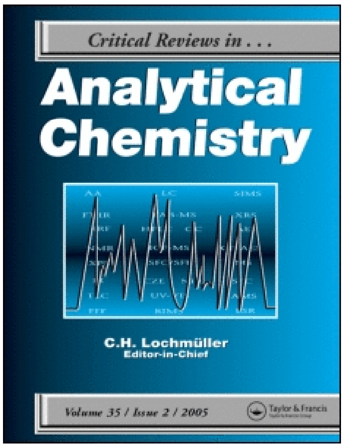

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J. Sánchez[a]; M. del Valle[a]
[a] Grup de Sensors i Biosensors, Departament de Química, Universitat Autònoma de Barcelona, Bellaterra, Catalonia, Spain

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Determination of Anionic Surfactants Employing Potentiometric Sensors—A Review

J. Sánchez and M. del Valle
Grup de Sensors i Biosensors, Departament de Química, Universitat Autònoma de Barcelona, Bellaterra, Catalonia, Spain

This article describes the ongoing evolution of potentiometric sensors as employed in the field of anionic surfactants, beginning with the first reports published in the 1960s. Although the 1970s saw an increased use of such devices due to the adoption of PVC matrices, it is only relatively recently that commercial electrodes for these species have been available to industry. The latest developments, particularly the study of new polymer formulations and their application to other transducing devices, are also discussed.

Keywords anionic surfactants, ion-selective electrodes, potentiometric sensors

INTRODUCTION

Anionic surfactants are a common feature of modern households, being found in soap, toothpaste, washing liquid, and laundry detergents. They also have many industrial applications as they act as good cleaning agents, are readily soluble in water, and are inexpensive for purchase. The most common anionic surfactants are the alkylsulfates and the alkylbenzenesulfonates.

In terms of activity, a study carried out in the more industrialized world (including Western Europe, United States, and Japan) reported these products to be most widely used in cleaning and laundry processes (48.3%), followed by cosmetics and pharmacy products (7.7%), and the mining industry (7.7%), as well as numerous minority applications in, among others, the textile, colorings, food and polymer industries (1).

The two main world markets, the U.S. and Europe, show comparable patterns of consumption due to their similar levels of industrial development and the increasingly evident phenomenon of economic globalisation. To date, both markets have relied heavily on the use of anionic surfactants, for both technical and cost reasons. However, it is likely that over the coming years nonionic and amphoteric surfactants will progressively take the place of anionic surfactants, while cationic surfactants will continue to be used in a small, stable specialized segment of the market. Available data indicate that the volume of sales for the U.S. laundry detergent market was $4.7 billion in 1999 and, for the same market, the consumption of surfactants reached $7.2 million tons in 2002. In the European domestic market, the absolute figures for such consumption are higher because of the larger population; also it shows a trend toward greater growth (2, 3).

The diversity of existing anionic surfactants and their wide presence in both industrial products and the environment creates the need for analytic tools that facilitate their control or monitoring. Several monographs are currently available on the determination of detergents (4–7).

Since the first volumetric procedure was reported in 1948 by Epton, volumetric methods have become industry's standard approach for determining anionic surfactants (ISO 2271, ISO 2871-1 and ISO 2871-2), there being only a few variations between the different methods (8–11). These determinations are based on two-phase (one aqueous and one organic) volumetric titration using a standard solution of a cationic detergent, usually Hyamine 1622. Despite being widely used, however, there are a number of disadvantages to two-phase titration, in particular: (1) the long analytic time required, from 15 to 45 min; (2) the use of toxic solvents; (3) the need to perform blanks runs; (4) problems of interference in the matrix; and (5) the degree of subjectivity in determining the end point of the titration (12).

In contrast to Epton's classical two-phase titration there are several advantages to the use of surfactant selective electrodes, especially: (1) routine analysis can be easily automated and the procedure simplified, thus reducing analysis times to 2–5 min per sample; (2) the analysis complies with good laboratory practices; (3) lower consumption of reagents, without the need for

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Address correspondence to M. del Valle, Grup de Sensors i Biosensors (GSB), Departament de Química, Universitat Autònoma de Barcelona, Bellaterra E-08193, Catalonia, Spain. E-mail: manel.delvalle@uab.es

problematic solvents; (4) greater reliability in determining the end point (less subjective), the accuracy being equivalent to that obtained by standard methods; (5) the elimination of problems associated with the possible turbidity or coloring of the sample; (6) sample preparation is usually unnecessary, except for a possible dilution in order to create the ideal conditions for titration and make any necessary adjustments to pH; and (7) both anionic and cationic surfactants are normally responsive (13).

The use of selective electrodes in the analysis of detergents offers a viable alternative to standard procedures and, being simpler and more environmentally-friendly, they will become a competitive presence in the field of industrial monitoring once research shows that the technique is able to produce similar results to other methods (14). At present, one of the most important limitations of the technique concerns the direct determination of low concentrations, making it unsuitable for environmental monitoring if there is no prior preconcentration stage; in addition, the life of the devices is limited by the gradual loss of their response characteristics.

DEVELOPMENT OF POTENTIOMETRIC SENSORS

The first reports on the use of potentiometric sensors for determining anionic surfactants date back to the 1960s and 1970s, when, in the absence of selective electrodes for such surfactants, researchers proposed measuring these species through the interference they caused in other electrodes, especially the ion-selective electrode (ISE) of the calcium ion (15–19). Other proposed indirect alternatives included the use of the nitrate ISE in the ASTM D-4251-88 standard method (20) and employing ISEs based on tetraphenylborate (21).

The arrival of liquid membranes specifically designed to evaluate anionic surfactants, along with the consolidation of PVC membranes, ushered in a second stage of development featuring many different kinds of sensor. These, in turn, gave rise to the first commercial ISEs for anionic surfactants, something that industry had been calling for for many years as a potential alternative to the classical titration methods used in the analysis of both raw materials and final products.

Although the appearance of these commercial devices led, during a number of years, to less research being carried out into new membranes, the recent development of flow injection analysis (FIA) potentiometric techniques, the design of photocurable and electropolymerizable membranes, the introduction of microelectronic technology (in particular, ion-selective field effect transistors—ISFETs), and the growing interest in environmental problems are combining to revive research in the field of new potentiometric sensors for these species; it is in this context that previous contributions must be situated.

Among published reports there are some that can be considered particularly relevant due to their influence on subsequent lines of research and application. Figure 1 shows the evolutionary study of this field of sensors and lists chronologically what can be considered some of the most significant contributions.

The limited number of research groups working in this field means that scientific output is relatively low, as illustrated by the number of publications listed in the most oft consulted bibliographic databases (Figure 2).

With respect to the geographical distribution of contributions, analysis of the *CAPlus* and *Medline* databases for indexed publications (since the 1990s) related to the design of potentiometric sensors for anionic surfactants and their applications (ISE, ISFET, FIA, titration, physico-chemical studies, etc.) reveals a small number of research groups working in this area, most activity being carried out in Europe (Figure 3).

