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An impedimetric chemical sensor for determination of detergents residues

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ABSTRACT

A new impedimetric sensor based on an interdigitated electrode array with electrode digits located at the bottom of microcapillaries formed in silicon dioxide is presented. Microcapillaries are opened at the top, so that in contact with an electrolyte solution the ac current flows close to the surface of the capillary wall from one electrode to another and is significantly affected by changes in the surface conductance at the SiO_2/electrolyte interface. Adsorption of detergents on the sensor surface affects the charge distribution in the electrical double layer and thus the surface conductance. These changes are registered by measuring impedance. Effect of surface adsorption of ionic and non-ionic surfactants on the sensor impedance is studied. The sensor is shown to be able to measure commercial detergents residues in a tap water starting from 5 ppm even in solutions with high electrolyte conductivity.

1. Introduction

In a sustainable society there is a permanent demand of "green" environmentally friendly products among which are typical for any household washing and dish-washing machines. Modern machines use various sensor systems for controlling the washing process to make it energy efficient and water saving. However, there exists a need for sensors that can be used to measure detergents or surfactants residues [1,2]. Such a sensor could be helpful in reducing the number of rinsing cycles or reducing the amount of water used for rinsing, resulting in both saved water and energy. It also could guarantee safe levels of residue detergent in the washed laundry.

Modern detergents can comprise 20 or more ingredients [3] but all the formulations contain surfactants — molecules, which due to the combination of hydrophilic and hydrophobic moieties within the same molecule show amphiphilic character. This property gives surfactants ability to concentrate at interfaces. There is a large variety of surfactants that are generally classified according to their hydrophilic component as non-ionic, anionic, cationic, or amphoteric. Typical laundry or dishwash detergent formulations contain up to 35% of anionic detergents and 1–5% of non-ionic detergents [3,4]. Among anionic detergents the most commonly used are linear alkyl benzene sulfonates, and fatty alcohol ethoxylates are the most typical non-ionic surfactants in detergents formulations [3–5].

There are numerous analytical methods and techniques that may be used for chemical analysis of surfactants [4–8] that include infra red and nuclear magnetic resonance spectroscopy, spectrophotometry, high performance liquid chromatography (HPLC), ion chromatography and others. Measurements of ionic and non-ionic surfactants may be performed by titration using potentiometric sensors [6–10] or with biosensors [11–13]. However, all these methods require expensive laboratory equipment and qualified personal and are not suitable for in-line or at-line measurements.

To measure detergent concentration in washing machines optical systems based on surface-plasmon resonance (SPR) phenomenon have been proposed [14–16]. Optical methods of detection are quite expensive, so commonly to control the amount of detergent in the washing machines different sensors and systems based on measuring the conductivity of the washing liquid with a detergent are used [17,18]. A conventional conductivity sensor is formed by two metal electrodes. When a voltage is applied externally between two electrodes, an electric current is generated which corresponds to the conductivity of the washing liquid, which depends on the concentration of the detergent. Thus, the electric current value, which can also be converted to impedance, is used to measure the concentration of the detergent present.

Disadvantages of methods based on the conductivity measurement arise from the fact that conductivity of the washing water depends on the concentration of detergent in cases when the final concentration is high. In the rinse cycle, when the concentration of detergent decreases, the conductivity of the solution will depend on the conductivity of the water itself and not on the present detergent residues. Therefore, these methods are useful for dispensing and dosing the detergents, but not to control their residues.

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An interesting approach was proposed by a Swedish group which used voltammetric electronic tongue to determine amounts of detergents in process water from washing machines [2,19]. However, authors conclude that there are no ways to distinguish between supporting electrolytes or the anionic surfactant with the electronic tongue. Thus, for process control the simpler conductivity meter will perform equally well.

Earlier we have reported [20–23] a new impedimetric device that is very sensitive to the presence of charged molecules (e.g. antigens, DNA, large polycations and polyanions) at its surface and that may be used as a transducer for the development of different sensors and biosensors. The objective of the present work was to study the sensor response to the presence of surfactants in water solutions.

