CHAPTER I

LITERATURE SURVEY

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I.1. An introduction on electroanalytical chemistry

Electroanalytical chemistry encompasses a group of quantitative analytical methods that were based upon the electrical properties of a solution of the analyte when it was made part of an electrochemical cell. Electroanalytical techniques were capable of producing exceptionally low detection limits and a wealth of characterization information describing electrochemically addressable systems. Such information included the stoichiometry and rate of interfacial charge transfer, rate of mass transfer, extent of adsorption or chemisorptions, and rates and equilibrium constants for chemical reactions [1,2].

Electroanalytical methods had certain general advantages over other types of procedures. First, electrochemical measurements were often specific for a particular oxidation state of an element. A second important advantage of electrochemical methods was that the instrumentation was relatively inexpensive. A third feature of certain electrochemical methods, which might be an advantage or a disadvantage, was that they provided information about activities rather than concentrations of chemical species.

Electrochemical measurements were classified according to physical parameter (potential, current, conductance ...etc) involved in the transduction process [1,2].

Among these methods, potentiometric determination using ion-selective electrodes were selected to determine some cationic and anionic surfactants in this study.

I.2. Ion selective electrodes

Ion selective electrodes (ISEs) were electrochemical sensors that allow potentiometric determination of the activity of certain ions in the presence of other ions in the sample solution. Potentiometric sensors were essentially passive electrochemical devices, in which changes in the electromotive force (emf) were

monitored under virtually, zero current conditions. In so-called direct potentiometry, the emf was ideally a function of the activity of only one chosen sample ion so that it could be selectively assessed in the presence of other ions. Achieving sufficient selectivity to measure one ion in the presence of others had long been the main focus of research in this field[3].

ISEs had found fast applications in diverse fields of analysis, being of low cost, selective, sensitive and applicable over a wide range of experimental conditions. A wide variety of clinically [4, 5] and environmentally [6] important analytes [7-9] were now routinely monitored using ISEs based on impregnated polymeric membranes.

I.3. Types of ion-selective electrodes

Ion selective electrodes could be classified according to the nature of the sensing membrane to many types. These types include homogeneous and heterogeneous solid state membranes, liquid membranes and gas electrodes. Brief descriptions of the major categories were given and a more detailed discussion was oriented to the heterogeneous solid state membrane electrodes, membrane and solid contact electrodes as they were the main direction of the present work.
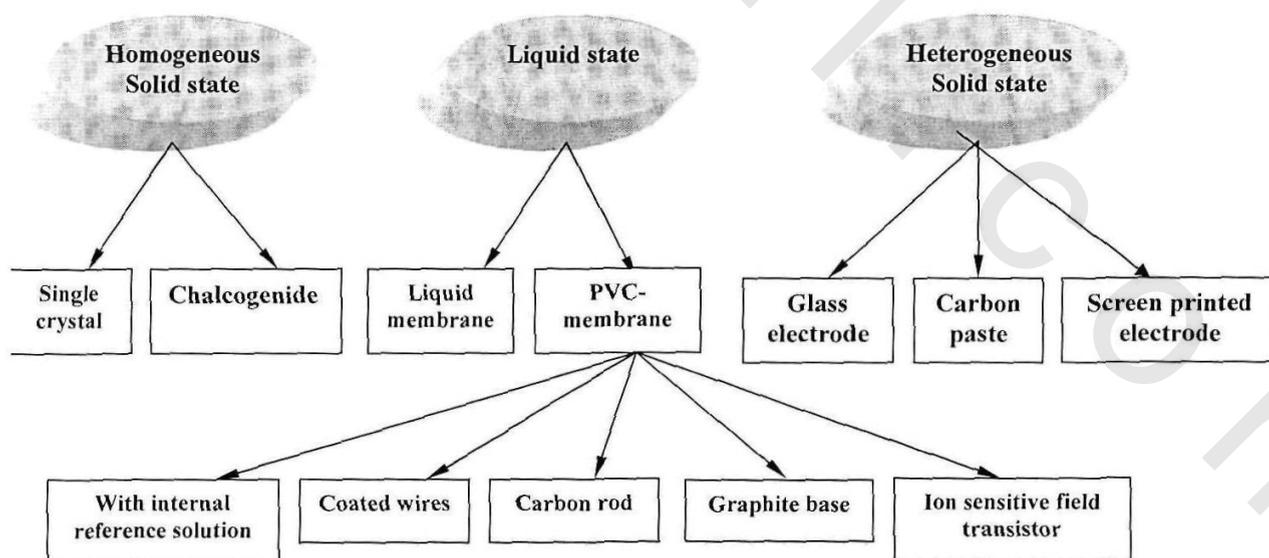
I.3.1. Homogeneous solid state membrane electrodes

The sensing membrane of these electrodes was a disk cut from a single crystal or a pressed pellet of polycrystalline or amorphous inorganic precipitate(s). This category included several commercialized electrodes, most successfully, fluoride electrode [10] based on lanthanum fluoride single crystal that could be considered as one of the few truly ion specific electrodes as only hydroxide ions resulted in significant interference which could be eliminated by lowering the pH to the acidic values.

Membranes for halide electrodes were prepared by pressing either pure silver sulfide or a 1:1 silver halide and silver sulfide. In these membranes, silver ions are the mobile ionic species and the electrode potential depends on the silver ion activity and the response to sulfide or halide ions is resulted from the dependence of the surface activity of silver ion on these species by the equation

$$E_{membrane} = E^o + 0.059 \log_{10} a^{Ag^+}$$

Chalcogenide membranes were prepared by pressing mixture of silver sulfides and metal selenides or telluride's. This type of electrodes is suitable for metals that form hygroscopic sulfide or the sulfide analog show no or poor responses.

I.3.2. Liquid state electrodes

I.3.2.1. Liquid membrane electrodes

The customary type of liquid membrane electrode was that in which the membrane was composed of a water-immiscible organic solvent containing the ion of interest in the form of ion pair. The membrane was interposed between a standard (internal) and the test (external) ion solutions, where the voltage being measured for the complete electrochemical cell which comprised the membrane separating internal and external electrolytes as well as the two (internal and external) references electrodes [11-15]. In early designed liquid membrane electrode, the organic phase of these membranes was an organic solvent, placed between two aqueous phases in bulk or with the support of a thin, porous cellulose sheet, sintered glass, or the like.

The nature of the organic solvent was used to determine the extraction parameter of the ion-pair and consequently, the electrode selectivity towards the ion of interest [11-17]. The membrane plasticizers must be of:

i- low solubility in water; ii- low vapour pressure; iii- high viscosity and suitable polarity "dielectric constant" to dissolve the electroactive material. Nitrobenzene was the popular membrane solvent in the home-made ion selective electrode [12, 18]. Other organic solvents were also applied such as o-nitrotolune, as well as other aromatic-nitro compounds namely 4-ethylnitrobenzene, 4-nitro-m-xylene and p-nitrocumarene.

