

Potentiometric Analysis of Surfactants

Zühre ŞENTÜRK*, Marc GERLACHE**, Jean-Michel KAUFFMANN**^o

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Summary : The aim of this review is to summarize the current trends in potentiometric sensors for the determination of surfactants. Several ion-selective electrode designs and compositions applicable for volumetric titrations with potentiometric end point detection or for direct potentiometry are described.

Key words: Surfactant, potentiometry, ion-selective electrodes

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Yüzey Aktif Maddelerin Potansiyometrik Analizi

Özet : Bu derlemede yüzey aktif maddelerin tayininde kullanılan potansiyometrik sensörlerdeki gelişmeler özetlenmektedir. Direkt potansiyometride veya dönüm noktası belirteci olarak volümetrik titrasyonlarda kullanılan çeşitli iyon seçimli elektrot şekil ve bileşimleri açıklanmıştır.

Anahtar kelimeler: Yüzey aktif madde, potansiyometri, iyon seçimli elektrotlar

INTRODUCTION

Surface active substances, commonly referred to as "surfactants", are amphiphilic compounds used as active ingredients in a variety of laundry and cleaning products, hard surface cleaners and shampoos, and also used in chemistry and biochemistry research laboratories¹.

Surfactants are organic chemicals which, when added to a mixed system such as water and air or water and soil, induce a decrease of the air/water interfacial tension. This property is related to the presence of both a hydrophobic non-polar part (mostly a hydrocarbon chain with 7 to 20 carbon atoms) and a highly polar or ionized part involving one or more functional groups in a single structure². Depending on the nature of the polar group within the molecule, sur-

factants are classified mainly as anionic, cationic, non-ionic and amphoteric.

Over the years, the use of surfactants has increased considerably. Annual world-wide consumption of surfactants was 2.5 million metric tons in 1993². The widespread use of them for domestic and industrial cleaning has resulted in serious environmental pollution problems. They are primarily used in aqueous solutions which are later introduced into the environment via waste water discharge. The harmful effects of surfactants on aquatic organisms are well known. In addition to their foaming properties, caused by their accumulation on the water surface, they impede the mass transfer of oxygen, which reduces the auto-cleaning power of water³. Further, surfactants can inhibit the growth of microalgae by interfering with their metabolism^{4,5}.

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Although the concentrations of surfactants found in water have decreased considerably as a result of the change to more biodegradable substances⁶, they are still one of the most common organic pollutants in natural waters. The determination of surfactants is highly important in plant production control, in environmental monitoring and in the analysis of formulations in the cosmetic and pharmaceutical industries.

A commonly used procedure for the determination of surfactants is the so-called two-phase titration which is widely adopted as standard method⁷⁻¹⁰. This technique is based on the formation of a lipophilic ion-pair between the surfactant and the titrant (a lipophilic ion that has an opposite charge), which is then extracted into an organic hydrophobic solvent (chloroform). The end point is detected visually with a suitable color indicator, which forms an extractable ion-pair with the titrant after the equivalence point has been reached. Although two-phase titrations are simple and useful methods, they have, however, several drawbacks, including the requirement of running blank tests, matrix interferences, subjective errors in the end point detection, increased analysis duration and use of chlorinated solvents.

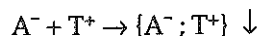
Alternative analytical methods for the determination of surfactants have been reported, of which the most important are spectrophotometry¹¹⁻¹⁴, spectrofluorimetry¹³, thin-layer chromatography¹⁵, gas chromatography¹⁶⁻¹⁷, high pressure liquid chromatography¹⁷⁻²⁰, capillary electrophoresis²¹, tensammetry²²⁻²⁴, amperometry^{23,25-28}, voltammetry^{29,30}, and potentiometry.

Trends and recent applications of potentiometry in the determination of the various types of surfactants are summarized in the present paper.

POTENTIOMETRY

Potentiometric titrations of surfactants in the presence of ion-selective electrodes (ISEs) are good alternatives to the two-phase titration and can avoid the disadvantages of the two-phase titration³¹⁻³³.

