The Quartz Crystal Microbalance as a Tool for the Study of a "Liquidlike Layer" at the Ice/Metal Interface

Vladimir Tsionsky,* Leonid Daikhin, Dmitrij Zagidulin,[†] Michael Urbakh, and Eliezer Gileadi

School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel-Aviv University, Ramat-Aviv 69978, Israel

The admittance of the quartz crystal microbalance (QCM) was used to study properties of a liquidlike layer (LLL) at the gold/frozen electrolyte interface. It was shown that in a certain range of temperature, below the melting point, the resonance of the QCM is readily detectable suggesting the presence of a LLL. Treatment of the experimental data within the framework of the models proposed here allowed us to conclude that, depending on the temperature, the LLL exists in two states: at temperatures above −4 °C, it can be considered as a viscous liquid, while at lower temperatures down to −7 °C, it behaves as a viscoelastic medium. Data handling enabled us to evaluate the temperature dependence of the thickness of the LLL, which increases from a few tens of nanometers at −7 °C up to ca. 200 nm at −1 °C in the systems studied here (aqueous solutions of 0.1 M Na_2SO_4 and 0.1 M $HClO_4$).

Introduction

Liquidlike layers (LLL) can exist on the surface of ice below the melting point.[1−4] One of the main characteristics of the LLL is the dependence of its average thickness on temperature. The experimental results available show a wide range of thickness. This is caused by the difference of the physical and chemical properties of systems studied, ice in contact with water vapor, with metals, with quartz surfaces of different roughness, etc. Another source of such diversity may be the different experimental methods employed to estimate the thickness, which reflect somewhat different properties of the system.

In the course of the long history of studying the LLL, various experimental methods have been employed. Among them are "dynamic" measurements[4−9] that are sensitive to the hydrodynamic properties of the layer (e.g., viscosity). On the other hand, measurements by ellipsometry,[10] photoelectron spectroscopy,[11] and nuclear magnetic resonance[12] are determined by other properties of the LLL. As a result, the hydrodynamic thickness of the layer can differ from the thickness relevant for its spectroscopic response.[13]

In a recent publication,[14] we studied the LLL employing, for the first time, the quartz crystal microbalance (QCM) technique. This technique belongs to the group of dynamic measurements.

The QCM is a quartz resonator plate covered on both sides with metal electrodes. There are two well-known landmarks in the development of the QCM as a powerful tool for the study of interfacial phenomena and its use as the active element of sensors for various applications.

First was the introduction of the QCM in 1959 by Sauerbrey,[15] which represented a major step in our ability to weigh matter rigidly attached to the vibrating surface of the QCM in the gas phase with a sensitivity of up to 1−2 ng/cm². Until then, routine measurements allowed an accuracy of 0.1 mg, and highly

sensitive measurements could be made with an accuracy limit of 0.3 μg under carefully controlled experimental conditions (cf. ref 16).

The second important step was taken in 1981 by Nomura et al.,[17] who showed that the QCM could also be used in liquids, and by Bruckenstein,[18] who first used the QCM in electrochemistry. Now the literature devoted to applications of the QCM and its electrochemical analogue, the EQCM, is wide and diverse (cf. refs 19−21). It includes both experimental and theoretical studies. It has long been recognized that the response of the QCM depends not only on the mass loading and the viscosity and density of the fluid in contact with it but also on the roughness of the surface, its morphology, and the characteristic interfacial properties of the fluid.

In our recent publication,[14] it was shown that the QCM in contact with ice or with frozen electrolyte at temperatures well below the melting point shows detectable resonance. It was also demonstrated that the parameters of the resonance depend strongly on temperature and, in the case of electrolyte, on the potential applied across the interface. In the cited publication, two main points were emphasized: (i) the QCM response proves the existence of the "liquidlike" layer (LLL), and (ii) the QCM could be used as a tool to study the properties of this layer.

It should be noted that until now most of experimental and theoretical studies have been performed for the case in which a vibrating resonator, with or without a film, was immersed in an infinite viscous medium.

In the case of the LLL, one has quite a different situation: a thin layer of liquid (or quasi-liquid) is confined between the vibrating surface of the resonator and a fixed motionless surface of solid ice or frozen electrolyte. To explore the results of the QCM measurements in such confined geometry, one has to establish relationships between the measured shift and width of the resonance and the properties of the confined layer at the interfaces. A similar configuration was studied theoretically in ref 22 in which the response of the QCM in contact with a liquid layer confined between an ideally flat vibrating surface and the slightly rough immobile surface was calculated. Below, we shall

