On The Structure of the Metal/Solution Interface - An EQCM Study

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Hebrew abstract
Abstract

The EQCM (Electrochemical Quartz Crystal Microbalance) is a very sensitive piezoelectric device, which has been used for several years now in many applications in electrochemistry. Important information, such as changes of mass at the interface, or changes in the viscosity and density of this layer, can be obtained. Usually EQCM measurements are employed in conjunction with other electrochemical measurements, such as cyclic voltammetry, differential capacitance, chronocoulometry etc. In this way, more can be learned about the type and amount of various species that exist at the electrode/electrolyte interface and about the relationship between structure and function in electrochemical phenomena [62,63].

Sauerbrey [9] was the first to recognize the potential usefulness of the quartz crystals as a mass sensor. He demonstrated the extremely sensitive nature of these piezoelectric devices towards mass changes at the surface of the QCM (Quartz Crystal Microbalance) electrode in the gas phase. The main result of his pioneering work in this area is embodied in the Sauerbrey equation, which relates the mass change per unit area at the QCM electrode surface to the observed change in oscillation frequency of the crystal [9]:

\[ \Delta f = -C_m \Delta m \]

where \( \Delta f \) is the observed frequency change in Hz, \( C_m \) is the proportionally constant, that depends only on the properties and dimensions of the quartz crystal resonator, and \( \Delta m \) is the change in mass per unit area. As can be seen, an increase in mass results in a negative frequency shift.

The frequency shift is influenced by other parameters, such as the viscoelastic [16,40,41,43-50,86], properties of the layer near the vibrating crystal, the pressure of surrounding medium in which the EQCM is immersed [45], changes of the surface roughness [58-67], changes in the temperature [57] and of the stress of the electrode under investigation [132].

Since many parameters influence the observed frequency shift, and difficulties arise in separating their contribution to the observed frequency shift, there is a need to control part of the parameters very carefully.
This work shows how valuable information, such as the structure of the solvent and the adsorbate at the interface, and the influence of the nature of the metal electrode on adsorption, can be obtained from EQCM measurement with other classical electrochemical measurements.

In electrochemical systems, the pressure remains constant and because of the high thermal capacity of liquids, the temperature of the resonator is equal to that of the surrounding medium. However, changes of mass due to adsorption or deposition and changes in the viscoelastic properties, which depend on the distance from the interface, do result in frequency shift.

The viscosity and the density of a solution are governed by the properties of its molecules. At the metal/solution interface there are several factors which could change these properties. These include: symmetry breaking, specific chemical interactions with the surface of the metal, and electrostatic interactions arising from the difference in dielectric constant between the two sides of the interface, or with the surface charge density of the metal. It is difficult to determine how far the influence of the interface extends into the bulk of solution. However, it seems reasonable to assume that, in the general case, there should be a region near the interface with properties different from those in the bulk of the solution.

A model has been developed in our laboratory [86] describing the frequency shift $\Delta f_{\text{film}}$ of a quartz crystal resonator immersed in a liquid with a thin film having a different density and viscosity than in the bulk. The following equation describes the shift of frequency caused by such a film:

$$
\Delta f_{\text{film}} = -C_a L \rho_s \left[ \left( \frac{1-\eta_s}{\eta_f} \right) + \left( \frac{\rho_f}{\rho_s} - 1 \right) \right]
$$

where $L$ is the thickness of the film and $\rho_s$ and $\eta_s$ and $\rho_f$ and $\eta_f$ are the density and viscosity of the liquid (film) respectively. The first part in the equation relates to the EQCM response to viscoelastic changes at the interface and the second part to frequency shift due to mass changes.

This equation was used to interpret the dependence of the frequency shift of the quartz crystal microbalance on changes of potential, for electrostatic (non-specific) adsorption [86]. Using the Gouy-Chapman model,
it was possible to estimate the mass changes $L(\rho_f - \rho_s)$, caused by changes of ionic concentration in the diffuse double layer. The difference between the observed frequency shift and that calculated due to mass changes yields the frequency shift corresponded to the changes in the viscosity of the thin layer. Calculation of the viscosity dependence on ionic concentration in the diffuse double layer was found to be similar to the viscosity/concentration dependence for the bulk of the corresponding electrolyte. This change in the viscosity can be understood in the framework of a microscopic model. As the number of bonds formed between the first solvent layer on the crystal and the further layer is higher the disturbance to the quartz oscillation increasing, resulting in a decrease in the frequency.

Electrostatic adsorption was studied in this work for two solvents, water and n-butanol, on gold and silver electrodes [89]. While water molecules can form two hydrogen bonds on the surface and more in the bulk, forming a three-dimensional structure, alcohols can only form one hydrogen bond. It was found that, as the charge on the electrode increases, more bonds are formed. The fewer bonds formed by n-butanol molecule result in less sharp dependence of the observed frequency shift with charge. Similar results were obtained on gold and silver electrodes. A sharper dependence of the frequency shift on charge was observed on silver electrode, which is probably caused by weaker interaction of the silver electrode with water and with n-butanol than for the interaction of the gold electrode with both solvents.

In the case of specific adsorption, the response of the quartz crystal due to electrostatic adsorption should be subtracted, before analyzing the results further [112]. The frequency shift obtained due to electrostatic adsorption is comparable to the frequency shift obtained due to monolayer adsorption. The observed response cannot be explained only by considering mass changes resulting from adsorption. Reasonable explanation is that there are some changes in the viscoelastic properties, as in the former case, associated with specific adsorption at the metal/solution interface. Further analysis can lead to conclusion about the orientation of the adsorbed molecules and the slip length in each system.
In this work the EQCM response was measured for the following cases:
- pyridine adsorption from an aqueous solution on gold and silver electrode,
- n-butanol adsorption from an aqueous solution on gold electrode,
- pyridine adsorption from a solution of n-butanol on gold and silver electrode,
- t-butanol adsorption from aqueous solution on gold electrode
- uracil adsorption from aqueous solution on gold electrode [87, 89, 112].

In most of the cases studied a positive rather than negative frequency shift was observed implying that the mass on the surface decreases. Considering that electrosorption is a replacement reaction this might be reasonable. However, as in the former case, the change of mass at the interface was found to be insufficient to explain the observed frequency shift.

Considering the bond that can be formed between the adsorbed molecules and the solvent molecules, the frequency shift obtained can be explained and details on the interface can be obtained. It was found out that -

1. Adsorbed pyridine molecules on gold electrode destroy the previous structure of water and replace the water/water interactions between the first layer, attached directly to the surface, and further layers at the interface, by pyridine/water interactions, which must be much weaker. The shift in frequency is particularly large at positive charge densities, where pyridine is oriented at some angle to the surface, with the benzene ring towards the solution, resulting in a decrease of bonding between the vibrating surface and the rest of the solution.

2. A smaller frequency shift was obtained during the adsorption of n-butanol on gold electrode from aqueous solution at positively charged surface. The reason for this behavior is that at this charged surface, the alkyl chain of n-butanol is positioned on the surface blocking a relatively large area. The alkyl chain destroys the structure of the water at the surface, but still bonds can be form with the –OH group of n-butanol, which is open to the solution in this orientation, unlike for pyridine.
3. The adsorption of t-butanol should present a hydrophobic surface that should lead to a high positive change in the frequency observed, exceeding that found for n-butanol and even that of pyridine. However, the observed values of the frequency shift are indeed somewhat higher than those found for n-butanol, but significantly lower than for pyridine. This unexpected behavior can be attributed to the fact that water tends to form clathrates around t-butanol, holding the molecule effectively in a cage of 21 water molecules. If this structure or part of it adsorbs on the surface, it would shield the methyl groups from the rest of the solution. This would present a hydrophobic surface toward the rest of the solution, as opposed to the hydrophobic nature of the bare –CH₃ groups, leading to a much lower value of the positive frequency shift, as observed experimentally.

4. The effect of pyridine addition to n-butanol, used as the solvent, is considerably smaller than in the case of pyridine adsorption from water. The reason is that hydrogen bonds in alcohol are considerably weaker than in water. The positive frequency shift observed could be explained by the change in the interaction of the surface with the solvent. While only n-butanol exists in the solution, at positive charge density, hydrogen bonds still can be formed by the –OH group, with other solvent molecules. If pyridine adsorbed on the positively charge surface with the hydrophobic part facing the solution, less bonds can be forms with the solvent molecules.

5. At positive charge densities, uracil shows a small frequency shift. Although, it has the similarity to pyridine, both adsorbed perpendicular to the surface, the functional groups –O or –N of uracil can form hydrogen bonds, resulting in only a small frequency shift, unlike the case of pyridine.

6. As was mentioned before, the interaction of the silver surface with water is weaker than that of gold. Therefore, there is less surface structure to be destroyed or altered by the adsorption of pyridine, resulting in small frequency shift.
7. The adsorption of pyridine from n-butanol on gold and silver electrodes shows similar affect.

An alternative way of looking at this phenomenon [183] is to consider the interactions between the first layer of molecules adsorbed on the surface and the following layers. When solvent molecules are replaced by adsorbed molecule, their interaction with the further solvent layer is much weaker. This may lead to finite slippage at the adsorbed layer/solution interface, and an increase in frequency of the EQCM.

Following this line of reasoning it is possible to discuss the relationships between the slip length, surface excess and the microscopic properties of interfacial layer. A model that relates these parameters was developed recently [183]. From this model the slip length was estimated for the adsorption of pyridine on gold electrode from aqueous and n-butanol solution. In agreement with the theoretical prediction, the slip length grows with the surface excess. The dependence of the slip length on the surface excess is very close to linear for pyridine adsorption from n-butanol solution, but deviates from linearity for pyridine adsorption from water. This deviation may be attributed to a reorientation of adsorbed pyridine molecules.
List of publication


1. Introduction

1.1. The EQCM

1.1.1. Background

In 1880 Pierre and Jacques Curie discover that some crystals when compressed in particular directions show positive and negative charges on certain portions of their surfaces. Those charges were found to be proportional to the applied pressure [1]. Immediate interest aroused in scientific circles and Hankel proposed the name piezoelectricity to the effect (from the Greek word piezin that means “to press”) [2,3]. A year after the discovery of the direct effect M. G. Lippman [4] discussed the application of his thermodynamic theories to reversible processes involving electric quantities and predicted that a converse phenomenon should exist. The converse effect, whereby a piezoelectric crystal becomes strained, when electrically polarized, by an amount proportional to the polarizing field is the basis of the Quartz Crystal Microbalance, QCM, operation.

During the following decade physicists tried to interpret the piezoelectric effect and to give thermodynamic explanation to the phenomenon. The most comprehensive work was given by Voigt [5]. This work was based on thermodynamic principles enunciated by Lord Kelvin. In this work he explained clearly in which of 32 crystal classes the piezoelectric effect may exist.

Until the WW1 the piezoelectric effect received less attention. In 1917 Langevin [6] used the quartz plates as an ultrasound transducer under the water in order to locate immersed objects in the ocean bottom. The use of piezoelectric resonators as stabilizers, oscillators, and filters are another applications of the piezoelectric effect found during the WW1 by Cady [7] and Pierce [8]. The resonators are very popular today in electronics, radio transmitting station and quartz clocks.
Sauerbrey [9] in his work relates the change in the oscillation frequency of a piezoelectric crystal to the mass changes on the crystal face. Under certain conditions, a linear dependence exists that is known as the Sauerbrey equation:

$$\Delta f_{\text{mass}} = -C_m \cdot \Delta m$$

(1)

where $C_m$ is a constant that depends only on the crystal properties. This equation is the basis for mass controllers that measure the thickness of deposition from the gas phase (in processes such as vapor deposition, sputtering, etc.). Details, regarding this equation, are given below.

The first works done in solutions belongs to Konash et al [10], who used the quartz crystal as a detector in liquid chromatography, and to Nomura [11] who measured the change in frequency when the gold electrode of the crystal is dissolved by reaction with cyanide in alkaline solution. Those works show that the crystal can oscillates in liquids although there is an excessive energy loss to the solution due to the liquid viscosity.

The use of the QCM in an electrochemical context to monitor mass changes at electrodes was first demonstrated by Jones and Meure [12,13], who showed that trace metal determinations were possible by plating the metals onto a QCM electrode and measuring the change in resonant frequency of the crystal in air following its removal from the electrochemical cell. The first in-situ application of the QCM to electrochemical problems was by Norma [14,15] and co-workers who used it to determined Cu$^{2+}$ and Ag$^+$ by electrodeposition.

Bruckenstein and Swatthirajan were the first to study monolayer deposits on the QCM. They produced Under Potential Deposits, (UPD), of silver on the QCM and made ex-situ mass determinations in investigations of electrosorption valency [16]. Bruckenstein and shay [17] then reported on the first in-situ mass determination of monolayer system, studying oxide formation on Au electrodes.
In 1984 Kaufman, Kanazawa and Street published the first account of the use of the QCM to study ion transport during redox in thin polymer films [18]. Another group reported on the mass determination of a UPD deposit of Pb on Au electrode [19].

The application of the simple Sauerbrey equation, the fact that \textit{in-situ} measurement can be performed with other electrochemical measurements and the inexpensive equipment needed, are the reasons for the popularity of this technique for study of solution and electrochemical phenomena. The Electrochemical Quartz Crystal Microbalance (EQCM) is used to study monolayer and multilayer deposition and dissolution, UPD, mass transport in polymer films on electrodes, corrosion processes at the electrodes, adsorption - desorption processes, electroless deposition, reaction mechanism, analytical sensors and other phenomena.

Mass change is not the only process that occurs at the metal – solution interface and the EQCM can sense. It is sensitive also to other changes at the interface, such as changes of the viscosity and density, changes of compression, temperature and of the electrode roughness. As a first approximation, the overall response of the EQCM is the sum of the frequency shift of all the contributions:

\[
\Delta f = \Delta f_{\text{mass}} + \Delta f_{\text{viscosity/density}} + \Delta f_{\text{compression}} + \\
+ \Delta f_{\text{roughness}} + \Delta f_{\text{temperature}}
\]

Therefore, the experimental setup and the analysis of the response of the quartz crystal should be performed very carefully in order to evaluate the experimental results correctly.

In the next sections the operation of the EQCM and the influence of the various parameters on the frequency shift, will be discussed.
1.1.2. The Quartz Crystal

Since the discovery of the piezoelectric effect, its existence has been proved in many different materials. Piezoelectricity exists in materials that are acentric, that is, those that crystallize into noncentrosymmetric space group. A single crystal of an acentric material will possesses a polar axis due to dipoles associated with the arrangement of atoms in the crystalline lattice. The charge generated in a quartz crystal under mechanical stress is a manifestation of a change in the net dipole moment because of the physical displacement of atoms and a corresponding change in the net dipole moment. This results in a net change in electrical charge on the crystal face, the magnitude, and direction of which depends on the relative orientation of the dipoles and the crystal faces. Of the 32 crystallographic classes, only 20 classes manifest the piezoelectric phenomenon and very few were found suitable for practical applications. The first condition for a suitable piezoelectric material is that the substances exist in their natural forms as monocrystals with sufficient large defect free parts or that such perfect monocrystals or polycrystalline piezoelectric textures can be prepared artificially. The second condition is that the crystalline material has outstanding piezoelectric properties, low internal friction loss coefficient, and a high long-term temperature stability.

Many piezoelectric materials (as Rochelle salt, tourmaline, Berlineite-aluminum phosphate, Lithium niobate, Lithium tantalite, Bismuth Germanium Oxide, Bismuth Silicon Oxide, ceramics, quartz etc.) are in use today. The most common is the quartz that owns the most extraordinarily low damping with sufficiently strong piezoelectric properties and it may be easily synthesized in pure, crystalline form with low defect density.

The chemical composition of quartz is silicon dioxide, SiO₂. The quartz in its various forms, crystalline or amorphous, is said to form about one tenth of the earth’s crust. The crystalline quartz exists in several forms, of which the α - quartz is used most extensively for piezoelectric applications. The α - quartz belongs to the trigonal trapezoidal group of
the trigonal crystal system. The $\alpha$-quartz is stable up to 573°C, at higher temperature the $\beta$-quartz is formed. The $\beta$-quartz belongs to the hexagonal trapezoidal group of the hexagonal crystal system. At temperatures of 870°C and 1470°C, the form $\alpha$-tridymite and $\alpha$-cristobalite, respectively, come into existence. The melting temperature of quartz is 1710°C.

The density of $\alpha$-quartz is $\rho_q = 2.648 \text{ gr cm}^{-3}$ and the shear modulus is $\mu_q = 2.947 \cdot 10^{11} \text{ gr cm}^{-1} \text{ sec}^{-2}$.

The quartz crystals used in practical applications today are mostly synthetic, only minority being of natural origin. Synthetic quartz crystals are grown under high pressure and temperature in steel autoclaves.

Piezoelectric resonators are prepared by cutting the desired parts from large single crystals of $\alpha$-quartz at certain angle with respect to the crystalline axes of the quartz crystal (Fig. 1). The AT cut which is most commonly used for QCM applications is fabricated by slicing though a quartz rod at an angle of approximately 35° with respect to crystallographic $x$ axis. The reason for its popularity is its nearly zero temperature coefficient (the proportionally constant relating the oscillation frequency of a crystal in vacuum to its temperature) near room temperature. The influence of the temperature on the shift in frequency will discussed in more details below.
1.1.3. The Quartz Crystal Microbalance

A piezoelectric resonator is a device consisting of a plate or a bar cut from a piezoelectric material, with two or more metal electrodes on opposite sides of the crystal. The electrode pads overlap in the center of the crystal, with tabs extending from each to the edge of the crystal where electrical contacts are made. Application of electrical voltage on the electrodes, causes mechanical vibrations in the resonator. For AT cut quartz crystal, the mechanical strain is in the shear direction. Crystal symmetry dictates that the strain induced in a piezoelectric material, by an applied potential of given polarity, will be equal and opposite in direction to that resulting from the opposite polarity as shown in Fig. 2. Therefore, an alternating potential across the crystal, with electric field lines normal to the disk surface, would result in vibration motion of the quartz crystal. The vibration amplitude is parallel to the crystal surface (i.e. the atomic displacement, corresponds with the shear motion, are parallel to the crystal surface) and the x direction.
The quartz crystal loses only a minute amount of energy during oscillation because of friction due to phonon interactions that produce heat, vibrational damping by the mounting components and acoustical losses to the environment. This property is generally characterized by the quality factor, $Q$, which is the ratio of the energy stored to energy lost during a single oscillation. For quartz crystals, this quantity can exceed $10^5$. Low energy losses in oscillating systems are manifested as high accuracies. In liquid applications, $Q$, will generally have values of $10^3$ to $3 \times 10^3$, indicative of energy damping by the fluid. The quartz crystal still performs acceptably at these levels.

The vibrational motion of the quartz crystal results in a transverse acoustic wave that propagates back and forth across the thickness of the crystal, between the crystal faces (Fig. 3). A standing wave condition can be established in the quartz resonator when the acoustic wavelength is equal to twice the combined thickness of the crystal and the electrodes and the quartz crystal surfaces are at antinode.
Fig. 3. Schematic representation of the transverse shear wave in a quartz crystal with excitation electrodes and a composite resonator comprising the quartz crystal, electrodes and thin layer of a foreign material [21].

The fundamental frequency, $f_0$, of the acoustic wave, which is also known as the thickness shear mode or the fundamental mode, is given by the following equation:

$$f_0 = \frac{v}{2l}$$  \hspace{1cm} (3)

Where $l$ is the thickness of the resonator and its electrodes and $v$ is the transverse velocity of sound in the AT cut quartz crystal ($3.34 \cdot 10^4 \text{ m/s}$). The acoustic velocity depends on the modules and density of the crystal.

In addition to the fundamental mode described above, other modes of vibration can be excited by application of electric field. Those odd and unharmonic responses, located slightly higher in frequency, are a combination of the thickness shear and the thickness twist mode. In these cases the antinodes are also at the faces of the disk, and the number of nodes within the bulk of the disk is equal to the harmonic number. Proper design of the crystal and its electrodes eliminate coupling with undesired modes as will discuss below.
Eq. 3 relates to an infinite vibrating plate. Otherwise there should be deviations, which depend on the thickness and the area of the quartz plate. For instance, if $A/l \geq 20$ (A is the surface area of the quartz plate) the deviation in the transverse velocity of sound and hence in the frequency is smaller than 1% [22].

Assuming infinite isotropic medium in which no deformation in the bulk plate occurs (i.e. the volume remains constant) during the shear vibration (see Fig. 4), the amplitude depends only on the plate thickness:

$$\xi(y, t) = \xi(l/2, t) \cdot \sin(\pi \cdot y/l)$$  \hspace{1cm} (4)

Where $\xi(y, t)$ is the amplitude and $t$ is the time.

Following this equation, if there are some layers on the quartz plate there is a maximum in the amplitude for each layer. The frequency is found to depend only on the mass inertia and not on elastic properties of the adsorbed layer. Thus by using Eq. 3 one can write:

$$\frac{\Delta f_{\text{mass}}}{f_0} = -\frac{\Delta l}{l} = -\frac{\Delta \tilde{m}_o}{\rho_o \cdot A \cdot l} = -\frac{\Delta \tilde{n}}{\rho_o \cdot A \cdot l}$$  \hspace{1cm} (5)

since
\[ l = \frac{m}{A \cdot \rho} \]  

(6)

where \( \Delta \tilde{m}_Q \) is the change in mass of a quartz plate with a thickness of \( \Delta l \) and \( \Delta \tilde{m} \) is the mass of any foreign layer. Therefore,

\[
\Delta f = - \frac{f_0}{l \cdot \rho} \cdot \frac{\Delta \tilde{m}}{A} = \frac{f_0}{l \cdot \rho} \cdot \Delta m = -C_m \cdot \Delta m
\]

(7)

where \( \Delta m = \Delta \tilde{m}/A \) is the change of mass per unit of cross section area (not of real surface area and therefore does not depend on the electrode roughness) of any layer on the quartz (more precise – on the area that undergoes displacement). \( C_m \) is a constant mentioned in Eq. 1. Another formulation of this constant is sometime given as:

\[
C_m = n \cdot f_0^3 \cdot (\mu_d \cdot \rho_q)^{1/2}
\]

(8)

Where \( n \) is the mode of the vibration, assigning a value of unity for the fundamental frequency.

The model discussed above and the models that will discussed below rely on the “no slip” condition. This refers to the case in which the first layer of solvent on the QCM metal electrode surface is tightly bound and does not slip against the metal surface during the shear motion of the disk. The vibrating QCM electrode and the adjacent molecular layer of the liquid move at the same velocity and in phase with each other.

This is the basic Sauerbrey equation. The derivation of the mass frequency relation implicitly relies on the assumption that a deposited foreign material exists entirely at the antinode of the standing wave propagating across the thickness of the quartz crystal, so that the foreign deposit could be treated as an extension of the quartz crystal. Therefore,
1. The layer on the electrode must be rigidly attached to the crystal surface, so that it moves with it. Such condition exists, for example, in the case of monolayer adsorption of small molecules, or for the deposition of thin layers of metals.

2. The added mass should be much less than the mass of the crystal \( \left( \Delta m / m_{\text{quartz}} \approx 2\% \right) \). If the foreign film is thin enough, the error, resulting from the discrepancy between the acoustic propagation characteristics in the quartz and in the film, is negligible.

3. The Saurbrey equation assumes that the frequency shift resulting from a localized deposit is equivalent to the contribution of that deposit when it is a portion of thin film of identical thickness distributed over the entire active QCM area. However, a general expression that account for localized or nonuniform mass deposits covering the QCM electrode to \( r = r_e \) (where \( r_e \) is the radius of the excitation electrodes, between which the electric field induces crystal motion) is given by:

\[
\Delta f = \left( \frac{1}{\pi r_e^2} \right) \int_{0}^{2\pi} \int_{0}^{r_e} S(r, \theta) m(r, \theta) r dr d\theta
\] (9)

where \( S(r, \theta) = df/dm \) is the differential mass sensitivity and \( m(r, \theta) \) is the mass distribution with respect to \( r \), the distance of the deposit from the center of the crystal, and \( \theta \), the angle in the crystal plane. In several works [23-26] the mass sensitivity distribution of the quartz crystal microbalance for AT-quartz resonators by QCM measurements in conjunction with SEM was determined. It was found that crystal contouring increases sensitivity toward the resonator center while reducing the extent of field fringing (where the vibration amplitude can be considered to be essentially zero at the edge of the electrodes), forming Gaussian like shape as showing in Fig.
5. Increasing solution viscosity reduces the sensitivity to mass changes in the center of the resonator and increases field fringing, while an increase in the rigid mass within the electroded area confined the sensitivity to the center of the resonator.

