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Superviscosity and electroviscous effects at an electrode/aqueous electrolyte interface: An atomic force microscope study

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ABSTRACT

Several authors observed in the past a larger than twofold increase in viscosity of *organic* liquids under the influence of an electric field of the order of 10^6 V/m. This was called electro viscous effect (EVE). Significantly higher electric fields, of up to 10^8 – 10^9 V/m, arise in the electric double layer in solutions close to an electrode. Therefore, the viscosity can be expected to increase at strongly charged liquid–solid interfaces. In more recent years, it was also observed that even in the absence of an externally controlled electric field the viscosity of water can be up to 10^7 times higher close to a hydrophilic surface than in the bulk (“hydrophilic forces”). Here, we present electrochemical atomic force microscopy (EC-AFM) measurements by which we can overcome the critical threshold of the electric field $H = 10^6$ V/m by the control of the potentials applied to both a conducting sample and a conducting tip immersed in solution. Using the EC-AFM, we have investigated for the first time the EVE in an aqueous electrolyte. We can show that by controlling the applied potential, we can control the viscosity and the thickness of the super viscous liquid layer close to the solid interface. Using this technique, we are further able to separate effects on viscosity induced by the hydrophilicity of the surfaces, by the strong nanoconfinement of the liquid between tip and surface, and by the applied electric field.

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1. Introduction

Investigations of the interaction between solid materials across water suggest that the water structure can be disturbed tens of angstroms away from solid surfaces. A hydration or interphase layer, whose structure and properties are significantly different from those of the bulk liquid, has been predicted. The role played by such a structured water in colloidal science, and the distance that such ordering extends from a surface are hotly debated. Beyond several nanometers from the surface continuum-based theories are expected to hold, as predicted by the DLVO (Derjaguin–Landau–Verwey–Overbeek) theory [1]. However, within a few molecular diameters from a solid surface, the confined liquid can no longer be regarded as a continuum, and its molecular nature is expected to come into play. One of the indicators of the structuring could be, e.g., a change of the effective viscosity of the liquid.

Recent atomic force microscope (AFM) and interfacial force microscope (IFM) studies [2–5] show that a surface can induce a drastic increase in the effective viscosity of water in its close proximity. Force profiles acquired in pure water with the IFM between

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a gold sample and a gold tip, both functionalized with self-assembled monolayers (SAM) of differently terminated alkane thiols, indicate the presence of an “interphase” water generating a repulsive hydration force [2]. The interphase layer extended up to 5 nm from the surfaces and had an effective viscosity up to 7 orders of magnitude greater than that of bulk water. Further measurements done in pure water confirmed the existence of such a highly viscous interphase of water on *hydrophilic surfaces only* [3]. In fact, SAM-functionalized surfaces have a regular surface texture in the sub-nanometer scale that could influence the structure of the interphase. However, a similar high effective viscosity was also found by Zhu and coworkers [4] on *bare hydrophilic surfaces* (amorphous silica flat and oxidized tungsten tip). Analogous results were also obtained in a work by Riedo and coworkers [5] for highly purified water confined between a silicon tip and glass and mica samples; the probed viscosity of the interphase water film was 4 orders of magnitude higher than bulk water. On a *bare hydrophobic* graphite surface, no increased viscosity was measured. Apart from pure water, a similar higher effective viscosity was also found in aqueous electrolyte. Force profiles acquired between a flat mica surface and a silicon nitride tip or a silicon oxide microsphere revealed the existence of a layer of water and ions “strongly bound” to the surfaces, and of several more fragile and “loosely bound” layers of water molecules, ions and hydrated ions on top

of the first layer [6,7]. Here, too the probed viscosity was reported to be higher at the surface. Most of these data suggest that an important criterion for the formation of the highly viscous interphase in aqueous solutions is the degree of hydrophilicity of the surfaces.

Years before the measurements reported earlier, the hypothesis of the presence of a super viscous layer (SVL) at the interface between a metal (mercury) electrode and a polar solvent – dimethylsulfoxide (DMSO) containing 0.04 M of Et_4N^+ – was suggested [8]. The SVL at the electrode was held responsible for a non-symmetric protonation of the symmetric electro-generated pentadienyl anion, because of its slow-down reorientation to the equilibrium state (inheritance of orientation of *unsymmetrical* parent molecules). Gradual shifting of the electrochemical process away from the electrode into the bulk solution resulted in a progressive decrease in the anomaly, until its complete vanishing [8]. This allowed to theoretically estimate the viscosity of the SVL as a function of the distance from the electrode [9]. A kinetic analysis of the process using the Frenkel's microscopic theory of viscosity [10,11] lead to the conclusion that the SVL is more than 10^4 – 10^6 times as viscous as the bulk solution [9]. The formation of the SVL was explained [8,9] by the *structuring* of the highly polarized DMSO in the *strong electric field* of the electrical double layer (EDL).

Results of *direct* viscometric measurements in thin microchannels, across which a high voltage was applied, provide an argument in favor of such an explanation. First, Andrade and Dodd (channel height of 200 μm , gold electrodes in contact with liquid) [12] and then Ostapenko (channel height of 700 μm , with or without direct contact between the electrodes and the liquid) [13] reported an increase in the measured viscosity for a number of liquids under the influence of an electric field. The increase in viscosity under the influence of an electrical field called *electro viscous effect* (EVE) was up to $C = \eta_e/\eta \approx 2$ for the highest field strength applied in the order of 10^6 V/m; η and η_e are the dynamic viscosities of the liquid before and after applying the electric field, respectively. Somewhat smaller C -values were found in the experiments carried out *without contact* between one of electrodes and the liquid [13]. Occurrence of the EVE *also for organic liquids* is supported recently by experimental results by Luo and coworkers [14].

