Adsorption of benzyldimethyldodecylammonium chloride onto stainless steel using the quartz crystal microbalance and the depletion methods: an optimisation study

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Keywords

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Abstract

The adsorption behaviour of benzyldimethyldodecylammonium chloride (C12BDMAC) corrosion inhibitor from aqueous solutions onto a stainless steel surface has been investigated using the Quartz Crystal Microbalance (QCM) technique and the depletion-HPLC method. Three different experimental procedures were used to carry out the adsorption measurements using the QCM. The results revealed that the employed experimental procedure had a marked influence on both of the measured frequency and dissipation energy changes. Additionally, the measured changes in the normalized frequency and dissipation changes were found to be overtone-dependent. The adsorbed amounts determined by QCM were higher than those determined by depletion due to strong contributions from the bulk liquid properties. The direct application of the measured frequency shifts corresponding to the lowest dissipation changes, $\Delta f_{lowestD}$, in the Sauerbrey equation was effective in minimising these contributions within an acceptable experimental tolerance. A correction procedure, based on the Kanazawa equation, has been proposed and applied successfully to separate the contribution from the bulk effects to the calculated adsorbed mass. The adsorption isotherms obtained from the corrected frequency shifts and the depletion method were perfectly matched over the whole range of concentrations investigated.

1. Introduction

Corrosion is one of the most common, costly and widespread industrial problems in the oil and gas production industry [1]. Oilfield corrosion manifests itself in several forms among which carbon dioxide corrosion and hydrogen sulphide corrosion in the produced fluids and oxygen corrosion in water injection systems are by far the most predominant forms of attack encountered in oil and gas production [2]. Corrosion control methods in oilfield systems include cathodic protection, protective coatings, chemical inhibitors (organic and inorganic molecules), plastic or cement liners, use of special alloys, solids removal and removal of corrosive gases [1, 3]. Organic corrosion inhibitors are strongly polar molecules, with many being based on nitrogen, such as amines [4], amides [5], imidazolines [6] or quaternary ammonium salts [7-9] and compounds containing P, S and O elements [3]. The use of organic corrosion inhibitors is one of the most cost-effective methods of protecting internal corrosion of carbon steel pipelines for oil transportation [3, 10]. They are typically surface-active agents due to the presence of hydrophilic and hydrophobic moieties within the same molecule. Surfactant corrosion inhibitors work by adsorbing at a corroding metal surface from an aqueous solution; the film adsorbed at the metal-water surface then acts as a waterproof barrier between the corrosive aqueous phase and the metal surface [11, 12]. Hence, studying the adsorption behaviour of surfactant corrosion inhibitors at solid-liquid interfaces provides important information about their action mechanism of action, which in turn helps in improving their efficiency.

The Quartz Crystal Microbalance (QCM) technique is currently experiencing rapid growth in the real-time monitoring of surfactant adsorption at the solid-liquid interface [13]. It involves the simultaneous measurement of changes in the resonance frequency and the dissipation energy of the crystal employed. The change in frequency is used to calculate the amount of adsorbed surfactant by applying the Sauerbrey equation [14]. Moreover, the measured dissipation changes provide additional information about the viscoelastic properties of the adsorbed surfactant layer. The high sensitivity, the low detection limit and the real-time monitoring of mass changes make the QCM a very attractive technique for studying the adsorption characteristics of surfactant molecules at the steel-water interface [15, 16].

Most reported QCM investigations have assumed ideal rigid layer behaviour, using the Sauerbrey model when interpreting frequency changes [17-19]. It is important to remember, however, that the QCM measures frequency changes and not mass changes. Additionally, in the liquid medium, the QCM frequency is highly dependent on the environment of the quartz crystal. Accordingly, the mass sensed by the QCM and the adsorbed amount detected by other techniques were found to be different. Several studies have been shown that direct application of the Sauerbrey equation to surfactant adsorption from liquids results in overestimating the adsorbed mass [17-22]. Stalgren *et al.* [18] studied the adsorption of hexaethylene glycol mono-*n*-tetradecyl ether ($C_{14}EO_6$) onto silica by the QCM and ellipsometry techniques. They reported that the frequency shift obtained from the QCM measurement results in an overestimation of the adsorbed mass. This was attributed to water molecules that are coupled to the adsorbed layer due to hydration of the polar region of the surfactant and other water molecules that for other reasons are trapped within the adsorbed layer. A similar observation has been reported by Knag *et al.* [22] during their adsorption studies of alkyl trimethyl ammonium bromides with alkyl groups from n-decyl to n-hexadecyl onto iron and cementite using the QCM. Caruso *et al.* [21] investigated the adsorption of octaethylene glycol monododecyl ether ($C_{12}E_8$) onto hydrophobic gold and hydrophilic chromium oxide surfaces from aqueous solution using the QCM and Surface Plasmon Resonance (SPR). They found that the amount of $C_{12}E_8$ adsorbed, estimated using the QCM, is 80% greater than that determined by the SPR. In addition to the water bonded to the adsorbed surfactant molecules, the overestimation of the adsorbed mass determined by the Sauerbrey equation has been mainly attributed to the changes in the density and viscosity of solutions, which is commonly known in the literature as the ‘‘bulk effect’’. In the liquid phase, the shear motion of the crystal generates a shear wave, which penetrates into the contacting liquid. This wave is dampened by energy dissipations, due to the viscosity and density of the liquid, resulting in a further decrease in the resonant frequency of the crystal. Therefore, when a QCM crystal contacts a liquid, the frequency shift has contributions from both the mass adsorbed and the bulk liquid properties [23-25]. In addition, some authors have pointed out that surface roughness affects the resonant frequency and results in an overestimation in the adsorbed mass calculated by the Sauerbrey equation [26, 27]. Several authors have attributed the overestimation in the mass calculated from the Sauerbrey equation to the corresponding changes in surface roughness during the adsorption process [27-29]. Rechendorff *et al.* [29] have studied how the frequency and dissipation responses of a QCM depend on the roughness of the surface when it is exposed to liquids with different density and viscosity values. Their main conclusions were that a surface with rms roughness below about 3 nm does not result in frequency and dissipation responses different from a flat surface, whereas surface roughness larger than about 6 nm influences the frequency shift significantly.

On the other hand, the application of the Sauerbrey equation may result in an underestimation of the adsorbed mass as reported by several adsorption studies of polymer or biomolecules [30-35]. This has been attributed mainly to the formation of strongly damped viscoelastic films, which do not follow the shear motion rigidly but are deformed because of the shear motion [33-35]. Several theoretical viscoelastic models, which make use of frequency and dissipation data collected at multiple overtones, have been developed to overcome the Sauerbrey model limitations. The Voigt based model [36, 37] and the Johannsmann model [38, 39] have been used widely in modelling the measured shifts in frequency and dissipation of viscoelastic adsorbed films [34, 40].These theoretical models describe viscoelastic films by four parameters; thickness, density, and two shear modulus components. Usually, the effective density, ρ_{eff}, or the effective thickness, d_{eff}, is required as an input in the models. Consequently, the mass determined by the Voigt or Johannsmann models corresponds to the total mass of the film, including both adsorbed molecules and coupled water. Hence, to determine the actual effective film mass of the adsorbed species of interest, the mass of water has to be measured independently using another technique.

Despite the number of studies done on the adsorption of surfactants and macromolecules onto solid surfaces using the QCM, the literature lacks a detailed study that shows how the employed experimental protocols, the measured frequency shifts at different overtones and the analysis of the obtained data could be used to interpret and overcome those aforementioned limitations exhibited by this technique. In previous studies, we have investigated the adsorption characteristics of the homologous series of alkylbenzyldimethylammonium chloride (CnBDMAC) corrosion inhibitors with alkyl chain lengths from 10 to 16 carbons onto C1018 mild steel [41], iron sulphide [9], barium sulphate [9], silica particles [9], sand particles [9, 41] and iron carbonate powder [8, 9] using the depletion method. Lately, we showed how the adsorption isotherm of hexadecylbenzyldimethylammonium chloride (C16BDMAC) combined with measurements of the steel corrosion rate providing an effective method for the quantitative prediction of the inhibitor effectiveness in the presence of sand as a competitor surface [8].

In the current work, we study the adsorption behaviour of benzyldimethyldodecylammonium chloride C12BDMAC corrosion inhibitor from aqueous solutions onto stainless steel surface using the QCM technique and the depletion method. We have investigated the effect of employing different experimental protocols or flow regimes on the measured frequency shifts and dissipation changes during the adsorption process. In addition, we investigated how the measured frequency and dissipation changes vary with the overtone number, and changes in the bulk properties of the tested surfactant solutions. Moreover, detailed analyses of the measured QCM data, using Sauerbrey and Kanazawa models, were carried out and compared with the adsorption data determined by the depletion method. Corrections for changes in density and viscosity of surfactant solutions were used to overcome the overestimation in the amount adsorbed, measured by the QCM method. The main aim of this work is to optimise (i) the experimental procedures used to carry out the adsorption measurements; (ii) the treatment and analysis of measured data to provide a simple and applicable method to overcome or reduce the overestimation in the adsorbed mass determined by the QCM.

2. Experimental

2.1. *Materials*

Water was purified by an Elga Prima reverse osmosis unit, and then treated with a Milli-Q reagent water system. The produced water had a resistivity of 18 MΩ cm or greater. Dodecylbenzyldimethylammonium chloride surfactant (C12BDMAC, >99%, Fluka) was used as received unless otherwise was stated. Stainless steel powder (type 316L), having an average particle size of 32 μm, was purchased from Sandvik Osprey Ltd., UK. **Error! Reference source not found.** shows a scanning electron micrograph of the used 316L stainless steel powder recorded using an EVO 60 SEM (Carl Zeiss SMT AG, Germany) instrument equipped with an INCA Energy 350 EDX detector (Oxford Instruments, UK).