During a titration, the ionic surfactant to be determined and the titrant form a stable, nonpolar complex that precipitates in the water sample:



The electrodes are sensitive to the variation of either the analyte or the titrant concentration, so the structure of the titrant influences greatly the titration data. Standard solutions of very different reagents have been used as titrants in surfactant analysis. As a rule, all reagents forming water-insoluble ion-pairs with surfactants can be tested for titrants. If they are sufficiently stable and water-soluble, they can form a convenient standard solution. For anionic surfactants, a bulky cationic surfactant is usually used as titrant and vice-versa.

The best suited substances for the titration and detection of cationic surfactants are sodium lauryl sulfate³⁴⁻³⁶ or tetraphenylborate³⁶⁻³⁸. For the determination of anionic surfactants, Hyamine 1622^{34,39-42}, cetyl pyridinium chloride⁴² and TEGO[®]trant A100^{43,44} are appropriate. Since TEGO[®]trant A100 is more hydrophobic and produces higher potentiometric steps compared to Hyamine 1622, it permits the detection of alkyl sulfates with shorter chain lengths i.e., less lipophilic molecules (Fig.1). This is the reason why this new substance has almost totally replaced the standard Hyamine 1622⁴³.

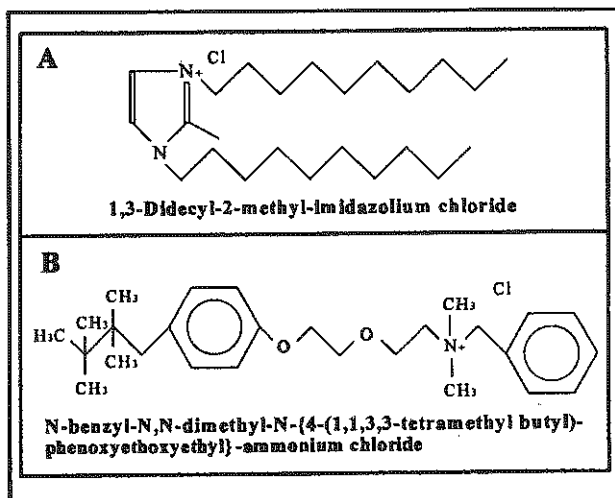


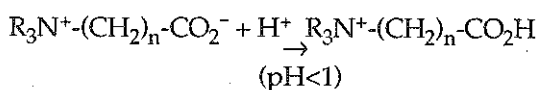
Figure 1. Structures of Hyamine 1622 (A) and TEGO[®] trant A100 (B)

The titration curves obtained with alkyl sulfates and alkyl benzene sulfonates are very similar to conventional acid/base titrations with well marked titration end points. Alkyl ether sulfates, especially those with a higher number of ethylene oxide units, show worse

titration curves with more noise, less steep potential steps, and more deformed baselines.

The titration of ethoxylated nonionic surfactants is based on the complexation of bivalent cations such as Ba^{2+} , with the polyethoxylate chains of the surfactant molecule^{45,46}. The resulting cationic complex can be titrated with tetraphenylborate^{47,48}.

Amphoteric surfactants, which are composed of a hydrophobic chain ended with two different polar groups, can only be titrated if they are converted to their cationic form in a strongly acidic media^{43,49}.



Due to the low pH required, anionic surfactants can not be used any longer as titrant of amphoteric surfactants because they will be protonated (sulfonates) or even hydrolyzed (sulfates), hence tetraphenylborate is the titrant of choice.

The progress which has been made in potentiometric titration of surfactants is closely related to the above mentioned titration reagents but also to the development of optimized ISEs. As already said, surfactant-selective electrodes are specially designed sensors to monitor the changes of surfactant ions activity in the solution.

In ISEs sensitive to ionic surfactants, the sensing membrane contains an ion associate (ion-pair) of the type C^+A^- in which A^- is an anionic surfactant and C^+ is a positively charged counter ion (e.g. a cationic surfactant). This kind of ISE is suitable for the detection of both A^- and C^+ .

