

ORIGINAL PAPER

Marc Gerlache · Zühre Senturk · Guy Quarin
Jean-Michel Kauffmann

Self-assembled monolayer gold electrode for surfactant analysis

Received: 28 January 1997 / Accepted: 7 March 1997

Abstract A gold electrode coated with a self-assembled monolayer of octane-thiol (SAM/Au) has been used as an amperometric detector for the determination of surfactants. This detector operated in the presence of a high percentage of organic solvent and was adapted to an HPLC System. At the SAM/Au, the electrochemical response of an electroactive tracer (potassium ferricyanide) was completely inhibited, but, in the presence of a cationic surfactant, the electrochemical reduction was progressively restored. In flow injection analysis, using the SAM/Au in an amperometric flow-through detector polarised at 0.0 V vs Ag/AgCl, a linear response ($i = f\{\text{[surfactant]}\}$) was observed for cationic surfactants e.g. cetylpyridinium chloride in the concentration range 2×10^{-6} – 1×10^{-3} M. The electrochemical data along with the determination of the ion pair stoichiometry between the redox tracer and the surfactant suggest an electrochemical response related to ion pair formation and governed by electron transfer by tunneling effect.

Key words Self-assembled monolayer · Gold · Surfactant · Amperometry · Flow injection analysis

Introduction

Surfactants are important industrial and environmental chemicals, which can be classified in four groups: anionic (AS), cationic (CS), non-ionic (NI) and zwitterionic species. Anionic surfactants are mainly used at the industrial level, but the cationic surfactants are becoming

increasingly important in softeners, household products, cosmetics, etc [1–3]. The wide consumption of these substances is leading to a growing need to control their concentration in environmental water for reasons of toxicity and/or biodegradability [4–8]. Usually, the analysis of ionic surfactants in environmental and industrial samples is performed by a colorimetric two-phase titration [2]. This technique, however, is time-consuming, difficult for automation, not suitable in turbid solutions, and uses toxic chlorinated solvents, etc [2, 9–11].

Other more elaborate instrumental methods for the determination of surfactants have been published: GC or GC/MS after thermal decomposition [12, 13], thin-layer chromatography [14, 15], HPLC with conductometric or postcolumn extraction and UV detection [3, 16–20], capillary electrophoresis [3, 21], electrochemical methods [22] including tensammetry [23–26], potentiometry with ion-selective electrodes [27–32], and amperometry [33–35]. During the last decade, self-assembled monolayer (SAM) modified metallic electrodes have attracted substantial interest in analytical chemistry [36–43]. SAMs of alkanethiol on gold have already been briefly described for the determination of surfactants [36, 37], but little information regarding the mechanism of the response and the lifetime and stability of such gold modified electrodes in aqueous and organic solvents is available. Here, we characterize and optimize a SAM gold electrode obtained by the formation of a strong chemical bond between a polycrystalline gold electrode and the sulfur atom of a judiciously selected alkane thiol. This electrode is incorporated in an amperometric flow injection analysis (FIA) apparatus in which the carrier contains an electroactive tracer. The latter is not detected at the SAM gold electrode (SAM/Au) because of diffusional restriction created by the densely packed alkanethiol monolayer. An ionic surfactant injected into the FIA carrier will interact with the redox marker and allow its detection at the SAM/Au polarized at a suitable potential. The determination of surfactant concentration by HPLC has been successfully realized.

M. Gerlache · Z. Senturk¹ · G. Quarin · J.-M. Kauffmann (✉)
Institut de Pharmacie, Université Libre de Bruxelles,
Campus Plaine 205/6, Bvd du Triomphe, 1050 Brussels, Belgium
Tel.: +32-2-650-52-15; Fax: +32-2-650-52-25;
e-mail: jmkauf@resulb.ulb.ac.be

¹ On leave from the University of Ankara

Experimental

Chemicals

All reagents were of analytical grade and were used without further purification. Cetyl-, tetradecyl- and dodecyl-pyridinium chloride (CPC, TPC, DPC) were from Fluka. Cetyltrimethylammonium chloride (CTA), dodecylbenzenesulfonic acid (DBSA), sodium lauryl sulphate (SLS) and the organic solvents were from Acros (Belgium). Ethanol and methanol were from Merck, Triton X100 (TX100) was from Sigma and the diester of triethanolamine quaternized with a dimethyl sulphate (an esterquat with a molecular weight of 820) and the ethoxylated alcohol (EO), were from Colgate-Palmolive. A 3- μm diamond slurry with PM Mecaprex solvent and a polishing solution (SPM Mecaprex) were provided by Presi Mecaprex (Grenoble, France).