2.2. Methods

2.2.1. Adsorption of C12BDMAC onto steel using the QCM

A QCM with dissipation monitoring instrument, Q-Sense E4 system, from Q-Sense, Sweden, was used for the *in-situ* adsorption of C12BDMAC from aqueous solution onto stainless steel coated crystals. The Q-Sense E4 includes four sensors that can be used in parallel configuration and they are temperature-controlled. A peristaltic pump, Ismatec IPC-N 4, Germany, was used to deliver surfactant solutions to the chambers that contain the crystals. The flow rate used in our experiments was 0.267 mL/min. All parts are connected with Teflon tubing and the internal volume of the tubing plus the measurement chamber is about 1 mL per module [42]. Four stainless steel-coated crystals were purchased from Q-Sense. The quartz crystal, 0.3 mm in thickness and 14 mm in diameter, is coated with 50 nm SS2343 type stainless steel with a projected surface area of 1cm^2 [42].

The resonant frequency of the crystal depends on the mass of the crystal. Therefore, when a substance is adsorbed on to the crystal, the frequency decreases. If the adsorbed mass is small compared to the mass of the crystal, evenly distributed and rigidly attached with no slip or deformation due to the oscillatory motion, the decrease in frequency *(Δf)* is proportional to the adsorbed mass *(Δm)* on the crystal according to the Sauerbrey equation [14]:

$$\Delta m = -\frac{A\sqrt{\mu_q \rho_q}\,\Delta f}{2nf_o^{\,2}} = -\frac{C\Delta f}{n} \tag{1}$$

where C is a constant equal to 17.7 ng cm^{-2} Hz^{-1} for a quartz crystal with surface area A equal to 1 cm^2 and a fundamental frequency, f_o, of 5 MHz, μ_q is the elastic shear modulus of quartz (2.947×10^{11} g cm^{-1} s^{-2}), ρ_q is the quartz density (2.65 g cm^{-3}), and n is the overtone number (1, 3, 5, ...).

The resonant frequency of a 5 MHz quartz crystal can be measured with a precision of about 0.01 Hz in vacuum and 0.1 Hz in liquids according to the manufacturer [42]. Accordingly, very small masses on the nano-gram scale could be measured by the QCM. The sensitivity factor of the QCM increased by a factor of *n* by operating at any of its *n* overtones and it increases with the square of the fundamental frequency, f_o [43].

The device measures the variation in dissipation energy factor, ΔD, simultaneously with the frequency change and reflects the viscoelastic properties of the adsorbed layer. The dissipation energy factor is defined as the ratio between the energy dissipated per oscillation cycle, $E_{dissipated}$, and the net stored energy in the oscillating system, E_{stored}. The more viscous the adsorbed layer is the more energy is lost from the oscillation. The dissipation factor is a dimensionless quantity and is given by the following equation [44]:

$$D = E_{dissipated} / 2 \pi E_{stored} \quad (2)$$

All the QCM parts in contact with surfactant solution were pre-rinsed with ethanol solution (96%) and dried with nitrogen gas. The stainless steel-coated crystals were cleaned by a hot basic piranha solution having a 5:1:1 mixture of water, ammonium hydroxide and hydrogen peroxide for 5 minutes. The crystals were then cleaned with ethanol using an ultrasonic cleaner for 10 minutes. Finally, the crystals were thoroughly rinsed with Milli-Q water, flushed with nitrogen and dried in an oven for about 15 min. Freshly cleaned crystals were used immediately. The purpose of this extensive cleaning was to remove any organic contaminants that may be present on the crystal surface prior to the contact with surfactant solutions. After drying, the crystals were inserted into the measurement chamber and the chamber was filled with gas-free deionised Milli-Q water. A steady baseline was obtained for at least 30 minutes prior to starting the experiment. Dissolved gases in surfactant solutions were removed by sonication and vacuum degassing prior to the adsorption measurements. The presence of dissolved gases results in high noise levels in the measured frequency shifts (See Figure S1 in the supplementary information).

Three different protocols have been investigated to carry out the adsorption measurement under the same experimental conditions of surfactant concentration, sample volume, temperature and flow rate. These protocols are the stepwise protocol, the batch protocol and the loop protocol. The stepwise protocol involves measuring the shift in the frequency of aqueous surfactant solutions of increasing concentration going from the lowest to the highest concentration without rinsing the coated crystals between additions. In this protocol, Milli-Q water was first injected continuously in the QCM module until stable Δf and ΔD baselines were achieved. Afterwards, the lowest surfactant concentration was pumped until a plateau value was attained. The next higher surfactant concentration was then pumped onto the same crystal without stopping the device or cleaning the crystal until equilibrium was reached. This was repeated until the whole range of surfactant concentrations to be investigated was done. The crystal was then flushed with deionised water and cleaned for further usage.

A similar experimental procedure to the stepwise protocol was employed in the batch protocol, except the device was stopped and the crystal was removed from the flow cell and cleaned between measurements for each surfactant concentration. Finally, in the loop protocol, the frequency shift was monitored individually for each surfactant concentration similar to the batch protocol. However, in the loop protocol the surfactant solution was made to pass over the crystal in a closed circuit (instead of passing a fresh solution) until equilibrium was attained. A schematic diagram describing the three different experimental protocols or flow patterns is shown in Figure S2.

2.2.2. Adsorption of C12BDMAC onto steel using the depletion method

The adsorption isotherms of the C12BDMAC corrosion inhibitor from aqueous solution onto the powder surfaces were determined by measuring the extent of depletion of solution concentration following adsorption. Solutions containing C12BDMAC at known initial concentrations were prepared. Weighed amounts of steel powder were added to the solutions (60 mL) in polystyrene bottles and equilibrated with stirring in a thermostted bath for four hours. Glass bottles were not used to avoid possible complications arising from the strong adsorption of the cationic CnBDMAC onto the glass walls. Following adsorption equilibration, the samples were decanted and centrifuged using an Eppendorf MiniSpin plus (Centrifuge, UK) at 14000 rpm for 10 min to remove all solid particles prior to analysis to measure the final, depleted concentration of C12BDMAC using high performance liquid chromatography (HPLC). A Shimadazu liquid chromatograph equipped with an LC-6A pump and a 759A absorbance detector (Applied Biosystems) operating at 262 nm was used for the measurements. A SPHERISORB 5 μm CN (25 x 0.46 cm) column was used at a mobile phase flow rate of 2 mL/min and sample injection volume of 20 μL. The mobile phase was a mixture of 70 vol.% acetonitrile and 30 vol.% of 0.2 M aqueous sodium acetate adjusted to pH 5.0 with acetic acid. The calibration plots of the C12BDMAC response peak integral versus concentration were accurately linear over the C12BDMAC concentration ranges used (typically 1×10^{-8} to 1×10^{-2} M). The correlation coefficients r^2 of the calibration plots were all higher than 0.98. In deriving the final adsorption isotherms, two points were carefully checked. Firstly, samples equilibrated for different times in excess of 4 hours produced identical results demonstrating that equilibrium adsorption was achieved within 4 hours.

Secondly, measurements made for samples containing different ratios of C12BDMAC to solid powder produced entirely self-consistent results.

2.2.3. Surface area determination of stainless steel particles using the BET method

The specific surface area of 316L steel powder was determined using the nitrogen gas adsorption isotherm, analysed according to the Brunauer, Emmett and Teller (BET) method [45, 46]. The nitrogen adsorption isotherm was measured at 77 K using a TriStar 3000 Analyzer, manufactured by Micromeritics, UK. The specific surface area of 316L stainless steel powder, derived from the BET isotherm, was 0.130 $\underline{+}$ 0.001 m^2 g^{-1}.

2.2.4. Density and viscosity measurements of surfactant solutions

The density and viscosity measurements were performed to determine the bulk properties of aqueous surfactant solutions at different concentrations. At least three density and viscosity measurements were performed for each solution, and averaged values were reported and used for the calculations. The densities (ρ, g mL^{-1}) of surfactant solutions were determined using a DMA 35 density meter (Anton Paar, UK) at 25 °C. The kinematic viscosities (ν, mm^2 s^{-1}) of aqueous surfactant solutions were determined using an Ubbelohde Viscometer (SCHOTT Instruments, Germany) with a calibrated capillary constant of 0.0035 mm^2 s^{-2} at 25 °C. The dynamic viscosities (η, mPa) of the solutions were calculated by multiplying the measured kinematic viscosities by the measured densities. The measured densities and viscosities of surfactant solutions are presented in Table S1.

3. Results and Discussion

3.1. Effect of the experimental protocol

The choice of an experimental procedure has a marked influence on the measured frequency and dissipation changes detected by the QCM. We have studied the effect of employing different experimental protocols on the measured frequency shifts and dissipation changes during the adsorption of different C12BDMAC concentrations from aqueous solution onto stainless steel-coated crystals at 25 °C. Figure 2 shows the measured changes in the frequency during the adsorption process of different C12BDMAC concentrations as a function of time using the stepwise protocol. In this figure, the plotted shift in frequency is the normalized shift in frequency with respect to the overtone, $\Delta f/n$, not the absolute one and n corresponds to the third overtone. The arrows shown in the figure indicate the time at which each surfactant concentration was introduced into the device chamber. The numbers shown above the arrows refer to the normalized surfactant concentrations with respect to the cmc of C12BDMAC (7 mM).