In addition to potentiometric titrations, techniques based on direct potentiometric measurements using ISEs and referring to a calibration curve are also applicable for surfactant determination. However, the errors in direct potentiometry are usually much larger than in potentiometric titrations. The latter need however an increased time demands and consumption of chemicals used as titrants.

Since the late fifties, non-specific potentiometric electrodes have been used such as the Craine's silver electrode^{50,51} and the Heyrovski's mercury-plated plat-

inum electrode⁵². At present, there are three different types of ISEs developed for titrimetric determination of surfactants: liquid membrane ISEs, polymeric membrane ISEs and polymeric-coated wire ISEs.

Liquid-membrane ISEs

Liquid-membrane surfactant selective electrodes can be prepared by using a glass tube sealed at the end with a Teflon membrane or a hydrophobic glass frit impregnated by the sensing solution³¹. This solution is a surfactant ion-pair, such as hexadecyltrimethylammonium dodecyl sulfate, dissolved in a hydrophobic organic solvent, such as nitrobenzene. The bulk of the tube is filled with a diluted solution of an anionic surfactant in the presence of a little amount of Cl^- ion. A Ag/AgCl reference electrode is inserted into this internal solution (Fig. 2a). The potentiometric measurements are performed classically using a second (external) reference potentiometric electrode such as a Ag/AgCl or a saturated calomel electrode⁵³. Various kind of ISEs with liquid membranes have been developed in the past^{39,54-56}.

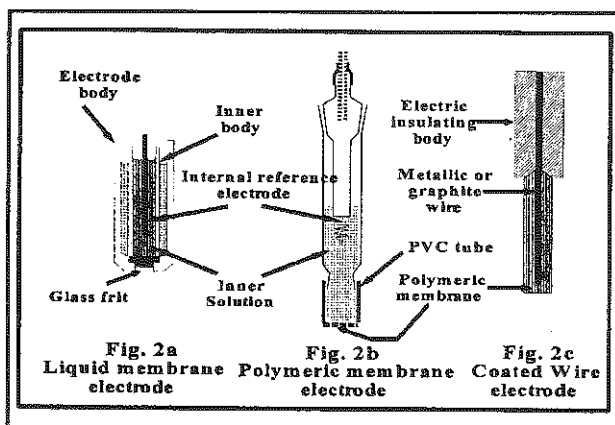


Figure 2. Schematic structures of the three types of ion-selective electrodes.

Sap and co-workers⁴⁰ proposed a new type of selective electrode based on the cationic complex Fe(II)-bis[2,4,6-tri(2-pyridyl)-1,3,5-triazine] for the analysis of anionic surfactants. The electrode showed a Nernstian response within the activity range comprised between 7.1×10^{-6} and 1.4×10^{-3} M of lauryl sulfate. The electrode was also used as end-point detector in potentiometric titration of ionic surfactants with a high potential jump. Campanella et al⁵⁷ obtained an electrode sensitive to anionic surfactant concentration,

made from a liquid-membrane consisting of a solution of benzyldimethylcetylammmonium cholate in 1-decanol, with a Ag/AgCl reference. Szczepaniak and Ren⁵⁸ utilized another liquid-membrane electrode which employs a solution of mercurated polystyrene as ion-exchanger for the analysis of anionic surfactants and soaps.

A liquid-membrane electrode, suitable for monitoring the titration of cationics with tetraphenylborate, was made using the nitroxyline solution of tetrapentylammmonium tetraphenylborate⁵⁹. Anghel et al³⁹ presented the results obtained in the analysis of cosmetic products with the first application of surfactant selective electrodes. Potentiometric titration with ISEs gave better results comparing to two-phase titration.

Liquid-membrane surfactant selective electrodes show a serious drawback due to a risk of progressive membrane active compound dissolution in the aqueous test medium, leading to poor response stability. This is especially dramatic when the surfactant concentrations are above the critical micelle concentration³¹. Ishibashi et al⁶⁰ used Crystal Violet as ion-exchange site in the membrane for the sulfonate ISEs. As expected from its relatively hydrophobic functional groups, the Crystal Violet molecule limits the dissolution of the sensing component in the aqueous medium.

