

Flow Injection Analysis of Surfactants Using Surfactant-Selective Electrode Detector

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Abstract

The determination of anionic, cationic and nonionic surfactants in aqueous solutions is very important in the field of both production control of surfactant and monitoring of environmental water. This review summarizes methods for the determination of anionic, cationic and nonionic surfactants by the flow injection analysis based on a surfactant-selective electrode detector.

Keywords Flow injection analysis, surfactant-selective electrode, anionic, cationic and nonionic surfactants.

1. Introduction

A number of workers have reported the determination methods for ionic surfactants by direct potentiometry and potentiometric titrimetry using surfactant-selective liquid membrane electrodes. A liquid membrane or a plasticized poly (vinyl chloride) (PVC) membrane, which incorporates an ion-pair of an ion-exchanger with an objective surfactant ion, is usually used as the sensitive membrane for surfactant ion-selective electrodes[1-3]. One of drawbacks of this kind of electrode is deterioration of the electrode membrane, which is known to be caused by leak of the ion exchanger from the membrane to sample solutions for long-term use.

In our earlier studies, an electrode based on an *o*-nitrophenyl octyl ether (*o*-NPOE)-plasticized PVC membrane with no added ion-exchanger showed a Nernstian response to both cationic and anionic surfactants and several hydrophobic ions [4-7]. The response mechanism of the *o*-NPOE-plasticized PVC membrane electrode to ionic surfactants is interesting because the electrode shows a Nernstian response to ionic surfactants, in spite of the fact that no ion-exchanger is added to the sensing membrane.

In this review, firstly the response characteristics of the surfactant-selective electrode based on the *o*-NPOE-plasticized PVC membrane developed by us are described with respect to linearity, selectivity, response time and lifetime. Finally, the applications of the electrode to flow injection determination of ionic surfactant and nonionic surfactants are also described by utilizing a flow-through type surfactant-selective electrode detector [8-12].

2. The response characteristics of the surfactant-selective electrode[4, 5]

2.1 Preparation of a plasticized PVC membrane sensitive to ionic surfactant

An *o*-NPOE-plasticized PVC membrane with no added ion-exchanger was prepared as follows: *o*-NPOE (1.0g) and PVC powder (0.4g) were dissolved in tetrahydrofuran (THF). The resulting solution was poured onto a flat-bottomed glass dish (6.8cm i.d.). The THF was evaporated by standing at room temperature for 48h to give a mother membrane. The thickness of the resulting PVC membrane was ca. 0.2 mm.

2.2 Fabrication of the electrode and measurement of the membrane potential

A 0.6 cm diameter disk was cut from the mother membrane and attached to the end of a PVC chip (Denki

Kagaku Keiki Co.) using a THF solution of PVC as an adhesive. A solution consisting of 5.0×10^{-3} M NaCl and 5.0×10^{-3} M sodium dodecylsulfate (NaDS) and an Ag-AgCl electrode were used as an inner solution and an inner reference electrode.

2.3 Response of the *o*-NPOE plasticized PVC membrane electrode to ionic surfactants

Figure 1 shows the potential responses of the *o*-NPOE plasticized PVC membrane electrode to dodecylsulfate (DS⁻) and dodecyltrimethylammonium (DTA⁺) ions. The electrode showed a Nernstian response with a slope of 58mV decade⁻¹ for DS⁻ ion from 1.0×10^{-6} to 8.0×10^{-3} M.

A deviation of the potential from the Nernstian response in the higher concentration than 8.0×10^{-3} M was observed. The deviation corresponds to the micelle formation of DS⁻ ion. For DTA⁺ ion, the electrode showed approximately a Nernstian response with a slope of 50mV decade⁻¹ from 1.0×10^{-6} to 1.0×10^{-2} M. The electrode showed approximately a constant potential in concentrations above 1.0×10^{-2} M, which is due to the micelle formation of DTA⁺ ion.