Clearly, the introduction of the surfactant solution results in lowering the frequency of the oscillating crystal due to the adsorption of surfactant molecules on the steel surface (Figure 2). The magnitude of the frequency shift Δf, increases with the increase in the surfactant concentration up to the cmc. Upon increasing the surfactant concentration beyond the cmc, the magnitude of Δf decreases. The maximum in Δf at the cmc, has been attributed to the presence of impurities in the used surfactant as inferred by the presence of a minimum in the surface tension isotherm at the same concentration. A significant minimum in the surface tension isotherm is observed for C12BDMAC. An experiment has been carried out to purify C12BDMAC by re-crystallization three times from hot ethyl acetate solution. The product was dried over calcium chloride under vacuum for 24 hours before the measurement. The surface tension isotherms for received and purified C12BDMAC samples are shown in Figure S3. The purified C12BDMAC has been used throughout the rest of this study.

Noticeably, flushing the crystals with water did not bring the measured frequency back to the starting baseline (where $\Delta f \approx 0$) before pumping surfactant solution. This may be attributed to an instrumental drift in the measured frequency over the time course of the measurement. According to the manufacturer, the frequency of a clean 5 MHz crystal sensor operating in a liquid at 25 °C drifts by up to about 1.5 Hz hour^{-1} and the corresponding drift in the measured dissipation is 2×10^{-7} per hour, when measured at the 15 MHz harmonic (i.e. at the third overtone) [42].

The changes in the frequency accompanying the adsorption of different C12BDMAC concentrations on the crystal as a function of time using the batch protocol are shown in Figure 3(a). The recorded shift in the frequency corresponds to the change in the third overtone. Similar to the stepwise protocol, the introduction of surfactant solution lowers the frequency of the oscillation and the magnitude of this shift increases with increasing surfactant concentration. However, the stepwise protocol gave rise to higher Δf values than those measured by the batch protocol. For example, the magnitude of Δf measured using the batch protocol at 7 mM C12BDMAC was about -13 Hz, whereas the stepwise protocol gave rise to a value of about -35 Hz.

Finally, the effect of using the loop protocol on the measured Δf during the adsorption of C12BDMAC onto the stainless steel-coated crystal is shown in Figure 3(b). Similar to the two other protocols, the frequency of the oscillated crystal decreases upon the introduction of surfactant solution and, in general, this decrease is directly proportional to the mass of adsorbed surfactant.

A comparison of the frequency shifts, measured using the three different protocols, as a function of the normalized C12BDMAC concentration is shown in Figure 4(a). The presented frequency shift, $(\Delta f/n)_{average}$, shown in this figure is the arithmetic mean of the normalized frequency changes measured at the 3rd, 5th, 7th, 9th, 11th and 13th overtones for two different crystals oscillating simultaneously. The average frequency change, $\Delta f_{average}$, is given by the following equations:

$$\Delta f_{average} = \frac{\Delta f_{1st} + \Delta f_{2nd}}{2} \tag{3}$$

$$\Delta f_{1st} = \left(\frac{\frac{\Delta f_3}{3} + \frac{\Delta f_5}{5} + \frac{\Delta f_7}{7} + \frac{\Delta f_9}{9} + \frac{\Delta f_{11}}{11} + \frac{\Delta f_{13}}{13}}{6} \right)_{1st} \tag{4}$$

$$\Delta f_{2nd} = \left(\frac{\frac{\Delta f_3}{3} + \frac{\Delta f_5}{5} + \frac{\Delta f_7}{7} + \frac{\Delta f_9}{9} + \frac{\Delta f_{11}}{11} + \frac{\Delta f_{13}}{13}}{6} \right)_{2nd} \tag{5}$$

where Δf_{1st} and Δf_{2nd} refer to the averages of the normalized frequency changes at the 3rd, 5th, 7th, 9th, 11th and 13th overtones for the first and the second crystals, respectively.

The error bars shown in Figure 4(a) represent the standard deviations of the shifts in frequency detected by the two crystals Δf_{1st} and Δf_{2nd}. The corresponding average changes in the dissipation, $\Delta D_{average}$, during the adsorption process are given in Figure 4(b). It is clear from Figure 4(a) that values of $\Delta f_{average}$, measured using the three tested experimental protocols, show an obvious divergence among them. This in turn indicates that the employed experimental protocol affects the measured QCM data and therefore will result in dissimilar adsorption data. The average frequency shifts detected by the stepwise protocol were larger than those measured by the batch and loop protocols by a factor three in most cases. For example, the value of $\Delta f_{average}$ measured by the stepwise protocol, at the cmc, was about -35 Hz and those measured by the batch and loop protocols were about -11 and -12 Hz, respectively.

A similar result has been reported by Lundgren *et al.* [40] during the adsorption of the unsaturated fatty acid linolenic acid from non-aqueous solution onto stainless steel-coated crystals using the QCM. They found that the measured frequency changes obtained by increasing the concentration stepwisely to differ from those obtained by injecting one given concentration per experiment by about 8%. The measured $\Delta D_{average}$ by the loop protocol was found to be less than 1×10^{-6} up to surfactant concentrations of about 0.8 times the cmc.

The aforementioned observation applies also to the measured dissipation changes determined by the three protocols. At low surfactant concentrations, the values of $\Delta D_{average}$ measured by the three protocols are similar and show no significant differences. At higher surfactant concentrations, the stepwise protocol gave rise to higher dissipation values compared to the other two protocols. For example, the measured $\Delta D_{average}$ by the stepwise protocol, at the cmc was about 8×10^{-6} and those measured by the batch and loop protocols were about 1.8×10^{-6} and 1.2×10^{-6}, respectively. The dissipation change values provide information about how rapidly the energy of the oscillating crystal is given up to the surroundings. Firmly attached, smooth and homogeneous layers give rise to a low dissipation, whereas loosely bound, rough and extended layers containing much solvent result in a high dissipation [44, 47]. Low dissipation values indicate that the QCM senses the mass adsorbed as a rigid mass and not as a viscoelastic layer. The adsorbed species are generally recognized as viscoelastic when the dissipation change is more than 1×10^{-6} [37, 39, 48]. Noticeably, the values of $\Delta D_{average}$ measured by the loop protocol were the lowest compared to the other protocols for most of the investigated surfactant concentrations. Accordingly, the use of the loop protocol would be more convenient than the other two protocols for studying the adsorption of C12BDMAC onto solid surfaces by the QCM technique.

These differences in the measured values of $\Delta f_{average}$ and $\Delta D_{average}$ by the three tested protocols will result in similar variations in the adsorbed masses detected or sensed by the QCM. This may be attributed to variations in the amounts of entrained or coupled water in the adsorbed surfactant assemblies caused by differences in the amounts and/or structures of adsorbed molecules. The amount of surfactant adsorbed as well as the structure they adopt on a surface is highly dependent on the history of that surface. In the stepwise protocol, it believed that the pre-adsorbed C12BDMAC molecules on the crystal surface, at the lower surfactant concentrations, results in an increased adsorption level and different adsorbed structures from those exhibited by the batch and loop protocols upon the introduction of the higher surfactant concentrations. This is not likely to occur in the batch and loop protocols as surfactant molecules are being adsorbed on a free surface with no aged film of pre-adsorbed surfactant molecules [17, 49].

The stepwise protocol has been used extensively in most of the QCM studies of surfactant adsorption onto solid surfaces [18, 19, 22, 49-51]. Arguably, the use of this protocol is one of the reasons that the adsorbed amounts determined by the QCM are higher than those determined by other methods such as ellipsometry [18], surface plasmon resonance [19, 21, 50], optical reflectometry [49] and the depletion method [20]. This is because the experimental procedures employed in the latter techniques are similar to that of the loop protocol and under static conditions, *i.e.* with no flow of surfactant solution. Additionally, the QCM senses the water content of the adsorbed structures, while other adsorption methods do not normally detect changes in the adsorbed solvent. The adsorbed water content can be of different kinds; it can be hydration shells or water trapped in cavities or enclosed spaces in the solid surface.

3.2. Choice of the overtone

The process of selecting an overtone, at which the changes in frequency and dissipation will be monitored, is crucial for the success and accuracy of the QCM measurement. For adsorption from a gas phase, no differences exist among the measured $\Delta f/n$ values regardless of which overtone is used and the same observation applies to the dissipation changes $\Delta D/n$ as well [24, 44]. On the contrary, for adsorption from liquids, the measured $\Delta f/n$ and $\Delta D/n$ values vary with the overtone number. Figure 5 shows the changes in the normalized frequency and dissipation of the fundamental frequency, Δf_o, and the overtone number 3, 5 and 13 as a function of time, on moving stainless steel-coated crystal from air to Milli-Q water at 25 °C. The arrow refers to the time at which Milli-Q water was pumped. As shown, the measured changes in the normalized frequency change and dissipation in the presence of air, are not overtone-dependent whereas they become overtone-dependent upon the introduction of water into the system. Similarly, the measured changes in the normalized frequency and dissipation of C12BDMAC solutions are overtone-dependent. Figure 6 shows how the normalized frequency shifts and dissipation changes vary with the overtone number during the adsorption of an aqueous solution of C12BDMAC with concentration of 0.8 times the cmc, using the loop protocol. For example, the $\Delta f/n$ value measured at the third overtone is about -10 Hz and that at the seventh and ninth overtones are -9.5 and -8.2 Hz, respectively.

