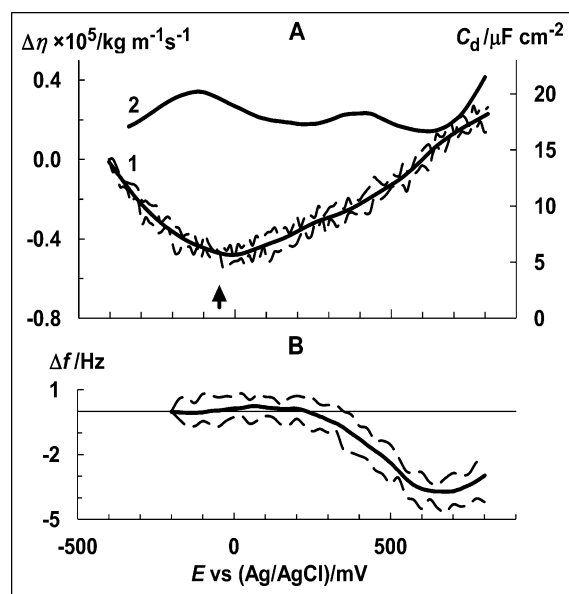
Figure 2. (A) Interfacial viscosity change (1), calculated from dual-resonator data, with its error ranges (dashed curves) vs potential of gold electrode in 0.1 M NaBF$_4$ aqueous solution (dE/dt=100 mV/s, θ=21.56±0.02°C); dependence of double layer capacitance (2) on the potential for Au electrode (gold coated non-textured face of quartz resonator) in 0.1 M NaBF$_4$ aqueous solution; arrow shows the approximate position of the *pzc*. (B) resonant frequency change due to mass change, calculated from admittance data, with its error ranges (dashed curves) vs potential of gold electrode in 0.1 M NaBF$_4$ aqueous solution, θ=19.81±0.03°C.
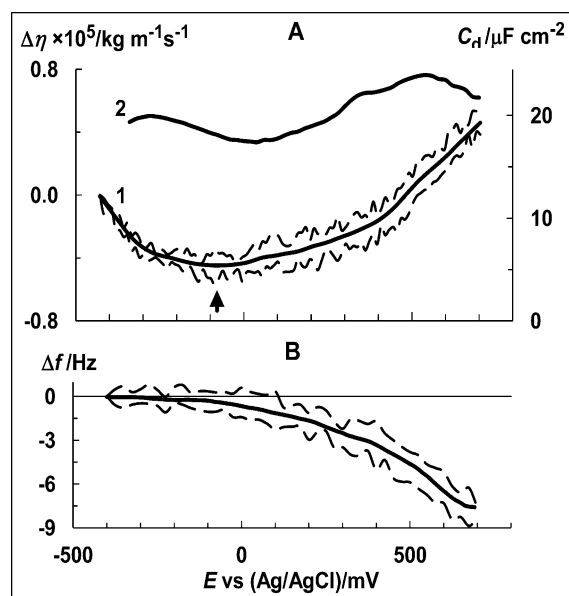
Figure 3. (A) Interfacial viscosity change (1), calculated from dual-resonator data, with its error ranges (dashed curves) vs potential of gold electrode in 0.1 M Na$_2$SO$_4$ aqueous solution (dE/dt=100 mV/s, θ=22.31±0.02°C); dependence of double layer capacitance (2) on the potential for Au electrode (gold coated non-textured face of quartz resonator) in 0.1 M Na$_2$SO$_4$ aqueous solution; arrow shows the approximate position of the *pzc*. (B) resonant frequency change due to mass change, calculated from admittance data, with its error ranges (dashed curves) vs potential of gold electrode in 0.1 M Na$_2$SO$_4$ aqueous solution, θ=20.48±0.03°C.

The arrows in Figs. 1A − 3A show the approximate position of the *pzc* of gold electrode in investigated solutions as reported in electrochemical literature [17]. In addition, the dependences of double layer capacitances on the potential for Au electrode (gold coated non-textured face of quartz resonator) were calculated (curves 2 in Figs. 1A − 3A) from EIS data measured in the same solutions. For calculations, the Randles equivalent circuit was used where both the double layer capacitor and the constant phase element (*CPE*) were tested. The reason for testing *CPE* was the polycrystalline nature and possible porosity of gold electrode manufactured by vacuum coating the quartz resonator. For Randles circuit, the relationship between C_d and *CPE* is $C_d = (CPE_p \times R_p)^{1/n} / R_p$ [18] where R$_p$ is a polarization resistance and n is the parameter with values between 0 and 1. It is usually assumed that $CPE_p \approx C_d$, when n > 0.95. Analysis of EIS data according to the Randles circuit produced n from 0.93 to 0.96 for all solutions. Hence, the n values are located in critical region. This could be one of the reasons why the minima, which could be associated with the *pzc*, are ill defined in all three dependences of C_d on the potential shown in Figs. 1A − 3A. Nonetheless, the comparison of obtained potential dependences of interfacial viscosity and double layer capacitance, considering the values of reported *pzc* values, allows to correlate the decrease of interfacial viscosity with the decrease of surface charge of electrode.

