Flow Injection Determination of Dodecylsulfate Using a Dodecylsulfate-Selective Plasticized Poly(Vinyl Chloride) Membrane Electrode Detector

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Abstract

A potentiometric flow injection determination method for dodecylsulfate (DS^-) ion was proposed by utilizing a flow-through type DS^- ion-selective electrode detector. The sensing membrane of the electrode was o-nitrophenyl octyl ether-plasticized poly(vinyl chloride) membrane without added ion exchanger. The peak-shape response of the electrode detector was obtained for injected the DS^- ion sample. A linear relationship was found between peak height and logarithmic concentration of the DS^- ion with a Nernstian slope of $52mV$ decade $^{-1}$ in a concentration range from 1.0×10^{-5} M to 1.0×10^{-3} M. In the concentration range from 1.0×10^{-6} M to 1.0×10^{-5} M, the peak height was found to be linear against the concentration of the DS^- ion. The detection limit of the present method for the DS^- ion was 5×10^{-7} M. The relative standard deviation for 5 injections of a 6×10^{-6} M DS^- ion solution was 1.3 % and the sampling rate was ca. 10 samples h^{-1}. The present method was free from the interference of nonionic surfactants and inorganic electrolytes for the determination of the DS^- ion.

Keywords : anionic surfactants, flow injection analysis, dodecylsulfate-selective electrode.

Introduction

Anionic surfactants are widely used as detergents. The determination of anionic surfactants in aqueous solutions is very important in many fields, such as process control of anionic surfactants and monitoring of environmental water. Solvent extraction-spectrophotometric methods based on the formation of an ion-pair with a dye ion and extraction of the resulting ion-pair into a suitable organic solvent have been widely used for the determination of anionic surfactants. [1-3] However, the procedures used in these batch methods are complicated and time-consuming. The drawbacks of these methods have been overcome by adapting the flow injection analysis(FIA) method. [4,5] The solvent extraction-spectrophotometric FIA method has provided faster and more reproducible assays of anionic surfactants. However, the FIA method requires a segmentor and a phase separator for

construction of the manifold and still needs a poisonous organic solvent, although an amount of solvent consumption in the FIA method is much smaller than that in the batch method. A simple FIA method for the determination of anionic surfactants without an extraction step is desirable on the viewpoint of health of analysts. Kina *et al*. found that anionic surfactants such as dodecylbenzenesulfonate reacts with 3,6-bis(dimethylamino)-10-dodecylacridinium ion (AO-10-D) to quench the fluorescence of AO-10-D in an aqueous solution and applied this reaction to the FIA of anionic surfactants. [6] An FIA method utilizing a surfactant ion-selective electrode (ISE) is a promising method for the determination of surfactants with respect to ease of handling, high reproducibility and high sampling rate. [7,8] However, one of the drawbacks of this method is short life-time of the ISE, which is thought to be caused by dissolution of the ion-exchanger from the electrode membrane with the surfactants in a sample solution.

In previous paper [9,10], we reported that a surfactant ISE based on a poly (vinyl chloride) membrane plasticized with *o*-nitrophenyl octyl ether shows the Nernstian response to anionic surfactants as well as to cationic surfactants. The electrode has high selectivity for the surfactant ions over inorganic ions and low selectivity amomg the same kinds of surfactant ions. This means that, for example, the electrode shows a similar sensitivity to alkylsulfate surfactants. The most remarkable characteristics of the electrode is that the electrode has a longer life-time than does a conventional surfactant-ISE in which the membrane contains an ion-exchanger. This electrode was capable to use continuously for more than 6 months in surfactant solutions. [11] The long-term stability of the electrode may be due to the fact that no ion-exchanger is added to the electrode membrane. Futhermore, our plasticized PVC membrane electrode was applied to a flow-through detector for a flow analysis of surfactants; simultaneous determination of anionic surfactants by high performance liquid chromatography [10] and the determination of cationic and nonionic surfactants by the FIA method. [12-14]

In this paper, we wish to report an application of our plasticized PVC membrane electrode to the FIA of an anionic surfactant, dodecylsulfate (DS⁻) ion.

Experimental

Chemicals. Sodium dodecylsulfate of guaranteed grade was obtained from Wako Pure Chemicals Co. *O*-nitrophenyl octyl ether (*o*-NPOE), used as a plasticizer for the preparation of a PVC membrane of the DS⁻-ISE, was obtained from Dojindo Laboratories. PVC (degree of polymerization: 1100) was obtained from Wako Pure Chemicals Co. Triton X-100 was also obtained from Wako Pure Chemicals Co. and used as a nonionic surfactant sample. All other chemicals were analytical reagent grade.

