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New tetradecyltrimethylammonium-selective electrodes: Surface composition and topography as correlated with electrode’s life span

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ABSTRACT

Two conventional plastic membrane electrodes that are selective for the tetradecyltrimethylammonium cation (TTA) have been prepared. The ion exchangers of these sensors were the ion associate, TTA-PT, and the ion aggregate, TTA-PSS, where PT and PSS are phosphotungstate and polystyrene sulfonate, respectively. The following performance characteristics of the TTA-PT- and TTA-PSS-containing electrodes were found: conditioning time of 30 and 20 min; potential response of 58.2 and 61.1 mV/TTA concentration decade; rectilinear concentration ranges of 2.0×10^{-5}–5.0×10^{-2} and 1.5×10^{-5}–7.9×10^{-2} mol L^{-1}; average working pH ranges of 4.0–10.5 and 3.8–10.7; life spans of 20 and 28 weeks, and isothermal temperature coefficients of 4.44×10^{-4} and 6.10×10^{-4} V/°C, respectively. Both electrodes exhibited high selectivity for TTA with an increasing number of inorganic and quaternary ammonium surfactant cations. These electrodes have been successfully applied to assay an antiseptic formulation containing TTA. Surface analyses using electron microscopy and X-ray photoelectron spectroscopy were used to determine the cause of the limited life span of plastic membrane electrodes.

1. Introduction

Cationic surfactants are widely used in the manufacture of many commercial products and pharmaceutical formulations, including textile softeners, anti-corrosion agents, disinfectants, cosmetics and household cleaning products [1–4]. However, the growing consumption of these compounds has a negative environmental impact. This resulted in growing concern to establish procedures to detect and monitor these compounds in the environment and to assay them in products for quality control purposes. Tetradecyltrimethylammonium bromide (TTAB) is one of the most important cationic surfactants. It has diverse applications especially as a preservative in many cosmetic and pharmaceutical products and as an effective antiseptic compound [5]. Many patents [6] have been reported that describe the cleaning formulations composed of TTAB, a chelant, and alcohol solvent mixtures. TTAB has also been a main component in lysing reagent for blood analysis [7]. Therefore, a simple and reliable technique is needed to determine the concentration of TTAB in products for the purpose of quality control in manufacturing companies [8]. The most suitable technique for this purpose is potentiometric sensing. Although many ion-selective electrodes have been developed for surfactants in the last three decades [9–12], very little has yet been reported about TTAB electrodes. A coated-wire TTAB electrode based on carboxylated PVC was constructed [13] and its response was examined over several months. However, no other performance characteristics of the electrode, such as the effect of pH, selectivity, or possible applications, were studied in this work. The purity of cetrimide, a composite containing TTAB, was analyzed [14] by an assay method according to a procedure in the European Pharmacopoeia. This method involved the conversion of TTAB to the iodide analogue (TTAI) by adding an excess of KI standard solution and back titrating with iodate solution. The TTAB concentration was also determined by titrating against a standard solution of perchloric acid [15] and silver nitrate [16]. It is evident that these methods do not allow for the direct determination of the presence of TTAB and are applicable to neither in-field nor in-line analyses.

Oppositely charged surfactants and polyelectrolytes have a strong tendency to bind to one another [17]. This tendency is quantified by the critical aggregation concentration (CAC) which is the surfactant concentration at which this surfactant and the poly-charged ion begin to aggregate [18,19]. Upon mixing these two oppositely charged species, the surface tension of the surfactant/polyionic molecules mixture decreases with increasing surfactant concentration and reaches a clear break point at which the aggregate starts to precipitate. At this point the surfactant/polyelectrolyte attraction overcomes their solubility and the aggregate solid phase starts to separate from the solvent [20]. This establishes an equilibrium system between the liquid gel and the

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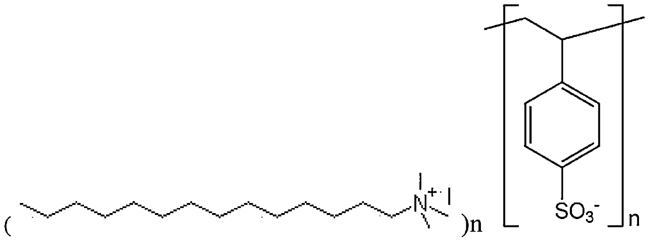

Scheme 1. TTA-PSS ion aggregate.

precipitating phase, which depends on the strength of the head groups of the poly-charged ion.

Polystyrene sulfonate (PSS) is a typical poly-charged anion of highly lipophilic polymeric chains (the degree of polymerization is 340). It interacts strongly with cationic surfactants to form aggregates at very low critical aggregation concentrations [19,21]. This is attributed to the specific hydrophobic interaction of the aromatic rings of the PSS-anion and the non-polar interior of the surfactant micelles [22].

