M. SAK-BOSNAR *et al.*: Non-Electrochemical Sensors in Biotechnology, *Food Technol. Biotechnol.* 42 (3) 207–212 (2004)

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Surfactant Sensors in Biotechnology
Part 2 – Non-Electrochemical Sensors

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Summary

An overview on non-electrochemical surfactant sensors is given with special attention to work published since 1993. In the first part the importance of surfactants in modern biotechnology is stressed out and works on electrochemical surfactant sensors have been summarised. In this part the research of non-electrochemical surfactant sensors is reported, primarily optochemical and piezoelectric surfactant sensors. Papers investigating some specific interactions of potential interest for surfactant sensors are reported as well.

Key words: surfactants, sensors, optochemical, electric, piezoelectric, biotechnology

Introduction

The importance of surfactants in industrial biotechnology has been reviewed in the first part of electrochemical sensors (*1*). In this part the works of non-electrochemical surfactant sensors since 1993 are reviewed.

Optochemical Surfactant Sensors

Optochemical surfactant sensors are mainly sensors with optical fibers and spectrometric detection. Some examples of photometric titrations are also given.

The cyanine dye Merocyanine 540 (MC 540) was incorporated as an optical sensor into small and large unilamellar phospholipid vesicles. The absorption spectrum of the amphipathic dye was used to monitor the sublytic and lytic actions of the non-ionic detergent Triton X-100 on model membrane systems. The maximum absorption wavelength (λ_{max}) of the monomer band is sensitive to micropolarity changes, while dimeric formation is related to environmental polarity, as well as to vesicle curvature. Triton X-100 incorporation into the bilayer leads to a more polar environment in the hydrocarbon region near the interface, so that solubilisation is accompanied by a blue-shift of λ_{max} and a decrease in the monomer/dimer area ratio. It is concluded that MC 540 is a sensitive and informative optical probe, supplying information along an unusually broad range of detergent/lipid ratios (*2*).

An instrument was designed, assembled and validated with the aim of measuring macroscopic properties of foams (such as foamability and stability) under high pressures and moderate temperatures (up to 105 bar and 425 K, respectively). The device makes use of infrared sensors to detect the foam forefront position as it is generated by gas sparging in the foaming solution. Traditional direct observation used in foam experiments at ambient conditions is therefore circumvented and the instrument can be set up in an appropriate place and monitored remotely so as to reduce the risks involved in high-pressure and high-temperature operations. A series of fluorosurfactants (cationic, anionic, and non-ionic)

were used to validate the instrument, and the effect of temperature on foamability, foam stability and foam quality was discussed. Finally, synergistic effects were observed with respect to the foam behaviour of different mixtures of the studied surfactants (*3*).

A photometric titration method for cationic surfactants with tetrabromophenolphthalein ethyl ester (TBPE) as an indicator was developed. In the presence of a non--ionic surfactant (Triton X-100), TBPE was dissolved in an acidic aqueous medium, giving a yellow colour in the acidic form (TBPE⁻H⁺). When a bulky cation (Q⁺) was added, TBPE⁻H⁺ reacted with Q⁺ to form an ion associate (Q⁺·TBPE⁻), and the colour changed from yellow to blue. This colour reaction was used for the detection of the end-point. Direct and indirect titration methods for the determination of cationic surfactants were examined. Dodecylbenzene sulphonate ion (DBS⁻) was used as a titrant for cationic surfactants in the direct titration. The colour changed from blue to yellow at pH=3.6, and the absorbance changes were monitored with an optical fibre sensor with a 630 nm interference filter. Benzyldimethyltetradecylammonium (zephiramine) ion was found to be the preferred titrant in the indirect titration. The titrant was added to a solution of cationic surfactant containing a known excess amount of anionic surfactant DBS⁻ at pH=3.6. Cationic surfactants at concentrations from $5 \cdot 10^{-6}$ to 10^{-3} M could be determined (*4*).