Flow Injection Analysis. Figure 1 shows a schematic diagram of the FIA system for the DS⁻ ion. The flow system is composed of a double plunger pump equipped with a sample injector (Sanuki Industry Co., DMX-2300T), a flow-through type ISE detector (Denki Kagaku Keiki, DKK, FLC-12), an ion-meter (DKK, COM-20R) and a strip chart recorder (Nippon Densi Kagaku Co., Unicorder U-228). The flow-through type DS⁻-ISE detector consists of the DS⁻-ISE based on a plasticized PVC membrane and a reference electrode (DKK, 4401L). The details of preparation of the DS⁻-ISE membrane were described in previous papers. [10,11] A sample solution (200 μl) of the

DS⁻ ion was injected into a water stream (carrier: CS). This stream was subsequently merged with a reagent solution (RS) stream of a mixed solution of 1×10^{-6} M NaDS and 2×10^{-1} M LiCl adjusted to pH 4.0 by a 0.1 M CH₃COOH/CH₃COONa buffer. LiCl was added as a supporting electrolyte to the reagent solution to minimize streaming potential, which affects the response of the electrode detector. The flow rates of the streams of CS and RS were 1.0 ml min⁻¹. The potential difference between the DS⁻-ISE 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.

Results and discussion

The effect of pH of the reagent solution on the sensitivity to the DS⁻ ion

The response of the DS⁻-ISE used in this work is influenced by pH of the sample solution because the electrode is slightly sensitive to OH⁻ ion, as reported previously.[11] At first, the effect of pH of the reagent solution on the sensitivity of the electrode detector to the DS⁻ ion was examined by using three reagent solutions of different pH. The results are shown in Fig. 2. In the cases that pH of the reagent solution was 4.0 and 6.0, the DS⁻-ISE detector showed the Nernstian response to the DS⁻ ion in the concentration range from 10^{-5} M to 10^{-3} M. The sensitivity of the electrode detector obtained with the reagent solution of pH 4.0 was slightly higher than that obtained with the reagent solution of pH 6.0. On the other hand, in the case that pH of the reagent solution was 9.0, the detector showed the sub-Nernstian response to the 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 DS⁻-ISE was interfered with OH⁻ ion in the reagent solution. This interference from the OH⁻ ion made the baseline potential of the DS⁻-ISE shift to negative direction, when the reagent solution of pH 9.0 was used. Indeed, the baseline potentials were 360, 344 and 212 mV, when pHs of the reagent solution were 4.0, 6.0 and 9.0, respectively. The baseline potential of the detector was maintained constant by adding 10^{-6} M DS⁻ ion to the reagent solution. However, the decrease in the
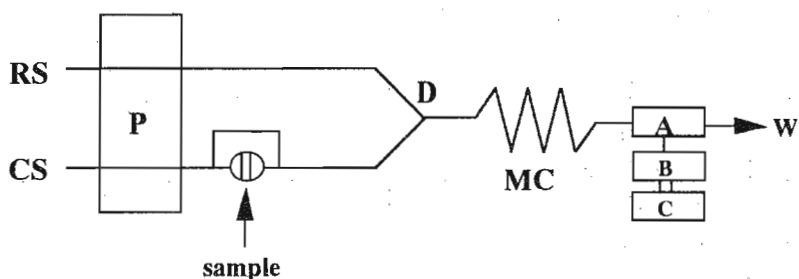

Figure 1 Flow diagram for determination of dodecylsulfate ion. CS; carrier solution (distilled and deionized water, 1.0 ml min⁻¹), RS; reagent solution (a mixed solution of 1×10^{-6} M NaDS and 2×10^{-1} M LiCl adjusted to pH 4.0 by 0.1 M CH₃COOH/CH₃COONa buffer, 1.0 ml min⁻¹), MC; mixing coil (i.d. 0.5mm x 100cm), A; flow-through type dodecylsulfate-selective electrode detector, B; ion-meter, C; recorder, D; confluence point, P; pump, W; waste, sample volume; 200μl.

baseline potential with the reagent solution of pH 9.0 may be due to 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 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 decreases as pH of the reagent solution increased. From the results, the reagent solution adjusted to pH 4.0 was used in subsequent experiments.

The effect of coexisting nonionic surfactant and inorganic electrolytes in the sample solution for the determination of the DS⁻ ion

Real samples such as wastewater and commercial detergents often contain both anionic and nonionic surfactants as well as inorganic electrolytes. Therefore, the effect of these coexisting species on the determination of anionic surfactants should be examined in order to apply the present method to the determination of anionic surfactants in real samples. Table 1 shows the effect of nonionic surfactant, Triton X-100, on the determination of 1×10^{-5} M DS⁻ ion. In the case that NaCl was used as the supporting electrolyte in the reagent solution, the coexistence of Triton X-100 at 2 and 5 times excess to the DS⁻ ion did not interfere with the determination of the DS⁻ ion. However, the coexistence of Triton X-100 at more than 10 times excess to the DS⁻ ion gave a serious negative error for the determination of the DS⁻ ion. For example, the coexistence of Triton X-100 at 10 times and 20 times excess to the 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 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 media containing alkali and alkaline earth metal ions.[14,15] 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 Triton X-100 in the anionic surfactant of the DS⁻ ion 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 Li⁺ ion than with Na⁺
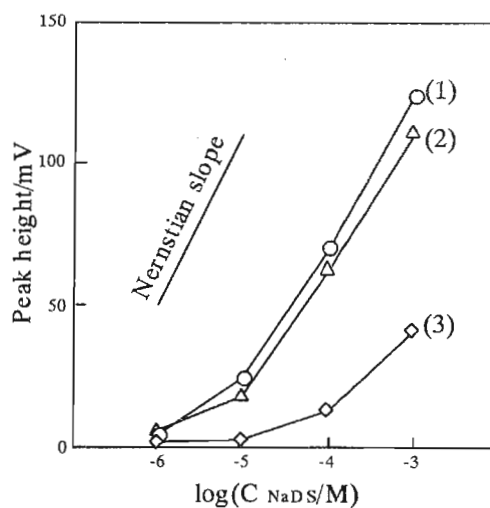

