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ORIGINAL CONTRIBUTION

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Effect of ionic surfactants on the oscillation frequency of one-electrode-separated piezoelectric quartz crystals modified with chitosan and its derivative

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Abstract From the pH dependence of oscillation frequencies of one-electrode-separated piezoelectric quartz crystals (ESPQC's) modified with chitosan and *N*-(1,3-dicarboxypropyl) chitosan (DCPC) in buffer solutions, it was deduced that the chitosan and DCPC films on an ESPQC contained water and that the water content depended on pH. Contrary to the expectation based on the Sauerbrey equation, the binding of ionic surfactants to chitosan and DCPC films increased the frequencies. This apparently abnormal phenomenon was explained by the release of water in swollen films. The frequency of the DCPC-modified ESPQC increased on addition of sodium dodecyl sulfate and hexadecyltrimethylammonium chloride at pH lower and higher, respectively, than 7.8. A linear relationship between surfactant concentration and frequency shift, whose slope depended on only the chain length of the surfactant alkyl group, was obtained in the range 5–50 μmol dm^{-3} hexadecyltrimethylammonium chloride. The DCPC-modified ESPQC can be used for a quantitative determination of cationic surfactants in this concentration range.

Keywords Chitosan and chitosan derivative · Hexadecyltrimethylammonium chloride · One-electrode-separated piezoelectric quartz crystal · Quantitative determination of cationic surfactants

Introduction

A piezoelectric quartz crystal (PQC) has been used for quantitative determinations of atmospheric trace components and volatile organic substances [1] and is usually called a quartz crystal microbalance (QCM), since Sauerbrey suggested its utilization as a microbalance in 1959 [2]. Furthermore, after Nomura and Miemura [3] and Konash and Bastiaans [4] independently reported that a PQC oscillated even in solutions in 1980, it has been utilized in many fields of colloid science [5], biochemistry, environmental science and others. Although what is generally used as the QCM is a normal PQC sandwiched between a pair of metal electrodes, a one-electrode-separated PQC (ESPQC) with an electrode only on one side [6] and an electrodeless PQC [7] have also been contrived. If surfaces of a metal electrode and a quartz crystal itself are not of relevance or interest, their surfaces are coated or modified with a suitable solid layer or polymer. For examples, Caruso et al. [8] converted a gold electrode surface of a QCM into that of chromium oxide to investigate the adsorption of a nonionic surfactant, and we chemically modified a quartz crystal surface of an ESPQC with *N*-(2-pyridylmethyl) chitosan (PMC) to concentrate selectively and determine a silver(I) ion [9].

Chitosan, an N-deacetylated derivative of chitin (poly *N*-acetyl-D-glucosamine), can complex with metal ions and has been widely used as an absorption reagent for

the concentration and separation of metal ions [10]. Although the binding mechanism of metal ions to chitosan is not fully understood yet, it is likely that the chitosan–metal cations complex is formed primarily through the amine groups as ligands [11]. Of course, anions can also be bound to chitosan by an electrostatic attraction to protonated amino groups. It has been reported that dodecyl sulfate anions are bound cooperatively to chitosan dissolved in acidic solution [12].

In a previous paper [13] we showed that a copper(II) cation and a dodecyl sulfate anion increased the oscillation frequency of the PQC coated with chitosan by being bound to chitosan. However this result was contrary to the expectation based on the Sauerbrey equation, i.e. the decrease in frequency with increasing mass loading. The reason was conjectured to be the desorption of absorbed water on the chitosan film induced by the binding of ions, but the mechanism remains unsolved.

In the present work we prepared three types of ESPQC coated with chitosan and modified chemically with chitosan and *N*-(1,3-dicarboxypropyl) chitosan (DCPC), and examined the pH dependence of their oscillation frequencies in aqueous solutions in order to reveal their oscillation characteristics, particularly from the viewpoint of the dependence of the water content of the chitosan film on its net charge. Furthermore, we investigated the effect of binding of ionic surfactants, sodium dodecyl sulfate (SDS) and hexadecyltrimethylammonium chloride (CTAC), to the chitosan and its derivative films on oscillation frequencies of two chemically modified ESPQC's, and examined their utilizability for a quantitative determination of ionic surfactant.

Experimental

Materials

Reagents for modifications of PQC, chitosan 1,000 (degree of N-deacetylation 75–90%), (3-aminopropyl)triethoxysilane, glutaraldehyde and 2-oxoglutaric acid were purchased from Wako Pure Chemical Industries, and were used without purification. Analytical reagent-grade SDS, CTAC and all other chemicals were also obtained from Wako Pure Chemical Industries, and were used without any purification.

Standard stock solutions of surfactants were prepared with deionized water and were diluted to test solutions when used. All other solutions were also prepared with deionized water.