Liquid Membranes

The first potentiometric sensors selective for anionic surfactants were described at the time when supported liquid membrane devices were being developed. These used a sensor solution formulated as an ion exchange system based on ion pairs employed in detergents. Thus, Coetzee and Freiser reported

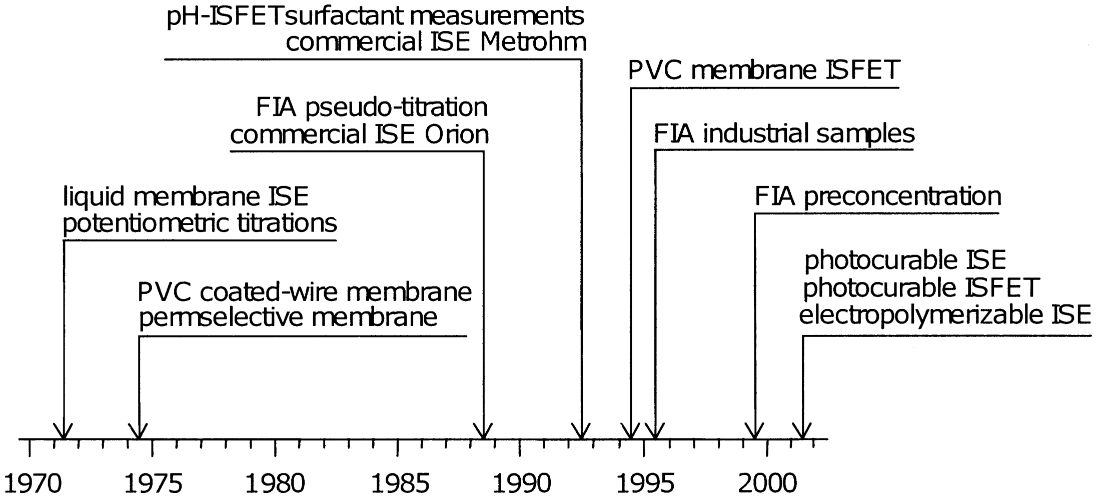

FIG. 1. Outstanding milestones along the development of potentiometric sensors for anionic surfactants.

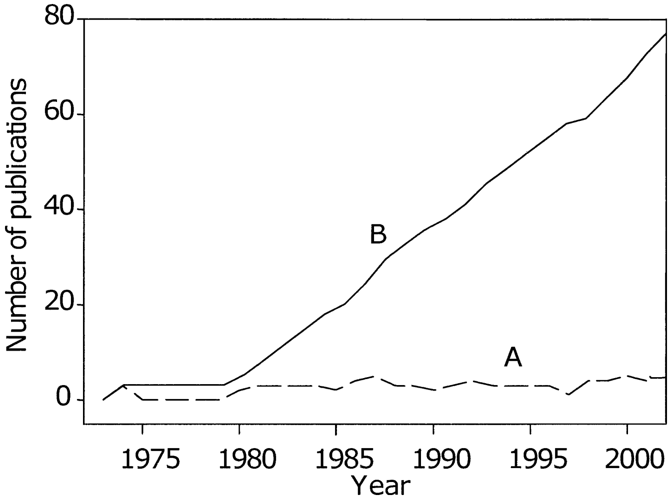

FIG. 2. Evolution of the number of publications referred to the study of potentiometric sensors for anionic surfactants and their applications. Information extracted from *CAPlus* and *Medline*. (A) Number of annual publications; (B) Number of total publications (cumulated).

a fairly universal system for the potentiometric detection of multiple anions based on the association that these were able to form with the trioctylmethylammonium ion in a 1-decanol medium (22, 23). Among the many ions assayed the system was also found to be responsive to *p*-toluensulfonate. However, the first truly selective electrodes designed specifically for anionic surfactants were probably those developed by Gavach and Bertrand in 1971, which were also used to determine values of the critical micellar concentration in various anionic surfactants (24).

A second important contribution was that of Birch and Clarke, researchers at Unilever Ltd. (England), who developed electrodes that responded to dodecylsulfate (25). Their applications included the potentiometric titration of various commercial detergents (26) and the monitoring of dodecylsulfate anion adsorption over numerous polymers and proteins (27).

In Japan, devices with a potentiometric response to anionic surfactants were created using ion pairs prepared from cationic colorants such as Crystal Violet (28) or other triphenylmethane derivatives (29). A noteworthy degree of selectivity was shown and reports described applications in potentiometric titration. In a subsequent study the same authors prepared a membrane formed by an ion pair comprising a surfactant cation and anion (30). When the electrode was used in the potentiometric titration of anionic detergents it showed excellent titration curves because the sensor material responded to both the anionic detergent being titrated and the titrant.

In a different approach Ciocan and Anghel (31) prepared a liquid membrane for dodecylsulfate using a Co^{3+} complex. The usual anions showed no interference and, by means of the pH of the medium, the selectivity of the response toward other surfactants could be heightened. The authors report the titration of various alkylsulfates (between C8 and C18), either alone or in binary mixtures (31). In a similar vein and three years later, Anghel and Popescu applied for a Romanian patent for a liquid membrane able to contain various metallic complexes, suitable for determining anionic detergents in oil residues (32).

At the same time, Hara's group reported a new membrane composition in which the addition of an alkylphenol allowed the membrane's selective response to be adjusted; this enabled the resolution of alkylsulfate mixtures by means of a single potentiometric titration, even though with other combinations this

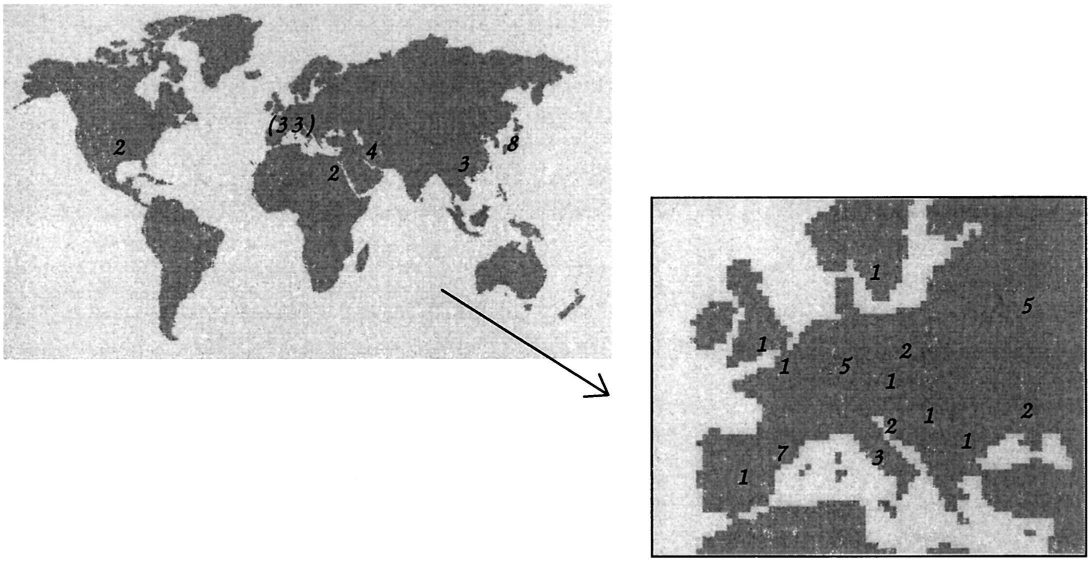

FIG. 3. Geographical distribution of the number of publications referred to potentiometric sensors for anionic surfactants and their applications beginning in the 1990 decade. *Source*: Indexed references from the *CAPlus* and *Medline* databases.

