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review

Surfactant Sensors in Biotechnology
Part 1 – Electrochemical Sensors

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Summary

An overview on electrochemical surfactant sensors is given with special attention to papers published since 1993. The importance of surfactants in modern biotechnology is stressed out. Electrochemical sensors are usually divided according to the measured physical quantity to potentiometric, amperometric, conductometric and impedimetric surfactant sensors. The last ones are very few. Potentiometric surfactant sensors are the most numerous due to their simplicity and versatility. They can be used either as end-point titration sensors or as direct E_{MF} measurement sensors, in batch or flow-through mode. Some amperometric surfactant sensors are true biosensors that use microorganisms or living cells.

Key words: surfactants, sensors, electrochemical, potentiometric, conductometric, ISFET sensors, amperometric, biotechnology

Introduction

Surfactants have long been among the most versatile of process chemicals in industrial biotechnology. Biosurfactants are the most promising compounds in this regard. A review on the synthesis of biosurfactants was given (*1–3*) and a review on natural surfactants with emphasis on the work published since 1998 has been reported (*4*).

Biosurfactants, biotransformation, biodegradation and bioavailability are the keywords of modern biotechnology (*5,6*). The most important uses of surfactants are given in continuation.

Surfactants are frequently used in a variety of textile technology and biotechnology. The use of enzymes in detergents (primarily protease and amylase) needs biotechnological skills to solve problems like enzyme production and isolation, enzyme storage stability and preserving the activity, thermostability, pH stability *etc.* (*7*).

The application of surfactants in the development of new materials is also important. Protectively and functionally coated magnetic nanoparticles are of special interest due to their important technological application in diverse fields ranging from biotechnology to transportation (*8*). It has been found that surfactants stabilize the new materials such as metal nanoclusters (*9*). A new technology for enzyme encapsulation in small multilamelar vesicles of surfactant, called spherulites, is also reported (*10*). Colloidal gas aphrons are microbubbles encapsulated by surfactant multilayers. A range of exciting biotechnological applications has been identified, including the recovery of cells, proteins and other biological

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molecules, and the enhancement of gas transfer in bioreactors and bioremediation (*11*). In the last years a number of advances have been made in the understanding of high-pressure phase behaviour of lipid and surfactant systems in particular phospholipid bilayers, which can serve as model biomembrane systems (*12*). Surfactant membranes have been used in textile and food industries, hydrometallurgy, medicine, biotechnology and environmental protection in the separation of hydrocarbons and gases, and in the concentration and separation of amino acids, metal ions and other mixtures and suspensions (*13*). The latest research provides basic knowledge about some properties of systems that contain sugar surfactants, especially with respect to the properties of microemulsions (*14*).

Some specific surfactant properties have also been investigated. Low concentration of non-ionic surfactants and organic solvents can increase the activity of some enzymes such as cholesterol oxidase. The effect of non-ionic surfactants Thesit and Triton X-100, and of propan-2-ol (used as a substrate solubiliser) on the activity of the cholesterol oxidases from *Streptomyces hygroscopicus* (SCO) and *Brevibacterium sterolicum* (BCO) was studied. Low concentrations of Thesit lead to an increase of the activity with both enzymes; at higher surfactant concentrations the opposite effect occurred. Triton X-100 inactivates both enzymes at all concentrations. It is deduced that these surfactants exert their effects by interaction with the enzymes and not by affecting micellar phenomena. Other organic solvents induce results similar to those obtained with SCO and propan-2-ol. A significant difference between the two cholesterol oxidases emerges when stability is tested at 25 °C and in the presence of different concentrations of propan-2-ol: BCO activity is rapidly inactivated, whereas SCO still has 70 % of the initial activity after 5 h in the presence of 30 % propan-2-ol. From the obtained results, SCO seems to be the catalyst of choice in comparison with BCO for the exploitation of cholesterol oxidases in biotechnology and applied biochemistry (*15*). Surfactant activity of the strain itself is also an important biotechnological property (*16*). DNA from salmon testes, two hydrolysing enzyme proteases and α-amylase were successfully extracted by reversed micelles that are formed by a cationic surfactant in isooctane and other organic solvents (*17,18*). Irreversible protein aggregation is affected by surfactants (*19*) and unusual thermoprecipitation behaviour of some soluble polymers in the presence of some surfactants was found (*20*), challenging some of the earlier assumptions concerning the effects of low surfactant concentration.

Succinic acid, derived from fermentation of agricultural carbohydrates, has a special market in industries producing food and pharmaceutical products, surfactants and detergents, green solvents, biodegradable plastics, and ingredients to stimulate animal and plant growth. New developments in end-product recovery biotechnology, including water-splitting electrodialysis and liquid/liquid extraction, have lowered the cost of succinic acid production (*21*).

The importance of surfactant sensors is evident in environmental control of surfactant waste water (*22–25*).

Medical and healthcare application of biosurfactants is also an important issue. Antiviral activity of surfactin, a cyclic lipopeptide antibiotic and biosurfactant, was discovered (*26*). Cationic surfactants are promising in medicine and biology (*27*). Self-perceived sensory responses to soap and synthetic detergent bars correlate with clinical signs of irritation. Epidemiological studies indicate that after using soaps and other personal care products, many consumers experience irritation. In 50 % of the cases the feelings of skin dryness, itching, and stinging occur in the absence of visible signs of irritation. The relation between self-perceived sensory responses of panellists to cleansing products and clinical signs of irritation has been determined. Sensory evaluations of irritation yield additional information on soap and detergent irritancy beyond clinical observations and expand understanding of the irritation process (*28*).