Materials

Cyclic voltammetry (CV) was performed on a BAS 100B electrochemical analyzer coupled to a cell stand BAS-C2. A three-electrode cell configuration comprised the gold working electrode (BAS, 3 mm diameter), an Ag/AgCl NaCl 3 M reference electrode, and a platinum wire as counter electrode. The flow system (for the FIA) consisted of a Perkin-Elmer pump (series 10) with an injection loop of 20 μl , a BAS LC-CC-5 working cell, an amperometric detector BAS LC-4b and a Kipp and Zonnen BD-41 recorder. The working gold electrode in the FIA was a dual 3-mm diameter model BAS MF 1004. The FIA detector comprised a stainless steel counter electrode and an Ag/AgCl NaCl 3 M reference electrode. The HPLC column was a Keystone Prism RP 150 \times 4.6 mm with a porosity of 5 μm (no. 155/321). All the experiments were made at room temperature (20 ± 2 $^{\circ}\text{C}$) with a flow rate of 1 ml min^{-1} .

Preparation of the SAM gold electrode

Before each modification, the gold electrode surface must be carefully cleaned to be free of any adsorbed species [39, 40]. The electrode was manually polished with a 3- μm diamond slurry in the presence of the PM Mecaprex solvent on a nylon disk for 2 min. After a thorough rinsing with deionized water, the electrode was polished for a further 2 min in the presence of SPM Mecaprex solution. After 5 min of sonication in a water bath, the cleanliness of the electrode was checked by cyclic voltammetry of a 5-mM $\text{Fe}(\text{CN})_6^{3-}$ solution in 0.25 M HAc/Ac $^-$, pH 4.7, in the presence of 0.1 M KCl. The presence of sodium chloride gives better reversibility of the redox tracer. If the peak potential separation ($E_{\text{pa}} - E_{\text{pc}}$) of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ deviated from reversible behavior (ΔE_{p} close to 60 mV), all the polishing procedure was repeated. When the ferri/ferrocyanide couple approached quasi-reversibility (ΔE_{p} about 70 mV), the polishing procedure was repeated once more. Then, the electrode was cleaned in deionized water in an ultrasonic bath and dried with pure ethanol. Subsequently, the electrode was soaked overnight in a 10 mM octanethiol ethanolic solution. After completion of the modification, the electrode was rinsed with ethanol and sonicated in an ethanol bath for at least 5 min to remove any physically adsorbed octanethiol.

Results and discussion

Cyclic voltammograms (scan rate 100 mV s^{-1}) of 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ recorded in a HAc/Ac $^-$ buffer (pH 4.7) in the presence of 0.1 M KCl at a gold electrode before (a)

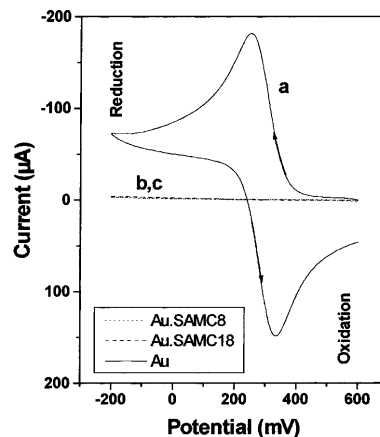


Fig. 1a-c Cyclic voltammograms (100 mV s^{-1}) of 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$, pH 4.7, HAc/Ac $^-$ buffer + 0.1 M KCl: **a** bare gold (Au) electrode, **b** octane-thiol SAM/Au, **c** octadecane-thiol SAM/Au electrode