The same group devised a simple and rapid automatic photometric titration method for the determination of anionic surfactants in a one-phase aqueous system with the same indicator TBPE. The titrant, distearyldimethylammonium ion, was added to an anionic surfactant solution at pH=3.2, and the absorbance changes (from yellow to blue) were monitored by a fiber-optic sensor with a 630 nm interference filter. The end-points were read from the inflection points with differential curves. Anionic surfactants at concentrations from 10^{-6} to 10^{-3} M could be determined by the proposed method. The relative standard deviations of various anionic surfactants were between 0.3 and 0.4 %. The proposed method was applied to some practical samples, and the results, except for those of anionic surfactants possessing polyoxyethylene groups, were in good agreement with the results of the JIS titration method (Epton method) and a solvent extraction method with ethyl violet (*5*).

Two different fiber optic sensors were developed for the determination of hydrogen sulphide at ppb concentration levels using some surfactants in the substrate. A probe-type fiber optic sensor coated with polyethylene oxide containing 0.5 M CdCl₂ and a fiber optic sensor utilising 0.5 M CdCl₂-pretreated filter paper as solid substrate were constructed. In the first type, CdCl₂-polyethylene oxide (PEO) mixture was coated onto the tip of a fiber optic probe and the probe was exposed to H₂S. The methodology is based on the measurement of CdS fluorescence on the surface. Detection limit (3 σ) of the PEO-coated fiber optic system was 36.0 ppb for H₂S and the precision at 0.552 ppm level was 29 % relative standard deviation (RSD). For the fiber optic system utilising CdCl₂-pretreated filter paper, two different configurations were devised and evaluated, a bifurcated fiber optic sensor and a single fiber optic sensor. Similar figures were obtained with these two systems; the detection limit (3 σ) was 4.0 ppb for the bifurcated fiber optic

sensor and 4.3 ppb for the single fiber optic sensor, and both sensors had linear responses in the range of 0.032–1.0 ppm. Their precisions at 0.299 ppm level were also very similar, 10 and 11 % RSD, respectively, for the bifurcated and single fiber systems. In addition to the fiber optic sensors developed, various surfactants (sodium dodecyl sulphate, Aerosol OT, Aerosol A102, Aerosol 501), some cellulosic substances (sodium carboxymethylcellulose, ethylcellulose, hydroxypropylmethylcellulose, ethylhydroxyethylcellulose, α-cellulose) and several water--soluble polymers (polyacrylic acid, polyethylene oxide (PEO) and polyvinyl alcohol (PVA)) were dissolved in proper solvents and after mixing with 0.5 M CdCl₂ were spread over glass slides. These novel solid substrates were exposed to H₂S and fluorescence signal on the surfaces of the glass slides was measured with a luminescence spectrometer (*6*).

The effect of non-ionic surfactants Triton X-100 and Brij 35 on the response of calcium, potassium and sodium optical sensors was studied. The addition of surfactants increases the optical response. The polymeric films doped only with chromofores were found useful for determination of non-ionic surfactants (*7*).

A simple U-shape optical fiber probe for determination of critical micelle concentration, using evanescent adsorption effect, has been described. Finding of critical micelle concentration point was also possible (*8*).

An optical chemical sensor has been developed for the determination of Tween 60 in aqueous solution based on the fluorescence enhancement of tetraphenylporphyrin (H₂TPP) immobilized in a plasticised polyvinyl chloride (PVC) membrane. The fluorescence enhancement of sensing membrane results from an associated complex formation between H₂TPP and Tween 60. With the optimum condition described, from 8 to 100 µg/mL Tween 60 in the sample solution can be determined. The response time of the sensor is within 1.0 min. In addition to the high reproducibility and reversibility of the fluorescence signal, the sensor also exhibits good selectivity over other common surfactants except for Tween 80 (*9*).