Due to all these, the importance of surfactants in biotechnology is obvious. In this review a most frequently used, simple and inexpensive electrochemical surfactant sensors are given, with special attention to the papers published since 1993. An earlier overview of electrochemical techniques, namely potentiometry, amperometry, tensammetry, electrocapillary measurements and biosensors applied for the determination of surfactants was given in 1996 (*29*). The electrochemical surfactant sensors are usually divided according to the measured physical quantity in potentiometric, amperometric, conductometric and impedimetric ones.

Electrochemical Surfactant Sensors

Potentiometric surfactant sensors

Potentiometric surfactant sensors are used mainly as titration end-point sensors, although some direct potentiometric sensors have also been reported. The most popular sensors in this group are the coated wire-type, liquid membrane and ISFET (ion-selective field effect transistor) sensors. The sensors are suitable for determination of ionic (cationic and anionic), as well as non-ionic surfactants. They can be used discontinuously in batch mode or continuously in flow injection analysis (FIA) mode. Although the aim of this overview was to focus on papers published since 1993, some important earlier papers are also mentioned.

The first papers on surfactant-sensitive electrodes appeared in the early 1970s. Gavach *et al.* (*30,31*) were probably the first to apply liquid membrane-based ion-selective electrodes (ISE) for titration of long chain alkyl methyl ammonium salts with sodium tetraphenyl borate. Birch *et al.* (*32–34*) were also among the first researchers to use liquid ion-exchange electrodes responsive to ionic surfactants. Fogg *et al.* (*35*) used silicone rubber surfactant electrode. Cotrell used a coated wire polyvinyl chloride (PVC) electrode for determination of low concentration of surfactants (*36*). An extensive article on potentiometric titration based on ion pair formation was published by Vytras (*37*). The same author published an excellent overview on coated wire electrodes in the analysis of surfactants (*38*), and his research group was very active in the field especially during the 1980s and dealt a lot with surfactant electrodes using cetylammonium and cetylpyridinium bromide as surfactant-sensitive materials (*39–44*). In 1997 the Vytras' group demonstrated that carbon paste-based electrodes can also be used as potentiometric sensors to monitor the surfactant titrations, with the main advantage of these electrodes being their suitability for titrations in very low Ohmic resistance systems (*45*). A lot of information on surfactant sensors can also be found in the book »Analysis of Surfactants« (*46*).

Coated wire and liquid membrane surfactant sensors

The distinction between coated wire and liquid membrane surfactant sensors is fuzzy. Both types operate with ISE membranes. Liquid membrane can be a misleading term because these membranes are usually »solid«, mainly for practical reasons. However, the mobile »sites« are complexing agents that are dissolved in a suitable solvent and usually trapped in a matrix gel.

The determination of the concentration of anionic and cationic surfactants by titration with an ion-selective electrode as end-point titration sensor has been described. It is shown that the same electrode can be used for non-ionic surfactants and surfactant mixtures. Before titrating the non-ionic surfactant with sodium tetraphenyl borate an activation with barium chloride must be carried out. Surfactants with more than 10 ethylene oxide groups give well reproducible results. The concentrations of mixtures of anionic and non-ionic surfactants can be determined as exactly and simply as the pure surfactant (*47*).

A planar all-solid-state electrode for the titrimetric analysis of ionic surfactants has been developed and characterised. The electrode is fabricated by lamination of suitable electrode structures that are sandwiched between flexible plastic foils. The zeolite-polymer membrane containing zeolite mass fraction of 50 % of the faujasite type is cast onto an exposed gold film surface to form the surfactant-sensitive electrode. The very fast potentiometric response of the sensor can be exploited for potentiometric titration of surfactants. The electrode assembly exhibits shelf lives longer than 3 months under room temperature and dry conditions. The practical utility of the disposable all-solid-state electrodes is demonstrated in terms of titrimetric determinations of anionic surfactants in commercial detergents (*48*).

The potentiometric behaviour of coated wire electrodes based on dodecylbenzene sulphonate-doped polypyrrole (PPy-DBS) and Hyamine as ion exchanger was investigated. Two types of coated wire electrodes made of PVC-PPy-DBS and PVC-Hyamine-DBS, elasticised with *o*-nitrophenyl octyl ether showed the Nernstian behaviour (with respective calibration slopes of about 58 and 60 mV per decade) over the DBS^- concentration range of $3.0\cdot10^{-6}$ to $1.1\cdot10^{-3}$ M and $5.0\cdot10^{-6}$ to $1.3\cdot10^{-3}$ M, respectively. The potentiometric response was independent from the pH of the test solution in the pH range of 3–10. The response time of electrodes was fast (10 s for both types of electrode), and the electrodes can be used for at least 3 months without any significant changes in the potential. The potentiometric selectivity coefficients for the PPy-DBS based electrode revealed a significant improvement as compared to the electrode made by conventional Hyamine-DBS anion-exchanger. The proposed electrode was used for the determination of DBS^- ion in some commercial detergents. The results of the potentiometric determinations were in satisfactory agreement with those obtained by a standard method (two-phase titration) (*49*).

Two surfactant sensors, based on ion-pair 1:1 water-insoluble salts, have also been prepared using Hyamine 1622 or tetradodecylammonium as cationic and dodecylbenzene sulphonate as anionic surfactant. Sensing materials were incorporated in a PVC matrix containing *o*-nitrophenyl octyl ether as a solvent mediator and applied on a support of conductive resin without inner reference solution. The responses of these electrodes to sodium dodecyl sulphate (lauryl sulphate) and sodium dodecylbenzene sulphonate as well as the interferences of several common inorganic anions and anionic surfactants have been examined. The main parameters of the evaluation of these electrodes and response times are presented and its behaviour is discussed. These membranes show good performance for use as a general potentiometric sensor responsive to anionic surfactants (*50*).