and after modification with octane-thiol (b) and octadecane-thiol (c) are shown in Fig. 1. At both SAM-gold electrodes, the ferricyanide redox behavior is totally inhibited over the potential range +600 to -200 mV. It appears that the C $_8$ -SAM and the C $_{18}$ -SAM recordings are indistinguishable from each other. Further experiments use the octanethiol SAM, since this gives better sensitivity for surfactants – a property related to its shorter alkanethiol chain length, i.e. better electron tunneling efficiency (see below). If a cationic surfactant (CS) is added to the buffer solution, the reduction of the tracer $\text{Fe}(\text{CN})_6^{3-}$ reappears. However, in comparison to the bare electrode, the peak potential is significantly shifted towards more negative values and the current is lower (Fig. 2). By increasing the CS concentration, the shape of the reduction peak progressively approaches the behavior obtained at the bare gold electrode. On repeating the above cyclic voltammetric experiments

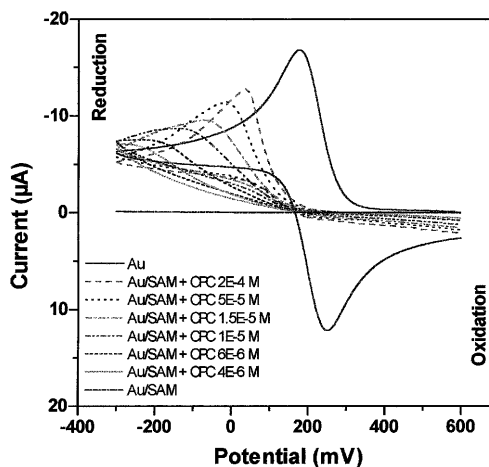


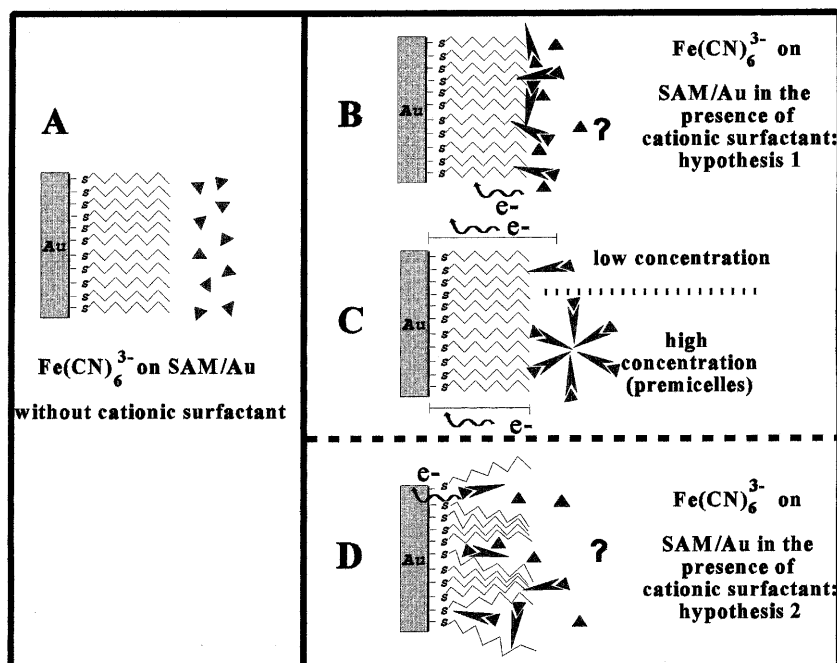
Fig. 2 Influence of the cationic surfactant (CPC) concentration on the electrochemical response of 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$, pH 4.7, HAc/Ac $^-$ buffer, 0.1 M KCl and 20% acetone: C $_8$ SAM/Au

