

## LETTERS

### Evidence for the Existence of a “Liquid-Like Layer” between a Metal Electrode and a Frozen Aqueous Electrolyte

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The quartz-crystal microbalance (QCM) was used to study premelting at the ice/gold and the frozen electrolyte/gold interfaces. It was shown that in a certain range of temperature, below the melting point, (i) the resonance of the QCM is readily detectable (at temperatures lower than this temperature range the QCM did not show any resonance), (ii) the parameters of the resonance depend on temperature, and (iii) the shape of the resonance is very different from that observed for the QCM in contact with liquids. The observed phenomena were ascribed to the existence of a liquid-like layer (LLL) between ice or frozen electrolyte and the gold surface. It was shown that for the frozen electrolyte/gold interface the parameters of the QCM resonance depend on potential. The latter, in turn, shows that the properties of the LLL could be controlled by the electrochemical potential of the metal/electrolyte interface.

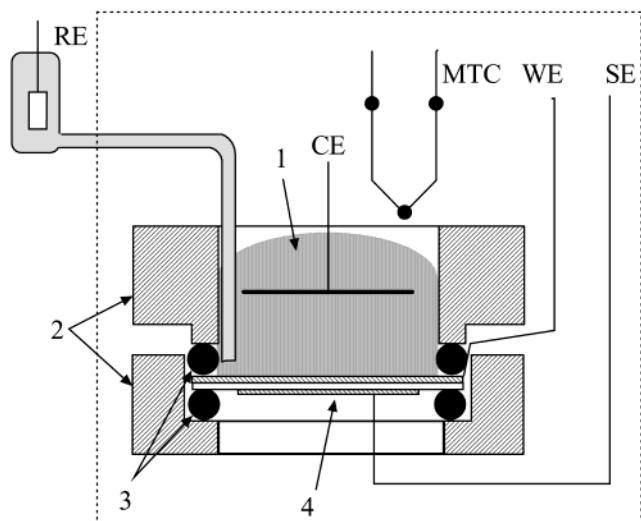
#### Introduction

The liquid-like layer (LLL) on the surface of ice or between ice and a solid phase, and the reasons for its existence, have generated interest among both theoreticians and experimentalists for more than 150 years.<sup>1–3</sup> The list of different techniques used to prove the existence of such a layer and to determine its properties, particularly its thickness, is very long.<sup>2,4–6</sup> Among authors of these studies one can find investigators in different fields. However, there are no electrochemists among them, except Michael Faraday,<sup>1</sup> who was both one of the founders of the field of electrochemistry and the first to suggest the idea of a LLL. In the time of Faraday, it may have been too early to correlate between these two fields, but it is obvious now that they are related, because both deal with the region where two different phases make contact. Moreover, it is well-known now

that electrochemical phenomena can be studied in frozen electrolytes (see, e.g., refs 7–10). In electrochemistry, one considers the metal/electrolyte interface, but there are only a few papers in which the ice/metal interface was studied<sup>6,11–13</sup> and where the existence of a LLL was confirmed. At the interface between two phases, there is always a potential drop, induced by the thermodynamic properties of the phases, adsorption phenomena, and reactions taking place at the interface. Although the absolute value of this potential drop is not accessible experimentally, changes in it are routinely measured and controlled in electrochemical studies. In the earlier studies mentioned above,<sup>6,11–13</sup> this potential was not controlled. A priori it is impossible to tell whether this is important, because the characteristic length of the LLL is not well-known. Values given in the literature (see, e.g., ref 5), based both on theoretical calculations and experiments, can vary from 1 to 100 nm and could be much larger than the characteristic length that controls charge transfer, adsorption, and other electrochemical phenomena taking place at the interface, under the influence of the

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**Figure 1.** Schematic representation of the cell. 1. Electrolyte (or water); 2. Teflon holder; 3. Viton O-rings; 4. Gold-covered quartz crystal resonator. RE and CE, reference and counter electrodes, respectively; WE (working electrode) and SE (supporting electrode) are used to induce vibration in the quartz crystal resonator, and to connect it to devices: Network analyzer and potentiostat. MTC, the micro thermocouple.

potential drop between the two phases. For example, the thickness of the Helmholtz layer, where charge transfer takes place, is of the order of 0.5 nm, and that of the diffuse double layer in 0.1 M electrolyte is only about 1 nm.

