Amperometric Determination of Surfactants Using a Gold Electrode Modified with a Self-Assembled Monolayer of Stearylthiol

Tetsuo KAWAGUCHI, Yuji YAMAUCHI, Hatsuo MAEDA and Hidenobu OHMORI

Faculty of Pharmaceutical Sciences, Osaka University, Yamadaoka, Suita, Osaka 565, Japan

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Surfactants, which find many applications as emulsifiers and solubilizers, are also environmental pollutants. Considerable attention has thus been focused on their detection and/or determination.¹ High-performance liquid chromatography (HPLC) has been recommended as an effective technique for this purpose. However, except for certain surfactants with characteristic UV absorption² or fluorescence³, the detection of most surfactants by HPLC has been performed with refractive-index detectors⁴ whose sensitivity and selectivity are not always satisfactory. Although a postcolumn detector based on ion-pair extraction was shown to give reasonable results⁵, a simpler and more facile method seems to be worthy of investigation.

We recently reported that the structure of a Langmuir-Blodgett (LB) membrane cast on a glassy carbon plate is distorted by surfactants to change its permeability to $\text{Fe}(\text{CN})_6^{3-}$ used as a marker ion.⁶ This finding suggested the possibility of electrochemical detection of surfactants by a solid electrode modified with a lipid membrane. LB membranes, however, are too fragile to be utilized in the flow system of an HPLC detector. On the other hand, alkanethiols form stable self-assembled monolayers (SAMs) on a gold surface.^{7,8} A novel electrochemical detection of surfactants could thus be attained if the permeability of an SAM to marker ions is affected by surfactants in a manner similar to that of an LB membrane. We discuss in this communication how the electrochemical response of an SAM-coated gold electrode towards marker ions, $\text{Fe}(\text{CN})_6^{3-}$ and Fe^{3+} , depends on the structure of the surfactants as well as their concentrations.

The SAM-coated electrode was prepared as follows. A gold disk electrode (1.6 mm ϕ) polished with 0.05 μm alumina was treated by multiple triangular potential sweeps (-0.2 – $+1.8$ V vs. Ag/AgCl, 10 V s^{-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 10 mM stearylthiol ($\text{CH}_3(\text{CH}_2)_{17}\text{SH}$) for 10 h. The thiol-coated electrode was then washed by keeping it in ethanol for 30 min followed by air-drying.

The amperometric response of the SAM-coated

electrode to the marker ions (5 mM) in aqueous KCl (0.1 M) was examined by measuring the steady-state reduction currents (I and I^0) due to the marker ions at 0.0 V vs. Ag/AgCl, where I refers to the current in the presence and I^0 to that in the absence of the surfactants. The I^0 values were 10 and 50 nA for $\text{Fe}(\text{CN})_6^{3-}$ and Fe^{3+} , respectively. Figures 1 and 2 show the dependence of the current ratio (I/I^0) on the concentration of surfactants with hydrophobic C-12 alkyl chain, $\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3\text{Br}$ (1), $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4\text{Na}$ (2), $\text{CH}_3(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_{23}\text{OH}$ (3), and $\text{CH}_3(\text{CH}_2)_{11}\text{OH}$ (4). When $\text{Fe}(\text{CN})_6^{3-}$ was employed as the marker, an increase in the I/I^0 value with the concentration was observed for only the cationic surfactant 1 (Fig. 1). A reverse behavior was noted with the cationic marker (Fe^{3+}): the current ratio increased in the presence of the anionic surfactant 2 (Fig. 2). In the case of an unmodified gold electrode, the effect of any of surfactants 1–4 on the current ratio was essentially negligible. Since the coexistence of a surfactant with a charge opposite to that of the marker ion causes an increase in the current ratio, it is suggested that an ion-

Fig. 1 Effects of surfactants with a hydrophobic C-12 alkyl chain on the amperometric response of an SAM-coated gold electrode to $\text{Fe}(\text{CN})_6^{3-}$ in aqueous KCl (0.1 M) containing $\text{K}_3\text{Fe}(\text{CN})_6$ (5 mM). ●, surfactant 1; ○, 2; △, 3; □, 4.

Fig. 2 Effects of surfactants with a hydrophobic C-12 alkyl chain on the amperometric response of an SAM-coated gold electrode to Fe^{3+} in aqueous KCl (0.1 M) containing FeCl_3 (5 mM). ●, surfactant 1; ○, 2; △, 3, □, 4.

pair is formed between the two species to facilitate access of the latter ion to the electrode surface from the aqueous phase through the SAM. The origin of the observed phenomenon can thus be considered to be similar to that of ion-pair extraction. When the charge of the surfactant was zero, or identical to that of the marker ion, the current ratio gradually decreased with the surfactant concentration. These results indicate that all of the surfactants will penetrate into the SAM and, except for those charged oppositely to the marker ion, will hamper access of the marker ion to the electrode surface.

In order to determine the possibility of applying the present results to the determination of surfactants, the dependence of the current ratio on the surfactant concentration was investigated. As can be seen in Fig. 3, linear relationships were obtained between the logarithms of the two variables for the reduction of $\text{Fe}(\text{CN})_6^{3-}$ in the presence of one of the three cationic surfactants⁹, 1, $\text{CH}_3(\text{CH}_2)_9\text{N}(\text{CH}_3)_3\text{Br}$ (5), and $\text{CH}_3(\text{CH}_2)_{13}\text{N}(\text{CH}_3)_3\text{Br}$ (6). The concentration at which the straight line intersects the abscissa decreases with an increase in the alkyl chain length of the surfactants, indicating that an increase in the hydrophobicity of the surfactant results in an increase in the number of ion-pairs transferring into the SAM.

The SAM-coated electrode employed can be readily prepared with reasonable stability and reproducibility to repeated measurements, and will be a convenient tool for the determination of surfactants. A restriction of the

Fig. 3 Logarithmic plots of the current ratio as a function of the surfactant concentration in aqueous KCl (0.1 M) containing $\text{K}_3\text{Fe}(\text{CN})_6$ (5 mM). ●, surfactant 1; △, 5; ○, 6.

present method can be encountered with samples contaminated by thiols and/or disulfides, which would strongly interact with the gold electrode to give erroneous results. The application of the SAM-coated electrode as a detector of surfactants in an HPLC system is in progress.

References and Notes

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9. At present, the reason for the logarithmic correlation of the two variables is not known, but should be explored further.

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