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* Corresponding author. E-mail: tsionsky@post.tau.ac.il.
† Permanent address: Institute of Chemistry, Gostauto 9, Vilnius LT-2600, Lithuania.
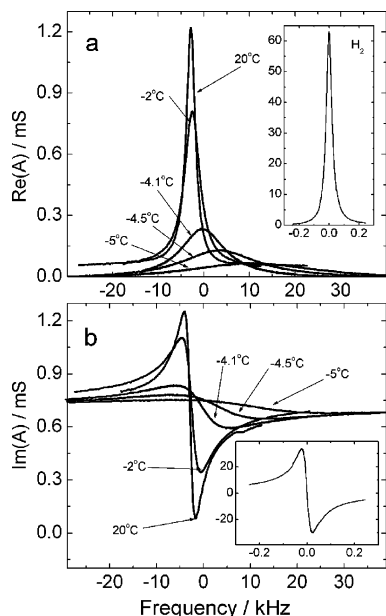
Figure 1. Dependence of the (a) real and (b) imaginary parts of the admittance of the quartz-crystal resonator on frequency in hydrogen atmosphere (insets) and in 0.1 M Na_2SO_4 aqueous solution at different temperatures as indicated.

Figure 2. Dependences of (a) the frequency shift, Δf, and (b) the width of resonance, Γ, on temperature obtained in 0.1 M aqueous solutions of (○) $HClO_4$ and (●) Na_2SO_4. Dashed lines designated 3 indicate the QCM response in supercooled solutions.

explain the main features of the response of the QCM in contact with the LLL, employing a more detailed model that takes into account the roughness of the vibrating surface. This roughness will be characterized by the same parameters as those in our previous studies of the response of the QCM immersed in an infinite liquid.

Experimental Methods

Measurements were conducted with an AT-cut 6 MHz quartz crystal resonator, which was attached to the bottom of the cell. The crystal, 1.5 cm diameter, purchased from Intellmetrics, was cradled between Viton O-rings to prevent leakage of the liquid. It was coated with a thin layer of titanium under the gold coating to improve adherence. The electrode in contact with the liquid in the cell had an exposed diameter of about 1.2 cm, determined by the O-ring. The height of the liquid above the crystal was about 0.5 cm. A container with the cell was purged with helium and placed in the thermostat. The temperature was controlled to within ±0.05 °C and measured with microresistance thermometers.

A Hewlett-Packard network analyzer type 5100A was used both to induce vibrations and to measure the admittance spectrum of the QCM. One of the electrodes of the QCM, which was in contact with the solution, was grounded. Under all experimental conditions, the observed resonance was always the only resonance in vicinity of 6 MHz. The two parameters measured were the real and the imaginary parts of the admittance. Further details of the experimental procedure employed are given in our previous publication.[14]

Experimental Data

In Figure 1, we show an example of data on the real (Re(A)) and the imaginary (Im(A)) parts of the admittance of the QCM as a function of frequency at different temperatures. The response is characterized by two parameters, the frequency shift (Δf) and the width of the resonance (Γ). Δf is defined as the difference of frequencies corresponding to maxima of the plots of Re(A) vs frequency obtained in the systems studied and that

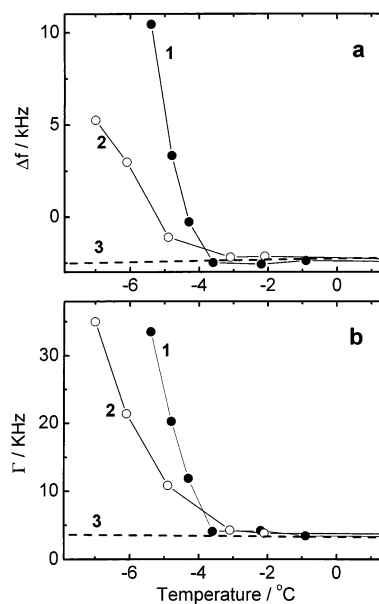observed under minimum loading. The fundamental frequency in the latter case was measured in hydrogen at 1 atm, in which the loss of energy due to the viscosity of the surrounding medium is negligible for any surface roughness, see ref 23. In other words, in Figure 1, the fundamental frequency observed in the gas phase is assigned a value of zero. The temperature dependence of admittance of the QCM in gas phase is a few orders less than that in studied systems and could be neglected. The second parameter, Γ, is defined as a difference between frequencies corresponding to the minimum and the maximum on the plot of Im(A) vs frequency. Because the admittance in hydrogen is very high and Γ is very small compared to the values of these parameters in the liquid, they are presented as insets in Figure 1. It is seen that below the melting point, where the bulk of the fluid in contact with the QCM is solid, the quartz resonator still vibrates and shows well-detectable resonance.

In Figure 1a, we note that the admittance decreases with decreasing temperature and the width increases. This is to be expected because the viscosity and density both increase. However, the resonance frequency increases with decreasing temperature in the same range, contrary to the behavior usually observed when the QCM is in contact with an infinite liquid. Moreover, it is noted that below a certain temperature the resonance frequency is higher than that in hydrogen at 1 atm. The last two observations cannot be explained by any model that takes into account only changes of viscosity and density of the fluid with temperature. This is characteristic of the existence of a LLL in contact with the vibrating surface of the QCM and can be interpreted by taking into account the viscoelastic properties of this layer, as will be discussed herein.