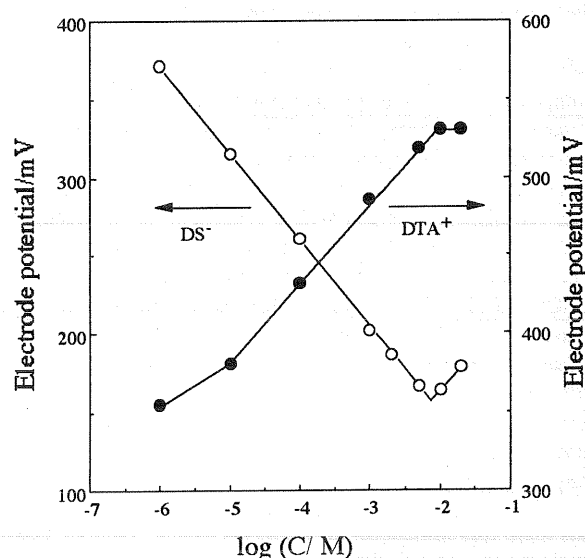


Fig. 1 Potential response of the *o*-NPOE-plasticized PVC membrane electrode for dodecylsulfate (DS⁻) and dodecyltrimethylammonium (DTA⁺) ions.

The break points correspond to the critical micelle concentration (CMC) of DS⁻ and DTA⁺ ions and agree well with reported CMC values for DS⁻ and DTA⁺ ions.

The response time of the electrode was within 10s both for instant increase from 1.0×10^{-5} to 5.5×10^{-5} M and for decrease from 1.0×10^{-4} to 5.0×10^{-5} M. The potential of the electrode was independent of the pH variation in the range from pH 2 to 7 for 1.0×10^{-5} M or 1.0×10^{-4} M DS⁻ solutions and in the range from pH 2 to 9 for 1.0×10^{-3} M and 5.0×10^{-3} M DS⁻ solutions.

The selectivity of the electrode for DS⁻ ion against several diverse ions was examined by a mixed solution method. The selectivity coefficient values shown in Table 1 indicate that the electrode is excellently selective for DS⁻ ion over inorganic anions, but interferences of other surfactants are great.

Table 1 Selectivity coefficients of the DS⁻ ion-selective electrode

Coexisting ion j	$K_{DS^-}^{j,m}$
Cl ⁻	$< 1 \times 10^{-5}$
Br ⁻	$< 1 \times 10^{-5}$
I ⁻	5×10^{-5}
NO ₃ ⁻	1×10^{-5}
ClO ₄ ⁻	3×10^{-3}
Tetradecylsulfate ion	6.4
Dodecylbenzenesulfonate ion	4.7

3. A potentiometric flow injection determination of ionic surfactants and nonionic surfactants utilizing a flow-through type surfactant-selective electrode detector[8-12]

3.1 Flow injection determination of anionic surfactants using the surfactant-selective electrode detector [8]

The FIA manifold for the determination of anionic surfactants consists of a two-channel system, which is composed of a double plunger pump equipped with a sample injector, a flow-through type surfactant-selective electrode, an ion-meter and a strip chart recorder. A sample solution (200 μ l) of DS⁻ ion was injected into a water stream (CS). This stream was subsequently merged with a reagent solution stream (RS) of a mixed solution of 1.0×10^{-6} M NaDS and 2.0×10^{-1} M LiCl. The pH of the RS solution was adjusted to 4.0 by a 0.1 M CHCOOH/CH₃COONa buffer. LiCl was added as a supporting electrolyte to RS to minimize a streaming potential, which affects the response of the electrode detector. The potential difference between the surfactant-selective electrode and the reference electrode was measured using the ion-meter and the peak-shaped response signals of the detector were fed to the strip chart recorder.