Surfactants have been shown to inhibit the anaerobic digestion process severely, with the methanogenic microorganisms being the most affected. The diverse nature of surfactants used even in one (*e.g.* textile finishing) plant sometimes makes an on-line determination of surfactants very difficult and expensive. Therefore, a fast on-line determination of inhibitory effects on the acidogenic microorganisms (first step of the degradation cascade) can help to give an early warning signal or to calculate a »pseudo«-surfactant concentration. A titration technique was successfully employed to measure the surfactant inhibition in a laboratory-scale acidification reactor. Additional experiments demonstrate (using sodium dodecylsulphate as the model substance) how inhibitory effects (and strategies to overcome inhibitory effects) can be investigated efficiently (*51*).

Ion-selective electrodes of the coated-wire type were used in potentiometric titrations of polypropylene glycols, copolymers of ethylene oxide and propylene oxide and non-ionic surfactants based on oxyalkylated fatty alcohols and furfuryl alcohol. The titration with a standard solution of sodium tetraphenyl borate is based on precipitation of ternary compounds in the presence of bivalent metal ions, among which barium(II) salts are preferable. The signal stabilization time during titrations depends on the length of the polyoxypropylene chain. Moreover, the results indicate that an average of 6.2 oxypropylene units corresponds to one tetraphenyl borate ion, *i.e.* 12.4 units per each barium(II) ion. For the analysis of detergents or other samples of practical importance, the use of empirical titration equivalents is recommended (*52*).

A potentiometric titration method for the direct determination of anionic polyelectrolytes, using a plasticised PVC membrane electrode, is described. A cationic surfactant solution is used as titrant. The method is based on ion association between the anionic polyelectrolyte in the sample and the cationic surfactant in the titrant. The end-point is detected as a sharp potential change due to an increase in the concentration of the free cationic surfactant at the equivalence point. The sharpness of the titration curve at the end-point is compared for several cationic surfactants. A solution of octadecylammonium (stearyltrimethylammonium) ion has been found to be superior (*53*).

A plasticised PVC membrane electrode sensitive to dodecylbenzene sulphonate (DBS^-) ion is applied for the determination of anionic polyelectrolytes such as PVSK by potentiometric titration, using a Cat-floc solution as a titrant. The end-point of the titration is detected as the potential jump of the plasticised PVC membrane electrode caused by decrease in the concentration of DBS^- ions added to the sample solution as a marker ion, due to the ion association reaction between the DBS^- ion and polydiallyldimethylammonium chloride (Cat-floc). The effects of the concentration of DBS^- ions, coexisting surfactants and electrolytes in the sample solution and pH of the sample on the degree of the potential jump at the end-point were examined. A linear relationship between the concentration of anionic polyelectrolyte and the end-point volume of the titrant exists in the concentration range from $2\cdot10^{-5}$ to $4\cdot10^{-4}$ M for potassium polyvinyl sulphate (PVSK), alginate, and carrageenan. End-point detection of the potentiometric titration of anionic polyelectrolytes using an anionic surfactant-selective plasticised PVC membrane electrode and an anionic surfactant as a marker ion was successfully achieved (*54*).

Similarly, a plasticised PVC membrane electrode sensitive to octadecylammonium (stearyltrimethylammonium) ion is applied for the determination of cationic polyelectrolytes such as Cat-floc by potentiometric titration, using a PVSK solution as a titrant. A linear relationship between the concentration of cationic polyelectrolyte and the end-point volume of the titrant exists in the concentration range from $2\cdot10^{-5}$ to $4\cdot10^{-4}$ M for Cat-floc, glycol chitosan, and methylglycol chitosan (*55*).

Sensing material tetrahexadecylammonium dodecyl sulphate was synthesised and used for the construction of a coated wire-type surfactant sensitive electrode, using a PVC matrix and graphite-polytetraflouro-ethylene (PTFE) as the conducting substrate. The electrode was used for the potentiometric titration of mixtures of soaps with anionic surfactants. The standard solution of cationic surfactant, CTMAB, was used as the titrant. Individual soaps were titrated in alkaline solution (pH=10.5), while for the titration of their mixtures with anionic surfactants two titrations of equal volumes of analyte were needed. By titration in alkaline solution both anionic surfactant and soap were detected, whereas the titration in acidic solution (pH=2.5) detected only anionic surfactants with strongly acidic groups. From the difference in titrant volume used for the alkaline and the acidic medium, the soap content in the mixture can be calculated (*56*).

E_{MF} methods using a surfactant selective electrode have been used to investigate the binding of the cationic surfactant CTMAB with the polymers polypropylene oxide, polyvinylmethyl ether, and ethyl(hydroxyethyl) cellulose. The data show that significant binding takes place and critical concentrations associated with the onset of binding and the saturation of the polymers with bound surfactant have been determined (*57*).