2. Experimental section

2.1. Microcapillary device design and fabrication

As presented earlier [21–23], the device was fabricated using conventional microelectronic techniques. Silicon wafer covered with a thermally grown silicon dioxide layer of 2500 nm was used as a substrate. A 230 nm thick layer of tantalum silicide ($TaSi_2$), which is a highly conductive material, is deposited by magnetron sputtering. The first photolithographic step defines collector bars and digits of two electrodes. The patterning is done by a reactive ion etching technique. This results in an interdigitated electrode array (IDEA) with 216 digits of 3 μm width and 3 μm gap between the adjacent electrode digits. The electrode digits are 1.5 mm long and the aperture between the adjacent digits is 1.4 mm.

To form the contact pads 1 μm of aluminum is deposited and patterned using standard photolithographic and etching steps leaving metal only at extremes of the two collector bars.

In the final step the wafer with formed IDEA devices is covered with a 4 μm thick silicon oxide layer deposited by a low pressure chemical vapor deposition (LPCVD). This material is virtually the SiO_2 but with a lower density compared to thermally grown silicon oxide or quartz. Photolithography is used to define the trenches to be opened in the oxide layer over the electrodes digits and over contact pads. These zones are opened by deep reactive ion etching (DRIE), which permits to obtain nearly vertical walls. In this way capillaries are formed in silicon dioxide over the electrode digits. The capillaries over each electrode digit are 3 μm wide, 4 μm high, 1.5 mm long and are opened at their top. Fabricated device is schematically presented in Fig. 1A.

After being cut from the wafer the sensors are glued to a printed circuit board (PCB) substrate with copper leads and are wire bonded for electrical connections. Contact pads and wires were encapsulated using epoxy resin.

2.2. Impedance measurements

Characterization of sensors was performed by impedance measurements in a 100 Hz–1000 kHz frequency range with a 25 mV (amplitude) voltage excitation using QuadTech 7600 Plus precision LCR meter. Z-Plot/Z-View software package (Scribner Associates, Southern Pines, NC, USA) was used for impedance data treatment and an electrical equivalent circuit fitting. Measurements were performed by immersing sensors into a beaker with 10 mL of a test solution. Concentration of the solution components was changed by adding a known volume of prepared stock solutions. All experiments were carried out at controlled temperature of 25 ± 0.5 °C in a thermostatic laboratory environment. At least two identical sensors of each type were tested in the experiments.

The conductivity of test solutions was controlled with a commercial conductimeter EC-Meter GLP 31+ (Crison).

2.3. Chemicals

As an ionic surfactant sodium dodecyl benzene sulfonate (NaDBS) from Sigma-Aldrich was used. Decaethylene glycol monododecyl ether (polyoxyethylene 10 lauryl ether, C12E10, Sigma-Aldrich) was used as a non-ionic surfactant. Commercial detergents were purchased at a local supermarket.

Test solutions were prepared using deionised water and analytical grade chemicals. In experiments with commercial detergents tap water was used to prepare detergent solutions.

3. Results and discussion

3.1. Physical model of the device and its equivalent electrical circuit

When a tangential electric field is applied at the solid/solution interface, due to a higher concentration of ions within the electricalal double layer (EDL), the local electric current can be higher than that typical of the bulk electrolyte solution. For a long time it was considered that surface conductivity is associated only with migration of ions accumulated within diffuse part of the EDL. Accumulated experimental evidence obliged to revise the EDL model of the solid/liquid interface [24,25] and to assume that under electric potential gradient part of ions which can migrate under the electric field is located in a stagnant layer of EDL. The current density in both surface layers is determined by concentration and mobility of ions. It may be noted that ion mobility

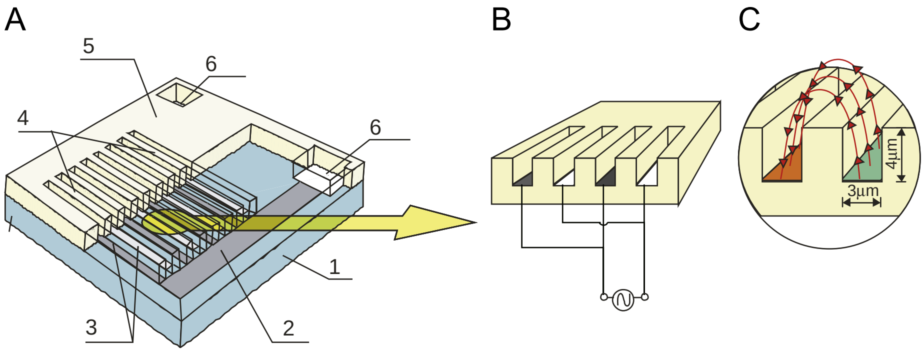

Fig. 1. (A) Design of the studied device with microcapillaries on its surface (1—isolating substrate, 2—electrode collector bar, 3—electrodes digits, 4—microcapillaries opened over electrode digits, 5—silicon dioxide cover layer, 6—contact pads). (B) Electrical connection scheme. (C) Electrical field lines passing over the barrier separating two electrode digits are shown.