The response of the surfactant-selective electrode used in this work was influenced by pH of the sample solution because the electrode was slightly sensitive to OH⁻ ion. At first, the effect of pH of the reagent solution was examined on the sensitivity of the electrode detector to DS⁻ ion by using three reagent solutions with different pH. In the cases that pH of the reagent solution was 4.0 and 6.0, the surfactant-selective electrode detector showed a Nernstian response to DS⁻ ion in

the concentration range from 1.0×10^{-5} M to 1.0×10^{-3} M. The sensitivity of the electrode detector obtained with RS of pH 4.0 was slightly higher than that obtained with RS of pH 6.0. On the other hand, in the case that pH of the reagent solution was 9.0, the detector showed a sub-Nernstian response to DS⁻ ion with a slope of 25mV decade⁻¹ in the same concentration range as for the reagent solutions of pH 4.0 and 6.0. This is due to the fact that the baseline potential was shifted to a negative direction, when the reagent solution of pH 9.0 was used. The baseline potential of the electrode detector was maintained constant by adding 1.0×10^{-6} M DS⁻ ion to the reagent solution. However, the decrease in the baseline potential with the reagent solution of pH 9.0 may be due to the fact that the OH⁻ ion interfered with the electrode response. Since a peak for the injected DS⁻ solution appeared in the negative direction from the baseline potential, the shift of the baseline potential of the electrode detector to a negative direction is unfavorable to detect the peak for the DS⁻ sample sensitively. Therefore, the peak heights from the baseline potential for the DS⁻ ion decrease as the pH of the reagent solution increased. From the results, the reagent solution of pH 4.0 was used.

The effect of nonionic surfactant, Triton X-100, was examined on the determination of 1.0×10^{-5} M DS⁻ ion. In the case that NaCl was used as the supporting electrolyte, the coexistence of Triton X-100 at 2 and 5 times excess to a DS⁻ ion did not interfere in the determination of the DS⁻ ion. However, the coexistence of Triton X-100 at more than 10 times excess to DS⁻ ion gave a serious negative error for the determination of DS⁻ ion. For example, the coexistence of Triton X-100 at 10 times and 20 times excess to a DS⁻ ion gave a negative error of -30% and -50%, respectively. The interference from Triton X-100 can be explained as follows; nonionic surfactants are known to behave as cationic surfactants by complex formation of poly (oxyethylene) moiety of the nonionic surfactants with the metal ion. In this case, Triton X-100 forms a complex with a Na⁺ ion in the reagent solution. Since the electrode used in this work responds to both anionic surfactants and cationic surfactants, the electrode shows a cationic response to nonionic surfactant in a media containing alkali and alkaline earth metal ions. The cationic response means that a peak is observed in the positive direction from the baseline potential in the FIA system. Therefore, the coexistence of the nonionic surfactant such as

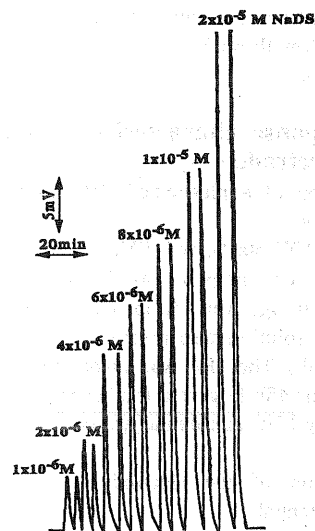


Fig. 2 Typical calibration peaks for DS⁻ ion in the concentration range from 1.0×10^{-6} to 2.0×10^{-5} M.

Triton X-100 in the anionic surfactant shows a negative error. This negative error, however, could be completely eliminated by using LiCl as the supporting electrolyte in the reagent solution. This may be due to a lower complex formation ability of Triton X-100 with a Li⁺ ion than with a Na⁺ ion. From these results, LiCl was used as the supporting electrolyte of the reagent solution.

The effect of coexisting electrolytes on the determination of 1.0×10^{-5} M DS⁻ ion was examined. The coexistence of common cations and anions at 500 times excess to DS⁻ ion did not interfere in the determination of DS⁻ ion.