Close examination of Figure 1b shows that the width of the resonance, Γ, increases sharply with decreasing temperature. This increase is very large compared to the changes observed for supercooled liquid water in the same range of temperatures.

Lines 1 and 2 in Figure 2 show the temperature dependences of Δf and Γ in 0.1 M solutions of Na_2SO_4 and $HClO_4$, respectively. Line 3 shows the data observed for supercooled liquid in the same range of temperature. It should be noted here

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that for low electrolyte concentrations, the data obtained in supercooled solutions and in pure water coincide.

Both the resonance frequency and the width of the resonance increase sharply below about −4 °C, when the QCM is in contact with a LLL (lines 1 and 2). In contrast, these parameters seem to be constant in supercooled liquid in the same range of temperature (line 3). A closer look reveals that the frequency shown by line 3 does decrease somewhat with decreasing temperature, and the width increases, but these changes are negligible compared to those obtained in the presence of the LLL and can barely be noticed on the scale used in Figure 2.

It should be recalled that the value of zero on the scale of frequency in Figure 2a corresponds to the resonance frequency in hydrogen at 1 atm, hence, that $\Delta f = 0$ corresponds to unloaded QCM. The observation of a *higher* resonance frequency when the QCM is in contact with the LLL at low temperatures is unique and will be discussed later.

State of Frozen Electrolyte

The choice of aqueous solutions of $HClO_4$ and Na_2SO_4 for our experiments was dictated by the following considerations. First, the specific adsorption of both SO_4^{2-} and ClO_4^- on gold is very small, at least at room temperature. Admittedly this does not ensure that the same applies for temperatures at or below the melting point of ice, but it can be expected that it will be smaller than that for other ions, Cl^-, for example, that are specifically adsorbed even at room temperatures.[24] We also assumed that these anions are not adsorbed at the surface of ice and of frozen electrolyte, although we do not have experimental evidence to support this assumption. Second, we chose these two electrolytes because of the large difference in their phase diagrams. Thus, the eutectic temperature for $HClO_4$ is −60 °C, while that for Na_2SO_4 is −1.2 °C.[25] It follows that in the range of temperature of −2 to −7 °C used in our present experiments a solution of Na_2SO_4 is a solid, consisting of ice and crystals of $Na_2SO_4·10H_2O$, while in a solution of $HClO_4$ there is a mixture of solid and liquid phases, if the system is at equilibrium, and the ratio of volumes of liquid to solid changes from about 20% at −2 °C to 7% at −7 °C.

It may be argued that in 0.1 M $HClO_4$, the response of the QCM could be a result of the interaction of the vibrating surface with a mixture of liquid and solid phases and does not necessarily prove the existence of a true LLL. However, the fact that in the temperature range of −2 to −7 °C the response of the QCM in contact with a solution of $HClO_4$ is very similar to that in contact with a solution of Na_2SO_4, where there should be no liquid phase according to the equilibrium phase diagram, indicates that it is the interaction of the LLL with the surface of the QCM that is observed in both cases.

The way in which the experiments were performed: the liquid was first supercooled carefully to a temperature of −12 to −15 °C and then frozen suddenly. Such fast freezing yields a nonequilibrium solid state. Hence $HClO_4$ is trapped more or less homogeneously in the frozen phase. It should be noted that at this stage of the experiment, the QCM response disappears in both systems because the volume ratio of liquid to solid is equal or very close to zero. The QCM resumes vibrating only at a higher temperature of at least −7 °C and after a relatively long time of about 1 h, which is apparently needed to allow the formation of the LLL. This explains the fact that the results observed in the two electrolytes tested are similar. The responses of the QCM in both systems (which is very different from that
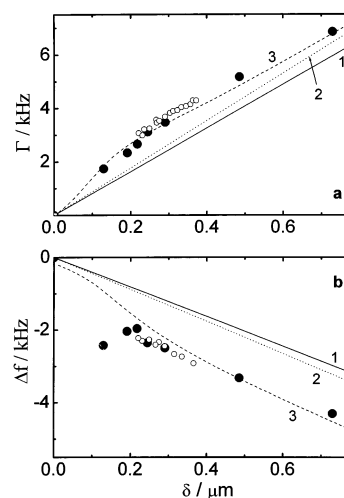

Figure 3. Dependences of (a) the width of resonance, Γ, and (b) the frequency shift, Δf, of the QCM immersed in (●) liquids of different densities and viscosities and (○) supercooled water at different temperatures. Lines designated 1 indicate expected responses of the QCM with ideally flat surface; lines designated 2 indicate expected responses of the QCM with surface having only slight roughness; lines designated 3 indicate expected responses of the QCM with the surface that has both slight and strong roughness.

observed in any liquid) support our claim that we are observing the effect of the LLL on the response of the QCM in both electrolytes.