TABLE 1
Liquid membrane electrodes for anionic surfactants

Year	Composition of the membrane	Applications	References
1968/9	$TOMA^+$ TS^- in 1-decanol	1	22,23
1971	$HDPy^+$ A^- in nitrobenzene ($A^- = DS^-$, $TPBS^-$, $DOSS^-$)	1,2,3	24
1972	$HDTMA^+$ DS^- in nitrobenzene	1,3	25
1973	CV^+ A^- in nitrobenzene or 1,2-dichloroethane ($A^- = BS^-$, TS^-, NS^-)	1,3	28
1973/4	$HDPy^+$ DS^- in *o*-dichlorobenzene	1,2,3	26,27
1978	$DMGPCo^{3+}$ DS^- in *o*-dichlorobenzene	1,2	31
1980	$HDTMA^+$ DS^- in *o*-dichlorobenzene/*p*-tert-octylphenol	1,2	33
1980	VB^+ DBS^- in nitrobenzene	1,2	29
1981	Metal complex containing Fe or Ru, Os, Ag or Co in *o*-dichlorobenzene/1-decanol	2	32
1982	Hy^+ TPB^- in nitrobenzene	1,2	30
1984	$HDTBA^+$ A^- in *o*-dichlorobenzene/hexachlorobenzene/4-bromoacetanilide ($A^- = OS^-$, dS^-)	1,2,3	34
1987	$HDDMBA^+$ Ch^- in 1-decanol	1,2	35
1994	Mercurated polystyrene in 1,1,2,2-tetrachloroethane	1,3	36
2003	$HDPy^+$ DS^- in acetophenone	1,2,3	37

Applications: (1) Response characteristics, Calibration curves; (2) Potentiometric titrations; (3) Physico-chemical studies.

Abbreviations (in alphabetic order): A^-, generic surfactant anion; BS^-, benzenesulfonate; Ch^- cholate; CV^+, crystal violet; DBS^-, dodecylbenzenesulfonate; $DMGPCo^{3+}$, bis(dimethylglyoxime)-1,10-phenanthroline cobaltate(III); $DOSS^-$, dioctylsulfosuccinate; dS^-, decylsulfate; DS^-, dodecylsulfate; $HDDMBA^+$, hexadecyldimethylbenzylammonium; $HDPy^+$, hexadecylpyridinium; $HDTBA^+$, hexadecyltributylammonium; $HDTMA^+$, hexadecyltrimethylammonium (or cetyltrimethylammonium, CTA^+); Hy^+, Hyamine 1622; NS^-, α-naphthalenesulfonate; OS^-, octyl sulfate; $TOMA^+$, trioctylmethylammonium; TPB^-, tetraphenylborate; $TPBS^-$, tetrapropylenebenzenesulfonate; TS^-, *p*-toluenesulfonate; VB^+, Victoria blue.

procedure gave the total amount of anionic surfactants (33). This type of electrode was subsequently studied again by Kresheck et al., who by including various additives in the formulation, managed to increase the ionisation of the ionizable components, thus enabling the determination of analytes such as octylsulfate and decylsulfate (34).

Campanella showed how a membrane developed for the cholate ion (derived from a biliary acid) enabled the determination of certain anionic surfactants, in particular, dodecylsulfate, dodecylbenzenesulfonate and dioctylsulfosuccinate. The linear working ranges were somewhat reduced and the observed sensitivity varied between 55 and 75 mV/dec (35).

Despite the fact that electrodes based on liquid membranes seem to be being used less and less there have been two recent contributions along this line. Szczepaniak used a new polymeric sensor, a mercurated polystyrene, to study the physico-chemical properties of solutions of the most common anionic surfactants and to enable their potentiometric titration (36). This sensor also showed a weak response to anions such as Cl^- and NO_3^-. Finally, Arvand-Barmchi et al., using already described sensor materials, provided the first report of super-Nernstian responses (108 ± 2 mV/decade) at low concentrations of dodecylsulfate (1.0×10^{-9} to 1.0×10^{-6} M) (37).

Despite being easy to build, liquid membrane electrodes have proved ineffective for many applications. The main limitations result from the lack of mechanical robustness and the loss of response stability, due to the progressive loss of the sensor material in the aqueous solution under study. Nevertheless, at the time they were of interest for thermodynamic studies of detergent solutions and in establishing potentiometric titration methodologies in the laboratory. The need for continuous recalibration, due to the temporal variability of their response, makes it difficult to apply liquid membranes in direct potentiometric techniques. By way of a summary, Table 1 shows the evolution of those liquid membranes considered to be of most interest.

PVC Polymeric Membranes

Since the first reports by Moody and Thomas showing the possibility of keeping liquid membranes immobilized on PVC there has been a rapid development of new sensor formulations (38, 39).

The most widely used formulation has followed the guidelines of its discoverers and consists, basically, in the preparation of sensor membranes with three components: ionophore, plasticizer and PVC. Figure 4 shows the typical formulation of a PVC membrane. It is assumed that the basic analytical response of the membrane depends mainly on there being a suitable combination of the plasticizer and the electroactive substance. Secondarily, the selectivity of the ISE may be easily altered by modifying the relative proportions of the membrane components.

The plasticizer, in particular, has a dual function: It acts both as a liquefying agent, enabling the homogenous solubilization

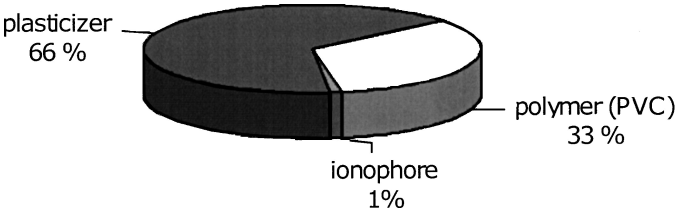

FIG. 4. Typical formulation for a PVC matrix potentiometric membrane.

of the membrane's ion pair, and serves to modify the value of the distribution constant of the ion pair used. The proportion of plasticizer used must be optimized in order to minimize the electrical asymmetry of the membrane, to keep the sensor as clean as possible, and to stop it leaching to the aqueous phase (40). The nature of the plasticizer has a marked influence on sensitivity, the linear range and the possible response to interferents, and must be chemically compatible with both the polymer and the sensor material; it must also reduce the value of the membrane's electrical resistance. As will be seen below in the discussion of the various assayed formulations, the most popular plasticizers for PVC membranes are currently *o*-nitrophenyloctyl ether and *o*-nitrophenylphenyl ether (41).

A further advantage of polymeric membranes is that they can be adapted to various electrode designs, the choice of one form or another determining the potential applications of devices. In what follows, we describe the various contributions made in this field.

Conventional ISEs

The most widely used method for preparing these devices involves dissolving the sensor cocktail in an appropriate organic solvent, such as tetrahydrofuran or cyclohexanone. The evaporation at room temperature of this mixture produces films that can be sliced and mounted on the body of an electrode filled with a reference system, normally Ag|AgCl. These selective electrodes, regardless of whether they include an internal reference solution, are known as "conventional ISEs".

In terms of conventional ISEs the first PVC membrane to respond to a surfactant species was described by Ishibashi et al. in 1973, who reported the characterization of a membrane using the species 1-naphthalenesulfonate (42). The first selective electrode with a PVC membrane designed specifically for anionic surfactants was described the following year and patented by the group of Tanaka in Japan (43, 44). The membrane's sensor material comprised a mixture of two ion pairs, formed by the ferroin cation with an alkylbenzenesulfonate and perchlorate. The response obtained during the study of alkylbenzenesulfonate solutions was found to be between 10^{-6} M and 10^{-2} M of primary ion, although the sensors selectivity and reproducibility fell short of the ideal.

Much better results were obtained with the membrane described three years later by Cutler et al., who used the association between an anionic and a cationic surfactant as an ionophore (45). This electrode responded generally to ionic surfactants, although it showed low selectivity between different surfactants of the same charge; however, it was found to last longer than other electrodes previously described in the literature.