Apparatus

An ESPQC [6] consisting of a quartz crystal plate of AT cut with a fundamental frequency (F_0) of 9 MHz (Kyushu Dentsu Co.) and a platinum plate electrode on only one side of the quartz crystal plate was used. It was connected to a transistor oscillator and 6.0 V was applied with a direct current voltage power supply (Metronix, 532B). The frequency of the ESPQC was read with a frequency counter (Iwasaki Communication, SC7204) and recorded with a personal computer. Measurements were carried out in a flow cell and the solution temperature was controlled with a thermostated bath (TAIYO, C-650).

Modification of the ESPQC with chitosan and its derivative

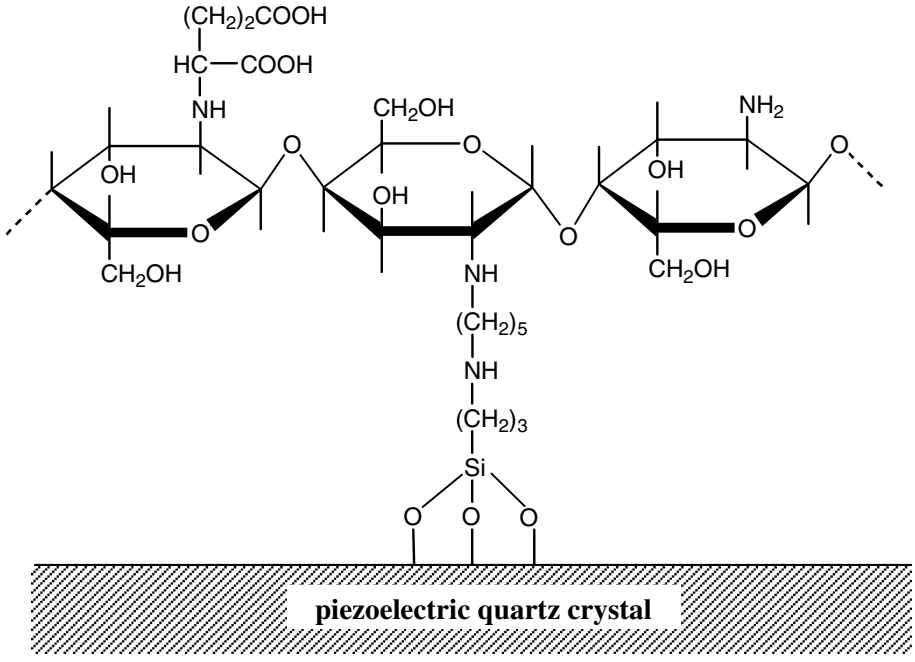
The ESPQC chemically modified with DCPC was obtained as described previously [9]. Prior to surface modification, the quartz crystal plate was soaked in 2 mol dm^{-3} sodium hydroxide solution for 3 min, washed with acetone and deionized water, and then dried. The ESPQC was soaked in 10% (3-aminopropyl)triethoxysilane [14] acetone solution for 2 h, dried at 100 °C for 1 h, and washed again with acetone. After that, it was immersed in 0.1 mol dm^{-3} phosphate buffer solution (pH 7.0) containing 5% glutaraldehyde for 2 h, washed with water, soaked in 5% acetic acid solution containing 0.5% chitosan overnight, immersed in 5% acetic acid solution containing 5% 2-oxoalutaric acid [15] overnight, and then treated with 0.3% $NaBH_4$ solution. The DCPC-modified ESPQC obtained was washed with water and acetone and then dried before being used. The expected microscopic structure of the DCPC-modified ESPQC is shown schematically in Scheme 1.

In addition to the DCPC-modified ESPQC, we used two other types of ESPQC: a chitosan-modified ESPQC and a chitosan-coated ESPQC. The former was the ESPQC chemically modified with chitosan in the same way as just described. The latter was the ESPQC coated with chitosan as described previously [13].

Procedure

All measurements were done for solutions flowing through a flow cell to maintain their properties such as electric conductivity, density, and viscosity during the measurement, because a frequency shift of the PQC depends on these properties [3, 16]. This procedure can also avoid a frequency shift due to an adhesion of dust and so on, which often happens when a PQC is taken out from a solution and exposed to air to change the test solution.

A blank solution of ammonium chloride buffer or phosphate buffer was pumped through a flow cell containing one of those ESPQC's. When the frequency



Scheme 1 Microscopic structure of the *N*-(1,3-dicarboxypropyl) chitosan modified one-electrode-separated piezoelectric quartz crystal

became constant (F_1), a sample solution of ionic surfactants containing the same buffer as the blank solution was pumped in place of it. The frequency (F_2) was recorded for 5 min. This recording time was not enough for F_2 to reach a constant value, but we selected 5 min with reference to our previous studies [9, 13] because our final aim was the utilization of an ESPQC as an easy method for determining ionic surfactant quantitatively. Then the sample solution was changed to the blank solution again. The frequency shift resulting from binding of surfactant (ΔF) was defined as $\Delta F \equiv F_2 - F_1$.