The central instrument used in the present work is the electrochemical quartz crystal microbalance (EQCM), which has been used widely in electrochemical studies for the past 20 years.<sup>14–16</sup> The admittance of the quartz resonator (the EQCM) immersed in a liquid reflects all phenomena taking place in the layer nearest to vibrating surface. The thickness of this layer is characterized by the velocity decay length, which is typically about 100–300 nm, depending on the properties of the resonator itself and the liquid in contact with it. Because this is of the same order of magnitude as the characteristic length of the LLL, the EQCM is very suitable to study this phenomenon, although the EQCM was shown to be sensitive also to changes in the diffuse double layer.<sup>17,18</sup> The measured admittance of the EQCM contains information on the mass deposited or adsorbed on its surface and on the density and viscosity of the liquid in a layer of thickness, which is of the order of magnitude of the velocity decay length.

A gold electrode in contact with dilute aqueous perchloric acid solution is one of the most thoroughly studied and best understood systems in electrochemistry. This system was therefore employed in the current paper to study the LLL with the EQCM and specifically to determine the influence of the electrical field at the interface on this phenomenon.

## Experimental Section

All measurements were performed in a one-compartment electrochemical cell with three electrodes (Figure 1), which was closed at the bottom by the quartz-crystal resonator (AT-cut type, with a fundamental frequency of about 6 MHz, diameter 15 mm, purchased from Intellmetrics). The crystal was cradled between Viton O-rings to prevent leakage. One side of the crystal resonator was coated with gold in its center (diameter 7 mm). The other side, the upper in Figure 1, was coated completely by gold and was used as the working electrode (the diameter of the part exposed to the solution was 12 mm,

determined by the O-ring). The details of pretreatment of the quartz crystal resonator and the measurements of its admittance were described in our previous publications.<sup>19–21</sup> Below, we characterize the properties of the EQCM by its resonance frequency,  $f_0$ , and the width of resonance  $\Gamma$ , (i.e., the width of the real part of the admittance plot at half-height), calculated from the raw data obtained with a Hewlett-Packard Network Analyzer, type 5100A (see ref 19). The height of the column of the electrolyte was 5 mm, and it contained another gold electrode, serving as the counter electrode. The reference electrode, RHE (reversible hydrogen electrode), maintained at room temperature, was connected to the cell by a thin Teflon tube, as shown in Figure 1. All of the parts marked by a dashed rectangle were placed in a hermetically sealed container purged continuously with pure helium. The temperature was controlled to within  $\pm 0.05^\circ$  of the stated values.

A microthermocouple was placed at a distance of a few mm above the meniscus of the electrolyte. The other junction of this thermocouple was far above the meniscus and was less sensitive to the temperature of the electrolyte. A zero reading of this thermocouple indicates that thermal equilibrium has been established. A spike is generated by a phase transition in the liquid, which, in the present case, indicates the beginning of freezing or of melting of the electrolyte.