using the same SAM/Au, identical behavior is observed, indicating the stability of the SAM in the presence of surfactants. We may note that reoxidation of the $\text{Fe}(\text{CN})_6^{4-}$ formed is not detectable even in the presence of high CS concentrations. If the anodic scan of the CV is extended to +900 mV, reoxidation is still not observed. Higher positive potentials have not been investigated because of SAM/Au instability (oxidative desorption of the monolayer). A possible explanation of the lack of ferrocyanide oxidation may be related to the formation of an ion pair with definite stoichiometry: $[\text{Fe}(\text{CN})_6^{3-}/\text{CPC}]$ and $[\text{Fe}(\text{CN})_6^{4-}/\text{CPC}]$. Such ion pairs are readily formed and precipitate out at high concentrations. By potentiometric titration of a ferricyanide or a ferrocyanide solution with CPC as titrant (using an ion-selective electrode as end point detector [31]) a stoichiometry of 1:3 for $[\text{Fe}(\text{CN})_6^{3-}/\text{CPC}]$ or 1:4 for $[\text{Fe}(\text{CN})_6^{4-}/\text{CPC}]$ is determined. Interestingly, both ion pairs show reversible behavior at the bare gold electrode and in the presence of the octanethiol monolayer at the Au/SAM, the ferro/CPC oxidation is inhibited but not the ferri/CPC reduction. The presence of one additional CPC molecule in the structure of the ferrocyanide ion pair $[\text{Fe}(\text{CN})_6^{4-}/\text{CPC}]$ can change its electronic configuration and thus its geometry, so that the ferrocyanide oxidation is inhibited at the SAM/Au. Actually, if the electronic transfer is realized by the tunneling effect, as will be discussed below, the electron path length may be longer in the 1:4 structure than in the 1:3 structure, and the transfer less efficient (exponential decrease of transfer rate with distance between donor and acceptor [44]).

When the CS is replaced by an anionic surfactant (AS) (SLS) or a nonionic surfactant (NS) (TX100), the

results are completely different. Whatever the SLS or TX100 concentration in solution, the cyclic voltammogram of $\text{Fe}(\text{CN})_6^{3-}$ shows no faradaic process, i.e. no reduction and no reoxidation peak is observed. In fact, in the absence of a surfactant, the monolayer represents a physical barrier between the gold surface and the electroactive tracer $\text{Fe}(\text{CN})_6^{3-}$ in solution. Here, despite the presence of an AS or NS, the tracer cannot diffuse to the gold surface and cannot be reduced (Fig. 3A). These results may be interpreted by considering that when a surfactant is added to the solution, lipophilic interaction between the alkyl chain of the SAM and the hydrophobic part of the surfactant occurs. In addition, there is some interaction between $\text{Fe}(\text{CN})_6^{3-}$ ions and the charged surfactant. If the charge of the surfactant is positive, the tracer will be attached to the hydrophilic part of the CS to form an ion pair. At this stage, two hypotheses are possible. In the first one, the ion pair and the surfactant adsorption allow the $\text{Fe}(\text{CN})_6^{3-}$ ions to approach closer to the SAM, giving rise to an electronic transfer by tunneling along the alkyl chain (Fig. 3B). By raising the CS concentration in solution, an increase in the slope of the ferricyanide reduction peak is observed in cyclic voltammetry. This might be interpreted by postulating a distinct orientation of the ion pair on the SAM, where a closer proximity of the ion pair is observed at high concentrations of CS (Fig. 3C). A second hypothesis might explain the electroreduction of the marker in the presence of CS. The surfactant might disorganize the SAM and allow the ion pair to diffuse through the monolayer allowing the reduction of ferricyanide at the gold surface electrode (Fig. 3D). However, there are several possible objections to the second interpretation:

Fig. 3 A-D Schematic drawing of the $\text{Fe}(\text{CN})_6^{3-}$ behavior at the SAM/Au (A) in the absence or (B, C, D) presence of a cationic surfactants. In the first hypothesis, the adsorption of the ion pair induces the electronic transfer by tunneling along the alkyl chain (B). Because of the premicelles formation at high CS concentration, the path length of the electronic transfer becomes shorter and the reduction rate of the ferricyanide ions increases (C). In the second hypothesis, the CSs disorganise the SAM and the ion pair diffuses through the “fluidized” monolayer



1. The amount and size of any pinholes between the chains of the SAM are likely to be small compared to the ionic pair size.