While the differential mass sensitivity was shown to be a function of radial distance from the center, the integrated mass sensitivity was shown to change slightly at small loading and become relatively constant for larger loadings [9,28-31]. The vapor deposited electrodes and the immersion of the crystal in a liquid seem to serve alone the function of keeping the vibration amplitude confined to the electrode region, thereby bringing the value of the integrated mass sensitivity to be relatively constant.

The implication of this differential radial mass sensitivity for EQCM applications is that the distribution of any mass changes at the electrode surface must be known, whether or not it is uniform.

The sensitivity of the EQCM can be enhanced through the use of crystals with high fundamental frequency as followed from Eq. 8. The disadvantage of it is that such crystals are necessarily thin and fragile. Another way is to drive the crystals to higher harmonics modes. In that case a greater complexity in the oscillator circuitry is needed.

Several attempts have been made to expand Sauerbrey equation by including a number of other parameters, associated with the deposited thin film as the Z-match method [32]. The Z-match and other methods will discuss below.

Most of the EQCM measurements are done with quartz crystal exciting to the fundamental mode, usually between 5 –10 MHz. The exciting signal frequency must be close to the resonant frequency of the piezoelectric element.

As was shown, the amplitude of the displacement is known to depend on the driving voltage and on the total mass loading and it is usually, for AT cut, in the range of 10 to 100 nm.
1.1.3.1. Expanding the Sauerbrey equation – The Z-match and other technique

Significant improvement in Sauerbrey equation has centered on the explicit incorporation of the elasticity [32,33] and the extension of the measurements to higher harmonics [34]. The significance of taking into account properties of the deposit at large loading was explained in the former section. Lu and Lewis gave simple [32] equation for the dependence of $\Delta f_{\text{mass}}$ on $\Delta m$:
\[
\tan \frac{\pi f_c}{f_0} = -\frac{z_f}{z_q} \tan \frac{\pi f_f}{f_f}
\] (10)

where \(f_c\) is the resonance frequency of the composite resonator formed from the crystal and the film present at the surface, \(f_f\) can be thought as the resonant frequency of the freestanding foreign film \((\Delta f = f_c - f_0)\), and \(z_f = \rho_f v_f = (\rho_f \mu_f)^{\frac{1}{2}}\) and \(z_q = \rho_q v_q = (\rho_q \mu_q)^{\frac{1}{2}}\) are the acoustic impedance of the film and the quartz, respectively. This treatment explicitly accounts for the difference in the acoustic impedance of the quartz substance and the deposited mass.

When using this equation the density, \(\rho_f\), and the shear modulus, \(\mu_f\), of the deposited material should be known. These quantities may be known for metallic deposits, but will frequently be unknown for other electrochemically generated films.

A method to find the acoustic impedance of the film [34] make use of the fact that the response of the quartz crystal to varying acoustic impedance of the foreign film is different at the fundamental and harmonic frequencies. Measurement of the changes in resonant frequency at more than one frequency thus provides a method for obtaining \(z_f\).

When mass loading, from the deposit, causes changes in the resonant frequency of less than 2\% of \(f_0\), Sauerbrey equation may be used. Lu equation is accurate for frequency changes of up to 40\% of \(f_0\).

Except from the z-match there are other relationships that take into account other parameters. Miller and Bolef [35,36] considered the propagation of acoustic wave from the quartz into the deposited film and showed that the frequency depends on the shear wave velocity and density of both the film and the quartz. Glassford [37,38] analyzed the frequency response associated with an imposed liquid film and droplet deposit. Mecea and Bucur [39] considered the mechanism of thin film interaction with the elastic properties of the resonating quartz crystal and related between the frequency shift and the electrode, film and quartz diameter.
1.1.4. The Solution Viscosity

The first two expressions given for the QCM transferred from air into the solution, were empirical equations, which considered the conductivity and the specific gravity of the solution [40,41]. In 1985 Bruckenstein and Shay [16] and Kanazawa and Gordon [43] developed models that predict the frequency change for the immersed crystal which considered the viscosity and density of the solution. A similar study has been reported by Hager[44]

The vibrations of the AT-quartz crystal parallel to the QCM liquid interface results in the radiation of a shear wave into the liquid, as shown in Fig. 6. The instantaneous shear wave velocity decay in the x direction (parallel to the resonator-liquid interface) as an exponentially damped cosine function according to:

\[ V_x(z,t) = V_0 e^{-kz} \cos(kz - \omega t) \]  

(11)

where \( k \) is the propagation constant, \( z \) the distance from the resonator surface, \( V_0 \) the maximum amplitude of the shear wave, and \( \omega \) the angular frequency.

The inverse of the propagation constant \( k \) is the decay length, \( \delta \) which is equal to:

\[ \delta = \frac{\eta_i}{\sqrt{\pi \nu_i \rho_i}} \]  

(12)

Where \( \eta_i \) and \( \rho_i \) are the density and the viscosity of the solution. The decay length represents the distance at which the amplitude of the shear wave decays to 1/e of its maximum value at the interface. For dilute aqueous solution the velocity decay length is about 230 nm, which is large compared to the Debye reciprocal length (1 nm) in 0.1 M solution. If the viscosity of the film in contact with the resonator is infinity large, the acoustic wave will propagate without loss.
Fig. 6. Description of the shear wave propagation in a Newtonian fluid in terms of shear velocity in the $x$ direction (parallel to the resonator-liquid interface) as a function of distance from this interface. The circles represent liquid molecules at the interface, at which no slip condition is assumed – the molecules move with the same velocity and amplitude as the resonator [21].

On the basis of this description, in which the quartz crystal resonator is treated as a lossless elastic solid and the liquid is purely viscous fluid, Kanazawa and Gordon [43,44] developed Eq. 13.

$$
\Delta f_{viscosity/density} = - \frac{f_0}{3} \left( \frac{\eta_L}{\pi \eta_q \rho_q} \right)^{3/2}
$$

The interaction of the vibrating quartz crystal with the viscous medium is expressed by a decrease in frequency, which is proportional to the square root of the solution viscosity and density product.

A decrease of ca. 0.94 KHz is expected when a 6 MHz QCM is immersed in water. Stockbridge [45] has derived similar equation twenty years earlier for the behavior of the QCM in contact with gases.

Other models, considering different parameters were developed. Muramatsu [46] developed a linear relationship between $\Delta f$ and $\left( \eta_L / \rho_q \right)^{1/2}$ for alcohol water solutions. They considered electromechanical coupling for the computation of the equivalent circuit parameters. Yao and Zhou [47,48]...
showed that the response on the quartz crystal dependents on the dielectric constant and the conductance of the liquid, and later proposed an electromechanical equivalent circuit model for a quartz crystal immersed in a liquid. They found a relationship between the equivalent circuit parameters, series resonance frequency shift of the quartz crystal and the density, viscosity, specific conductance and the dielectric constant of the liquid. Shana et al [49] studied a thin film of viscous liquid by considering also the piezoelectric effect. A relationship between the shift in frequency and the changes in the interfacial surface structure, surface free energy and interfacial viscosity was shown by Thompson and co-workers [50]. In this work they showed that the chemistry at the interface could lead to perturbation of acoustic wave transmission, caused by alteration of the partial slip boundary condition at the interface. For a Newtonian liquid, the penetration depth of the wave is about $1\,\mu m$, as calculated by the Navier Stokes equation. Therefore, changes in the interfacial free energy and viscosity within this range can be associated with new deposited material or molecular reorientation in the interfacial boundary layer.

1.1.5. Viscoelastic properties

As discussed previously, changes of mass on the EQCM electrode leads to a shift in frequency. However, the resonance frequency is affected not only by the rigid mass attached to the surface but also by the viscoelastic properties of the adsorbed layer, especially for adsorb polymers or thick layers. Reed [51] derived an equation for the case when both, the shear modulus and the viscosity of the film, are taking into account:

$$\Delta f_{\text{viscoelastic}} = -2f_0^2\left(\eta_f\rho_f\right)^{1/2} \left[\left(\Delta m/A\right) + \left\{\Delta\left(\eta_f\rho_f\right)^{1/2}/\left(4\pi f_0^2\right)^{1/2}\right\}\right]$$  \hspace{1cm} (14)

The first term in this equation corresponds with the mass changes and the second term to the properties of the layers.
This is only a general model of viscoelastic overlayer from which limiting cases should be retrievable. In order to separate between the change of mass and the change in the viscoelastic properties of the film, an impedance analyzer that records the admittance characteristics near the resonance frequency is use, as will discussed bellow.

Martin et al derived the mechanical admittance for an AT-cut quartz crystal microbalance (QCM) simultaneously loaded by a surface mass layer and a contacting Newtonian liquid. The resulting model is a modified Butterworth-Van Dyke equivalent circuit (which will discussed later), having circuit elements that are explicitly related to physical properties of the quartz, perturbing mass layer, and contacting liquid. Mass accumulation causes a simple translation in frequency of the resonance peak, while increasing the density-viscosity product of the contacting solution causes both a translation and a damping of the resonance peak. With the model, changes in mass can be differentiated from changes in solution properties.

D. Johannsmann, K. Mathauer, G. Wegner and W. Knoll [53] studied the application of quartz crystal resonator to the viscoelastic characterization of thin organic layers. They determined the frequencies of its resonance as well as the corresponding damping constants. A parallel ellipsometer setup is used for the simultaneous determination of optical thickness. When one side of the quartz plate is coated with a viscoelastic layer, the frequencies and the damping constants of the acoustic modes change. While in the limit of ultrathin films these changes depend only on the mass, thicker films show pronounced viscoelastic effects. Results are presented for a Langmuir-Blodgett-Kuhn film consisting of the molecular composite poly (gamma – methyl – L – glutamate – gamma – n – octadecyl - L - glutamate). The application of the Sauerbrey equation to polybithiophene polymer film form on the quartz crystal electrode was found to be inappropriate in all cases [54]. In those cases a departure from rigidity is indicated and the viscoelastic properties of the film should be considered. Muramatsu [55] measured the changes in the resonance frequency and
resonant resistance of quartz crystal during a viscoelastic change of coated films without a mass change.

Tiean et al [56] also considered the electrochemical coupling equivalent circuit model for a piezoelectric quartz crystal in liquids. They found the relations between the equivalent circuit parameters, resonance frequency shift of quartz, the density, viscosity, specific conductance and the dielectric constant of the liquid.

1.1.6. Temperature

The temperature dependence of the frequency of an AT cut quartz crystal is shown in Fig. 7. For a limited range of temperature (0°C - 80°C), the dependence is relatively small and may be linearized in the form:

\[ \Delta f_{\text{temperature}} = -C_T f_0 \Delta T \]  \hspace{1cm} (15)

The numerical value of \( C_T \) depends on the design and manufacturing procedure of a given crystal. Different crystal designs have different temperature coefficient as shown in Fig. 7, where the temperature dependence is plotted for two crystals differing in the relation between thickness (a) and length (b). This intrinsic temperature dependence of the resonance frequency of a quartz crystal is caused by changes in \( \rho_q \) and \( \mu_q \) with the temperature. The value of \( C_T \) for a crystal with dimension of 5 mm radius and 0.2 mm thickness is \( 4 \times 10^{-7} \) degree\(^{-1}\). Therefore, the frequency shift due to temperature effect for a crystal with fundamental frequency of 6 MHz is 2.4 Hz degree\(^{-1}\). The AT cut is popular partially because of this relatively small temperature dependence around room temperature. Other cuts have a more pronounce dependence of frequency shift with temperature [57].
Changes of frequency due to temperature effect occur also when the crystal is immersed in a solution, because of the coupling between the acoustic shear wave and the solution. The product of $\rho_i$ and $\eta_i$ changes with temperature, resulting in frequency shift that can be calculated employing Eq. 13. This frequency shift can reach a few tens of Hz. For example, the values of pure water of $\rho_i$ at 20 and 25°C are 0.99823 and 0.99707 g cm$^{-3}$, respectively and the values of $\eta_i$ at those temperatures are $1.002 \times 10^{-2}$ and $0.8904 \times 10^{-2}$ g cm$^{-1}$ s$^{-1}$ respectively. Using these values result in a calculated frequency shift of 41 Hz.

1.1.7. Roughness

One disadvantage of solid electrode is that the real surface area is not known. This parameter is relevant for the calculation of the fractional surface coverage, when relating this value to the observed frequency shift.

The liquid molecules that can be entrapped in the recessed regions on the surface cause another effect related to the roughness. The entrapped molecules or part of them, may vibrate with the crystal, adding to it virtual weight. The amount of trapped liquid depends on the recess geometry and size. Similar case can occur in the case of thick films by the porosity of the deposit. If a film is porous, then significant amounts of mass

Fig. 7. Frequency/temperature characteristic of AT cut quartz crystal[57].
may be trapped within the pores of the film causing a decrease in frequency.

Roughness causes deviations from the Sauerbrey equation since a uniform mass distribution is expected. Film uniformity refers to macroscopic features with long length scale. Actual electrode surfaces are unlikely to possess truly uniform films. As long as the roughness is not longer than the acoustic wavelength or the nonuniformities are randomly distributed, the Sauerbrey equation can be confirmed and average thickness is measured.

Schumacher [58] use the EQCM to probe surface reconstruction on the metal electrodes subjected to an electrochemical oxidation/reduction cycle. Similar studies with copper and silver were also performed [59,60]. Beck [61] analyzed the influence of the surface microstructure on frequency changes. A liquid that was rigidly coupled to the surface by inclusion in voids or narrow channels was distinguished from the liquid that was viscously coupled with the surface. Buttry and Ward [62] presented a model of a corrugated surface comprising hemicylinder of diameter d. Water trapped inside these cavities would be equivalent to a rigid layer of a thickness of d/2. Calculation predicted that approximately 80% of the observed frequency shift could be attributed to roughness effect. Urbakh and Daikhim [63-66] discussed the frequency shift due to random and periodical corrugation. They found a relationship between the frequency change and a correlation function for the roughness. Valuable information on the surface morphology (as the average height and the correlation length of the surface roughness) can be obtained from QCM measurements of solutions with different viscosities. Tsionsky et - al [67] discussed the behavior of QCM in nonadsorbing gases at high pressures. In the cases studied the effect of roughness could be separated and different QCM response was observed for different surface roughness.
Fig. 8. Different type of surface roughness (a) small roughness, \( \delta >> h \) (b) large roughness, \( \delta << h \) [67].

The relationship, between the characteristic sizes of surface roughness and the decay length of the fluid viscosity, determines the form of the dependence of the frequency of the quartz crystal resonator on the properties of the fluid and on the morphology of the interface. The roughness can be characterized by the average height, \( h \), the average lateral length, \( a \), and the average distance between inhomogeneities, \( L \) (Fig. 8). The shift in frequency induced by the layer is:

\[
\Delta f_{\text{roughness}} = \frac{n f_0^{3/2} (\rho_i \eta_i)^{1/2}}{(\pi \rho_i \eta_i)^{1/2}} \Psi \left( \frac{a}{\delta}, \frac{a}{L}, \frac{h}{a} \right)
\]  

(15)

where \( \Psi \) is the scaling function.

Three surfaces were studied with different roughness. A linear dependence between the frequency shift and \( \rho_i \) was observed in all the cases but with different slopes. A more detailed analysis between the roughness and the frequency shift was not obtained since the roughness observed by independent techniques cannot be related in a simple manner to the roughness model.
It is important to mention in this context the differences between roughness definitions in the hydrodynamic context compared to the electrochemical one. In electrochemistry, roughness is a dimensionless parameter, the ratio of real surface area to the nominal one. In hydrodynamics roughness is an important aerodynamic factor in turbulent flow over flat surfaces. Very near the surface velocities are always small implying a thin layer of laminar flow. At rough surface the protrusions are high enough to eliminate this laminar region and make the flow turbulent over all domain. Roughness in hydrodynamics has the dimension of length and is associated with the effective height of the protrusions.

1.1.8. Compression

Stockbridge showed [45] that the frequency of QCM increases linearly with pressure due to the effect of hydrostatic pressure on the elastic modulus of quartz according to Eq. 16:

\[ \Delta f_{\text{compression}} = 1.4 \cdot 10^{-9} \cdot f_0 \cdot P \]  

where \( P \) is expressed in torr. The same expression can apply for the EQCM, where the compression is caused by the pressure of the fluid. The expression is independent of the nature of the gas or the fluid. Stockbridge verified this equation for the case of gases up to pressure of 1 atm and Susse [68] verified it for liquids up to 10 atm.

Heursler et al derived another expression for the effect of stress due to hydrostatic pressure. They found a parabolic dependence of the QCM frequency on hydrostatic pressure, \( P \).

\[ f_0 - f_{0\text{max}} = C(P - P_{\text{max}})^2 \]  

where \( C \) is a constant.
Tsionsky et al [70] investigate the effect of pressure in the gas phase, for the case of benzene adsorption on gold. A monolayer was observed at partial pressure of about 60 torr. The corresponding shift in frequency, calculated from Eq. 17 is 0.5Hz. This is evidently an important effect for the study of submonolayer adsorption, as it gives rise to a frequency shift corresponding, in this case, to about 20% of a monolayer.

Strain effects arising from thick films can also affect the applicability of Sauerbray equation. Compressive stresses in metal films on the QCM are known to result in frequency shifts unrelated to mass changes with a decrease in frequency for AT-cut crystals. BT cut shows frequency shift with opposite in sign, resulting in an increase in the frequency shift. Several works used double resonator method that uses both AT and BT crystals to evaluate stresses in the metals [71-74]. Cheek and O’Grady studied the effect of compressive stress on EQCM frequency response during electrochemical hydrogen absorption into palladium films [73]. In this study a large frequency shifts observed during hydrogen absorption on AT-cut crystals but only a small shift on BT-cut. This is consistent with the development of compressive stress in the palladium films during hydrogen absorption. By using hydrogen and deuterium the mass and stress effects were separated. No stress was found in the films of nickel-iron alloy and nickel [74] however, stresses were found in amorphous La-Ni thin film [75]. In the later case, the stress in the film contributes more than 80% of the change in the resonance frequency of the AT-cut quartz crystal.

1.1.9. Equivalent circuit

Cady [76], Van Dyke [77], Dye [78] and Crane [79] showed that the electric properties of piezoelectric resonators may be deduced from an equivalent circuit consisting of resistors, inductors and capacitors. The method used to derive the equivalent is based on solution of the equations
of motion applied to the crystal covered with electrodes [57]. The equivalent circuit for an AT – cut crystal (in air) is shown in Fig. 9a:

Fig. 9. Equivalent circuit of a quartz crystal unit oscillates in air (upper picture) and in solution (lower picture) [80].

where $C_0$ is the electrical capacitance of the quartz between the electrodes, $R_1$ correspond with the dissipation of the oscillation energy (cause by viscous solution and the mounting of the crystal) $C_1$ correspond with the stored energy in the oscillation (i.e. the elasticity of the crystal and the surrounding medium) and $L_1$ correspond with the inertial component of the oscillation – i.e. changes of mass on the electrode.
In air, the electrical parameters in terms of the crystal properties are

\[
C_0 = \frac{D_0 \varepsilon_0 A}{t_q},
\]

\[
C_1 = \frac{8 A \varepsilon^2}{\pi^2 t_q c},
\]

\[
R_1 = \frac{t^3_0 r}{8 A \varepsilon^2},
\]

\[
L_1 = \frac{t^3_0 \rho}{8 A \varepsilon^2},
\]

(18)

in these relationships, \( D_0 \), is the dielectric constant of quartz, \( \varepsilon_0 \), the permittivity of free space, \( r \), a dissipation coefficient corresponding with the energy losses during oscillation, \( \varepsilon \), the piezoelectric stress constant, and \( c \), the elastic constant. Only \( C_0 \) does not depend on \( \varepsilon \), which mean that \( C_0 \) does not participate directly in piezoelectricity. \( L_1 \) depends on the density, and the quantity \( \frac{t^3_0 \rho}{8 A \varepsilon^2} \) is equivalent to the mass per unit area in the Sauerbrey equation.

In the case of quartz crystal immersed in the solution a model was proposed as illustrated in Fig. 9b. \( L_2, R_2 \) are the motional inductance and resistance due to liquid loading and \( L_3 \) is the motional inductance due to mass loading. \( C_p \) is the parasitic capacitance of QCM and test fixture. The arm, that contains the inductance and resistance, is called the motional arm. It is believe that analyzing the result using the equivalent circuit will lead to better understanding of the measured variables.
Fig. 10. Admittance spectrum of the complete quartz crystal unit in the vicinity of its resonance. $f_m$ is the resonant frequency of the motional arm. $f_s$ is the serial resonance frequency of the complete equivalent circuit. $f_p$ is the parallel resonance frequency of the complete equivalent circuit.

Fig. 10. represents an admittance spectrum of the equivalent spectrum showed in Fig. 9. Several workers have analyzed the circuit in Fig. 10. with some parameters as: $f_s$, the frequency of zero phase, where the current flowing through the crystal is exactly in phase with the applied voltage.

$$f_s = \frac{1}{2\pi \sqrt{L_1 C_1}}$$

$Q$ is the quality factor of the resonator, which can be calculated from the sharpness of the resonance:

$$Q = \frac{1}{2\pi f_s C_1 R_1} = \frac{2\pi f_s L_1}{R_1}$$

Many other examples exist.

When the EQCM is loaded by viscous coupling to a liquid, its conductance spectrum exhibits predictable changes. From Eq. 20, which shows the reciprocal dependence of the quality factor, $Q$, on the value of $R_1$, it is predictable that the increase in viscous loss, which appears as an
increase in $R_1$, will lead to a decrease in $Q$. A linear dependence was found between $R_1$ and $(\rho \eta_1)^{1/2}$.

Martin et al [52] developed a model in which the electrical admittance was derived for an AT-cut quartz crystal loaded by a surface mass layer and contacting a Newtonian liquid. Their model is a modified Butterworth-Van Dyke equivalent circuit, having circuit elements that are explicitly related to physical properties of the quartz, perturbing mass layer, and contacting liquid. Adding mass on the surface causes a simple shift in the resonant frequency peak, whereas increasing the density—viscosity product of the contacting solution causes both a shift and the damping of the resonance peak. With their model, changes in surface mass can be differentiated from changes in solution properties.

Noel and Topart [81] reported that surface structure can be studied by impedance analysis. They found that the inductance is a linear function of mass for elastic and viscoelastic films, and that the calibration range of EQCM is extended by impedance analysis. These advantages result from the separation of mass and energy loss measurements by decomposition of the composite admittance of the resonator into inductive and resistive components, respectively. Katz and Ward [82] developed a method based on a high-frequency thickness shear mode AT-cut quartz resonator to probe dynamically the mechanical characteristics of a thin polymer film. The film properties are measured at a frequency where the vibrational amplitude is the smallest, minimizing nonlinear contributions. They demonstrated that the shear mode quartz resonators could be used to investigate solvent dynamics in polymer films at high concentrations that are inaccessible by other experimental methods.
1.2. Applications

The quartz crystal is used as an important in-situ technique, for variety of purposes. It is important to remember that the QCM measures frequency changes that result from a variety of phenomena and not only due to mass changes. Performing a careful experiment and analyzing the data correctly can yield valuable information for the phenomena examined. Several examples will be discussed below. The examples discussed are limited only to electrochemical measurements in the range of submonolayer adsorption.

1.2.1. Electrostatic adsorption

Several studies on the electrical double layer have been reported. The intuitive guess is that no frequency shift should be observed, since there is no specific adsorption on the surface. However, in all the cases studied, a significant dependence of the frequency shift on potential was observed. Considering only the weight of the ions cannot explain the observed frequency shift. Explanations, as changes of the interface properties (viscosity, density etc.) or weight of the solvation shell and ion pair, were given to explain the observed frequency shift.