Developing the idea described in Ref. [15], we present here electrochemical atomic force microscope (EC-AFM) measurements for investigating the EVE in the electric double layer close to an electrode. Such a technique allows measuring in liquids, including *aqueous electrolytes*, strongly nanoconfined between a flat sample and an approaching tip, at electric field strengths up to 10^8 – 10^9 V/m. First results of investigations of the pre-electrode viscosity are presented later.

2. Experimental section

The force measurements were carried out on an atomic force microscope (AFM) (Nanowizard, JPK Instruments AG, Berlin, Germany). Two types of cantilevers were used. In experiment (A), we used a V-shaped silicon nitride cantilever (NanoProbe, Veeco Instruments, Santa Barbara, CA) with spring constant $k_c = 0.26$ N/m and tip radius $R = 220$ nm; in experiment (B), we used a silicon cantilever (Olympus) with $k_c = 1.1$ N/m and $R = 16$ nm. The spring constants of the cantilevers were measured by the thermal noise method [16,17]. The radii of the tips were determined from scanning electron microscopy (SEM) images (LEO 1530 Gemini, Zeiss-LEO GmbH, Oberkochen, Germany).

The EC-AFM-cell was developed and built in house. The electrical diagram is shown in Fig. 1. The cell consisted of a PTFE base and a ring-shaped cover with a built in Au-disc sample (area $S = 1.54$ cm²). The cantilever used in (A) was gold coated on the

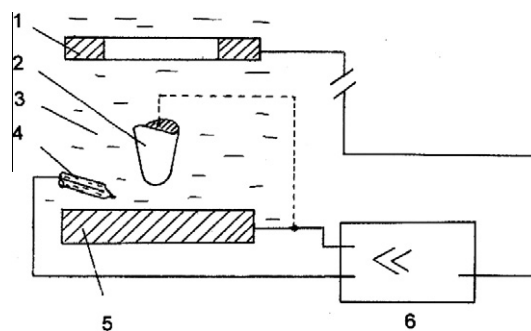


Fig. 1. Scheme of the experimental setup: (1) auxiliary electrode (AE); (2) cantilever tip; (3) aqueous electrolyte; (4) reference electrode (RE); (5) sample; (6) potentiostat.

tip and on the back side by sputtering (*symmetrical* sample-tip system, 4-electrode EC-AFM-cell). Both sample and tip could be used as working electrodes (WEs) with a separate potential control by a bi-potentiostat, or they could be short-circuited and used as equipotential WE (see Fig. 1). In experiment (B), the tip of the cantilever was not gold coated (*unsymmetrical* sample-tip system, 3-electrode EC-AFM-cell), and only the sample acted as WE. The auxiliary electrode (AE) was a 1-mm-thick gold wire. The reference electrode (RE) was a Ag/AgCl electrode (Flexible Dri-RefTM, WPI Germany GmbH). We used a scanning potentiostat (Model 362, EG&G, Princeton Applied Research, USA). The potentials in this work are given vs. the saturated calomel electrode (SCE) or in some cases vs. potential of zero charge (pzc). They are called E and E^z , respectively.

The electrodes (sample and cantilever tip) were made by deposition of a gold film. Polished single crystal silicon was used as sample substrate. Surfaces were first plasma cleaned at medium power (30 W) for 60 s (PDC-002, Harrick Scientific Inc., Pleasantville, NY). Then, they were coated with 5 nm chromium (for promoting adhesion) and 60 nm gold by means of thermal evaporation. Process parameters were the following: deposition rate of 0.2 nm/s and pressure of 2×10^{-5} mbar (MED-20, BAL-TEC AG, Balzers, Liechtenstein). The *rms* roughness of the gold electrodes was always below 2 nm, as measured by atomic force microscopy in contact mode over areas of 2×2 μm^2 . Just prior to the measurement, the cantilever, the cantilever holder, and the sample were cleaned in argon plasma for 60 s.

Unlike in Refs. [2,3,18], we did not coat the gold electrodes by alkane thiol SAMs for two reasons. Firstly, their nano-texture could change the structure of the water layer close to them, and secondly, it narrows the range of potentials applicable to the surfaces because of the desorption of SAM-molecules depending on the potential of the electrode in the both anodic and (primarily) cathodic regions [19].

Two aqueous electrolyte solutions were used and prepared from analytical grade NaF in Milli-Q water (resistivity of 18.2 M Ω cm⁻¹) purified by a commercial system (Milli-Q Gradient, Millipore Corp., Billerica, MA). NaF was chosen because there is no specific adsorption of the two ions on the gold surface [20,21], even of different crystallographic structures including the poly-crystalline gold surfaces we are using. Further, for NaF, anion and cation are of similar size, so that we can reduce additional water structuring effects by electrolyte. Prior to each experiment, argon was bubbled through the electrolyte solution for 20 min to purge the solution from air; then, the cell was filled with the solution. During the filling and the measurements, the cell was flooded with argon in order to prevent absorption of air oxygen into the liquid.

In fact, there are several experimental difficulties for working with clean gold surfaces. We took special measures to prevent a possible contamination/oxidation. Even if we cannot rule out com-

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