A β-cyclodextrin derivative (CD-NA) bearing 7 negatively charged naphthoate chromophores is shown to strongly interact with cationic surfactants. In the absence of a surfactant, the CD-NA emission spectrum is composed of two bands; one is assigned to the normal fluorescence and the other to the fluorescence of intramolecular excimers. Interaction with a cationic surfactant leads to a drop in excimer emission. CD-NA can be used to detect cetyltrimethylammonium chloride (cetyl=hexadecyl) and cetylpyridinium chloride in an aqueous solution at concentrations as low as a few µM and up to about 50 µM. The interaction between CD-NA and cationic surfactants can be interpreted by a micellisation process induced by CD-NA rather than by the formation of 1:1 inclusion complexes (*10*).

A novel and simple kind of optode for monitoring anionic surfactants was developed by using 1,2-benzo--7-(diethylamino)-3-(octadecanoylimino)-phenoxazine (ETH 5294) immobilized in a thin plasticised PVC membrane. The response to anionic surfactants was the result of an ion-pair coextraction of the surfactant anion and a proton. On exposure to anionic surfactants, the red ETH 5294, in its neutral form, was converted to a blue ETH 5294 in its protonated form, inducing an absorbance spec-

tral change of the membrane. When the fixed exposure time (4 min) and non-stirring detection modes are used in a buffer solution of pH=7.5, absorbance or absorbance ratio (at 535 and 660 nm) of a membrane of 4 µm thickness changes, depending on the anionic surfactant concentration, exemplified by sodium dodecyl sulphate and sodium dodecylbenzene sulphonate. The linear ranges of the method were between $5 \cdot 10^{-5}$ and 10^{-2} M and $2 \cdot 10^{-5}$ to 10^{-3} M, respectively. The sensing membrane showed a good selectivity over cationic surfactants and some common anions including acetate, iodide and nitrate (*11*).

The photophysical properties of 11-(4-N,N-dimethyl-aminophthalimido)-undecanoic acid (DAPL), a surfactant covalently labelled with a fluorophore, in homogeneous and micellar media have been reported. The remarkable sensitivity of the fluorescence properties of DAPL to the polarity of the media is attributed to the existence of a low-lying non-fluorescent twisted intramolecular charge transfer state. DAPL was found to be an excellent fluorescence sensor for following the micellar aggregation process. Although DAPL shows enhanced binding with the micelles, the quenching experiments and the fluorescence spectral and intensity data clearly indicate that the fluorescing moiety does not penetrate into the non-polar core region of the micelles even though the fluorophore is covalently attached to the non-polar end group of the fatty acid. It is unambiguously established from the fluorescence data that both of the terminal groups of DAPL are located in the interfacial region of the micelles by folding of the long polymethylene chain (*12*).

Electric Surfactant Sensors

Piezoelectric surfactant sensors

Determination of surfactant adsorbed on a quartz surface by an electrode-separated piezoelectric sensor and *in situ* method to determine the adsorption density of cetylpyridinium bromide on a quartz surface is proposed by use of an electrode-separated piezoelectric sensor. The correlation between the frequency shift and the mass load on the quartz surface was investigated. The dependence of the adsorption density and adsorption rate on pH and ionic strength have been reported (*13*).

The partition coefficients of 1-alkanols (1-butanol to 1-heptanol) between ionic micelles and water, expressed in the mol ratio scale (K-N) and in the mol fraction scale (K-X), were measured at 25 °C by using polymer-coated piezoelectric gas sensors. While K-N is constant over the concentration range measured, K-X decreases with increasing mol fraction of the 1-alkanols in micelles. It is demonstrated that K-N is equal to the value of K-X at infinite dilution. The dependence of the partition coefficient on the chain length of the cationic surfactants is explained in terms of the micellar electrostatic potential change on solubilisation (*14*).