A supported liquid and a PVC-based membrane selective for dodecyl sulphate (DS^-) ion is described. The active element is a membrane containing a dissolved ion association complex of DS^- with cetylpyridinium (CP^+) cation. The supported liquid membrane electrode (acetophenone as solvent) showed a Nernstian response towards the DS^- anion over the concentration range of sodium dodecyl sulphate (SDS) from $8.3\cdot10^{-3}$ to $1.0\cdot10^{-6}$ M at 25 °C. The proposed electrode also showed a supra-Nernstian potential response of (108±2) mV/decade at low concentrations from $1.0\cdot10^{-9}$ to $1.0\cdot10^{-6}$ M. Moreover, this electrode showed good selectivity and precision (RSD $\leq$ 2.0 %), and was usable within the pH range of 4.0–6.8. The proposed electrode revealed a lower limit of detection of $6.3\cdot10^{-7}$ M and improved selectivity in comparison with some previously reported DS^- ion selective electrodes. The liquid membrane electrode may find application in the direct determination of SDS by the standard addition method at pH=5.0, and in the physicochemical studies of surfactant solutions (*58*).

A new sensor for anionic surfactants with a membrane consisting of mass fraction of 33 % PVC, 66 % dioctylphthalate (DOP) plasticiser, and 1 % tridodecylmethylammonium chloride (TDMAC) is developed and used for flow injection analysis. The sensor displays a working response range from $5\cdot10^{-7}$ to $5\cdot10^{-3}$ M dodecylbenzene sulphonate (DBS) with a Nernstian slope of (58.5±0.2) mV/decade, a response time of 30 s and a detection limit of $1.5\cdot10^{-7}$ M DBS^- ions. Selectivity measurements with different anionic species indicate good membrane selectivity towards DBS^-. The sensor is used to measure anionic surfactants (DBS) in different wastewater samples, commercial detergent products, and for monitoring the rate of surfactant biodegradation in sewage treatment plants. The results obtained agree fairly well with the data obtained by the standard extraction-spectrophotometric method. The proposed potentiometric method offers the advantages of simplicity, accuracy, automation feasibility, and applicability to turbid and coloured sample solutions (*59*).

Dodecyl sulphate-doped polypyrrole (PPy-DS) was prepared electrochemically by anodic polymerisation of pyrrole in the presence of dodecyl sulphate (DS^-) ions in aqueous solution and used as a DS^- sensor. The electrode made with PVC-PPy-DS membrane, plasticised with 2-nitrophenyl octyl ether showed the Nernstian behaviour (57.5 mV/decade) from over 10^{-5} to $7\cdot10^{-3}$ M DS^- with a detection limit of $5\cdot10^{-6}$ M. The response time of the electrode is in the order of a few seconds and can be used for at least six months without any divergence. The electrode is highly selective to DS^- ions over diverse inorganic anions (*60*).

Selectivity of liquid membrane electrode based on mercurated polystyrene as ion-exchanger to anionic surfactants and soaps was investigated. An electrode that employs a solution of mercurated polystyrene in 1,1',2,2'-tetrachloroethane as the sensor in a liquid-state membrane has been developed. The electrode was tested toward some common anions, anionic surfactants, and soaps. This electrode displays an unusually high level of selectivity for anionic surfactants, in particular to bis(2-ethylhexyl)sodium sulphosuccinate, sodium dodecylbenzene sulphonate, and sodium dodecyl sulphate, over many common anions, such as NO_3^-, ClO_4^-, F^-, Cl^- and Br^-. The electrode may find application in the analysis of surfactants, as an indicator electrode in the potentiometric titration and in the physicochemical studies of surfactant solutions (*61*).

Lipophilic α-, β- and γ-cyclodextrins (CDs) have been systematically analysed in order to establish their selective binding to onium ions and some surfactants. A peroctylated cyclodextrin provides a size-selective cavity for the binding and detection of onium ions, as well as some surfactants. Potentiometric α-, β- and γ-cyclodextrin-based electrodes selectively sense NH_4^+, NMe_4^+ and NEt_4^+ ions and some surfactants (*62*).

Functionalised, lipophilic α-, β- and γ-cyclodextrins were synthesised and their suitability as onium ion-selective potentiometric sensors were investigated. The phenomenon of complexation was evidenced by ^1H and ^{14}N nuclear magnetic resonance relaxation-time measurements and by electrospray mass spectrometry. Nernstian responses were also evident for acetylcholine chloride, dopamine hydrochloride and the surfactant myristyltrimethylammonium bromide. The response of 'blank' membrane electrodes comprising PVC, solvent mediator, and additive was compared to the equivalent electrode response for membranes containing functionalised cyclodextrins. In each instance, the electrode response was substantially enhanced and stabilised by the presence of the lipophilic cyclodextrin. The effect of using either 1.0 mM NMe_4Cl or 0.01 M analyte as inner filling solution was compared, and, with 1.0 mM NH_4Cl, was found to enhance electrode performance (*63*).

The main electrochemical and performance characteristics of solid-contact sensors for cationic surfactants based on an organic hexadecylpyridiniumtetraphenyl borate (cetylpyridiniumtetraphenyl borate) ion exchanger were determined. It was found that the surface of the sensors for cationic surfactants can be modified with PVC molecular sieves. The modified electrodes can separately determine alkylpyridinium homologues with different lengths of hydrocarbon radicals (C_{10}–C_{18}) (*64*).

Potentiometric ion-selective electrodes (ISEs) sensitive to non-ionic surfactants of the polyethoxylate type were improved. The constructed ISEs were all-solid-state sensors with plasticised PVC membranes. The sensing material was a tetraphenyl borate salt of the barium complex with a polyethoxylate non-ionic surfactant. As membrane component, the complex ions of two polyethoxylates of the nonylphenoxy type, which differed in the number of oxyethylene units (5 or 12), were used. Two different plasticisers, *o*-nitrophenyl octyl ether and *o*-nitrophenyl phenyl ether, were tested. The response of these electrodes to different non-ionic surfactants and the interference effect of several species have been evaluated. For all types of the tested electrodes, the sensitivities shown were 30.0 mV/decade and the limit of detection was 10^{-5} M when a nonylphenoxyde with 12 oxyethylene units was used as standard (*65*).