The polyelectrolyte-surfactant aggregates have diverse applications in drug delivery, cosmetic formulations, and rheological modification [23,24]. However, none of these aggregates have yet been used as an exchanger in an ion-selective electrode, although they can provide multiple-sites for the phase boundary exchange of the targeted species. Moreover, this type of aggregate has a highly lipophilic organic part and many electrostatic bonds between TTAB and PSS.

The ion associate, hexadecypyridinium-phosphotungstate (HDP-PT) was used in 1988 as a novel exchanger in HDP-selective electrode [25]. This exchanger exhibited better performance characteristics than those electrodes based on ion pairs as the exchanger. Since 1988 many other ion associates of pharmaceutical cationic species [26–30], and surfactants [31,32], have been used for the same purpose.

The success of ion associates as exchangers was attributed to their higher lipophilicity and the greater number of sites available for ionic exchange as compared to ion pairs. In the present work, an ion aggregate composed of TTA with the polyelectrolyte, polystyrene sulfonate (PSS) is introduced as a novel exchanger for TTA in its electrode (Scheme 1). The polymeric nature of this ion aggregate makes the potential applications of this ion aggregate promising because it can provide a large number of ion exchange sites.

2. Experimental

2.1. Reagents and materials

Sodium (polystyrene sulfonate) (NaPSS) of molar mass 70,000 g/mol (Sigma Aldrich), phosphotungstic acid (PTA) (Fluka), tetradecyltrimethylammonium bromide (TTAB) (Sigma Aldrich), dioctyl phthalate (DOP) (Fluka), poly(vinyl chloride) (PVC) of high molecular weight (Fluka), tetrahydrofuran (THF) (Sigma Aldrich), and Savlon antiseptic cream (Novartis Consumer Health, Horsham, RH12 5AB, UK) were used. All aqueous solutions were prepared in bi-distilled water. The TTA-PT ion associate was prepared as previously described [25] and its purity was checked by elemental analysis. The results revealed a stoichiometric ratio of 3:1 (TTA:PT). The TTA-PSS aggregate was prepared by adding 100 mL solution containing 3.31 g (9.84 mmol) TTAB drop-wise with continuous stirring into 100 mL aqueous solution containing 2.00 g (2.85×10^{-2} mmol) of NaPSS. The spongy white precipitate was filtered and thoroughly washed with distilled water until it was free of Cl^- ions, as tested by $AgNO_3$ solution. The product was dried under vacuum and subjected to IR and elemental analyses. The results revealed the formation of ion aggregates in which more than 99% of the negatively charged sites in the PSS poly-anion are statically bonded to TTA cationic species.

2.2. Construction of the electrodes

The electrodes were prepared as previously described [26] using membranes of different compositions (Table 1).

2.3. Potentiometric measurements

The following assembly was used to measure the potential:

Ag|AgCl|internal solution|membrane|test solution||AgCl|Ag

The measuring instrument was an Orion, Model 420A pH/mV meter. A Caron circulator thermostat was used to control the temperature of the test solution. The method of obtaining the calibration graph was similar to that described previously [25].

2.4. Selectivity

The selectivity coefficients of the TTA-selective electrodes ($K_{\text{pot}}^{\text{TTA},j^{z+}}$) towards different inorganic and quaternary ammonium cationic species, j^{z+}, were determined by the separate solution (SSM) [33] and matched potential methods (MPM) [34].

2.5. Analytical application

The antiseptic cream (Savlon, Novartis Consumer Health, Horsham, RH12 5AB, UK), was assayed by applying the standard addition method using the TTA-electrodes as sensors. An accurately weighed sample of the cream was dispersed in 0.1 mol L^{-1} HNO_3 solution and the greasy material was extracted with petroleum ether. The aqueous layer containing TTA was collected using a separating funnel and its pH adjusted to 6.0 with NaOH solution; then the volume was increased to 100 mL with bi-distilled water.

2.6. X-ray photoelectron spectroscopy (XPS)

XPS spectra were recorded on a model VG ESCALAB 200 (UK) spectrometer using Mg Kα radiation (1253.6 eV) and operated at 300 W (15 kV, 20 mA). The spectra acquisition and processing were carried out by means of an Eclipse V 2.1 data system (UK). The plastic membrane of the electrode was carefully cut out and introduced into the preparation chamber with the sample holder, degassed until a pressure of about 10^{-6} Torr was achieved, and was then transferred into the analysis chamber. The analyses were carried out under the following conditions: analysis chamber pressure of 10^{-9}–10^{-10} Torr, step size of 0.1 eV, dwell time of 100 ms, pass energy of 20 eV, and a source of Mg Kα in the large-area mode. All binding energy values were determined with respect to the C 1s line (284.6 eV), which originates from adventitious carbon. The depth profiling was performed with an Ar ion gun with 5 kV energy and a 1 μA sample current.

2.7. Electron microscopy

The surface topography of membranes cut from new and exhausted electrodes was studied by a ZEISS-variable pressure field emission scanning electron microscope model SUPRA 50VP.