Results and discussion

pH dependences of frequencies of three ESPQC's

In previous work [9], the frequencies of normal PQC's coated with chitosan, PMC and polystyrene were measured in air and water. The frequencies (F) of these coated normal PQC's in air and the polystyrene-coated one in water decreased with increasing weight of the coatings according to the Sauerbrey equation [2],

$$F - F_0 = -2.3 \times 10^6 F_0^2 (\Delta m/A),$$

where Δm is the change in mass loading and A is the area of the PQC, whereas for the chitosan-coated and PMC-coated normal PQC's in water the rate of frequency decrease was about 3 times larger than that predicted from the Sauerbrey equation. Therefore we concluded that chitosan and its derivative films on PQC absorbed water of approximately twice their weight and became swollen in water. This is supported by the result of Singh and Ray [17] that a chitosan film contains solvent of weight 1.1 times its own weight in 0.1 mol dm^{-3} phosphate buffer solution (pH 7.4). It is well known that the degree of swelling of gels having ionizable groups depends on the degree of ionization [18]. Moreover, Chen et al. [19] recently reported a pH-sensitive gel based on carboxymethyl chitosan and gelatin. Therefore we investigated the pH dependence of the oscillation frequency of each ESPQC.

The oscillation frequency of the chitosan-modified ESPQC increased with increasing pH of the solution and was almost constant above pH 8, as shown in Fig. 1a. At lower pH more amino groups of chitosan are protonated and the electrostatic repulsion between them causes the chitosan film to extend and swell to a greater degree. Consequently, this pH dependence of the frequency of the chitosan-modified ESPQC indicates that the mass of water penetrating into the chitosan film contributes to the mass loading on the ESPQC. Above pH 8 most of the amino groups have released protons and, therefore, the oscillation frequency hardly depends on pH. If the Sauerbrey equation (Eq. 1) holds in this case, though the frequency should depend not only on a mass loading but also on solution properties such as electric conductivity, density, and viscosity [3, 16], the amount of water absorbed can be estimated to be 1.0 μg when the decrease in pH from 8.88 to 4.65 swells the chitosan film.

In contrast to the chitosan-modified ESPQC, the frequency of chitosan-coated ESPQC decreased with increasing pH of the solution, as also shown in Fig. 1a. Moreover, the oscillation frequency no longer returned

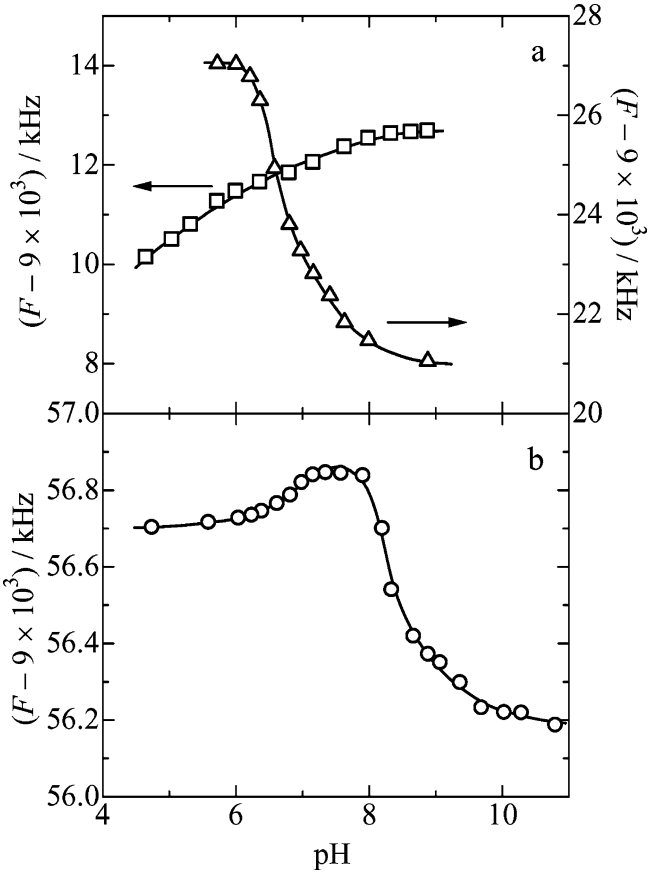


Fig. 1 pH dependence of the oscillation frequency of **a** one-electrode-separated piezoelectric quartz crystals (*ESPQC's*) coated (*open triangles*) and modified (*open squares*) with chitosan in 20 mmol dm^{-3} phosphate buffer solution containing 10 mmol dm^{-3} KCl and **b** an *N*-(1,3-dicarboxypropyl) chitosan (*DCPC*)-modified ESPQC in 20 mmol dm^{-3} phosphate solution or 40 mmol dm^{-3} ammonium chloride buffer solution containing KCl as a supporting electrolyte at 25 °C. Flow rate 4.0 cm^3 min^{-1}