Solid-contact potentiometric sensors based on ion pairs of hexadecylpyridinium (cetylpyridinium) with dodecyl sulphate and tetraphenyl borate for various surfactants were prepared. The main electroanalytical parameters of sensors were determined. Procedures for the potentiometric determination of non-ionic surfactants in wastewater, cationic surfactants in hair rinses, and separate determination of non-ionic and anionic surfactants in shampoos and synthetic detergents were developed (*66*).

An all-solid-state surfactant sensitive electrode has been prepared, based on a teflonised graphite conducting substrate coated with plasticised PVC membrane containing a new synthesised tetrahexadecylammonium-dodecyl sulphate as anionic surfactant sensing material. The electrode exhibited Nernstian response (58.1 mV/decade) for dodecylbenzene sulphonate and a near-Nernstian response (64.2 mV/decade) for dodecyl sulphate. The electrode was used as end-point indicator for potentiometric surfactant titrations. The selectivity coefficients related to the common inorganic and organic anions have been calculated by modelling of Nikolskii-Eisenman equation. Several commercial surfactants have also been titrated. The electrode enables the titration of shorter hydrocarbon chain anionic surfactants as well (*67*).

A novel hexadecylpyridinium chloride (cetylpyridinium chloride, CPC)-selective membrane sensor consisting of cetylpyridinium-ferric thiocyanate ion pairs dispersed in a PVC matrix placticised with dioctylphthalate is described. The electrode shows a stable, near-Nernstian response for 10^{-3} to 10^{-6} M CPC at 25 °C over the pH range of 1–6 with a cationic slope of (57.5±0.4) mV/decade. The lower detection limit is $8\cdot10^{-7}$ M and the response time is 30–60 s. Selectivity coefficients for CPC relative to a number of interfering substances were investigated. There is negligible interference from many cations, anions and pharmaceutical excipients; however, CTMAB interfered significantly. The determination of 0.5–350 μg/mL of CPC in aqueous solutions shows an average recovery of 98.5 % and a mean relative standard deviation of 1.6 % at 56.0 μg/mL. The direct determination of CPC in Ezafluor mouthwash gave results that compare favourably with those obtained by the British Pharmacopoeia method. Precipitation titrations involving CPC as titrant are monitored with a CP sensor. The CP electrode has been utilized as an end-point indicator electrode for the determination of anionic surfactants in some commercial detergents (*68*).

Three new kinds of ion-selective polymeric membranes (ISEs) sensitive to cationic surfactants were fabricated and characterised. These new sensors use benzyldimethylhexadecylammonium reineckate, dodecyl-trimethylammonium reineckate or hexadecylpyridinium phosphotungstate as exchangers, dispersed in a PVC matrix. ISEs display a linearity range for common cationic surfactants between about 10^{-6} and 10^{-4} M, satisfactory fast response (≤ 60 s) and moderately sub-Nernstian slope values (*69*).

A new, simple, sensitive, low cost and rapid potentiometric method for direct determination of ultra-trace amounts of sodium dodecyl sulphate (SDS) with a new DS^- selective electrode is reported. The electrode was prepared by electropolymerisation of aniline in acidified DS^- ions on the surface of a Pt electrode. The cyclic voltammetry (CV) was used for electropolymerisation of polyaniline (PA) in the potential range of –200 to 1000 mV *vs.* Ag/AgCl. This sensor showed a Nernstian behaviour of (59.0±2.3) mV/decade over a very wide linear range ($1.0\cdot10^{-9}$–$3.0\cdot10^{-6}$ M) with a detection limit of

$1.0\cdot10^{-9}$ M. The response time of the electrode was 15 s for $1.0\cdot10^{-7}$ M of analyte. The electrode can be used for 4 weeks without any major deviations in the pH range of 3.5–9.8. The selectivity of electrode to DS^{-} over some organic, inorganic and anionic surfactants was investigated with the fixed primary ion method. The results show that the electrode is highly selective to DS^{-} ions over other ions. The proposed electrode was applied to the determination of DS^{-} in real samples (*70*).

A novel method for the determination of non-ionic surfactants is described. The polyoxyethylene portion of non-ionic surfactants forms pseudo-crown compounds in the presence of barium ions. The Orion surfactant electrode is used as the end-point indicator in titrations of these compounds with sodium tetraphenylborate. Stoichiometric constants for the reaction of barium non-ionic complexes with sodium tetraphenylborate have been established. The results of titrations of several non-ionic surfactants indicate that an average of 5.16 oxyethylene units will form a complex with one tetraphenylborate ion. Empirical titration factors have also been established for several classes of non-ionic surfactants and used in the analysis for the non-ionic content of commercial detergent products. An average recovery of 96.4 % was obtained in the analysis of three standard detergent products. The described method has been used successfully in the routine determination of non-ionic surfactants (*71*).

Various polymer coatings have been investigated for the protection of mercury thin-film electrodes in the square wave anodic stripping voltammetry of environmental samples using batch injection analysis, with the injection of untreated 50-μL samples directly over the sensing electrode. Polymer coatings studied include those with controlled porosity, and cation-exchange polymers based on sulphonated polymers. Of the polymers tested, films of approximately 1 μm thickness made from Nafion mixed with 5 % polyvinyl sulphonic acid were found to give the best results in tests with the model surfactants Triton X-100, detergent, sodium dodecyl sulphate and protein standard. The validity of the approach is demonstrated by application to real samples (*72*).