within the immobile compact part of the EDL may be quite high, comparable to those of the bulk of water solution [26,27].

Adsorption of charged molecules at the interface alters the charge distribution and thus the surface conductivity. Surfactants are known to adsorb easily on the silicon dioxide surface [28] affecting the structure and charge distribution in the double layer.

Analyzing the possible electrical equivalent circuit of the microcapillary system presented in Fig. 2A and taking into consideration that the surface conductivity may play an important role, we may distinguish the following components which are presented in Fig. 2B. R_C is the contact resistance introduced by wires and collector bars of the electrodes; C_G is the geometrical (stray) capacitance between two interdigitated electrodes in a water solution; R_S is the resistance of the bulk water solution between two electrodes of the array; $\mathrm{CPE_{DL}}$ is a constant phase element [20,29] associated with the capacitance of the electrical double layer at the electrode–water solution interface. The solution bulk resistance, R_S, is in parallel with the resistance of the surface layer, R_{SURF}, and a capacitive element, C_{SURF}, between two resistances which can be interpreted as an interfacial capacitance between the surface of the barrier and the solution bulk.

Analysis of the impedance spectra of the equivalent circuit (EC) in Fig. 2B shows that at high frequencies the impedance will be determined by the parallel RC combination of the stray capacitance, C_G, and the resistance R, which is a parallel combination of bulk and surface resistances. In the low frequency range the impedance will mainly depend on the series combination of R_{SURF} and C_{SURF}. An example of simulated spectra for different values of R_{B} and R_{SURF} is presented in Fig. 3.

When the resistance parallel to the stray capacitance is large a semicircle appears at high frequencies. Its intercept with the Z_{REAL} axes on the left side gives the R_C value. The intercept on the right side gives the value of the parallel combination of R_B and R_{SURF}. If the value of the resistance is small the semicircle does not appear in the established frequency range (dashed line in Fig. 3). At low frequencies the impedance in both cases depends mainly on the series combination of R_{SURF} and C_{SURF} as it follows from the spectra presented in Fig. 4. This means that the trend in changes of the surface resistance may be studied in-situ by measuring changes in time of the serial resistance at fixed frequency. This is very important as dynamic processes and their kinetics may be studied in real time.

3.2. Adsorption of individual ionic and non-ionic surfactants

The silicon dioxide surface of the studied devices is hydrophilic and in contact with water solutions capillaries are easily filled with the solution. Before performing the tests impedance spectra

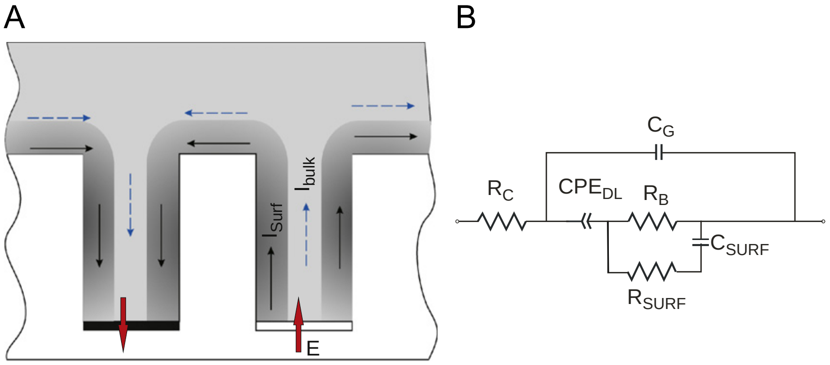

Fig. 2. (A)—electrical current paths in the microcapillary sensor (surface and bulk zones are marked). B—the electrical equivalent circuits used for impedance spectra fitting.