The electroactive materials used in these membranes were divided into three main classes [19]: ion exchangers, neutral carriers, and charged carriers. In the liquid ion exchanger electrode, the electroactive material was usually the salt (ion pair) with a highly lipophilic cation or anion to allow solubility of the resulted ion-pairs in the membrane solvent. Another category of liquid membrane electrode was based on neutral carriers. These were lipophilic, multifunctional compound with active groups which were primarily alternating ether and/or keto oxygen that could form a cage for the positively charged ions.

A well-known example of these types was the calcium electrode described by Ross [20], which was based on calcium didecylphosphate dissolved in di-n-octyl phenyl phosphonate. Many other publications had been found covering the work of liquid membranes including electrodes to perchlorate [21] in pharmaceutical analysis.

I.3.2.2. Polyvinyl chloride (PVC) membrane electrodes

I.3.2.2.1. PVC-membrane electrode with internal reference solution

Moody et al [22] introduced a more convenient approach for membrane electrodes, in the new approach, the membrane components (electroactive material, supporting polymer and plasticizer) were dissolved in tetrahydrofuran or cyclohexanone at room temperature and after evaporation of the solvents, a homogeneous polymeric membrane with thickness ~0.2 mm was formed. Since, these membranes contained ~70% (w/w) plasticizer and because the plasticized polymer behaved like a viscous liquid, the properties of the electrode were very similar to the original liquid membrane electrode. However, the polymeric matrix

could be considered as a microporous net or a close netting, respectively, the vacancies of which were occupied by the plasticizer in which the electroactive material was dissolved [17]. The produced membranes were carefully mounted on the polished end of PVC or glass tubing field with an inner electrolyte of the analyte ion of interest [22] with the internal reference electrode.

The fundamental requirements for polymeric materials used in polymeric plastic membrane electrode were discussed by Fiedler and Ruzicka [23]. Based on this study, many polymers were used as a polymeric support such as polyvinyl chloride, polyurethane, silicone rubber, polystyrene and polymethyl methacrylate. PVC was the most commonly used polymer matrix for sensors of the liquid ion exchanger and neutral carrier ionophors types, because it gave homogeneous, solid and flexible membranes. Also membranes prepared from PVC as polymeric materials had the advantages of their electrochemical compatibility with a host of sensor material cocktails based on liquid ion-exchanger and their appropriate plasting solvent mediators [24].

It was well known that, in the preparation of PVC, it was necessary to add the appropriate plasticizer in order to obtain the best potential response. The role of plasticizers in plastic membrane electrode might be considered analogous to that of organic solvent in liquid membrane electrodes, as it would determine the electrode selectivity towards the ion of interest, slope of the calibration graph as well as the membrane resistance.

When the liquid and/or plastic membrane electrodes were used to monitor the titrations based on ion-pair formation, the magnitude of both the potential break and sharpness at the inflexion point of the titration curve was pre-determined by the solubility of the corresponding ion-pair into the membrane solvent. Vytras et al [25] found that the potential break (ΔE) in the titration of N-alkyl-n-ethylpyrrolidinium with tetraphenylborate was affected by the nature of membrane plasticizer. The results showed that nitrophenyl ethers gave the highest ΔE, which might be due to its high polarity. More recently [17], the same author used coated wires electrodes in the potentiometric titration for testing new plasticizers. It was found that, from 15 nitro compounds in this study, nitrophenyloctyl ether proved to be the most suitable

from both criteria (the life time of the electrode as well as the value of the potential break).

A good deal of interest had developed during the past four decades in prospective use of PVC electrodes for monitoring various ions. These electrodes were applied for the determination of metal ions [26-27], organic compounds as well as surfactant analysis [28–32] and pharmaceuticals [33-34].

I.3.2.2.2. Solid contact ion selective electrodes

The increased interest in using ISEs had led to the development of new sensor materials that show high selectivity for a variety of anions and cations and new methods for the construction of electrodes from these materials. For routine analysis, the symmetric configuration was generally preferred in which the sensing membrane came in direct contact with two aqueous solutions, the internal one with fixed ion activity and the external one with the ion activity to be measured. Although the symmetric ISEs had found a wide range of applications [26-27, 35-38], they still had certain inherent limitations, they were mechanically complicated, and thus difficult to be manufactured in small size. The internal reference solution increased the system impedance and the electrode response time, in addition to the shorter lifetime due to leaching of the electroactive material throughout both solutions in contact with the membrane, and finally due to the internal compartment, they couldn't with stand high pressure [39]. Several attempts had been made to eliminate the internal reference solution in the ISEs. Examples of these new types of sensors design included the coated wire electrodes; graphite rod, graphite-based electrodes and the ion selective field effect transistors.

3.2.2.2.1. Coated wire ISEs

A new kind of all solid-state electrodes sensors, were reported which refer to a type of ISEs in which the internal reference element is in direct contact with the electroactive membrane matrix and thus contain no aqueous solution. Due mainly to the elimination of the internal reference solution, these electrodes will have certain advantageous such as their small size, faster responses, and ability to operate in higher pressure environment where the symmetric ISEs might be damaged.

The first group of the simplified sensors mentioned above covered those of

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so-called coated wire construction type (CWE). This type of electrodes was first reported by Cattrall and Freiser in 1971 [40], in the new approach the metal wire was coated with a solution of PVC in THF containing also a suitable electroactive material. After evaporation of the solvent, a metal wire coated with a PVC film was produced. Although different materials such as platinum, silver or sliver chloride and aluminum [41] could serve as central conductors, an extensive study dealing with the application of CWISE in ion pair formation based titration [41] had shown that when the wire support didn't react with the membrane components, it had no substantial influence on the shape of the titration curve.

Vytras et al [42-44] had described the preparation of simple aluminum CWE type elements where the instructions for their use in the ion-pair-based titrations of many species included surfactants [43, 45] using different membranes. Steven and Freiser [46] recommended CW cadmium selective electrode based on bidentate neutral carrier as this electrode exhibited a Nernstian response with a detection limit of 10^{-6} M. As reported in numerous papers [47], these devices became attractive because of the ease with which it could be fabricated and manipulated.

Another approach of solid contact electrodes [48] was that at which the sensitive electroactive membrane was in direct contact with metallic disk as conductor. In this type, the solution of the electroactive material and PVC solution was poured on the surface of silver epoxy resin [49], silver [50] or silver-silver chloride disk electrode [51] and after evaporation of the solvent the membrane came in direct contact to the metal surface.

3.2.2.2.2. Graphite rod electrodes

Several workers had been able to construct electrodes which function without internal reference solutions. Ruzicka et al [52] had described electrodes in which the ionic sensitive materials, which might be either an electroactive solid or a solution of an electroactive species dissolved in water, immiscible organic solvent and coated the surface of a graphite substrate. Ansaldi and Epstein [53] recommenced the direct connection of PVC sensitive membrane for surfactant on one end of graphite rod where the produced electrode functions without an internal reference solution. The described electrode gave a response in the concentration range from 10^{-2} to

10^{-6} M surfactant. Coated carbon rod electrodes were prepared for the determination of many species like anionic or cationic surfactants [54-55].