Membranes constituted of polymers of differing intrinsic chemical compositions as well as PVC membranes variously modified with plasticising agents were assessed as potential blood contacting interfaces for the use of enzyme electrode. PVC membranes modified with the non-ionic surfactants Tween 80 or Triton X-100 and anionic bis(2-ethylhexyl)hydrogenphosphate exhibited superior biocompatibility over the commercially available porous polycarbonate and Cuprophan haemodialysis membranes. A cationic surfactant (tricaprylylmethylammonium chloride)-modified PVC membrane exhibited the worst biocompatibility (*73*).

The influence of non-ionic surfactants, *i.e.* Tween 20, Triton X-100 and PEG 10 000, on the response of cholinesterase-based potentiometric biosensors and their sensitivity towards reversible and irreversible inhibitors was investigated. Acetyl- and butyrylcholinesterases were immobilised on nylon, cellulose nitrate films and tracing paper and were introduced into an assembly of potentiometric biosensors. The effect of surface-active compounds depends on the hydrophilic properties and porosity of the enzyme support material and the inhibition mechanism. In the range of mass per volume (m/V) ratio 0.002 to 0.3 % the surfactants show a reversible inhibiting effect on biosensor response. At lower concentrations (down to mass per volume ratio 10^{-4} %) the surfactants alter the analytical characteristics of reversible and irreversible inhibitor determination. The use of surface-active additives improves the biosensor selectivity in multi-component media (*74*).

Determination of the number of oxyethyl groups in non-ionic surfactants using ion-selective electrodes has also been reported (*75*).

ISFET surfactant sensors

An ISFET device selective to anionic detergents, based on a PVC-sebacate membrane, containing benzyldimethylcetylammonium cholate as exchanger has been prepared, characterised and applied for the determination of some anionic surfactants in standard aqueous solutions and in authentic matrices (lake and sea water). The linearity range extends over 3–4 decades depending on the examined surfactant, within the range between about 10^{-6} and 10^{-3} M in all cases. The results are compared with those obtained by the previously described liquid and polymeric membrane sensors, based on the same exchanger (76).

The preparation of a new ISFET device based on a photocurable membrane sensitive to anionic surfactants is described. The membrane is formed by an urethane-acrylate matrix with 2-cyanophenyl octyl ether as the plasticiser. When compared to conventional ion-selective electrodes, the prepared ISFETs do not show significant differences in sensitivity and reproducibility. When calibrating with dodecylbenzene sulphonate (DBS) the prepared ISFETs show a Nernstian behaviour, with a slope of 57.5 mV/decade. The linear working range is from $1.0\cdot10^{-3}$ to $3.0\cdot10^{-6}$ M DBS and the detection limit is $1.2\cdot10^{-6}$ M. The response times were below 0.7 min in all cases (95 % of the step change). Photodegradation processes using titanium dioxide dispersions were monitored for two common anionic surfactants: DBS, being aromatic, and the more alkylic dodecyl sulphate, DS. The determination of surfactant concentration was performed following a standard addition method, using ISFETs as sensors, and without any previous separation stages. The degradation kinetics in both cases are first-order processes, with half-life times $t_{1/2}$=31.5 min for DBS and 52.0 min for DS (*77*).

Similarly, the same authors reported the preparation of photocurable polymer membranes selective to anionic surfactants and their application to all-solid state ion-selective electrodes. A preliminary trial employing chemically modified field effect transistor (CHEMFET) devices is also shown. Membranes were based, as in a previous work, on a urethane-acrylate polymer and used 2-cyanophenyl octyl ether (CPOE) as a plasticiser compatible with the photocuring process. These membranes were highly selective to the anionic surfactants assayed, while common inorganic anions did not interfere. Several membrane compositions were obtained using a mass fraction of CPOE between 44 and 48 %. A membrane with a general-purpose formulation is fully characterised and calibration results for anionic surfactants such as dodecylbenzene sulphonate (DBS), tetrapropylenebenzene sulphonate and dodecyl sulphate, or cationic surfactants such as Hyamine 1622 and cetyltrimethylammonium ion are presented. With the primary DBS ion the slope of 58.1 mV/decade was obtained. A linear response between 10^{-3} M and $3\cdot10^{-6}$ M, a detection limit corresponding to 0.26 ppm DBS ($7.9\cdot10^{-7}$ M) and a slope precision of 2.8 % RSD between days were obtained (*78*).

Development of a new ISFET sensor for anionic surfactants was reported with the application to potentiometric titrations. The developed devices showed a lifetime longer than 4 months, improving the reported values of PVC membrane-ISFETs. Other characteristics are Nernstian slopes from 59 to 62 mV/decade, detection limits of about 10^{-6} M and good linearity. They also showed response to several anionic surfactant species and to the reagent used for the potentiometric titration. This allowed the measurement of the overall anionic surfactant content in different samples. The devices were useful in the range from 0.02 to 10 mM for dodecylbenzene sulphonate solutions. End-point potential jumps up to 250 mV were obtained in the titrations. The reproducibility, expressed as relative standard deviation, was estimated, using a standard 4 mM sodium dodecyl sulphate solution, as 1.45 % (N=14). Finally, in a comparative study, there were no significant differences between the results produced with the standard, two-phase titration method and the proposed potentiometric titration method using surfactant ISFETs as end-point indicators (*79*).

Three new ISFET devices based on polymeric selective membranes sensitive to cationic surfactants have been fabricated and characterised. These new sensors use a PVC-sebacate matrix incorporating benzyldimethyl-hexadecylammonium reineckate, dodecyltrimethylammonium reineckate and hexadecylpyridinium phosphotungstate, respectively, as exchangers. Determinations of cationic surfactants in authentic aqueous matrices of environmental interest have been carried out using the new sensor with the best performance. Furthermore, the critical micellar concentration (CMC) of some cationic surfactants has also been evaluated (*80*).

