A Novel Approach for Direct Measurement of the Thickness of the Liquid-like Layer at the Ice/Solid Interface

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Received: December 10, 2003; In Final Form: April 27, 2004

A device allowing direct optical measurement of the displacement was employed to measure the thickness of the liquid-like layer. The data were correlated with calculations of the thickness based on admittance data of the quartz crystal microbalance, measured simultaneously. Agreement between the two independent measurements lends strong support for the validity of the models assumed in our calculations. The approach developed here allows the direct measurement of the thickness of the LLL in the range of a few tens up to few hundreds of nanometers.

Introduction

Liquid-like layers (LLL) exist on the surface of some solid substances in contact with their vapors or with foreign substrates, below the melting point of these substances.[1−5] A central problem in the understanding of this phenomenon is the determination of the thickness of the LLL. The list of experimental methods employed for studying the LLL on ice and frozen electrolytes is long: ellipsometry,[6] photoelectron spectroscopy,[7] magnetic resonance,[8] infrared study,[9,10] wire regelation in ice,[3] observation of movement of ice along the quartz surface,[11−13] the tip of an atomic force microscope along an ice surface,[14] or flow in a LLL between ice and solid polymer.[15] In our recent publications,[16,17] we showed that the quartz crystal microbalance (QCM) can also be successfully employed to study this phenomenon.

In all cases discussed so far, the thickness of the LLL was calculated indirectly from experimental data of other properties of the LLL, making some assumptions or employing suitable models. For example, in our recent work[17] we studied the LLL employing the QCM. What was measured directly was the admittance of the QCM: its resonance frequency and the width of resonance. The calculations of the thickness of the LLL were made on theoretical grounds—models that describe the behavior of the resonator under corresponding conditions.[17] Such an approach is typical to all experimental studies of the LLL mentioned above. As such, a natural question always presents itself: how adequate is the model in describing the real situation?

In the present communication we describe an attempt at direct measurement of the thickness of the LLL. We compare these measurements with calculations of the thickness based on QCM admittance data measured simultaneously, based on the models presented in our previous work.[17]

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Experimental Section

The experimental arrangement is shown in Figure 1. It is similar to the construction described in our previous work.[16] We again use a quartz crystal resonator disk (AT-cut type, with a fundamental frequency of about 6 MHz, diameter 15 mm, purchased from Intellemetrics). Both surfaces are coated with 0.1 μm gold films. This resonator is gently cradled between two Viton O-rings, to prevent leakage (marked in Figure 1 as **QCM** and **2**, respectively). The upper Teflon cylindrical part (**1**) is filled with water (or other studied solution) up to 5−10 mm height. The scheme does not show details, which allow preparation and supply of liquid to part **1**, which is kept during the experiment under helium at ambient pressure. The lower part consists of three elements: a cylinder (**3**), the sensing tip of the optical displacement sensor (**OT**), and its holder (**4**). Figure 1 is a schematic presentation and does not show many details of the setup, such as electrical connectors to the resonator (**QCM**), the system of the precise adjusting of optical tip, temperature probe, etc. All the setup was placed in a thermostat and the temperature was controlled to within ±0.05° of the stated values. Figure 1 is not drawn to scale, since the thickness of the LLL is orders of magnitude smaller than any dimensions of the other parts, shown in Figure 1. We suggest that the LLL exists at all surfaces where ice or frozen electrolyte makes contact with other substances, be it gold on the surface of the QCM, Viton O-rings or Teflon cylinder **1**. Of course, the thickness of the LLL on these contacts could be different.

The fiber-optic displacement sensor used in this work is Model D20, PHILTEC, Inc, with a measuring range 10 and 60 μm and sensitivity of 87 mV/μm. Its principle of operation is based on measuring interference of light of a laser emission diode (880 nm) reflected from the surface. The best resolution in our experimental setup was about 0.01 μm. The distance between the lower surface of the **QCM** and the **OT** was usually in the range 25 and 35 μm.