The preparation of a universal solid state ISE was early mentioned by Ruzicka *et al* [52, 56]. Their construction was based on the formation and in situ application of a mobile carrier membrane onto a polymer substrate loaded with conductive material particles, which acted as an-internal solid contact. The procedure involved was straight and easily implemented, and had so far been used to construct various electrodes selective for ions such as anionic or cationic surfactants using different types of charged and neutral carries, mediator solvents and solid contact (epoxy resin loaded with silver or graphite). Due to the increase of the interest of the composite electrodes, recent reviews were published describing the properties, electrochemical behaviour and applications of such electrodes for analysis [57-58].

I.3.3. Heterogeneous solid state membrane electrodes

I.3.3.1.Carbon paste electrodes

In 1958, Adams published a preliminary report; in which he introduced a new type of solid carbon electrode for voltammetry [59-60]. The author called this electrode a "Carbon Paste Electrode, CPE". Carbon paste electrodes were originally introduced in electroanalytical chemistry to obtain an electrode with properties similar to those of the traditional mercury dropping electrodes, which had, as known some limitation when used in the area of more positive potentials, caused by anodic dissolution of mercury.

Carbon paste was composed of carbon powder mixed with a suitable binder that is why these sensors were currently classified as the so-called heterogeneous carbon electrode. The binder was formed by an organic liquid "pasting liquid" which should be little volatile, immiscible with water, sufficiently chemically inert and also electrochemically inactive. From among the substances currently used, tricresyl phosphate were recommended in case of ISE potentiometry [61]. It should be mentioned that qualitatively new CPEs had been obtained by mixing carbon powder with more polar liquids used as plasticizers in PVC membrane electrodes [62, 63].

Potential of such an electrode [64] was predominantly governed by ion exchange at the interface between carbon paste and sample solution resulting in Donnan potential as given by the equation shown below

$$\Delta_{\Phi d} = \frac{RT}{Z_i F} \ln \frac{a_i \text{ (sample)}}{a_i \text{ (paste)}}$$

Earlier, the CPEs were also classified as special type of solid and/or carbon electrodes. From the point of view of potentiometry, the electrodes were now classified among the ion-selective electrodes with a liquid membrane as the pasting liquid present as a very thin film surrounding the carbon particles and exhibit usually good extraction ability against ion-associates composed of lipophilic species. When compared with other ion selective electrodes (including CWISEs), the CPEs had an advantage of much lower ohmic resistance (less than 10 Ω instead up to MΩ for electrodes based on plastic membranes) [65]. In addition, the equilibrium voltage was stabilized during much shorter times which could probably be caused by a quick diffusion of ions into the very thin film of pasting liquid coated onto small particles of carbon powder as confirmed by microscopic studies [66].

Vytras et al [47, 65, 67] suggested the carbon paste electrodes (CPEs) as a very useful end point indicator electrode in the potentiometric titration of surfactants, when compared with similar PVC membrane electrodes and CWE, CPEs had the advantages of very low ohmic resistance, the very short response time in addition to the ease of fabrication and regeneration as well as long functional lifetime.

Carbon paste electrodes (CPEs) had been used in analytical chemistry for many years as useful materials for the fabrication of various electrometric sensors, as indicated in some recent reviews [65, 68-69]. With regard to potentiometry, Mesaric and Dahman [70] were probably the first to use electrodes filled with carbon paste. The paste mixture based on carbon powder with both Nujol or Paraffin wax, and containing a precipitate of silver halide and silver sulfide exhibited a nearly Nernstian response for both halide and silver ions. Other potentiometric applications of carbon paste electrodes were also mentioned for the potentiometric determination of anionic or cationic surfactants [71-73]

I.3.3.2.Glass electrodes

These were the oldest and best-known ion selective electrodes, made of various multi component glasses. The glass membrane electrode was viewed as consisting of three distinct regions:

Internal solution	hydrated glass layer	dry glass layer	hydrated glass layer	test solution

Hydration was accompanied by a reaction in which singly charged cations of the glass were exchanged for hydrogen ion of solution (H^+_{aq} + Na^+ glass = Na^+ aq + H^+ glass). The thickness of the dry glass layer was of the order $50\mu m$, whereas thickness of the hydrated layer was found to vary between $100.0\ \mu m$ depending on the composition of the glass and nature of the solution in which it was immersed. The potential developed was given by [19]:

$$E_{membrane} = E^o + 0.059 \log_{10} a^{H+}$$

where: a^{H+} was the activity of the hydrogen ion in the external solution, K^o contained the logarithm of the activity of the internal solution and asymmetry potential, which was caused by strains in the curved membrane structure.

Although glass electrodes belonged to the category of ion selective membrane electrodes, their applications were classed with traditional sensors. Few papers [74-75] described the use of these electrodes for the determination of cationic surfactants and other univalent cations with tetraphenylborate titrant.

I.3.3.3. Screen-printed electrodes

I.3.3.3.1. General considerations

Although carbon paste electrodes continued to play a major role in the development of analytical procedures applicable in laboratory or to test some new analytical methodologies, their relative large size diminish their commercialization. Also, due to the liquid nature of these carbon pastes, it was not directly possible to roll tapes of these types of sensor, thus solid-like sensors were needed. This can be achieved by mixing a polymer with graphite particles and a solvent. This mixture can be spread or printed on a tape substrate. The solvent was then evaporated during a curing stage, leading to a conductive carbon track made of percolated graphitic

particles binded by the polymer. While thick-film carbon electrodes could be proposed as a solution to the lack of commercial viability of electrochemical (bio) sensors for decentralized monitoring of trace metals, organic pollutants, or biologically important compounds.

The preparation of disposable strips made of thick-film carbon electrodes [76], most often prepared according to the screen-printing micro-fabrication technology, appeared somewhat as a revolution in the production of extremely inexpensive heterogeneous carbon electrochemical sensors, as discussed in some well-documented overviews [77-83]. They usually exist in planar devices realized by depositing layers of different electro-conductive and insulating composite materials with controlled thickness and shape on ceramic or plastic substrates. Almost each kind of analytical application involving the use of bulky CPEs could be adapted to the single use of thick-film carbon electrodes and sensors. In particular, the latter could be easily modified by a wide range of suitable chemical or biological compounds, either in the whole thick-film volume (modifier incorporation in the course of sensor preparation) or at its surface (post-treatment).

Historically, the first reports on single-use disposable strip electrodes were dealing with amperometric biosensors at the end of 1980s, but the major developments of bio-chemically modified screen-printed carbon electrodes appeared following the impulse of pioneering works by Wring, Hart and coworkers [81, 84-85], as well as by the Wang's group [86-89]. The sensors were named according to their production technique, quite generally "screen printed electrodes" (SPEs), or better, when carbon was the electro-conductive matter, "screen printed carbon electrodes" (SPCEs). An even more characteristic name often appearing in literature was "thick-film electrodes" (TFEs), which described better their physical dimensions as thick-films. "

I.3.3.3.2. Composition, preparation and testing

i- Fabrication

Solid-state, mechanically robust, and planar sensors could be constructed by thick-film technology. The fabrication process implied the sequential deposition of thick-films on a solid substrate, commonly by screen printing, which was a versatile

technique enabling the preparation of devices showing a wide range of configurations, likely to use many different materials, and compatible with several modification strategies as well as integration in more sophisticated instruments e.g., portable analyzers [77]. Even if the level of complexity of the fabrication procedure depended on the type of device and the target application, some general guidelines might be given on how screen-printed carbon electrodes were built.