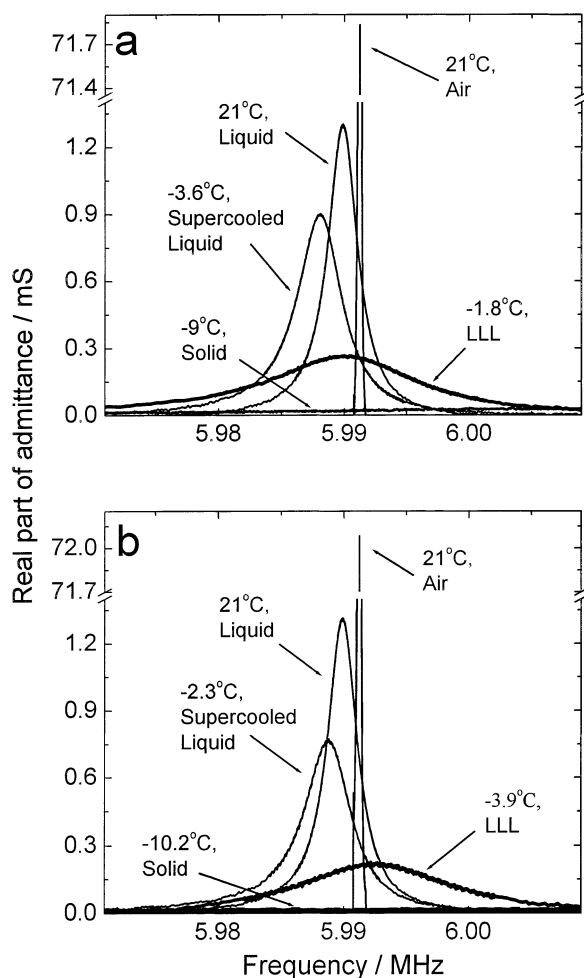
In all experiments, Milli-Q water with a specific resistance of 18.3 MOhm/cm and perchloric acid (Merck, pure) were used.

## Results and Discussion

Figure 2 shows the real part of the admittance of the quartz-crystal resonator as a function of frequency, in the vicinity of the resonance frequency, under different conditions, as marked. In air at room temperature, the admittance is high and the width of the resonance is very narrow, of the order of a few tens of hertz. When filled with pure distilled water (Figure 2a) at the same temperature, the resonance frequency is shifted to lower values and the width of the resonance is increased dramatically, to about 3 kHz (the exact value is of no significance here, because it depends on the surface structure of the electrode in contact with the aqueous phase, but for a given crystal, the changes in the width of the resonance are very important, as will be discussed below). When the temperature was lowered carefully, forming supercooled water at  $-3.6^\circ\text{C}$ , the width of the resonance increased further (to 4 kHz), and the resonance frequency was shifted to a lower value. This behavior is readily understood in terms of the increased viscosity of the medium in which the EQCM is immersed and is associated with an increase of damping of the vibrations of the quartz-crystal resonator with increasing viscosity of the fluid.<sup>14–16</sup>

When the water was frozen, as evidenced by a sharp spike in the voltage of the micro thermocouple, the EQCM response collapsed and transformed as shown for  $(-9^\circ\text{C})$ . There was no resonance when the temperature was increased after that up to  $-3^\circ\text{C}$ . However, when the temperature was set between  $-3^\circ\text{C}$  and a temperature somewhat lower than  $0^\circ\text{C}$ , usually for 1–1.5 h, resonance was restored, but its appearance was quite different from that obtained with liquid water. A typical curve observed in this region is shown for  $-1.8^\circ\text{C}$ . This resonance was found to be stable indefinitely. Restoring the resonance was not accompanied by any response of the microthermocouple, indicating that no phase transition had taken place, and the bulk was still solid.

It could be argued that the vibrating quartz crystal resonator might be a source of heat that would melt a thin layer of ice at the surface. This possibility was discarded for the following



**Figure 2.** Dependence of the real part of the impedance of the quartz-crystal resonator on frequency in air, liquid, ice, and LLL at different temperatures, as indicated. a, water; b, 0.1 M aqueous solution of HClO<sub>4</sub>.

reasons: (i) The thermocouples do not show any changes of temperature when a voltage was applied to the quartz crystal resonator. (ii) When the temperature was lowered to about  $-10^{\circ}\text{C}$ , then raised to a value where a LLL exists ( $-1.8^{\circ}\text{C}$  in pure water and  $-3.9^{\circ}\text{C}$  in the solution of the electrolyte, cf. Figure 2), and held there for 1–1.5 h, the crystal started vibration immediately upon application of a voltage, irrespective of whether a voltage had been applied during this waiting period. (iii) Calculations based on the known parameters of the system (the impedance of the crystal, the applied voltage, the geometry of the cell, and the thermal conductivity of ice and of the gas layer between it and the thermocouple) showed that the increase of temperature at the crystal/ice interface could not exceed  $0.05^{\circ}$ . (iv) The voltage applied to the quartz resonator was 1 V peak to peak in all regular measurements. A test, in which this voltage was decreased by as much as 2 orders of magnitude, yielded no significant change in the reading of the thermocouples or in the response of the quartz resonator in the region where a LLL is formed.