At the beginning of the 1980s a number of reports were published that took a different approach and reconsidered the classical three-component formulation for sensors. Indeed, a membrane comprised solely of a polymeric matrix and a suitable plasticizer was found, after a period of "learning," to be capable of providing satisfactory results in potentiometric titrations. This work was based on the idea that it is the ion pair which is formed during the titration, the carrier agent which will be incorporated into the membrane. Thus, by means of the first titrations the membrane will gradually become saturated with the ion pair until an optimum level is reached in the plasticizer, determined by the corresponding value of the distribution constant. Furthermore, this progressive incorporation avoids an overconcentration in the membrane, which could lead to deterioration in its detection limit. If the titration system is eventually modified only two or three new titrations will be necessary to re-establish the balance for the new ion pair (46).

Dilley, a researcher with Shell Chemicals, reported a membrane comprising PVC and tricresylphosphate. The electrodes containing it showed a working life of at least five months and were used to determine the active anionic material in detergents, the results being similar to those obtained using Epton's method (47). A few years later Ishibashi described a different formulation of the two components, using *o*-nitrophenyloctyl ether as the plasticizer (48). The published data revealed the membrane to have a sub-Nernstian response to lipophilic ions, including a number of surfactant agents such as dodecyltrimethylammonium, dodecylsulfate, and tetradecylsulfate ions. Among inorganic ions, only the interference of perchlorate was important.

An ionophore initially developed by Campanella's group for cholate determination was subsequently used with the standard approach for preparing polymeric membranes. The results obtained with the new form were similar to those for the liquid membranes already described (49).

An extensive study aimed at investigating various forms of ionic surfactants was presented in Barcelona in 1992 during the VI Jornadas de la Detergencia (6th Annual Meeting on Detergency) (50). The study, carried out by Buschmann and Schulz, demonstrated a new sensor membrane, plasticized with *o*-nitrophenyloctyl ether and containing an additive to improve electrical conductivity, that required no preconditioning. Good results were obtained in the potentiometric titration of the ISEs prepared, solutions of dodecylsulfate, and Hyamine being used as the anionic and cationic standards, respectively.

The following year a report described the synthesis of various ionophores for anionic surfactants with the use of the ion pair formed by tetradodecylammonium and dodecylbenzenesulfonate in order that they be incorporated into PVC membranes plasticized with *o*-nitrophenyloctyl ether (51). One of the most

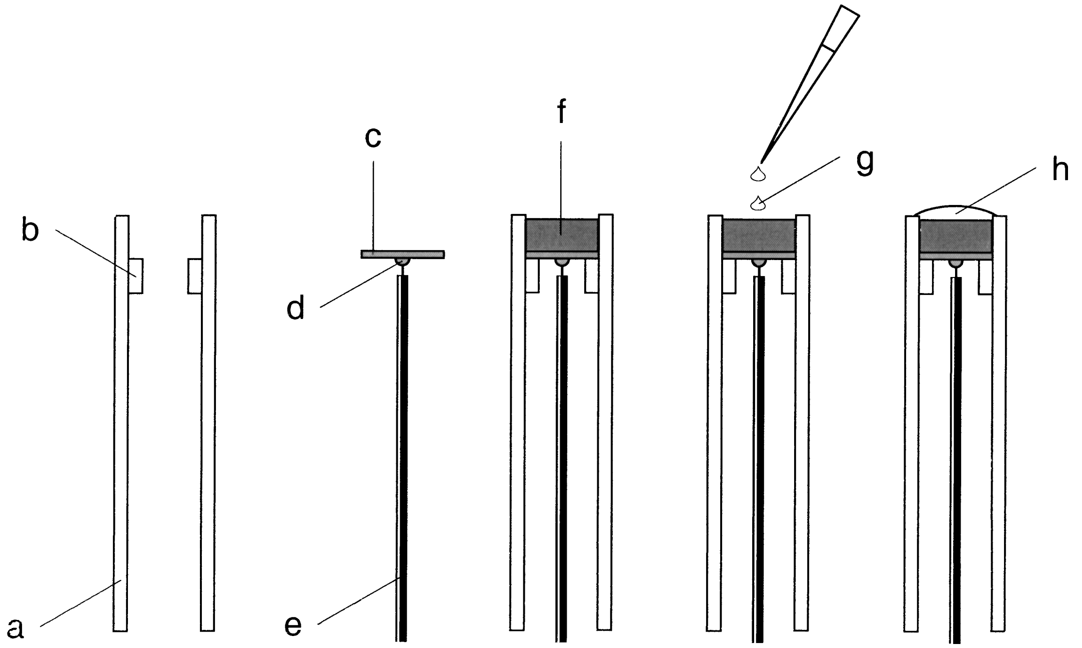

FIG. 5. Construction of all-solid-state ion-selective electrodes employing a polymeric membrane. (a) perspex tube; (b) inner PVC ring; (c) cupper disc; (d) solder; (e) shielded cable; (f) deposition of the conductive paste; (g) deposition of the cocktail membrane; (h) sensing membrane.

interesting characteristics of these electrodes proved to be the direct application of the sensor membrane onto a conductive surface of optimized epoxy/graphite, thus avoiding the need for an internal liquid reference system and, at the same time, enabling the possibility of using the electrodes for a variety of applications (see schematic in Figure 5). The new formulations gave good results when compared with an Orion surfactant ISE, showing better selectivity and dynamic response characteristics. Subsequently, these electrodes enabled the automated titration of anionic surfactants in routine analysis, giving comparable values to the reference method (52).

At the beginning of the 1990s, Metrohm began to commercialize its first ISEs for detergents. Its sales strategy involved supplying a complete titration system that included a new titrant for anionic surfactants, a product registered as TEGOtrant A100. Gerlache et al. designed a membrane that included this cation within the ionophore and, using the same TEGOtrant A100 solutions in the titration, obtained good results in the potentiometric determination of household detergents, in accordance with the two-phase titration (53). Since their use as titrants has already been mentioned, Figure 6 shows the structure of the two cationic standards most widely used for the potentiometric titration of anionic surfactants, namely, Hyamine 1622 and TEGOTrant A100.

Coated-Wire Electrodes

Another design adopted by these polymeric membranes is that of coated-wire electrodes, which appeared at the beginning of the 1970s (54,55). These devices have been quite widely used in the laboratory due to their simplicity and low preparation costs. The basic procedure for producing the membrane involves repeatedly introducing a conductive material (a wire of Pt, Ag, Cu, or Al, or a graphite rod) into a sensor cocktail and allowing the solution that forms the membrane to evaporate (after each immersion) until a polymeric film of an acceptable thickness is obtained.

Among the characteristics of these electrodes, it is worth noting that their potentials drift significantly over time and,

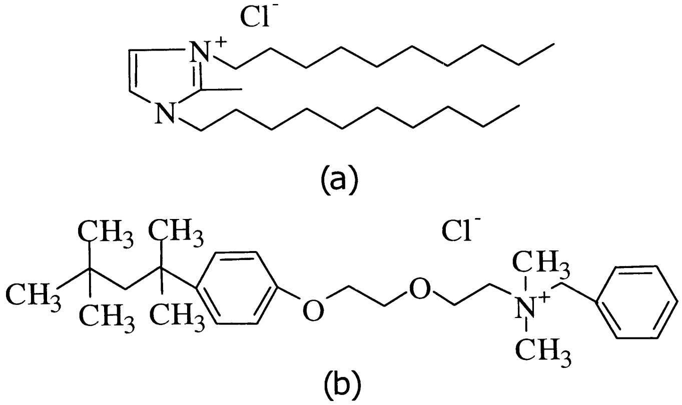

FIG. 6. Chemical structure of standards used as cationic surfactants. (a) 1,3-didecyl-2-methyl-imidazolium chloride (TEGOtrant A100); (b) benzyldimethyl[2-[2-(p-1,1,3,3-tetramethylbutylphenoxy)ethoxy]ethyl]ammonium chloride (Hyamine 1622).

moreover, tend to be irreproducible, even when the formulation of the coating includes a suitable exchange complex. However, these electrodes are very useful for detecting the end point in titrations where all that is required is a sufficient potential jump. For other requirements conventional membrane electrodes provide better results.