The adsorption of two non-ionic surfactants on hydrophobic gold and hydrophilic chromium oxide surfaces from aqueous solution has been investigated using a quartz crystal microbalance (QCM) and surface plasmon resonance (SPR). Adsorption isotherms for a nonyl phenol ethoxylate with average ethylene oxide chain length of 9 (N9) on gold and for octaethylene glycol monododecyl ether (GMDE) on both gold and chromi-

um oxide surfaces have been measured by QCM. Isotherms for N9 and GMDE on the gold surface can be described by Langmuir adsorption, while that of GMDE on the chromium oxide surface was S-type. Complementary SPR experiments of GMDE adsorption onto gold suggest that the resonance frequency change of the QCM crystal in solution with adsorbed GMDE (at saturation coverage) is 80 % greater than that predicted by the Sauerbrey equation for air measurements. This implies a 2.08 Hz/ng change for the QCM in contact with aqueous solution. This calibration factor was used to calculate the saturated surface coverage for the surfactants (and hence area per surfactant) at the solid/liquid interface. These data are in good agreement with those reported in the literature for N9 and GMDE adsorbed onto various hydrophobic and hydrophilic surfaces (*15*).

A method for probing the interaction process between ionic surfactant and protein was developed with a series piezoelectric quartz crystal (SPQC) sensing technique. It was based on the sensitive response of the SPQC sensor to the change in solution conductivity. The method was used to examine the interaction process of two surfactants, cetyltrimethylammonium bromide and sodium dodecyl sulphate, with lysozyme in aqueous solution. The obtained experimental results were in agreement with those of other reference methods. It was shown that the new method developed here was a useful and promising tool for probing the ionic surfactant-protein interaction process and might find more applications in similar studies (*16*).

The measurement of the kinetics of adsorption of sodium dodecyl sulphate (SDS), an anionic surfactant, onto a quartz surface with a pre-adsorbed layer of Ca^{2+} as an ion bridge, using an electrode-separated piezoelectric sensor (ESPS) is reported. An impedance analysis method was employed to characterise the responses of the ESPS. The impedance and frequency parameters of the ESPS were examined as functions of the conductivity, permittivity, viscosity and density of the liquid. The adsorption process of SDS onto the quartz surface resulted in an increase in both mass and energy dissipation of the oscillating quartz crystal. The adsorption densities could be estimated by the ESPS method after taking into consideration the effects of surface viscosity and roughness. The adsorption and desorption rate constants of SDS onto the quartz surface were calculated as k_a=(88.1±0.26) M/s and k_d=(4.92±0.53)·10^{-3} s^{-1}, respectively, based on the Langmuirs model. ESPS was shown to be a powerful means of examining anionic surfactant adsorption to the solid/liquid interface (*17*).

The same group used ESPS and the same principle on the quartz crystal surface in a direct contact with the liquid phase. With the pre-adsorption of Ca^{2+} as the ionic bridge, anionic surfactant can adsorb on the negatively charged quartz surface (pH>2.0). The adsorption process of sodium dodecylbenzene sulphonate (SDBS) was monitored in real time with the ESPS method. It was shown that the adsorption of SDBS on quartz surface by Ca^{2+} inducement was reversible with respect to the dilution of solution phase. The adsorption and desorption rate constants were estimated to be k_a=(108.4 ±6.4) M/s and k_d=(2.57±0.32)·10^{-3} s^{-1}, respectively. The observed adsorption densities in the ESPS method were significantly greater than the true ones. The influence of

surface roughness of the quartz disc on adsorption densities should be corrected by adding a calibration coefficient in the Sauerbrey equation. The saturation adsorption density is 0.223 μg/cm^2 for SDBS on quartz surface. Double layer occurs for the adsorption of SDBS on quartz surface (*18*).

A piezoelectric quartz crystal (PQC) sensor to investigate the non-specific adsorption of fibrinogen (FN) and sodium dodecyl sulphate (SDS) onto a self-assembled monolayer (SAM) of alkane thiols on gold was described. The change in adsorption mass was monitored *in situ* by the PQC sensor. A kinetics model was proposed to describe the adsorption of the FN and SDS on the hydrophobic SAM surface. The adsorption kinetic parameters were determined from the responses of the PQC. The adsorption and desorption rate constants of the FN on the SAM surface were estimated to be $(6.18\pm0.53)\cdot10^3$ M/s and $(6.74\pm0.72)\cdot10^{-3}$ s^{-1}, respectively. The rate constants for the adsorption and desorption of SDS on the SAM are (24.3 ± 1.4) M/s and $(1.52\pm0.11)\cdot10^{-2}$ s^{-1}, respectively. The adsorption of SDS on the SAM was reversible. The fractional coverage of the FN on the SAM surface was estimated from kinetic analysis to be 42–86 % for the FN concentration range of 25–400 μg/mL. Over 80 % of the FN is irreversibly adsorbed on the SAM surface with respect to dilution of the bulk phase. The fraction of reversibly adsorbed FN increases with the bulk concentration of FN (*19*).