Response of the QCM in Liquids

Consider the response of the QCM in different liquids, including supercooled water. In the next section, these results will be used as a reference point for the description of its response when in contact with the LLL. In Figure 3, we show the dependences of Δf and Γ on the properties of different liquids. Each liquid is characterized by a velocity decay length, $\delta = (\eta/(\pi f \rho))^{1/2}$, where ρ and η are the density and the viscosity of the liquid and f is the fundamental frequency of the QCM. Closed circles in Figure 3 represent data obtained in liquids having different values of ρ and η at 25 °C (see ref 26 for details). Open circles represent data obtained in water (including supercooled water) in the temperature range of −10 to +25 °C. It is seen that for given roughness the QCM response is determined mainly by the value δ. For a given value of this parameter, it is similar for supercooled water and for different liquids at temperatures above their melting points.

The theory describing the dependence of the response of an ideally flat QCM on the properties of the liquid in contact with it is well-known from the works of Kanazawa,[27,28] and its predictions are shown by lines 1 in Figure 3. Clearly, the experimental data shown here deviate significantly from this theory. Recently, we demonstrated[26] that surface roughness should be taken into account to fit experimental results to theory. The effect of roughness leads to increased contributions of dissipation and inertia to the QCM signal. However, as in the case of flat surfaces, the viscosity and density, expressed by the parameter δ, are the only properties of any liquid that determine the QCM signal at rough surfaces.

Analyzing the data obtained for the LLL, we use the model for the QCM response at rough surfaces that has proven itself useful for the QCM immersed in liquids. In a subsequent section, we point out briefly the main characteristics of this model. It is well-known that real surfaces have complex morphologies and can best be characterized as having multiscale roughness. An
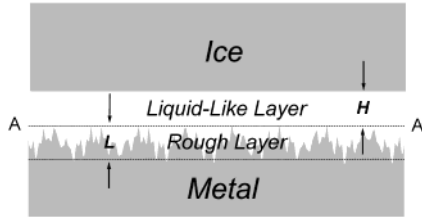
Figure 4. Schematic presentation of the LLL confined between a flat surface of ice and a rough surface of metal, see text.

approximate description of rough surfaces, which is based on a two-scale roughness model of the interfaces, one scale corresponding to *slight* roughness and another to the *strong* roughness, was proposed. Slight roughness is defined such that the deviations of an interface from some average reference plane are much smaller than the lateral characteristic length. For strong roughness, on the other hand, the "amplitude" and "period" of repetitions are of the same order of magnitude. The effect of slight roughness on the QCM signal has been considered within the perturbation theory, while the effect of strong roughness has been described within an approach based on the Brinkman equation for a liquid flow in the interfacial region. This combined approach allowed us to derive an analytic equation for the description of the QCM response in liquids, which could be employed to treat the experimental data obtained over a wide range of viscosities and densities of liquids. An example of such description is represented by curves 3 in Figure 3. Curves 1 are the QCM response expected for an ideally flat vibrating surface, and curves 2 describe the response expected for a surface with slight roughness. It should be noted that in the region of parameters corresponding to data obtained in water ($\delta = 0.2-0.4\ \mu$m) the contribution of slight roughness is relatively small and the deviation of the response from that calculated for an ideally flat surface can be associated mainly with strong roughness.

The Liquidlike Layer as a Viscous Medium

Figure 4 shows a schematic sketch of the system with the LLL located between a flat surface of ice and the rough surface of the vibrating resonator. H and L are the thickness of the part of the LLL that lies above the rough surface (above the line AA) and the thickness of strong roughness layer, respectively.

Comparison of the theory of the response of the QCM assuming a model of two-scale roughness with the experimental data obtained at room temperature [26] shows that the surface has strong roughness, that is, roughness with high local curvature, which may comprise pores, cavities, and the like. The sign of the local curvature of such surface elements is negative. As a result, the melting point of ice inside the rough surface layer may be lower than the bulk melting point (Thomson−Gibbs effect),[3] while the influence of slight roughness on the melting point can be neglected. Thus, it is not unreasonable to assume that the solution inside pores of strong roughness does not freeze at all temperatures used in these experiment. Thus, a change of the liquid layer thickness with temperature takes place mostly due to surface melting of ice above the rough region.

The model derived herein and the schematic representation of the surface shown in Figure 4 imply the following: (i) The influence of slight roughness on the surface melting of ice is negligible. Hence, the interface can be treated, in the context of the response of the QCM in contact with a LLL, as having only strong roughness. (ii) Water inside the intricate structure of the layer of strong roughness (having a thickness L as shown in Figure 4) has a lower melting point than bulk water and is

hence in the liquid phase in the range of temperatures studied here. We also assume that the surface of ice is ideally flat and the density and viscosity of the fluid are uniform everywhere between the ice and metal surface, including the rough layer. Under these assumptions, the equations of motion in the above confined region can be written in the following form:[29,30]

(a) The wave equation for shear waves in the quartz resonator is

$$-\omega^2 \rho_q u(z,\omega) = \mu_q \frac{d^2 u(z,\omega)}{dz^2} \tag{1}$$

where ρ_q and μ_q are the density and shear modulus of the quartz crystal and $u(z,t) = u(z,\omega)\exp(i\omega t)$ is the displacement in the quartz.