3.2. Reliability of interfacial viscosity data obtained from dual-resonator measurements

Reliability of interfacial viscosity density changes with potential (curves 1 in Figs. 1A - 3A), obtained by using dual-resonator technique, is conditioned by several factors. The one is the validity of the assumption that frequency shifts are solely determined by the properties of interfacial liquid and the other is the character of the roughness of electrode surface.

The validity of the said assumption can be tested by using quartz resonator admittance analysis, which allows to differentiate the electrode mass change from liquid properties. Using resonator with non-textured vacuum deposited gold layer, admittance measurements were performed in 25 mV steps in the potential region from -200 to +800 mV for perchloric acid and sodium tetrafluoroborate solutions and from -400 to +700 mV for sodium sulphate solutions. At one potential**,** during 15 s admittance magnitude and phase angle frequency spectra were recorded 6 times. Then the analysis of every recorded set of admittance data was performed as described previously [7, 15], where the surface of resonator was assumed as being ideally smooth. When such ideal resonator is placed into a viscous medium and when mass is added, under non-slip, constant temperature and pressure conditions the total frequency shift is [19]

$$\Delta f_t = \Delta f_m + \Delta f_{\rho,\eta} = -\frac{2f_0^2}{(\rho_q \mu_q)^{1/2}} \left[\frac{\Delta M}{A} + \left(\frac{\rho_L \eta_L}{4\pi f_0} \right)^{1/2} \right] \qquad (3)$$

The relationship between the parameters of the Butterworth-Van Dyke equivalent circuit of such resonator and liquid density-viscosity product $\rho_L \eta_L$ is [14]

$$\rho_L \eta_L = (64/\pi)\rho_q \mu_q (K^2)^2 f_0 C_0^2 R_2^2 \qquad (4)$$

where ρ_q and μ_q are the density and the shear modulus of AT-cut of quartz, respectively; K^2 is the electromechanical coupling constant for AT-cut quartz; f_0 is the resonant frequency of quartz resonator; C_0 is the static capacitance of quartz resonator and R_2 is the equivalent resistance characterising the contact of quartz resonator with liquid.

Analysis of admittance data together with eqs. (3) and (4) allowed to separate frequency change due to added mass change from the frequency change due to change of interfacial liquid properties. In Figs. 1B-3B, the changes of Δf_m with potential change are shown as differences $\Delta f = \Delta f_m^E - \Delta f_m^{E_{in}}$. The character of frequency changes due to mass change with potential (Figs. 1B-3B) shows that there are potential ranges where frequency changes can be considered as determined only by the properties of interfacial liquid when potential is scanned into positive direction. Comparison of curves 1 in Figs. 1A–3A with the frequency changes due to mass change with potential (Figs. 1B-3B) allows to conclude that dual-resonator data on interfacial viscosity can be considered as credible in potential ranges where the change of added mass is insignificant: from $E_{in} = -200$ mV to approximately +250 mV for perchloric acid and sodium tetrafluoroborate solutions; from $E_{in} = -400$ mV to approximately -50 mV for sulphate solution.

Another factor, which influences the reliability of interfacial viscosity data, is the character of the roughness of electrode surface. It was briefly discussed in section 2.1. These considerations show that quantitative data on interfacial liquid properties obtained from dual-quartz resonator

measurements and conclusions inferred from quartz resonator admittance analysis should be treated reservedly. The approximation of ideally smooth resonator was used because the existing theories provide a description for rough surfaces in two limiting cases of slight and rough surfaces but much is left to be developed for a quantitative interpretation of data obtained for real surfaces [11].

Nevertheless, conclusions, inferred from the results of quartz resonator measurements of the electrode potential effect on viscosity of perchloric acid, tetrafluoroborate and sulphate aqueous solutions at a gold electrode, are in agreement with the results of our previous studies [7, 8]. In all solutions investigated, the minima of interfacial viscosity are located close to the *pzc* of gold electrode in these solutions. It should be noted that the established potentials of the minima of interfacial viscosity are in the potential ranges where the changes of anion adsorption are negligible.