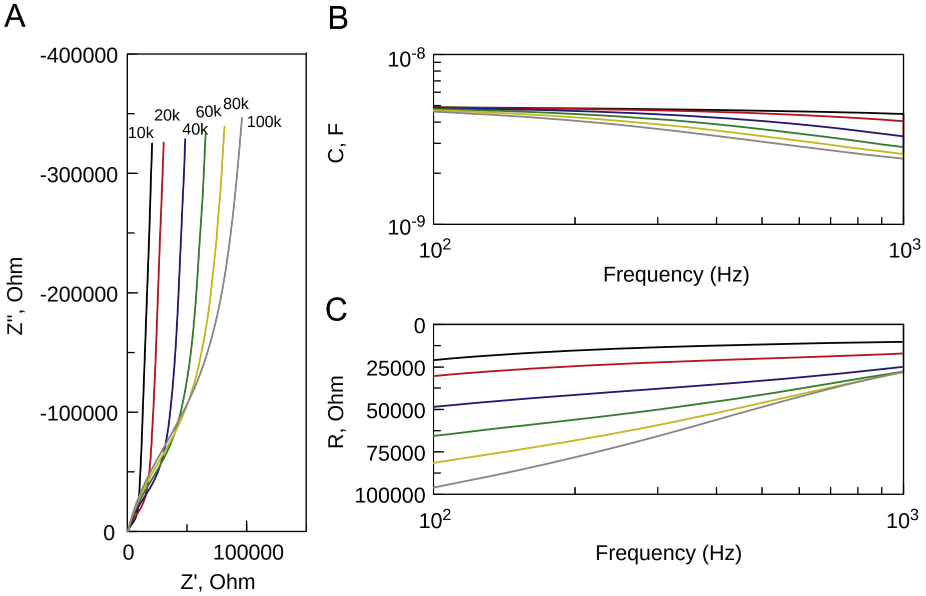

Fig. 3. Simulation of the impedance spectra of the EC in Fig. 2B. The components values are: R_C—125 Ω, C_G—68 pF, $\mathrm{CPE_{DL}}$—56 nF, C_{SURF}—1.4 nF, R_B and R_{SURF} 50 Ω and 20 kΩ (dashed line) and 20 kΩ and 20 kΩ (solid line), respectively.

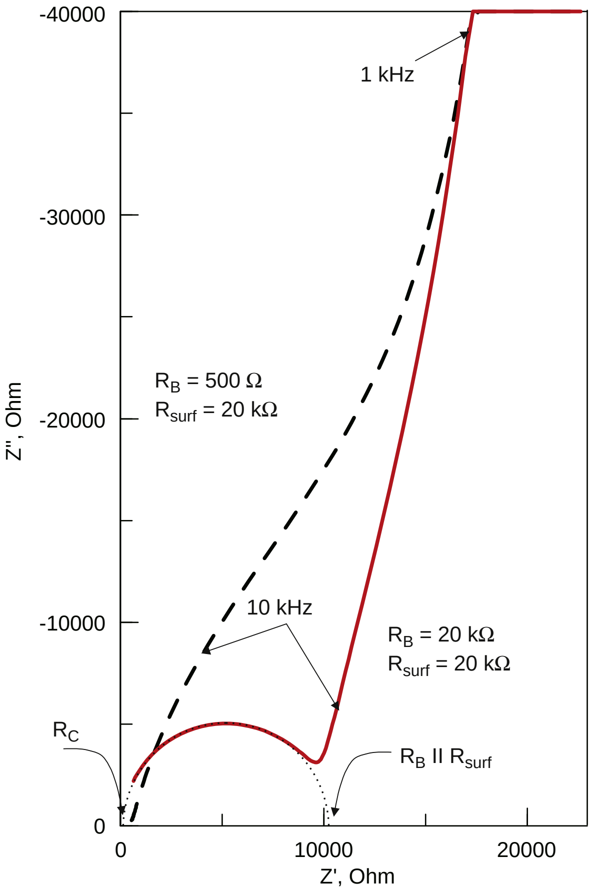

Fig. 4. Simulation of the impedance spectra of the EC with the components values : R_C–125 Ω, C_G– 68 pF, CPE_{DL}–56 nF, C_{SURF}–1.4 nF. Dashed line—R_B and R_{SURF} 500 Ω, respectively and 20 kΩ; solid line—R_B and R_{SUR} –20 kΩ and 20 kΩ, respectively. R_B II R_{SURF} denotes parallel combination resistance value.