(b) The Brinkman equation for liquid motion in the rough surface layer is

$$i\omega\rho v(z,\omega) = \eta \frac{d^2}{dz^2} v(z,\omega) + \eta \xi_H^{-2}[V_0 - v(z,\omega)] \tag{2}$$

where ρ and η are the density and viscosity of the liquid, ξ_H is the characteristic length of the "porous" medium,[31] and V_0 and $v(z,\omega)$ are the amplitude of the velocity of the quartz surface and velocity, $v(z,t) = v(z,\omega)\exp(i\omega t)$, of the liquid, respectively.

(c) The equation for movement in the LLL is

$$i\omega\rho v_l(z,\omega) = \eta \frac{d^2 v_l(z,\omega)}{dz^2} \tag{3}$$

where $v_l(z,t) = v_l(z,\omega)\exp(i\omega t)$ is the velocity of liquid in the layer.

The boundary conditions for solving the above equations are derived from the requirement that continuity of the velocities and stresses must be satisfied at all interfaces. In addition, at the free resonator surface, the stress equals zero, and at the ice surface, the liquid velocity equals zero. One can solve these equations together with the above boundary conditions and find the velocity distributions. The response of the QCM is found from considerations of conservation of energy in the system.[30] The following expressions for the response of the QCM are obtained

$$\Delta f = -\frac{2f^2\rho}{(\mu_q\rho_q)^{1/2}} \operatorname{Re}\left(\frac{1}{q_0 g(H)} + \frac{L}{\xi_H^2 q_1^2} - \frac{1}{W_1}\frac{1}{\xi_H^2 q_1^2} \times \right.$$
$$\left. \left\{ \frac{2q_0}{q_1}[\cosh(q_1 L) - 1] + \xi_H^2\left(\frac{q_1^2}{g(H)} - q_0^2 g(H)\right)\sinh(q_1 L) \right\} \right) \tag{4}$$

$$\Gamma = -\frac{4f^2\rho}{(\mu_q\rho_q)^{1/2}} \operatorname{Im}\left(\frac{1}{q_0 g(H)} + \frac{L}{\xi_H^2 q_1^2} - \frac{1}{W_1}\frac{1}{\xi_H^2 q_1^2} \times \right.$$
$$\left. \left\{ \frac{2q_0}{q_1}[\cosh(q_1 L) - 1] + \xi_H^2\left(\frac{q_1^2}{g(H)} - q_0^2 g(H)\right)\sinh(q_1 L) \right\} \right) \tag{5}$$

Here $W_1 = q_0 \sinh(q_1 L) + q_1 g(H)\cosh(q_1 L)$, $q_0^2 = i\omega\rho/\eta$, $q_1^2 = q_0^2 + 1/\xi_H^2$, and $g(H) = \tan(q_0 H)$.

In the limit of thick LLL, the value of H tends to infinity, and eqs 4 and 5 are simplified to the equations describing the behavior of the QCM with only strong roughness in contact with semiinfinite liquid, see refs 29 and 30. In that case, the
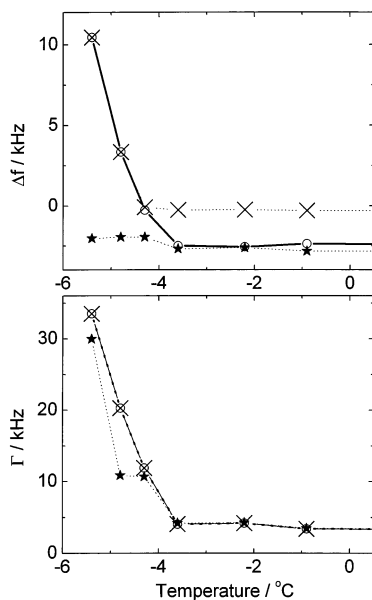
Figure 5. Comparison of experimentally obtained QCM responses in 0.1 M Na_2SO_4 aqueous solution ($\bigcirc$,—) with predictions of models: ($\bigstar$,···) liquidlike layer as a viscous medium ; ($\times$,···) liquidlike layer as a viscoelastic medium.

equations contain two adjustable parameters that characterized the surface roughness, ξ_H and L, which can be determined by measuring Γ and Δf in liquids of known values of ρ and η under experimental conditions in which the ice phase does not exist and hence $H = \infty$. Then, ξ_H and L can be used to fit the experimental data obtained at temperatures at which the LLL exists. Supposing that ρ and η are the same as those in supercooled water, there is only one adjustable parameter, H. Results of such fittings are shown by stars in Figure 5. Open circles show experimental data. It is evident that the preceding model allows us to explain the data obtained for temperatures higher than −4 °C only. At lower temperatures, the model prediction becomes inconsistent with the experiment.

