

## Surfactant-Selective Electrode Based on Plasticized Poly(vinyl chloride) Membrane and Its Application

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The surfactant-selective electrode based on the poly(vinyl chloride) membrane plasticized with *o*-nitrophenyl octyl ether shows the Nernstian response to anionic surfactants as well as to cationic ones, e.g., the dodecylsulfate ion and the dodecyltrimethyl ammonium ion. The response time of the electrode is in the order of a few seconds. The electrode is highly selective to the dodecylsulfate ion over inorganic anions. The dodecylsulfate ion selective electrode was applied to the successive potentiometric detection of surfactants by high performance liquid chromatography. Four alkylsulfates were successfully detected with the electrode, after being separately eluted with water-methanol mixture through the reversed phase packing column. The electrode was shown to be useful for the determination of critical micelle concentrations of surfactants in the presence of electrolytes.

**Keywords** Surfactant-selective electrode, PVC membrane, *o*-NPOE, ion selective electrode detector, HPLC, critical micelle concentration

Development of rapid and highly sensitive analytical methods of surfactants has been required, since those are pollutants in the environmental water. The surfactant-selective electrodes offer an attractive method for the surfactant analysis.<sup>4-11,13,17</sup> Most of these electrode membranes incorporate a pair of an ion exchange site with an objective surfactant. Therefore deterioration of an electrode membrane is caused by a leak of an ion exchanger from the membrane to sample solutions. On the other hand, Higuchi *et al.*<sup>1-3</sup> reported that there are electrodes with plastic membranes highly sensitive to oleophilic ions even if they do not apparently incorporate an ion exchange site and a counter ion within the membrane. The electrode with the poly(vinyl chloride) membrane plasticized with *N,N*-dimethyloleamide showed the Nernstian response to the tetrabutylammonium ion down to  $10^{-5}$  M. However, they obtained no good electrode membranes sensitive to oleophilic anions. Only the nylon-based membrane plasticized with phenol showed near the Nernstian response for the tetraphenylborate anion in the concentration range from  $10^{-4}$  to  $10^{-5}$  M. In the previous paper<sup>17</sup>, the authors reported that the poly(vinyl chloride) membrane electrode plasticized with *o*-nitrophenyl octyl ether (*o*-NPOE) was an excellently selective not only to cationic surfactants, but also to anionic surfactants.

The present paper reports the details of performance of this electrode such as sensitivity, selectivity, response

time, and the effect of pH on the electrode potential. Applications of this electrode to the determination of the critical micelle concentration of the dodecylsulfate ion and to the detector in high performance liquid chromatography (HPLC) were also described.

### Experimental

#### Reagents

Sodium dodecylsulfate (NaDS)(Kishida Chemical Co.) was used after twice recrystallization from reagent grade methanol (Kishida Chemical Co.). Sodium tetradecylsulfate (Kanto Chemical Co.) and sodium cetyl sulfate (Tokyo Kasei Kogyo Co.) were used without purification. Sodium cetyl sulfate was a mixture of sodium tetradecylsulfate (1%), sodium cetyl sulfate (56%) and sodium octadecylsulfate (43%). Dodecyltrimethyl ammonium bromide (DoTA<sup>+</sup>Br<sup>-</sup>) (Tokyo Kasei Kogyo Co.) of the guaranteed grade and the poly(vinyl chloride)(Kishida Chemical Co.) were used without purification. All other chemicals of reagent grade were used also without purification. Distilled and deionized water was used throughout the experimental work.

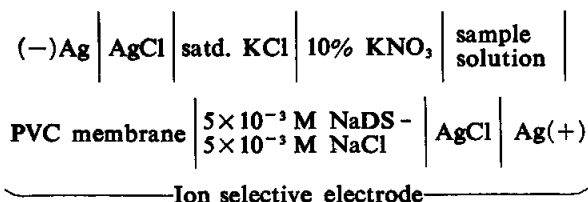
#### Preparation of the PVC membrane

Four hundred milligram of the PVC powder together with 1.0 g of a plasticizer was dissolved into 10 ml of

tetrahydrofuran (THF). The resulted THF solution was poured onto a flat-bottomed glass dish of an inside diameter 6.8 cm. The solvent THF was allowed to evaporate under 48 h standing at room temperature. The thickness of the membrane obtained was about 0.2 mm.