Similar observations have been reported by Bordes *et al.* [19] during the adsorption of amino acid-based surfactants onto silica surfaces using the QCM. They found that the measured frequency shifts are overtone-dependent with the values decreasing with an increase in the overtone number. Additionally, very strong dissipation changes were also reported. They attributed this behaviour to a strong contribution from the bulk effect. These differences in the measured $\Delta f/n$ values at the different overtones indicate that the adsorbed surfactant layer is not rigid but rather a viscoelastic film [17-20]. Accordingly, applying these measured $\Delta f/n$ values in the Sauerbrey equation will result in different adsorbed masses. The question arises here about which one of these measured frequency shifts at different overtones should be used to study the adsorption process. No reported studies have employed the frequency shifts measured at the fundamental frequency of the QCM, as noise levels and baseline drift are not stable [49, 52]. Moreover, because the sensitivity increases as the square of frequency, the sensitivity is enhanced when the resonator is operated at a higher overtone [16]. Nearly all of the reported studies on the adsorption of surfactants onto solid surfaces by the QCM have used the measured frequency shifts at the third overtone [17-19, 49-51] despite the existence of differences between the measured normalized frequency shifts at different overtones.

In order to minimize these differences and their impact on the calculated masses from the Sauerbrey equation, three different measured values of the recorded frequency shifts at different overtones were tested. These three different values are: the shift in the frequency of the third overtone, Δf_3; the average shift in frequencies of all overtones, $\Delta f_{average}$; and the shift in the frequency of the overtone with the lowest dissipation energy, $\Delta f_{lowestD}$. Our goal is to find which one of these quantities gives rise to the closest value to the actual adsorbed mass when estimated using the Sauerbrey equation. The actual mass of adsorbed surfactant will be determined with the aid of the depletion method under the same experimental conditions. In addition, the dissipation change values corresponding to each of the aforementioned frequency changes have been measured. These values are; dissipation change of the third overtone, ΔD_3; average dissipation change of the all overtones, $\Delta D_{average}$; and dissipation change of the overtone with the lowest dissipation energy, $\Delta D_{lowestD}$.

The variation in the values of Δf_3, $\Delta f_{average}$ and $\Delta f_{lowestD}$ versus aqueous C12BDMAC concentrations, measured by the loop protocol, is shown in **Error! Reference source not found.**(a). The values represented in this figure are the averages of two measurements running simultaneously on two different stainless steel-coated crystals. As seen, the magnitudes of the three frequency shifts are different and these differences increase with increasing surfactant concentration. The magnitude of Δf_3 is the highest followed by $\Delta f_{average}$ and $\Delta f_{lowestD}$ over the entire investigated concentration range. For example, the measured Δf_3 at the cmc is about -11 Hz, and that for $\Delta f_{average}$ and $\Delta f_{lowestD}$ are about -9 and -6 Hz, respectively.

The corresponding variations in the dissipation values are shown in **Error! Reference source not found.**(b). The three measured dissipation changes do not agree as shown in the figure. The values of ΔD_3 give rise to higher values than those for $\Delta D_{average}$ and $\Delta D_{lowestD}$ over the entire studied concentration range. For example, the measured ΔD_3 at the cmc is about 1.52×10^{-6}, and that for $\Delta D_{average}$ and ΔD_{lowest} are about 1.40×10^{-6} and 1.13×10^{-6}, respectively.

3.3. *Data analysis using the Sauerbrey model*

The Sauerbrey model is used routinely to convert the measured frequency shift into an adsorbed mass. In this model, the adsorbed surfactant layer is assumed to adsorb rigidly onto the adsorbent surface. The measured frequency shifts $\Delta f_{average}$ and $\Delta f_{lowestD}$, determined by the loop protocol, were applied in the Sauerbrey equation to calculate the mass of adsorbed surfactant, $\Delta m_{Sauerbrey}$. The calculated $\Delta m_{Sauerbrey}$ values (in ng cm^{-2}) were then converted into the corresponding adsorbed amount $\Gamma_{Sauerbrey}$ (in molecules nm^{-2}) using the following equation:

$$\Gamma_{\mathrm{Sauerbrey}} = \frac{\Delta \mathrm{m}_{\mathrm{Sauerbrey}} \times \mathrm{N_A} \times 10^{-14}}{\mathrm{M_{wt}}} \tag{6}$$

where N_A is Avogadro’s number and M_{wt} is the molecular weight of the surfactant.

Additionally, the adsorption of C12BDMAC surfactant molecules onto 316L stainless steel particles was studied using the depletion method. This study has been carried out under the same experimental conditions used for the QCM and using 316L stainless steel powder, which has the same composition as the employed stainless steel-coated crystals. The amounts of C12BDMAC adsorbed onto 316L steel particles using the depletion method were compared to those determined by the QCM and are shown in **Error! Reference source not found.**. The experimentally determined adsorption isotherms were fitted to the two-stage Langmuir model (solid lines) to compare the amounts adsorbed by the two techniques quantitatively using the following equation:

$$\Gamma = \Gamma_{1\,(\mathrm{max})} \frac{\mathrm{k_1 C_{eq}}}{1+\mathrm{k_1 C_{eq}}} + \Gamma_{2\,(\mathrm{max})} \frac{\mathrm{k_2 C_{eq}}}{1+\mathrm{k_2 C_{eq}}} \tag{7}$$

where k_1 and k_2 are the equilibrium adsorption constants in the first and second stages in M^{-1} units, $C_{eq.}$ is the surfactant equilibrium concentration in M units and $\Gamma_{1\,(max)}$ and $\Gamma_{2\,(max)}$ are the maximum amount adsorbed corresponding to the first and the second layers, respectively. The fitting parameters used to fit the experimentally determined adsorption isotherms to the two-stage Langmuir model are given in Table S2. As shown in **Error! Reference source not found.**, the adsorption isotherm calculated using the measured frequency shifts $\Delta f_{average}$ gave rise to higher adsorption values than that determined by the depletion method. However, the values of adsorbed amount corresponding to $\Delta f_{lowestD}$ are the closest to those determined by the depletion method. For example, at a surfactant concentration of about 1 × 10^{-4} M, the amount adsorbed calculated from $\Delta f_{lowestD}$ and $\Delta f_{average}$ frequency shifts were about 0.2 and

0.5 molecules nm^{-2} respectively while the depletion method gave rise to a value of about 0.15 molecules nm^{-2}. At a surfactant concentration of about 7 × 10^{-3} M, the amount adsorbed calculated from $\Delta f_{lowestD}$ and $\Delta f_{average}$ frequency shifts were about 2 and 3.2 molecules nm^{-2} respectively while the depletion method gave rise to a value of about 1.2 molecules nm^{-2}. Despite the fact that the application of the measured frequency shifts $\Delta f_{lowestD}$ in the Sauerbrey equation was unable to overcome completely the overestimation in the adsorbed masses, arguably, it was successful in reducing it effectively to be within the experimental errors. This judgment is based on the fact, that the measured masses of adsorbed C12BDMAC using the depletion method have relative standard deviations, RSD, of about 15-20% over the studied concentration range. Additionally, the depletion method measures the mass of the dry adsorbed film in contrast to the QCM technique, which measures the mass of the wet adsorbed surfactant layer plus changes in the solvent adsorption.

The overestimation exhibited by the QCM could be attributed to changes in the density and viscosity of surfactant solutions. This means that the measured frequency shift is not entirely due to the adsorption of surfactant molecules and that it has an additional contribution from the solution bulk properties. Accordingly, a correction procedure is needed to work out the actual mass adsorbed on the crystal and to account for of these small differences in the measured adsorbed masses between the QCM and the depletion methods.

3.4. Data analysis considering the effects of the solution bulk properties using Kanazawa and Gordon equation

QCM is very sensitive not only to mass changes, at the crystal solution interface, or density and viscosity changes, but also to temperature changes and surface roughness. Accordingly, the overall frequency change may be expressed as follows [53]:

$$\Delta f = \Delta f_m + \Delta f_p + \Delta f_{\eta\rho} + \Delta f_r + \Delta f_T \tag{8}$$

where Δf_m is the mass effect caused by the added mass which is attached to the surface, Δf_p is the compression effect caused by changes of pressure of the fluid in contact with the quartz, $\Delta f_{\eta\rho}$ is the density and viscosity effect (which is referred to as the bulk effect), Δf_T is the temperature effect and Δf_r is the roughness effect. Additionally, in the QCM measurements, water (or any other liquid or solvent) may couple as an additional mass via direct hydration, viscous drag or entrapment in cavities in the adsorbed film. This means that the layer is essentially detected as a viscoelastic film composed of surfactant molecules and the coupled water. The typical amount of coupled water has been shown to vary significantly depending on the nature of the film, with mass-uptake estimations between a factor of 1.5 and 4 times larger than the molar mass of the adsorbed molecules [34, 54]. In the current experiments, the effects of pressure, temperature and roughness seem to be negligible as the experiments are carried out in a thermostatted flow cell at fixed temperature using a constant flow rate on the same crystal. This leaves us with the shift in frequency that may result due to the changes in density and viscosity (bulk effects) of tested solutions.

The frequency of an oscillating crystal in a liquid was found to be affected by the density and viscosity of the liquid. Kanazawa and Gordon [23] have developed a mathematical relationship which describes how the frequency of an oscillating crystal in a liquid will vary with changes in the bulk properties of the liquid and it is given by the following equation:

$$\Delta f = -\sqrt{n}\, f_0^{3/2} \left(\frac{\rho_l \eta_l}{\pi \mu_q \rho_q} \right)^{1/2} \tag{9}$$

where ρ_l and η_l are the density and viscosity of the liquid, ρ_q is the density of quartz and μ_q is the shear modulus of quartz.

Corrections based on this equation have been used in several studies [40, 55, 56] to eliminate the contribution of the bulk effect to the measured shifts in frequency. Lundgren *et al.* [40] studied the adsorption of the unsaturated fatty acid linolenic acid from non-aqueous solution onto stainless steel-coated crystals. They reported that above a concentration of 0.1 wt.% of the fatty acid, it is vital to make corrections for changes in bulk viscosity and density for these systems. They separated the bulk properties by independently measuring the density and the viscosity of the solutions and subtracted the contribution from the bulk using theoretical estimates of the expected frequency response. The corrected mass was then compared to the mass results from fitting the measured frequency shifts at different overtones to the Johannsmann model [38, 39]. Therefore, the actual adsorbed mass was not measured by other means and it is not clear which overtone has been used by Lundgren *et al.* for applying correction procedures.