At a temperature of about −4 to −5 °C, Δf changes its sign and becomes positive. Further decrease of temperature leads to a steep increase of both Δf and Γ. Thus, for temperatures below −5 °C, the resonance frequency exceeds its value for an unloaded quartz crystal (crystal immersed in hydrogen). This surprising behavior differs qualitatively from that observed for a QCM in contact with bulk liquids and, in particular, with supercooled solution. In the latter case, lowering the temperature leads to an increase of the viscosity, which causes an increase of dissipation and inertia in the liquid. Therefore the resonance frequency of a QCM immersed into a bulk liquid is always lower than that of an unloaded resonator. Positive values of Δf at low temperatures cannot be described in terms of viscosity and density.

We note that the increase of Δf is accompanied by the drastic increase of Γ. It reaches much higher values than one could observe even in liquids with very large viscosities, see Figure 3 and ref 26. If we fit different experimental data, it is possible to obtain a reasonable fit for Γ as shown in Figure 5b. However, for Δf, the discrepancy between the model and experiment at low temperatures is always very large. A model that takes into account only the viscous properties of a medium cannot explain this effect. The observed effect must hence have a different physical origin. A possible explanation could be based on the assumption that the LLL starts to exhibit viscoelastic properties when its thickness decreases. This effect has not been taken into consideration in the preceding model.

The Liquidlike Layer as a Viscoelastic Medium

To include the effect of elasticity, we consider the LLL as a viscoelastic medium confined between two flat interfaces. For simplicity, we neglect the roughness of the vibrating surface. The motion within the viscoelastic layer can be described by a wave equation with a shear modulus $\mu = \mu_1 + i\omega\eta$.[32] The imaginary part of μ describes the dissipation. The response of the QCM for such a configuration can be calculated following the procedure described in ref 22 for a viscous layer. The corresponding expressions for a viscoelastic layer can be written in the following form:

$$\Delta f = \frac{f^2\rho\delta}{\sqrt{\rho_q\mu_q}} \operatorname{Re}\left\{ i\sqrt{2\left(i+\frac{\mu_1}{\omega\eta}\right)} \coth\left[\frac{H}{\delta}\frac{i\sqrt{2}}{\sqrt{\left(i+\frac{\mu_1}{\omega\eta}\right)}}\right]\right\} \quad (6)$$

$$\Gamma = \frac{2f^2\rho\delta}{\sqrt{\rho_q\mu_q}} \operatorname{Im}\left\{ i\sqrt{2\left(i+\frac{\mu_1}{\omega\eta}\right)} \coth\left[\frac{H}{\delta}\frac{i\sqrt{2}}{\sqrt{\left(i+\frac{\mu_1}{\omega\eta}\right)}}\right]\right\} \quad (7)$$

Here μ_1 is the shear modulus of the LLL. Knowing the experimental values of Δf and Γ at a given temperature and assuming as above that ρ and η (and correspondingly $\delta = (\eta/(\pi f\rho))^{1/2}$) in the LLL are the same as those in supercooled solutions, one can calculate the parameters H and $\mu_1/(\omega\eta)$. The parameter $\omega\eta/\mu_1$ defines the loss tangent of the medium.[33] The results of calculations according eqs 6 and 7 are presented in Figure 5 by crosses. The results for the viscoelastic model differ qualitatively from those obtained for a viscous liquid layer. At low temperatures, the viscoelastic model allows us to explain the experimental data, but it does not fit the data above −4 °C.

It should be noted that the contribution of elasticity to the QCM signal far exceeds any possible effect of roughness. This justifies our approximation above, in which the roughness of the surface of the QCM was ignored for the purpose of the model to be applied at temperatures below −5 °C.

Summarizing our findings, we can conclude that the properties of the LLL change with decreasing temperature. For temperatures above −5 °C, it can be considered as a liquid phase, while for lower temperature, it exhibits elasticity, which is a characteristic property of solids. These changes of the LLL properties occur along with a decrease of its thickness and are most likely the result of this change of thickness. Deviations of properties of the LLL from those of liquids have been also observed in previous publications. For instance, studies of the basal plane of ice[34] have demonstrated that the LLL conserves a residual degree of order up to −1.8 °C.

In Figure 6, we show the thickness of the LLL, which was found from a comparison of theoretical models with the experimental data. In doing so, we used the viscoelastic model for temperatures below −5 °C and the viscous model for temperatures above −4 °C. We do not show results in the immediate vicinity of the transition temperature where a more complex model should be used. Open signs correspond to the viscous model of the LLL, and closed signs correspond to the viscoelastic model of the LLL. The main tendency is evident: as the temperature approaches the melting point, the thickness of the LLL increases. Moreover, thicknesses calculated using different models converge, yielding a monotonic dependence of thickness on temperature.