Liquid-membrane ISEs have been applied in volumetric titrations for end point detection, however, they are not suited practically in direct potentiometric measurements of surfactants because of a need of frequent recalibrations.

Polymeric membrane ISEs

The construction of polymer membrane electrodes consists to use, instead of the porous and fragile disc of liquid membranes, a film of plastic membrane (0.2 - 0.3 mm thick)⁶¹. Such electrodes are physically more robust than liquid-membrane electrodes, and also less subjected to solubilization in the aqueous media in which they are immersed (Fig. 2b). The membrane composition consists of the polymeric matrix, the sensing component and a plasticizer. Poly(vinylchloride)(PVC) is by far the most commonly used polymer matrix. The membrane film is usually pre-

pared by slowly evaporating an organic solvent, such as tetrahydrofuran (THF) or cyclohexanone, at room temperature (20°C), from a solution of PVC containing a high level of plasticizer and the electroactive substance. Then, the membrane is mounted on the end of PVC or glass-tubing filled with an inner electrolyte solution containing the ion of interest and completed with an internal reference electrode (e.g. Ag/AgCl)⁶²⁻⁶⁴.

The selectivity of ISEs can be significantly altered by changing the relative proportions of the electrode membrane's component. One of the major components of the electrode membrane is the plasticizer, which mainly acts as a fluidizer allowing homogeneous solubilization and mobility diffusion of the ion-pair inside the membrane. The amount of plasticizer must be properly optimized in order to minimize electrical asymmetry of the membrane, and to limit fouling of the sensor (e.g. by proteins). At high concentrations, the plasticizer may leak out of the membrane and create these problems. Better membranes are generally obtained by implementing two or three plasticizer components. If the composition of polymer is around 70:30 percent (plasticizer: PVC), it is a single phase homogeneous mixture, and referred to as "solvent polymeric" type⁶³. This kind of polymer generally exhibits liquid-membrane properties.

Proper use of the plasticizer allows one to control the value of the electrode/solution distribution ratio of the particular C^+A^- ion-pair employed as an ion-exchanger. The analytical performance of such electrodes is strongly dependent on a suitable combination of plasticizer and electroactive substance. The nature of the plasticizer has a marked influence on the response slope, linear domain and also on the selectivity of PVC membrane electrodes⁶⁵. The plasticizer must be chemically compatible with both the polymer and the sensing material, thereby reducing the electrical resistance of the polymeric bead of the film. The most frequently used plasticizer of PVC membranes are *o*-nitrophenyl octyl ether (NPOE)^{35,38,49,65-69} and *o*-nitrophenyl phenyl ether (NPPE)^{45,46,65,70}.

In general, it is desirable that polymeric membranes have a glass transition temperature (T_g) below room temperature. The plasticizers used in association with the sensor are effective in reducing the glass transi-

tion temperature. It is noted that the Tg of PVC (+81°C) falls to -65°C when it is mixed with 70 % NPOE.

Some of the earliest PVC-based ISEs developed for the detection of other ions, such as calcium^{71,72} and nitrate^{32,73}, were adapted for the surfactant titrations. With the exception of such investigations, most electrodes have been based on a polymeric membrane designed deliberately to be anionic or cationic surfactant-specific^{44,74-82}. Some characteristics of a new type of PVC based ISE developed by Gerlache et al⁴⁴, comprising an ion-pair between sodium lauryl sulfate and TEGO® trant A100, are summarized in Table 1. Several ISEs, of similar conception, specifically constructed for ionic surfactant analysis have been commercially launched in the last few years, such as Orion model 93-42^{35,68}, ASTEC model TSE 01/91^{35,42}, and more recently, the Metrohm "High Sense Tenside" ISE^{35,42-44,49}. The most promising of the commercial ISEs appears to be the "High Sense Tenside" electrode, which is suitable for working in titration mode for more than 7 months with a relative standard deviation comprised between 0.2 and 1.3 % for anionic surfactants. Useful over a wide pH range (1-12), the response of the electrode makes it suitable for the determination of a soap/alkyl sulfonate or amine/quaternary ammonium mixture.

Table 1. Analytical figures of merit of a new PVC-ISE suitable in direct potentiometric measurements⁴⁴.