2. In FIA (see below), the return to the base line after an injection of CS is rapid.

3. With this model, it is difficult to explain why the $\text{Fe}(\text{CN})_6^{4-}$ formed is not reoxidized.

4. AS and NS show no SAM monolayer perturbation.

When the added surfactant is negative, there is an electrostatic repulsion of the tracer from the SAM/solution interface, and the reduction of the ferricyanide evidently cannot occur.

The attractive property of the SAM-electrode studied is the inherent stability of the SAM under hydrodynamic conditions. A study of the amperometric response of the tracer $[\text{Fe}(\text{CN})_6^{3-}]$ as a function of the applied potential in an FIA system has been carried out (Fig. 4). The carrier is fixed at pH 4.7 using acetate buffer containing 1×10^{-5} M $\text{Fe}(\text{CN})_6^{3-}$, 0.1 M KCl and 20% acetone. A maximum current response is observed at -300 mV. A similar hydrodynamic voltammogram, though of much higher intensity, is obtained in the presence of CPC. The low response observed in the absence of CPC (Fig. 4) must be attributed to some defects in the SAMs.

To minimise the oxygen reduction interference, a potential of 0.0 V is preferably applied. A linear response ($i = f([\text{CPC}])$) (Table 1) of the reduction current to the CS concentration is obtained for cationic surfactants such as CTA and CPC (also TPC and DPC) between 5×10^{-6} and 1×10^{-3} M, 2.5×10^{-6} and

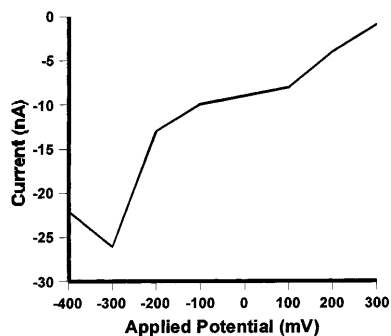


Fig. 4 Amperometric response of the SAM/Au electrode as a function of the applied potential in an FIA system (carrier: pH 4.7, acetate buffer, 0.1 M KCl, 1×10^{-5} M $\text{K}_3\text{Fe}(\text{CN})_6$ and 20% acetone), flow rate 1 ml min^{-1}

Table 1 Equations for the linear portions of the curves A, B and C in Fig. 5 for concentrations expressed in M and current in nA

	A	B	C
Intercept (nA)	1.476	0.269	0.564
Slope (nA M^{-1})	149117	26389	62276
r	0.996	0.9999	0.996
Standard deviation	1.16	0.06	0.14

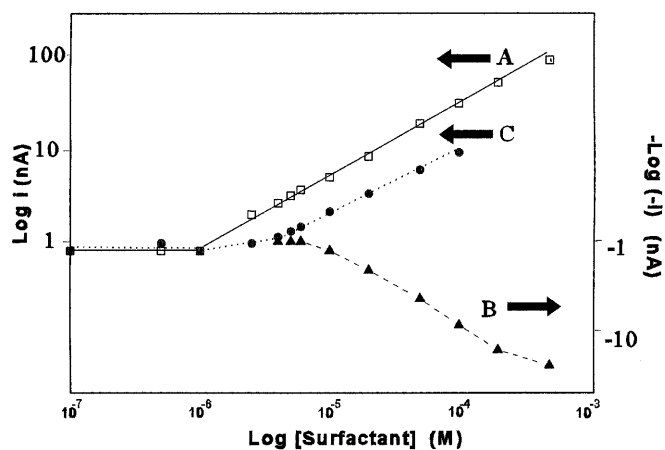


Fig. 5 Calibration curve obtained at a $\text{C}_8\text{SAM}/\text{Au}$ ($E_{\text{appl.}} = 0.0 \text{ V}$) for **A** CPC and **B** SLS injections in an FIA system (carrier: pH 4.7, acetate buffer, 0.1 M KCl, 1×10^{-5} M $\text{K}_3\text{Fe}(\text{CN})_6$, and 20% acetone), flow rate 1 ml min^{-1} . The capacitive component of the amperometric signal for CPC injections is reported on curve C

1×10^{-3} M, respectively (Fig. 5a), with a detection limit of 2×10^{-6} for both. The response time is less than 2 s, and the RSD, for several injections ($N = 9$) of a 3×10^{-5} M CS solution, is 1%. Some other CSs such as TPC and DPC have been determined by this technique. The quantitative results obtained are similar to those obtained with the CPC and CTA. To complete our investigation, we have tried to analyze an esterquat (a new kind of CS), the diester of triethanolamine quaternized with dimethyl sulphate (MW 820). With this molecule, the limit of detection is around 6×10^{-4} M and the linear region was between 8×10^{-4} and 6×10^{-3} M.