The authors of ref 9 tried to plot all currently available data regarding the thickness of the LLL in one figure. They found
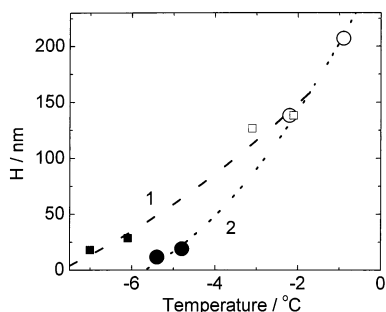
Figure 6. Thickness of the LLL calculated by fitting experimental data (solutions of 0.1 M (□) Na_2SO_4 or (○) $HClO_4$) with models of liquidlike layer as a viscous medium (open symbols) and liquidlike layer as a viscoelastic medium (filled symbols).

large differences between the values of the thickness of the LLL obtained by different techniques and in different systems (ice/vapor, ice/quartz, ice/metal, etc.). Our results fall within the range of existing data. We agree with the authors of ref 9 that care must be exercised in comparing thickness obtained by different techniques and for different systems.

Considering Figure 6, we note that the thickness of the LLL obtained for temperatures at which it exhibits viscoelastic properties depends significantly on the electrolyte. At −5 °C, for example, the thickness calculated is ca. 16 and 54 nm for 0.1 M solutions of Na_2SO_4 and $HClO_4$, respectively. Existing data are not sufficient to clarify the origin of this difference. In particular, experiments involving the metal/electrolyte interface can be considered reliable only if the interface is under potential control. Otherwise, the surface charge density and adsorption processes are not controlled and may not be reproducible. The latter is relevant to all work published so far in which the LLL at the metal/ice or metal/electrolyte interface has been studied.[4,35−37] The fact that the QCM response in the case of the LLL can depend strongly on the applied potential was shown in our previous publication.[14] The experimental data shown herein were obtained under open-circuit conditions, that is, the metal/solution interface was not polarized. Under these conditions, the potential established at the metal/electrolyte interface is close to 0.40 ± 0.02 V vs SHE. The dependence of the response of the QCM on potential will be discussed in a future publication. In the present paper, we only attempt to develop an initial understanding of the response of the QCM in the presence of the LLL as a function of temperature.

Fitting the experimental data to eqs 6 and 7, which describe the response of the viscoelastic LLL, we found not only the thickness of LLL (H) but also the parameter of the loss tangent, $\omega\eta/\mu_1$. The calculated values of the shear modulus, obtained from this parameter, lie in the range of $(1.0-2.5) \times 10^4$ Pa. These values are much smaller than those of polycrystalline ice, which is 3.4×10^9 Pa (see ref 38) but are commensurate with values found for organic polymer films, which lie in a wide range of 10^3-10^6 Pa.[32,39,40]

Conclusion

We have demonstrated for the first time that the properties of a liquidlike layer at a metal/frozen electrolyte interface can be studied by the QCM technique. It was observed that at temperatures well below the melting point of the electrolyte, in the range of −2 to −7 °C, the QCM immersed in a frozen electrolyte shows detectable resonance, the parameters of which depend strongly on temperature. This observation suggests the presence of a LLL at the solid/frozen electrolyte interface. A model was developed that establishes the relationships between

the measured shift in frequency and width of the resonance and the properties of the LLL confined between two solid surfaces. Treatment of the experimental data within the framework of the proposed model allowed us to conclude that for temperatures above −4 °C the layer can be considered as a viscous liquid with a viscosity close to that of supercooled water at the same temperature. Further decrease of temperature leads to a change of the state of the LLL that can be modeled as a viscoelastic medium, rather than a viscous liquid. Data handling enabled us to evaluate the temperature dependence of the thickness of the LLL. The results obtained demonstrate that applications of the QCM and its electrochemical equivalent, the EQCM, could open new and promising opportunities for studies of the LLL. In particular, an interaction of the LLL with surfaces can be readily modified in situ in electrochemical experiment where the potential, as well as the excess surface charge density and all kinds of adsorption, can be controlled. Further work in this direction is under way in our laboratory.