In principal, a screen (masque with openings representing the shape of the electrode film, in the simplest case a rectangle) of a defined thickness (usually some 20 to 100 μm) was put on a support, commonly an insulator, and a carbon ink was wiped over the screen in a way that the openings were filled with the ink. This could be done either manually or preferably with a screen-printing device, which were commercially available as semi-automatic or fully automatic instruments. The sensor-to-sensor repeatability seemed better for the instrumental production. Usually a whole array of sensors was printed in a single patch featuring their mass production.

After the printing process, the screen was removed and the printed electrode films were cured until the electrode material had solidified. If desired, printing could be repeated after curing the films either to place other electrodes, insulating layers or other layers with specific functions (protective layers, enzyme layers, layers to improve the wettability, layers with immobilized reagents, etc.) on the already printed layers and/or on the support. The various configurations used in the design of screen-printed electrodes (single or multiple layers; single-, two-, or three-electrode devices; one-step configuration of composite layer(s)) had been reviewed in case of enzymatic thick-film biosensors [90]. It illustrated the case of the simplest configuration (one single carbon strip) as well as an example of a three electrode device, showing that their typical size was about 3-4 cm length and 0.5-1 cm wide.

ii- Carbon inks

The printed electrode fabrication requires an ink as a precursor, which was typically a mixture, containing at least three components: 1) conductive particles having electroactive sites, 2) a polymer that can bind together these particles [91] and

3) a solvent. This is producing, after curing, a thick conducting track with surface electroactive sites.

Carbon inks can be simply fabricated by mixing these three components, different types of graphitic powders being commercially available. These particles are generally in a flake shape or spherical with overall dimensions of about 1 μm.

Occasionally studies were published describing the preparation of carbon inks [81], but usually commercially available inks were used because they had been already widely tested and optimized under various conditions. The disadvantage of commercial preparations was that their composition was unknown in many respects, because they were secret recipes of the producer. But on the other hand, due to the needs of the customers, different varieties were very often offered (e.g., inks particularly suited for the preparation of biosensors) to meet the requirements of the user and often the companies were also very willing to adapt inks to special wishes of the buyer. From the companies offering such inks, arbitrarily two would be mentioned here, i.e., Acheson, Dupont, Ercon (USA), or Gwent Electronics (GB) [92].

The carbon ink for screen printing purposes was very similar to carbon pastes where the pasting liquid had been replaced by another liquid matrix, which would solidify after the curing process. The matrix might be a polymer, e.g., polycarbonate, cellulose acetate [81], dissolved in a proper organic solvent such as cyclohexanone, ethylene glycol, acetone, ethyl cellulose, terpineol, among others, or a monomer (optionally with co-polymers) which could be polymerized photolytically or thermally.

Other conductive inks based on metallic conductors (containing powdered metals such as gold, silver, or platinum) were also commercially available. They had been used in connection to carbon-based screen-printed sensors to include either (pseudo-) reference or auxiliary electrodes beside the carbon film in the final device. Note that these inks could also be used for electrical connections.

Finally, insulating inks were also commercially available and used to print an insulating layer on the device to define the electrode surface area expected to contact the solution, at one end of the strip, and the connection pads at the other end

for transducing and conversing signals.

The nature of the carbon ink was a key parameter affecting the performance of screen-printed carbon electrodes and therefore, the final composition of the carbon composite layer. Wang et al [92] had studied this in detail. Also, from the analytical point of view, the performance of single-use sensors produced from different carbon inks was strongly dependent on the electroanalytical technique used (variable background contributions) and the target application. Nevertheless, thick-film carbon sensors had been shown to offer attractive performance in pulse-voltammetric, amperometric, and stripping operations, trace analysis of various inorganic ions and organic compounds, environmental pollutants, as well as the determination of numerous biologically important molecules.

iii- Supports

The support was in most cases an insulator onto which the working electrode (optionally with other electrodes and/or layers) was printed. Basically its choice was not very critical, but of course it must fulfill at least two requirements: it must fit to the concepts of the sensing assay (flexibility, rigidity, mechanical and chemical stability, etc.) and it must guarantee that the printed layers adhered strongly enough to it to provide the necessary mechanical stability. Thus, plastic and ceramic materials were most commonly used, such as polyvinyl chloride, PVC (see, e.g.[81, 87, 89, 93-97]), polycarbonate [98-100], polyester [101], or sintered aluminum oxide (see, e.g., [92, 102-106]).

iv- Structure

The structure of thick-film carbon electrodes was similar to carbon paste, where carbon particles with diameters of around 10 μm were embedded in an insulating matrix. The matrix was not a liquid in this case, but a rigid polymer, and the overall sensor showed much less bulk dimensions, but resembles more a thick membrane. Therefore there were some criterions, which distinguished them from CPEs, so that the results obtained with SPCEs might also differ significantly. Whereas sorption on CPEs was often rather comparable to extraction, such liquid-liquid partitioning processes were not or to a lesser extent occurring with SPEs

supposing that the matrix was free of plasticizers.

v- Characteristics

In their electrochemical behaviour, SPCEs showed a behaviour comparable to CPEs, which was not surprising due to their similar heterogeneous structure. Electron transfer processes were retarded due to the presence of the insulating phase, producing signal broadening and deviating Nernstian behaviour. In this sense thick-film electrode (in the same way as CPEs) was not a very suitable object for theoretical electrochemical investigations. Compared to carbon paste electrodes, they showed higher background currents (mostly in the microampere range compared to nanoamperes with CPEs) and higher resistivity of the electrode material. The latter disadvantage was sometimes circumvented by printing a silver layer first (to create high conductivity on the support, silver inks were also commercially available) and upon this the carbon layer (possessing a more noble character than Ag from an electrochemical viewpoint), which improved the electrical characteristics. But care had to be taken that silver would not diffuse through the carbon film and deteriorate the analytical performance of the sensor.

I.3.3.3.3. Advantages

1. Optimized manufacturing sensor-to-sensor repeatability of production in one batch or through different batches was only within few percent of RSD, which could be kept low or parameterized and eliminated by accompanying calibrating functions.

2. The potential for mass production at low cost made them ideal for industrial commercial production.

3. Improved mechanical stability and robustness.

4. Small sample volume (10-50 µl).

5. Long shelf life time.

6. High flexibility provides a precise control over the product dimensions.

7. Excellent uniformity

8. High reliability and reproducibility.

They were designed for application in the field with portable small instruments.

I.4. Potentiometry

Generally, carbon substrate electrodes could operate according to various mechanisms, depending on the properties of the materials that impart selectivity toward the target species [107]. It should be mentioned first that applications of carbon electrodes in potentiometry had a long tradition; basic information could be found in an extensive review [108]. Presently, widely used carbon electrodes could be grouped into four main classes: pyrolytic graphite, polycrystalline graphite, glassy carbon, and carbon fibers. This list neither was in historical order nor implies popularity but rather was organized according to the complexity of the carbon material with the most ordered graphite first [109].