Interestingly, if the surfactant injected into the FIA system is an AS such as SLS or DBSA, an electrochemical signal appears also. However, the response is oriented in the opposite direction to that observed with CSs (Fig. 6), i.e. an anodic response is observed in agreement with the literature [36]. The sensitivity of the response and the linear range for these molecules are less attractive than those obtained with CSs. Actually, the current observed for ASs clearly has a capacitive origin, since no oxidable species is present in the carrier solution. With the adsorption of ASs, the SAM takes a

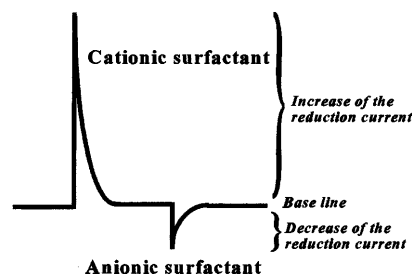


Fig. 6 Orientation of the amperometric response at the $\text{C}_8\text{SAM}/\text{Au}$ ($E_{\text{appl.}} = 0.0 \text{ V}$) in an FIA system for the injection of **a** CPC and **b** SLS (carrier: pH 4.7, acetate buffer, 0.1 M KCl, 1×10^{-5} M $\text{K}_3\text{Fe}(\text{CN})_6$ and 20% acetone)

negative charge, and this induces a positive charge at the gold electrode surface. If at 0.0 V the electrode potential is more positive than the zero point of charge, the amplitude of the transient current (capacitive current) will increase with an increase of the AS concentration. When CSs are injected, the observed current variations are considerably higher. In this case, the electrode surface is negative, and a faradaic current of high amplitude is superimposed on the capacitive component of the observed current (Fig. 5). No detectable response is obtained for NSs (TX100 and the EO) even at high concentration (1×10^{-3} M). It should be mentioned that recent work took advantage of the capacitive response of surfactants at SAM/Au for the study of surfactant adsorption [45] and for the development of a sensor for lipolytic enzymes based on the capacitive recording [46].

As desired for possible on-site environmental detection applications, the SAM electrode must be free of interference. A number of experiments were carried out where several possible interfering species (at a concentration of 10 mM) were added to a 0.1 mM CPC or CTA solution and injected into the FIA. For a large number of inorganic interfering ions, the electrode still offers good selectivity (Table 2). Among the possible interferents tested, only those having an electrical charge greater than ± 3 actually do interfere. This observation must be related to the formation of the ion pair between the CS and the marker. When the charge of the ionic interferent is high, the ion pair formation between CS and ferricyanide is greatly affected, yet because of the low concentration of this kind of ion in natural samples, they do not interfere in the analysis. In industry, the presence of polyphosphate ions in the analyzed media is not unusual, and these can become an important source of error if they are not previously eliminated. In terms of lifetime, if a cationic surfactant standard sample is injected twice a day in the FIA apparatus, the same electrode can be used for more than 1 week without renewing the SAM. Only a small decrease of the linear range (± 5 –7% in 1 week) and a very small shift of the slope (+5%) are observed. With a 1×10^{-5} M CPC solution permanently present in the carrier, the electrode shows a drift of less than 5% after 12 h of continuous use.