The experiment was conducted as follows. The liquid was first frozen by lowering the temperature to −10 or −12 °C. At that temperature the resonance of the QCM becomes undetectable, as described in our previous publication.[16] Next, the

10.1021/jp031299l CCC: $27.50
Published on Web 05/28/2004

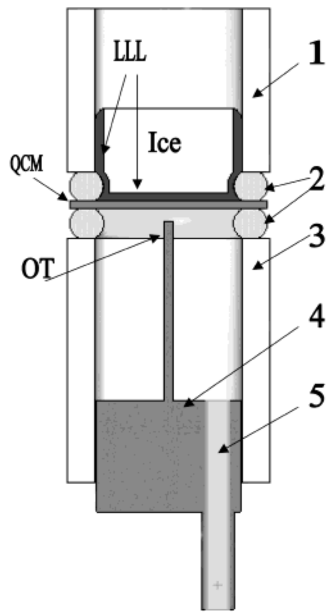

Figure 1. Schematic representation of the cell. **1** and **3**: Teflon cylinders; **2**: Viton O-rings: **4**: Holder of the optical displacement sensor OT; **5**: tube to apply pressure. QCM, quartz crystal resonator plate; LLL, liquid-like layer between block of ice and other parts of the cell. The parts in this figure, including the LLL thickness, are not drawn to scale.

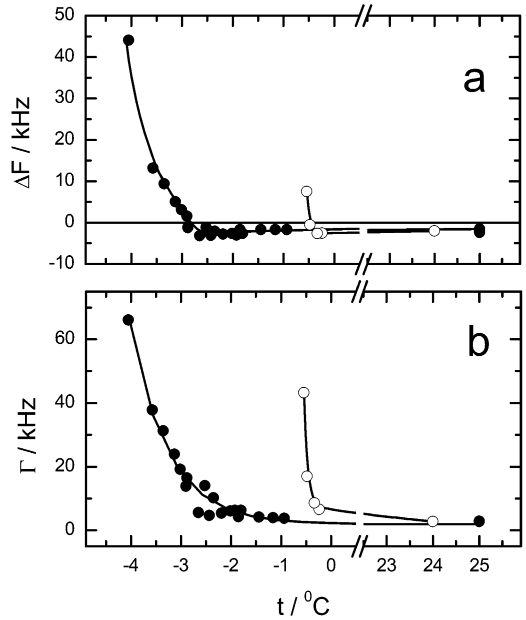

Figure 2. Dependences of the frequency shift, ΔF (a) and of the width of resonance, Γ (b) on temperature, obtained for LLL at the surface of frozen 10 mM aqueous solutions of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ (closed circles) and for LLL at the surface of ice (open circles).

temperature was increased to a value where we are going to study the system with the LLL. Restoring a steady resonance, stable in time, indicating equilibrium in the system LLL, ice, and gold electrode of the QCM, takes about an hour. After measuring the stable admittance of the resonator, pressure was applied through tube **5** and the readings of the optical displacement sensor and the QCM admittance were taken simultaneously. Admittance parameters were measured with E5100A Network Analyzer (Agilent Technologies).

In this study we used pure water or an aqueous solution of 10 mM $K_4Fe(CN)_6$ + 10 mM $K_3Fe(CN)_6$. Figure 2 shows the dependence of the resonance frequency, ΔF,[21] and the width of resonance, Γ, on temperature. The shape of both curves shown is similar to those as obtained for 0.1 M aqueous solutions of $HClO_4$ and Na_2SO_4, studied in refs 16,17. At some characteristic temperature, different for different systems, ΔF takes positive value. This is indicative of a major change in the properties of the fluid in the LLL—at higher temperatures it behaves as a usual viscous liquid, while at lower temperatures it exhibits viscoelastic properties, as discussed in our previous publication.[17]

The ferro-/ferricyanide system was chosen because the exchange current of this redox-couple is high,[18] and a constant potential is maintained at the gold/solution interface. This is very important, because the properties of the LLL depend on electrode potential as shown earlier.[16] The dependence shown in Figure 2 for ferro-/ferricyanide is reproducible. In contrast, the pure ice/LLL/gold system exhibits less reproducibility, because there is no way to control the electrode potential across the interface, and very small quantities of impurities could drastically change the nature of the metal surface. As a result, the characteristic temperature where $\Delta F = 0$ varies in different experiments from -0.5 °C to -2 °C. It should be noted that freezing at low temperatures is not a well-controlled process and accumulation of impurities at the interfaces could depend on the rate and other peculiarities of the freezing process. In the presence of electrolyte the freezing process is more stable and reproducible. The above reasoning may explain the broad range of literature data on the thickness of the LLL and its dependence on temperature. However, the purpose of the present communication is to demonstrate a method of direct measurements of the thickness of the LLL, and the reproducibility of the system is of lesser importance here.