I.5. Surfactants and lipophilic modifiers

Several kinds of surfactants (long-chain alkylamines or alkylsulfonates, quaternized amine derivatives as cetyltrimethylammonium or cetylpyridinium [110-137]), had been introduced in CPEs. Owing to their amphiphilic properties, these modifiers were well dispersed into the paste and could be applied to adsorptive stripping voltammetry of organic compounds and even to the pre-concentration analysis of ionic species via open circuit accumulation by ion-pair formation. Similar pre-concentration behaviour towards organic compounds was also reported for diphenylether-modified CPE [138]. Natural lipids were also incorporated into CPEs including stearic acid [139-144] as well as other fatty acids and phospholipids [136, 145- 156]. This was carried out either to pre-concentrate lipophilic analytes or to mimic the living cell membrane structure in the goal to investigate the drug-membrane interactions. These modified electrodes also found applications in the enzyme-based biosensors [156].

I.6. Advantages and disadvantages of ion-selective electrodes

The huge reviews about the application of ISEs [158-160] indicate the advantages of ISEs. The most important advantage property of ISEs was that they measure activity directly, not concentration. The linear working range of many electrodes was quite large; generally, from 10^{-3}- 10^{-6} mol. Electrodes would function well in colored or turbid samples so they were more effective than the

spectrophotometric measurements. For most ISEs the equilibrium state was reached in less than a minute, this rapidity made it suitable for kinetic studies and for monitoring change in flowing process streams. The equipment used was simple, quite inexpensive, and could be made portable for field operations. The most common disadvantage of ISEs was that they were subjected to rather large number of interferences; the selectivity coefficient could be used as a useful index to assess the selectivity of all ISEs towards different ions in relation to their primary ions.

I.7. Literature survey on the determination of surfactants.

Surfactants were organic amphiphilic compounds, which considerably change the surface properties of the liquids in which they were dissolved. Surfactant was comprised of two parts: a hydrophilic part: polar head, and a lipophilic part constituted of one or more linear hydrocarbonated chains with a $(CH_2)_n$ motif. Two categories of surfactants could be distinguished according to the nature of the polar group: it was an ionic (anionic or cationic) surfactant if this group was charged or it was a non-ionic surfactant if this group was neutral.

Surfactants were important in various phenomena of interfacial science and continued to be critical in many applications including household or industrial cleaners and cosmetics (agrochemicals, emulsion polymerization, paper manufacturing, water treatment, oil recovery, fire fighting and plastic manufacturing [161]). At the present time most tensioactive products used, were biodegradable, their accumulation, or accumulation of their biodegrading products in natural waters, induces water pollution which could, in extreme conditions, leads to the destruction of the surface water fauna and flora [162-163]. Handling of surfactants for use, formulation or production needed simple and reliable analytical to determine their quantity in reaction media. The literature devoted to the determination of surfactants was greatly expanding and a number of applications were oriented towards the analysis of environmental samples and in quality control of manufactured products [164-165].

The most widely used technique in surfactant analysis was the so-called two-phase titration. In this method, the surfactant was extracted in an organic

hydrophobic solvent ($CHCl_3$) as a lipophilic ion-pair formed with the titrant. The latter was generally a surfactant of opposite charge. The titration was carried out in the presence of an ionic dye (or a mixture of ionic dyes) which coloured the organic layer differently in the presence of an excess of anionic or cationic surfactant [164, 166]. This procedure was currently used as a standard method; however, it suffered from several drawbacks such as [167].

1- Formation of an emulsion during titration (risks of errors in visual end-point detection).

2- Lack of efficiency for surfactant having a short carbon chain length.

3- Turbidity of the solution when analyzing a complex sample.

4- Interference by many components such as ClO_4^-, SCN^-, and NO_3^-.

5- Toxicity of the chlorinated organic solvent ($CHCl_3$).

6- Time consuming.

7- Automation was difficult.

Many other methods had been developed for the determination of surfactants. This review was intended to provide an overview of recent analytical methods devoted to the surfactants analysis.

I.7.1. Determination of anionic surfactants

Anionic surfactants were produced in large amounts and widely used for industrial and domestic purposes, including laundry powders, household cleaning products, and emulsifiers for industrial solvent cleaners, biochemistry research laboratories, agricultural and horticultural chemical delivery systems [168]. Such a wide application of surfactants might result in the pollution of surface water. Although most anionic surfactants in use today were biodegradable and essentially nontoxic to humans [169]. A need still exists for effective monitoring of these compounds. Aside from the visul pollution (in the form of foaming) associated with surfactant use, the environmental impact of surfactant release in natural water systems could be much more serious. Numerous techniques had been adapted for the determination of anionic surfactants; hence, the development of highly sensitive and rapid methods for determination of trace amounts of surfactants was of considerable interest such as:

I.7.1.1. Titrimetric methods:

The purity of sodium dodecylsulfate (SDS) was checked by acid hydrolysis of the substance and back-titration with standard sodium hydroxide solution [168]. Hilp[169] had titrated SDS in aqueous medium with cetylpyridinium tetrachlorozincate as standard solution and methyl orange or bromophenolblue as indicator.

I.7.1.2. Potentiometric methods

Sandchez and Delvalle [170] had prepared a new ion-selective field-effect transistor (ISFET) based on a photocurable membrane sensitive to anionic surfactants sodium dodecylbenzensulfonate (SDBS) and sodium dodecylsulfate (SDS). The determination of the surfactants concentration was performed following a standard addition methodology using ISFETs as sensors and without any previous separation stages.

Matersic-Puac et al [171] had prepared an all solid-state surfactant sensitive electrode based on a teflonized graphite conducting substrate coated with plasticized PVC-membrane containing a new synthesized tetrahexyldecyl-ammoniumdodecylsulfate as anionic surfactant sensing material. The electrode was used as end-point indicator for potentiometric surfactants titration. Sensors for anionic surfactants with PVC membranes containing dodecylbenzenesulfonate [172] or tridodecylmethylammonium chloride [173] were developed and used for the potentiometric flow injection analysis of dodecylbenzenesulfonate (DBS). The sensors were used to measure anion DBS⁻ in different waste water samples, commercial detergent products and for monitoring the rate of surfactant biodegradation in sewage treated plants.

I.7.1.3. Spectrophotometric methods

Imasaka et al [174] had determined SDS by visible semiconductor laser fluorimetry after solvent extraction with Rhodamine 800. SDS and SDBS were simultaneously determined spectrophotometrically [175] using 1-stearyl-4-(4-aminonaphthylazo)-pyridinium bromide reagent. The sample solution was treated sequentially with citrate buffer, 0.4% polyoxythylene and 0.1 mM reagent, and the absorbancies were measured at 424 and 445 nm for determination of SDBS and SDS, respectively.