The first coated-wire electrode for anionic surfactants was prepared by Fujinaga et al. in 1974 by adapting the experience gained by some group members using the same ionophore over liquid membranes (22, 56). On this occasion the electrode showed important interference with inorganic ions and overall responses to various alkylbenzenesulfonates. Vytras was the first to report a device coated with a two-component membrane (57). After testing various PVC plasticizers, some of which were already described in the literature, the author concluded that devices incorporating *o*-nitrophenyloctyl ether produced steeper and more symmetrical titration curves; he, thus, recommended their use in the titration of both anionic and cationic surfactants.

Dowle et al., with the backing of the company ICI, developed a solid-state electrode by coating a graphite rod with a polymeric membrane. In terms of its application they devised a technique for the titration of both anionic and cationic surfactants resulting from the elution of commercial samples by ionic exchange, in combined media of chlorhydric acid/ethanol (58, 59).

The research groups from the universities of Osijek (former Yugoslavia) and Pécs (Hungary) have worked on various electroactive elements for detergent electrodes. Starting from a PVC membrane plasticized with tricresylphosphate, they have applied various combinations of surfactant cations and anions, and, following a comparative study, chose the association between Hyamine and dodecylsulfate as the most suitable ion pair for potentiometric determinations (60, 61).

Garrison and Phillippi, researchers at Clorox Co. (USA), used an ionic exchange material comprising, basically, the two-phase titration indicators dimidium bromide and disulphine blue to prepare coated-wire electrodes useful for the titration of many kinds of detergents. Although these devices and their applications have been patented there are, to our knowledge, no references in the scientific literature that describe or discuss their response characteristics (62).

Szczepaniak took an ionophore developed initially for liquid membranes and used it in plasticized PVC systems, observing the effect of different plasticizers (63). Among these, Nernstian responses were achieved with *o*-nitrophenyloctyl ether and dibutyl phthalate, there being high selectivity for various anionic surfactants. Although the study illustrates the possibility of carrying out various potentiometric titrations the fact that the response is highly dependent on the pH of the medium limits the potential applications of the membrane.

In another study, Vytras tested a new PVC membrane plasticized with 2,4-dinitrophenyloctyl ether which offered the possibility of titrating various kinds of surfactant, even in mixed systems. However, despite their great potential the electrodes prepared proved only to be of interest in research laboratories (64).

More recently, Mategic-Puac et al. developed a membrane based on a PVC matrix incorporating the sensor material tetrahexadecylammonium dodecylsulfate. This new membrane, applied over a conductive surface of teflonated graphite, enabled the determination of both soaps and mixtures of soaps with other anionic detergents, hexadecyltrimethylammonium bromide being used as the titrating agent and the pH of the test medium being adjusted accordingly (65).

Flow Injection Potentiometry

Another methodological problem is that associated with potentiometric detection in continuous flow. In terms of determining anionic surfactants, research contributions have been very limited; this is due mainly to the experimental problems associated with the flow system, having to adapt electrodes to the new manifolds, and, with respect to potential environmental applications, the intrinsic limited response shown by these devices at low concentrations.

The first study to report the potentiometric Flow Injection Analysis (FIA) detection of anionic detergents was that of Frend et al. in 1983 (18). This work was derived from the observed effect of anionic surfactants on calcium ISEs mentioned above.

Using membranes developed for anionic surfactants Dowle et al. (66) reported in 1988 the results of some pseudotitrations in flow based on the use of tubular electrodes comprising graphite tubes coated on the inside with a membrane designed previously by the same researchers (58). Although the flow system responded to different surfactants the presence of certain hydrodynamic problems, resulting from the electrode design, and an unstable response, due to the choice of membrane, meant that the electrodes showed poor precision and lasted only a few weeks.

Subsequently, systems for building selective electrodes developed by the Sensor and Biosensor Group at the Universitat Autònoma in Barcelona served as the basis for a number of simple and versatile all-solid-state potentiometric detectors for continuous flow measurements and applicable to anionic surfactants (67). The tubular electrodes, containing a previously studied formulation (51), were used to monitor commercial alkylsulfates found in metal plate cleaning baths. The process of collecting and processing data, using a PC incorporated into the system, enabled 30 samples/h to be analysed, with relative errors of around 1.1% and excellent reproducibility. By way of an example, Figure 7 shows a simple FIA set-up for the automated determination of anionic surfactants using potentiometric sensors.

Gerlache et al. reported a possible application for the online measurement of anionic detergents in surface water, taking advantage of the good behavior shown by the membrane in potentiometric titrations (53). However, the adaptation of a conventional electrode for flow measurements and the detection limit of the membrane itself, within the concentration range of the analytes to be determined, appear to place significant

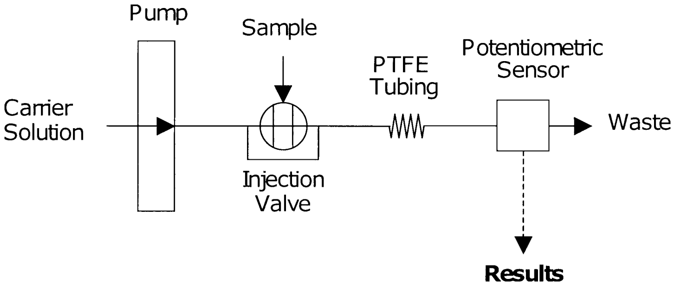

FIG. 7. FIA manifold for the determination of surfactants employing the FIA technique with potentiometric detection.

limitations on the described assembly. An alternative approach is to use the membrane as a potentiometric detector (wall-jet design) in a microflow HPLC system (68). Here, the ability to respond to multiple anionic surfactants makes the device a potential detector for this group of substances and, moreover, one that may respond in various orders of magnitude, due to the way the response varies with the logarithm of the species concentration. Furthermore, in this case the technique used has the advantage of being able to discriminate between the different components of commercial formulations.

Martínez-Barrachina et al., using online preconcentration columns, devised the first FIA potentiometric system able to determine traces of these species in real matrices (69). The application, based on the use of previously studied tubular electrodes (67), reduces by 1–2 orders of magnitude the detection limit of the membranes described for these species, enabling the quantification of small concentrations (0.1 μM of dodecylsulfate) in favorable analytic conditions, with a speed of analysis of 10 samples/h and accuracy variation of around 2 percent (RSD). This research has led to the design and development of an automatic analyzer for anionic surfactants, one that is suitable for environmental measurements.

Likewise, it has been shown that anionic surfactants in environmental samples can be determined using low-cost electrodes—that are easy to make and store—by coating a graphite rod with a PVC membrane. The lineal range indicated is between 10^{-3} and 10^{-6} M and the system is able to determine 50–80 samples/h (70). More recently, Hassan et al. described a new sensor for anionic surfactants developed and used for FIA. The sensor is used satisfactorily to measure dodecylbenzene sulfonate anion in different wastewater samples, commercial detergent products, and for monitoring the rate of surfactant biodegradation in sewage treatment plants (71).