Table 1
Concentration and conductivity of NaDBS and C12E10 surfactants used in experiments.

C, mg/l	NaDBS			C12E10		
	C, mM/l	Test 1 κ, μS/cm	Test 2 κ, μS/cm	C, mM/l	Test 3 κ, μS/cm	Test 4 κ, μS/cm
0	0	30.1	298		31.5	302
1	0.0029	30.6	299	0.0016	31.7	303
10	0.029	35.1	301	0.016	32.1	301
20	0.057	39.4	302	0.032	31.8	299
40	0.115	48.5	307	0.064	31.4	293
60	0.172	57.3	312	0.096	31.0	288
80	0.230	65.6	316	0.128	30.6	283
100	0.287	73.6	320	0.16	30.2	278

of all the sensors are measured in 10^{-5} M KCl solution. The spectra typically coincide one with another, which means that no air bubbles are entrapped within the capillaries.

Adsorption of surfactants was studied in KCl solutions at two different ionic strengths, 0.011 mM and 2.06 mM. The 1 g/l stock solution of surfactants prepared on a subsequent KCl solution background was added to the test solution using a micropipette to change the surfactant concentration. Concentrations of test solutions and their respective conductivities are presented in Table 1. The background KCl solutions initial conductivities were 30 μS/cm (Test 1 and 3) and 300 μS/cm (Test 2 and 4). Addition of anionic surfactant leads to solutions with higher conductivity, while in the case of non-ionic surfactant it diminishes. After changing the surfactant concentration in a beaker under stirring sensors were left for 5 min for surfactant adsorption and then the impedance spectra were measured. Preliminary measurements of impedance in time showed that changes associated with surfactant adsorption occur within 2–3 min, so we assume that after 5 min of contact with test solution the interface is at equilibrium.

EC on Fig. 2B was used for spectra fitting to extract the component values. The fitting quality was evaluated by chi-squared (χ^2) values, which were between $1 \cdot 10^{-4}$ and $1 \cdot 10^{-5}$ in the whole frequency range from 100 Hz to 1 MHz. The chi-squared value is the square of the standard deviation between the original data and the calculated spectrum and represents an evaluation of the goodness of fit. Performed fitting gave values of R_B and R_{SURF} with relative errors of 0.4–1.0% and 1.5–5%, respectively. This error range corresponds to all the spectra measured. Higher R_{SURF} fitting errors were noted in highly conductive solutions where this parameter has less influence on the spectra shape than in poorly conducting solutions. The surface conductance is an inverse of thus determined R_{SURF} value.

Adsorption of surfactants onto a silicon dioxide surface [30–33] takes place at concentrations below critical micelle concentration (CMC), which is 1.36 mM for C12E10 [34] and between 2 and 3 mM for NaDBS [30], and depends on various factors, one of which is the solution ionic strength.

Effect of non-ionic surfactant adsorption on the silicon dioxide surface of the sensor on the determined surface resistance is presented in Fig. 5. At low background electrolyte concentration adsorption of first surfactant molecules provoke drop of the resistance which increases at higher surfactant concentrations approaching the saturation at concentrations close to CMC. The dominant interaction between non-ionic surfactants and the hydrophilic surface of silica is due to hydrogen bonding of the ether oxygens of the ethylene oxide group and the surface [35]. Blocking of ionized hydroxyl groups at the surface will reduce the surface charge and thus the compensating charge within the EDL which should lead to higher surface resistance. However, the adsorption of non-ionic surfactants on oxides and other hydroxyl terminated surfaces leads to preferential orientation of the polar headgroup towards the surface [36], so that first adsorbed molecules may induce more charge in the EDL in the case of low background electrolyte concentration. Due to low overall surface resistance at higher ionic strength, this effect is not visible.

Adsorption of anionic sodium dodecyl benzene sulfonate introduces negative charges to the silicon dioxide surface. Cations attracted from the solution to the surface reduce the surface resistance as it follows from the data presented in Fig. 6. Once again, this effect is more profound in solutions with low electrolyte concentration as the relative change of the cations concentration within the EDL is higher.

