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Gold Electrode Modified with a Self-Assembled Monolayer of Thiols as an Electrochemical Detector for Ionic Surfactants

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Effects of ionic surfactants on the amperometric response of Fe(CN)$_6^{3-}$ at a gold electrode modified with the self-assembled monolayer (SAM) of an alkanethiol were examined in a flow system using an aqueous solution of a supporting electrolyte as the mobile phase. The response was enhanced by a cationic surfactant but depressed by an anionic surfactant, being detected as a positive and a negative peak, respectively. Octyl- and decylthiol were suited for the electrode modifier, and LiCl or NaCl was the electrolyte of choice. With 5% aqueous MeOH containing NaCl (0.1 M) and $K_3Fe(CN)_6$ (5 mM) as the mobile phase, the amperometric peak area was linearly correlated with the concentration of surfactants, indicating that the SAM-modified electrode is a prospect as a detector for surfactants in high-performance liquid chromatography.

Keywords surfactant; amperometric detection; alkanethiolmodified gold electrode; self-assembled monolayer; flow system

We previously reported the determination of ionic surfactants using a gold electrode modified with stearylthiol self-assembled monolayer (SAM).$^{1)}$ On cyclic voltammetry at the gold electrode, the SAM inhibited the redox reactions of Fe(CN)$_6^{3-}$ and Fe^{3+}, the marker ions, in a stationary aqueous solution. When a cationic or an anionic surfactant was added to the solution, the voltammetric response of the anionic or the cationic marker ion, respectively, was recovered, and the extent of recovery was dependent on the alkyl-chain length and the concentation of the surfactant.

In the present study, we examined the applicability of the SAM-coated electrode as an electrochemical detector for ionic surfactants in high-performance liquid chromatography (HPLC). HPLC is recommended as an effective technique for the analysis of surfactants$^{2)}$ and various methods of their detection have been proposed.$^{3-6)}$ However, a simpler and more facile method seems worthy of investigation.

Experimental

All the chemicals used were of reagent grade and were used without further purification. Deionized and distilled water was used throughout.

The flow injection system consisted of a plunger pump (Shimadzu Model LC-5A), an injection valve with 20 ml sample loop, interconnecting Teflon tubing, and an electrochemical detector (Shimadzu L-ECD-6A, using only the detector cell-compartment) equipped with a gold electrode modified with a SAM of thiol. No separation column was connected to the system, since the primary object of this study was to clarify how a SAM-coated electrode would respond to surfactants in a flow system. The SAM-coated electrode was prepared as follows. A gold disk electrode (Johnson Matthey Japan Co., Ltd., 2.0 mmø) polished with 0.05 mm alumina was treated by multiple triangular potential sweeps (−0.2—+1.8 V *vs*. Ag/AgCl, 10 Vs^{-1}) in 1 M H_2SO_4 for 10 min. After being rinsed with distilled water, the electrode was immersed in an ethanolic solution of a thiol (10 mM) for 10 h. The thiol-coated electrode was then washed by immersing it in ethanol for 30 min followed by air-drying.

An aqueous sample solution was injected into the mobile phase consisting of water or a mixture of water and methanol containing a supporting electrolyte (0.1 M). The marker, $K_3Fe(CN)_6$, was added either to the sample solution or to the mobile phase depending on the experimental purpose. The potential of the detector electrode was kept at 0.0 V *vs*. Ag/AgCl, at which Fe(CN)$_6^{-3}$ is reduced to Fe(CN)$_6^{4-}$, by a Hokuto high sensitive potentiostat HECS 318.

Results and Discussion

Figure 1 shows typical response peaks of a cationic surfactant $CH_3(CH_2)_{11}N(CH_3)_3Br$ (**1**) and an anionic surfactant $CH_3(CH_2)_{11}SO_4Na$ (**2**) at the gold electrode modified with dodecyl thiol with $K_3Fe(CN)_6$ as the marker in the mobile phase. The surfactant **1** gave a positive peak, while a negative peak was observed for **2**. These results are consistent with those obtained in a stationary solution.$^{1)}$ The cationic surfactant **1** injected in the mobile phase will penetrate into the SAM to bring a positive charge to the monolayer, and the permeability of Fe(CN)$_6^{3-}$ ion to the SAM will be enhanced by an electrostatic effect and/or by an ion-pair formation. On the contrary, transfer of the anionic surfactant **2** into the SAM will result in a steric and electrostatic repulsion toward the marker anion to reduce its flux to the electrode surface. These results suggest that both cationic and anionic surfactants can be detected by the present method. The response time seems rather slow under the conditions described in Fig. 1, but the time decreased with the increase of MeOH content in the mobile phase.