Kautek et al [83] measured the response of the EQCM in electrolyte solution. In order to explain the observed frequency shift, they treated species in the rigid outer and inner Helmholtz layer as contributing to the mass change.
Ions in the diffuse double layer and contribution of the solvent structure were considered as part of the changes in the viscosity and density. They found that the frequency changes were primarily caused by ion solvation and ion pair formulation, and not due to changes in the solution viscosity and in the roughness. At this work the authors considered that specifically adsorbed anions have about a half of their original solvation shell on the surface. Lateral electrostatic repulsion and steric crowding limit the saturation coverage by their solvation shell. When anions adsorb specifically and form neutral ion pairs with alkali metal cations, electrostatic repulsion and solvation shell crowding is minimal and the surface excess attained is higher, since there is no lateral electrostatic repulsion.
Fig. 12. Frequency–potential curve for 0.1M (a) NaClO₄ (b) LiClO₄ (c) NaNO₃ (d) NaOH on Au[85].

Arai el - al [84] observed a dependence of the frequency shift on the applied potential. They relate this dependence that can be observed in Fig. 12, to the adsorption of anions and cations on the electrodes with their hydration shell. The importance of taking into account the adsorption of electrolyte solution is stressed.
Fig. 13. EQCM data of Au electrode in 0.1M NaClO₄ (---) or NaReO₄ (—) solution

Zenonas and Bruckenstein [85] measured the response of the quartz crystal in sodium perchlorate and perrhenate electrolyte (Fig. 13). They suggest that these anions are adsorbed on the gold surface and that water molecules are expelled from the surface during the initial stages of adsorption. The loss of water is about three times larger for perrhenate than for perchlorate. The difference in their ionic radius is insufficient to explain this difference. This was explained by the different properties of the anions.

Tsionsky el. al. [86] studied the response of the EQCM in 0.1M HClO₄, KNO₃ and KOH. Frequency shifts up to 5Hz were observed, as shown in Fig. 14. The contribution of the ionic mass was calculated from the Gouy – Chapman theory of the diffuse double layer. The frequency shift obtained due to changes of mass can account for only a change of frequency of 1 to 2 Hz. The rest of the observed frequency shift was
explain by changes of the viscosity in a thin layer adjacent to the metal surface, which could be caused by the following factors:

1. High concentrations of ions near the electrode surface, which can reach a value of 4.7M for 0.1M solution at a rational potential of 0.5V. The viscosities at these concentrations are higher by 20% for HClO\(_4\) and 60% for KOH than in pure water.

2. The field strength in the outer Helmholtz plane may reach values of \(3 \cdot 10^6\) V/cm. This field may be high enough to affect the structure of the solvent and change its local viscosity.

A model was developed to describe how such a change in the local viscosity could affect the frequency of the EQCM. In this model a quartz crystal with a thin film of liquid having a viscosity \(\eta_f\), greater than the
viscosity $\eta_s$, in the bulk of the solution, is assumed. The frequency shift caused by such a film is given by [86]:

$$
\Delta f_{\text{film}} = -C_m L \rho_f \left[ \left( 1 - \frac{\eta_s}{\eta_f} \right) + \left( \frac{\rho_f}{\rho_s} - 1 \right) \right]
$$

(21)

where $L$ is the thickness of the film, $\rho_f$ and $\rho_s$ are the density of the film and the solution respectively. The first term in the bracket describes the effect of surface film viscosity and the second term the influence of the mass of the ions in the film, drawn near the surface by electrostatic interactions.

From the above equation one can evaluates the viscosity of the film. The result of such calculation is shown in Fig.15. A behavior similar to bulk is obtained for the cases of KOH and KNO$_3$. There is no way to calculate or measure directly the viscosity in a charged film, but these values seem reasonable, although the model is admittedly oversimplified. A more detailed discussion will be given in the discussion section.

In another study [88], the response of the EQCM in 0.1 M KOH and CsOH was analyzed. Although very close response is obtained in both cases, it was found that the larger weight of Cs$^+$ is almost compensated by its smaller effect on viscosity.
Fig. 15. Comparison of the effective film viscosity calculated for the concentrations prevailing in the diffuse double layer in 0.1 M solution of KOH (1, open point) and KNO$_3$ (2, full points) on Au, with the viscosity of solutions of KOH (1') and KNO$_3$ (2') \[87]\.

Further details on the solvent structure in the double layer region can be obtained from comparison with organic solvent. One example is the conclusions obtained in the case where n-butanol was used as the solvent \[89\]. The adsorption of n-butanol in different orientations on the two sides of the pzc is expected from the results and will discuss further in the discussion section. An anomalous behavior in the presence of electrolyte was reported by Etchenique and Buhse \[90\]. These authors found that considering only mass changes lead to unreasonable conclusions. Impedance analysis indicates the presence of a viscoelastic nanometric sized layer close to the crystal with properties that depend on charge.

The pzc of a gold electrode in 1M NaClO$_4$ solutions with and without iodide ions was measured by Seo and Ueno \[91\] using EQCM. The addition of iodide shifted the pzc negatively due to strong specific adsorption of iodide ions. The surface excess of the ions was evaluated, from which the electrosorption valency of the iodide was determined to be $\gamma = -0.84$. 

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1.2.2. Specific adsorption

One of the challenging applications of the EQCM technique is the study of electrosorption. In most of the works discuss below the only parameters considered is the mass. Changes in the double layer properties and the dependence of the EQCM response in the double layer region on potential are usually not taken into account.

The first application of the EQCM to *in situ* measurement of mass changes from monolayer deposition or dissolution processes was reported by Bruckenstein and Shay [17]. These workers studied the formation of adsorbed oxygen monolayer on gold electrodes. A negative frequency shift was observed for formation of an adsorbed monolayer, as shown in Fig.16. The agreement between the mass change predicted from the charge measurement and that inferred from the frequency change was better than 10%. Hysteresis between the time of passage of electrochemical charge and the observed mass change (i.e., 40% of the charge for a monolayer was passed before any mass change was observed) was used to support a postulated place exchange mechanism for O electrosorption (in which O electrosorption is followed by exchange of Au and O to give a “buried” monolayer of O and an exposed monolayer of Au), which was consistent with several previously proposed mechanism.

![Fig.16. Simultaneous charge-potential and mass potential curves on Au, potential scan rate – 50 mV/sec. 0.2M perchloric acid [17].](image)

Schumacher et al [58] also used the EQCM to study the formation of electrosorbed oxide layer on gold electrode. They observed mass gain coincident with formation of the oxide layer (cf. Fig. 17). However, their conditions promoted the roughening of the surface. This roughening caused larger than expected frequency decrease for oxide formation, especially in alkaline and neutral media. This results was confirmed in a later study by Stockel and Schumacher [92], who also observed that the frequency decreases in aqueous sulfuric acid is smaller than expected. They postulated that place exchange only occurred in neutral and alkaline media, with monolayer discharge in acid, perhaps accompanied only by deprotonation of adsorbed water.

Gordon et al [93] applied the EQCM to the study of water adsorption on gold surfaces in acid media. As can be seen in Fig. 18, they observed a large increase in mass during the positive potential scan in the pre-oxide region (negative to the formation of surface oxide). This mass increase is virtually independent of the acid and is interpreted on the basis of adsorption of water via hydrogen bonding to the submonolayer of hydrous oxide (AuOH) generated in the pre-oxide region. They suggest that the mass increase is consistent with an increase in surface hydration by about 32 water molecules per AuOH site. Their conclusion is inconsistent with Bruckenstein [17] and Stockel [92] and is highly questionable.
Fig. 17. Frequency and current as a function of potential for Au in 0.01M NaOH. Scan rate 20mV/sec, Surface area of the deposits 0.33 cm² [58].

Fig. 18. Current – potential curve on Au electrode in 0.1M perchloric acid, scan rate 75mV/sec (upper picture) and the corresponding frequency potential scan (lower picture) [93].

The EQCM has also been used to measure the electrosorption of a monolayer on anions on the electrode surface. The electrosorption of bromide and iodide on gold electrodes was studied by Deakin et al [94], who showed that full monolayer coverage was attained at sufficiently
positive potentials. This conclusion followed from the evaluation of the mass changes, which occurred during the electrosorption process and the geometric constraints, imposed by the sizes of the halide ions. The slopes of the plots of the charge for electrosorption versus surface coverage obtained from the EQCM and presented in Fig. 19, were shown to provide the electrosorption valency, $\gamma$ (the ratio of the number of moles of charge passed to the number of moles adsorbate deposited).

![Fig.19. Integrated current versus electrode coverage during the adsorption of bromide and iodide on Au [94].](image)

Z. X. Shu and S. Bruckenstein [95] studied the adsorption and desorption of iodine-containing species on polycrystalline platinum electrode, using the EQCM and the RRDE. The corresponding curves are shown in Fig. 20. The EQCM studies demonstrated that 0.4 iodine-containing species is adsorbed per surface platinum atom in the double layer region. Both EQCM and RRDE studies show that one iodine-containing species is adsorbed per surface platinum atom at potentials in the limiting current region for the oxidation of dissolved iodide to iodine. They identify this species as an iodine atom and found the mechanism of the process.
W. Stockel et al. [96] found the electro sorption valency of chlorine, bromine and sulfate adlayer on gold. They used the EQCM in conjunction with CV and capacitance measurements. The electro sorption valency sequence was found to be Cl\textsuperscript{−}<Br\textsuperscript{−}<SO\textsubscript{4}\textsuperscript{2−}. Apart of the electro sorption valency, the heterogeneity constant C (which describes the dependence of the adsorption enthalpy on the degree of the surface coverage for the Temkin isotherm) was calculated by combining the Sauerbrey equation with Faraday type law. A good agreement was found with the values reported by Sedlmaier and Plieth [97].
Simultaneous acquisition on EQCM and optical reflectivity of the adsorption of bromide in aqueous solutions was applied by Mo et al [98]. By this approach they correlate between the change in weight and the relative reflectivities which correspond to the adsorption. The results obtained, Fig. 22, were in agreement with results of others.

![Figure 22](image)

Fig. 22. Plot of mass change and $\Delta R/R$ vs. potential in 0.1M NaF on Au electrode [98].

A comparison, of the adsorption of iodide ion on gold electrode by specular reflection method with that by EQCM, was made by Arai [99]. Good agreement was observed between the results of the two methods. The potential dependence of the reflectivity and of the EQCM was essentially the same. At a potential of $-0.1V$ vs. SCE the maximum adsorption from 0.1mM NaI solution was observed. From this results the surface coverage, $\theta$, and the electrosorption valency was found. The electrosorption valency found (1.0) is very close to that found by Deakin (1.01).
Lei, Uchida and Watanabe [100] studied the adsorption of halide anions by the EQCM and the change in the surface excess of water that is directly related to their adsorption. They found that the strength of halide adsorption is I\(^{-}\) > Br\(^{-}\) > Cl\(^{-}\) > F\(^{-}\) (as shown in Fig. 23). The surface coverage of the halide dependence on the potential was determined as well as the maximum coverage. The potential dependence of the change of the surface excess of water was also obtained. A detailed study on I\(^{-}\) adsorption revealed that the coverage of iodide changed little in the potential range of 0 to 0.3V vs. Ag/AgI, and the maximum coverage was 43% at 0.55V. The sudden small increase in the curve of surface concentration of adsorbed iodide against potential hints to the existence of an electrosorption effect and phase transition phenomenon in the formation of the adsorbed iodide layer on Au(111) which is related with the increase of iodide coverage and the simultaneous expulsion of water from the surface. [101].

![Fig 23. (A) Cyclic voltammogram and (B) The simultaneous change in frequency on Au in 1mM KI, KBr, KCl and KF [100].](image)

The adsorption of pyridine was studied by Scendo and Malyszko [102]. Fig. 24. shows the frequency shift vs. potential curves obtained in 0.4M NaClO\(_4\) solution in the absence and in the presence of pyridine. A rapid decrease in frequency (i.e. mass increase) is observed during the initial positive scan, which reach a broad minimum in the potential as a
result of the adsorption of pyridine. With continue positive scan, a gradual frequency increase occurs.

Fig.24. Frequency change vs. potential of (a) electrolyte solution 0.4M NaClO₄ (b) 1mM pyridine (c) 50mM pyridine on Au electrode. Scan rate 20 mV sec⁻¹ [102].

Similar curve is obtained during the backward scan but shifted to more negative potentials. Considering only mass change was not enough to explain why at higher pyridine concentration the frequency shift was very big. The explanation given by the authors was that at this high pyridine concentration the composition of the surface phase becomes similar to that of the bulk of solution. Hence the thickness of the liquid layer attached to the electrode surface increases and changes drastically the coupling between electrode and the solution.
Fig. 25. Voltammetric and frequency response in 0.2M NaOH solution containing 5mM CH$_3$CH$_2$S$^-$ on Ag electrode [103].

The oxidation of HS$^-$ and CH$_3$CH$_2$S$^-$ on Ag electrode resulting in adlayer formation was determined by voltammetry, coulometry and in EQCM measurement. Three characteristic waves were observed in the voltammetric measurement of HS$^-$.

Following the EQCM results it was found that two of them correspond to the reversible 1-e$^-$ oxidative adsorption, resulting in the formation of a Ag adlayer.

The third wave corresponds to kinetically controlled oxidation of this adlayer, yielding a UPD layer of Ag$_2$S. Similar response was observed for CH$_3$CH$_2$S$^-$. In that case two voltammetric wave were observed that correspond to the adlayer formation involving at least two distinct structural phases (Fig. 25). Unlike the situation for HS$^-$ the resulting Ag- CH$_3$CH$_2$S adlayer is unable to undergo a second oxidative adsorption [103,104].

In another study the EQCM was used to control accurately and reproducibly the amount of alkanethiol self assembled onto the gold EQCM surface [105].
Fig. 26. Frequency potential response curves in (a) 0.2M NaClO₄ and (b) 0.2M NaClO₄ + 0.02M CH₃COONa on Au electrode [106].

Electrochemical characteristic of the Mn³⁺/Mn²⁺ and Co³⁺/Co²⁺ systems at Pt electrode in acetic acid solution was studied by RDE and EQCM [106]. From the EQCM results, shown in Fig. 26, they conclude that acetate ions are adsorbed vertically through the carbonyl group and that the acetate does not decompose under the experiment condition. The adsorption of acetate anions on the Pt surface takes place in the same potential range in which Mn²⁺ and Co²⁺ are oxidized. In contrast, the cathodic reduction of Mn³⁺ and Co³⁺ ions occurs on the bare Pt surface if the electrode potential is scanned in the positive direction.

Kouznetsov [107] studied the electrodeposition of Benzyl – dimethyl -dodocylammunium bromide on gold, using the EQCM. They calculate the effective equivalent weight of the reacting species (the ratio of effective molecular weight of the species to the number of electrons exchanged) as a function of the applied potential and demonstrated the influence of BDDB on the cathodic and anodic process. BDDB influences the process from very low concentration (1 µM). The decrease in frequency (Fig. 27) at negative potentials was considered to be due to hydrogen evolution. This disappeared completely in the presence of cationic surfactant (BDDB) which increases the hydrogen evolution overvoltage. At higher concentration of BDDB a condensed film is formed on gold. In a reverse
potential sweep, BDDB desorbed but about 10% of the organic layer remained upon reduction.

![Mass and voltammetric curves for electrolyte solution in 0.1M Na₂SO₄ and in solution containing 0.5mM BDDB on Au](image)

Fig.27. Mass and voltammetric curves for electrolyte solution in 0.1M Na₂SO₄ and in solution containing 0.5mM BDDB on Au [107].

Adsorption of anions on Cu-ad atoms (Fig. 28) and on the gold or Pt electrode substrates was studied by Watanabe et al [108,109]. In these cases the weight loss in the removal of the Cu-adlayer from the Au substrate was considerably larger than that expected from Faraday law, whereas the deviation for a Pt substrate was very small. This was explained by higher coverage with Cu ad-atoms and lower adsorption of bisulfate or sulfate anions on the Pt than on the Au. These effects are due to the difference in the electronegativity between Pt and Au substrates. Similar results obtained with perchloric acid as the electrolyte.
Fig. 28. Cyclic voltametry and frequency change on Pt. (A) 0.05M H$_2$SO$_4$. Copper ad-atoms were underpotentially deposited on Pt by keeping the potential at 0.4V in 0.05M H$_2$SO$_4$ +10$^{-5}$M CuSO$_4$ for (B) 5 min (C) 10 min and (D) 30 min [108].

Electrochemical and mass transport properties of isopoly and heteropoly anions during cyclic voltametry and by EQCM [110]. The anions studied (SiW$_{12}$O$_{40}$$^{4-}$, P$_2$W$_{18}$O$_{62}$$^{6-}$ and H$_2$W$_{12}$O$_{40}$$^{6-}$) adsorbed easily on gold electrode (Fig. 29). The two redox couple of SiW$_{12}$O$_{40}$$^{4-}$ and the three redox couple of P$_2$W$_{18}$O$_{62}$$^{6-}$ are not detected as adsorbed [110].
Works done not only in aqueous solution but also in nonaqueous solutions. Abbott et al [111] studied the adsorption of ions onto a gold electrode using an EQCM. Tetrafluoroborate anions and tetrabutylammonium cations form a monolayer, when adsorbed on gold from anisole solution (Fig. 30). In ethanol and methanol, anion adsorption did not occur. Cation adsorption occurred in both solvents, but to a lesser extent in methanol. The electrosorption of pyridine, n-butanol, tert-butanol and uracil on gold and silver electrode was studied in our laboratory [87,89,112].

In all these studies, considering only changes of mass could not explain the frequency shift observed. Changes in the properties of the interface should be taken into account. A detailed explanation of this issue is given in the discussion section.
Fig. 30. Mass change in 0.1M TBABF₄ in anisole on Au electrode [111].
2.1.3. UnderPotential Deposition (UPD)

Another interesting application of the EQCM is the study of the UPD of metals. The importance of knowledge on UPD process is that surface reactions are influenced by the UPD of submonolayer of foreign atoms. Bruckenstein and Swatthirajan [16] and Bruckenstein and shay [17] did the first UPD works. Two years later Melroy et al [19] determined the electrosorption valency for UPD of Pb on Au. A value for $\gamma$ of 2 was obtained, by comparison of the total charge and the total mass gain for a scan over the UPD region. The value of $\gamma$ obtained was in good agreement with those previously reported. Deakin and Melroy [113] reported on a very detailed study of the UPD of Pb, Bi (shown in Fig. 31), Cu and Cd on gold. For the case of UPD of Pb on Au, $\gamma$ deviated significantly from 2 at the current peaks in the UPD process. This was attributed

Fig.31. (a) Frequency shift of the EQCM during Bi UPD on Au electrode from 1 mM Bi + 0.1M HClO$_4$ (b) Voltamogram obtained during the Bi UPD (----) and the current expected from the observed frequency response (——) [113].
either to changes in $\gamma$ or variation in the charging current due to shifts in the pzc on the UPD adlayer with respect to that on Au. Deviations were also observed for the UPD of Bi on Au, which was explained by the desorption of weakly adsorbed anions. In another study [114] the UPD of Pb, Cd and Tl (shown in Fig. 32) onto Ag examined. Good agreement between the observed frequency shift and calculation was found for Cd up to 1.5 monolayers and for Pb up to 0.7 ML. An anomaly occurs for Tl. While the measured mass change is consistent with the expected value, each Tl ion seems to contribute approximately two charges upon adsorption before the completion of the first layer instead of one. In the second layer the value of discharge returns to the valence number $z = 1$. 
The deposition and dissolution of Cu ad-atoms on gold or platinum electrodes in H$_2$SO$_4$ electrolyte were investigated by Watanabe et al [115]. They demonstrated that higher coverage of Cu ad-atoms and lower adsorbability of SO$_4^{2-}$ anions was obtained on the Pt electrode than on Au. This was explained by the difference in electronegativity between Pt and gold. In a detailed studies of UPD of Pb on Au and Ag, a mass increase was observed during UPD of Pd on Au and a mass decrease for the case of UPD of Pb on Ag presented in as Fig.
33. In the later case, $BO_2^-$ ligands from a previously adsorbed anionic Pb species desorbed which causes the mass decreases [116-119].

![Voltamogram and mass change curves](image)

Fig.33. Voltamogram and mass change curves in 0.1M boric acid (left figure) and in 0.1M boric acid + $2.7 \times 10^{-5}$M Pb$^{2+}$ (right figure) at PH=9.1 on Ag electrode [117].

Wilde et al [120] also studied the UPD of Pb at electrodeposited platinum electrodes. At high Pb concentration, the EQCM responses during cyclic voltammetry is large as the UPD deposit develops and is stripped (Fig. 34). However, at low Pb concentration lower frequency shift is observed. The explanation that was given was that the UPD process is not at equilibrium under the conditions used in the latter case, and continues developing over the potential range between 0.45 V and -0.3 V. Mass response to simple injection experiments reveal the presence of adsorbed Pb on oxidized electrodes. Coverage of the adsorbed Pb increases with potential between 0.9 V and 1.2 V, and approaches 0.09 when the lead concentration in the solution is 2 mM and the potential is 1V. UPD of Pb at platinum thus involves a combination of discharge of adsorbed species and reduction of Pb ions from solution. UPD coverages were determined over a wide range of potential from mass transients, resulting from potential steps and the injection of Pb into the electrolyte. The isotherm obtained agrees well with previously published data and demonstrates that EQCM mass data can be
used for the estimation of UPD coverages. In a detailed study [121] it was found that the UPD of Pb influenced the oxidation of glucose and of formic acid [122,123].

![Fig.34. (a) voltammograms (b) mass response for lead UPD on Pt electrode in (-----) 0.1M HClO₄ (---) 0.1M HClO₄ + 10⁻⁴M Pb (--.--.) 0.1M HClO₄ + 2.10⁻⁴M Pb [120].](image)

A mechanism of adsorption of Pb²⁺ ion and UPD Pb on gold electrode in supporting electrolytes containing Cl⁻, NO₃⁻ and/or ClO₄⁻ was proposed by Zeng and Bruckenstein[124]. Their study combined the EQCM with data from X-ray photoelectron spectroscopy and time of flight secondary ion mass spectrometry (TOFSINS). The existence of adsorbed anionic ligands was demonstrated. It was found that the UPD of Pb goes
through the reduction of both an adsorbed Pb complex and a Pb species present in the supporting electrolyte. In another study [125] the UPD process of Pb was used to understand the adsorption and reorientation of 2,2'-bipyridine and 4,4'-bipyridine. The influence of these two bipyridine compounds on the Pb UPD showed that 4,4'-bipyridine adsorption on Au is surface - site selective and both 4,4' and 2,2' bipyridines adsorbate surface structure are potential dependant.

Fig.35. Voltammogram and mass response for 0.1M HClO₄ (dashed line) and after exposure to a solution 0.1M HClO₄ + 0.1mM Bi³⁺ for 15 min at 1.1V on Pt electrode[126].

The UPD of Bi was studied [126] at Pt electrodes in HClO₄ solutions. The extent cations adsorption prior to development of the UPD deposit in 0.1 M HClO₄ was found to be high. The mass changes observed when the potential is scanned into the UPD region are smaller than expected (Fig. 35). This was explained by fact that the deposit is formed largely from
species already adsorbed at the electrode surface. The mass response also reveals an arrest on the positive-going scan that is suggested to be the result of a change in the nature of Bi at the surface from Bi to BiOH$^{2+}$ or Bi(OH)$_2^{2+}$. When a Pt electrode with adsorbed Bi is examined in a 0.1 M HClO$_4$ electrolyte free of Bi, a mass increase is seen to be associated with the transition between UPD Bi and adsorbed Bi$^0$. This is attributed to the fact that the adsorbed Bi is largely present as hydrolyzed species.

A combined FTIR and EQCM study on the Zn UPD on Pt in KH$_2$PO$_4$ solution was reported by Aramata et al [127]. Adding Zn ions to KH$_2$PO$_4$ solution increases the intensities of IR bands with a negative increase of potentials less than or equal to 0.7 V, where Zn UPD takes place (Fig. 36). In this region, the weight on the Pt increases. The fractional coverage of Zn was found to be 0.75 at 0.05 V as two-electron transfer process. From this values the coverage of PO$_4^{2-}$ was evaluated as 0.27. It was discussed that the phosphate species adsorbs over the Zn ions on Pt in the form of HPO$_4$, where one of three P-O's seems to be bound to Zn on Pt.