to the initial value when the pH of the solution was lowered below 8 and then returned to the initial pH. The cause of the frequency increase with decreasing pH is similar to that of the frequency increase of QCM deposited with a Langmuir–Blodgett film at its phase-transition temperature from the solid to the liquid-crystalline state, i.e., the slipping between swollen hydrophilic interlayers in the liquid-crystalline state of the Langmuir–Blodgett film [20]. In this case, parts of the chitosan chain gradually dissolve into solution as a loop or tail with decreasing pH, because chitosan, soluble in an acidic solution, is not bound chemically to the ESPQC. Since such loops or tails dangling in solution can move considerably freely, the slipping would occur between the chitosan film and the layer of solution containing them and consequently increase the frequency.

The pH dependence of the frequency of the ESPQC modified with DCPC having both carboxyl groups and unchanged amino groups is shown in Fig. 1b. As the pH of the solution increased, the frequency gradually increased, reached a maximum around pH 7.8 (pH_{max}) and then decreased. The frequency increase with increasing pH below pH_{max} is due to the dissociation of ammonium groups of DCPC as in the case of the chitosan-modified ESPQC. On the other hand, the frequency decrease with increasing pH above pH_{max} is attributed to the dissociation of carboxyl groups of DCPC. pH_{max} can be regarded as an isoelectric point of the synthesized DCPC. Consequently anionic and cationic surfactants are expected to bind to the DCPC film at pH lower and higher than pH_{max}, about 7.8, respectively.

The amounts of water absorbed by the DCPC film are estimated to be 0.06 μg when the pH increases from 4.74 to pH_{max} and 0.27 μg when the pH decreases from 10.80 to pH_{max}. The latter value, arising from the dissociation of carboxyl groups, is larger than the former value, arising from the dissociation of ammonium groups, and this suggests that there are more carboxyl groups than amino groups in the DCPC film. These amounts of water absorbed smaller than the amount for the chitosan-modified ESPQC suggest that even at pH_{max} the DCPC film has many ionized groups, though its total charge is zero, and swells more than the chitosan film.

Time variation of the frequency of the ESPQC's in aqueous solutions of ionic surfactants

Frequency shifts, ΔF, of the DCPC-modified ESPQC with time after the blank solution had been exchanged with the SDS and CTAC solutions are shown in Fig. 2. The pH values of the blank and surfactant solutions were adjusted to 7.0 with a phosphate buffer for SDS and to 9.6 with an ammonium chloride buffer for CTAC. At surfactant concentrations lower than 0.7 mmol dm^{-3} for SDS and 0.1 mmol dm^{-3} for CTAC, the frequency shift monotonously increased. When the blank solution was flowed again, the frequency shift monotonously decreased and finally returned to the initial value, 0. The increase of frequency shift is attributed to binding of surfactant ions to functional groups of DCPC with opposite charge. Such binding reduces the net charge of DCPC and should shrink the DCPC film. Therefore, the mass loading on the ESPQC decreases and its frequency increases since some of the water included in the film is released. Flowing the blank solution again causes the dissociation of surfactant ions from DCPC and, therefore, the DCPC film returns to the initial state.

At higher concentrations of ionic surfactants, the frequency shift versus time plots had two peaks. The first peak can be explained by the same processes as the