Table 2 Variation of the amperometric signal recorded at an SAM/Au electrode in the presence of interferents

Interferent cation	Signal variation	Interferent anion	Signal variation
K ⁺ (KCl)	/	Cl ⁻ (KCl)	/
Na ⁺ (NaCl)	/	Br ⁻ (KBr)	/
Ca ²⁺ (CaCl ₂ · 2H ₂ O)	/	NO ₃ ⁻ (KNO ₃)	/
Mg ²⁺ (MgCl ₂ · 6H ₂ O)	/	CO ₃ ²⁻ (K ₂ CO ₃)	/
Sr ²⁺ (SrCl ₂ · 6H ₂ O)	/	H ₃ BO ₃	/
Li ⁺ (LiNO ₃)	/	Na ₅ P ₃ O ₁₀	-43%
Co ³⁺ (CoCl ₃)	+5%	H ₂ PO ₄ ⁻ (KH ₂ PO ₄)	/
Cu ²⁺ (CuCl ₂)	/		
Al ³⁺ (AlCl ₃ · 2H ₂ O)	+7%		

In the surfactant industry, it is not unusual to determine the different surfactants in a complex mixture. It would be interesting to achieve the determination on-line following a separation step which is usually realized by HPLC. The mobile phase is generally a mixture of different organic solvents with or without water [3, 47]. In the literature, non-aqueous solvents such as a methanol, THF and hexane solution in different proportions are used as the mobile phase for the HPLC separation of a complex mixture of cationic surfactants [47]. In order to know if our electrode was able to work in such conditions, a new series of experiments was carried out. First, a saturated Fe(CN)₆³⁻ methanol solution was prepared at 22 °C. The FIA carrier consisted of 1 mM trichloroacetic acid as supporting electrolyte in methanol + ferricyanide:THF:hexane in the ratio 1:3:3 v/v. The exact Fe(CN)₆³⁻ concentration in the carrier was determined by colorimetric titration [48] and was found to be 2.1×10^{-6} M. Between 2×10^{-6} and 3×10^{-4} M CPC, the measured current is directly proportional to the CPC concentration, with an RSD of ± 2 –3%. The background current obtained under such conditions is very low (-0.8 nA), but is stable for only 150 min after which it becomes irreproducible.

Another mobile phase tested in HPLC was an aqueous phase containing 75% acetonitrile [3]. After a postcolumn dilution, the carrier consisted of 37.5% of acetonitrile in 5×10^{-3} M acetate buffer pH 4.7, 0.1 M KCl and 1×10^{-5} M Fe(CN)₆³⁻. The reduction current is linear with respect to the injected CPC, in the concentration range 5×10^{-6} – 1×10^{-3} M. As previously mentioned, the base line is very low and stable. Within 16 h of continuous use, the base line rose from -1.3 to -2.0 nA. The injection of a mouthwash sample, containing CPC as disinfectant, gives an amperometric response, after a retention time of 6.5 min, in good agreement with the UV response. However, the SAM/Au electrode is less sensitive to additional compounds in the sample such as perfumes or other chromophoric products, which are also monitored by the UV detector. The ASs (SLS and DBSA) give a small current variation (capacitive origin) linearly related to their concentration between 2.5×10^{-4} and 2×10^{-3} M.

Conclusion

The good operational stability of an octane-thiol SAM/Au electrode (more than 10 days), its wide linear response range towards cationic surfactants in a flow-through detector (FIA), and the possibility of using this electrode as an amperometric detector after HPLC makes this modified electrode a complementary alternative to UV detection of cationic surfactants.

Acknowledgements Thanks are expressed to the Ministry of Walloon District for the application of the FIRST programme JC0161CG2860 and to the Brussels Capital Region for a "Research in Brussels" Grant (Z.S). Acknowledgments are also

expressed to the R and D Colgate-Palmolive European Center (Milmort-Belgium) for their help and to BAS (Lafayette USA) for instrumentation support.