Caruso *et al.* [20, 21] have used the calibration method for correcting the adsorbed mass calculated by the Sauerbrey equation. They investigated the adsorption of a series of polyethylene glycol monododecyl ethers ($C_{12}E_n$, n = 3, 5, and 8) from benzene onto silica surfaces using the QCM and depletion methods. Corrected frequency shifts for $C_{12}E_3$, $C_{12}E_5$ and $C_{12}E_8$ yielded calibration factors of 1.06, 1.05 and 4.8 for the QCM, respectively. Despite the success of the calibration method in correcting the overestimated mass, it suffers from a serious drawback, as the determined calibration factor is specific and limited for the system to which the correction has been made.

Recently, Bordes and Hook [57] have used two different approaches to quantify the bulk response during the adsorption of Triton X100 at the gold-water interface. The first approach involves the use of a non-adsorbing surface (silica), yielding a calibration curve for the concentration dependent bulk effect. In the second method they claimed that the overtone-dependent QCM-D response, originates from changes in the bulk differs, from that induced by the adsorbed layer of the surfactants. They assumed that the bulk solution and the adsorbed surfactants could be treated as a Newtonian liquid and an acoustically rigid film. However, in the case of polymer adsorption, this is not necessarily the case and one may question whether the bulk solution remains Newtonian at high concentrations. Accordingly, this approach of separating the bulk effect from the measured frequency shifts becomes more complicated.

In the current work, we attempt to develop a simple correction procedure based on equation (9) to quantify and separate the bulk effect from the measured frequency shifts by the loop protocol. When a 5 MHz QCM crystal with a smooth surface is moved from air into contact with deionised water at 25 °C, the frequency should shift to a lower value by about 672 Hz according to equation (9). This value is based on a measured viscosity of about 0.885 cP and density of 0.995 g cm^{-3} for the deionised water used in this work. In practice, a larger frequency shift of up to 2000Hz may be expected, depending on the surface roughness of the employed crystal. The effect of roughness is also related indirectly to the viscosity and density, since the hydrodynamic flow regime at the surface is altered as a result of roughness [53]. As shown in **Error! Reference source not found.**, the measured shift in the fundamental frequency Δf_0, on moving a stainless steel-coated crystal from air to Milli-Q water at 25 °C was about 716 Hz, which indicates the roughness of the crystal surface is low as it is reasonably close to the value calculated from equation (9) for a smooth QCM surface. Noticeably, the measured $\Delta f/n$ and $\Delta D/n$ values are overtone-dependent, in accordance with this equation. A comparison between the experimentally determined frequency shifts at different overtones, and those calculated using the Kanazawa equation, on moving the stainless steel-coated crystal from air to Milli-Q water at 25 °C is shown in **Error! Reference source not found.**. It can be seen that the measured frequency changes are in a good agreement with the calculated values using the Kanazawa equation for a smooth crystal surface. Similarly, the changes in the frequency brought about by different C12BDMAC aqueous solutions were calculated using equation (9) with the density and viscosity values given in Table S1. **Error! Reference source not found.** shows a comparison between the calculated frequency shifts $\Delta f_{lowestDK}$, which correspond to the changes in the solution bulk properties, and those experimentally determined by the loop protocol $\Delta f_{lowestD}$. The calculated $\Delta f_{lowestDK}$ correspond to changes in the frequency of the 13th overtone –the frequency of the lowest dissipation change calculated using equation (9).

To obtain the corrected frequency shifts in which changes in the solution bulk properties have been accounted for, the following procedure was applied. Firstly, the calculated shift in frequency for water was subtracted from the corresponding calculated shift in frequency for the aqueous surfactant solution, $\Delta f_{lowestDK}$. Secondly, the resulting frequency shift was then subtracted from the measured frequency shift, $\Delta f_{lowestD}$ and a frequency shift corrected for the changes in bulk properties, *corrected* $\Delta f_{lowestD}$ was obtained and is presented in **Error! Reference source not found.**.

The corrected frequency shifts were then applied in the Sauerbrey equation to calculate the corrected mass of adsorbed surfactant. **Error! Reference source not found.** shows a comparison between adsorption isotherms for C12BDMAC using the corrected QCM data to those determined by the depletion method. Two different corrected masses were calculated using the corrected frequency shifts for the overtone with the lowest dissipation change $\Delta f_{lowestD}$ and that for the average of changes of all the overtones $\Delta f_{average}$. The adsorption isotherms obtained from the *corrected* $\Delta f_{lowestD}$ and the depletion method are perfectly superimposed over the whole range of investigated surfactant concentration. On the contrary, the adsorption isotherm obtained from the *corrected* $\Delta f_{average}$ gives rise to higher values than those determined by the depletion method. Obviously, the figure demonstrates the success of the employed correction procedure in (i) removing completely the contribution from the bulk effect and (ii) the determination of the true mass of the adsorbed surfactant of C12BDMAC onto stainless steel surfaces using the QCM.

4. Conclusions

The optimization of QCM for studying the adsorption behaviour of the cationic surfactant benzyldimethyldodecylammonium chloride at the stainless steel-water interface has been investigated. The different experimental procedures used have been shown to have a marked influence on both the measured frequency shifts and dissipation energy changes. The stepwise protocol gave rise to the highest values of the average frequency shifts followed by those for the batch and loop protocols. The measured changes in the dissipation energy using the loop protocol were the lowest in value. These differences in the measured values of Δf

and *ΔD* by the three tested protocols may be attributed to variations in the amounts of entrained or coupled water in the adsorbed surfactant assemblies caused by differences in the amounts and/or structures of adsorbed molecules. In the stepwise protocol, it believed that the pre-adsorbed C12BDMAC molecules on the crystal surface, at the lower surfactant concentrations, and the longer equilibrium time result in an increased adsorption level and different adsorbed structures from those exhibited by the batch and loop protocols upon the introduction of the higher surfactant concentrations. The measured normalized frequency shifts were found to vary with the overtone number. This indicates that measured frequency shifts are not only due to the mass of adsorbed surfactant but also have contributions from the bulk solution properties. The use of the measured frequency shifts with the lowest dissipation using the loop protocol reduces effectively the differences in the derived adsorbed amounts between the QCM and depletion methods. We also show that the contribution of the bulk effect in the QCM measurements is removed completely by using a correction procedure based on Kanazawa and Gordon equation.

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Figures

Figure 1. Scanning electron micrograph of 316L stainless steel particles.

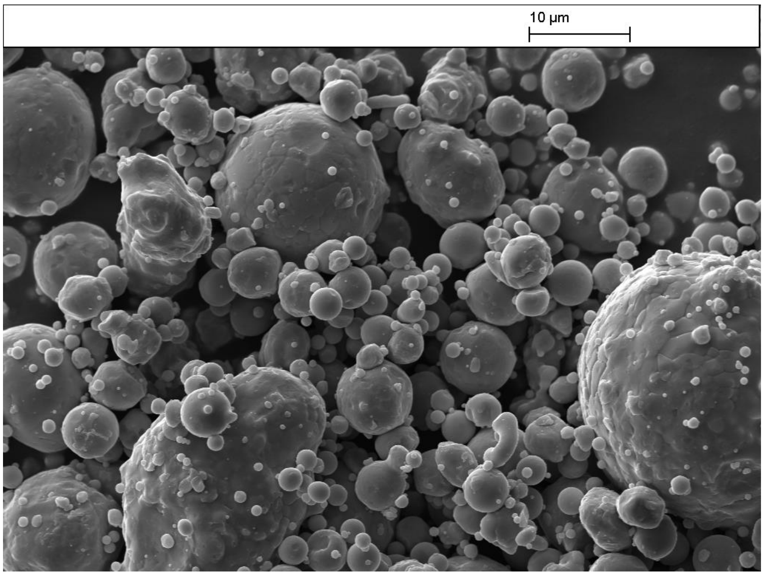

Figure 2. Changes in the frequency as a function of time during the adsorption of different C12BDMAC concentrations from aqueous solution onto stainless steel coated crystals at 25°C, at the third overtone, using the stepwise protocol. The arrows indicate the time at which each concentration was introduced. The numbers refer to the normalized surfactant concentration with respect to the cmc (7 mM).