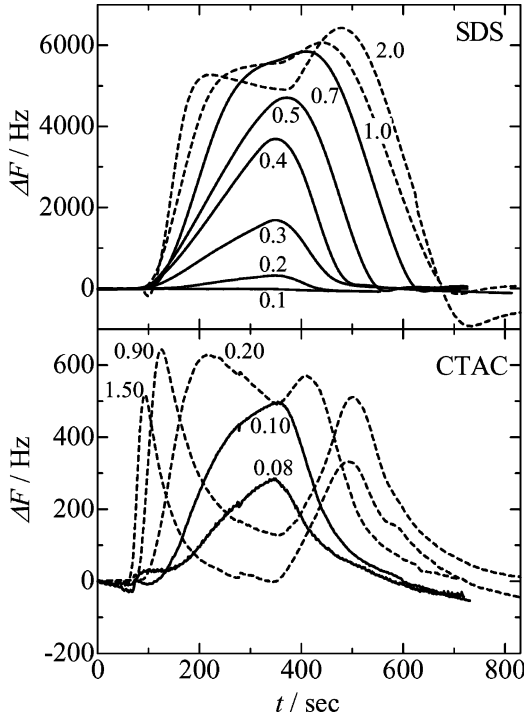


Fig. 2 Time variations of the frequency of the DCPC-modified ESPQC when the surfactant solutions were pumped through the flow cell for 5 min. The *numbers* represent surfactant concentrations in millimoles per cubic decimetre. Sodium dodecyl sulfate (*SDS*) in 20 mmol dm^{-3} phosphate buffer solution (pH 7.0); hexadecyltrimethylammonium chloride (*CTAC*) in 40 mmol dm^{-3} ammonium chloride buffer solution (pH 9.6). Other conditions as for Fig. 1b

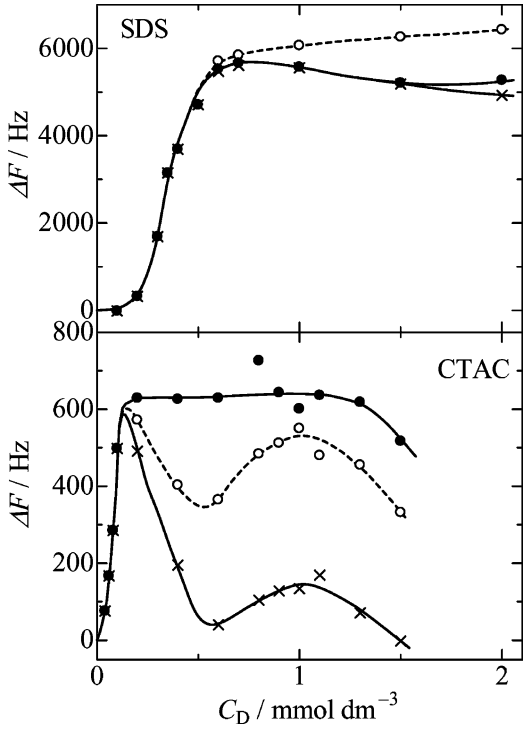


Fig. 3 Dependence on surfactant concentration of surfactant-induced frequency shift, ΔF_{max} (*closed circles*), ΔF_b (*crosses*) and ΔF_{2nd} (*open circles*). All conditions as for Fig. 2

binding processes of surfactant ions to a polyelectrolyte or an ionic gel in equilibrium, i.e., the initiation process and the cooperative process [21], although our system is not in equilibrium. At first after the blank solution is exchanged for the surfactant solution, the frequency increases since surfactant ions are electrostatically bound to oppositely charged groups of DCPC and the DCPC film releases water molecules as at the lower surfactant concentrations. As the amount of surfactant ion bound on DCPC increases, however, the surfactant ion is cooperatively bound to a binding site adjacent to an occupied site on DCPC, the increase of mass loading due to the cooperative binding of surfactants exceeds the decrease of mass loading due to the release of water molecules, and therefore the frequency decreases. The second peak could be attributed to the reverse processes.

Figure 2 shows that the maximum frequency shift due to SDS is about 10 times larger than that due to CTAC, and appears to indicate that there are more amino groups than carboxyl groups in the DCPC film in contrast to the result in Fig. 1b. This contradiction may suggest the possibility that the mechanism of frequency shift caused by ionic surfactant binding is more complicated than that described earlier.

The frequency shifts of the chitosan-coated and chitosan-modified ESPQC's in SDS solutions changed with time in the same manner, although they are not shown in Fig. 2.

Dependence of frequency shift on surfactant concentration

The frequency shifts at the maximum in surfactant solution (ΔF_{max}), just before the sample solution was exchanged for the blank solution (ΔF_b), and at the second peak (ΔF_{2nd}) are shown in Fig. 3 as a function of surfactant concentration. At surfactant concentrations lower than 0.6 mmol dm^{-3} for SDS and 0.2 mmol dm^{-3} for CTAC, the frequency shift versus time plot has only a maximum just before the exchange of sample solution for blank solution, so ΔF_{max} coincides with ΔF_b and ΔF_{2nd} does not exist.