Experiments conducted with an electrolyte (Figure 2b), instead of pure distilled water, exhibited very similar behavior, although the numerical values of the parameters of the resonance were somewhat different and the temperature range where resonance was restored in the frozen electrolyte was found to depend on the nature of the electrolyte and its concentration in solution. Thus, for a 0.1 M aqueous solution of HClO<sub>4</sub>, these

temperatures lie between  $-5.5$  and  $-2^{\circ}\text{C}$ . At higher temperatures, the resonance curves did not differ from those obtained in liquid at the same temperatures. Being a two-component system, an aqueous solution of 0.1 M HClO<sub>4</sub>, it is much more complex than pure water. It is fully liquid at temperatures higher than  $-0.5^{\circ}\text{C}$  and fully solid at  $-60^{\circ}\text{C}$ .<sup>22</sup> Nevertheless, the evident similarity of the data obtained in pure water and in the electrolyte confirms that working with both systems one is dealing with the same phenomenon: the existence of a LLL between the metal and the frozen liquid.

Consider the peculiarities of the resonance presented by the curves shown for the LLL:

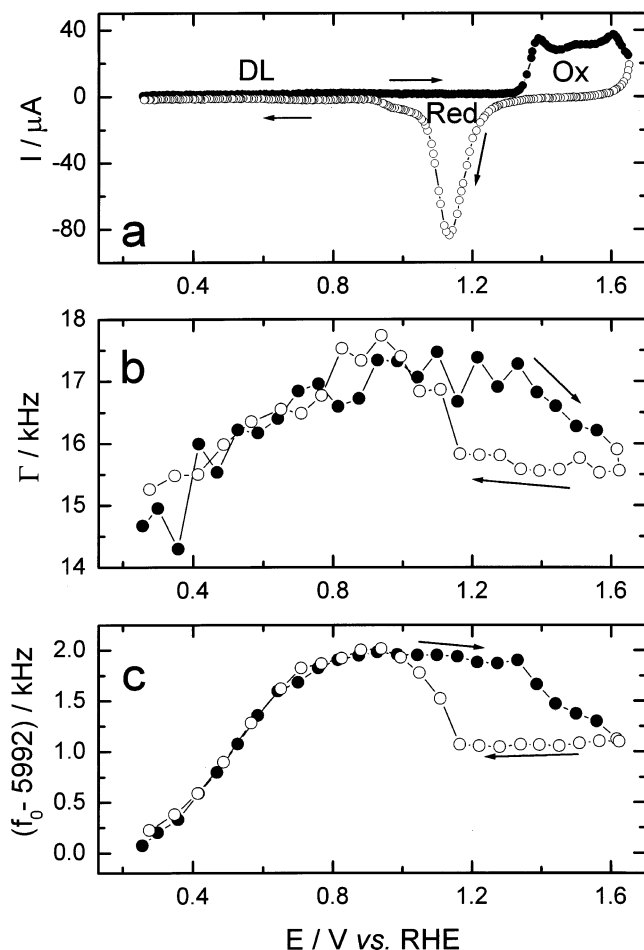
i. Just as the resonance observed in liquid at different temperatures and in the gas phase, these resonance curves represent true single resonance: there is no resonance splitting and the complex-plane plot of the imaginary part of the admittance vs the real part is a true circle.

ii. Increase of the viscosity and/or density of a liquid should lead to widening of the resonance and a decrease of both the resonance frequency and the absolute value of the admittance, as seen by comparing the curves for  $21^{\circ}\text{C}$  and for supercooled liquids. The curves marked as LLL are shifted to higher frequencies (which would normally indicate a decrease in viscosity and density), yet the resonance is much wider and the admittance is significantly lower than in supercooled liquids at a similar temperature, (which could be interpreted as an increase in viscosity and density).