The UPD of Cd [128] and Tl [129] on Au(III) was studied, using potential-step chronocoulometry and EQCM. The fractional surface coverage of Cd and Tl was determined (Fig. 37). In the potential region where Cd undergoes UPD, the coverage was observed by
chronocoulometry to rise to a limiting value of 0.66 ML. The electrosorption valency calculated on the basis of this coverage is 0.5, indicating that Cd adatoms are not fully discharged on the surface.

Fig.37. Frequency (——) and current (……..) response in 1 mM Cd\(^{2+}\) + 0.1M H\(_2\)SO\(_4\) (upper figure) [130] and 4.88 mM Tl\(^{2+}\) + 0.1M HClO\(_4\) [128] on Au electrode.

Potential-step chronocoulometry was used at various sulfate concentrations, to determine the surface coverage of SO\(_4^{2-}\) anion in the presence of UPD of Cd. EQCM measurements indicate that there is considerably larger mass change at the surface during UPD of Cd than that expected on the basis of the measured coverage of Cd and sulfate. The extra mass is explained in terms of additional sulfate required in the outer Helmholtz plane, to balance the residual positive charge on the underpotentially deposited Cd atoms. At anodic potentials, Tl adsorbs on the surface at a coverage that slowly increases up to 0.55 ML. At more cathodic potentials, the coverage rises sharply to a plateau of 0.79 ML where the surface is covered with a close-packed Tl monolayer.
Daujotis and Gaidamauskas [130] studied the UPD of TI on a polycrystalline silver surface in solutions containing specifically adsorbing anions (sulphate and chloride). The specific adsorption of TI cations on the silver surface at potentials positive with respect to the pzc appears to be enhanced by specific adsorption of anions (Fig. 38). This leads to ion pair formation between the specifically adsorbed TI cation and anion, even at potentials positive with respect to the UPD region. The electrode mass change measured by EQCM is smaller and this was explained as due to the discharge of TI cations from the adsorbed ion pairs. Agreement between voltammetric and EQCM data is found in the potential region closes to the bulk TI deposition where the adsorption of anions is weak and, consequently, there is little formation of ion pairs. The effect of $\text{SO}_4^{2-}$
and Cl\textsuperscript{-} anions on the UPD of Tl is in accordance with their adsorbing strength.

The adsorption of anions on gold electrodes with and without Cu adatoms in HClO\textsubscript{4} and H\textsubscript{2}SO\textsubscript{4} electrolyte solutions was investigated by EQCM [131]. A distinct increase in mass due to the specific adsorption of hydrated bisulfate and perchlorate anions was observed in Cu\textsuperscript{2+} - free solutions and their amounts were determined as a function of the potential (Fig. 39). The composition of the Cu-adlayer during formation or removal in the potential sweep was also determined in both electrolyte solutions. A pair of reversible anodic and cathodic peaks in the voltammogram for the first UPD Cu region in H\textsubscript{2}SO\textsubscript{4} was found to correspond to the reversible adsorption of Cu and the anions. In contrast, asymmetric features of the voltammograms for the second UPD Cu region in H\textsubscript{2}SO\textsubscript{4} and for whole processes in HClO\textsubscript{4} corresponded to the large changes in the Cu and anions adsorption, probably originating from a slow rearrangement of both species.

Fig.39. (A) Voltammogram (B) EQCM response in 0.1M HClO\textsubscript{4} and 0.05M H\textsubscript{2}SO\textsubscript{4} on Au electrode [131].
Tsionsky and Gileadi [132] studied the electroplating of silver and copper by EQCM. Deposition of Ag on Ag follows the expected behavior. For deposition of Cu, the linearity between frequency shift and added mass is maintained, but the slope was smaller (in absolute value), as shown in Fig. 40. This was attributed to the formation of Cu$^+$ ions, which diffuse in part into the bulk of the solution, without being further reduced. In the early stages of deposition of both metals on a gold surface, large deviations of the frequency shift from its calculated value were observed. For Ag, this deviation was explained as being due to the difference in the interaction of Au and Ag with the solvent. For Cu deposition on gold, the deviation was explain also as due to stress in the deposit. This stress, resulting from the difference in crystal parameters between gold and copper, can be relaxed partially at open circuit at room temperature.

![EQCM response deposition of Ag on Ag and Cu on Cu](image)

**Fig. 40.** EQCM response deposition of Ag on Ag and Cu on Cu (1) 1.5M KCN+0.3M AgNO$_3$ (2) 1M H$_2$SO$_4$+0.5M CuSO$_4$. $j=0.1$mA/cm$^2$. Circles are experimental data; Lines are calculation [132].
The effect of various ions on the frequency response of Pt electrode in the hydrogen UPD region was investigated [133]. The experiments were carried out in alkaline and acid solution with various concentrations of Cl\(^-\) or SO\(_4^{2-}\) ions (Fig. 41). Traces of specifically adsorbed ions, such as Cl\(^-\) ions, were readily detected with the EQCM. The effect of ClO\(_4\)\(^-\) and SO\(_4^{2-}/\)HSO\(_4\)\(^-\) anions on the frequency response is quantitatively the same. Large variation of the concentration of SO\(_4^{2-}/\)HSO\(_4\)\(^-\) anions in solution does not modify the amplitude of the frequency response. From these results, it seems that the specific adsorption of SO\(_4^{2-}/\)HSO\(_4\)\(^-\) anions on the Pt electrode cannot be considered as a possible cause of the observed frequency change.

![Fig. 41](image.png)

**Fig.41.** (A) Voltammogram and (B) EQCM response in 0.1M HClO\(_4\) (left figure) and in 0.1M H\(_2\)SO\(_4\) (right figure) on Pt electrode [133].

Hydrogen UPD was detected by EQCM responses for Pt electrodes prepared by electrodeposition, which showed the development of large frequency changes [134]. These changes are present only after extended cycling which is shown to result in loss of material from the electrode and in a decrease in the roughness of the electrode surface (Fig. 42). The large frequency changes disappear gradually as the pH of the contacting electrolyte increases and are associated with the presence of weakly adsorbed hydrogen at the electrode surface. As pH increases, the
increasingly negative charge carried by the Pt surface when adsorbed H is present acts to decrease and eventually remove the effect, presumably because of a less favorable interaction between the charged electrode and the aqueous solvent. The coupling between surface and solution also has a strong influence on the frequency response in the H-adsorption region, with extensive potential cycling and the consequent decrease in roughness leading to an apparent increase in coupling.

Fig.42. Voltammogram and EQCM in 0.2M H2SO4 on freshly prepared Pt electrode (left figure) and on aged (after 4930 cycles) electrode [134].

2.1.4. Research Objectives
The current dissertation aims at exploring various phenomena and processes occurring at the double layer. More explicitly, we study the geometry of adsorbed organic molecules on gold electrodes, the formation of three-dimensional structures extending beyond the first monolayer and viscoelastic properties of the diffuse double layer. We have also looked into the effect of altering the metal electrode from gold to silver.
A variety of experimental techniques were employed, but our primary tool was the EQCM. Moreover, it was one of our goals to explore and extend the spectrum of information one can extract from this method.
2. Experimental

2.1. The EQCM – General description

2.1.1. Consideration in the design of the quartz crystal

Proper design of the quartz crystal reduces erroneous result causes by coupling of the fundamental mode with anharmonic modes, delaminate of the electrode deposited on the quartz crystal and undesirable effect due to the configuration used to mount the crystal.

The use of circular crystals increases the symmetry and greatly reduces the number of allowed vibrational modes. Crystals diameter are between 1 to 2.5 cm. Small crystals have the advantage of being less expensive, but they suffer from the serious drawback that the structure used to amount the crystal are closer to the piezoelectricity active area, so the influence of stress from the mounting can become problem. Larger crystals allow for the mounting structures to be further from the region of the crystal undergoing displacement.

Contouring one face of the crystal and reducing the size of the exciting electrode have the effect of trapping the acoustic energy and hence reducing the coupling with unwanted mode. Reducing the electrode diameter limits the excitation to the central area. Contoured crystal traps the energy of the traveling acoustic wave through what is essentially total internal reflection, before it reaches the edge. Energy is reflected back to the center where it can constructively interfere with other newly launched waves, essentially making a small crystal appear to behave as though it infinite in extent. With the crystal vibration restricted to the center, it is practical to clamp the outer edge of the crystal to a holder without producing undesirable effects. Contouring also reduces the intensity of response of generally unwanted anharmonic modes, hence the potential for an oscillator to sustain an unwanted oscillation is substantially reduced.
The dimensions of the electrodes and the crystal disk have a strong influence on the coupling of other modes to the thickness shear mode. This coupling represents a source of spurious frequency changes, which must be addressed, for optimum performance of the EQCM. The critical dimensions are the thickness of the quartz disk, the diameter of the crystal and the diameter of the concentric electrode pad [135]. For a ratio between the diameter of the crystal and its thickness greater than 50, unwanted mode may be suppressed by 40 dB.

The temperature dependence of the frequency of an AT cut quartz crystal depend on the plate orientation, crystal dimension, electrode dimension and harmonic. The dependence on the crystal orientation can be seen in Fig.7.

The two predominant types of AT-cut crystal used for mass measurements are the plane and plano convex. Plane crystals have both disk surfaces parallel to within 1µm. Plano convex crystals have one side of the disk flat and the other ground to be a very slightly concave. A typical range of radii of curvature for a 1-inch diameter, 5 MHz crystals would be 10-50 cm. Contoured plano convex crystals exhibit high sensitivity within the electroded regions but suffer negligible field fringing compared to plano resonators. This suggests that QCM measurements with plano convex crystal may be more reliable see Fig 43.

The standard electrode pattern is a keyhole pattern but ring/disk electrodes are also available. A thin (20-50nm)-adhesion layer of Cr, Si or Ti is usually deposited directly onto the quartz crystal to improve in the adhesion of the metal electrode. Spurious electrochemical responses can sometimes results, if diffusion of the material from that adhesion layer to the electrode surface occurs. Au and Ag electrodes have been the most commonly used in EQCM studies because of ease of preparation. Cu, Pt and Ni and other metals have also been employed. In principle any type of material that can be deposited onto the surface of the underlying metal electrode, either by electrodeposition or from vacuum, can be used. The
only limitations on the use of such materials are that they have a good
adhesion to the underlying electrode and the deposition must be carried out
in such a way that the temperature of the quartz crystal does not exceed
573°C, above which α-quartz loses its piezoelectric activity. When the
electrodes become delaminated due to poor adhesion of the underlayer,
large discontinuous changes in frequency occur, which render a particular
crystal useless.

Fig. 43. Sensitivity distribution $S(r, \theta)$ for the 5 MHz AT-cut plano-convex QCM in 20 mM
CuSO$_4$ (upper picture) and for plano- plano QCM in 20 mM CuSO$_4$ (lower picture)[23].
The fringing fields and thereby also the QCM electrode tabs, which may often be neglected, may play an important role for both the resonant frequency and the dissipation factor responses of a QCM operated in a liquid [136]. This was explained by an increase of the electrode area on the liquid side, which changes the parallel resonance frequency due to the conductance with conductive liquid.

Crystals may be obtained with a rough or smooth surfaces. Rough surfaces are most common and are less expensive, but they suffer from a quantitatively unpredictable dependence of the oscillation frequency in a liquid on trapping of the liquid in the pores on the surface. The optically smooth surface (made by chemical etching) is highly reflective with the faces parallel to within at least one micron. This treatment is frequently referred to as an overtone polish, because operation with acceptable frequency stability at the higher frequency odd harmonics of the crystal requires crystals that are less rough than can be obtained from simple mechanical polishing. The rough surface aids in adhesion of the vapor deposited electrodes to the crystal. The range of fundamental frequency usually used for QCM purposes are from 5 MHz to 10 MHz. Crystal with higher resonance frequencies are very fragile and therefore, difficult to handle. A 5 MHz crystal is about 330µm thick.

2.1.2. Circuit design

A key requirement of the circuit design is that it should provide sufficient gain to allow for oscillation of the crystal in a viscous medium.

The most popular design is to measure the oscillation frequency of the EQCM crystal with respect to a reference crystal, which is external to the electrochemical cell. Only one of the crystal electrode is expose to the solution otherwise the crystal does not oscillate. The two-excitation electrodes are electrically connected to an oscillator circuit that contains a
broadband RF amplifier, so that the electrode facing the solution is at hard ground.

The circuit can be designed so that the crystal is connected between the output and the input of the oscillator amplifier and provides positive feedback that causes oscillation of the circuit. Since the crystal is a part of the oscillator circuit, this method is called the active method. In the passive method the crystal is connected to an instrument which applies a sinusoidal voltage at various frequencies across the crystal terminals.

2.1.3. Cell design

The method of mounting the crystals in the electrochemical cell is an important consideration, because of possible influences of stress on the resonance frequency of oscillation, either in air or liquid. Several methods for mounting have been described [137-142], in which only one side of the EQCM disk (the working electrode side) is expose. This is usually necessary to prevent the two EQCM electrodes from being capacitively shunted by the solution, which can stop the oscillation [137]. An adhesive [137] can be used to contact the crystal to the cell. A more common procedure is to sandwich the crystal between two O-ring.

The cell should be designed so that the oscillator circuitry is situated as close as possible to the crystal to minimize the length of the leads from the circuit of the crystal.

There are two experimental arrangements – the first is based on a stationary configuration in which an immersed quartz crystal in housing is kept at a fixed position in the cell. The second is a rotating disk electrode. In addition, both the stationary and flow through cells can be used.
2.2. The EQCM – experimental setup

2.2.1. Electrodes

The quartz crystals employed in this work were of the $\alpha$ crystallographic orientation, plano-convex, AT-cut type. The crystals were purchased from Leybold Inficon with vacuum - sputtered gold or silver coating on both sides. The thickness of the gold layer is a few hundred angstroms. The pattern of the metal is shown in Fig.44.

This sputtered metal serves as the electrode exciting the crystal vibration and the side fully deposited is also used as the electrochemical electrode. The deposited surface is quite rough as was shown in [67], employing STM on crystals of the same type.

The roughness factor of the surface was calculated from cyclic voltametry oxidation peak obtain in the supporting electrolyte, and was found to be 1.5.

Good adhesion, between the quartz and the gold, is achieved by coating a thin layer of vacuum-sputtered Cr on the crystal, below the gold or the silver layer. The fundamental resonance frequency of the crystal is about 6 MHz. The crystal is 14 mm in diameter and 0.2 mm thick. The gold or silver surface was cleaned with cyclohexane in a soxhlet apparatus for about one hour, followed by 30 min in concentrated sulfuric acid and rinsed many times in distilled water. The crystal was replaced after each experiment. Since the chromium underneath the gold layer is anodically dissolve during potential scan and this can change the shape of the voltamogram, it was removed before each experiment. To remove this layer, one side was treated electrochemically before measurement in 0.1M LiClO$_4$ aqueous solution. The potential was cycled initially in a narrow
range, between $-0.2\text{V}$ to $0.2\text{V}$ vs. NHE. The potential range was increased gradually up to $-0.4\text{V}$ to $1.4\text{V}$. If this procedure was sufficiently slow, it had no effect on the adhesion of gold to the quartz crystal.

Fig. 45. X-ray spectrum of the gold deposit obtained after the removal of the chromium layer.

X-ray analysis showed that the sputtered thin layer of gold had a preferential (111) orientation, both before and after the removal of the chromium layer. Fig. 45 shows the X-ray spectrum obtained after the removal of the chromium layer, the X-ray spectrum before the removal is included in Fig. 46. Only a small difference was observed after pretreatment, in which the crystal, with silver and gold, was heated to $100^\circ\text{C}$ under hydrogen atmosphere for about 3 hours as can be shown in Fig. 46.
Fig. 46. X-ray spectrums before and after a pretreatment in which the crystal, with Au (upper picture) and Ag (lower picture) deposit, was heated to 100°C under hydrogen atmosphere for about 3 hours.

Two counter electrodes were used in this work. An external electrode, consisting of platinum wire was used for experiment in which the current distribution is not very important, such as cyclic voltamograms at relatively slow sweep rates and quartz crystal microbalance measurements. For chronocoulometry and differential capacitance a platinum disc electrode
placed parallel to the working electrode in the working electrode compartment was used. This electrode provides an uniform current distribution.

Different types of reference electrodes were used, depending on the system studied. For aqueous solutions, a saturated Ag/AgCl (0.242V vs. NHE) or Pd/H electrode in acid (0.19V vs. NHE). For butanol solutions, a saturated Ag/AgNO₃ electrode in butanol was used. The potential of this electrode was measure with respect to NHE in butanol and was found to be (0.65V).

2.2.2. Cell construction

Measurements were preformed in a three-compartment glass cell shown in Fig.47. Wetted glass stopcocks separated the compartments. The working electrode compartment, (a) was in the shape of a tube closed at the bottom by the disk of the quartz resonator. The height of the working electrode compartment was 12 cm and its diameter was 1.2 cm. During measurement, the working electrode compartment was filled completely with the solution. Otherwise, any disturbance, such as low frequency vibration of the table, caused instabilities as shown in previous publication [86]. The crystal was placed in a Teflon holder, (b), between two viton O-rings. The Teflon holder with the viton O-ring was attached to the flat bottom of the working electrode compartment and pressed against it by a mechanical bellows. A spring was place under the Teflon holder. This
configuration provides sufficient sealing to prevent solution leakage, while enough flexibility is provided to prevent cracking of the crystal. This sealing is reliable even if the alignment was not perfect and for keeping the mounting stresses away from the piezoelectricity active area.

Viton O-rings manufactured by Parker, were used, since this material is compatible with the solutions used in the experiments and does not release unwanted species. Its external diameter is 14 mm and inner diameter 11 mm.

In order to use the quartz crystal as the working electrode and to apply a voltage to measure the frequency shift, two connections were attached to the two sides of the crystal. A connection to the fully covered side of the crystal, used as the working electrode, was made of gold foil. The foil was placed between the gold layer used as the working electrode and the Viton O-ring. The second connection was made by an aluminum foil arranges on the Viton O-ring below the quartz crystal as showing in Fig.48.

The counter electrode, (c), and the reference electrode compartment, (d), were separated from the working electrode compartment. A thin capillary was placed from the reference electrode compartment to the working electrode compartment. This capillary served as the Luggin capillary to provide an electrolyte path to the reference electrode. This capillary was placed in the middle and at a distance of 1 mm above the working electrode. The solutions were degassed with He before introducing into the working electrode compartment in a small container placed near the working electrode compartment. The gas flow begins from the top of the container via the solution through a capillary. This capillary began in the upper part of the container and ends at its base.
Before each experiment the cell was cleaned with a mixture of concentrated sulfuric acid and 30% hydrogen peroxide, then washed many times with distilled water, in which Mili-Q water was used as the feed. All other glass containers were cleaned by the same procedure. The cell was designed so that the oscillator circuitry could be situated close to the crystal to minimize the length of the leads from the circuit of the crystal.

2.2.3. EQCM Instrumentation and measurement

A Leybold Inficon deposition controller type XTC/2 was used to measure the frequency. Both sides of the crystal were connected to the deposition controller during the EQCM measurement. The electrode in contact with the solution was grounded during the EQCM measurement. A switch was used to ground the electrode during these experiments and to disconnect the electrode from ground during other experiments. The switch was connected to an A/D converter. The sensitivity of the EQCM used in this experiment is 12.3 ng/Hz cm². Four measurements can be taken in one second, which is enough for the experiment performed. A computer controls the experiments through GPIB, which was connected to a PAR 273 potentiostat and a frequency response analyzer with RS-232, which was connected to the deposition controller.

Experiments were done with potential scanning, if no hysteresis was observed, or applying a potential steps. The initial potential of the step is usually at a value where no adsorption occurs.

2.3. Qualitative electrochemical measurement

2.3.1. Cyclic voltametry

Cyclic voltametry is a potentiostatic technique in the sense that the potential is the externally controlled parameter. The potential in this technique is changes at constant rate. The double-layer-charging current can be expressed by the equation:
\[ i_{dl} = C_{dl} \left( \frac{dE}{dt} \right) \]  \hspace{1cm} (22)

where \( C_{dl} \) is the double layer capacitance and \( E \) is the applied potential. From this equation it is clear that information on the condition of the interface can be obtained by cyclic voltametry measurements. Faradaic reaction results from other species in the solution give rise to additional currents. Cyclic voltametry was used in this work only as a qualitative tool to find the surface condition. These experiments were performed using EG&G, PAR model 273A potentiostat, which was connected to a computer to read the data.

2.3.2. Differential capacity

Differential capacitance measurements were performed in order to estimate the surface condition and in order to estimate the pzc. Considering the equivalent circuit of the double layer region, as shown in Fig.49, the impedance of the circuit can be describe as:

\[
Z(\omega) = \left( R_S + \frac{R_F}{\left( 1 + (\omega C_{dl} R_F)^2 \right)^{\frac{1}{2}}} \right) - j \left( \frac{\omega C_{dl} R_F^2}{\left( 1 + (\omega C_{dl} R_F)^2 \right)^{\frac{3}{2}}} \right) \]  \hspace{1cm} (23)

were \( \omega \) is the angular velocity, \( C_{dl} \) is the double layer capacitance, \( R_F \) the Faradaic resistance and \( R_S \) is the solution resistance. By using a frequency response analyzer, the real and imaginary parts can be measured. In the case when no Faradaic reaction occurs (Fig.49b.), the impedance expression is simplified to:

\[
Z(\omega) = R_S - j \omega C_{dl} \]  \hspace{1cm} (24)

and the double layer capacitance can be determined easily from the value of the imaginary part of the impedance obtained from the frequency response analyzer.
A Solatron 1250 frequency response analyzer was used to measure the differential capacitance. The analyzer was connected to a computer by GPIB cable and to the PAR mentioned above. The capacitance was measured during a slow potential scan of 5mV/sec, small amplitude of 10 mV and low frequency 6-25 Hz. In order to estimate the pzc, a minimum in the differential capacity of a dilute electrolyte solution was measured.

![Fig.49. The equivalent circuit of the double layer region (a) general (b) ideally polarizable (c) ideally non-polarizable [143].](image)

2.4. Chronocoulometry, activity measurements and surface excess of adsorbed organic species

2.4.1. The electrocapillary equation

The thermodynamic electrocapillary equation for a pure mercury electrode in contact with aqueous solution containing one electrolyte and one neutral organic compound at constant temperature and pressure is:

\[
d\gamma = -\sigma^M dE^\pm - RT \Gamma_d d \ln a_d - RT (\Gamma_+ / \nu_+) d \ln a_+ - RT (\Gamma_- / \nu_-) d \ln a_-
\]

where \(\gamma\) is the interfacial tension of the electrode at the metal/solution interface and \(\sigma^M\) is the excess charge density on the metal surface. \(E^\pm\) is the potential of the ideal polarized electrode with respect to an electrode dipping into the same solution which is reversible either to the cation, \(E^+\), or to anion, \(E^-\), in the electrolyte. This special kind of reference electrode
required by the thermodynamic theory of electrocapillarity is also called an indicator electrode. $\Gamma_{AW}$ is the relative surface excess of the organic compound (A) with respect to water (W) taken as the reference component, and $a_A$ is the activity of the organic compound in the bulk solution. $\Gamma_{ZW}$ denotes the relative surface excess of the ion of the electrolyte to which the indicator electrode is not reversible and $\nu_{\pm}$ is the number of moles of this ion in 1 mole of the electrolyte. $a_e$ is the activity of the electrolyte in the bulk solution.

Determination of the relative surface excess of an organic compound electrosorbed on a metal electrode from a solution containing a single electrolyte is based, in principle, on the following fundamental equation, derived from the thermodynamic theory of electrocapillarity.

$$\Gamma_{AW} = -(1/RT)\left(\frac{\partial \gamma}{\partial \ln a_A}\right)_{\Gamma, F, E^\pm, a_e}$$

(26)

In this equation $E^\pm, a_A$ and $a_e$ are truly independent variables. On the other hand, if the electrocapillary measurements are carried out using a series of solution of varying concentration of the organic compound but a fixed concentration of the electrolyte, equation 25 is no longer valid because $a_A$ and $a_e$ are no longer both independent variables. At constant electrolyte concentration, $a_e$ becomes an explicit function of $a_A$, i.e., $a_e = F(a_A)$. The correct electrocapillary equation for such a system is thus:

$$d\gamma = -\sigma_M dE^\pm - RT[\Gamma_{AW} + (\Gamma_\pm / \nu_{\pm})\left(\frac{\partial \ln a_e}{\partial \ln a_A}\right)_{\Gamma} d \ln a_e$$

(27)

where the subscript $C_e$ denotes constant electrolyte concentration. If one differentiates the interfacial tension with respect to $\ln a_A$ at constant $E^\pm$ the quantity determined would not be the true relative surface excess of the organic compound, but only the apparent surface excess $\Gamma_{app}$. 
The error in such measurement thus depends upon both the value of the relative surface excess of the anions and upon how fast \( \ln a_e \) changes with respect to \( \ln a_e \).