For SDS, ΔF_{max} and ΔF_b increased monotonously with increasing concentration below 0.6 mmol dm^{-3}, but decreased slightly above it. At lower concentrations the degree of shrinking of the DCPC film due to surfactant binding and the resulting positive frequency shift depend on surfactant concentration, because the surfactant concentration determines the amount of surfactant bound to DCPC for the fixed time, 5 min. The nearly constant

ΔF_{max} at higher concentrations where two peaks appeared results because the surfactant concentration cannot affect the amount of bound surfactant, m_{max}, at which the increase in the rate of mass loading due to surfactant binding balances the decrease in the rate of mass loading due to water release. As the surfactant concentration increases, the time required for the amount of bound surfactant to reach m_{max} should be shorter and Fig. 2 shows that this is the case. ΔF_b is the frequency shift when the amount of bound surfactant exceeds m_{max} and, therefore, is slightly smaller than ΔF_{max}.

In the case of CTAC, ΔF_{max} and ΔF_b increased monotonously with increasing concentration below 0.2 mmol dm^{-3}. Above this, ΔF_{max} was almost constant, except that it decreased by about 100 Hz at 1.5 mmol dm^{-3}. In contrast, ΔF_b decreased at first, increased by about 150 Hz in the concentration range 0.6–1.0 mmol dm^{-3} and then decreased again. The critical micelle concentration (cmc) of CTAC in buffer solution is estimated to be 0.2 mmol dm^{-3} by the Corrin–Harkins equation, $\log C_0 = -0.61\log(C_0 + C_S) - 4.78$, where C_0 is the cmc and C_S is the salt concentration in moles per cubic decimetre, obtained from data in water and aqueous NaCl solution [22]. The complex dependence of ΔF_b on surfactant concentration is attributed to the formation of CTAC micelles, because it was not observed for SDS, whose cmc in buffer solution is higher than 3 mmol dm^{-3} [23], but its detailed mechanism remains to be clarified.

In both cases ΔF_{2nd} did not agree with ΔF_{max}. This fact suggests that the release processes of surfactant causing the second peak are not quite the same as the reverse of its binding processes causing the first peak, but the details are still unknown.

In the following sections, we will consider only ΔF_{max} exhibiting the simplest concentration dependence.

Influences of pH and buffer concentration on surfactant-induced frequency shift

Figure 4 shows that the pH dependence of the SDS-induced frequency shift, ΔF_{max}, is the same for the chitosan-coated and the chitosan-modified ESPQC's, although the pH dependence of the frequency of the former was opposite to that of the latter, as shown in Fig. 1a. α in the inset in Fig. 4 is the degree of dissociation of chitosan NH_3^+ groups, which is roughly estimated by the Henderson–Hasselbalch equation assuming their p K_a to be 6.5 [24] and ignoring the contribution of electrostatic potential. ΔF_{max} is constant below pH 7.5 ($\alpha = 0.91$), but decreases with increasing pH above it and then becomes almost 0 above pH 8.5 ($\alpha = 0.99$). This suggests that at least 1% protonation of chitosan amino groups is required for the anionic surfactant SDS to bind to chitosan

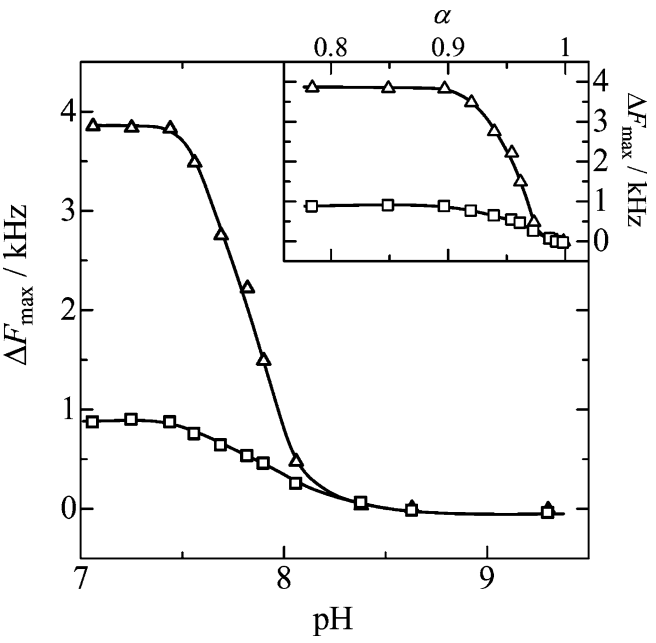


Fig. 4 Frequency shifts, ΔF_{max}, of an ESPQC coated (*open triangles*) and modified (*open squares*) with chitosan in various pH of phosphate buffer solution containing 1 mmol dm^{-3} SDS. Other conditions as for Fig. 1a. The *inset* shows the dependence of ΔF_{max} on the degree of dissociation of chitosan NH_3^+ groups

film. The larger frequency shift of the chitosan-coated ESPQC is caused by the thicker chitosan film and/or the partial dissolution of the chitosan chain.