Restoring the resonance in the frozen liquid, in the absence of any sign of a phase transition, is a strong indication for the appearance of a liquid or a LLL at the surface, whereas the bulk of the liquid is still frozen, in accordance with existing evidence in the literature.<sup>3,5</sup> However, this is the first time, to our knowledge, that this phenomenon has been observed using a quartz crystal resonator.

In Figure 3, we show data obtained with 0.1 M aqueous solution of HClO<sub>4</sub>, which was first frozen and then heated to  $-3.9^{\circ}\text{C}$ , where we suggest the existence of a LLL. The electrochemical behavior of this system at  $-3.9^{\circ}\text{C}$  is very similar to that usually observed in the same electrolyte at room temperatures, see for example ref 23. As the electrode potential was increased linearly with time up to 1.30 V vs RHE, only a very small current, corresponding to charging of the electrical double layer, was observed (the region marked DL in Figure 3a). The increased anodic current in the region marked "Ox" corresponds to formation of a surface oxide layer on gold. On reversing the direction of the potential scan, a cathodic current peak, corresponding to the reduction of this surface oxide, is observed (marked as "Red"), followed by a small cathodic current associated with double-layer charging. Similar cycling voltammograms were obtained at all temperatures in the electrolyte above the melting point, in supercooled electrolyte as well as in frozen electrolyte, where the existence of the LLL is indicated by the ability of the quartz-crystal resonator to vibrate. Such behavior is not unusual and has been demonstrated in other electrochemical systems, where the electrode/electrolyte interface shows no discontinuity at the melting point.<sup>7–10</sup> Some subtle changes do exist, of course, and will be discussed elsewhere.

In Figure 3, parts b and c, we show the variation of the width of the resonance and the resonance frequency with potential, respectively, taken simultaneously with the cyclic voltammogram shown in Figure 3a. These data were obtained at a potential scan rate of 10 mV/s, but data taken in the range of 5–20 mV/s were found to be the same, within experimental error.



**Figure 3.** Response of a gold-covered EQCM immersed at  $-3.9^\circ\text{C}$  in 0.1 M aqueous solution of  $\text{HClO}_4$  vs potential.  $V = 10$  mV/sec: a. Current vs potential. DL, double layer region. "Ox" and "Red", surface oxide formation and its reduction, respectively; b. width of resonance ( $\Gamma$ ) and c. fundamental frequency ( $f_0$ ) as a function of potential. Open and closed circles correspond to different directions of potential scan, as shown by the arrows.

The response of the EQCM with potential in this system at room temperature has been well-documented.<sup>14–16</sup> The frequency change observed in the same range of potential does not exceed a few tens of hertz, compared to changes in the range of a few kHz shown in Figure 3c. Moreover, the width of resonance for the same gold surface in the electrolyte solution at room temperature is about 3 kHz, independent of potential.<sup>23</sup> Our experiments showed the same behavior, as long as the electrolyte was liquid, over a wide range of temperature, even when the liquid was supercooled.

Consider the peculiar response of the quartz-crystal resonator for frozen electrolyte with a LLL.

The width of the resonance shown in Figure 3b is in the range of about 14–18 kHz, compared to a value of about 3 kHz observed for the same electrode at room temperature.

The width is a function of potential, changing as much as 3 kHz over the range measured here, whereas it is essentially independent of potential in liquid electrolyte.

Cycling the potential of a gold electrode in this range allows us to study the effect of the nature of the surface on the response of the EQCM. Sweeping in the anodic direction, the surface is bare up to a potential of about 1.30 V RHE and becomes completely covered by a surface oxide by the time the potential has reached a value of 1.60 V, RHE. Oxidation of the surface is, however, quite irreversible. Thus, on the return (cathodic)

sweep, removal of the oxide does not start until a potential of about 1.30 V RHE has been reached. In the region between 1.3 and 1.6 V, it is possible to study the response of the EQCM on a surface, which is initially bare and becomes gradually covered by an oxide (during the anodic sweep) and on a surface completely covered by an oxide (during the cathodic peak).