3.3. On the change of viscosity within the solution layer at electrode surface

In introduction, it has been mentioned that in piezoelectric resonator measurement interfacial properties are determined by averaging over the velocity decay length scale of the damped shear wave radiated into the liquid by the resonator [11] and that this decay length δ is equal to 250 nm in water at 20°C when f=5 MHz [12]. The contribution of solution viscosity to averaged viscosity sensed by piezoelectric resonator should be the function of the distance from resonator surface. This function should be of the form of exponential decay as the shear wave evanescently decays from resonator surface into liquid according to exponential law [10, 11]. In this way, the average viscosity $\langle \eta \rangle$ can be written as follows

$$\langle \eta \rangle = \int_0^\infty \eta(z) \exp(-z/\delta) dz \bigg/ \int_0^\infty \exp(-z/\delta) dz \tag{5}$$

where $\eta(z)$ denotes the viscosity as a function of the distance from resonator surface.

Further, some simple model assumptions are used for providing function $\eta(z)$ with an explicit form. First, the thickness of solution layer at electrode surface where the viscosity is different from the bulk value must be known. Measurements done in water confirmed the existence of a highly viscous interphase of water on hydrophilic surfaces [1, 2] without any external potential applied. Electrochemical atomic force microscope study [6] has shown that the viscosity of 0.1 M NaF solution decays exponentially within the interphase layer, the thickness of which ranges from 2 nm near the *pzc* to 5 nm at potentials approximately 1 V away.

Denoting characteristic length scale as δ^*, viscosity dependence on the distance from electrode z can be approximated by

$$\eta(z) = \Delta \eta^{\mathrm{s}} \exp(-z/\delta^*) + \eta_{\mathrm{b}} \tag{6}$$

where $\Delta \eta^{\mathrm{s}}$ is the difference between the viscosity of water layer in close vicinity to the electrode surface and bulk viscosity η_{b}.

Introduction of eq. (6) into eq. (5) and then integration gives

$$\langle \eta \rangle = \Delta \eta^{\mathrm{s}} \delta^* \big/ (\delta^* + \delta) + \eta_{\mathrm{b}} \approx \Delta \eta^{S} \delta^* \big/ \delta + \eta_{\mathrm{b}} \tag{7}$$

In this equation, both $\Delta\eta^{\mathrm{S}}$ and δ^* are dependent on the potential. When δ is assumed to be equal to 250 nm and the maximum decrease of the average viscosity with potential change is approximately equal to 0.5% of the bulk value (see curves 1 in Figs. 1A-3A), eqn. (7) yields

$$\langle\eta\rangle_{\mathrm{pzc}} - \langle\eta\rangle_{E_{\mathrm{in}}} \approx \Delta\eta^{\mathrm{S}}_{\mathrm{pzc}}\delta^*_{\mathrm{pzc}}/\delta - \Delta\eta^{\mathrm{S}}_{E_{\mathrm{in}}}\delta^*_{E_{in}}/\delta \approx 5\cdot10^{-3}\eta_{\mathrm{b}} \tag{8}$$

Inspection of these approximate calculations shows that a decrease of the average viscosity is caused by a decrease of the product of $\Delta\eta^{\mathrm{S}}$ and δ^* with a change of potential towards *pzc*. The change of δ^* alone would be able to cause the observed average viscosity change considering reported data on the potential dependent thickness of the layer where the viscosity change occurs [6].

4. CONCLUSION

Piezoelectric resonator measurements in perchloric acid, sodium tetrafluoroborate and sodium sulphate solutions show a decrease of interfacial viscosity of anion solutions, when gold electrode potential is polarized towards *pzc*. A maximum decrease of interfacial viscosity of all solutions investigated, which is equal to approximately 0.5% the bulk viscosity, has been observed at the *pzc*. The findings of present work together with earlier reported measurements in hexafluorophosphate, perchlorate and chloride solutions provide strong support in favour of assumption that the change of interfacial viscosity of anion solutions at gold electrode with potential change is mostly governed by changing electrode surface charge. The influence of anion nature probably appears indirectly through participation of anions in determining surface charge.

For testing the reliability of interfacial viscosity dependences on the potential measured by dual-resonator technique, these measurements were complemented with quartz resonator admittance analysis. It confirmed the reliability of potential dependences of interfacial viscosity during positive polarisation up to the potentials exceeding the potential at which interfacial viscosity minimum were observed. Further polarisation causes noticeable anion adsorption what distorts interfacial viscosity measurements.

The findings of present work provide with additional arguments the earlier conclusion [7, 8] that by controlling the applied potential, it is possible to control the viscosity of liquid layer close to the solid interface what increases the ability to actively manipulate a wall-bounded liquid flow field to effect a desired change.

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