Xie et al [176] had used rhodamine B for the flourimetric determination of SDS in environmental water samples. Samples were treated with rhodamine B in 2.5 M H_2SO_4, diluted with water and extracted with $CHCl_3$. The fluorescence intensity of the extract was measured at 600 nm.

A study using a UV-vis spectral correction technique on the interaction of anionic surfactants with nile blue and safranine T was reported [177]. The result showed that aggregation of the dyes on the surfactant surface obeyed Langmuir isothermal absorption and these interaction were used to develop a method for the determination of anionic surfactants in water with detection limits of 0.03-0.07 µ mol.

A kinetic method for the determination of SDS was reported [178]. The method was based on its inhibitory effect on aniline blue-thiosulfate reaction. The reaction was followed spectrophotometrically by measuring the change in absorbance at 601 nm using a fixed time method. The calibration curve was linear in the range of 3-40 µg/ml and detection limit was 1.7 µg/ml.

Chen et al [179] had applied the resonance rayleigh scattering (RRS) spectra of ethyl violet-anionic surfactant systems for the determination of some surfactants. Anionic surfactants reacted with ethyl violet in weak acid media to form ion association complexes, while resulted in an increase of resonance rayleigh scattering and an appearance of a new RRS spectrum. The maximum RRS peaks were at 330 and 508 nm and the detection limit for SDS was 2.5 µg /L.

Many spectrophotometric methods were adopted for the determination of SDS including the method based on the association reaction of the surfactant with naphthyldiphenylmethane [180], reaction with Victoria blue [181] in phosphate buffer and reaction with bromocresol purple [182] in pressure of CTABr.

I.7.1.4. Chromatographic methods

Campbell et al [183] had developed a gas chromatographic method to accurately quantitate SDS in aqueous biomedical samples. The method was based on the quantitative conversion of SDS to I-dodecanol in the GC injection part at elevated temperature, and the thermal degradation product I-dodecanol was analysed to determine SDS concentration.

Mixtures of nonionic surfactants namely polyethylene oxide and dodecylsulphate in water were simultaneously analysed by reversed-phase liquid chromatography [184]. A fractional factorial design was used to optimize the separation process as a trace enrichment procedure to determine very low concentrations of SDS.

Schroder [185] had analysed mixtures of surfactants containing SDS in biological waste water samples by flow injection mass-spectrometry, liquid chromatography-mass spectrometry and tandem mass spectrometry. Ion-chromatographic technique [186] was used successfully for the determination of anionic surfactants (e.g. SDS) by using Dionex-10 ion chromatograph with a column of a surface modified low-capacity anion exchanger and a suppressor column of a high-capacity cation exchanger.

SDS was determined in toothpastes using ion chromatography in combination with electrospray mass spectrometry [187], ion-pair HPLC [188] and TLC [189].

I.7.2. Determination of cetylpyridinium chloride (CPCl)

I.7.2.1. Potentiometric methods

Chernova and coworkers had potentiometrically titrated CPCl against anionic surfactants using solid state electrodes [190]. The electrode comprised a PVC tube with internal graphite rod and an ion-exchange resin membrane containing the Cu-H redox system. The electrode response was linear from 5 mM to 0.1 M surfactant. Jazkova et al [191] used perchlorate and fluoroborate ion-selective carbon paste electrodes for both direct potentiometric measurements and potentiometric titration of perchlorate or fluoroborate with 0.1 M CPCl. The electrodes had a rapid response, low resistance and limits of detections and selectivity similar to the limits of commercial membrane electrodes.

Kulapin et al [192] prepared a modified potentiometric sensor for the selective determination of some cationic surfactants including CPCl. The sensors were based on dibutylphthalate plasticized PVC films which contained a cetylpyridinium-tetrphenylborate ion exchanger and were coated with molecular sieves with different pore sizes.

I.7.2.2. Spectrophotometric methods

Tananaiko and Todradze [193] used the extractive spectrophotometric technique for the determination of CPCl in the range of 5 to 35 μg ml^{-1} with a coefficient of variation of < 0.25%. The method was based upon the formation of CPCl sulpharsazen complex in, an aqueous medium at pH 7, which is very extractable into nitrobenzene and spectrophotometric measuremed at 560 nm. In anther approach CPCl formed ternary (1:1:1) complex with bromocresol green and qunidine [194]. which was extracted into 1.2-dichloroethane and measured spectrophotometrically at 633 nm.

Liu [195] treated CPCl or other cationic surfactants with potassium hydrogen phthalate/ HCl buffer of pH 2.6 and aqueous eosin solution. The double scattering and antidouble scattering intensities of the ionic associate were measured at 620 and 352 nm, respectively, using a fluorescence spectrophotometer. The calibration graph was linear up to 200 $\mu g/L$ of CPCl.

Some quaternary ammonium salts including CPCl were determined spectrophotometrically by treating the sample with ethanolic quercetin solution and N-bromosuccinimide at pH 5. The mixture was extracted into dichloroethane and the organic phase was dried over anhydrous Na_2SO_4 and the absorbence was measured at an appropriate wavelength. Beer's law was obeyed for 5-30 $\mu g/ml$ and the detection limits were 1-3.7 $\mu g/ml$ [196].

Patel [197] adopted a flow-injection analysis method for the determination of cationic surfactants in environmental samples. Cationic surfactant solution was injected into a carrier stream of H_2O which merged with a stream of 0.15 mM Fe (III) in 0.005 M HNO_3, followed by merging with a stream of 0.7 M NH_4SCN. The absorbance of the resulting Fe(III)-SCN- surfactant ternary complex was measured at 475 nm.

I.7.2.3. Chromatographic methods

Binder and coworkers [198] used the reaction gas chromatographic technique for the determination of CPCl on a Chromosorb 102 column with flame ionization detector. CPCl was cleaved to pyridine and chlorohexadecane in the injection port at 400°C, while the pyridine was determined over the range of 100-600 ppm.

Benassi et al [199] determined CPCl in pharmaceutical and cosmetic products by reversed-phase ion-pair HPLC. The applicability of the method was demonstrated by analyzing different commercial or laboratory product samples with different concentrations.

Haruyana and Okaya [200] developed HPLC method for the determination of CPCl and other cationic preservatives in cosmetics. The sample was dissolved in THF or methanol and applied to a Bond-Elut SCX cartridge. After washing with methanol the analytes were eluted with 0.1 M $NaClO_4$/methanol and detected spectrophotometrically at 263 nm.

Quaternary ammonium compounds including CPCl in candy-based lozenges were determined by capillary electrophoresis [201] and HPLC [202]. Mixtures of cationic surfactants containing CPCl were analysed by capillary zone electrophoresis and micellar electrokinetic chromatography with deoxycholate micelles in the presence of large solvent concentrations [203].

I.7.2.4. Voltammetric methods

Adeloju and Shaw [204] determined CPCl at ultratrace level by indirect stripping voltammetry on a hanging Hg drop electrode. The calibration graph was linear up to 65 mg/L with detection limit of 10 µg/L. The method was applied to the analysis of CPCl in disinfectants, lozenges and mouth wash.