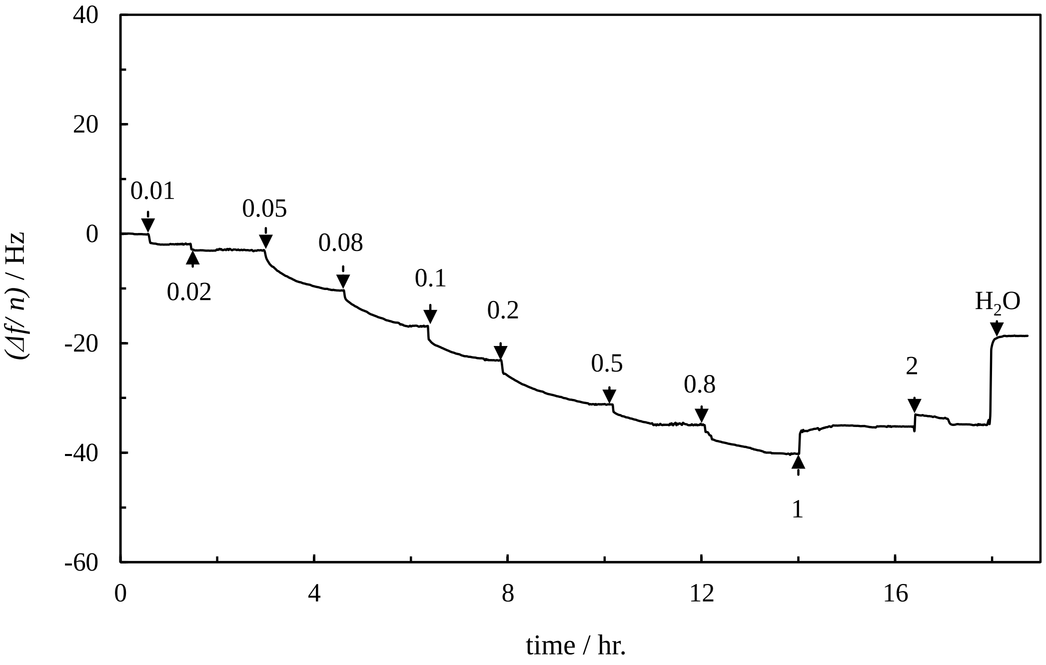

Figure 3. Frequency changes as a function of time during the adsorption of C12BDMAC onto stainless steel-coated crystals at 25°C, at the third overtone, using (a) the batch protocol and (b) the loop protocol.

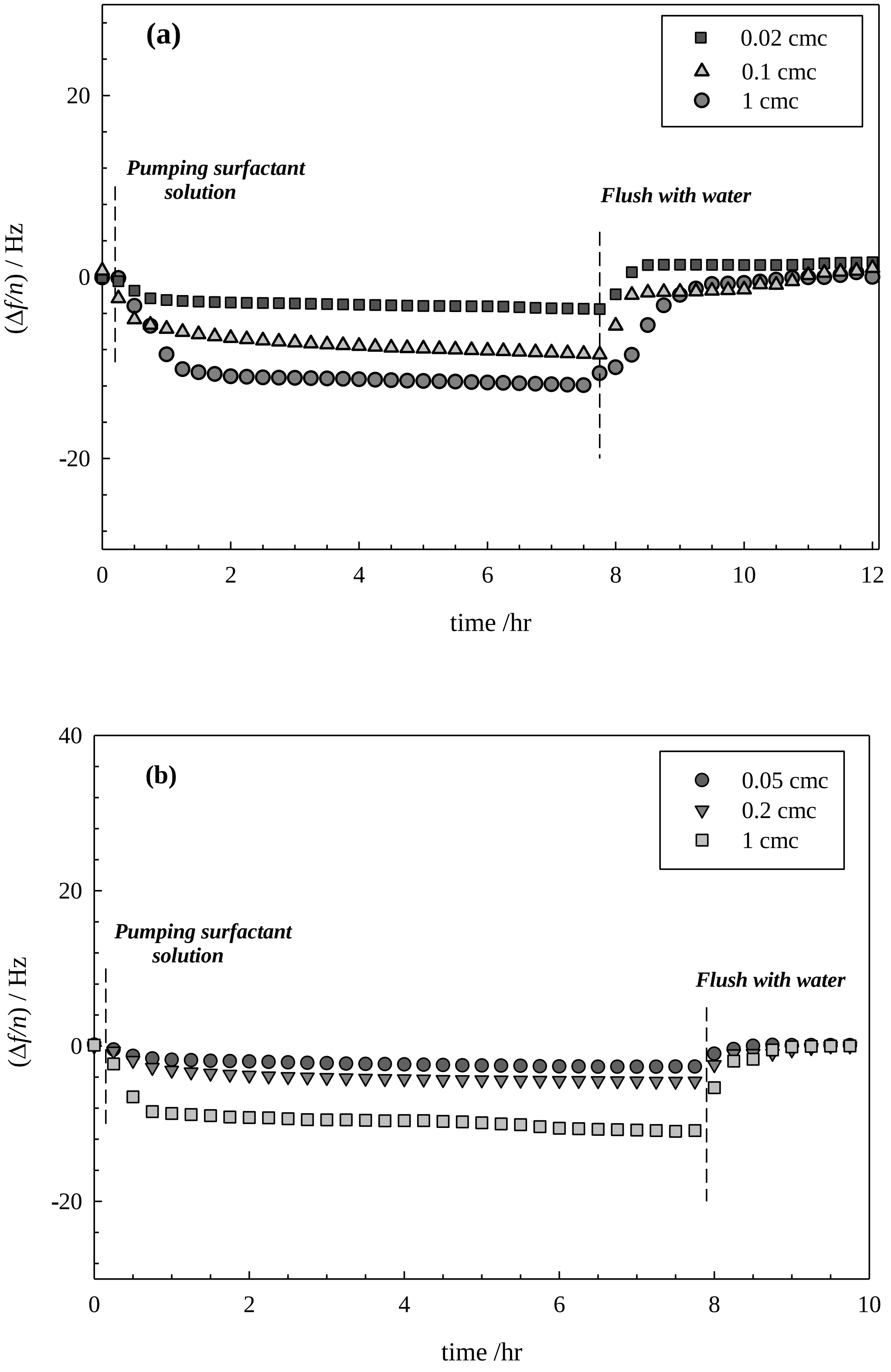

Figure 4. Variation of (a) the average frequency shift and (b) the average dissipation change as a function of the normalized C12BDMAC concentration, during the adsorption from aqueous solution onto stainless steel-coated crystals at 25 °C using different protocols.

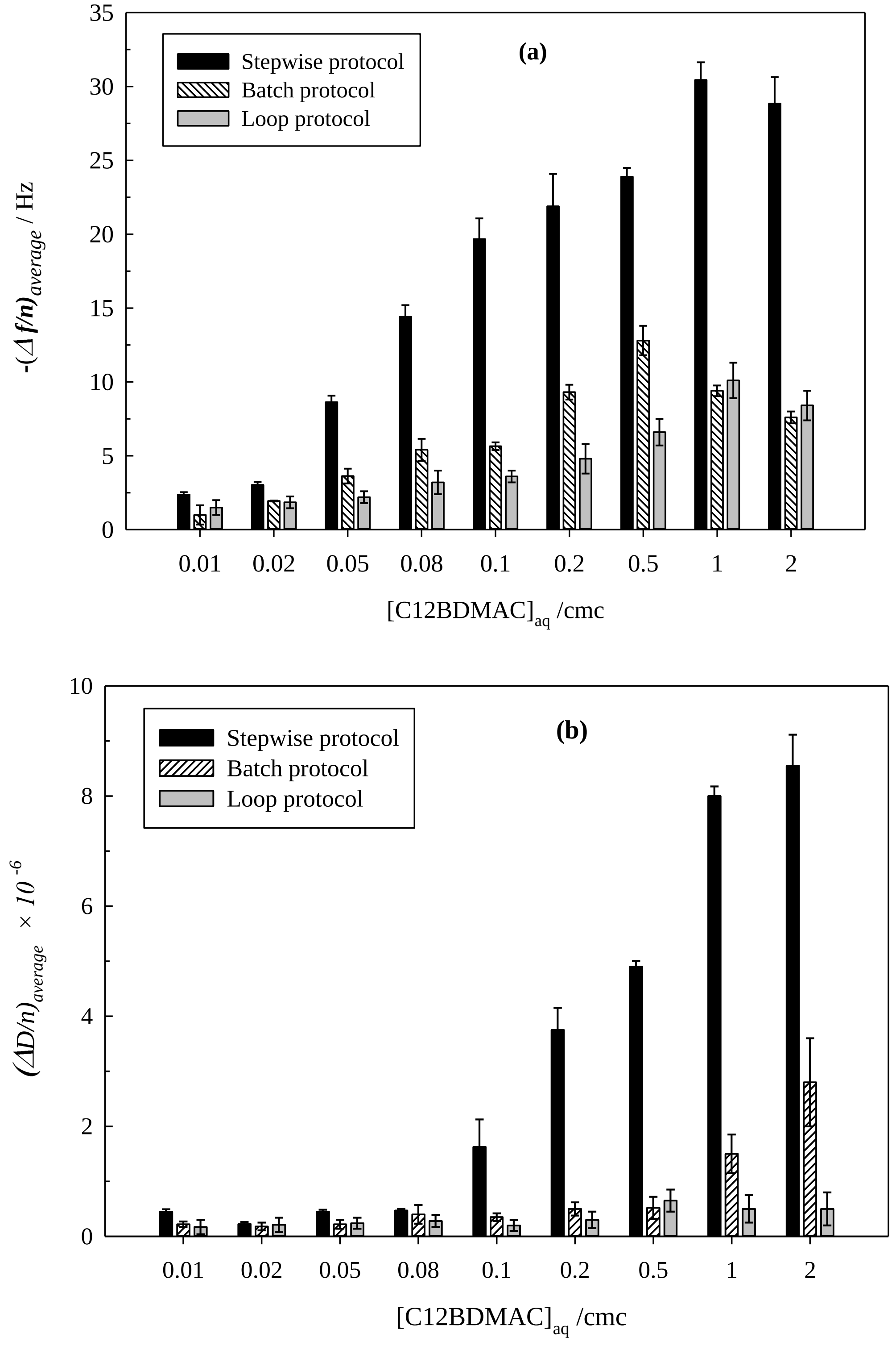

Figure 5. Changes in the normalized frequency, Δf_n, and dissipation, ΔD_n, as a function of time on moving stainless steel-coated crystal from air to Milli-Q water at 25 °C. The arrow refers to the time at which Milli-Q water was introduced.