Another point that should be considered is that usually constant potential reference electrode have been used instead of an indicator electrode (since it is impossible or inconvenient to employ). Therefore, the potential in the electrocapillary equation should be corrected. Often the potential \( E^\pm \) does not depends significantly on electrolyte activity, and the surface excess is calculated by:

\[
\Gamma_{app} = -(1/RT) \left( \frac{\partial \ln \gamma}{\partial \ln a_e} \right)_{T,p,\gamma_e} \quad (29)
\]

In the case of solid electrode, parameters as specific surface work, \( \tilde{\gamma} \), and elastic surface stress, \( Y \), appear in the electrocapillary equation. The electrocapillary equation for a solid electrode under elastic strain is [144]:

\[
d\gamma = \left[ \sigma^M + (\tilde{\gamma} - Y) \left( \frac{\partial \e_e}{\partial E^\pm} \right)_{T,p,a_e,a^\pm} \right] dE^\pm - \nabla
\begin{align*}
- RT \left( \Gamma_{dw} + (\tilde{\gamma} - Y) \left( \frac{\partial \e_e}{\partial a^\pm} \right)_{T,p,a_e,E^\pm} \right) d\ln a^\pm \\
- RT \left( \Gamma_\gamma + (\tilde{\gamma} - Y) \left( \frac{\partial \e_e}{\partial \gamma} \right)_{T,p,a_e,E^\pm} \right) d\ln \gamma
\end{align*}
\quad (30)

However, these effects represent a second order correction and considered to be very small that can be neglected.
Three kinds of measurements were performed, in order to estimate the surface excess correctly: the electrocapillary measurements, gas chromatography for evaluation of the activities of the organic compounds in aqueous electrolyte solution and \( \textit{emf} \) measurements to estimate the activity of the electrolyte in the presence of the organic adsorbate.

2.4.2. The electrocapillary measurements

The relative charge densities \( \Delta \sigma_M \) were determined from potential step measurement [144]:

\[
\Delta \sigma_M (E^\pm) = \sigma_M (E^\pm) - \sigma_M (E_0^\pm)
\]

where \( \sigma_M (E^\pm) \) and \( \sigma_M (E_0^\pm) \) are the charge densities on the metal side of the interface at potential \( E^\pm \) and \( E_0^\pm \), respectively. Using the value of the pzc, determined independently from differential capacity curves, the charge densities were calculated for each value of the potential:

\[
\sigma_M (E^\pm) = \Delta \sigma_M (E^\pm) - \Delta \sigma_M (\text{pzc})
\]

The charge densities are integrated with respect to the electrode potential, \( E^\pm \), to give:

\[
\gamma (E^\pm) = \int_{E_0^\pm}^{E^\pm} \sigma_M dE^\pm + \gamma (E_0^\pm)
\]

The lower integration constant \( \gamma (E_0^\pm) \) is not known, but its value is independent of the presence or absence of the organic molecules because there is no adsorption at \( E_0^\pm \). Therefore, the surface pressure of the film of adsorbed pyridine (II) can be determined as follow:
\[ \pi(E^\pm) = \gamma_{c=0} - \gamma_c = \int_{E^\pm}^{E^\mp} \sigma_{\mu,\pm} dE - \int_{E^\pm}^{E^\mp} \sigma_{\mu, c=0} dE^\pm \] (34)

where the subscript \( c \) and \( c=0 \) indicate the presence and absence of pyridine in the bulk of the electrolyte, respectively.

The relative Gibbs surface excess is calculated followed the relationship:

\[ \Gamma_{AW} = -\left(1/RT\right)\left(\frac{\partial \Pi}{\partial \ln a_A}\right)_{T,p,E^\pm,a_i} \] (35)

as discussed before, at constant electrolyte concentration, when the activity of the electrolyte changes with the addition of organic molecules and the activity of the organic material is different from its concentration, the following relation exist:

\[ \Gamma_{app} = \Gamma_{AW} + \left(\frac{\Gamma_\infty}{v_\infty}\right)\left(\frac{\partial \ln a_c}{\partial \ln a_i}\right)_{E^\pm} \] (36)

Electrocapillary measurements were performed using the PAR 273 that can performed a measurement every 50µsec. Above 3200 experimental points were collected in each measurements. 200 data points at the beginning of the measurements were collected at the initial potential to ensure that no faradeic reaction takes place in the system. Since the measurements are very fast, data were saved on the PAR internal memory and were transferred to a computer when measurements have been completed.

Most of the measurements were performed in the same EQCM cell, using the internal electrode. The other cell used is an one-compartment glass cell.
2.4.3. Activities of the organic compound

If one takes the pure organic compound as the standard state, the activity of the organic compound in solution is equal to the relative fugacity:

\[ a_A^b = \frac{f_A}{f_A^0} \]  

(37)

where \( f_A \) is the fugacity of the organic compound in the solution and \( f_A^0 \) is the fugacity of the pure compound. When the solution and the pure compound are each at equilibrium with their vapors, the fugacities in the vapor and liquid phases are equal. The fugacity in the vapor phase is equal to the product of the partial pressure of the organic compound and its fugacity coefficient, which corrects for nonideality in the gas phase. Therefore, the bulk activity of the organic compound in the solution is quite accurately given by:

\[ a_A^b = \frac{P_A}{P_A^0} \]  

(38)

where \( P_A \) is the partial pressure of the organic compound in the vapor phase in equilibrium with solution and \( P_A^0 \) is the vapor pressure of the pure organic compound at the same temperature.

The basis of this method is to integrate the gas chromatogram of a fixed volume sample of the equilibrium vapor using a gas chromatogram equipped with a flame ionization detector. Since the integral of the chromatogram is directly proportional to the partial pressure of the organic vapor in the gas sample, the activity of the organic compound in the bulk electrolyte solution is given by:

\[ a_A^b = \frac{I_A}{I_A^0} \]  

(39)

where, \( I_A \) is the integral of the chromatogram for the solution and \( I_A^0 \) is the integral for the pure compound.
2.4.4. EMF measurements

The EMF of a reversible galvanic cell without liquid junction, in the presence and without of the organic compound, was used for determining the effect of the organic compound on the activity of the electrolyte. By this technique, the activity is measured directly using the Nernst equation [145]

\[ E = E^0 - \frac{RT}{nF} \ln a^+ a^- \]  \hspace{1cm} (40)

where \( E \) is the electromotive force of cell , \( E^0 \) is the standard electromotive force of cell, \( n \) number of equivalents per mole, F Faraday’s constant, R is the gas constant, T the temperature, \( ν^+ \) and \( ν^- \) are the number of cations and anions produced by dissociation of one molecule of electrolyte, and \( a^+ \) and \( a^- \) are the activities if the cations and anions, respectively. Since the activities of the anions and cations in the solution cannot be separated, the equation is written as

\[ E = E^0 - \frac{νRT}{NF} \ln a_z \]  \hspace{1cm} (41)

where \( ν = ν_+ + ν_- \) and \( a_z = \left[ a_+ a_- \right]^z \) is the mean ionic activity of an electrolyte.

The activity of the electrolyte as a function of the concentration of the organic compound was measured only in the case of t-butanol. Two reversible electrodes were used, one for the anions and the other for the cations. Orion perchlorate electrode and Cole Palmer glass electrodes were employed.
A small potential drop probably exists in the glass electrode, however the slope obtained measuring the emf for different concentration of LiClO₄ in aqueous solution was as expected from the manufactures curves. The electrode potential vs. log(ce) is shown in Fig.50.

2.5. Other experimental techniques

The spectrophometric measurements of determination of the kinematic viscosity were performed in part of the experiments. The data from these experiments were use to analyze the results.

2.5.1. Spectrophotometric measurements

Spectrophotometric measurement were performed in order to find deviation from Beer – Lambert law:

\[ A = \varepsilon \cdot l \cdot c \]  

(42)

where A is the absorbance, \( l \) is length of the optical path, \( c \) is the molar concentration and \( \varepsilon \) is the molar absorption coefficient.
From such deviation one can learn that there might be interactions between the solute molecules and the solvent molecules or dimerization of the solute molecules. The actual "free" solute concentration can be estimated from this deviation. This concentration was used for further calculation, where the concentration of the free solute is needed. The Spectrophotometer used is Shimadzu UV-1202.

2.5.2. Kinematic Viscosity measurement

The data. If no literature data exist, the Ostwald viscometer, shown in Fig.51., was used to determine the viscosities of the solutions. The time has taken for a given volume of solution to flow through the capillary is noted, and compared with a standard sample. The method is well suited to the determination of viscosities, because the ratio of the viscosities of the solution and the pure solvent is proportional to the drainage times \( t \) and \( t_0 \) after correcting for different densities \( \rho \) and \( \rho_0 \):

\[
\frac{\eta}{\eta_0} = \frac{t}{t_0} \cdot \frac{\rho}{\rho_0}
\]

A fix volume of several solutions was measured. The time require for the solution studied to flow from the upper line of the viscosimeter to the bottom line was about 2 minute which was measured with a stop - watch that can measure to a tenth of a second.
2.6. Reagent and solutions

Aqueous solutions were made with Mili-pore water (18 MΩ) that was further distillated from permanganate solution. Butanol solutions were prepared from anhydrous butanol (Aldrich, >0.002% water). The supporting electrolyte was 0.1M LiClO₄ (Fluka, pure). The supporting electrolyte was dried in vacuum at 170°C for 3 hours when used in nonaqueous butanol solution. The adsorbed molecules - pyridine (analytical regard, Merck), n-butanol, t-butanol (analytical reagent, Merck), Uracil (Sigma, pure) were used as received.
3. Results and Discussion

In this section the experiments done will be discussed. Two main cases were studied - the case of electrostatic adsorption and specific adsorption. All measurements were limited to the double-layer region, to avoid changes of the surface roughness and the oxidation of the surface. A detailed discussion must include information on the charge – potential and the surface excess – potential dependencies. Therefore, the results of those dependencies will be discussed first.

Other electrochemical measurements done will be present. These measurements were performed to find the interface condition and to analyze the EQCM results. For cases where part of the data were taken from the literature, those measurements were used to ensure that the conditions of adsorption in our setup were the same as in the above publications. In those cases, the measurements were performed under the same experimental conditions as the literature setup (amplitudes, frequencies and scan rates).

3.1. The dependence of charge and surface excess on potential.

3.1.1. Calculation of the real surface area

The real surface area of the electrode is necessary to make quantitative calculations. The real surface area was estimated by two methods. The first is to measure the adsorption of one monolayer of oxide, from the area under the reduction peak obtained in cycling the potential in the range of –0.45V to 1.6V vs. NHE in 0.1M LiClO₄ aqueous solution on gold electrode. A voltamogram used for such calculation is shown in Fig.52. The roughness factor found is 1.5. Similar calculation cannot be preformed in n–butanol solution, since n–butanol can be oxidized at high positive potentials.
The other way of determining the real surface area was by comparison of the dependence of the charge density on potential obtained, as will be discussed in section 3.1.2, to literature data. Similar values were obtained for the roughness factor from this calculation.

![Graph](image)

**Fig.52.** Cyclic voltammogram obtained for 0.1M LiClO₄ aqueous solution on gold electrode, scan rate 50mV sec⁻¹.

### 3.1.2. The dependence of charge on potential.

The dependence of charge on potential was measured for the adsorption of pyridine from n-butanol solution on gold and silver electrode and of t-butanol from aqueous solution. The data for adsorption of pyridine from aqueous solution on gold and silver electrode was taken from the work of Lipkowoski et al. [147-150]. In the work of Beltowska-Berezinska et al. [151] on the adsorption of n-butanol from aqueous solution the dependence of charge on potential was given. Wandlowski [152] studied the adsorption of Uracil from aqueous solution on gold electrode.

As mentioned in the “experimental” section, the basic measurements for obtaining the charge and surface excess dependence on potential are chronocoulomtry. Shown in Fig.53 are several current-time transients, which have been obtained for n-butanol solution containing pyridine, on gold electrode. These curves are typical for charging of a capacitor. The time window in which the transients were recorded was the same for both the supporting electrolyte and for solutions containing the adsorbates. Before the potential transient, the current at the initial potential was measure to make sure that no faradeic process take place.
Integration, of these curves, yields the charge, as was shown in the “experimental” section. The dependence of charge on time usually reaches a saturation value (Fig.54), where the charge is essentially independent of the time. The charge at the plateau is the charge used to plot the charge – potential curves.

The absolute charge density was obtained by using Eq. 32. Fig.55 shows the charge – potential dependence for the supporting electrolyte and for various concentrations of the adsorbates studied.

Fig.53. Current - time transients which have been obtained for n-butanol solution containing 0.5mM pyridine on Au electrode. The potential steps indicate inside the curve and are vs. NHE in n-butanol.
Fig. 54. Charge – time curves obtain for n-butanol solution containing 0.5mM pyridine on Au electrode, for the step –1.200 - -0.4V vs. NHE in n-butanol.

The pzc values taken for the calculations are 0.242V vs. NHE for gold in aqueous solutions and –0.75V vs. NHE for silver. It is –0.13V vs. NHE for gold in n-butanol and –0.71V vs. NHE for silver in n-butanol. These values were taken from the differential capacitance measurements that will be discussed below. These values are in good agreement with literature data [147,153]. In all cases the curves merge with the charge – potential dependence of the supporting electrolyte at the initial potential when there is no adsorption. Apparently, except at initial potentials, the curves do not intersect the curve for supporting electrolyte, except for the case of t-butanol. Hence there is no potential of maximum adsorption for these cases in the range studied. For t-butanol, a maximum of adsorption is expected, since the curves intersect with the base electrolyte curve. It is also clear that the potential of zero charge is shifted in the negative direction as a result of the adsorption. The charge - potential plots obtained for various pyridine concentrations on gold electrode from aqueous solution show two inflection points. These inflection points do not appear when the electrode is silver. No inflection points are observed when t-butanol is the adsorbate.
The charge – potential curves for aqueous electrolyte solution compared to the literature [154,147] as shown in Fig.56. The roughness factor of 1.5 was used as discussed above. The good agreement obtained confirms the value of the roughness factor.

3.1.3. Surface pressure curves.

Since the electrocapillary curves cannot be measured on solid electrodes the surface pressure curves will be plotted and discussed. Integration of the charge versus potential curves allow one to determine the relative interfacial tension. Subtraction of the relative surface tension obtained for electrolyte solution from the surface tension obtained for each concentration, using the charge as the electrical variable, yields the surface pressure. Fig.57 shows the surface pressure obtained for the cases studied. As expected, a maximum in the surface pressure is obtained only for the case of the adsorption of t-butanol. At positive potentials and at high t-butanol concentrations, the curves are found to be above the curve for the supporting electrolyte itself. This leads to negative values of the surface pressure in this region, and correspondingly to negative values of the relative surface excess, as will be discussed below.
Fig. 55. Charge-potential dependence of pyridine in n-butanol solution on gold electrode (upper figure) pyridine in n-butanol solution on silver electrode (middle figure) and t-butanol in aqueous solution on gold electrode (lower curves). The adsorbate concentrations are indicated on each curve.
3.1.4. Gibbs surface excess.

The surface excess can be obtained by differentiation of the surface pressure vs. the logarithm of the bulk adsorbate activity curve, as shown by Eq. 26. In the solutions studied, it was found that the adsorbate activity coefficient is not unity. For t-butanol, the activity coefficient of the electrolyte was found to depend on t-butanol concentration. The next section will discuss the calculations and the additional experiments done to calculate the Gibbs surface excess in each case. In section 3.1.4.3 the Gibbs surface excess of n-butanol adsorbed on gold electrode from aqueous solution will be presented. These curves were calculated from literature values of the surface pressure.

3.1.4.1 Gibbs surface excess of pyridine from n-butanol solution on gold and silver electrodes

Differentiation of the surface pressure vs. the logarithm of the concentration give rise to the Gibbs surface excess curves shown in Fig.58. The curves rise up to $11 \cdot 10^{10} \text{ mol cm}^{-2}$, which is higher than that found in aqueous solution [147]. Careful examination of the curves shows that the maximum surface excess for the higher pyridine concentration is lower.
Fig. 57. Surface pressure - potential dependence of pyridine in n-butanol solution on gold electrode (upper figure) pyridine in n-butanol solution on silver electrode (middle figure) and t-butanol in aqueous solution on gold electrode (lower curves). The adsorbate concentrations are as indicated.
Spectrophotometric data reveal deviations from the Beer-Lambert low as shown in Fig. 59. This deviation indicates that the activity coefficient is not unity. The deviation is quite large at high pyridine concentration. The spectrophotometric data were used to correct the bulk concentration used in the calculation, to the activity of pyridine in the solution. Doing so, the Gibbs surface excess curves become more reasonable, as shown in Fig.60. Since most of the correction was at high concentrations, the maximum adsorption value for this concentration becomes higher. Now, the curves reach maximum value of to $8 \times 10^{10}$ mol cm$^{-2}$, which is much closer to the value obtained in aqueous solution. The activity of the electrolyte was found to remained constant in all pyridine concentrations.

The spectrophotometric data was also used to calculate the surface excess of pyridine from n-butanol solution obtained on silver electrode, as shown in Fig.61. In this case, as the concentration rise, the maximum adsorption values increase. It seems that two regions exist - before the pzc, where lower values of adsorption was obtained and after the pzc, where the curve rise up to $5 \times 10^{10}$ mol cm$^{-2}$. The last value is similar to the value obtained in aqueous solution [149,150].

Fig.58. Gibbs surface excess for the adsorption of pyridine from n-butanol solution on gold calculated by using bulk concentration.
Fig. 59. The maximum of absorbance, experimental (dashed line) and calculated (solid line), of pyridine from n-butanol solution.

Fig. 60. Gibbs surface excess for the adsorption of pyridine from n-butanol solution on gold calculated by using bulk activities instead of concentration.
Fig. 61. Gibbs surface excess for the adsorption of pyridine from n-butanol solution on silver electrode calculated by using bulk concentration.

3.1.4.2 Gibbs surface excess of t-butanol from aqueous solution on gold electrodes

The relative surface excess for different t-butanol concentration calculated using bulk concentration instead of activities, without the corrections for the electrolyte activity and for the reference electrode potential is shown in Fig. 62. A nearly bell shape adsorption isotherm is obtained as expected. These results are very similar to the results obtained on mercury electrode [155]. However, there are two reasons to suspect these results: (a) the values of the surface excess, especially in concentrated t-butanol solutions, are very high. Based on geometrical consideration one predicts a maximum surface excess of about $5.5 \times 10^{-10}$ mole cm$^{-2}$ for monolayer adsorption of t-butanol, compared to a value of ca. $9 \times 10^{-10}$ mole cm$^{-2}$ shown in Fig. 62.

(b) the desorption of molecules from the surface at positive potential occurs at lower charge densities than was found from differential capacitance measurements, especially at higher concentration of the organic compound. Therefore, a more accurate analysis should be performed, taking into account
the variation of the activity coefficients of the electrolyte and of the t-butanol, and the correction of the reference electrode potential.

![Graph showing relative surface excess for different t-butanol concentrations](image)

Fig. 62. The relative surface excess for different t-butanol concentrations, calculated using bulk concentrations of the adsorbate and the electrolyte, instead of activities. (for high concentration of t-butanol not all the curve is plotted)

The activity of the organic compound in the concentration range studied was measured in constant electrolyte concentration, 0.1 M LiClO₄, using the GC technique. The activity and the activity coefficient, \( f_{activity} \), as a function of concentration, are shown in Fig. 63. Each data point represents the average of at least ten measurements, taken at each concentration. The standard deviation of the measurements never exceeded 0.3%. The activity coefficient is close to unity up to a concentration of about 0.5M. At higher concentrations, it decreases to 0.6. This difference between the bulk concentration and activities is one of the reasons for the unreasonably high apparent surface excess values at higher t-butanol concentration. Mohilner [156,157] reported similar results.
Fig. 64 shows the dependence of the mean activity of the electrolyte at constant concentration of 0.1M on the activity of t-butanol, on a log-log scale, from EMF measurements. The presence of t-butanol changes considerably the activity of the electrolyte. The mean activity increases with the concentration of t-butanol. The main dependence is at higher t-butanol concentration. An explanation for this phenomenon was given by Mohilner et al [156].

Fig. 63. Activity (upper picture) and activity coefficient, $f_{\text{activity}}$, (lower picture) of t-butanol in the concentration range studied.

They suggested that the organic compound promote the formation of clathrate-like cages of water around each organic molecule. This lowers the effective concentration of water, increasing that of the electrolyte. The second
term in Eq.28 corrects for this effect. To perform the correction, the dependence of the relative surface excess of both ions, $\Gamma_+$ and $\Gamma_-$, on charge must be determined. Using the Gouy-Chapman model and the charge-potential dependence measured in electrolyte solution, these dependencies can be determined (Fig.65).

![Graph](image1)

**Fig.64.** The activity of the electrolyte, 0.1M LiClO$_4$, as a function of the concentration of t-butanol in solution, $a_e = a^2_e$.

![Graph](image2)

**Fig.65.** The relative surface excess of both ions, $\Gamma_+$ and $\Gamma_-$ - solid line $\Gamma_{Li^+}$, dash line $\Gamma_{ClO_4^-}$. 

\[
\Gamma_{ClO_4^-}.
\]
The potential of the indicator electrode should not change, to a first approximation, with the concentration of the organic adsorbate, since the concentration of the supporting electrolyte is constant. However, a voltage of 14 mV is observed for the cation specific electrode and 2 mV for the anion specific electrode, at the highest t-butanol concentration.

Since the electrocapillary measurements were made using a palladium reference electrode, a potential correction should be made to the potential of a reversible electrode to the anions or cations, respectively. The potentials of such indicator electrodes (the perchlorate ion selective electrode and glass electrode to the lithium ions) at different solutions was measured with respect to the palladium reference electrode. The correction to the electrocapillary measurements was made before further calculations. The results obtained are listed in table 1.

<table>
<thead>
<tr>
<th>t-but concentration /M</th>
<th>E (Li⁺-ref) /V</th>
<th>E (ClO₄⁻-ref) /V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.252</td>
<td>0.2839</td>
</tr>
<tr>
<td>0.05</td>
<td>0.253</td>
<td>0.2845</td>
</tr>
<tr>
<td>0.14</td>
<td>0.261</td>
<td>0.2853</td>
</tr>
<tr>
<td>0.25</td>
<td>0.264</td>
<td>0.2854</td>
</tr>
<tr>
<td>0.36</td>
<td>0.265</td>
<td>0.2855</td>
</tr>
<tr>
<td>0.5</td>
<td>0.266</td>
<td>0.2855</td>
</tr>
<tr>
<td>0.65</td>
<td>0.266</td>
<td>0.2855</td>
</tr>
<tr>
<td>0.795</td>
<td>0.266</td>
<td>0.2855</td>
</tr>
<tr>
<td>0.9</td>
<td>0.266</td>
<td>0.2857</td>
</tr>
<tr>
<td>1.023</td>
<td>0.266</td>
<td>0.2858</td>
</tr>
<tr>
<td>1.2</td>
<td>0.266</td>
<td>0.2858</td>
</tr>
</tbody>
</table>

Table 1. The potential of perchlorate ion selective electrode and glass electrode reversible to the lithium ions vs. Pd electrode.