In order to find reasonable conditions for the determination of surfactants, factors affecting the response of the SAM-coated electrode were explored. First, the effects of alkyl-chain length of the thiol forming the SAM were examined. In this experiment, the marker was added

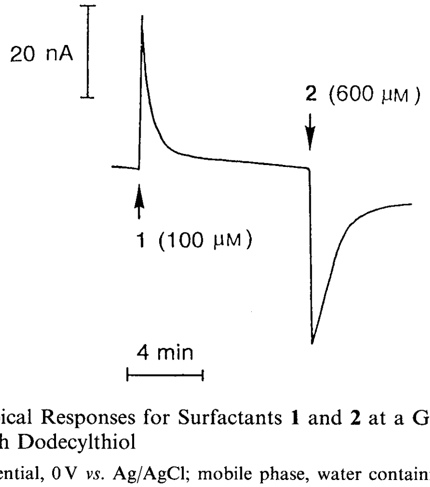

Fig. 1. Typical Responses for Surfactants **1** and **2** at a Gold Electrode Modified with Dodecylthiol

Applied potential, 0 V *vs*. Ag/AgCl; mobile phase, water containing KCl (0.1 M) and $K_3Fe(CN)_6$ (5 mM); flow rate, 1.0 ml/min.

Table I. Effects of Alkyl Chain Length of Thiol Employed as Electrode Modifier on the Electrochemical Response of $K_3Fe(CN)_6$ (5 mM)[a)]

Carbon No. of thiol	I'/I	I''/I' Surfactant 3	I''/I' Surfactant 1	I''/I' Surfactant 4
8	0.096	2.94	3.10	4.41
10	0.041	3.90	3.36	3.61
12	0.012	1.42	3.47	2.47
14	0.004	2.84	2.79	1.24
16	0.003	1.90	1.70	1.22

a) The concentrations of **3**, **1** and **4** were 3, 0.3 and 0.3 mM, respectively; applied potential, 0 V *vs.* Ag/AgCl; mobile phase, water containing KCl (0.1 M); flow rate, 1.0 ml/min.

Table II. Effects of Supporting Electrolyte and MeOH in the Mobile Phase upon the Electrochemical Response Induced by **1** at a Gold Electrode Modified with Dodecylthiol[a)]

Supporting electrolyte	I''/I'	MeOH content (%)[b)]	I''/I'
KCl	3.59	0	3.59
NaCl	5.75	5	3.45
LiCl	6.62	10	2.39
KBr	3.36	20	1.66
KNO_3	2.84	30	1.21
KSCN	1.62		
$NaClO_4$	1.46		

a) Applied potential, 0 V *vs.* Ag/AgCl; mobile phase, water containing a supporting electrolyte (0.1 M); flow rate, 1.0 ml/min; injected sample, aqueous solution of 5 mM $K_3Fe(CN)_6$ with (I'') or without surfactant **1** (0.3 mM) (I'). b) Supporting electrolyte, KCl.

in the sample solution and the peak current due to its reduction at the SAM-coated electrode (I') was compared with that at the unmodified gold electrode (I). The ratio of the peak currents, I'/I, then represents the efficiency of the SAM for blocking the approach of $Fe(CN)_6^{3-}$ to the electrode surface. As expected, the ratio decreased with increase in the alkyl-chain length of the thiol (Table I). When a cationic surfactant was present in the sample solution together with the marker, the blocking effect of the SAM was partially removed and the peak current at the coated electrode was recovered. Table I also includes the current ratio, I''/I', where I'' is the reduction current obtained in the presence of three cationic surfactants: $CH_3(CH_2)_nN(CH_3)_3Br$: $n=9$ (**3**), 11 (**1**), and 13 (**4**). The values of I'/I and I''/I' suggest that thiols with alkyl chain of 8 to 10 carbon atoms are suitable for modifying the electrode.

Table II summarizes the effects of supporting electrolyte in the mobile phase on the current ratio, I''/I': dodecyltrimethylammonium bromide **1** was employed as the surfactant. The effectiveness of the cations of supporting electrolytes to increase the current ratio was $Li^+ > Na^+ > K^+$, and that of the anions was $Cl^- > Br^- > NO_3^- > SCN^-$ in potassium salts, and $Cl^- > ClO_4^-$ in sodium salts. These orders are in accord with Hofmeister's series for cations and anions, respectively, which represent the hydration force of ions. Since the current ratio will depend on the degree of the mutual attraction between the cationic surfactant **1** and the marker anion, caused either electrostatically or by an ion-pair formation (see above), a cation of supporting electrolyte whose hydration force is small will inhibit the attraction by interacting strongly with the marker anion to bring about a current ratio of low value. An anion of supporting electrolyte with small hydration force will exert similar effects by interacting with the cationic surfactant. From the current ratio given in Table II, LiCl or NaCl is recommended as the supporting electrolyte.