Figure 2 Effect of pH of the reagent solution on the sensitivity of the dodecylsulfate-selective electrode detector.
pH of the reagent solution; (1) pH=4.0, (2) pH=6.0, (3) pH=9.0

Table1 Effect of nonionic surfactant, Triton X-100, on the determination of determination of 1×10^{-5} M NaDS

Concentration of Triton X-100/ M	Response potential*	
	Supporting electrolyte	
	NaCl	LiCl
0	100	100
2×10^{-5}	100	103
5×10^{-5}	93	99
1×10^{-4}	72	104
2×10^{-4}	51	98

*The response potential was expressed as relative value to that obtained for the DS⁻ sample without Triton X-100.

Table 2 Effect of coexisting electrolytes on the determination on the determination of 1×10^{-5} M NaDS

Coexisting electrolytes	Response potential*
none	100
5×10^{-3} M NH$_4$Cl	100
5×10^{-3} M KCl	101
5×10^{-3} M NaCl	105
5×10^{-3} M Na$_2$SO$_4$	105
5×10^{-3} M MgCl$_2$	94
5×10^{-3} M CaCl$_2$	96
5×10^{-3} M NaNO$_3$	102

*The response potential was expressed as relative value to that obtained for the DS⁻ sample without electrolytes.

ion. From these results, LiCl was used as the supporting electrolyte of the reagent solution in subsequent experiment. Effect of coexisting inorganic electrolytes in the sample for the determination of the DS⁻ ion was also examined. Table 2 shows the effect of coexisting electrolytes on the determination of 1×10^{-5} M DS⁻ ion. Table 2 indicates that the coexistence of common cations and anions at 500 times excess to the DS⁻ ion did not interfere with the determination of the DS⁻ ion.

Calibration curve

As can be seen from Fig. 3, a linear relationship exists between peak height and the concentration of the DS⁻ ion in the concentration range from 1×10^{-6} M to 1×10^{-5} M, when the mixed solution of 1×10^{-6} M NaDS and 2×10^{-1} M LiCl adjusted to pH 4.0 by 0.1 M CH$_3$COOH/ CH$_3$COONa was used as the reagent solution. The factor of linear regression of the calibration curve was 0.997. The detection limit, defined as the S/N=3 was ca. 5×10^{-7} M for the DS⁻ ion. The reproducibility of the peak heights was examined by five times injections of the 6×10^{-6} M NaDS solution, and the relative standard deviation was found to be 1.3%. The sampling rate was ca. 10 samples h^{-1}. An appreciable change in the selectivity of the DS⁻-ISE detector was not observed even
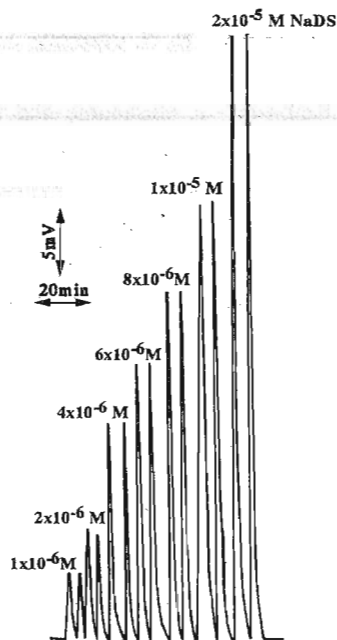

Figure 3 Typical calibration peaks for the DS⁻ ion in the concentration range from 1×10^{-6} to 2×10^{-5} M. Experimental conditions are identical as Fig. 1.

in continuous use for 6 months.

In conclusion, the DS⁻ ion is determined by the present FIA system utilizing the DS⁻ ion-selective plasticized PVC membrane electrode detector without interference from coexisting nonionic surfactants, common cations and anions in the sample solution. Since the present DS⁻-ISE shows a similar sensitivity to typical anionic surfactants such as dodecylbenzenesulfonate and bis(2-ethylhexyl) sulfosuccinate ions, the proposed FIA method can be applicable to the determination of total anionic surfactants. The system of the proposed FIA method is simpler than that of the FIA method based on solvent extraction. The segmentor, phase separator and the poisonous organic solvent are not required. The present method will be useful for the quality control of detergents manufacturing and for the determination of anionic surfactants in the environmental water.

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