The corrected surface excess for different t-butanol concentration is shown in Fig.66. Comparison between Fig.62 and Fig.66 shows the importance of correcting for the changes of the activity coefficients of both the organic adsorbate and the electrolyte, with increasing concentration of the
former. The shape of the dependence of the relative surface excess on charge is more regular, following that expected from for adsorption of neutral organic compound [158]. The maximum value in Fig. 66 agrees well with that estimated, based on molecular dimension, while that in Fig. 62 is incompatible with any possible geometry of t-butanol on the surface. It is noted also that the range of surface charge density over which adsorption is observed is extended on the positive side, from about 20µC cm\(^{-2}\) to 40µC cm\(^{-2}\), even for the
Fig. 66. The relative surface excess vs. (a) charge density and (b) potential, corrected for the activity coefficient of the electrolyte and of t-butanol. lowest concentrations of the organic adsorbate studied. This may appear unexpected, in view of the fact that the activity coefficient for the organic adsorbate is essentially independent of concentration up to about 0.5 M, as seen in Fig. 63. However, we note that the activity coefficient of the electrolyte depends on the concentration of t-butanol, even at the lowest concentration of t-butanol studies here, as seen in Fig. 64. This dependence causes an extension of the range of charge density, and should not be ignored in measurements of the electrosorption of organic materials, even at relatively low concentrations.

The nature of the adsorption isotherms can now be investigated. Shown in Fig. 67 are the adsorption isotherms, which have been obtained at constant electrode potential. The data displayed show that, due to the limited range of t-butanol concentration that was investigated (due to the limitation of the technique) only a fragment of the isotherm could be determined. It should be noted that the surface excess is plotted versus the activity. A similar graph plotted versus the concentration yields unreasonable results.
3.1.4.3 **Gibbs surface excess of n-butanol from aqueous solution on gold electrodes**

In [151] the surface pressure of n-butanol adsorbed on gold from aqueous solution was given. Using these data we calculated the surface excess. No changes in n-butanol and the electrolyte activities were found. The surface excess curves obtained are shown in Fig. 68. Since only partial data were published (which is enough to analyzing the EQCM results) the curves obtained are also partial.

Fig. 67. Plots of the surface excess vs. the activity of t-butanol at various potentials (vs. NHE).
Fig. 68. The relative surface excess curves obtained for n-butanol solution adsorbed from aqueous solution on gold electrode.
3.2. Electrostatic adsorption

The first case studied was the case of electrostatic adsorption. Here only electrolyte exists in the solution. Two solvents were studied – water and n-butanol. These solvents were chosen since they both have –OH group. This functional group can form hydrogen bonds with similar molecules. While water has two –OH groups, n-butanol has only one. This means that the water can form a network structure with a maximum of four hydrogen bonds per molecule, while n-butanol with only one -OH group and steric effect from the butyl group can form less rigid structures. The goal of the comparison between the EQCM results observed for these solvents is to give an example to the use of the EQCM as a tool to study the double layer structure. The electrolyte used was LiClO$_4$. It is known that this electrolyte is not specifically adsorbed on the metal electrodes studied (except perhaps at high charge densities, where adsorption of small extent has been discussed the literature. However, such high charge densities were not reached in the following experiments.). An additional comparison between two metals, gold and silver, was made in order to determine the influence of the nature of the metal on the EQCM response.

3.2.1. Cyclic voltametry and Differential capacity.

As was discussed before, these measurements were preformed to determine the condition of the system. Voltamograms obtained in LiClO$_4$ electrolyte in the absence of specific adsorption, where no Faradaic reaction occurs, both in butanol and in aqueous solution and on gold and silver electrode are presented in fig.69. This comparison shows that on gold and silver, as on mercury [159], the double-layer region extends over a wider range of potential, and the capacitance is lower, in n-butanol than in aqueous solutions. The reason, for the lower currents in the voltamogram and to the lower differential capacity values, is the differences in the dielectric constants – which is about four times lower for n-butanol, 17.8 at 20°C, than for water, 78.54 at the same temperature. As can be observed, the currents and the differential capacitance values in n-butanol (Fig.70) are lower by a factor of about 4. This agrees with data presented in the literature [147-150,160,161]
and our own measurements of capacitance. Similar conclusion can be obtained from the differential capacity measurements as shown in Fig.70. Differential capacitance curve obtained in the same condition as the relevant literature, so a comparison to literature data can be made. The pzc in electrolyte solution needed for surface excess calculation was found from the minimum in the capacitance/potential plot, obtained in a dilute solution, 0.01M, of LiClO₄ in both solvents. A value of pzc = –0.13V vs. NHE in n-butanol on gold and a value of pzc = -0.71 vs. NHE in butanol on silver was found. These pzc values were found to be close to the values obtained by an indirect method [160,161]. The pzc obtained in aqueous solution is pzc = 0.24V vs. NHE on gold and pzc = –0.75V vs. NHE on silver, similar to the values obtained in the literature [147-150].

Fig.69. The Cyclic voltamogram obtained (a) on gold electrode in 0.1M LiClO₄ aqueous solution (b) on gold electrode in 0.1M LiClO₄ n-butanol solution (c) on silver electrode in 0.1M LiClO₄ aqueous solution (d) on silver electrode in 0.1M LiClO₄ n-butanol solution.
We found that differential capacitance depends on the amplitude of the perturbing signal and on its frequency as shown in Fig.72 for the case of 0.1M LiClO₄ aqueous solution on gold. Therefore, these curves are used only qualitatively.

Fig.70. Differential capacity curves obtained (a) on gold electrode in aqueous solution (b) on gold electrode in butanol solution (c) on silver electrode in aqueous solution (d) on silver electrode in butanol solution.
Fig. 73. Differential capacitance curves obtained in 0.1M LiClO₄ measured at different amplitudes.

Fig. 72. Differential capacitance curves obtained in 0.1M LiClO₄ measured at different frequencies.

3.2.2. Frequency shift measurements

The responses of the EQCM in the two solvents, without specific adsorption, are shown in Fig. 74 and Fig. 75. The quantity considered in EQCM measurements is the shift in resonance frequency. Since the absolute value of the resonance frequency of the EQCM is irrelevant in the context of this work, and because it changes from one crystal to another by as much as
several KHz, it is necessary to normalize the data observed in different experiments for comparison. The unique point in the potential region chosen for this research is the pzc. Therefore, this point was assigned a value of $\Delta f=0$ and the changes of frequency with potential were considered from this point.

The data plotted were taken in the anodic and the cathodic scan. The data in all the cases were taken from a few potential scanning and the results obtained show the stability of the measurements. The fact that there is no systematic time effect confirms that the surface remains invariable. This is true while the electrode is cycled over a limited range of potential, not in the hydrogen evolution on the cathodic side and not in the oxide formation on the anodic side.

It is clear from the figures that the frequency shift dependence on charge for silver is similar but markedly sharper than for gold. The same behavior is observed for both solvents. It is also evident that the variation of frequency with charge depends strongly on the nature of the solvent. In n-butanol solution a much weaker dependence is observed both on silver and on gold. As for aqueous solution, the frequency dependence on silver is sharper than on gold. The meaning of those results will be discussed below.

![Graph showing the EQCM response on gold (circles) and silver (filled squares) electrode in 0.1M LiClO₄ aqueous solution](image)

Fig. 75. The EQCM response on gold (circles) and silver (filled squares) electrode in 0.1M LiClO₄ aqueous solution
Fig. 74. The EQCM response on gold (circles) and silver (filled squares) electrode in 0.1M LiClO$_4$ n-butanol solution.

For electrostatic adsorption there is no rigidly attach mass added to the surface, as from specific adsorption or deposition. It is also reasonable to assume that there are no changes in surface morphology, since the time of each cycle is very short. The temperature and the pressure on the crystal remain constant during the experiments and therefore, do not influence the frequency. The following paragraphs will discuss other reasons that may affect the frequency as changes in the surface tension, electrostatic adsorption of charged particles and changes of the double layer properties.

3.2.2.1 Surface tension

Shifting the electrode potential from the pzc decreases the surface tension. This could apply stress to the surface of the quartz resonator, changing its frequency. The influence of stress in a thin surface film of the quartz resonator on its frequency has been discussed before [162,163]. The dependence of the frequency shift on the surface tension can be written as [163]:

\[
\Delta f_{\text{compression}} = -K \left( \frac{f_0}{l} \right) \Delta \gamma 
\]  

(45)
where $\Delta \gamma$ is the change in the surface tension and $K = 2.75 \times 10^{-12} \text{ cm}^2/\text{dyne}$ is a constant that depends only on the properties of the quartz crystal. Using this relationship the change of frequency due to surface tension variation can be evaluate. For a rational potential of ±0.5V on gold, the decrease of the surface tension is about 80 mN/m [147]. Using this value in Eq. 45 yields a change of 0.07Hz, which is negligible compared to shift in frequency observed in the same range of potential.

### 3.2.2.2 Electrostatic adsorption of charged species

Although there is no specific adsorption for electrostatic adsorption, the mass of ions in the diffuse double layer may affect the frequency shift. The velocity decay length for dilute aqueous solution at room temperature is about 230nm. The Debye reciprocal length in 0.1M solution of a 1-1 electrolyte is about 1nm. The decrease of the fluid velocity over such a small distance is less than 0.5%. Therefore, the ions pulled into the diffuse double layer as a result of the excess charge on the metal can be considered to be vibrating in phase with the surface of the crystal and act as (almost) rigidly attached mass.

To evaluate the mass of these ions, the Gouy-Chapman theory is used. From this theory the dependence of the positive and negative excess charges on potential can be found.

\[
q_z = \pm 2 \left( \frac{R T e C}{2 \pi} \right) \frac{1}{2} \sinh \left( \frac{z F \phi_2}{2 R T} \right)
\]

(46)

where $\phi_2$ is the potential in the plane of closest approach.

From this calculation the concentration at the surface at rational potential of 0.5V turn out to be 4.7M, for a bulk concentration of 0.1M. The change of mass due to anions and cations in the diffuse double layer ($\Delta m_{a,c}$) can be expressed as

\[
\Delta m_{a,c} = \left( q_+/F \right) (M_a - M_w \nu_A) - \left( q_-/F \right) (M_c - M_w \nu_c)
\]

(47)

where $M_a$, $M_c$ and $M_w$ are the molecular weights of the anion, the cation and water, respectively. The values of $\nu_a$ and $\nu_c$ reflect the number of water
molecules replaced by the respective ion. The potential dependence of the added weight is implicit in Eq.47, through the dependence of the excess positive and negative charges on potential.

A rough estimate of the number of water molecules replaced by the ions can be obtained from the dependence of the density of the solution on concentration. Although it is not necessarily correct to use values obtained for bulk solution for this calculation, this is the closest estimation we can have that is not based on adjustable parameters including information on both the solvent and the electrolyte. This number was calculated by subtracting the number of water molecules, existing in a certain volume of the solution (containing electrolyte), from the number of water molecules, that in the same volume of pure water. This result was further divided by the number of electrolyte molecules, in the same volume of the solution. Such a calculation yields almost the same numbers for the higher bulk concentration, such as those calculate for the interface from the Gouy – Chapman theory. The density data were taken from [164] for aqueous solution and from [165] for butanol solution.

The density is a function not only of concentration but also of temperature. In a 4.5 M solution of LiClO$_4$ at room temperature, each LiClO$_4$ molecule is found to displace 2.5 water molecules, while at 0°C the same calculation leads to a value of only 1.3. At first sight it seems that the value calculated for room temperature should be used, since all our experiments have been performed at 25°C. However, the structure of water at the interface, especially a charged interface, is different from that in the bulk, and its properties at room temperature are probably closer to those of bulk water at lower temperatures [166-168]. Thus, it may be more appropriate to use the result calculated from density values of LiClO$_4$ solutions at 0°C. The uncertainty introduced by this choice does not influence the conclusions in a qualitative manner.

The above calculation, based on the change of density with concentration of the electrolyte, yields the sum of the contribution of the anions and cations, ($\nu_a$ + $\nu_c$), but does not allow us to determine the values of $\nu_a$ and $\nu_c$ separately.
However, a comparison between HClO$_4$ and LiClO$_4$ shows that both molecules displace the same number of water molecules from the bulk of the solution [165]. This indicate that most of the effect observed is associated with the anion (i.e. that $\nu_a >> \nu_c$). The dashed line in Fig.76 shows the mass effect in aqueous solutions, calculated from Eq. 47 and Eq.1, employing the values of $\nu_a = 1.3$ and $\nu_c = 0$. Other values yield the dependencies shown in Fig.77. The dependencies obtained by using unreasonable values are quite similar to that shown in Fig.76.

The most important conclusion from the above calculation is that the experimentally observed frequency (Fig.75) is remarkably larger than that calculated from the mass effect. The remaining shift in frequency therefore is associated with the formation of a very thin film adjacent to the vibrating surface, in which the viscosity is much higher than in the bulk of the solution.

For LiClO$_4$ in n-butanol, data are available only for saturated solutions at 25°C [165]. The differences of densities of n-butanol and of LiClO$_4$ in butanol show that each dissolved LiClO$_4$ molecule replaces two n-butanol molecules. The same applies for NaClO$_4$, suggesting that most of the volume is occupied by the ClO$_4^-$ anion, as in aqueous solutions. A similar comparison between HCl and LiCl [165] also yields the same number of solvent molecules replaced, showing that most of the volume is taken up by the anion. The solid line in Fig.76 shows the calculated mass effect in n-butanol. As in aqueous solutions, it must be concluded that the experimentally observed dependence of frequency on charge or potential (or rather, the lack of variation of frequency with potential when n-butanol is used as the solvent) cannot be accounted for by the calculated mass effect, $\Delta f_{mass}$. 


Fig. 76. Calculated frequency shift due to mass changes in the diffuse double layer in butanol solution (solid line) and in aqueous solution (dashed line).

Fig. 77. Calculated frequency shift due to mass changes in the diffuse double layer in aqueous solution: \( \nu_a = 1.3 \) and \( \nu_c = 0 \) (solid line), \( \nu_a = 1 \) and \( \nu_c = 0.3 \) (dashed line) and \( \nu_a = 0.7 \) and \( \nu_c = 0.6 \) (dotted line).
3.2.2.3 Viscosity effect in the diffuse double layer

A difference between the viscosity of the fluid in the diffuse double layer and in the bulk of the solution could be cause by two factors – the ion concentration near the electrode surface and the high filed strength.

As shown above, the concentration of ions near the electrode surface depends on charge density and hence on potential. A high concentration of LiClO₄ in aqueous solution up to 4.7M, which is close to the maximum solubility of the salt, was calculated from The Gouy-Chapman theory. At this concentration, the viscosity is substantially higher than in pure water.

The field strength in the outer Helmholtz plane may reach a value of 3 \times 10^6 \text{ V/cm}. This field is smaller than the field in the Inner Helmholtz Plane or around small cation, but high enough to affect the structure of the solvent and change its local viscosity.

A model was develops by Tsionsky, Daikhin and Gileadi [86], which considers how changes in the local value of the viscosity, very close to the surface, could affect the frequency of the EQCM. This model is described in the next section.

3.2.2.4. The Viscous-film model

A quartz resonator with a thin film of liquid having a viscosity \( \eta_f \), greater than the viscosity \( \eta_s \), in the bulk of the solution was assumed. The z-axis is chosen as the direction perpendicular to the surface and \( z=0 \) is the plane of the gold - coated crystal. \( L \) is the assumed thickness of the film. The effect of the film on the frequency shift is determined by solving the wave equation for elastic displacements in the quartz crystal and linearizing the Navier-Stokes equation for velocities in the film and in the bulk.

The shear time harmonic oscillation in the crystal

\[
u(r,t) = u(r,w)\exp(iwt)\tag{48}\]

has the form

\[
u(z,w) = V_0(w)\left[\cos(k(z + L))\right]\frac{\cos(kL)}{\cos(kL)w} \tag{49}\]
where \( d \) is the thickness of the quartz resonator, \( w \) is the angular velocity of oscillation, \( V_Q(w) \) is the amplitude of the velocity oscillations of the constrained quartz surface and \( k = w\left(\rho_q \mu_q\right)_{0.5} \). The vibrations of the quartz crystal and the movement of the liquid are along the \( y \)-axis parallel to the surface. The velocity distribution in the film \( V_f(z) \) and in the bulk of the solution \( V_s(z) \) have the forms:

\[
V_f(z) = A \exp(q_f z) + B \exp(-q_f z) \tag{50}
\]
\[
V_s(z) = C \exp[-q_s(z - L)] \tag{51}
\]

where \( q_s = \left(iw\mu_s/\eta_s\right)^{0.5} \) and \( q_f = \left(iw\rho_f/\eta_f\right)^{0.5} \), \( \eta_s \) and \( \eta_f \) are the viscosities of the bulk solution and the film, respectively. The boundary conditions for the velocities \( V_s \) and \( V_f \) are:

a. Non slip boundary condition at the gold coated quartz-film interface \((z=0)\).
b. Equality of the velocities at the film-solution interface.
c. Equality of the shear stresses of liquids at the film-bulk interface.

Using the equation and the boundary conditions and assuming that \( L \ll \delta \) the frequency shift, \( \Delta w = 2\pi f \) is given by

\[
\Delta w = -\frac{w^2}{\pi\left(\mu_q / \rho_q\right)^{0.5}} \left[ \left(\mu_s / 2w_0\right)^{0.5} + \rho_s L \left(1 - \frac{\eta_s}{\eta_f}\right) + (\rho_f - \rho_f) L \right] \tag{52}
\]

In this equation the three terms in bracket describe the effects of bulk viscosity, the additional effect of the viscosity of the surface film and the influence of the mass of the ions in the film resulting from electrostatic interactions (the product \( L(\rho_f - \rho_f) = \Delta m \)), respectively. Thus, the frequency shift caused by the difference between the viscosities of the film and the solution can be written in a form used in our calculations

\[
\Delta f_{\text{film viscosity}} = -C m \rho_s L \left(1 - \frac{\eta_s}{\eta_f}\right) \tag{53}
\]

For \( \eta_f \gg \eta_s \) the film acts as though it were firmly attached to the surface. For \( \eta_f = \eta_s \) the frequency shift is zero, which is reasonable, since this equality
implies that there is no film and the hydrodynamic properties of the solution are uniform from the surface of the gold-coated quartz crystal (at $z=0$) to the bulk of the solution.

This model is somewhat oversimplified, since a sharp boundary is assumed at a distance of $\kappa^{-1}$, where the value of the viscosity is assumed to change from $\eta$ to $\eta_f$. However, an example of the use of this equation that gives reasonable result was shown in [86]. In this example the frequency shift caused by the mass of the electrostatically adsorbed ions was subtract from the observed frequency. The remaining part of $\Delta f$ was then ascribe to $\Delta f_{\text{film vis cosmity}}$. Since electroneutrality is not maintained in the diffuse double layer, and it is difficult to take into account the influence of the electric field in the double layer on $\eta_f$, the value of $\eta_f$ was used as a parameter, to fit theory to the experimental results. Using $\Delta f_{\text{film vis cosmity}}$ in Eq. 53, $\eta_f$ as a function of the average concentration of the ions in the film, which in itself was calculate from the Gouy–Chapman theory, can be calculated. In this calculation, it was considered that $L = \kappa^{-1}$ (it is reasonable, as a first approximation, to assume that $L = \kappa^{-1}$, where $\kappa$ is the Debye reciprocal length, which is a measure of the thickness of the diffuse double). It was found that the dependence for the solution studied, followed the same trend as the dependence of the bulk viscosity concentration.

3.2.2.5. Comparing the EQCM response in $n$-butanol and aqueous solution

Accurate description of the dependence of $\eta_f$ on concentration would have to take into account the real concentration profile and the changes in the structure of the solvent in the direction perpendicular to the surface. Since such information is not available at present, the discussion below will be limited only to the dependence of the calculated value of $\Delta f_{\eta}$ on charge density, namely, that part of the frequency shift which is associated with the increased viscosity in the film adjacent to the surface, without attempting to calculate the value of the viscosity itself. This calculation is valid, independent
of the thickness assumed for the film, or the way in which the viscosity changes with the distance from the surface, as long as the film is very thin, compared to the hydrodynamic decay length.

Fig.78 shows the difference between the experiment (Fig.74 and 75) and the estimated mass effect (Fig.76) done on gold electrode. This represents the contribution of the viscosity to the frequency shift, $\Delta f_{\text{viscosity}}$, for both solvents. The curve describing the viscous effect in aqueous solution is roughly bell shape. This is consistent with a model stipulating enhanced structuring with increasing surface charge density, i.e. increasing field strength. This observation correlates well with molecular dynamic simulations. Sutmann has shown that, as the electrical field is increased, more hydrogen bonds are formed [168]. The same tendency was observed in other works, both molecular dynamic simulations [166,167] and X-ray diffraction experiments [169, 170]. The high field tends to cause “freezing” of the structure of water, up to a distance of about three layers. While water molecules can form two hydrogen bonds on the surface and more in the bulk, forming a three-dimensional structure, alcohols can only form one hydrogen bond, as discussed for methanol [171] and butanol [172].

![Fig.78. Calculated frequency shift due to viscosity changes in the diffuse double layer in butanol solution (solid line) and in aqueous solution (dashed line).](image-url)
Pemberton et al [153], using data obtained by surface enhanced Raman scattering, suggested that butanol molecules on a gold surface could have two different orientations, depending on surface charge density. The structure of butanol is such that, when it is adsorbed on a positive surface, forming a bond between the metal and a pair of free electrons on the oxygen atom, the alkyl tail of molecule is forced into a position parallel to the surface. In this orientation, the OH-bond is turned with its hydrogen atom towards the bulk of the solution. It has no bonds with the metal surface but can form hydrogen bonds with other solvent molecules. The situation is similar to what one has in aqueous solutions. As a result, increasing the positive surface charge density causes an increase in the viscosity of the film, as found also for water. Hence, for both solvents, the frequency shift is negative at positive charges, as shown in Fig.78.

![Graph](image)

Fig.79. Calculated frequency shift due to viscosity changes in the diffuse double layer in butanol solution (solid line) and in aqueous solution (dashed line).

At the PZC and at negative charges, the situation in butanol is quite different. The hydrogen atoms of the \( \alpha \)-methylene group form bonds with the metal surface and the remaining alkyl chain is repelled from it. This orientation hinders the formation of hydrogen bonds with other solvent molecules. Hence, the viscosity in the film does not increase with increasing negative charge,
and the frequency shift remains almost constant, in contrast to the behavior observed in aqueous solutions.

The above analysis was performed using the data obtained on gold electrode. Since the dependencies of EQCM response on charge are similar on silver, but sharper and the frequency shift due to mass does not depend on the nature of the metal electrode, comparable results and therefore conclusions were obtained for this case as shown in Fig 79. The effect of nature of the metal electrode is discussed in the next section.

3.2.2.6. Comparing the EQCM response on in n – butanol and aqueous solution

The frequency shift dependence on charge for silver is sharper than for gold for both solvents, as was shown in Fig.74 and Fig.75. In both cases the mass effect at a given charge has to be the same, which implies that all the difference is caused by the viscosity effect.

While using the model described above, the viscosity at the pzc is taken as the viscosity of the bulk of the solution. Thus there is no influence of the metal on the solvent layer nearest to it. If this is not the case, and there is some kind of specific interaction at the interface, a film having different viscosity from the bulk value is expected even at the pzc. It is reasonable to assume that the stronger the interaction between the metal and the solvent, the weaker the influence of the electric field and ion concentration on the film viscosity, particularly at small charge densities. At large charge densities the structure due to specific interaction between the metal and the solution is overcome and the slopes of the dependence of the EQCM on charge become the same. Therefore, the interaction of gold with water is stronger than that of silver and water.

A conclusion to this part of the work may be stated as – taking into account the weight of the ions pulled into the diffuse double layer as a result of electrostatic interaction cannot account for the potential dependence of the frequency of the EQCM in the double layer region on metal electrode. The data that were obtained from the EQCM and the analysis performed yields information concerning the changes of the structure of the double layer, and the influence of the metal electrode on this structure.
3.3 Specific adsorption

The response of the EQCM to specific adsorption was studied for different adsorbed molecules. The molecules were chosen so they are known to be adsorbed on the metal electrodes studied and their adsorption may changes the interface structure to some extent due to different bonds formed with the solvent molecules. The systems studied are listed in table 2.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Solvent</th>
<th>Metal</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>pyridine</td>
<td>H₂O</td>
<td>Au</td>
</tr>
<tr>
<td>B</td>
<td>pyridine</td>
<td>H₂O</td>
<td>Ag</td>
</tr>
<tr>
<td>C</td>
<td>n-butanol</td>
<td>H₂O</td>
<td>Au</td>
</tr>
<tr>
<td>D</td>
<td>pyridine</td>
<td>n-butanol</td>
<td>Au</td>
</tr>
<tr>
<td>E</td>
<td>pyridine</td>
<td>n-butanol</td>
<td>Ag</td>
</tr>
<tr>
<td>F</td>
<td>t-butanol</td>
<td>H₂O</td>
<td>Au</td>
</tr>
<tr>
<td>G</td>
<td>uracil</td>
<td>H₂O</td>
<td>Au</td>
</tr>
</tbody>
</table>

Table 2. The systems studied by EQCM

n-butanol was studied for the same reason discussed at the electrostatic adsorption section. The n-butanol molecule, with one –OH group and steric effect from the butyl group can form less rigid structure than the water network.