Working range, M (SLS)	$2 \times 10^{-6} - 5 \times 10^{-3}$
Limit of detection, M	1×10^{-6}
Slope, mV / decade of [SLS]	58.9
Reproducibility, mV (for a 1×10^{-4} M SLS)	255 ± 3
Response time, s	30
Sensitivity to inorganic salts	None

Much research has also been carried out in the area of potentiometric sensors for the determination of non-ionic surfactants. A plasticized PVC membrane electrode doped with a barium-nonionic (ethoxylated nonylphenol)-tetraphenylborate complex, was prepared for the ethoxylated surfactants^{45,46}. The application was oriented towards either direct po-

tentiometric measurement⁴⁵ or monitoring the titration of non-ionics⁸³. Ivanov and Pravshin⁸⁴ prepared a plasticized PVC membrane containing either the ternary complex cetylpyridinium/dodecylsulfonate/barium or the complex between tetraphenylborate and a nonionic surfactant. Ionic surfactants interfered in the titration. Gallegos⁴⁸ used the Orion ionic surfactant electrode as the end-point indicator for the titration of barium non-ionic complexes with sodium tetraphenylborate. Recently, Metrohm has launched a non-ionic surfactant electrode suitable for volumetric titration with tetraphenylborate.

Up to now, only very few methods for the titrimetric determination of amphoteric surfactants have been reported. Buschmann and Schulz⁴⁹ developed a direct titration procedure for amphoteric surfactants using a new type of PVC-membrane (PVC - NPOE - Ion carrier). The ion carrier was the ion associate of tetraphenyl phosphonium and tetraphenyl borate or the associate of cetylpyridinium and tetraphenyl borate. All surfactants could be titrated with a relative standard deviation (RSD) of 1.6 % . Simultaneous titrations of cationic and amphoteric surfactants were also possible.

Other structures for polymeric membrane electrodes are being searched at present by modifying the polymers chemically to confer them functional groups in order to make them more specific to a given surfactant. An example of a new generation of membrane electrodes is as follows⁸⁵ : the modified PVC, derivatized to contain either sulfonate or quaternary ammonium end groups, is dissolved in THF and precipitated in an aqueous solution containing the counter ion of the surfactant to be determined. After washing and drying, the PVC is mixed with a high molecular weight plasticizer (Elvaloy 742, m.w. 25,000) which makes the entire electrode membrane more stable.

All of the above-mentioned electrodes are based on a specific membrane composed of a homogeneous mixture of PVC, a plasticizer and the sensing material. Generally, the sensing material (e.g. an ion-pair formed by using an organic anion which gives an insoluble salt in water in the presence of a cationic surfactant) is dissolved in this kind of membrane. However, electrodes can also be constructed using

heterogeneous membranes, in which the carrier is insoluble. Laponite, a synthetic clay, has been successfully used as a surfactant carrier for electrodes specific to cationic surfactants^{86,87}.

Some researchers have also found that plasticized polymeric membranes without added sensing materials (blank membranes) respond to some ionic⁸⁸ and non-ionic⁸⁹ surfactants.

Recently, novel ion-selective electrodes for surfactants based on crown ethers, as neutral carrier ionophores incorporated into the electrode membrane, have been described^{38,81,90}.

Polymeric-coated wire ISEs

Besides the most common construction of the polymeric membrane electrodes, another way of preparing them consists to fix the polymeric membrane directly on a solid substrate, thus eliminating the internal electrolyte solution (Fig. 2c). These "coated wire electrodes" can be prepared simply by dipping the solid substrate into a solution containing the dissolved polymer (usually PVC), the plasticizer, and, if desired, an ion-pair, and allowing the solvent to evaporate. The solid substrate is a conductor, commonly, of metallic (platinum⁶⁶, aluminium^{47,91}, silver⁹², copper^{34,36,92}...) or graphite^{41,44} type, and it can be of any convenient geometric shape³⁷. These simple and inexpensive electrodes can be used advantageously as sensors in ion-pair formation-based titration of surfactants of various type. Cationic surfactants titrated with sodium tetraphenylborate yield titration curves with sharp potential breaks^{80,93}. For the determination of anionic surfactants, lipophilic cationic titrants such as those based on quaternary ammonium or pyridinium salts are used^{66,72,94}.