The difference is indeed remarkable. During the anodic sweep, the width rises initially, reaching a constant value in the double layer region, at about 0.9 V, RHE, and remains constant as long as the surface remains essentially bare, up to a potential of about 1.30 V. As oxide formation starts, the width of the resonance starts to decrease until a full oxide layer has been formed. On the reverse (cathodic) sweep, the width remains remarkably constant down to a potential of 1.30 V, as long as the oxide layer remains essentially intact, as judged from Figure 3a. It then rises rapidly and retraces the values obtained in the double layer region during the anodic sweep, both measured on a bare surface.

The variation of the resonance frequency with potential, shown in Figure 3c, emphasizes further the effect of the nature of the surface on the response of the EQCM. First we note that the resonance frequency changes by as much as 2 kHz with potential, about 2 orders of magnitude more than the change observed in liquid electrolyte over the same range of potential. Second, in the oxide formation and reduction regions, hysteresis is very clearly seen, showing the effect of the formation of the oxide layer on the resonance frequency: at 1.3 V RHE, the width of the resonance and the frequency shift are both very different for the bare and the oxide-covered surfaces. We note also that on the bare gold surface in the double region both the resonance frequency and the width are quite reversible, independent of the direction of sweep.

To the best of our knowledge, this is the first case in which the effect of applied potential, and the resulting high field imposed across the interface, on the behavior of a liquid like layer (LLL) in a frozen electrolyte has been reported. Moreover, employing a gold electrode in the appropriate potential region allowed us also to compare the LLL on a bare gold electrode with that observed for an oxide covered surface, in terms of its effect on the response of the EQCM.

It seems evident that the changes of the admittance of the EQCM must be associated with changes of the structure of the interface, specifically the viscosity, density, and thickness of the LLL. The effects observed are quite large, much exceeding that which could be expected for adsorption phenomena or changes of concentration in the diffuse double layer region. The corresponding theory has not yet been developed. Moreover, other additional experiments will have to be devised, to estimate the thickness of the LLL, which is one of the central issues in describing the phenomenon of the formation of a LLL.

The theory of a vibrating resonator immersed in a viscous medium of infinite depth has been developed.<sup>14–16,24–27</sup> The system of interest here consists of three-layers: a vibrating gold surface, a fixed motionless surface of the frozen electrolyte, and a LLL in between. A theoretical model related to this case was considered for two flat surfaces, one fixed and the other vibrating, with a thin liquid layer confined between them.<sup>28</sup> However, this applies rigorously only if the thickness of the liquid layer is known and its properties are assumed to be homogeneous throughout the gap between the two solids, conditions that may not apply to the LLL considered here. This model and further experimental results of the kind described above will be discussed in a following publication.



In studies of the LLL by different techniques, the influence of impurities on the properties of such layers, in particular on their thickness, has been taken into account. In theoretical consideration,<sup>29</sup> the existence of the LLL was accepted. A dramatic influence of the nature of the substrate/ice interface, and of small amounts of electrolyte, on the thickness of the LLL were predicted. Unfortunately, the metal/ice interface was not considered in the above study. Hence, the results obtained from theory cannot be applied directly to the system reported in the present paper. The role of impurities will undoubtedly become an important issue in the study of LLL at the metal/frozen electrolyte interface, when methods for determining the parameters of the LLL employing the QCM, combined with electrochemical control of the interface, will be developed.

The main purpose of the present communication is to demonstrate the potential of the QCM (including its operation in the electrochemical mode) for studies of the LLL over a wide range of experimental conditions.

### Conclusion

Measurements of the admittance of the quartz crystal resonator show that at temperatures just below the melting point of aqueous electrolyte, or even of pure water, a liquid or a LLL exists between the gold electrode and the frozen electrolyte, which allows the EQCM to resonate. Moreover, the admittance of the quartz-crystal resonator in such systems depends on the applied potential and on the nature of the surface. This indicates that the properties of the LLL are strongly controlled by the properties of the metal electrode in contact with the frozen electrolyte phase.

There are many open questions, but a clear correlation between the nature of the surface, the electric field across the interface, and the properties of the LLL has been demonstrated. It was also shown that this behavior can be studied experimentally under a broad range of experimental conditions, and the effects observed are large (compared to effect of submonolayer phenomena on the EQCM) and reproducible.

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