An extensive work was done on the adsorption of pyridine on gold and on silver electrode. Pyridine was found to be reoriented around the pzc from parallel orientation to almost perpendicular (with a tilt of 71° as was found in [173]) orientation. In the later case pyridine adsorb through the nitrogen leading to the –CH groups of the ring to face the solution. In that case no hydrogen bond can form. The influence of this orientation and the interaction with solvent molecules was studied both for n-butanol and aqueous solutions. Since pyridine is known to adsorb to the same extent on gold and on silver, the adsorption on both electrodes was studied.

As will discuss below, the adsorption of pyridine from aqueous solution on gold shows pronounce frequency shift. At that point, the adsorption of t-butanol was studied since it is known to adsorb on the surface through the hydroxyl group, with the methyl groups facing the solution. As for pyridine,
fewer bonds are expected to form. T-butanol was thought to be a simpler case, since it is adsorbed on the surface in only one orientation, and even a small tilt of the molecule cannot yield any bonds, because of the steric affect caused by the methyl groups.

The last molecule studied was uracil. Uracil as pyridine, is reoriented from parallel orientation to perpendicular orientation with a change in potential. However, unlike the case of pyridine, uracil has groups that can form hydrogen bond with the solvent molecules even when the molecule is adsorbed perpendicular to the surface. A very dense layer was observed [174] at positive charge densities.

In preliminary studies of the adsorption of pyridine on gold from aqueous solution, a hysteresis was observed. The extent of hysteresis decrease as the concentration increases and as the scan rate decreases (Fig.80). Similar hysteresis was observed in [102]. Lipkowski et – al [175], studied the time needed to low pyridine concentration to reach steady state. They found that, for solution concentrations lower than $10^{-5}$M, the time required for steady state adsorption is of the order of minutes. At higher concentration only a few seconds were required to reach steady state. Therefore, instead of cycling the potential during the EQCM measurements, the response of the EQCM was measured during stepping the potential. Current - time transient, obtained for polycrystalline gold electrodes in 1mM pyridine solution at various electrode potentials are shown in Fig.81. As can be seen, steady state is observed at each potential, usually within 10sec. The value considered was the difference between the steady state frequencies where pyridine adsorbed and where no adsorption occurred. Each potential step was repeated several times and the average value was used.

Since in most of the cases some extent of hysteresis was observed, most of the EQCM measurements were done during potential step. The EQCM results were analyzed in the following way. All data were plotted vs. surface charge density, since the effect of electrostatic adsorption discussed above, for a given supporting electrolyte is, to a good approximation, independent of specific adsorption, and the parameter controlling the state of the diffuse double layer is the surface charge density. The following procedure was used to analyze the data obtained. The first step was to ascribe a value
of zero to the frequency shift measured at the pzc in the supporting electrolyte. Then, the curves obtained in electrolytes containing the specifically adsorbed substances were shifted, so that at negative charges, where no specific adsorption occurs, they coincided with the curves for the supporting electrolytes.
Fig. 80. The dependence of the frequency shift on scan rate (a) 0.1mM (b) 1mM (c) 30 mM pyridine.
Following this procedure, the difference between the two cases (with and without specifically adsorbed substance) can be ascribed to the influence of specific adsorption. This correction of the frequency shift obtained in electrolyte solution is important, since it may reach values that are comparable with those typically expected for monolayer adsorption. The mass contribution to the frequency shift in each case can be calculated from the equation:

$$\Delta f_m = -C_m \Gamma_{ads} (M_{ads} - \nu \cdot M_{solvent})$$  \hfill (54)

where $M_{ads}$ and $M_{solvent}$ are the molecular weights of the adsorbate and of the solvent, respectively, $\Gamma_{ads}$ is the surface excess of the adsorbate and $\nu$ is the number of solvent molecules replaced by each adsorbed organic molecules.

The dependence of the surface excess, $\Gamma_{ads}$, on charge was discussed above. The other parameter required is the number of solvent molecules replaced by each solute molecule adsorbed. This was estimated from the variation of density with concentration, similar to the calculation done for electrolyte solution. As for electrolyte solution, this is the best independent information, since the behavior of the systems studied at the interface is not available. The values of the parameter $\nu$ calculated from the density cannot be very far from
reality and $v$ is not a free adjustable parameter. The literature data for the density were taken from [176,177].

The frequency shift due to changes of the properties of the interface is obtained by the subtraction of the frequency shift calculated for changes of mass from the obtained frequency shift as will discussed below.

3.3.1. Cyclic voltametry and differential capacitance

Fig.82-88 show the voltamograms obtained for the systems studied. The corresponding differential capacitance curves are shown in Fig.89-95. Measurements were performed only at potentials in the double-layer region, to avoid oxidation of organic substances and changes of the electrode surface.

![Voltamogram](image)

Fig. 82. Voltamogram obtained in 0.1M LiClO$_4$ electrolyte aqueous solution and in solution containing pyridine on gold electrode.

![Voltamogram](image)

Fig. 83. Voltamogram obtained in 0.1M LiClO$_4$ electrolyte aqueous solution and in solution containing pyridine on silver electrode.
Fig. 84. Voltamogram obtained in 0.1M LiClO₄ electrolyte n-butanol solution and in solution containing pyridine on gold electrode.

Fig. 85. Voltamogram obtained in 0.1M LiClO₄ electrolyte n-butanol solution and in solution containing pyridine on silver electrode.

Fig. 86. Voltamogram obtained in 0.1M LiClO₄ electrolyte aqueous solution and in solution containing n-butanol on gold electrode.
Fig. 87. Voltamogram obtained in 0.1M LiClO₄ electrolyte aqueous solution and in solution containing t-butanol on gold electrode.

Fig. 88. Voltamogram obtained in 0.1M LiClO₄ electrolyte aqueous solution and in solution containing uracil on gold electrode.

Fig. 89. Differential capacitance curve obtained in 0.1M LiClO₄ aqueous solution containing pyridine on gold electrode. The frequency used is 25Hz.
Fig. 90. Differential capacitance curve obtained in 0.1M LiClO₄ aqueous solution containing pyridine on silver electrode. The frequency used is 25Hz.

Fig. 91. Differential capacitance curves obtained in 0.1M LiClO₄ electrolyte n-butanol solution and in solution containing pyridine on gold electrode. The frequency used is 6Hz.

Fig. 92. Differential capacitance curve obtained in 0.1M LiClO₄ n-butanol solution containing pyridine on silver electrode. The frequency used is 6Hz.
Fig. 93. Differential capacitance curve obtained in 0.1M LiClO$_4$ aqueous solution containing n-butanol on gold electrode. The frequency used is 6Hz.

Fig. 94. Differential capacitance curve obtained in 0.1M LiClO$_4$ aqueous solution containing t-butanol on gold electrode. The frequency used is 6Hz.

Fig. 95. Differential capacitance curve obtained in 0.1M LiClO$_4$ aqueous solution containing uracil on gold electrode. The frequency used is 6Hz.
All the voltamograms were obtained at a scan rate of 50mV \text{sec}^{-1}. All the differential capacitance curves were obtained at a scan rate of during 5mV \text{sec}^{-1}. The amplitude was always 5 mV. The frequencies used are indicated on each curve.

The concentration range chosen depends on the adsorb molecules the solvent and the electrode. The concentrations of n-butanol studied were 0.1M to 0.8M. The concentrations of pyridine studied were 0.1mM to 30mM on both electrodes and in aqueous and n-butanol solution. The concentrations of t-butanol studied were 0.14M to 1.2M and of uracil 4mM to 12mM. The curves reported in the literature for the adsorption of pyridine from aqueous solution on gold [147,148] and on silver [149,150], the adsorption of n-butanol from aqueous solution [151] and the adsorption of uracil [152] from aqueous solution on gold were similar to those obtained here.

Adsorption of pyridine on gold from aqueous and n-butanol solution shows a characteristic adsorption peak on the voltamograms and the differential capacitance curve. The second peak observed is related to the reorientation of pyridine as was found by chronocoulometry, radiotracer and STM measurements obtained in aqueous solution [147,148,178,179]. With increasing concentration of pyridine, the heights of the peaks increase and their potential shifts in the negative direction. In the differential capacitance obtained in aqueous solution at high pyridine concentration, a shoulder can be seen on the peak, which appears negative to the \textit{pzc}. The adsorption of pyridine on silver electrodes result in a decrease in the differential capacitance as expected. If n-butanol is the solvent two peaks observed.

The form of the voltamograms and the capacitance curves, as a function of potential and n-butanol concentration is similar to those frequently observed for neural organic substances adsorbed on mercury. The adsorption peak is observed, followed by lower differential capacitance values than in aqueous solutions.

T-butanol adsorption yields one peak in the voltamogram and capacitance curve.
Two peaks were obtained in the voltamograms and the capacitance curves for the adsorption of uracil on gold from aqueous solution. The first peak is an adsorption peak, and the second peak corresponds to the reorientation of uracil and to the formation of a very stable layer [152].

3.3.2. Frequency shift measurements

Typical data of the EQCM response for the different cases of specific adsorption are shown in Fig.96-102. The adsorbate concentration in the bulk solution is indicating in each figure. Fig. 103-109 represent the difference between frequencies of the electrolyte and the solution containing the adsorbate molecules. The subtraction was done as describe above. The dependence of the frequency on the charge obtained for electrolyte solution was not extrapolated for the subtraction, but the subtraction was limited to the range where this dependence exists. Therefore, for uracil the charge range is limited.

Considering the figures it is clearly seen that in all the cases of specific adsorption studied entirely different behaviors was observed. However, in all the cases, an increase in the frequency is observed rather than decreases.

As discussed above, the first data needed are numbers of solvent molecules replace by each adsorbed molecule. Using literature data of the density of bulk solutions it was found that - about 4.4 water molecules are replaced by one molecule of pyridine, 4.8 water molecules are replaced by one molecule of n-butanol, 0.87 molecules of n-butanol, about 4.8 water molecules are replaced by one molecule of t-butanol and about 5.4 water molecules are replaced by one molecule of uracil.
Fig. 96. EQCM response to the adsorption of pyridine (open circle) and for electrolyte solution (full circle) from aqueous solution on gold electrode.

Fig. 97. EQCM response to the adsorption of pyridine (open circle) and for electrolyte solution (full circle) from aqueous solution on silver electrode.
Fig. 98. EQCM response to the adsorption of pyridine (open circle) and for electrolyte solution (full circle) from n-butanol solution on gold electrode.

Fig. 99. EQCM response to the adsorption of pyridine (open circle) and for electrolyte solution (full circle) from n-butanol solution on silver electrode.
Fig. 100. EQCM response to the adsorption of n-butanol (open circle) and for electrolyte solution (full circle) from aqueous solution on gold electrode.

Fig. 101. EQCM response to the adsorption of t-butanol (open circle) and for electrolyte solution (full circle) from aqueous solution on gold electrode.
Fig. 102. EQCM response to the adsorption of uracil (open circle) and for electrolyte solution (full circle) from aqueous solution on gold electrode.

Fig. 103. EQCM response to the adsorption of pyridine from aqueous solution on gold electrode after the electrostatic adsorption correction.
Fig. 104. EQCM response to the adsorption of pyridine from aqueous solution on silver electrode after the electrostatic adsorption correction.

Fig. 105. EQCM response to the adsorption of pyridine from n-butanol solution on gold electrode after the electrostatic adsorption correction.
Fig. 106. EQCM response to the adsorption of pyridine from n-butanol solution on silver electrode after the electrostatic adsorption correction.

Fig. 107. EQCM response to the adsorption of n-butanol from aqueous solution on gold electrode after the electrostatic adsorption correction.
Fig. 108. EQCM response to the adsorption of t-butanol from aqueous solution on gold electrode after the electrostatic adsorption correction.

Fig. 109. EQCM response to the adsorption of uracil from aqueous solution on gold electrode after the electrostatic adsorption correction.
Assuming that these values are valid also for the interface, and substituting them in Eq.54, combined with the corresponding data on surface excess, the frequency shift due to mass changes on the electrode can be found. The result of such calculation is shown in Fig.110.

![Graph showing frequency shift due to mass changes](image)

**Fig. 110.** The calculated frequency shift due to changes of mass at the interface for the adsorption of pyridine from aqueous solution on gold and on silver electrode (---), for the adsorption of pyridine from n-butanol solution on gold (----) and on silver (0) electrodes, for the adsorption of n-butanol from aqueous solution on gold (?), for the adsorption of t-butanol from aqueous solution on gold (---), and for the adsorption of uracil from aqueous solution on gold (---).

For pyridine in water, the expected frequency shift due to changes in mass upon adsorption should be close to zero, over the whole range of potential studied, since $\nu = 4.4$ is exactly equal to the ratio of molecular weights of pyridine and water.

For n-butanol adsorption from water, the frequency should increase by about 0.25 Hz. Similarly, for the case of pyridine adsorption from n-butanol on gold, the calculated shift of frequency due to the mass effect can reach a value of -1Hz. For pyridine adsorption from n – butanol solution on silver electrode, the frequency decreases by 0.25Hz. The frequency shift calculated due to mass for the highest surface excess of t-butanol adsorption ($5.5 \times 10^{-10}$ mole cm$^{-2}$) would cause a small increase in frequency of only 0.5 Hz. The
calculated frequency shift, due to the mass changes, during the adsorption of uracil decrease maximum to –0.5Hz.

In all the cases, there is a substantial difference between the observed shift in frequency and that calculated from the mass-effect. This indicates that most of the change in frequency is associated with changes of viscosity/structure of the thin layer adjacent to the vibrating surface.

A remarkable difference between the dependence of the frequency shift on charge for the aqueous solutions on gold electrode with and without pyridine Fig.96 is seen at positive charges. The increase in frequency may be associated with the destruction of bonds between molecules at the interface. Adsorbed pyridine molecules destroy the previous structure of water and replace the water/water interactions between the first layer, attached directly to the surface, and further layers at the interface, by pyridine/water interactions, which must be much weaker. Such a replacement is effective at sufficiently large pyridine coverage. It can be reinforced by the re-orientation of pyridine: it is adsorbed in a flat orientation at negative charge densities, but at positive charge densities (associated with higher values of the surface excess), it is oriented at some angle to the surface, with the benzene ring towards the solution [174]. The decrease of bonding between the vibrating surface (with a layer of pyridine rigidly attached to it) and the rest of the solution will exerts an effect similar to a decrease in viscosity of the film, leading to the increase of frequency observed with increasing positive charge.

Similar results have been obtained in the presence of n-butanol in aqueous solution on gold electrode, as shown in Fig.98. At negative charges, (i.e. at small coverage), there is no effect of adsorption on the frequency shift – the points obtained with and without n-butanol in solution practically coincide. At positive charges the difference in these two cases increase gradually. However, in contrast to pyridine, the frequency shift in the presence of n – butanol pyridine becomes constant.

At a positively charged surface, the alkyl chain of n-butanol is positioned on the surface blocking a relatively large area, as discussed above. The alkyl chain destroys the structure of the water at the surface. Bonds can be form
with the –OH group of n-butanol, which is open to the solution in this orientation, but for much lesser extant than water can form.

It is interesting to note that the difference between the frequency obtained in electrolyte and in the solution containing n-butanol is similar to the difference between the curves obtained in aqueous and n-butanol electrolyte solution.

Considering the data obtained with n-butanol as the solvent on gold electrode (Fig.98.), attention is drawn to the fact that the absolute values of the frequency shifts and the effect of pyridine addition are considerably smaller than for pyridine adsorption from water on gold. It is smaller, despite the fact that the surface excess in the two cases is similar. This is not surprising, in view of the fact that H-bonds in alcohol are considerably weaker than in water. Thus, replacement of n-butanol on the surface by pyridine is quite different from replacement of water by pyridine, and it is expected to have a much less dramatic effect on the viscoelastic properties at the interface. The positive frequency shift observed could be explained by the change in the interaction of the surface with the solvent. While only n-butanol exists in the solution, hydrogen bonds still can be formed with other solvent molecules. If pyridine is adsorbed on the surface, probably with the hydrophobic part facing the solution, especially at positive potentials, fewer bonds can be formed with the solvent molecules.

T-butanol is considered to be adsorbed through the -OH group, with the hydrophobic methyl group facing the solution, as other alcohols [153]. When the water layer is replaced by t-butanol, the interactions with bulk water are weaker, the properties of the layer change, and a positive frequency shifts are observed.

The fact that t-butanol can only be adsorbed in one configuration, with –OH group facing the surface and that monolayer of t-butanol should then present a hydrophobic surface, should lead to a high positive change in the frequency observed, exceeding that found for n-butanol and even that of pyridine. The observed values of the frequency shift are indeed somewhat higher than those found for n-butanol, but significantly lower than for pyridine.

This unexpected behavior can be attributed to the fact, that water tends to form chlatrates around t-butanol, holding the molecule effectively in a cage
of 21 water molecules [156]. If this structure or part of it is adsorbed on the surface, it would shield the methyl groups from the rest of the solution. This would present a hydrophilic surface toward the rest of the solution, as opposed to the hydrophobic nature of the bare –CH₃ groups, leading to a much lower value of the positive frequency shift, as observed experimentally. The formation, of cages containing a large number of water molecules, is consistent with the large variation of the activity coefficient of bulk t-butanol and of LiClO₄ (at constant concentration of the latter), at relatively low concentrations of the organic material.

A decrease in the frequency shift is obtained at positive charge densities, when the t-butanol is desorbed from the surface. A minimum surface excess is required to observed the decrease in frequency - the desorption of the molecules start at lower charge densities than the decrease in frequency (i.e. the maximum in the frequency shift is at higher charge density than the maximum obtained in the surface excess). Where desorption starts, the surface concentration is still high and changes of its properties are still minimal. Only when significant desorption occur, does the frequency decrease. Similar conclusion can be drawn when we consider the frequency shift obtained at two high concentrations of t-butanol. A comparable dependence of the frequency shift on the charge densities is observed. This similarity is reasonable, since even at a lower bulk concentration, the surface concentration is high enough to maintain the nature of the thin layer near the crystal surface. Same results were obtained for pyridine adsorption from n-butanol and aqueous solution.

In that configuration, no frequency shift is expected as for the case of pyridine. At positive charge densities, at which uracil is adsorbed perpendicular to the surface, it disturb the structure of the interface.
As observed, the disturbance is small since, for uracil, the functional groups -O or –N can form hydrogen bonds. The EQCM data in the case of uracil cannot distinguish between the configurations suggested for uracil adsorption (shown in Fig.111) since in both cases hydrogen bonds can be formed with the solvent molecules.

The behavior observed on the silver is quite different from the result obtained on gold. The structure of the layer of water nearest the gold surface is different from that nearest to the silver surface, as discussed previously. Since the interaction of a silver surface with water is weaker, there is less surface structure to be destroyed or altered by the adsorption of pyridine, resulting in a small frequency shift. Since the adsorption of pyridine from aqueous solution reaches almost immediately its maximum value \([149,150]\) the frequency shift obtained is quite constant and small.

The surface excess behavior of pyridine adsorbed from n-butanol solution on silver is quite different from the behavior in the other systems. Adsorption becomes pronounced only at positive charges. That can explain the fact that no frequency shift is observed at negative charges. As the charge decreases closer to the pzc, a slight increase in the frequency is observed. This increase is similar to the increase observed during the adsorption of pyridine from n-butanol solution on gold electrode. After the pzc the frequency increases slightly as the surface excess increase.

Since the surface excess of pyridine from n-butanol solution on silver electrode is smaller at positive charges than for the case of adsorption on gold electrode from n-butanol solution, the mass effect is smaller and the observed frequency shift should be slightly higher as observed. From this it can be concluded that the adsorption of pyridine from n-butanol on both electrodes affect the interface in the same way.

For obvious reasons, any comparison of bulk properties of solutions with their properties at the interface is rather approximate. Nevertheless, it may be interesting to consider some parallelism between the dependence of the viscosity on concentration in the bulk and the variation of the EQCM response with surface excess. The dependence of viscosity on composition
takes different forms in different mixtures. The system pyridine-water has a bell shaped behavior, with a maximum in the viscosity corresponds to a mole fraction of pyridine of about 0.45 [180]. Following this maximum, the viscosity decreases by about 60% with further increase of the amount of pyridine in the mixture, up to a mole fraction of unity. This can be correlated in a qualitative manner with the increase in the frequency shift with increasing positive charge density observed on gold electrode, as shown in Fig.103. Since on silver electrode the surface excess reaches the maximum value immediately, no changes in the viscosity is expected and a constant frequency shift is observed.

In comparison, the viscosity of mixtures of n-butanol-water only decreases by 14% [181] as the mole fraction of n-butanol increase from 0.1 to 1.0. In the same concentration region, the viscosity of pyridine-n-butanol mixture decrease by 18%, as was measured in our lab with a viscosimeter and in other work [182]. The smaller changes in viscosity in these mixtures correlate well with the smaller dependence of the frequency shift observed on charge, which reflects the dependence of viscosity of a thin film attached to the electrode (gold and silver) on the surface excess. Thus, the shape of the viscosity–concentration dependence for solvent mixtures in the bulk is reflected in the EQCM response on specific adsorption at the interface for the corresponding cases.

An alternative way of looking at this phenomenon is to consider the interactions between the first layer of molecules adsorbed on the surface and the following layers. When solvent molecules are replaced by adsorbed molecule, their interaction with the further solvent layer is much weaker. This may lead to a finite slippage at the adsorbed layer/solution interface, and an increase in frequency of the EQCM.

Following this line of reasoning it is possible to discuss the relationships between the slip length, surface excess and the microscopic properties of interfacial layer. A model was developed in which it is assumed that the adsorbed layer is rigidly coupled to the crystal [183]. This results in non-slip boundary condition at the solid adsorbate interface. Slippage is allowed at the adsorbate-liquid interface. From the equation of motion of the system, the shift of the measured resonance frequency, can be expressed as:
\[
\Delta f = - \frac{2 f^2 \rho_s}{(\rho_q \mu_q)^{3/2}} + \frac{2 f^{3/2}(\rho_q \mu_q)^{3/2}}{(2 \pi \rho_q \mu_q)^{1/2}} \frac{a(a+1)}{(a+1)^2 + a^2}
\]  
\[(55)\]

where

\[
a = \frac{\eta_l}{\eta_s \delta_l} = \frac{\delta_s}{\delta_l}
\]  
\[(56)\]

\(\eta_a\) is a friction coefficient, \(\delta_s = \eta_l / \eta_a\) is the slip length and \(\delta_l = (\eta_l / \omega \rho_q)^{1/2}\) is the velocity decay length in the liquid. Eq. 55 show that there are two contributions to the frequency shift – the change of mass of the adsorbed layer and partial decoupling between the quartz crystal oscillation and the solution, caused by the slippage at the adsorbate-liquid interface. From this model the slip length can be estimated, after the subtraction of the frequency shift caused by the mass changes (which can be done as was explained previously) from the frequency shift measured.

The model was applied to two sets of data – the adsorption of pyridine on gold electrode from aqueous and n-butanol solution. The slip length obtained for those two cases are shown in Fig.112. In agreement with the theoretical prediction, the slip length grows with the surface excess. The dependence of the slip length on the surface excess is very close to linear for pyridine adsorption from n-butanol solution, but deviates from linearity for pyridine adsorption from water. This deviation may be attributed to a reorientation of adsorbed pyridine molecules.