At these analytical conditions, a linear relationship exists between peak height and the concentration of DS⁻ ion in the concentration range from 1.0×10^{-6} M to 1.0×10^{-5} M. Figure 2 shows the typical FIA peaks for DS⁻ ion. The factor of linear regression of the calibration curve was 0.997. The detection limit was ca. 5.0×10^{-7} M for DS⁻ ion. The reproducibility of the peak heights was examined by five times injections of a 6.0×10^{-6} M NaDS solution, and the relative standard deviation was found to be 1.3%. The sampling rate was ca. 10 samples h⁻¹.

3.2 Flow injection determination of cationic surfactants using the surfactant-selective electrode detector [9]

Figure 3 shows a schematic diagram of FIA for cationic surfactants. The manifold consists of a three-channel system which is composed of two double plunger pumps equipped with a sample injector and without one, an anion-exchange column packed with Amberlite IRA-401 (Cl⁻ form, i.d. 2mm x 100mm), a flow-through type ion-selective electrode detector, an ion-meter and a strip chart recorder. A sample solution (100 μ l) of a cationic surfactant was injected into a methanol solution stream (methanol / H₂O = 50/50 (v/v, %)) (carrier: CS₁). Anionic surfactants coexisting in the sample solution were removed by an anion exchange column, and a cationic surfactant was eluted by a methanol / H₂O = 50/50 (v/v, %) solution. The sample zone, which contained a cationic surfactant, was merged with a mixed solution (RS) of 0.2 M LiCl solution and 1.0×10^{-7} M DTA. The pH of the RS solution was adjusted to 9.1 by a Tris-HCl buffer. This mixed stream was subsequently merged with a distilled and deionized water (CS₂). The LiCl was added as a supporting electrolyte to the solution of the RS stream to

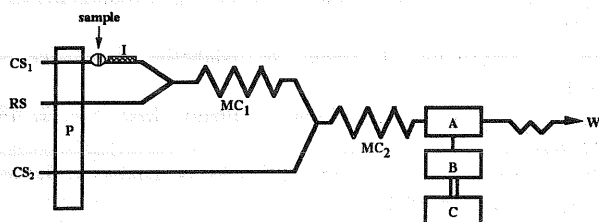


Fig. 3 Flow diagram for determination of cationic surfactants. CS₁; carrier solution (methanol-water (50/50, v/v, %)) (0.6ml min⁻¹), RS; reagent solution (0.2M LiCl solution and 10^{-7} M DTA. The pH of the reagent solution was adjusted to 9.1 by a Tris-HCl buffer (0.6ml min⁻¹), CS₂; distilled and deionized water (1.5ml min⁻¹), I; anion-exchange column packed with Amberlite IRA-401 (Cl⁻ form, i.d. 2mm x 100mm), MC₁; mixing coil (i.d. 0.5mm x 100cm), MC₂; mixing coil (i.d. 0.5mm x 100cm), A; flow-through type surfactant-selective electrode detector, B; ion-meter, C; recorder, P; pump, W; waste, sample volume; 100 μ l.

minimize a streaming potential for the electrode detector. The eluted DTA⁺ ion was detected by the surfactant-selective electrode detector.