A successful coated graphite electrode was constructed by Dowle et al⁴¹. It is based on a PVC membrane incorporating tritioyl phosphate and an appropriate surfactant salt (0.1 %). The electrode was used as end-point indicator for the potentiometric titration of industrial anionic and cationic surfactant samples in both aqueous and mixed-solvent systems^{41,95}. The authors reported a linear response range between 1×10^{-6} and 1×10^{-2} M of lauryl sulfate without any interference from inorganic salts. Later,

this electrode was redesigned to form a hollow graphite tube with the membrane coated on the inside wall⁹⁶. The use of this electrode as a flow-through electrode in conjunction with a reference electrode, enabled the manual potentiometric titration to be adapted to a flow injection pseudo-titration method. In this application, the mobile phase of the flow injection analysis (FIA) systems contained a constant concentration of the titrant, which can be either a cationic or an anionic surfactant. The sample, containing either an anionic or a cationic surfactant, is passed through a dilution chamber prior to mixing with the mobile phase. This detection system of flow-through electrode design is sensitive to ionic surfactants. The peak width, rather than the peak height, of the signal is proportional to the logarithm of the surfactant concentration. The disadvantage of the direct potentiometric system when compared with the manual titration is that the system must be calibrated according to the surfactant type. The reported electrode life is only 2-4 weeks. Alonso and co-workers⁹⁷ showed also the applicability of the developed tubular sensors in flow-injection systems for the determination of anionic surfactants in the 1×10^{-4} and 1×10^{-3} M range.

For the determination of non-ionic surfactants containing poly-oxyalkylene chains, the method used was based on the precipitation of tertiary compounds with sodium tetraphenylborate in the presence of a bivalent metal ion with an ionic radius higher than 100 pm⁴⁷. Only ampholytic surfactants could be titrated directly with sodium tetraphenylborate in acidic solution, in which they are cationic, using aluminium wire coated plasticized PVC membrane⁹¹. For the determination of some samples, however, back titration was found to be more convenient. The amphoteric surfactants were reached with an excess of tetraphenylborate, which is then back-titrated with a standard thallium (I) nitrate solution using the same electrode (coated Al) for the indication of the end-point⁹¹.

A PVC matrix membrane electrode in an all-solid-state graphite-epoxy support allowed for the titration of anionic surfactants at concentrations down to 10^{-5} M with an average value of potential jump of 140 mV⁶⁹.

CONCLUSION

In his recent book, Schmitt states³¹: "Today's surfactant-sensitive electrodes suffer from response which varies from day to day, and even from hour to hour". This explains that, in most cases, they have been used as indicators of the end point of volumetric titrations rather than in direct measurements relating potential to concentration. In potentiometric titrations, it is only important that the electrode shows a high potential jump at the end point. Thanks to commercially available automated titrators, improved surfactant-sensitive electrodes and specially designed titrating agents, the potentiometric titrations of surfactant can fulfill numerous practical needs encountered in industrial and environmental surfactant analyses⁹⁸. A few years ago, the potentiometric method has been adopted as standard analysis in the United States³². Thus the potentiometry of surfactants has been undoubtedly validated.

As stated by Schmitt³¹: "It is not an impossible dream that the electrochemical procedure for surfactant determination, as well as pH measurement, will consist of dipping an electrode into the test solution, measuring the electrode potential, and converting the potential data to a concentration value". This review addresses this statement by showing some successful trends in the area of direct potentiometric measurements using ISEs.

Operation of ISEs relies on the Nernst equation or, more precisely, on the Nikolsky-Eisenman equation which takes into account the fact that ISEs are not 100% specific but rather more or less selective to a given ionic species. This explains why trends in the use of ISEs are currently directed towards their use as detectors combined to high performance liquid chromatography⁷⁵ capillary electrophoresis⁹⁹ and in flow injection analysis^{89,100,101}.

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