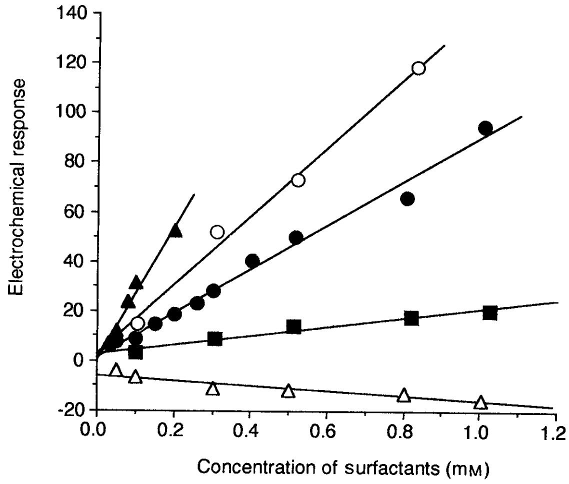

Fig. 2. Relation between the Concentration of Surfactants and the Electrochemical Response Detected at a Gold Electrode Modified with Octylthiol

Applied potential, 0 V *vs.* Ag/AgCl; mobile phase, 5% aqueous MeOH containing NaCl (0.1 M) and $K_3Fe(CN)_6$ (5 mM); flow rate, 1.0 ml/min. ●, surfactant **1**; ■, **3**; ▲, **4**; ○, **5**; △, **2**.

In the practical analysis of surfactants by HPLC, a reverse phase column is usually employed with a mixture of water and an organic solvent, such as MeOH and MeCN, as the mobile phase. The effects of MeOH in the mobile phase on the current ratio, therefore, were examined next; the surfactant **1** was again used. As seen from the results included in Table II, MeOH lowered the current ratio remarkably. In the presence of 30% MeOH, the current ratio approached unity, that is, the surfactant was no longer detectable under the conditions. As described above, the enhanced reduction current I'' of the marker ion relative to I' can be considered ascribable to the transfer of the surfactant into the SAM on the electrode surface. MeOH will depress the transfer by increasing the lipophilicity of the mobile phase. However, denaturation of the SAM did not take place when MeOH was added, and the response of the SAM-coated electrode to the surfactant was restored when the mobile phase was changed to water. The lowering of the current ratio by MeOH is not a crucial disadvantage in applying the present method to HPLC, because MeOH content in the mobile phase entering the detector can be regulated in the cell of the detector by postcolumn mixing of an aqueous marker solution.

Based on the results described so far, the indirect determination of surfactants in the flow system was attempted using 5% aqueous MeOH containing 0.1 M NaCl and 5 mM $K_3Fe(CN)_6$ as the mobile phase. An aqueous sample solution containing a surfactant was injected, and the electrochemical response (see Fig. 1) was monitored. As shown in Fig. 2, linear relationships were obtained between the concentration of surfactant and the electrochemical response expressed by the peak area: the standard deviation in the measured peak areas for repeated sample injection was less than 2%.[7] For the three cationic surfactants **1**, **3** and **4** with $-N^+(CH_3)_3$ group in common, the slope of the regression line increased with their alkylchain length, indicating that the effectiveness of a surfactant to be transferred into the SAM on the electrode will be enhanced by an increase in the lipophilicity of its alkyl chain. In the case of 1-dodecylpyridinium chloride (**5**), the slope of the line was larger than that for **1**, probably because the pyridinium group is smaller in size than the $-N^+(CH_3)_3$ group and **5** is transferred into the SAM more effectively. The slope for the surfactant **2** was negative because its electrochemical response was measured as a negative peak. The lower limit of detection for surfactants also depended on their alkyl-chain length for the same reason as for the slope: for example, the limit was *ca.* 10 and 100 mM for **1** and **3**, respectively.

In a stationary aqueous solution, the electrochemical response, which was expressed by the ratio of steady state reduction current of $Fe(CN)_6^{3-}$ in the presence and absence of a surfactant, was logarithmically related to the concentration of the surfactant. In the flow system, on the other hand, a linear relation was obtained between the two variables (Fig. 2). Although the apparent discrepancy must originate from a difference in the manner of monitoring the electrochemical response, a reasonable explanation is yet to be determined. Apart from this point, however, the gold electrode modified with a thiol of C8 or C10 alkyl chain is applicable to the indirect determination of various surfactants, though studies should continue to seek even better condition for the determination, including the choice of other electrode modifiers.

References and Notes

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7) At a freshly prepared electrode, the electrochemical response first decreased with the number of injections, but reached a constant value (*ca.* 80% of the initial value) when the number of injections exceeded 20. The results shown in Fig. 2 were obtained under the latter conditions.