References and Notes

(1) Fletcher, N. H. *Philos. Mag.* **1968**, *18*, 1287.
(2) Petrenko, V. F.; Whitworth, R. W. *Physics of Ice*; Oxford University Press: New York, 1999.
(3) Dash, J. G.; Fu, H. Y.; Wettlaufer, J. S. *Rep. Prog. Phys.* **1995**, *58*, 115.
(4) Gilpin, R. R. *J. Colloid Interface Sci.* **1980**, *77*, 435.
(5) Churaev, N. V.; Bardasov, S. A.; Sobolev, V. D. *Colloids Surf., A* **1993**, *79*, 11.
(6) Barer, S. S.; Churaev, N. V.; Derjaguin, B. V.; Kiseleva, O. A.; Sobolev, V. D. *J. Colloid Interface Sci.* **1980**, *74*, 173.
(7) Barer, S. S.; Kvlividze, V. I.; Sobolev, V. D.; Churaev, N. V.; Kurzaev, A. B. *Dokl. Akad. Nauk SSSR* **1977**, *235*, 601.
(8) Wilen, L. A.; Dash, J. G. *Phys. Rev. Lett.* **1995**, *74*, 5076.
(9) Pittenger, B.; Fain, S. C.; Cochran, M. J.; Donev, J. M. K.; Robertson, B. E.; Szuchmacher, A.; Overney, R. M. *Phys. Rev. B* **2001**, *6313*, 4102.
(10) Beaglehole, D.; Wilson, P. *J. Phys. Chem.* **1994**, *98*, 8096.
(11) Bluhm, H.; Ogletree, D. F.; Fadley, C. S.; Hussain, Z.; Salmeron, N. *J. Phys.: Condens. Matter* **2002**, *14*, L227-L233.
(12) Ishizaki, T.; Maruyama, M.; Furukawa, Y.; Dash, J. G. *J. Cryst. Growth* **1996**, *163*, 455.
(13) Domack, A.; Prucker, O.; Ruhe, J.; Johannsmann, D. *Phys. Rev. E* **1997**, *56*, 680.
(14) Tsionsky, V.; Zagidulin, D.; Gileadi, E. *J. Phys. Chem. B* **2002**, *106*, 13089.
(15) Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206.
(16) Moret, H.; Louwerix, E. In *Vacuum Microbalance Techniques*; Behrndt, K. H. N., Ed.; Plenum Press: New York, 1966; pp 59−75.
(17) Nomura, T.; Iijima, M. *Anal. Chim. Acta* **1981**, *131*, 97.
(18) Bruckenstein, S.; Shay, M. *Electrochim. Acta* **1985**, *30*, 1295.
(19) Buttry, D. A. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker Inc.: New York, 1991.
(20) Buttry, D. A. In *Electrochemical interfaces − modern techniques for in situ interface characterization*; Abruna, H. D., Ed.; VCH: New York, 1991; Chapter 10, pp 531−566.
(21) Tsionsky, V.; Daikhin, L.; Urbakh, M.; Gileadi, E. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, Basel, 2003; Vol. 22.
(22) Daikhin, L.; Urbakh, M. *Faraday Discuss.* **1997**, *107*, 27.
(23) Tsionsky, V.; Daikhin, L.; Urbakh, M.; Gileadi, E. *Langmuir* **1995**, *11*, 674.
(24) Habib, M. A.; Bockris, J. O. In *The Double Layer*; Bockris, J. O., Conway, B. E., Yeager, E., Eds; Comprehensive Treatise of Electrochemistry, Vol. 1; Plenum Press: New York, London, 1980; Chapter 4, pp 135−220.
(25) *Handbook of Chemistry*; Nikolsky, B. P., Ed.; Khimia: Moscow, Leningrad, 1962; pp 716−719.
(26) Daikhin, L.; Gileadi, E.; Katz, G.; Tsionsky, V.; Urbakh, M.; Zagidulin, D. *Anal. Chem.* **2002**, *74*, 554.
(27) Kanazawa, K. K.; Gordon, J. G. *Anal. Chim. Acta* **1985**, *175*, 99.
(28) Reed, C. E.; Kanazawa, K. K.; Kaufman, J. H. *J. Appl. Phys.* **1990**, *68*, 1993.

(29) Urbakh, M.; Daikhin, L. *Langmuir* **1994**, *10*, 2836.

(30) Daikhin, L.; Urbakh, M. *Langmuir* **1996**, *12*, 6354.

(31) Sahimi, M. *Rev. Mod. Phys.* **1993**, *65*, 1393.

(32) Kanazawa, K. K. *Faraday Discuss.* **1997**, *107*, 77.

(33) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.

(34) Golecki, I.; Jaccard, C. *J. Phys. C: Solid State Phys.* **1978**, *11*, 4229.

(35) Petrenko, V. F. *J. Appl. Phys.* **1998**, *84*, 261.

(36) Petrenko, V. F.; Qi, S. G. *J. Appl. Phys.* **1999**, *86*, 5450.

(37) Petrenko, V. F. *Abstr. Pap. Am. Chem. Soc.* **1998**, *215*, 178.

(38) Hobbs, P. V. *Ice Physics*; Clarendon Press: Oxford, U. K., 1974.

(39) Bandey, H. L.; Hillman, A. R.; Brown, M. J.; Martin, S. J. *Faraday Discuss.* **1997**, *107*, 105.

(40) Calvo, E. J.; Etchenique, R.; Bartlett, P. N.; Singhal, K.; Santamaria, C. *Faraday Discuss.* **1997**, *107*, 141.