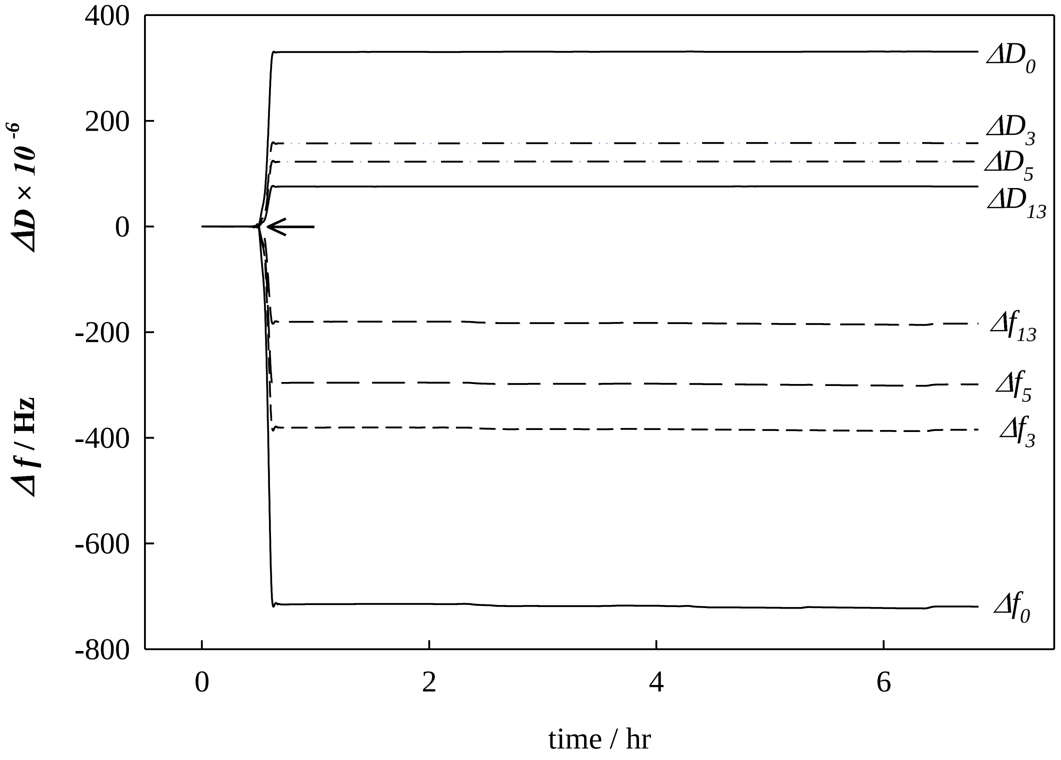

Figure 6. Changes in (a) the normalized frequency and (b) dissipation monitored at 3rd, 7th, 9th and 11th overtones as a function of time during the adsorption of an aqueous solution of C12BDMAC having concentration of 0.8 times the cmc onto a stainless steel-coated crystal at 25 °C using the loop protocol.

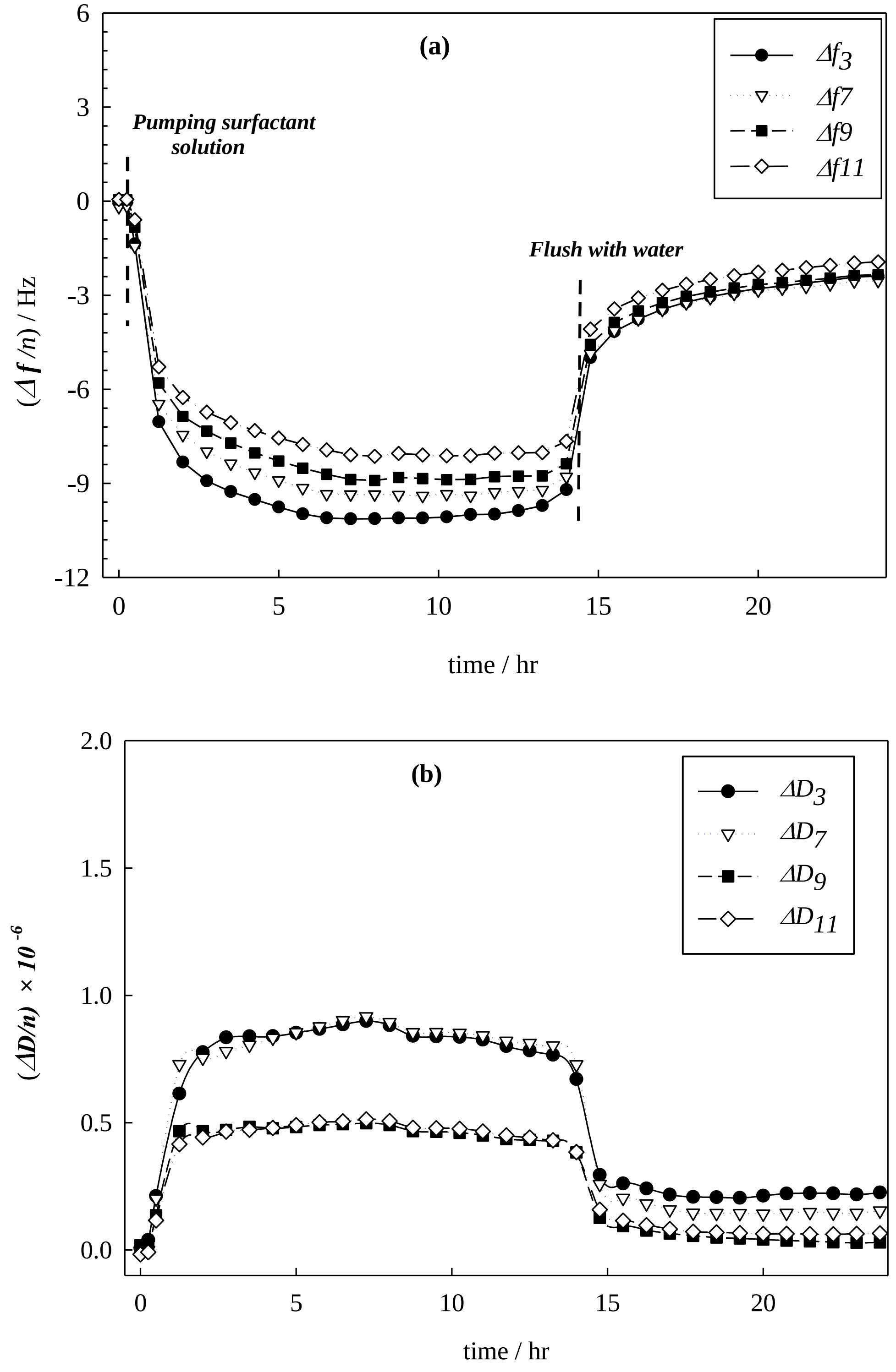

Figure 7. Variation of (a) different frequency shifts and (b) dissipation changes as a function of the normalized C12BDMAC concentration using the loop protocol.

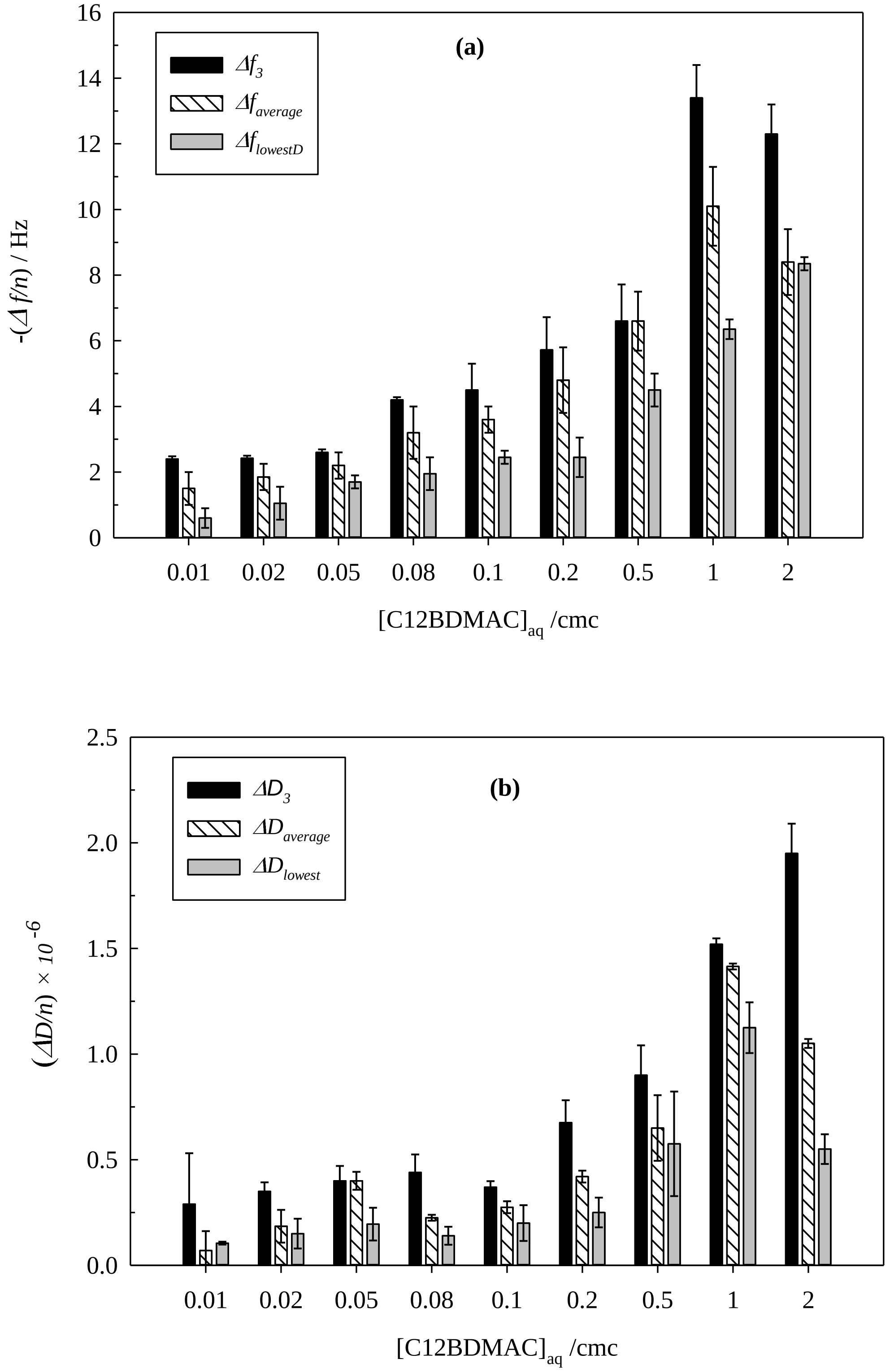

Figure 8. A comparison between the amounts of C12BDMAC adsorbed onto stainless steel surfaces determined experimentally by the QCM and the depletion method. The measured $\Delta f_{lowestD}$ and $\Delta f_{average}$ values were applied in the Sauerbrey equation to determine the amounts of surfactant adsorbed.