Zhao and Zeng [205] noticed that, in presence of L-cycteine, CPCl exhibited sensitive cathodic stripping peak at about ~1.2 V. (vs. SCE). The square root of the peak hight was linear with CPCl concentration over the range of 2-50 µM. This was developed for the determination of CPCl concentration.

I.7.3. Determination of cetyltrimethylammonium bromide (CTABr).

I.7.3.1. Titrimetric methods.

Narasimham et al [206] determined CTABr either alone or in the presence of Pb(II) and Cu(II) solutions by titration with standard sodium tetraphenylborate solution at pH 3 in the presence of methyl yellow indicator.

Massaccessi [207] determined quatermary ammonium compounds including cetyltrimethylammonium chloride in pharmaceutical formulations by visual titration with 0.01 M Sodium dodecylsulfate in NaOH or borate buffer using Azure A as

indicator or an indicator consisting of a mixture of Xylenol orange, $LaCl_3$ and a non ionic surfactant.

Lowy and Patrut [208] used heteropolyanions for the titration of CTABr in aqueous solution. The titrations were performed with a 5 mM aqueous solution of $K_8[P_2Co(II)MoW_{16}O_{61}(H_2O)].19H_2O$. Two methods were used: (i) biphase titration according to Reid et al [209] with visual detection and (ii) potentiometric titration at 25 °C with the use of a surfactant - ISE.

I.7.3.2. Potentiometric methods

Determination of surfactants of various types by potentiometric titration represents an ecologic alternative to the official two-phase titrimetric method [65]. For monitoring these titrations, simple and inexpensive electrodes could be used and, in addition, time needed for such determinations could extremely be shortened by introduction of automated titration procedures. Procedures for determination of cationic surfactants CTABr had been developed. The methods elaborated were reviewed with particular emphasis on recent investigations.

Fogg et al [210] prepared an electrode giving a steady potential response within 1 min with a potential concentration slope of 56 mV / concentration decade in the 10^{-5}-10^{-3} M range during the potentiometric titration of CTABr using precipitants such as sodium tetraphenylborate and potassium dichromate. The electrode did not respond to anionic surfactants.

Pathan [211] prepared an ion-selective electrode for CTA^+ determination consisting of silicon rubber membrane containing 40% by weight cetyltrimethylammoniumdodecyl sulphate. It was used primarily for the potentiometric titration of CTABr against SDS, sodium tetraphenylborate, ammonium reineckate, potassium hexacyanoferrate (III) and potassium dichromate.

Surfactant quaternary ammonium salts alone or in pharmaceutical preparations were determined [212] by potentiometric titration of their aqueous solutions against standard tetraphenylborate solution in an automatic titrator with an Ag-indicator electrode. The magnitude of the potential was reproduced to ±10 % by pretreating the Ag electrode in 6 M HNO_3 containing $NaNO_2$, rinsing and soaking it 2 min in magnetically stirred 1M KCN solution. Recoveries from aqueous

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solutions and pharmaceutical preparations were exhibiting a relative standard deviation of 1.1%.

Benoit et al [213] titrated CTABr against sodium tetraphenylborate potentiometrically using commercial ClO_4^- selective electrode. The method proved to be precise exhibiting a relative standard deviation of 1.1%.

Ninteen quaternary ammonium salts including CTABr and twenty five basic dyes were potentiometrically titrated aganist orange IV [214]. The indicator electrode was carbon rod coated with PVC membrane containing triheptyldodecylammonium iodide. The ammonium compounds containing alkyl groups of 14-18 carbon atoms showed well defined titration curves and the sensitivity of the method reached from 10^{-5} to 10^{-4} M.

A PVC membrane ion-selective electrode suitable for the potentiometric end point detection in the titration of cationic surfactants had been constructed [215]. The active substance of the electrode was the neutral carrier dibenzo-18-crown-6 using diisooctyl phthalate as plasticizer. The electrode had a pH working range from 2.0-12.0 with a Nernstian behaviour between 6.0×10^{-6} and 1.6×10^{-3} mol/L and high selectivity towards inorganic cations.

Qian et al [216] prepared PVC membrane electrode with the use of hexadecylbenzene sulphonate and tetraphenylborate as active materials. The electrode exhibited good stability and selectivity, with a rectilinear response being observed from 1 μM to 1 mM CTABr.

Badawy et al [217] prepared CTABr cation sensitive polymeric membrane electrode. The electroactive material was the ion-association complex of the cation $(CTA)^+$ with phosphotungstic acid (PTA). The electrode was applied in the determination of CTABr in aqueous solutions by standard additions and by potentiometric titration with PTA. Response was nearly Nernstian between 3.2 and 830 μM and was unaffected by pH changes in the range from 2.5 to 8.5. Recoveries of CTABr from a desinfectant solution were 102.8 and 97% by the standard addition and potentiometric methods, respectively.

Jin et al [218] prepared PVC-membrane electrode by dissolving fullerene (C_{60}) in a solution of PVC and diphenyl-(2-ethylhexyl) phosphate in THF and toluene and

adhering the membrane to the end of a PVC tube with PVC/THF solution. The electrode was used to determine CTABr in 1.5 M acetic acid. It exhibited a Nernstian response in the range from 5 mμ M to 10 mM CTABr. The detection limit was 0.55 mμ M. The response time was 1.5 min and it was stable for 2 months.

Badawy et al [219] prepared a PVC-membrane electrode selective for cetyldimethylethylammonium bromide (CDEA). The active element was a plasticized PVC membrane containing a dissolved ion associate complex of CDEA with phosphotungstic acid. The electrode showed a near-Nernstian response within the concentration range of 10^{-6} to 10^{-4}M CDEA.

Katsu [220] had evaluated eight dioxadicarboxylic diamides as ionophores in membrane-type ISE for hexylammonium ion. The PVC membrane was prepared using the selected ionophore and dioctylphthalate as plasticizer. The electrodes with these ionophores produced a near-Nernstian response to hexylammonium ions in 0.5 M MgCl$_2$. The detection limits were similar at 3 μM and the selectivities of these electrodes were much better than that of dibenzo-18-crown-6-electrode.

Patil [221] prepared an electrode sensitive to dodecyltrimethylammonium ion (DTA$^+$) and tetradecyltrimethylammonium ion (TTA$^+$). The electrode was used for determination of critical micelle concentration of tetradecyltrimethyl ammonium bromide in water. Moreover the electrode was tested in presence of non-aqueous polar solvents i.e. dimethylformamide (DMF) and dimethyl sulphoxide (DMSO) in water and was observed to be Nernstian within wide concentration range.

I.7.3.3. Spectrophotometric methods

Nakashima et al [222] titrated CTABr spectrophotometrically with potassium (polyvinyl) sulphate in the presence of toluidine blue as indicator and the variation in absorbance was followed at 640 nm. The titration curve broked sharply at the end point. The effects of pH, ionic strength, and initial concentration were examined.