Results and Discussion

Figure 3 presents data obtained with aqueous solution of ferro-/ferricyanide at -1.9 °C. Similar data were observed when working with pure water. When at some time t_s pressure (Figure 3a) was applied, the distance H_{OPT}, measured between **QCM** and **OT**, the optical sensor, increased (Figure 3e). At the same time the resonance frequency, ΔF, and the width of resonance, Γ, of the QCM also increase (Figure 3b and 3c, respectively). Decreasing the pressure to its original value (at time t_r) led to the reversal of all three measured parameters, ΔF, Γ, and H_{OPT}. Figure 3d shows the thickness, H_{QCM}, of the LLL, calculated from data in Figure 3b and 3c, on the basis of the model described earlier.[17] The value of H_{QCM} decreases sharply when pressure is applied and increases when it is relaxed. The main feature of the curves in Figure 3 is the sharp change at the initial moment, when pressure was changed, and the slow subsequent relaxation.

To understand this behavior it is necessary to take into account that parts **1**, **3**, and **4** (Figure 1) are rigidly fixed in their positions. Thus, when pressure is applied through tube **5**, only the quartz plate **QCM** can change its position: the O-rings (**2**) are the softest parts in the system. They are responding as springs—the upper one is compressed, and the lower one is stretched. Figure 4a shows how these "springs" respond. When the upper surface of the QCM-disk is in contact with a liquid phase, the dependence of the distance between the **OT** and **QCM** is proportional to the applied pressure (Lines 1 and 2). The lower the temperature, the larger the pressure that has to be applied to attain the same displacement—the O-rings became slightly more rigid at lower temperature. The latter is seen when comparing the slopes of Lines 1 and 2, obtained at different

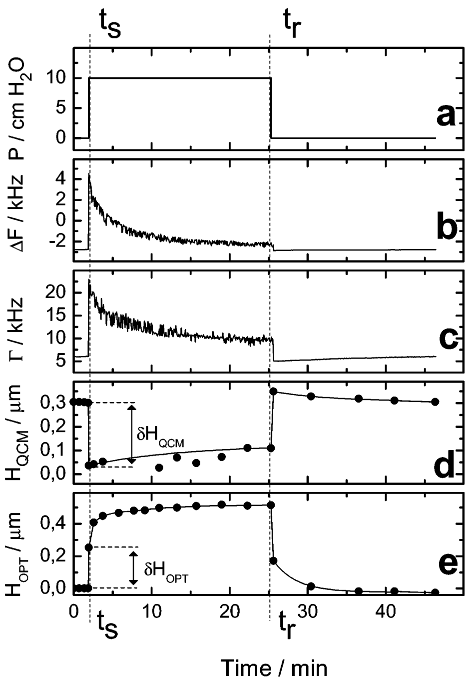

Figure 3. Dependences on time of applied pressure (a); frequency shift, ΔF (b); and width of resonance, Γ (c); the calculated thickness of the LLL, H_{QCM} (d); and readings of optical displacement device, H_{OPT} (e). t_s and t_r represent times when pressure was applied and relaxed, respectively. The data presented here were obtained with ferro-/ferricyanide at −1.9 °C.