The response of the surfactant-selective electrode is influenced by the pH of the sample solution because the electrode is slightly sensitive to a OH⁻ ion. At first, the effect of the pH of the reagent solution on the sensitivity of the electrode detector to DTA⁺ and DS⁻ ions was examined by using several reagent solutions with different pH. In the cases that the pH of the reagent solution was from 6.0 to 10.0, the surfactant-selective electrode detector showed a Nernstian response to DTA⁺ ion in the concentration range from 1.0×10^{-6} M to 1.0×10^{-3} M. The sensitivity of the electrode detector obtained with the reagent solution (pH 6.0 to 9.1) to a DTA⁺ ion was slightly higher than that obtained with the reagent solution of pH 4.0. On the other hand, in the case that a pH of the reagent solution was 9.1, the detector showed a sub-Nernstian response to DS⁻ ion with a slope of 25mV decade⁻¹ in the concentration range from 1.0×10^{-5} M to 1.0×10^{-3} M. For the case that the pH of the reagent solutions was 4.0 and 6.0, the detector showed a Nernstian response to DS⁻ ion in the concentration range from 1.0×10^{-6} M to 1.0×10^{-3} M. The results show that the optimal pH of the reagent solution is in a basic side for the determination of cationic surfactants in the presence of anionic surfactants. This is due to the fact that the baseline potential was shifted to a negative direction, when the reagent solution of pH 9.1 was used. Since a peak for the injected DTA⁺ solution appeared in the positive direction from the baseline potential, the shift of the baseline potential of the electrode detector to a negative direction is favorable to detect the peak for the DTA⁺ sample sensitively. Therefore, the peak heights from the baseline potential for DTA⁺ ion increased as the pH of the reagent solution increased. From the results, the reagent solution of pH 9.1 was used.

The effect of nonionic surfactant, Triton X-100, on the determination of 5.0×10^{-7} M DTA⁺ ion was examined. In the case that NH₄Cl was used as the supporting electrolyte in the reagent solution, the coexistence of Triton X-100 at 40 and 100 times excess to DTA⁺ ion gave a positive error of +20% and +30%, respectively. This positive error, however, could be completely eliminated by using LiCl as the supporting electrolyte in the reagent solution. From these results, LiCl was used as the supporting electrolyte of the reagent solution.

The effect of the coexisting electrolytes on the determination of 5.0×10^{-7} M DTA⁺ ion was examined. The coexistence of common cations and anions at 10^4 times excess to the DTA⁺ ion did not interfere in the determination of the DTA⁺ ion.

The effect of a coexisting anionic surfactant on the determination of 5.0×10^{-7} M DTA⁺ ion was examined. The coexistence of an anionic surfactant at 10^2 times excess to DTA⁺ ion did not interfere in the determination of DTA⁺ ion by using an anion-exchange column packed with Amberlite IRA-401 (Cl⁻ form, i.d. 2mm x 100mm).

Figure 4 shows the typical FIA peaks for DTA⁺ ion. A linear relationship with a slope of 45mV decade⁻¹ exists between a peak height and the logarithmic concentration of the DTA⁺ ion in the concentration range from 5.0×10^{-7} M to 1.0×10^{-5} M. The detection limit was ca. 1.0×10^{-8} M for DTA⁺ ion. The reproducibility of the peak heights was examined by ten times injections of the 5.0×10^{-7} M DTA⁺ solution, and the relative standard deviation was found to be 2.2%. The sampling rate was ca. 8-10 samples h⁻¹.

We applied the present method to determination of a cationic surfactant in river water. The recovery of a cationic surfactant added to river water was examined. For all of the samples examined in this work, the recovery of a DTA⁺ ion was ca. 98-108%. This result shows that the present method can be applied to determine a cationic surfactant in river water.

3.3 Flow injection determination of nonionic surfactants using the surfactant-selective electrode detector [10-12]

Since a nonionic surfactant (NIS) is expected to behave as a cationic surfactant by its complex formation with alkali metal or alkaline earth metal ions, we examined the response behavior of the surfactant-selective electrode to NISs in the presence of alkali and alkali metal ions. The electrode showed the almost same response to NISs as the cationic surfactants, which is consistent with our expectation. Based on the above finding, we have applied the electrode to the potentiometric detector for FIA of NIS using a barium chloride solution as a reagent stream.