The oscillation frequency equation for an electrode-separated piezoelectric sensor (ESPS) in a liquid phase was derived theoretically and verified experimentally. The dependences of the frequency shifts on conductivity, permittivity, density and viscosity of the liquid were investigated. The ESPS was applied to determine *in situ* the adsorption amount of hexadecyl trimethylammonium bromide on a quartz surface (*20*).

Simple methods of preparing the direct affinity sensors are proposed. Due to the self-consistent introduction of a hydrocarbon chain bound with oligonucleotide pentadecathymidylate into the hydrophobic region of surfactant bilayer or the adsorption of antibodies on the bilayer surface, the immobilizations of oligonucleotide or antibodies were carried out correspondingly. The responses were detected by impedance spectroscopy. Whereas the specific DNA-coupling caused the decrease of real part of impedance, the antibody-antigen interaction caused the increase of the real part. The obtained results give an opportunity for the development of impedimetric affinity sensors for clinical analysis or for the detection of various environmental pollutants (*21*).

In a separated-electrode piezoelectric sensor (SEPS), the two excitation electrodes were separated by solution layers. The oscillation ability of the SEPS depends obviously on the separation-distance between the two excitation electrodes. In a given solution, there is a maximum separation-distance (D_{max}) for the SEPS. If the separation-distance is >D_{max}, operation of the SEPS is not stable or even ceases to oscillate. The dependence of D_{max} value on conductivity of solution was investigated and explained. The SEPS was applied for the determination of the adsorption density of dicetyldimethylammonium bromide onto quartz surface (*22*).

The aim of this study was to determine the influence of surfactant on the particle-bubble interaction.

Therefore, an experimental set-up with which the interaction between colloidal particles and air bubbles in aqueous medium can be directly measured was constructed. The particles were attached to atomic force microscope cantilevers that served as force sensors. The separation between particle and bubble was adjusted with a calibrated piezotranslator. Force and distance resolution were 0.1 nN and 1 nm at full dynamic ranges of roughly 1 μN and 15 μm, respectively. With this set-up, the force between hydrophilic and hydrophobised silica particles (5 μm diameter) and an air bubble was measured. For both cases, the influence of dodecyltrimethylammonium bromide (DTAB) and sodium dodecyl sulphate (SDS) was determined. These surfactants were chosen because of their different electric charge and adsorption behaviour. DTAB is positively charged and adsorbs strongly to silica. SDS is negative and shows only negligible adsorption to silica. The measured forces could be interpreted in terms of the electrostatic double-layer force, the van der Waals repulsion, the hydration repulsion, a hydrophobic attraction, and the contact angle (*23*).

Capacitive surfactant sensor

Capacitive sensing devices are reported only very few. One attempt was reported where a capacitive sensing device was designed by using electropolymerised *o*-phenylenediamine (PPD) film as an isolating layer and was applied successfully to study the adsorption of Tween 80 onto the PPD film surface. The PPD was prepared with a cyclic voltammetry and the thickness of the PPD film was estimated as about (110$\pm$10) nm. The properties of the PPD insulating film were characterised with an electrochemical impedance method. The results show that the equivalent circuit model of this device is Randles type. The adsorption process of Tween 80 onto the PPD film was detected with the electrochemical impedance method. The result implies that the adsorption model of Tween 80 onto the PPD film appeared as pseudo Langmuir type and the adsorption equilibrium constant was 213.87 dm^3/g. The authors expect that the capacitive sensor will be a useful tool for the investigation of interface action (*24*).

Surfactant Interactions for Possible Sensor Use

In this chapter the papers investigating some interesting interactions for possible sensor applications are reported, together with some »true« biosensors.