#### Electrode potential measurement

Disks of about 0.4 cm diameter were cut out from the master membrane. One of these membranes was fitted to an ion selective electrode body furnished from Denki Kagaku Keiki Co. The THF solution of PVC was used as an adhesive for fixing the membrane to the electrode body. The electrode has the inner solution consisting of  $5 \times 10^{-3}$  M NaDS- $5 \times 10^{-3}$  M NaCl and a Ag/AgCl inner electrode. The response of the electrode to surfactants was examined by measuring electromotive force (emf) of the following electrochemical cell.



The measurement of emf was conducted by using an Orion Ionalyzer Model 801A at room temperature under agitation of a sample solution with a magnetic stirrer (200 r.p.m.). An effect of pH on the electrode potential was examined under an ionic strength 0.1 which was adjusted with an aliquot of 0.2 M sodium chloride. The pH of the DS<sup>-</sup> solution was adjusted by adding an appropriate amount of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide.

#### Ion selective electrode detector for HPLC

The flow-through type ion selective electrode detector furnished from Denki Kagaku Keiki Co., was used, which consisted of the ion selective electrode and the reference electrode. The ion selective electrode was fabricated in the same manner as described above. The KCl-saturated Ag/AgCl electrode was used for the reference electrode. The dead volume of the ion selective electrode chamber was about 10  $\mu$ l. The potential difference between two electrodes was measured with an Takeda Riken TR 8651 electrometer and a chromatogram was recorded by a strip chart recorder (Watanabe Co.).

#### Flow system

The HPLC system is shown in Fig. 1. The system is composed of two double plunger pumps (Yanako L-4000W and Sanuki Kogyo Co.), a sample injector (Rheodyne, Inc, Cotati, CA Model 7125), a separation column (i.d. 4.6 mm $\times$ 250 mm, TSK-gel-120T, Toyo Soda Co.) and an ion selective electrode detector.

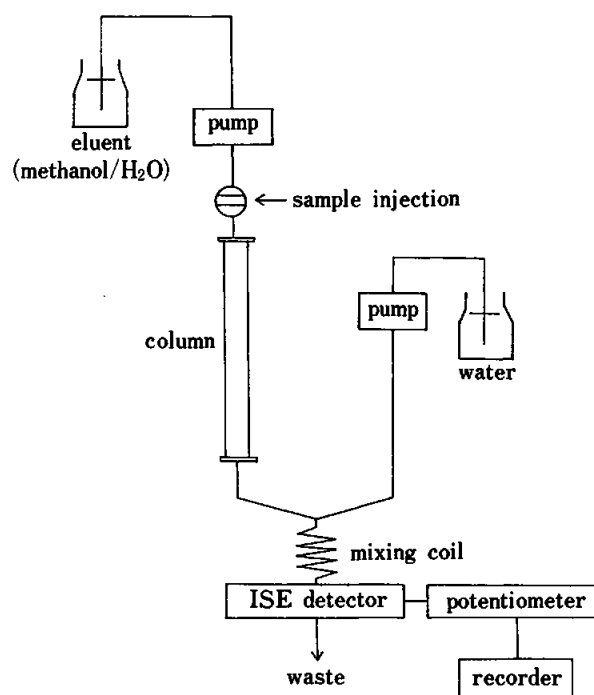


Fig. 1 Schematic diagram of chromatographic system.

Eluents used were mixtures of methanol with water (mixed ratios of methanol to water; 85/15 and 90/10, v/v). The injection volume of the sample was 200  $\mu$ l. An effluent from the separation column was diluted with the water stream in order to protect the membrane. For the flow injection analysis, the separation column and the water supply pump were removed from the HPLC system of Fig. 1.