For the DCPC-modified ESPQC, the same pH dependence of the SDS-induced frequency shift was observed, but the lowest pH value at which the frequency shift was approximately zero was lower than that for the chitosan-modified ESPQC (Fig. 5). On the other hand, the CTAC-induced frequency shift increased with increasing pH. These results support our conjecture mentioned earlier that the net charge of DCPC decreases from positive to negative with zero net charge around pH 7.8 as the pH increases. Moreover, the composite of two curves for SDS and CTAC is very similar to the vertical inverse of the curves in Fig. 1b, and supports our model that water molecules included in the DCPC film are released by surfactant binding.

The surfactant-induced frequency shift of the DCPC-modified ESPQC is plotted in Fig. 6 against the logarithm of the buffer concentration, C_b. When 2 mmol dm^{-3} SDS solution was pumped through the flow cell, a linear relationship between them was observed with a negative slope. This is caused by the decrease in the amount of water to be released by SDS binding, because the increase in the ionic strength causes the DCPC film to shrink. For 0.2 mmol dm^{-3} CTAC, the frequency shift also decreased with increasing buffer concentration, but the plot was

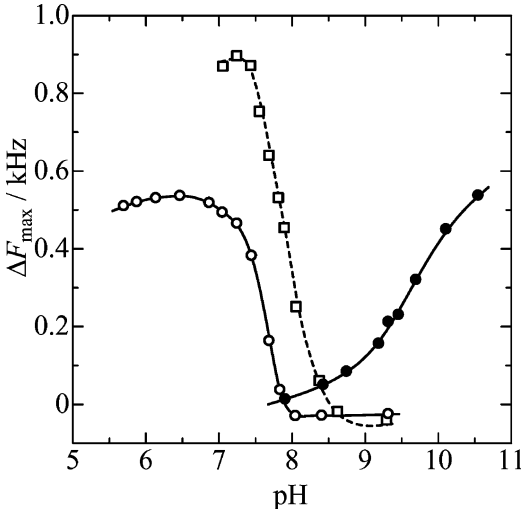


Fig. 5 pH dependence of the surfactant-induced frequency shift of the DCPC-modified ESPQC for 1 mmol dm^{-3} SDS (*open circles*) and for 0.2 mmol dm^{-3} CTAC (*closed circles*). Other conditions as for Fig. 2. SDS-induced frequency shifts of the chitosan-modified ESPQC (*open squares*) are also included for comparison

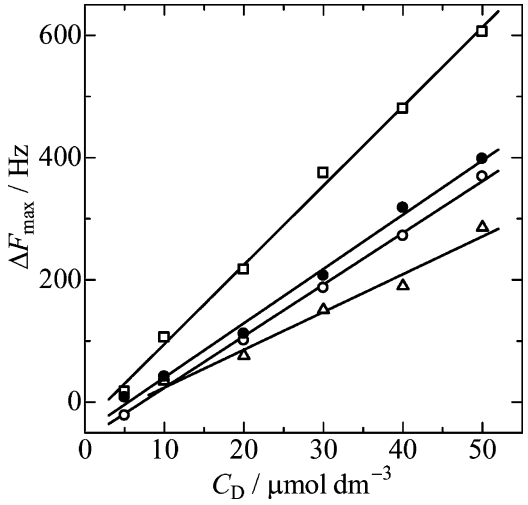


Fig. 7 Relationships between low surfactant concentration and surfactant-induced frequency shift of the DCPC-modified ESPQC in 60 mmol dm^{-3} ammonium chloride buffer solutions (pH 9.5) containing CTAC (*closed circles*), hexadecyltrimethylammonium bromide (*open circles*), octadecyltrimethylammonium chloride (*open squares*) and Zephiramine (*open triangles*). Other conditions as for Fig. 2

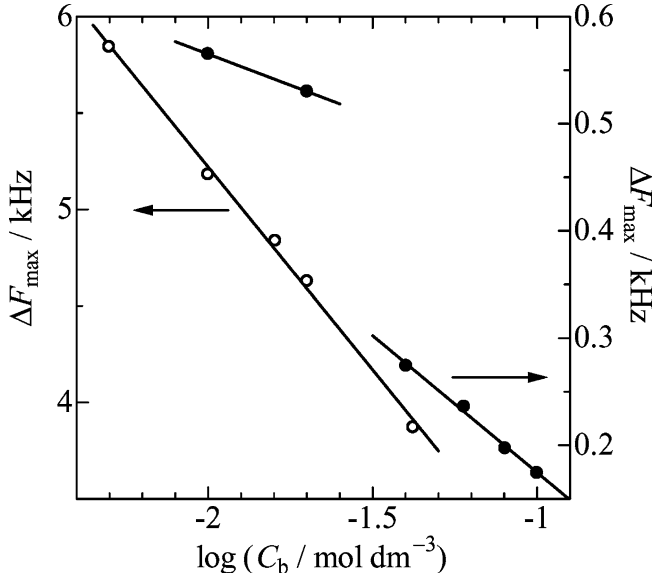


Fig. 6 Dependence on buffer concentration of the surfactant-induced frequency shift of the DCPC-modified ESPQC in phosphate buffer solutions (pH 7.4) containing 2 mmol dm^{-3} SDS (*open circles*) and in ammonium chloride buffer solutions (pH 9.4) containing 0.2 mmol dm^{-3} CTAC (*closed circles*). Other conditions as for Fig. 2