3.3. Adsorption of commercial detergents

Initial experiments were performed with a white-label commercial liquid laundry detergent. Test solutions were prepared with tap water which in Barcelona region is highly mineralized and has the conductivity of 300–400 μS/cm.

Experimental spectra obtained in solutions with different detergent concentrations are presented in Fig. 7. As the bulk solution conductivity in these experiments remains constant and high (300–400 μS/cm) the high frequency part of the spectra remains unchanged. However, the detergent concentration affects the impedance changes in a low frequency region that may be attributed to changes in a surface concentration of the adsorbed detergent. And indeed, fitting of the spectra with the equivalent

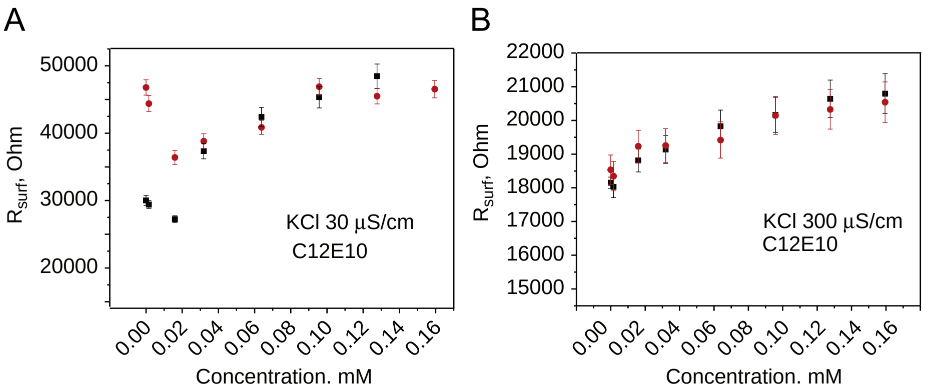

Fig. 5. Changes in the surface resistance due to adsorption of non-ionic surfactant C12E10 from KCl solutions with conductivity of 30 μS/cm (A) and 300 μS/cm (B). Results obtained on two sensors are presented. Error bars show the absolute error of the fitting.

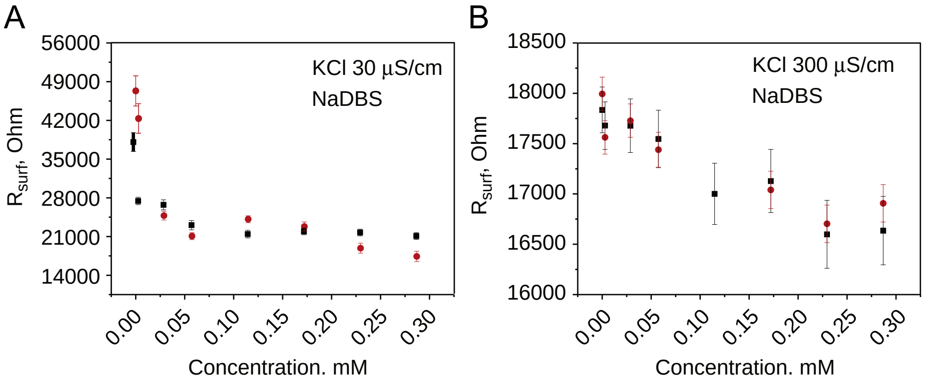

Fig. 6. Changes in the surface resistance due to adsorption of anionic surfactant NaDBS from KCl solutions with conductivity of 30 μS/cm (A) and 300 μS/cm (B). Results obtained on two sensors are presented. Error bars show the absolute error of the fitting.

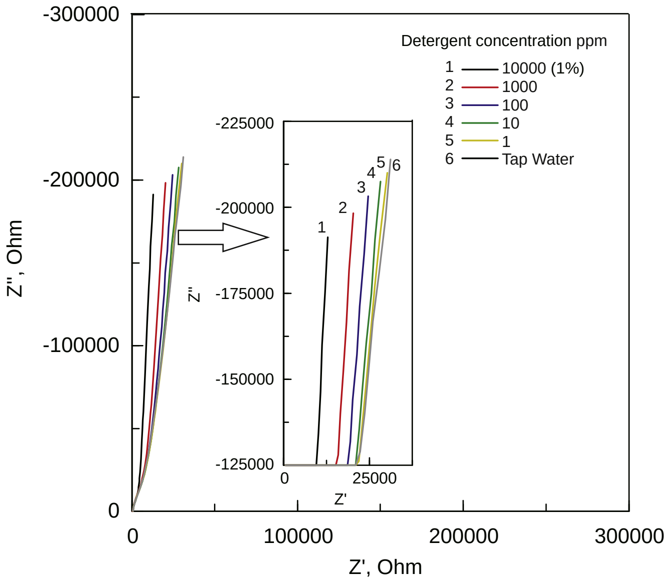

Fig. 7. Impedance spectra measured with the sensor in tap water with conductivity of 300–400 μS/cm at different detergent concentrations.