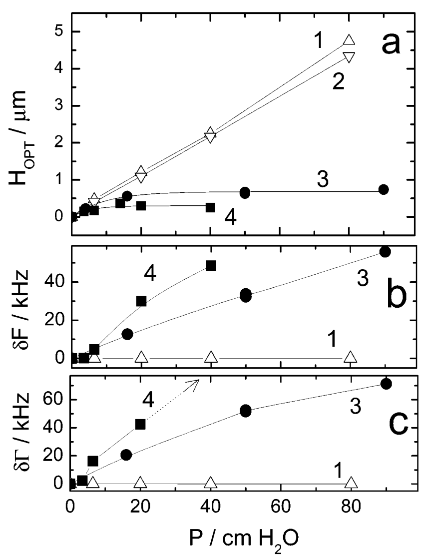

Figure 4. Dependences on pressure of (a) displacement measured by optical sensor, H_{OPT}; (b) changes of the frequency shift, δF; and (c) changes of the width of resonance, $\delta\Gamma$. **1** and **2**: data obtained with a quartz resonator in contact with water at room temperature and at −1.9 °C (supercooled), respectively. **3** and **4**: data obtained with LLL in contact with frozen electrolyte and with ice, respectively.

temperatures. However, curves 3 and 4 show quite different behavior. They were obtained in the presence of a LLL between the QCM and the solid phase of ice or frozen electrolyte. Such behavior indicates that the QCM plate responds as though it were set against a rigid wall. The ice block cannot be shifted upward, because of large contact area with the walls of cylinder **1**: the height of the ice block and its diameter were about 1 cm. The upper O-ring proves to be the most compliant part of the system. The fluid of the LLL between ice and quartz plate is squeezed out into the region between ice and the upper Viton O-ring. This relatively soft O-ring allows the changes of the configuration of the volume occupied by the fluid of the LLL. If this O-ring would be noncompressible, one could observe neither changes of H_{OPT} nor thinning of the LLL, as manifested in the decrease of calculated value of H_{QCM}.

Figures 4b and 4c show that the applied pressure does not change the resonance parameters when above the QCM there is liquid (curves 1). However, in the case of the LLL this pressure produces remarkable changes of both width of resonance and its fundamental frequency.[22] Note that upon application of a pressure step, both ΔF and Γ change abruptly and then start to relax toward their initial values, as shown in Figure 3b and 3c. The points used to build curves 3 and 4 of Figure 4 were the first points obtained after the pressure had been applied.

Two different processes determine the behavior of the system following application of pressure. One is melting of ice in contact with the QCM. Applying pressure we decreased the thickness of the LLL below its equilibrium value, characteristic for the temperature of the experiment. Following this perturbation, the system tries to return to equilibrium. The pressure difference below and above the ice induces another process—flow of the fluid of all the LLLs along the contacts of ice with the QCM surface, O-ring, and walls of the Teflon container. Evidently, fluid pressed out to the "free" upper surface of ice block is frozen there.

The resistance of the gap where the LLL flows is large, and there is always an additional pressure in the gap, larger than above the ice but smaller than under the QCM. Hence, when the pressure applied to the lower part of the system is relaxed (t_r in Figure 3), the QCM plate "jumps" down, again creating a nonequilibrium LLL, but thicker than characteristic for the given temperature. This generates a corresponding increase of the thickness of the LLL, making it thicker than at the beginning of the experiment (Figure 3d).

The processes taking place following changes in the applied pressure can be explained qualitatively, but quantitative interpretation could be extremely complex. Moreover, this behavior depends on minor details of the construction of the cell shown in Figure 1, and is of little importance for understanding the properties of the LLL per se. Hence, we are going to consider below only data obtained less than 3 s after the pressure has been changed.

The fact that curves 3 and 4 in Figure 4a reach a plateau at some pressure proves the existence of a LLL, even without taking into account the simultaneously measured response of the QCM. At the same time, the corresponding curves in Figures 4b and 4c increase monotonically. This increase of resonance parameters, when recalculated as changes of H_{QCM}, leads to changes of only a few tens of nanometers, which cannot be seen on the scale used in Figure 4a.