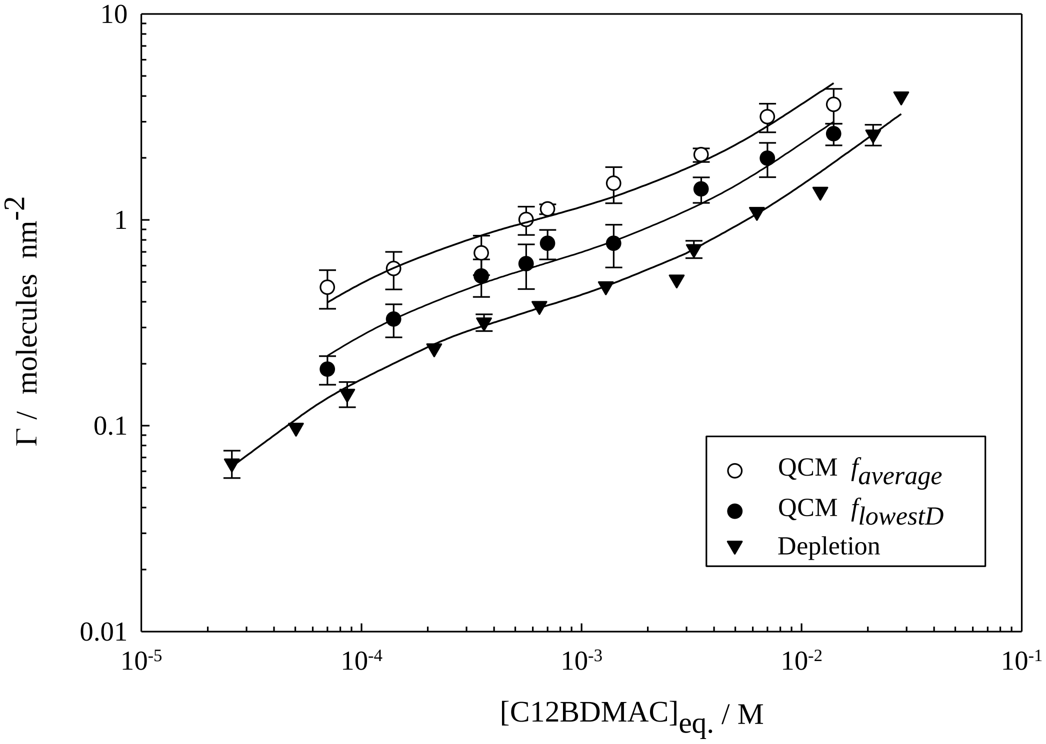

Figure 9. A comparison between the experimentally determined frequency shifts at different overtones and those predicted by equation (9) on moving a stainless steel coated-crystal from air to Milli-Q water at 25 °C. Δf_n corresponds to the change in the frequency of the n^{th} overtone.

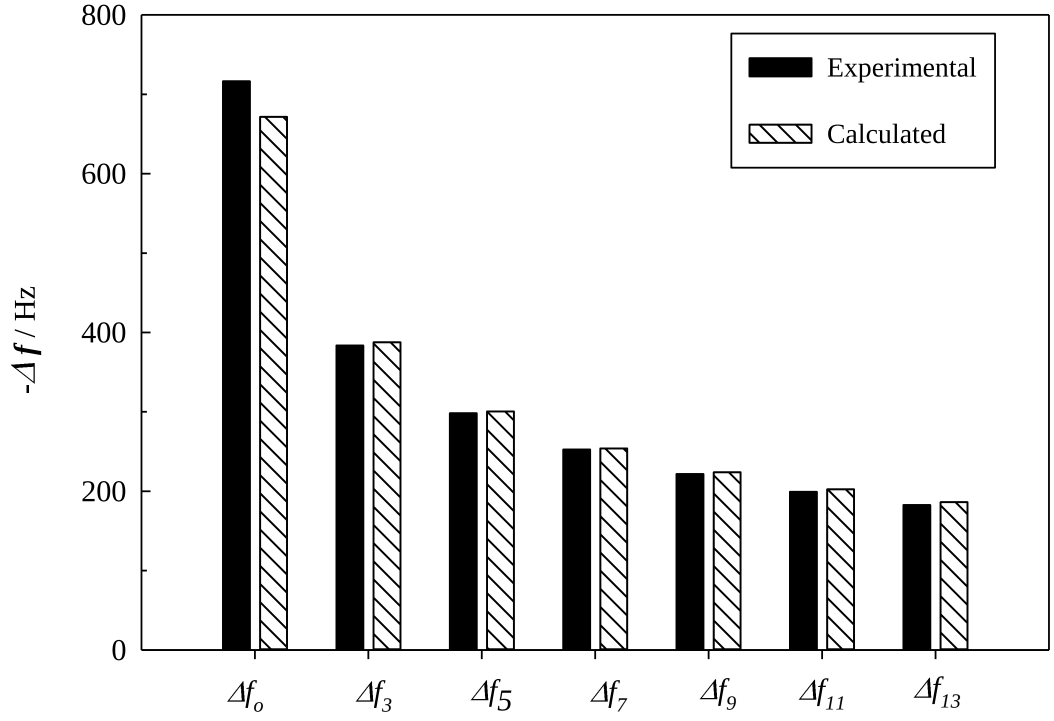

Figure 10. A comparison between the experimentally determined $\Delta f_{lowestD}$, the predicted frequency shifts calculated by equation (9) $\Delta f_{lowestDK}$ (bulk effect contribution) and the *corrected* $\Delta f_{lowestD}$ as a function of C12BDMAC concentration.

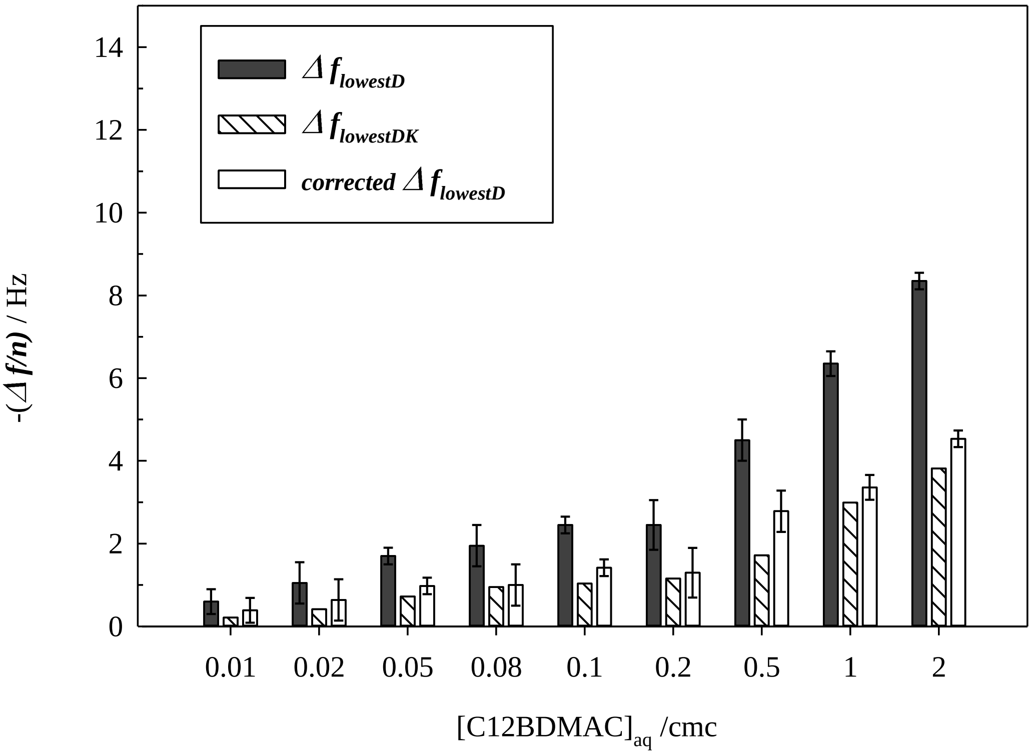

Figure 11. A comparison between the amounts of C12BDMAC adsorbed onto stainless steel surfaces determined by the QCM and the depletion method. The amounts adsorbed were calculated using *corrected* $\Delta f_{average}$ *and* $\Delta f_{lowestD}$ values in the Sauerbrey equation.