Surfactant sensors for FIA

Many potentiometric surfactant sensors, as well as amperometric ones, can be used as detectors in flow injection analysis (FIA).

An electrochemical sensor based on the incorporation of dodecyl sulphate (DDS) into polypyrrole (Ppy) by electropolymerisation of pyrrole in the presence of surfactant is described. The physicochemical characteristics of the Ppy-DDS electrode and its response against the alkali metal ions in cyclic voltammetry were studied. Application of this electrode as a sensor in flow-injection analysis and in high-performance ion chromatography is demonstrated. The electrode remains stable for several weeks with no evidence of chemical or mechanical damages (*81*).

The development of high-performance paraquat selective potentiometric sensors based on octamethyl cyclotetrasiloxane is described. In the fabrication of these sensors, the use of highly lipophilic PVC-based membrane components, namely plasticiser and anionic sites, is emphasised. The use of bis(1-butylpentyl)decane-1,1'-diyl-diglutarate (BBDG) and tetra-*n*-undecyl 3,3',4,4'-benzophenone tetracarboxylate (TBT) as plasticisers in conjunction with either sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NTB) or potassium tetrakis(4-chlorophenyl)borate (KTPB) as membrane additives all yielded functional paraquat selective chemical sensors of Nernstian slopes. A distinct advantage of the paraquat sensors described here was their resistance to fouling by surfactants as compared to earlier sensors that used *o*-nitrophenyl octyl ether (NPOE) as a plasticiser. The second part of this paper deals with the usage of the promising membrane systems described above when applied on the surface of platinum wire and subsequently used as a flow-through potentiometric detector. A brief description of the flow-through detector design and optimisation of the flow-injection analysis (FIA) set-up were also presented. Analysis of 0.01–0.1 mM paraquat dichloride in the backgrounds of well, river and lake waters when performed in the FIA mode gave excellent recoveries. A throughput of 85 samples/h can be achieved with this system (*82*).

An automated FIA system for the determination of low levels of anionic surfactants in river water and wastewater was developed. The system uses specially constructed tubular flow-through ion-selective electrodes (ISEs) as potentiometric sensors and on-line preconcentration techniques. The anionic surfactant ISEs employed are of the all-solid-state type with a plasticised PVC membrane. They show a general response to anionic surfactants with a lower limit of linear response of approximately 10^{-5} M, when used in direct determinations. However, their specificity is limited, which hampers their direct use with environmental samples. Therefore, the FIA system presented here includes a solid-phase extraction procedure for the purification and preconcentration of analytes. The FIA system was first applied for the determination of different types of anionic surfactant standards. Potentially interfering substances such as chloride, nitrate, and non-ionic surfactants were checked to verify that they did not interfere with the response of the system. Concentrations of approximately 10^{-7} M (0.03 ppm) of sodium dodecyl sulphate could be detected in the non-linear response region when 3 mL of sample was preconcentrated and eluted with 50 µL of acetonitrile in water volume fraction of 75 %. Precision was 2 % RSD (N=31) for 10^{-6} M sodium dodecyl sulphate standard solution and the sample throughput was 10 h^{-1}. The FIA system was then used for the determination of total anionic surfactants in river water and wastewater (*83*).

Samples obtained by gas-diffusion flow injection with a nonactin-based potentiometric sensor used as the detector for the ammonium ion were investigated. Analyses could be performed at a sampling rate of 25 h^{-1} and the cartridge was effective for at least 1000 injections of 50-µL samples in the concentration range of 1–180 mg/L. The procedure was applied to the analysis of wastewaters and was found to be efficient in removing ionic and non-ionic surfactants from acidified (pH=1) samples (*84*).

Amperometric surfactant sensors

Among amperometric surfactant sensors there are several true surfactant biosensors that employ microorganisms or cells.

A range of modified PVC membranes based on their permeability and selectivity to electrochemically active species has been characterised. The species are detected at an amperometric (two-electrode) cell in phosphate buffer solution. Diffusing species studied were paracetamol, catechol, ascorbic acid and hydrogen peroxide. Membrane modifying agents studied were cationic (Aliquat 336s) and non-ionic (Tween 80 and Triton X-100) surfactants. For the first time, surfactant combinations with the liquid crystal N-(4-methoxybenzylidene)-4-butyl-aniline were reported (*85*).

Bacteria-degraders as the base of an amperometric biosensor for detection of anionic surfactants have been investigated (*86*).

A *Pseudomonas rathonis T*-based amperometric biosensor was constructed for the detection of anionic surfactants. Microorganisms contained the plasmid for surfactant degradation. The sensor was highly sensitive to sodium dodecyl sulphate (SDS) and volgonat. The lower limit of SDS detection was within the range of 0.25–0.75 mg/L (*87*).

Amperometric sensor study of the selectivity of PVC membranes plasticised with surfactants and liquid crystals was reported (*88*).

Effects of non-ionic surfactants on electrochemical behaviour of ubiquinone and menaquinone incorporated in a carbon paste electrode were studied. A carbon paste electrode, in which the carbon particles were coated with a thin layer of a non-ionic surfactant, was constructed with a pasting liquid containing ubiquinone or menaquinone. Further, such a modification was applied for the preparation of an enzyme electrode in which the quinone molecule acts as a redox mediator and the influences on the sensitivity of the glucose biosensor were demonstrated (*89*).