circuit presented in Fig. 2B showed very good results with chi-squared (χ^2) values between $2\cdot10^{-4}$ and $9\cdot10^{-5}$ in the whole frequency range from 100 Hz to 1 MHz. Performed fitting gave values of R_B and R_{SURF} with relative errors of 0.4% and 3.5%, respectively. Typical R_B and R_{SURF} values obtained from the spectra were in the range of 300–400 Ω and 10–50 kOhm, respectively.

3.3.1. Real-time monitoring of sensor response at a fixed frequency

As show results presented above, impedance spectra measurements is a very useful technique that permits to characterize processes at the solid/liquid interface. However, this method does not satisfy the requirements of a chemical sensor concept, which relies on a single measurable quantity (e.g. electrical current, potential, frequency, etc.) that is dependant on an analyte concentration.

It may be noted that variations in the spectra on Fig. 7 as the detergent concentration changes are very close to the simulation results discussed in Section 3.1 and presented in Fig. 4A. At low frequencies the impedance mainly depends on the series combination of R_{SURF} and C_{SURF} of the equivalent circuit presented in Fig. 2B. This permitted us to perform real-time measurements at a fixed frequency of 200 Hz registering changes in the series resistance values. Obtained in this way response curve of the sensor is presented in Fig. 8.

The sensors response time is presented in Fig. 9 and is equal to 4 min. After the measurement cycle the sensor, being thoroughly rinsed with the water flow, returns to its initial values and is ready to be used in another measurement cycle.

The sensor response was tested in solutions of different commercial detergents in different aggregate states (powder, gel, liquid) for washing and dish-washing machines as well as in solutions containing technical detergent for cleaning-in-place (CIP) systems. Results are presented in Fig. 10. For all the detergents the response in the studied range of concentrations (0–0.1 g/l) was almost linear with a slope of -25 to -30 kOhm/g·l^{-1} of detergent, which is equivalent to -25 to -30 Ω/ppm. The detection limit was 3–5 ppm of a detergent.

It may be noted that the sensitivity of the sensor differs in pure anionic surfactant and in commercial detergents. This may be attributed to the presence of surfactants of different types in commercial formulations [3]. It is known that mixtures of surfactants often produce enhanced performance over the pure components [37]. Even in binary mixtures of different surfactants [32,34,38] synergetic effects often enhance the adsorption of detergents.

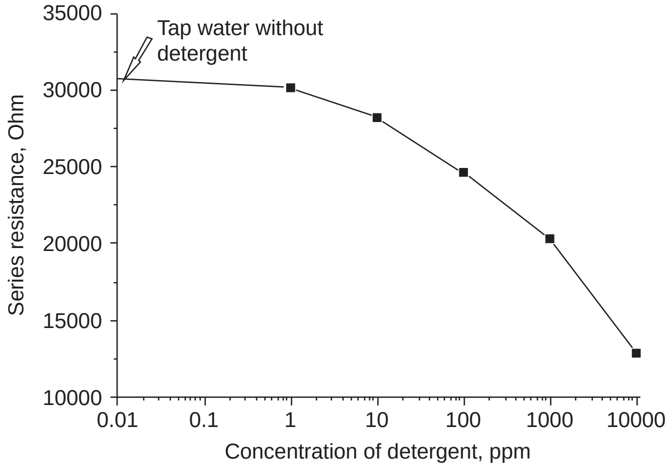

Fig. 8. Series resistance of RC combination determined in solutions with different detergent concentrations.