ChemFETs

In recent years a new area of study in the field of sensors is that concerning chemically modified field effect transistors, which are being introduced as an alternative to ion-selective electrodes due to the possibility of their rapid response, reduced size and potential low cost. Figure 8 shows a measurement system that uses an ISFET sensor. Unfortunately, the technology required

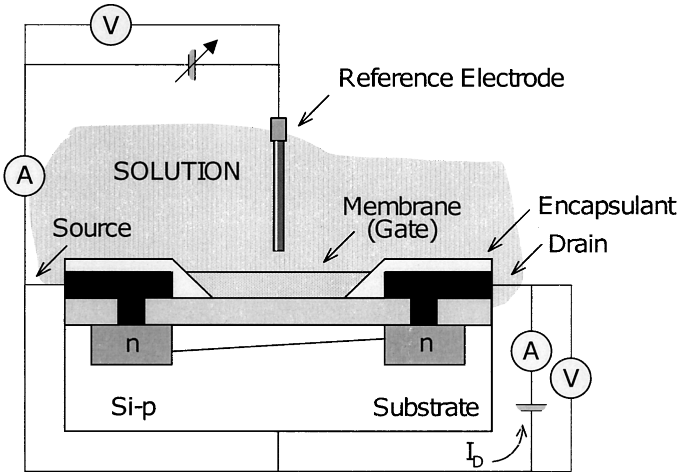

FIG. 8. Measuring scheme used with Ion Selective Field Effect Transistors (ISFET sensors).

and the difficulty of improving the working life of these devices means that few research groups have yet to explore this line of study.

The first ISFET measurements of anionic surfactants were reported by Masadome et al. in 1992, who used a simply assembly based on a pH ISFET immersed in a plasticizer (72). In this case, therefore, no membrane was applied to the device, the purpose being solely to establish the role of the plasticizer in the response mechanism of certain membranes developed by the same group and in which there was no ionophore (48).

Subsequently, a report was published on the application to ISFETs of a PVC membrane developed for the cholate ion, a design known as the ChemFET (73). These devices show super-Nernstian behavior and, surprisingly, the study found that the detection limit of the membrane designed by the authors for other formats was improved, the new design proving suitable for environmental analysis in continental and marine waters (49). Indeed, some of the improvements described in this report may result from the particular way in which the device was characterized, which was not entirely in keeping with IUPAC recommendations.

A PVC membrane ChemFET designed specifically for anionic surfactants was prepared in 1999, transferring the good results provided by the previously-designed membrane in potentiometric titrations and FIA systems (74). Having characterized the device's response to various surfactant anions and the cation Hyamine 1622, the authors described its application in the potentiometric titration of numerous anionic detergents and commercial samples containing them, the results obtained being perfectly consistent with the standard two-phase method. The suitability of the membrane is defined by the particular composition of the ionophore, which responds to both anionic surfactants and the test solution. Noteworthy characteristics of the device include its working life of over four months and its Nernstian response to the primary ion.

Other Membranes

Although most membranes described in the literature are developed over PVC matrices, other approaches have also begun to appear, mainly in an attempt to improve selectivity. A chronological summary of these approaches, in terms of both formulations and proposed applications, is shown in Table 2.

Initial efforts were focused on the study of membranes based on a silicon rubber matrix using the ion pair formed by hexadecyltrimethylammonium and dodecylsulfate as the electroactive material (75, 76). This electrode enabled the titration of millimolar solutions of dodecylsulfate with hexadecylpyridine bromide, mainly because of its response to the cation.

In 1977, at the time when PVC membranes were becoming widely used, Cutler et al. published an extensive comparative study in which they highlighted the strengths of PVC compared with other polymers in the preparation of membranes comprising the same ionophores and plasticizers, but based on polybutadiene, polymethylmetacrylate, and polystyrene matrices. Relatively acceptable results were only obtained when substituting vinyl polychloride with its equivalent vinyl polybromide (45). Following another research line the same authors sought to functionalise suitably the PVC chains in order to fix the electroactive material and, thus, avoid or reduce its progressive solubilisation. In the case of a membrane selective to anionic surfactants the synthesis involved, first, placing a nitrogen atom at the end of the polymer chain and then quaternizing it. Then, in a subsequent process, the anion fixed to the chain was exchanged for its corresponding surfactant anion. Despite the changes carried out the authors acknowledge that the problem of the loss of plasticizer into the aqueous medium remains to be resolved. Using a similar procedure Xu and Bloor recently prepared membranes with Nernstian behavior and a working life of over six months, the membranes being maintained in solutions of the primary ion between successive applications (77).

The group of Hayakawa recently reported modified PVC membranes synthesised by means of the co-polymerisation of vinyl chloride and 3-acrylamido-N,N-dimethylpropylamine in different ratios, followed by alkylation of the amine segments with methyl iodide. In mixtures of SDS and other surfactants the electrode response was examined and the selectivity coefficient (K^{pot}) for the added surfactant was determined. The charge density of the functional membrane altered the K^{pot}: the greater the charge density of the membrane, the greater the K^{pot} value. Two membrane electrodes with different K^{pot} were used to determine the concentration of each component in a binary surfactant mixture. They determined the concentration of the primary surfactant with reasonable accuracy, but there was a large error in determining the concentration of the secondary surfactant (78). The principle illustrated here, namely, the use of sensor matrices with cross sensitivity combined with the processing of complex data, represents clear progress in the field of sensors and, in our case, enables the determination and individual quantification of surfactant mixtures (79).

Recently, a number of studies have been published describing the use of mixed membranes comprising PVC and polypyrrole, the latter obtained by electropolymerisation. Alizadeh et al. reported a new dodecylsulfate sensor prepared electrochemically by anodic polymerization of pyrrole in the presence of dodecylsulfate ions in aqueous solution (80). The same researcher later synthesized the association between this conductive polymer and dodecylbenzenesulfonate as an electroactive material (81). This material forms part of the classical cocktail for membrane formation, with Hyamine as the additive. Although the membrane has been successfully tested in titrations of anionic detergents in different methanol/water media, its response is sub-Nernstian and highly dependent on the proportion of components used. An optimized formulation of this PVC membrane, incorporating the ion pair formed by polypyrrole and dodecylbenzenesulfonate as an anionic exchanger, has shown response characteristics as good as any reported to date (82).

In another approach, the groups of Kóvacs and Ivaska grew a coating of polypyrrole over a teflonized graphite tube with the aim of creating a solid and thermodynamically stable internal electrical contact (83). Different formulations, prepared in accordance with the usual proportions of the cocktail, were tested on this polymer and titrated in flow systems, this enabling the detection of anionic surfactants in the range 10^{-6} M to 10^{-3} M and the analysis of 30 samples/h.

More surprising were the findings reported recently by Mousavi et al., who described a new electrode for the dodecylsulfate anion based on the electropolymerization of aniline in the presence of the surfactant anion on a Pt surface (84). According to the authors, the new device shows Nernstian behaviour at trace levels, a linear working range of 1.0×10^{-9} to 3.0×10^{-6} M and a detection limit on the nM scale, improving by almost three concentration decades the best results published so far. Although certain aspects of the preparation are new, the materials of which the final device is comprised have already been implanted on other electrodes, and thus the results should be treated with caution as they do not cease to be exceptional. In another work, the same author has reported a new dodecylbenzenesulfonate sensor based on polyaniline-coated electrode. The device exhibits an excellent Nernstian slope over a wide concentration range (5.0×10^{-6} to 4.1×10^{-3} M). The proposed electrode revealed good sensitivities for dodecylbenzenesulfonate anion and can be used in the pH range of 5–10 in real samples (85).