Anionic surfactants and cationic surfactants coexisting in the sample solution were removed by the ion-exchange columns, Dowex 50W-X4 (Na⁺ form) / Bio Rad AG1-X4 (Cl⁻ form) = (1:1 (v/v), i.d. 2mm x 700mm) + Dowex 50W-X4 (Na⁺ form, i.d. 2mm x 100mm), and a nonionic surfactant was eluted by ethanol / H₂O = 50/50 (v/v, %) solution. The sample zone, which contained a nonionic surfactant, was merged with a mixed solution (RS) of 0.1M BaCl₂ solution and 1.0 x 10⁻⁵ M sodium tetraphenylborate. The pH of the RS solution was adjusted to 8.9 by a Tris-HCl buffer. This mixed stream was subsequently merged with a distilled and deionized water. The cationic complexes formed between the eluted nonionic surfactants and Ba²⁺ ion in RS solution were detected by the surfactant-selective electrode detector.

The effect of these coexisting inorganic electrolytes on the determination of nonionic surfactants should be examined. In the case that 0.1 M NaCl was used as the supporting electrolyte in the reagent solution, the coexistence of BaCl₂ at 10 times excess to the Triton X-100 gave a positive error of +50% (data not shown). The positive interference from BaCl₂ may be due to a higher complex formation ability of Triton X-100 with a Ba²⁺ ion than with a Na⁺ ion. The coexistence of common cations and anions at 10³ times excess to the Triton X-100 did not interfere with the determination of the Triton X-100, using BaCl₂ as the supporting electrolyte in the reagent solution. From these results, BaCl₂ was used as the supporting electrolyte of the reagent solution.

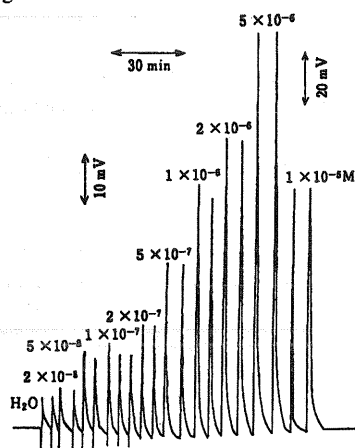


Fig. 4 Typical calibration peaks for DTA⁺ ion in the concentration range from 2.0 x 10⁻⁸ to 1.0 x 10⁻⁵ M.

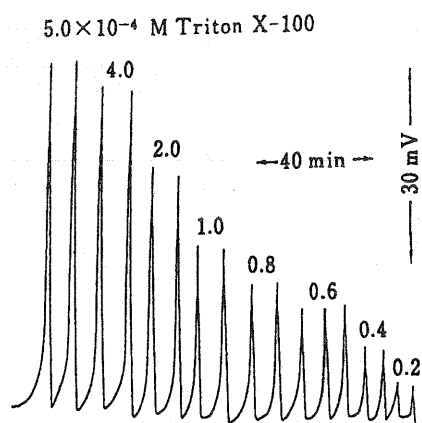


Fig. 5 Typical calibration peaks for Triton X-100 in the concentration range from 2.0 x 10⁻⁵ to 5.0 x 10⁻⁴ M.

The effect of coexisting ionic surfactant was examined on the determination of 1.0 x 10⁻⁴ M Triton X-100. The coexistence of an anionic surfactant and a cationic surfactant at 10² times excess to the Triton X-100 did not interfere in the determination of the Triton X-100 by using the ion-exchange columns.

Figure 5 shows the typical FIA peaks for Triton X-100. A linear relationship with a slope of 40mV decade⁻¹ existed between a peak height and the logarithmic concentration of Triton X-100 in the concentration range from 4.0 x 10⁻⁵ M to 5.0 x 10⁻⁴ M. The detection limit was ca. 1.0 x 10⁻⁵ M for Triton X-100. The reproducibility of the peak heights was examined by five times injections of the 6x10⁻⁵ M Triton X-100 solution, and the relative standard deviation was found to be 3%. The sampling rate was ca. 8-10 samples h⁻¹.

We applied the present method to the determination of a nonionic surfactant in commercial detergents. The recovery of a nonionic surfactant (Triton X-100) added to commercial detergents was examined. For all of the samples examined in this work, the recovery of the Triton X-100 was 95-99%. This result shows that the present method can be applied to determine a nonionic surfactant in commercial detergents.

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