A whole cell biosensor was constructed for the detection of anionic surfactants in aquatic environments. The analysis was rapid, convenient and did not require organic reagents. In this report, the application of sensor to river water samples was investigated when applied to environmental samples. Other organic substances present in river water may affect the measurement of linear alkylbenzene sulphonates. In order to deal with this problem, a correction system was developed using whole cells of *Trichosporon cutaneum*. This system was applied to 24-h continuous *in situ* monitoring in the Saka river (*25*).

Several strains belonging to genera Pseudomonas and Achromobacter, and characterised by the ability to degrade anionic surfactants were tested as potential bases of microbial biosensors for surfactant detection. The total amount of the substrates tested (including carbohy-

drates, alcohols, aromatics, organic acids, *etc.*) was equal to 60. The maximal signals were observed towards the anionic surfactants. Lower limit of detection for sodium dodecyl sulphate used as a model surfactant was in the field of 1 µM for all the strains. The created microbial biosensor model can extend the practical possibilities for rapid evaluation of surfactants in water media (*26*).

A novel whole cell biosensor was constructed for detection of anionic surfactants in an aquatic environment. The sensor response to linear alkyl benzene sulphonates was linear up to 6 mg/L, which is a range suitable for the detection of anionic surfactant concentration in polluted river water. Under optimum conditions, the sensor response time was less than 15 min. Anionic surfactant analysis was rapid and convenient and did not require organic reagents that are harmful to environment (*27*).

Associates of dodecyl sulphate with copper complexes of alkyl derivatives of diamines were investigated. Homologous series of ethylenediamine and 1,4-diaminobutane derivatives that contain from 1 to 4 hydrocarbon radicals at nitrogen atoms were synthesized. A photometric study of their complexes with copper(II) and of ion associates of the complexes with the anionic surfactant dodecyl sulphate was performed. The ion associates were isolated and introduced into the composition of ion-selective wire electrodes. In a series of diamines examined, the associate based on dialkylethylenediamine had the best properties as an electrode-active substance. The prepared electrodes measured the concentrations of sodium dodecyl sulphate in water in the analytical range from 10^{-6} to $8 \cdot 10^{-3}$ M (critical micelle concentration) and had highly stable characteristics and a long life time (7 to 8 months) (*28*).

Kinetics of polymer surfactant interactions and the effect of surfactant binding on the conformational dynamics of the polymer were explored in this work using surface plasmon resonance spectroscopy. Polyacrylic acid was modified with thiol to varying degrees so as to force the polymer to form different loop sizes upon adsorption on the gold SPR sensor surface. Dodecyltrimethylammonium chloride in solution was flown over the polymer-coated sensor surface and the binding followed in real time. It was found that the control of the loop size of the polymer on the solid surface enabled in turn the control of surfactant binding, with the largest loop allowing the maximum amount of surfactant to bind and *vice versa*. Studies using unmodified polymers suggested the possibility of sudden conformational rearrangement in the polymer network, with progress in surfactant binding. Furthermore, the reflectance of the SPR spectrum was found to increase upon surfactant binding, implying that there is a decreased efficiency of coupling of the incident radiation into the surface plasmon mode of the metal, which suggests that the surfactant actually penetrated the polymer matrix (*29*).

A PEG-containing surface coating was investigated as a means of controlling neurite outgrowth in the presence of serum. Various ratios of end-group-activated triblock copolymer Pluronic F108 were used to immobilise the extracellular matrix protein fibronectin (FN). Primary cultures of dorsal root ganglion neurons were cultured on F108-immobilised FN or, as a control, on FN adsorbed from solution directly to polystyrene. Polypropylene filament bundles treated with F108-immobilised FN supported robust outgrowth from explants of dorsal root ganglia, demonstrating the utility of the surface coating on clinically relevant materials with more complex shapes. The ability to control neuronal behaviours in a serum-resistant manner, coupled with enhanced biologic activity, demonstrates the potential for surfactant-based immobilization as a method for generating biointeractive materials for tissue engineering (*30*).