Figure 5 summarizes the data obtained in different experiments, taking into account the initial changes of δH_{OPT} and δH_{QCM}, as shown in Figure 3d and 3e. It includes data for water and a frozen aqueous solution of 10 mM $K_4Fe(CN)_6$ + 10 mM $K_3Fe(CN)_6$, and data obtained both by increasing and decreasing pressure. Line 1 is drawn as a reference, for the case, where $\delta H_{OPT} = \delta H_{QCM}$. For changes less than 300 nm the experimental points agree well with this line. *This is the central point of the present work*. It shows that the response of the optical displacement device, which directly measures the changes of distance, coincides with the changes of the thickness of the LLL, calculated from the response of the QCM. This supports the models used to calculate the LLL thickness from the experi-

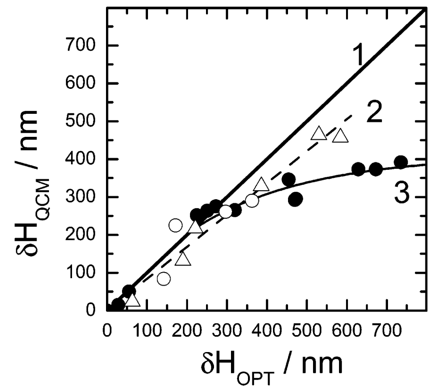

Figure 5. Plot of the change of distance calculated from the parameters of resonance, δH_{QCM}, as a function of the change of displacement measured by the optical sensor, δH_{OPT}. Circles represent measurements taken immediately after pressure was increased (open circles: ice at −0.24 °C; closed circles: frozen electrolyte at −1.9 °C). Triangles represent data obtained for frozen electrolyte (−1.9 °C) immediately after the pressure was relaxed.

mental data on the QCM response, despite some simplifying assumptions underlying these theoretical models.[17]

Let us consider the deviations of the experimental points from straight line 1 at $\delta H_{OPT} > 300$ nm. The circles were obtained when a relatively high pressure was applied, enough to compress the LLL from about 300 nm down to 20−30 nm or even to "collapse" it to the point that the resonance of the QCM could no longer be observed. The thickness of the LLL was changed by 1 order of magnitude or more, causing a large perturbation in equilibrium conditions. The rate of recovery of the LLL to its equilibrium state in this case is high and calls for rapid measuring of the resonance. However, the devices used in our experiment allowed us to obtain resonance data only every 3 s. Faster measurements would probably shift the experimental points closer to Line 1. When the pressure was decreased and the LLL thickness was increased by 300−400 nm from its initial value of about 100 nm, the relative change of thickness was much less than in the previous case. Hence, the corresponding points in the Figure 4 (open triangles at $\delta H_{opt} > 400$ nm) lay closer to Line 1.

Conclusion

In the book "Ice Physics", published in 1974, P. V. Hobbs[2] wrote (page 397) that: "The presence of a "liquid-like" layer on ice has not been detected by *direct* experimental methods. However, this is not surprising if the layer is only a few tens of angstroms thick and has properties intermediate between those of water and ice." Now it is evident that in some cases the thickness of the LLL could be much larger. In these cases, the technique described above could be suitable. We emphasize again that the fact that the readings of the optical displacement device reaches a plateau at some pressure (Figure 4a) proves the existence of the LLL. The agreement shown in Figure 5 between the thickness calculated from measurements of the parameters of the resonance and from the optical displacement device shows (a) that the models employed in the calculation are valid and (b) that the method proposed here could be used to measure the thickness of the LLL directly. It is evident that the accuracy of measurements could be improved by employing displacement devices of better quality, such as used in modern STM or AFM apparatus, allowing measurement of a much smaller thickness of the LLL at higher resolution.

Accurate and highly sensitive measurement of the thickness of liquid-like layers at different interfaces is of paramount importance for the understanding of this phenomenon, which has such long history, starting from works of Faraday[19] and Thompson.[20] We hope that the work presented here will encourage other experimentalists to search for additional, perhaps more accurate, methods for direct measurement of this parameter.

Acknowledgment. Financial support for this work by the Israel Science Foundation (Grant No. 2/01) is gratefully acknowledged.

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(21) Note that ΔF is the difference between the fundamental frequency of the resonator under given conditions and that of the unloaded resonator, i.e., a resonator having no contact with any viscous medium.
(22) At a pressure of 40 cm H_2O (for a LLL in contact with ice) the corresponding point for $\delta\Gamma$ (curve 4 in Figure 4c) is marked by an arrow. In this case, the LLL was so thin that vibrations of the resonator were impeded to the point where it become difficult to measure the resonance parameters and all we can state is that $\delta\Gamma$ is larger than 70 kHz.