Cetyltrimethylammonuim chloride (CTACl) was determined in mixture with non-ionic surfactants to 98.6-101.0% recovery by treating the mixture with potassium dichromate, [223] followed by dissolving the separated precipitate of CTA-dichromate in methanol and the absorbance of the resulting solution was measured at 335 nm. Up to 10 fold amounts of non-ionic surfactants and inorganic salts such

as NaCl and Na_2SO_4 did not affect the determination.

Saito et al.[224] determined CTABr by chelate formation with chromazurol S aluminate. A mixture of 10 ml sample of chromazurol S in ethyl alcohol and 1.5×10^{-4} M solution of potassium sulphate at pH 4.8 was left to stand for 20 min, then the absorbance was measured at 640 nm against the reagent blank. Beer's law was obeyed form 2.5 to 10 μg/mL.

Um and Lee [225] determined CTABr with tetrathiocyanato cobaltate(II) by an extraction-spectrophotomrtric method. The formed coloured complex was extracted by organic solvents and then identified by elemental analysis, IR and mass spectra.

A rapid method was developed for the determination of low concentrations of CTABr employing its colour reaction with eosin [226]. The analysis was carried out at pH 3.0 in aqueous ethanol containing a citrate buffer and the absorbance was determined at 535 nm.

A spectrophotometric method for determination of CTABr in natural water using bromophenol blue was described by Gorenc [227]. Interferences of dominant and trace anions present in water systems could be eliminated by ion exchange treatment. The method was successful in the concentration range 1-10 mg/L CTABr.

Several metals were precipitated as ion-pair complexes by CTABr in the presence of SCN-. The determination of CTABr was based on the extraction of its ion pair with the Fe(III)-SCN- complex into $CHCl_3$ [228]. Final measurement was done by molecular-absorption spectrophotometry at 487 nm versus $CHCl_3$ or by atomic absorption spectrophotometry (AAS) after mineralization of the extract.

El-Khateeb and Abdel-Moety [229] suggested a method for the determination of CTABr in pharmaceutical formulations by the hypochromic effect. The method was based on the partial decolourization of phosphate-buffere (pH 7.5) of bromothymol blue at 610 nm by means of the surfactant. The calibration graph was rectilinear from 0.5 to 3 mM surfactant. Methods were described for disinfectant solution, creams, eye-drop and tablets. Recovery of CTABr from standard solution and from pharmaceuticals was quantitative.

Marhold et al [230] determined CTABr by a sensitive fluorimetric method. Aliquotes containing 0.4 to 4 mμg/ml of cationic surfactant were treated with 1 ml

of aqueous 10 mμ M 8-octadecyloxypyrene-1,3,6-trisulphonate and the solution was measured (within 3 min) at 430 nm (excitation at 410 nm). Calibration graph for CTABr was rectilinear from 40 to 400 mg/ml with standard deviation of 3% (n = 5). No interference was observed for up to 10-fold excess of sodium dodecyl sulphate and quenching by Fe(III) was not significant below 50 mμM.

I.7.3.4. Chromatographic methods

Bettoni and Franchini [231] determined CTABr by passing aqueous solution or commercial preparations containing the quaternary ammonuim salt through a column of Dowex 50 w in the Ca (II) form after dilution with water. Ca (II) in the eluate (stoichiometrically equivalent to the amount of CTABr present in the original solution) was determined by atomic absorption spectrophotometry.

A useful analytical method for the determination of alkyltrimethylammonuim compounds by gas chromatography was established [232]. The method is based on degradation of the ammonium compounds with potassium tetrabutoxide in benzenedimethylsulphoxide (8:2) under reflux for 30 min giving a 1-olefin corresponding to the alkyl group as well as alkyltrimethyl amine from alkyltrimethylammonuim compounds. The 1-olefin was determined by gas chromatography equiped with a flame ionization detector. The method was applied to determine the ammonium compounds in commercial hair rinse liquid softening agents, and antistatic aerosol products.

I.7.3.5. Miscellaneous methods

CTABr was determined tensammetrically [233] in 0.1 M Na_2SO_4 using a multivariate calibration technique based on singular value decomposition and the HoKachap algorithm. Acceptable accuracy was obtained with a two-step calculation procedure in which calibration constants for the total concentration range of interest were used to guide the choice of a more specific set of calibration constants which were valid for much smaller concentration span. From 3 mμ M to 0.2 mM, CTABr could be determined.

CTABr was determined [234] at trace levels by indirect adsorptive polarography on a dropping Hg electrode. Corresponding calibration graph was linear up to 65 mg/L CTABr with detection limit of 5 mg/L. The method was applied to the

analysis of products such as disinfectant, lozenges and mouthwash. In some cases sample solution was subjected to clean up through a chromatographic column before analysis to eliminate matrix interference.

A method proposed by Yao et al [235] based on the ability of fast-anti-bombardment mass spectrometry (FAB MS) to analyse small amounts of polar or non-volatile compounds to directly obtain the mass spectra on paper. This involved adhering a scrap of paper containing the sample of interest to the FAB probe tip with a strip of double-faced adhesive tape before introducing the probe into the mass spectrometer to acquire FAB speenua in the usual manner. The detection limit of the method was 10 mg with respect to hexadecyl adhered to the FAB probe tip.

I.7.4. Miscellaneous methods for determination of surfactants

Most of these limitations could be overcomed by using ion selective electrodes (ISEs) as indicators in potentiometric titration of surfactants. Several excellent articles [12, 43, 236-239] reviewed the use of different types of electrodes for surfactant analysis.

A number of authors had described the surfactant sensitive electrodes usually based on a liquid/PVC membrane electrode [28-29, 240-245]. A drawback in the use of PVC membrane electrodes arised from the time consuming and inconsistent manual fabrication methods, difficult to be manufactured in small size, as well as the shorter life span of the electrode.

Vytras et al [65, 67, 247] suggested CPE as a very useful electrode in the potentiometric determination of surfactants. When compared with similar PVC membrane electrodes, CPEs had the advantages of very low Ohmic resistance, the very short response time in addition to the ease of fabrication and regeneration as well as long functional lifetime. Hand-made carbon paste mixtures (made of carbon powder and a liquid binder) were a soft and non-compact material that had to be packed into a special electrode holder offers a simple and quick renewal of the electrode material, which was one of the most distinct advantages of CPEs. However, designs and shapes of such electrodes were not suitable for every purpose as in the case of measurements in flowing streams or field monitoring with portable analyzers where the respective detection units require electrodes of special

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constructions. Usually, smaller dimensions and plane configuration of such electrodes were inevitable, which could be documented on recent trends in the development and applications of screen-printed sensors (SPEs).

Over the past few years, an interest had been increasing in the application of simple, rapid, inexpensive and disposable sensors in different fields such as clinical, environmental or industrial analysis [130, 248-252]. Disposable screen printed electrodes (SPEs) were ideally used for potentiometric determination of various species [253-256] using a commercial inks modified with different ionophores. The carbon ink for screen printing purposes was very similar to carbon pastes where the pasting liquid had been replaced by another liquid polymer matrix, which would be solid after the curing process. The disadvantage of commercial ink preparations was that their composition was unknown in many respects, because they were secret recipes of the producer and some of the ink component might interfere in the electrochemical measurements.