In terms of the application of membranes to other devices, particularly ISFETs, the solutions assayed on the selective electrodes present certain technical limitations. These include the manual process of applying membranes and the problems derived from their low adherence to the transistor gate (which may lead to variable responses being obtained among the different units prepared), a certain drift in the potential response, and, finally, a limited working life of, at best, a few months. These problems mainly limit the large-scale preparation of these new sensors. One of the strategies currently being considered in

TABLE 2
Other electrodes for anionic surfactants

Year	Composition of the membrane	Applications	Configuration	References
1973	PVC, DOP, TDDMBA$^+$ or TOMA$^+$, NS$^-$	1	A	42
1974	PVC, 1-decanol, TOMA$^+$ ABS$^-$	1,5	C	56
1974	Silicone, HDTMA$^+$ DS$^-$	2	A	75,76
1974/5	PVC, DOP, ABS$^-$/ClO$_{4^-}$ ferroin^{2+}	1	A	43,44
1977	PVC, TCP, HDTMA$^+$ DS$^-$ or PVC/PVC$^+$, TCP, DS$^-$	1,5	A	45
1980	PVC, TCP	2	A	47
1981	PVC, NPOE	2	C	57
1986	PVC, NPOE	1	A	48
1987/8	PVC, TCP, HDTMA$^+$ PS$^-$	1,2	C	58,59
1988	PVC, TCP, HDTMA$^+$ PS$^-$	2,4	D	66
1988	PVC, DOS, HDDMBA$^+$ Ch$^-$	1,3	A	49
1989	PVC, TCP, Hy$^+$ DS$^-$ or HDTMA$^+$ DS$^-$ or HDTMA$^+$ DDS$^-$ or HDTMA$^+$ ODS$^-$	1,2	C	60,61
1989	PVC, TCP, DMBr/DB	2	C	62
1990	PVC or PVC/PS, NPOE or DBP, mercurated polystyrene	1,2	C	63
1991	PVC, DNPOE	2	C	64
1992	PVC, NPOE, Na$^+$ TFMPB$^-$	2	A	50
1993/4	PVC, NPOE, TDA$^+$ DBS$^-$ or Hy$^+$ DBS$^-$	1,2	B	51,52
1994	PVC, DOS, HDDMBA$^+$ Ch$^-$	1	E	73
1995	PVC, NPOE, TDA$^+$ DBS$^-$	1,4	D	67
1997/8	PVC, NPOE, TEGO$^+$ DS$^-$	1,2,4	A, C	53,68
1999	PVC, NPOE, TDA$^+$ DBS$^-$	1,2	E	74
1999	PVC, NPOE, TDA$^+$ DBS$^-$	1,4	D	69
2000	PVC/PVC$^+$, Elvaloy 742, DS$^-$	1	C	77
2000	PVC, NPOE, PPy$^+$ DS$^-$	1	A	80
2001	PVC, NPOE, PPy$^+$ DBS$^-$, Hy$^+$ Cl$^-$	1,2	A	81
2001	PPy, PVC, NPOE, HDTMA$^+$ SS$^-$ or DDMA$^+$ TPB$^-$ or TOA$^+$ DS$^-$	1,4	B	83
2001	PU-Acr, HDDA, DMPAP, CPOE, TDA$^+$ DBS$^-$	1	B	86
2001	PU-Acr, HDDA, DMPAP, CPOE, TDA$^+$ DBS$^-$	1,3	E	87
2002	Pt | PA$^+$DS$^-$	1	C	84
2002	PVC, NPOE, THDA$^+$DS-	1,2	C	65
2002	PVC, DBP, NB, ThDA$^+$DBS$^-$	1,4	D	70
2003	PVC-ADPA, Elvaloy 742	1	B	78
2004	PVC, NPOE, PPy$^+$ DBS$^-$	1,2	C	82
2004	PVC, DOP, TDMAC	1,4	D	71
2004	Pt | PA$^+$DBS$^-$	1	C	85

Applications: (1) Response characteristics, Calibration curves; (2) Potentiometric titrations; (3) Incremental potentiometric methods; (4) Flow measurements; (5) Physico-chemical studies.

Configuration: (A) Conventional electrode with inner reference solution; (B) Conventional electrode without inner reference solution (all-solid-state); (C) Coated-wire electrode (CWE); (D) Tubular electrode, flow-through cell; (E) Ion-selective field-effect transistor (ISFET).

Abbreviations (in alphabetic order): ABS$^-$, alkylbenzenesulfonate; ADPA, 3-acrylamido- N,N-dimethylpropylamine; Ch$^-$, cholate; CPOE, 2-cyanophenyl octyl ether; DB, disulfine blue; DBP, dibutyl phthalate; DBS$^-$, dodecylbenzenesulfonate; DDMA$^+$, didodecyldimethyammonium; DDS$^-$, dodecansulfonate; DMBr, dimidium bromide; DMPAP, 2,2'-dimethoxy-2-phenylacetophenone; DNPOE, 2,4-dinitrophenyl n-octyl ether; DOP, dioctyl phthalate; DOS, bis(2-ethyllhexyl)sebacate (or dioctylsebacate); DS$^-$, dodecylsulfate; HDDA, hexanediol diacrylate; HDDMBA$^+$, hexadecyldimethylbenzylammonium; HDTMA$^+$, hexadecyltrimethylammonium; Hy$^+$, Hyamine 1622; NB, nitrobenzene; NPOE, *o*-nitrophenyloctyl ether; NS$^-$, α-naphtalenesulfonate; ODS$^-$, octadecylsulfate; PA$^+$, polyaniline; PPy, polypyrrole; PPy$^+$, doped polypyrrole; PS, polystyrene; PS$^-$, 1-pentanesulfonate; PU-Acr, acrylated polyurethane; PVC, poly(vinyl chloride); PVC$^+$, charged PVC; SS$^-$, 1-octadecanesulfonate (or stearyl sulfonate); TCP, tricresyl phosphate (or tritolyl phosphate); TDA$^+$, tetradodecylammonium; TDDMBA$^+$, tetradecyldimethylbenzylammonium; TDMAC, tridodecylmethylammonium chloride; TEGO$^+$, 1,3-didecyl-2-methyl-imidazolium (TEGOtrant^R A100); TFMPB$^-$, tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate; ThDA$^+$, triheptyldodecylammonium; THDA$^+$, tetrahexadecylammonium; TOA$^+$, tetraoctylammonium; TOMA$^+$, trioctylmethylammonium; TPB$^-$, tetraphenylborate.

response to these limitations involves reformulating the membranes in order to enable them to be implemented automatically, while one of the research lines being explored consists in designing membranes based on new photocurable polymers capable of being manipulated via photolithography procedures. Thus, in order to overcome these limitations the first photocurable membrane for anionic surfactants has now been prepared, characterized, and optimized (86). A novel feature of this membrane is that it includes a new polymeric matrix of urethane acrylate, plasticized with 2-cyanophenyloctyl ether, and the available experimental data suggest that this reproduces the good behavior of the *o*-nitrophenyloctyl ether present in PVC compositions. The membrane has been applied to ISFETs and enabled the clean and environmentally relevant monitoring of photodegradation processes using TiO_2 dispersions (87).