discontinuous around 30 mmol dm^{-3}. Since the cmc of CTAC in 40 mmol dm^{-3} buffer solution has been estimated to be 0.2 mmol dm^{-3}, this discontinuity is attributed to the micelle formation.

Frequency shift due to binding of various cationic surfactants at lower concentrations

Figure 3 shows that the CTAC-induced frequency shift of the DCPC-modified ESPQC increases almost linearly with increasing CTAC concentration from 0.04 to 0.10 mmol dm^{-3}. We investigated the concentration dependence of the frequency shift in the lower range of the CTAC concentration, 5–50 μmol dm^{-3}, and obtained a linear relationship,

$$\Delta F_{max}/\mathrm{Hz} = 8.88\left(C_D/\ \mu\ \mathrm{mol\ dm^{-3}}\right) - 48.5,$$

with a correlation coefficient, r, of 0.997 (Fig. 7).

For three other cationic surfactants linear relationships were also obtained:

$$\Delta F_{max}/\mathrm{Hz} = 8.45\left(C_D/\ \mu\ \mathrm{mol\ dm^{-3}}\right) - 61.1 \quad (r = 0.998)$$

for hexadecyltrimethylammonium bromide having a counterion different from that of CTAC,

$$\Delta F_{max}/\mathrm{Hz} = 12.96\left(C_D/\ \mu\ \mathrm{mol\ dm^{-3}}\right) - 34.6 \quad (r = 0.998)$$

for octadecyltrimethylammonium chloride with an alkyl chain two CH_2 groups longer than CTAC, and

$$\Delta F_{max}/\mathrm{Hz} = 6.18\left(C_D/\ \mu\ \mathrm{mol\ dm^{-3}}\right) - 38.0 \quad (r = 0.990)$$

for benzyldimethyltetradecylammonium chloride (Zephiramine) with an alkyl chain two CH_2 groups shorter and a head group bulkier than CTAC.

Since the slopes are almost the same and the intercepts differ only slightly from each other for CTAC and hexadecyltrimethylammonium bromide, the kind of counterion would hardly affect the surfactant-induced frequency shift. Furthermore, comparing CTAC with octadecyltrimethylammonium chloride and Zephiramine, we find that the slope increases by a factor of about 1.45 when the chain length of the surfactant alkyl group increases by two CH_2 groups, but the intercept changes only slightly. This increase in slope is attributed to the increasing amount of water released by surfactant binding, which is caused by the increasing amount of bound surfactant owing to its enhanced hydrophobicity and/or the enlargement of surfactant size. Therefore, it is concluded that the rate of increase in the frequency shift with surfactant concentration does not depend on the kind of counterion and the size of the head group but depends on the chain length of the surfactant, and the DCPC-modified ESPQC can be utilized for a quantitative determination of cationic surfactants in the range 5–50 μmol dm^{-3}.

Conclusions

The oscillation frequencies of ESPQC's modified chemically with chitosan and DCPC decreased as the pH of the solution decreased or increased from 8 and 7.8, respectively. These phenomena arise because the chitosan and DCPC films on an ESPQC contain water and the water content depends on pH, i.e., net charge of films. In contrast, the frequency of the ESPQC coated with chitosan increased with decreasing pH because of partial dissolution of chitosan chains.

Contrary to what we expected on the basis of the Sauerbrey equation, the binding of ionic surfactants to chitosan and DCPC films increased the frequencies of the ESPQC's. This apparently abnormal phenomenon can be explained by the release of water included in swollen films.

For the ESPQC modified with DCPC having both carboxyl groups and amino groups, an anionic surfactant SDS and a cationic surfactant CTAC induced a positive frequency shift at pH lower and higher, respectively, than 7.8. In the range 5–50 μmol dm^{-3} CTAC, a linear relationship was obtained between surfactant concentration and frequency shift. A comparison of CTAC with three other cationic surfactants indicates that the kind of counterion and the size of the head group hardly affect the linear relationship but the increase in alkyl chain length or hydrophobicity increases its slope. The DCPC-modified ESPQC can be utilized for a quantitative determination of cationic surfactants in the low concentration range.

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