The selective binding of charge diffuse alkyl and arylammonium ions relies on multiple weak interactions with a complementary synthetic receptor. Using appropriately sized lipophilic cyclodextrin derivatives, the chemoselective binding of alkylammonium ions such as dopamine, acetyl choline, guanidine, and long chain cationic surfactants may be achieved allowing their selective detection by either potentiometric or amperometric methods of analysis. Enantioselectivity in the binding of chiral β-hydroxyarylammonium ions, such as propranolol, allows chiral sensors to be developed. The selective detection of various clinically important analytes, such as imipramine, lignocaine and creatinine, has also been studied (*90*).

The applicability of the well-known three-parameter Hill equation for the description of calibration curves for potentiometric (detection of glucose, pesticides, urea) and amperometric (detection of surfactants, biphenyl, nitrite) biosensors has been analysed. The criterion for validity of the Hill equation has been proposed. The sources of errors at the determination of concentration of the analysed substance have been considered (*91*).

Ordered surfactant films on electrodes are promising for various applications, including catalysis, sensors and fundamental studies. Films were prepared by first casting the didodecyldimethylammonium bromide (DDAB) onto electrodes, then introducing the copper phthalocyanine tetrasulphonate (CuPCTS) by ion exchange from solution, or by casting the films as the CuPCTS(didodecyldimethylammonium) salt. The salt films were characterised by overlapped voltammetric peaks, while the ion exchanged films showed a well-resolved first reduction process. The analysis of voltammetric data at pH=12 showed that charge transport diffusion and electron transfer kinetics were significantly faster in the ion exchanger films than in the salt films. The fluid lamellar liquid crystal structure of the ion exchanged films facilitates charge transport compared to the salt films, which are not liquid crystalline (*92*).

Conductometric surfactant sensors

There is only one paper dealing with this type of surfactant sensors for on-line monitoring of the evolution of a number of particles in the emulsion polymerisation by conductivity measurements. The model developed was built on the assumption that surfactant is partitioned among the three principal phases of the polymerising latex. A soft-sensor strategy was then proposed for monitoring the number of polymer particles (N-P) by combining the conductivity model with the available conversion, temperature, and conductivity signals. The main objective was to validate the conductivity model in a broader range of operation conditions and to follow the evolution of N-P (nucleation/coagulation) on-line under different reaction conditions. A series of batch and semi-batch polymerisation runs was carried out aiming to evaluate the model performance when different solid content, surfactant concentration, and reactor temperatures are used. Results showed that the model was able to perform accurate predictions of N-P even when disturbances of ±2 °C in temperature and ±0.03 in monomer conversion took place during the polymerisation process (*93*).

Impedimetric surfactant sensors

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 immobilisations 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 the impedance, the antibody-antigen interaction caused its increase. The obtained results give an opportunity for the development of impedimetric affinity sensors for clinical analysis or for the detection of various environmental pollutants (*94*).

The simple methods for preparing the direct affinity sensors are proposed. The proposed method consists of the immobilisations of either oligonucleotide or antibodies as recognizing elements onto the surfactant bilayer. For DNA-sensor the immobilisation of oligonucleotide by spontaneous infiltration of hydrocarbon chain bound to oligonucleotide pentadecathymidylate into the hydrophobic region of surfactant bilayer was performed. The adsorption of antibodies on bilayer surface has resulted in immunosensor development. The direct detection of affinity interactions in both cases has been investigated by impedance spectroscopy. In both studies the significant changes in impedance spectra have been observed. The dynamics of the response manifestation have been followed by the specific DNA-coupling causing the decrease of real part of the impedance, whereas the antibody-antigen interaction caused the increase of the real part. The obtained results are promising for the development of impedimetric affinity sensors for clinical or environmental applications (*95*).

A few hundred ppm of water can cause detrimental changes in the lubricating properties of engine oil. Electrochemical sensors based on electrochemical impedance spectroscopy and cyclic voltammetry were utilized to detect water leaks and continuously monitor the time-dependent dynamics of water-oil interactions following the injection of water into industrial lubricant. Immediately following the injection, water molecules interacted with the oil additives (surfactants) forming a water-in-oil emulsion based on the inverse micelles. Emulsification was followed by gradual loss of water from the solution through evaporation and electrolysis. On-line data were used to characterise the dynamics of water micellisation, evaporation, and electrolysis. The values of kinetic rate constants and diffusion coefficients for the components of the water/oil system were determined. In order to support the experimental data and establish the kinetics of water-oil interactions, literature equations describing these interactions were adopted to develop a computational analysis model. The model illustrated the processes occurring in the water/oil system and resulted in an increased understanding of the recorded experimental data (*96*).

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Tenzidni senzori u biotehnologiji
1. Elektrokemijski senzori

Sažetak

U radu je dan literaturni pregled tenzidnih senzora od 1993. godine do danas te istaknuta njihova važnost u suvremenoj biotehnologiji. Elektrokemijski tenzidni senzori su najpopularniji zbog jednostavnosti priprave i pouzdanosti. Prema mjerenoj fizičkoj veličini uobičajena je podjela elektrokemijskih senzora na potenciometrijske, amperometrijske, konduktometrijske i impedanciometrijske. Potenciometrijski tenzidni senzori su najčešći a mogu se primijeniti diskontinuirano i kontinuirano. Također postoje kao detektori titracijske završne točke ili za izravna mjerenja elektromotorne sile. Najmanje su značajni konduktometrijski i impedanciometrijski senzori, dok među amperometrijskim tenzidnim senzorima ima i »pravih« biosenzora s mikroorganizmima ili stanicama živih bića.