Commercial Electrodes for Anionic Surfactants

There are three main companies involved in the manufacture of selective electrodes for anionic surfactants, although others have sought to develop them and many firms sell them (88). However, some of these products are restricted to limited geographical areas due to the minor presence of some manufacturers in the international market.

The first commercial electrode for surfactants was designed by the U.S. firm Orion Research (now Thermo Electron Corporation, Beverly, MA) and launched in 1988. The electrode was marketed as model 9342BN and, at first, was available as part of the Orion 960 Autochemistry Surfactant System, providing an automated alternative to the manual methods widely used at the time. The procedures offered by the company were mainly centerd on the routine determination of anionic surfactants in industrial monitoring, and for household products such as toothpaste, shampoos, and domestic cleaning agents; the titration time under favorable conditions was 2 to 5 min (89).

Electrode 9342BN responds to both anionic and cationic surfactants and is designed to be used in potentiometric titrations (90). According to manufacturer's data, it is a plastic membrane indicator electrode noteworthy for its working range (between 2 and 12 units) and its detection limit for anionic surfactants, around 10^{-5} M. During use, the analytic requirements are determined by the type and concentration (between 10^{-2} M and 10^{-5} M) of the detergent samples. For anionic, sulfate, and sulfonate samples the titration is carried out with Hyamine 1622, the sample being acidified, if necessary, with HCl or citric acid ($2.5 < \text{pH} < 4.5$). In the case of determining cationic detergents, the pH must be around 3 and can be corrected through the addition of the same acids; standard solutions of sodium dodecylsulfate are used as the titrant. The manufacturer's general recommendations include the need to dilute the samples as much as possible and to prevent, by gentle shaking, an excessive froth from forming, as this may lead to erroneous results. Orion procedures also recommend using an additive, Triton^{R} X-100 (a non-ionic surfactant), in all samples in order to help keep the membrane clean and in good working conditions, along with the use of acidulated water to clean the electrode between different samples (91). This electrode has been used by various researchers in the study of new applications (92).

The advantages of using this electrode include its objectivity in determining the end point of titrations, the reduced analysis time and the elimination of harmful organic solvents from the analytic procedures. Despite this, however, potentiometric techniques were not immediately introduced into the routine analysis of detergents. One of the reasons for this was resistance to change on the part of quality control laboratories, which had been relying for many years on widely used and well-known methods. A second problem was related to slight discrepancies in the results obtained via the two methods in the analysis of certain real samples.

In terms of the European market, by 1975 the Swiss company Metrohm had already begun to recommend the use of PVC-based ISEs (for nitrate, calcium, and tetrafluoroborate) in detergent titrations. This company currently offers the widest range of selective electrodes for surfactants, as well as numerous applications (93, 94). The first electrode specifically designed by Metrohm for surfactants was launched in 1992 (the 6.0504.150 High Sense Surfactant Electrode). This was followed in 1995 by the NIO Surfactant Electrode 6.0507.010, for nonionic surfactants, and the Ionic Surfactant Electrode 6.0507.120; 1996 saw the launch of the Surfactrode Resistant 6.0507.130 for the two-phase potentiometric titration of ionic surfactants, followed in 1998 by the Surfactrode Refill 6.0507.140, for the same kind of application. The latter two electrodes are resistant to organic solvent media, the only ones with such characteristics to be commercially available (95). Below, we will focus on the range of these commercial electrodes for use with ionic surfactants.

The High Sense Surfactant Electrode is based on a typical three-component PVC membrane. Anionic detergents (except for soaps) are titrated with this electrode at $\text{pH} = 3$, the use of TEGOtrant^{R} A100 standard solutions being recommended. If the sample matrix contains nonionic surfactants (as is commonly the case in many household products) then the addition of methanol to the medium produces titration curves that are easier to interpret.

For the determination of surfactant ions in aqueous medium Metrohm currently proposes using the Ionic Surfactant Electrode, which is now available in a solid-state design. Experience with the first model, the High Sense, showed that the electrode lost its electroactive material during its working life, this being the result of the ion exchange equilibriums to which it was subjected. The new design, comprising a long graphite rod coated with a PVC membrane, produces comparable results with a longer working life.

Some of the limitations associated with the use of the above-mentioned electrodes are overcome by the Surfactrodes. The first of these, the Surfactrode Resistant, contains, as an electroactive element, ionically-modified silicone acrylate polymerized over a conductive material (graphite); this prevents it from being eliminated by organic solvents. In the second model, the Surfactrode

Refill, the ionophore is incorporated into the electrode in the form of a conductive paste, optimized for use in two-phase titrations with the continuous regeneration of the membrane, giving the electrode a rapid response. This model is usually applied in the titration of samples where the pH is greater than 10 (such as soaps).

According to the the manufacturer's information, these new electrodes work well in complex matrices, are resistant in organic media (in the presence of alcohols, ketones, hydrocarbons, and chlorinated solvents), and enable the work to be carried out in a similar way to the classical two-phase Epton titration.

It should be kept in mind that the Epton titration (ISO 2271) remains the reference method in the industrial monitoring of surfactants and control laboratories insist that new potentiometric methods are first compared with the standard procedure before being used in its place (11). To this end, in Spring 1998, an extensive European interlaboratory project, involving the Comité Européen des agents de Surface et leurs Intermédiaires Organiques (CESIO), the Association Internationale de la Savonnerie, de la Détergence et des Produits d'Entretien (AISE), and the Gemeinschafts-Ausschuss Tenside (GAT), compared the Metrohm electrodes Surfactrode Resistant and Surfactrode Refill with the manual Epton method. The good correspondence between the results obtained in the analysis of various anionic surfactants and detergent samples has opened the door to the development of new European standard analytic procedures (14).

As a third source, in the U.S. market, the Phoenix Electrode Company (Houston, TX) has recently presented two new electrodes for ionic surfactants, namely, models SUR1501 (indicating electrode) and SUR1502 (combined electrode) (96). These devices, identical in terms of the characteristics of the polymeric membrane, show a similar response to various surfactants (as is common with this type of electrode) and, as an alternative, can be mounted in a FlowThru system. The manufacturer lists the following characteristics as being most noteworthy: a wide working range, from 1 to 12000 ppm (10^{-5} a 5×10^{-2} M); a working pH range between 2 and 12; a reproducibility of ±2 percent in measurements; and a response time (95%) of 30 s (no information is given for any of these characteristics regarding the species and determination conditions to which these data apply). The electrodes are also designed for potentiometric titrations of ionic surfactants using standard solutions of Hyamine or dodecylsulfate, providing, under favourable conditions, potential jumps at the equivalence point of over 200 mV.

SUMMARY

After three decades of continuous research into the potentiometric detection of anionic surfactants the field has matured to such an extent that numerous analytic problems can now be resolved. The most notable application, demonstrated by many research groups, involves the use of potentiometric sensors in the determination of anionic surfactants, rather than the standard two-phase titration. In such cases, potentiometric titration offers a cleaner and more objective alternative that can easily be performed automatically. Compared with other techniques, which are often more expensive and complicated and may require prepreparation of the sample, the use of potentiometric membranes—whether fitted to selective electrodes or ISFETs, and in both discrete and flow titrations—offers an already proven alternative. In addition, a wide range of such electrodes are now commercially available, providing numerous applications in the analysis of household and industrial products; therefore, these devices are not restricted solely to research settings.

In coming years, new research lines will seek to optimize existing PVC formulations and include new electropolymerizable and photocurable materials into membranes; this will help to improve selectivity and enable these sensors to be more widely used.

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