References

1. Fabry B, Nickel D (1994) *J Com Esp Deterg* 25: 65
2. Schmitt TM (1992) *Analysis of surfactants*. Dekker, New York
3. Cross J, Singer EJ (1994) *Cationic surfactants; analytical and biological evaluation*. Dekker, New York
4. Grammo A, Ekelund R, Magnusson K, Berggren M (1989) *Envir Pollut* 59: 115
5. Lewis MA (1991) *Water Res* 25: 101
6. Ahel M, McEvoy J, Giger W (1993) *Envir Pollut* 79: 243
7. Ahel M, Giger W, Koch M (1994) *Water Res* 28: 1131
8. Field JA, Field TM, Poiger T, Siegrist H, Giger W (1994) *Water Res* 29: 1301
9. Thomas JDR (1986) *Anal Chim Acta* 180: 289
10. Reid VW, Longman GF, Heineth E (1967) *Tenside Deterg* 4: 292
11. Koenig H, Walldorf E (1978) *Fresenius Z Anal Chem* 189: 177
12. König H, Stroebel W (1983) *Fresenius Z Anal Chem* 314: 143
13. Linhart K, Wrabertz K (1978) *Tenside Deterg* 15: 19
14. Michelsen ER (1978) *Tenside Deterg* 15: 169
15. Kruse A, Buschmann N, Cammann K (1994) *J Planar Chromatogr* 7: 22
16. Levsen K, Emmrich M, Behnert S (1993) *Fresenius Z Anal Chem* 346: 732
17. Kawase J, Takao Y, Tsuji K (1983) *J Chromatogr* 262: 408
18. Kawase J, Veno H, Tsuji K (1983) *J Chromatogr* 264: 415
19. Kawase J, Veno H, Tsuji K (1984) *J Chromatogr* 267: 133
20. Kawase J, Veno H, Tsuji K (1984) *J Chromatogr* 267: 149
21. Chen S, Pietrzyk DJ (1993) *Anal Chem* 65: 2270
22. Gerlache M, Kauffmann JM, Quarin G, Viré JC, Bryant GA, Talbot JM (1996) *Talanta* 43: 507
23. Szymanski A, Lukaszewski Z (1994) *Anal Chim Acta* 293: 77
24. Szymanski A, Wyrwas B, Lukaszewski Z *Anal Chim Acta* (in press)
25. Wyrwas B, Szymanski A, Lukaszewski Z (1994) *Talanta* 41: 1529
26. Bersier PM, Bersier J (1988) *Analyst* 113: 3
27. Buschmann N, Schulz R (1992) *Tenside Deterg* 29: 128
28. Vytras K, Dvorakova V, Zeman I (1989) *Analyst* 114: 1435
29. Shulz R, Gerhards R (1994) *Intern Lab* 10: 10
30. Lowy DA, Patrut A, Walter ME (1993) *Process and Control Quality* 4: 125
31. Gerlache M, Senturk Z, Viré JC, Kauffmann JM *Anal Chim Acta* (in press)
32. Vytras K, Kalous J, Jezkova J (1997) *Egypt J Anal Chem* 6: (in press)
33. Zutic V, Cosovic B, Kozarac Z (1977) *J Electroanal Chem* 78: 113
34. Adeloju SB, Shaw SJ (1994) *Electroanalysis* 6: 645
35. Schimdt T, Emons H (1994) *Electroanalysis* 3: 543
36. Kawaguchi T, Yamauchi Y, Maeda H, Ohmori H (1993) *Chem Pharm Bull* 41: 1601
37. Kawaguchi T, Yamauchi Y, Maeda H, Ohmori H (1992) *Anal Sciences* 8: 691
38. Dubois LH, Nuzzo RG (1992) *Ann Rev Phys Chem* 43: 437
39. Yang Z, Gonzales-Cortés A, Jourquin G, Viré JC, Kauffmann JM, Delplancke JL (1995) *Biosensors and Bioelectron* 10: 789
40. Takehara K, Takemura H, Ide Y (1994) *Electrochim Acta* 39: 817
41. Widrig CA, Chung C, Porter MD (1991) *J Electroanal Chem* 310: 335
42. Creager SE, Rowe GK (1994) *J Electroanal Chem* 370: 203
43. Malem F, Mandler D (1993) *Anal Chem* 65: 3741
44. Marcus RA, Sutin N (1985) *Biochim Biophys Acta* 811: 265
45. Krause C, Mirsky VM, Heckman KD (1996) *Langmuir* 12: 6059
46. Mirsky VM, Krause C, Heckman KD (1996) *Thin Solid Films* 284-85: 939
47. Wilkes AJ, Walraven G, Talbot JM (1992) *J Am Oil Chem Soc* 69: 609
48. Vogel AI (1961) *Quantitative inorganic analysis*, 3rd edn. Longmans, London, p 37