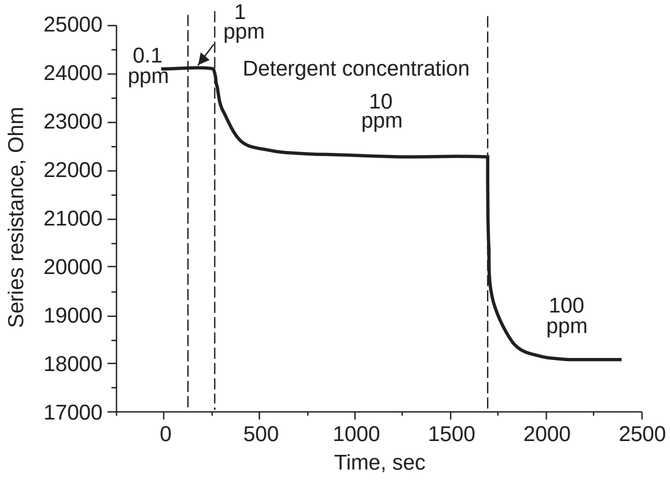

Fig. 9. Response time of the sensor to the change in the detergent concentration.

4. Conclusions

Most techniques that can determine adsorbed surfactant layers are only suitable for equilibrium measurements or in the case of slow kinetics. Techniques that respond rapidly to sub-monolayer changes in the mass of an adsorbed film, such as optical reflectometry and ellipsometry [39,40], surface plasmon resonance and quartz crystal microbalance [41] measurements may be used for in-situ measurements. However, the last two are limited to metal surfaces. We have proposed a new device based on impedimetric measurements in a microcapillary interdigitated structure that can be successfully used for these purposes. The functional mechanism of the device is based on the measurement of changes in surface conductivity at the microcapillary walls that are affected by electrical charge redistribution at the interface due to the adsorption of surfactants. In principle, the same effect of charging of the double layer on adsorption of surfactants on metal electrodes was exploited in the work of Olsson et al. [2], who applied the square wave pulse voltammetry to register the initial current flow which depends strongly on the charging of the species close to the electrode surface.

The sensor responds to the adsorption of anionic as well as non-ionic surfactants though the response is oppositely directed. Adsorption of NaDBS introduces negative charges to the surface which are compensated within the EDL by attracting mobile cations which results in higher surface conductivity. In the case of non-ionic surfactants the surface conductivity diminishes as organic molecules block the surface silanol groups.

The sensor was tested in solutions of different commercial household detergents for washing and dishwashing machines. Though detergent formulations usually contain surfactants of different types the sensor response is the same as in the presence of anionic surfactants. In the studied concentrations range (0–0.1 g/l) the response is almost linear with a slope of -25 to -30 kOhm/g·l^{-1} of the detergent. The detection limit is 3–5 ppm of a detergent even in water with high electrolyte conductivity. This suggests that the new sensor can be used to control detergents residues in the rinsing cycles. The sensor is very robust and simple and can be used for practical applications, e.g. in washing and dishwashing machines.

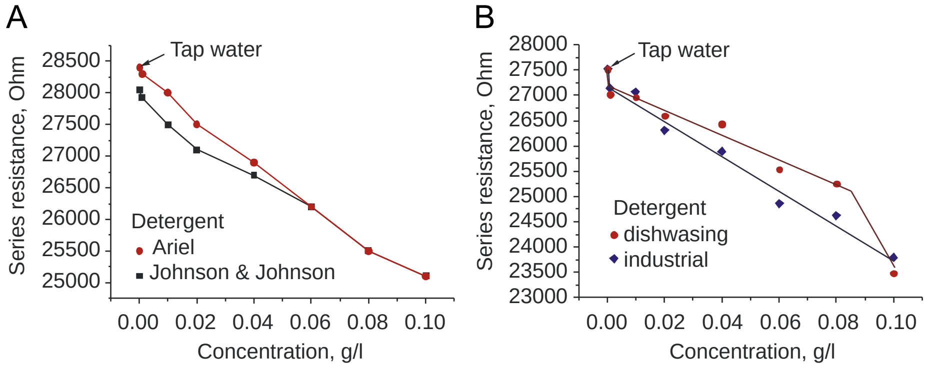

Fig. 10. Sensor response to concentration of different commercial detergents in tap water solutions. (A) circles—Ariel laundry detergent (liquid), squares—Johnson&Johnson laundry detergent (gel); (B) circles—dishwashing detergent (powder), squares—Cleaning-in-place industrial detergent (liquid).

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