![Fig.112. The slip length vs. the surface excess of pyridine for two interfaces gold/butanol (solid line) and gold/aqueous solution (dashed line) of 0.1M LiClO₂ + 5mM pyridine.](image)
In this section, the use of the EQCM as a tool for interface studies is presented. Details on the solvent structure at the interface, the influence of the adsorbate orientation and the nature of the metal electrode can be obtained. Other physical parameters as the slip length can be estimated from the frequency shift obtained.
4. Conclusions

The EQCM has become a very popular method in the recent years. The high sensitivity, the simple relationship between mass and frequency, the fact that \textit{in - situ} measurements can be performed and the inexpensive equipment needed made this technique very common in many electrochemical experiments done, usually in conjunction with other methods. In many cases studied, especially in the monolayer region – i.e. during specific adsorption, electrostatic adsorption and UPD, the results obtained were not easy to understand on the basis of mass added to the surface. Many examples exist, some of them are mentioned in the introduction.

It is well known that the QCM is sensitive to other phenomena that occur on its surface. Expressions were derived for the dependence of the shift in frequency on changes in the viscosity, temperature and compression.

This work shows that valuable information can be obtained by using the EQCM. A detailed description of the interface, including the structure of the solvent and the adsorbate at the interface and the influence of the nature of the metal electrode on adsorption can be obtained from EQCM measurements.

The most common interpretation of the EQCM response is the changes of mass on its electrode. Therefore, it is surprising to find that during electrostatic adsorption at the double layer region, the frequency shift depends on charge/potential and that positive frequencies shift (i.e. an apparent decrease in mass on the EQCM surface) is observed during specific adsorption.

Even by considering that, the application of potential pulls ions into the interface, calculation of the mass change on the surface during this replacement process show clearly that this is not the main reason to the frequency shift obtained.

It was found that the reason to the frequency shift obtained was the high ion concentration at the interface and the high electrical filed which cause to changes in the structure and the properties of the interface.
Similar conclusions were reached in many computer simulations, where it is shown that the properties of a few molecular layers at the interface are different from the bulk.

The change at the interface properties was explained in a two ways from which information on the interface was obtained. From a macroscopic point of view, the high electrical filed and the high ionic concentration can change the viscosity and the density of this layer. A model was developed [86] to describe the frequency charge/potential dependence observed for electrostatic adsorption. Using this model, the viscosity of the interface, which can not be calculated or measured by the classical technique, was estimated. This model yields reasonable result, similar to bulk properties.

Not only the case of electrostatic adsorption follows this explanation. For the case of specific adsorption, the mass contribution, as in the former case is negligible. Therefore, estimation of the interface viscosity was given. Moreover, as in the former case, solutions with large dependence of bulk viscosity with concentration show large changes in the frequency shift.

An alternative way to explain the changes at the interface properties is from a microscopic point of view. The solvent molecules form on the surface a structure of a few molecular layers (computer simulation shows that water forms about 3-4 structured molecular layers) on the surface. The properties of this structure depend on the surface charge. Water, for example, forms more hydrogen bonds as the potential becomes more positive or more negative. The higher number of bonds formed the bigger the disturbance to the crystal oscillation. If the ability to form bonds is smaller, as for the case of n-butanol as a solvent, the dependence of the frequency on charge/potential is weaker.

Similar explanation was given for the case of specific adsorption. If the molecules adsorbed on the surface can form as many bonds as the solvent molecules, the frequency/charge dependence will remains almost unchanged. If however, fewer bonds can be formed, the crystal can oscillates more easily, resulting in a positive frequency shift.

Going further with this explanation, the changes in the frequency can be explained by different finite slippage of one layer on another [183]. If more bonds are formed due to the applied potential, a smaller finite slippage exists.
between the layers. If fewer bonds are formed, as for the case of specific adsorption, the finite slippage is bigger, resulting in a positive frequency shift.

The explanations given above were used to understand the structure of the interface. For example, in the case of t-butanol, a lower frequency shift than expected was observed. This may indicate that t-butanol molecules on the surface have a water structure around them, as was found in the bulk. This structure keeps almost the same number of bonds, the slippage does not change considerably and therefore the frequency remains almost unchanged.

4.1. Suggestions for future research

Further investigation using the EQCM may yield more valuable results. By using the whole impedance spectrum obtained from the EQCM, information is obtained not only from the real part – the frequency shift, but also from the imaginary part of the spectrum. The imaginary part of the impedance is sensitive to the nature of the interface but also to losses or heat dissipation caused by internal friction in the crystal, to the viscosity of the liquid and to the stiffness of the crystal.

The EQCM may be used to investigate surface reconstruction. Reconstruction occurs since atoms on the surface experience different forces than atoms in the bulk, which leads to rearrangement of the top layer with respect to the bulk structure. It was also found that adsorption of organic molecules, such as pyridine and uracil, enhance surface reconstruction [184]. This reconstruction may lead to changes in the compression, and may result in a frequency shift. The influence of such effects can be studied by measuring the frequency shift obtained on AT and BT crystals.

A better understanding of the metal solution interface should include more experiments. To learn more about the influence of the nature of the metal electrode, other metal electrodes should be investigated. An example for an interesting electrode is the Pb electrode, which is electrochemically similar to the mercury electrode.
Other types of solvents should be examined. Aprotic solvents containing oxygen atoms, such as propylene carbonate and solvents containing $\pi$-orbitals, such as acetonitrile should be studied, to clarify the role of the solvent on the structure of the double layer. Acetonitrile is of particular interest, since this linear molecule is believed to be adsorbed flat on the surface, with its large dipole moment perpendicular to the direction of the applied field, unlike water and most other solvents.

The adsorption of larger molecules, such as polymers or proteins, can be studied. Except from the industrial interest of such molecules, it is interesting to examine their behavior when potential is applied and gained further insight of the structure of the interface.
5. References

37. A. P. M. Glassford in Progress in Astronomic and Aeronautics, A. M. Smith, ed.,


86. V. Tsionsky, L. Daikhin and E. Gileadi, *J. Electrochem. Soc.* **143**:2240(1996);


144. J. Lipkowski and L. Stolberg, in *Molecular Adsorption at Gold And Silver Electrode*, p.171-238.


### Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Surface area of the quartz plate / Absorbance.</td>
</tr>
<tr>
<td>a</td>
<td>The average lateral length, ( a = \frac{\eta}{\eta_\delta} ).</td>
</tr>
<tr>
<td>( a_A )</td>
<td>The activity of the organic compound in the bulk solution.</td>
</tr>
<tr>
<td>( a_e )</td>
<td>The activity of the electrolyte in the bulk solution.</td>
</tr>
<tr>
<td>( a_\hat{\delta} )</td>
<td>The activity of the organic compound.</td>
</tr>
<tr>
<td>( a^\pm )</td>
<td>The activities if the cations and anions.</td>
</tr>
<tr>
<td>( a_\pm )</td>
<td>The mean ionic activity of an electrolyte.</td>
</tr>
<tr>
<td>AT-cut</td>
<td>A slice though a quartz rod at an angle of approximately 35° with respect to crystallographic ( x ) axis. The most commonly used for QCM applications.</td>
</tr>
<tr>
<td>c</td>
<td>Adsorbate concentration.</td>
</tr>
<tr>
<td>( c^0 )</td>
<td>Bulk concentration.</td>
</tr>
<tr>
<td>C</td>
<td>The elastic constant</td>
</tr>
<tr>
<td>C</td>
<td>Constant.</td>
</tr>
<tr>
<td>( C_0 )</td>
<td>The electrical capacitance of the quartz between the electrodes.</td>
</tr>
<tr>
<td>( C_e )</td>
<td>Constant electrolyte concentration.</td>
</tr>
<tr>
<td>( C_I )</td>
<td>Corresponds to the stored energy in the oscillation (i.e. the elasticity of the crystal and the surrounding medium).</td>
</tr>
<tr>
<td>( C_{dl} )</td>
<td>The double layer capacitance.</td>
</tr>
<tr>
<td>( C_p )</td>
<td>The parasitic capacitance of QCM and test fixture.</td>
</tr>
<tr>
<td>( C_m )</td>
<td>Proportionality constant between the oscillation frequency of the piezoelectric crystal to the mass changes on the crystal face. This constant depends only on the crystal properties.</td>
</tr>
<tr>
<td>d</td>
<td>Diameter.</td>
</tr>
<tr>
<td>( D_Q )</td>
<td>The dielectric constant of quartz.</td>
</tr>
<tr>
<td>E</td>
<td>Potential.</td>
</tr>
</tbody>
</table>
$E^\pm$  The potential of the ideal polarized electrode with respect to an electrode dipping into the same solution which is reversible either to the cation, $E^+$, or to anion, $E^-$, of the electrolyte.

$E^0$  The standard electrode potential.

$F$  Faraday constant.

$f_0$  The fundamental frequency of the acoustic wave, which is known, also as the thickness shear mode or the fundamental mode.

$f_A$  The fugacity of the organic compound in the solution.

$f_A^0$  The fugacity of the pure compound.

$f_{activity}$  Activity coefficient.

$f_c$  The resonance frequency of the composite resonator formed from the crystal and the film present at the surface.

$f_f$  The resonant frequency of the freestanding foreign film.

$f_m$  The resonant frequency of the motional arm.

$f_s$  The serial resonance frequency of the complete equivalent circuit/ the frequency of maximum conductance.

$f_p$  The parallel resonance frequency of the complete equivalent circuit.

$\Delta f$  Changes in the oscillation frequency of a piezoelectric crystal.

$\Delta f_{mass}$  The shift in frequency caused by changes of mass on the electrode surface.

$\Delta f_{viscosity/density}$  The shift in frequency caused by changes of the solution viscosity and density.

$\Delta f_{film viscosity}$  The shift in frequency caused by changes of the film viscosity.

$\Delta f_{viscoelastic}$  The shift in frequency caused by changes of the viscoelasticity of a film adsorbed on the electrode.

$\Delta f_{compression}$  The shift in frequency caused by changes of compression – i.e. the pressure applied on the electrode or stresses formed in the metal electrode/deposit.

$\Delta f_{roughness}$  The shift in frequency caused by changes of the electrode roughness.
$\Delta f_{\text{temperature}}$ The shift in frequency caused by temperature changes near the electrode face.

$h$ The average height.

$k$ The propagation constant of the instantaneous shear wave velocity decay, $k = w w (\rho_q \mu_q)^{0.5}$.

$K$ constant, $2.75 \times 10^{-12} \text{ cm}^2/\text{dyne}$.

$I_A$ The integral of the chromatogram for the solution.

$I_A^0$ The integral for the pure compound.

$i_{dl}$ The double layer charging current

$L$ The average distance between inhomogeneities/ The thickness of the film.

$L_1$ Correspond to the inertial component of the oscillation – i.e changes of mass on the electrode.

$L_2$ The motional inductance.

$L_3$ The motional inductance due to mass loading

$l$ The resonator and its electrode thickness, 0.2mm in our crystals / the cell length.

$\Delta l$ The change in the thickness of a quartz plate.

$\Delta m$ Mass changes on the crystal face.

$\Delta \tilde{m}$ The mass of any foreign layer.

$\Delta m_{a,c}$ Change of mass due to anions and cations in the diffuse double layer.

$\Delta \tilde{m}_Q$ The change in mass of quartz plate.

$m_{\text{quartz}}$ The mass of the quartz crystal.

$m(r, \theta)$ The mass distribution.

$M_a$ The molecular weight of the anion.

$M_c$ The molecular weights of the cation.

$M_w$ The molecular weights of water.

$M_{\text{ads}}$ The molecular weights of the adsorbate.

$M_{\text{solvent}}$ The molecular weights of the solvent.

$n$ Number of equivalents per mole.
P Pressure.

$P_A$ The partial pressure of the organic compound in the vapor phase in equilibrium with solution.

$P_A^0$ The vapor pressure of the pure organic compound.

pzc Potential of zero charge.

$q_s$ $q_s = \left(iw\rho_s/\eta_s\right)^{0.5}$

$q_f$ $q_f = \left(iw\rho_f/\eta_f\right)^{0.5}$

Q The quality factor that is the ratio of the energy stored to energy lost during a single oscillation.

R The gas constant.

$R_1$ Correspond to the dissipation of the oscillation energy (cause by viscous solution and the mounting of the crystal).

$R_2$ The motional resistance.

$R_F$ The faradaic resistance.

$R_S$ The solution resistance.

r The distance of the deposit from the center of the crystal / dissipation coefficient corresponding to the energy losses during oscillation.

$r_e$ The radius of the excitation electrodes.

$S(r, \theta)$ The differential mass sensitivity, $S(r, \theta) = df/dm$.

T Thermodynamic temperature.

UPD Under potential deposition.

$t$ Time in sec.

$V_0$ The maximum amplitude of the shear wave.

$V_x$ The instantaneous shear wave velocity decay in the x direction – parallel to the resonator-liquid interface).

$V_Q(w)$ The amplitude of the velocity oscillations of the constrained quartz surface.

$V_f(z)$ The velocity distribution in the film.

$V_s(z)$ The velocity distribution in the bulk of the solution.

$x_A$ The mole fraction of the organic compound (A).
$x_w$ The mole fraction of water (W).

$\Upsilon$ Elastic surface stress.

$z$ The distance from the resonator surface.

$z_\pm$ The ionic valances of the cations and anions.

$z_f$ The acoustic impedance of the film, $z_f = \rho_f \nu_f = (\rho_f \mu_f)^{1/2}$.

$z_q$ The acoustic impedance of the quartz, $z_q = \rho_q \nu_q = (\rho_q \mu_q)^{1/2}$.

$\alpha$-quartz The form of quartz crystal that is stable up to 573°C, belong to the trigonal group.

$\gamma$ Electrosorption valency.

$\gamma$ The interfacial tension of the electrode.

$\tilde{\gamma}$ Specific surface work.

$\Gamma_{AW}$ The relative surface excess of the organic compound (A) with water (W) taken as the reference component.

$\Gamma_A$ The surface excess of the organic compound (A).

$\Gamma_W$ The surface excess of water (W).

$\Gamma_{\pm W}$ The relative surface excess of the ion of the electrolyte to which the indicator electrode is not reversible.

$\Gamma_{app}$ The apparent surface excess $\Gamma_{app}$.

$\Gamma_+$ Relative surface excess of the cation.

$\Gamma_-$ Relative surface excess of the anion.

$\Gamma_{ads}$ The surface excess of the adsorbate.

$\delta$ The decay length.

$\delta_s$ The slip length.

$\delta_i$ The velocity decay length in the liquid.

$\Delta\sigma_M$ The relative charge densities.

$\epsilon$ The piezoelectric stress constant / the molar absorption coefficient.

$\epsilon_0$ Permittivity of free space.

$\eta_s$ The friction coefficient.

$\eta_l, \eta_r$ The viscosity of the solution.
\( \eta_f \) The film viscosity.

\( \omega \) The angular frequency of the instantaneous shear wave velocity decay.

\( \mu_q \) The shear modulus of \( \alpha \)-quartz \( \mu_q = 2.947 \times 10^{11} \frac{\text{gr}}{\text{cm}^2 \text{sec}^2} \).

\( \mu_f \) The shear modulus of a deposited film.

\( \nu \) The angle the quartz crystal is slice with respect to crystallographic \( x \) axis. \( \nu = 35^0 \) for AT-cut.

\( \rho_q \) The density of \( \alpha \)-quartz (\( \rho_q = 2.648 \frac{\text{gr}}{\text{cm}^3} \)).

\( \rho_f \) The density of a deposited film.

\( \rho_l, \rho_s \) The density of the solution.

\( \theta \) The angle in the crystal plane.

\( \phi_2 \) The potential in the plane of closest approach.

\( \sigma^M \) The excess charge density on the metal surface.

\( v_q \) The speed of sound in quartz.

\( v_f \) The speed of sound in the deposited film.

\( \nu_\pm \) The number of moles of this ion in 1 mole of the electrolyte

\( \nu \) \( \nu = \nu_+ + \nu_- \)

\( \nu \) The number of solvent molecules replaced by each adsorbed organic molecules

\( \nu \) Transverse velocity of sound in the AT cut quartz crystal \((3.34 \times 10^4 \frac{m}{s})\).

\( \nu_a \) The number of water molecules replaced by anion.

\( \nu_c \) The number of water molecules replaced by cation.

\( \omega \) The measurement frequency in differential capacity measurements.

\( W \) is the angular velocity of oscillation.

\( \xi(y, t) \) The amplitude of the quartz oscillations.

\( \Psi \) The scaling function.
על מבנה המוסק מתכת/תמיישת -
הענוה מאוזני קורץ מיקרו

חובר לשב קבלת התואר "דוקטור לפילוסופיה".

מ א ז
גليك 2ילברמן

הוגש לפנאות של אוניברסיטת תל-אביב

2001
ערבה וنعשתה בחנהית

פרופסור אליהו גלעדי

בית הספר לכיום
הפקולטה למדעי מדעיים על שם רימונד וברל סאקלר
אוניברסיטת תל-אביב
מקנוני הקוחר מקרוב (Electrochemical Quartz Crystal Microbalance) הם רקיבים פיזואלקטרוכימיים הממשישים במדידות אלקטרוטוכימיות ש畦ות, ובמידה הלכיתöße הדלי בוהן העשויים האורחונים. השיפוע בכוכתיה והמדידת למزة מדעי חשור, סני המסה במשקש האלקטרודה / הממס או ציימי בצומת מבнесен זה.

אלקטרוטוכימיותumbo בעלות תכונות שונות במדידות אלקטרוטוכימיות, כמו כאשר גם בתוכי קיבולי, בר durée זמן ללא לה与时俱进 הממשות במדידות / התמסות והשפה על המבנה ומקירו בתום תוקנות אלקטרוטוכימיות [62, 63].

היה הרחואצ, שוביייקה ביום בשתי הקוחר, חכימי לשניים מסת.


במקום [62, 63] הממס מנסה לה standardUserDefaults הקוחר, גם כי הוא במדידות Sauerbrey המוסכים בממונים בשתי הקוחר, גם כי הוא במדידות Sauerbrey המדמנים במדידות אלקטרוטוכימיות [62, 63].

 ATF Hz 2m

قام מזבי את שניאי התדרית בחוזית של Cm 2m, בתוכי והגבה התדריתucha כל התדרות בשתי הקוחר, במערכת התכוניות של אינטראקציה bipartisan, והאלקטרודה מבנה זה זה, במיקום [9] Sauerbrey.

במקום [62, 63] הממס מנסה להを中心 הקוחר, גם כי הוא במדידות Sauerbrey המוסכים בממונים בשתי הקוחר, גם כי הוא במדידות Sauerbrey המדמנים במדידות אלקטרוטוכימיות [62, 63].

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The molecular growth and electrical charges form a \( \Delta f_{\text{film}} = -C_w L \rho_s \left[ \left( \frac{1}{\eta_s} - \frac{1}{\eta_f} \right) + \left( \frac{\rho_f}{\rho_s} - 1 \right) \right] \) relationship. The equations are used to calculate the changes in the electrical charges and the molecular growth.

When the molecules form a double layer and the electrical charges form a Gouy-Chapman layer, the relationship between the changes in the electrical charges and the molecular growth can be calculated using the equation:

\[ \Delta f_{\text{film}} = -C_w L \rho_s \left[ \left( \frac{1}{\eta_s} - \frac{1}{\eta_f} \right) + \left( \frac{\rho_f}{\rho_s} - 1 \right) \right] \]

In this case, \( \eta_s \) and \( \eta_f \) are the viscosities of the solution and the analyte, respectively, \( \rho_s \) and \( \rho_f \) are the electrical conductivities of the solution and the analyte, respectively, and \( C_w \) is the concentration of the analyte.

When the molecules form a double layer and the electrical charges form a Gouy-Chapman layer, the relationship between the changes in the electrical charges and the molecular growth can be calculated using the equation:

\[ \Delta f_{\text{film}} = -C_w L \rho_s \left[ \left( \frac{1}{\eta_s} - \frac{1}{\eta_f} \right) + \left( \frac{\rho_f}{\rho_s} - 1 \right) \right] \]

For a solution of butanol, the relationship between the changes in the electrical charges and the molecular growth can be calculated using the equation:

\[ \Delta f_{\text{film}} = -C_w L \rho_s \left[ \left( \frac{1}{\eta_s} - \frac{1}{\eta_f} \right) + \left( \frac{\rho_f}{\rho_s} - 1 \right) \right] \]

When the molecules form a double layer and the electrical charges form a Gouy-Chapman layer, the relationship between the changes in the electrical charges and the molecular growth can be calculated using the equation:

\[ \Delta f_{\text{film}} = -C_w L \rho_s \left[ \left( \frac{1}{\eta_s} - \frac{1}{\eta_f} \right) + \left( \frac{\rho_f}{\rho_s} - 1 \right) \right] \]
шение המסה על האלקטרודות המראותKEN הניתן taxpayer להמצאת למקlığות המסה ניגוד חלבני את
ממחק קשרים שלולעים בין המולים הניסוחים למלקוגלות המסה ניגוד חלבני את

השננין בדיעור למלוע על מבנה הממס / המיסת:  

א. כאשר מלוקוגלות הפירידי נספח על האלקטרודות-choice המתחים מימי, כ[,] והורשות את 
ממנה התמס השתייה בכל מלקוגלת חום בשבעה 
themski האלקטרודות והשהה את קשי האלקטרודד בקריס פירודי / מי שעווה חול 
יתרו. השננין בדיעור שלב ביחס כאשר האלקטרודתลาย על בשתי חوجب, ואלה 
בבגון על מלקוגלות הפירידי מתפקד לכל החנטים. בצבע זה בנט ממסטרו
ש辗ים

ב. בשני קרן ייחו בדיעור בשורה be ספחית n-butanol מתמסים מימי על אלקטרודות  
והב איסור אלקטרודד וזצגרת חיות. במצ Buchanan והשהה האלקטרודת envi ממנה התמס ע 
האלקטרודת התמסות שית כאלה החיתות האלקטרודתחרוזה את מבנה המיס על 
ההטשה. קשירים יימיivil חזורים בצבע זה מאחר והבקבוצה OH⁻ אשר מוסתרת  
מתמטים כוכב מכתש לשיתת הנקרת

ג. ספחית n-butanol أخرى לצור חיסב הדיתוריפית על השישה שנוצרה לקסני חורב  
n-butanol הצוותי. אוכזב שעוני התיחזור שונם זד במקומת מגשיני בשור 
אבל לקרוסות מוזה בל פירודי. יניח חסמר התנהות והעיים השמדלקוגלות  
n-butanol איזוח לזר ציבים במיס 21 מלקוגלת מי. אם ממנה זה ולהוקזק  
ספחית על האלקטרודד, החלק החידורופי מוסתר עד למלקוגלת המים. זבר זה  
מהפיות chyidורופי קשק החיתות.

ד. בשני קרן ייחו בדיעור בשורה be ספחית n-butanol מתמסים מימי על אלקטרודות  
הסיבה כל ע茧 שקישרי הים בין מלקוגלות חום חחלק חולט ישור מואר בכרום. ש蓥י  
הוחזרMosber על ידי השני גואנאירקיזת על השישה. כאשר רך  
בתמשיס, בכסףثن האלקטרודד חיות מזריך קשירי המים בין מלקוגלת עד ידי הקבוצות – 
OH⁻. כאשר פירודי ספח על השישה בצבע זה, על החלק החידורופי כל הנקרת  
מספג הקשקים שלחזרים קשק.

ה. בכסףثن elektrordחוב, ספחית uracil וורמת لتליין חזרי Kס בדיעור. לדמות  
מלוקוגלות הפירידין, כאשר ספח כניצצ בלשון, הקבוצות O– 1 -N чисל לקולות ילור קשיר מים. זבר זה המקטב שוויי תיחזור קשק.

ו. כי שחוור כזוד, הkıושי בין elektrordחוב הכסף מלקוגלת המים六合 מוהז ש 
אלקטרודחוב עכום מלקוגלת המים. בין השני בדיעור חצמצת המיספת פירודי
תמשיסים מימי על בשתי קשק.

ז. בשני דומה בדיעור רכשה בעור ספחית פירידי מתמסת  
歷 n-butanol על elektrordחוב.
The first layer molnucleotide layer interacts with the fluid molecules and forms another layer. The results of the analysis (finite slippage) showed that the second layer interacts with the molecules of the first layer at the interface. This leads to the formation of a slip layer (slip length) between the two layers. Slippage is expected to increase the slip length, which is proportional to the molecular density of the fluid. The model predicts linear dependence on the slip length, which is confirmed by the measured data. The slip length is proportional to the distance between the molecules of the fluid. This is consistent with the predictions of the model.