Organically and bioorganically doped sol-gel materials have attracted much attention due to their ability to reproduce solution molecular activities within the ceramic environment. This methodology was taken one step forward and conditions under which the dopant properties can be modified by the matrix were explored. Specifically, it was reported that the co-entrapment of the surfactant cetyltrimethylammonium bromide (CTAB, the modifier) at low concentrations, with an extensive series of pH indicators representing several key molecular families (the primary dopant) within tetramethoxysilane (TMOS)-derived silica sol-gel matrices, greatly modifies the indicating performance of the primary dopant. Thus, very large pK_i shifts of up to 3–4 orders of magnitude obtained upon the co-entrapment cause methyl orange (MO) to become an indicator for higher acidities and phenolphthalein for higher basicities, compared to their solution behaviour. In another example, the ΔpK_i between the two indicating transitions of alizarin increased from similar to 4.5 pK units in solution to similar to 10.5 pH units in the glass, transforming it into an indicator for both the high acidic and high basic pH ranges. In yet another example, the two indicating transitions of phenol red were shifted to a more acidic pH range, pushing the tail of the more acidic titration branch into the range of negative pH values. The indicators also proved highly sensitive in revealing the properties of the local environment created by the surfactant. The concentration- and humidity-dependent surfactant aggregation processes within the silica cage were probed with MO, and the results were compared with the behaviour of entrapped MO in sol-gel matrices of varying hydrophobicities, obtained by the copolymerisation of $CH_3Si(OCH_3)_3$ with TMOS at various ratios, with and without CTAB. It was shown that CTAB can be used to stabilize the microscopic structure of the material upon heat-drying. This provides a potential solution to the problem of continuing structural changes, which take place with sol-gel materials long after the completion of their synthesis (*31*).

Detection of cationic phenolic derivatives at a surfactant-doped screen-printed electrode for the indirect sensitive determination of alkaline phosphatase (AP) was presented. The enzyme-label alkaline phosphatase commonly used in immunoassay was recently detected at subfemtomolar concentration with a screen-printed electrode (SPE) coated with a Nafion film (*32*) through the catalytic transformation of an anionic substrate (aromatic monoester phosphate) to a cationic electroactive product (phenol substituted by a cationic function). In order to improve the technique, a new cation-exchanger-doped SPE was developed and its analytical performances were evaluated with several cationic phenolic products. The doped SPEs were prepared from a carbon ink loaded with the sodium salt of dodecylbenzene sulphonic acid. The anionic surfactant was strongly retained within the dry ink and it allowed the accumulation of nanomolar concentrations of cationic phenol derivatives to occur

through an ion-exchange process at the electrode surface. The accumulated phenol compounds were detected by the voltametric oxidation of their phenolic function. Preliminary results obtained with AP (detection limit of ca. 10^{-14} M) appear promising for enzyme immunoassays (*33*).

A thin uniform transparent film composed of the non--ionic surfactant Triton X-100 and of polyvinyl methyl ether with relative molecular mass of 30 000 has been deposited on a glass slide by dip-coating in a solution of reversed micelles in cyclohexane containing titanium(IV) tetraisopropoxide. Partial hydrolysis of the alkoxide assists in the attachment on the glass surface. Pyrene introduced in the film by original solubilisation in cyclohexane forms diffusion-controlled excimers which can be switched on and off by changing the temperature (*34*).

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Tenzidni senzori u biotehnologiji
2. Neelektrokemijski senzori

Sažetak

U radu je obuhvaćen pregled literaturnih radova o neelektrokemijskim tenzidnim senzorima od 1993. godine do danas. U 1. dijelu prikazana je važnost tenzida u suvremenoj biotehnologiji te dan pregled najvažnijih elektrokemijskih tenzidnih senzora. U ovom je dijelu prikazan pregled neelektrokemijskih tenzidnih senzora, u prvom redu optičkih i piezoelektričnih. Također su navedene neke zanimljive interakcije tenzida koje bi mogle biti korisne za razvoj tenzidnih senzora.