## Results and Discussion

#### Selection of the plasticizer

As reported previously<sup>17</sup>, the electrode showed the Nernstian response with a slope of 58 mV per decade for the DS<sup>-</sup> ion from  $1 \times 10^{-6}$  to  $8 \times 10^{-3}$  M. The potential showed a deviation from the Nernstian response in the higher concentration than  $8 \times 10^{-3}$  M, which corresponds to the micelle formation of the DS<sup>-</sup> ion. The potential for the DS<sup>-</sup> ion reached stable values within about 1 min in the concentration range from  $1 \times 10^{-5}$  M to the critical micelle concentration (C. M. C.). However, for surfactant concentrations above C. M. C., the electrode showed a very slow potential drift toward lower values. For the DoTA<sup>+</sup> ion, the electrode showed approximately the Nernstian response (*i.e.* a linear response with the potential slope of 50 mV per decade) from  $10^{-6}$  to  $10^{-2}$  M. The electrode showed approximately a constant potential in concentrations above  $10^{-2}$  M, which is due to from the micelle formation of the DoTA<sup>+</sup> ion. The PVC membrane electrode plasticized with tricresyl phosphate (TCP)

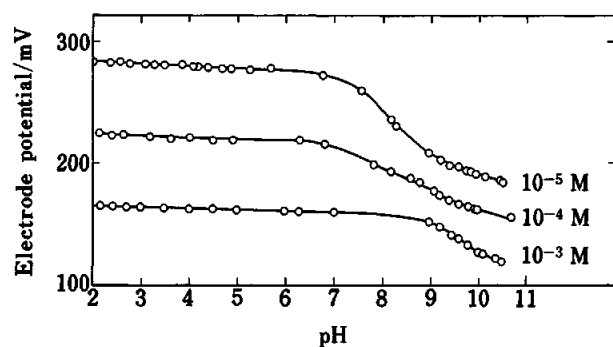


Fig. 2 Effect of pH on DS<sup>-</sup> ion selective electrode.

showed no reproducible response to the DS<sup>-</sup> ion and the DoTA<sup>+</sup> ion. The potential stability was inferior to that of the *o*-NPOE-plasticized PVC membrane electrode. Fluctuation and drift of the electrode potential for the DS<sup>-</sup> ion and the DoTA<sup>+</sup> ion were observed in the 10<sup>-6</sup> to 10<sup>-1</sup> M range. A dioctylphthalate-plasticized PVC membrane electrode showed a similarly inferior response to the TCP-plasticized PVC membrane electrode. These results show that *o*-NPOE is the best plasticizer among three plasticizers examined. All experimental results described below were obtained on the *o*-NPOE-plasticized PVC membrane electrode.

#### Response time

The response time was measured by changing concentrations of the DS<sup>-</sup> solution by instantly adding an aliquot of the water or the DS<sup>-</sup> solution of appropriate concentrations to the test solution. The response time for the DS<sup>-</sup> solution was about 10 s for instant increase from 1.0×10<sup>-5</sup> M to 5.5×10<sup>-5</sup> M and for decrease from 1.0×10<sup>-4</sup> M to 5.0×10<sup>-5</sup> M.

#### Effect of pH on electrode potential

As shown in Fig. 2, the potential of the DS<sup>-</sup> ion selective electrode is independent of the pH variation in the range from pH 2 to 7 for 1.0×10<sup>-5</sup> M or 1.0×10<sup>-4</sup> M DS<sup>-</sup> solutions and in the range from pH 2 to 9 for 1.0×10<sup>-3</sup> M and 5.0×10<sup>-3</sup> M DS<sup>-</sup>. The decrease of the electrode potential in an alkaline region shows that the electrode is interfered with the OH<sup>-</sup> ion.

#### Selectivity

The selectivity of the *o*-NPOE-plasticized PVC membrane electrode for the DS<sup>-</sup> ion was examined by the mixed solution method.<sup>12</sup> The electrode potential was measured for various concentrations of diverse ion. The selectivity coefficient values of Table 1 show that the electrode is excellently selective for the DS<sup>-</sup> ion over inorganic anions, but interferences of other surfactants are great.

#### Determination of the critical micelle concentration

The electrode is capable to determine the C.M.C. of

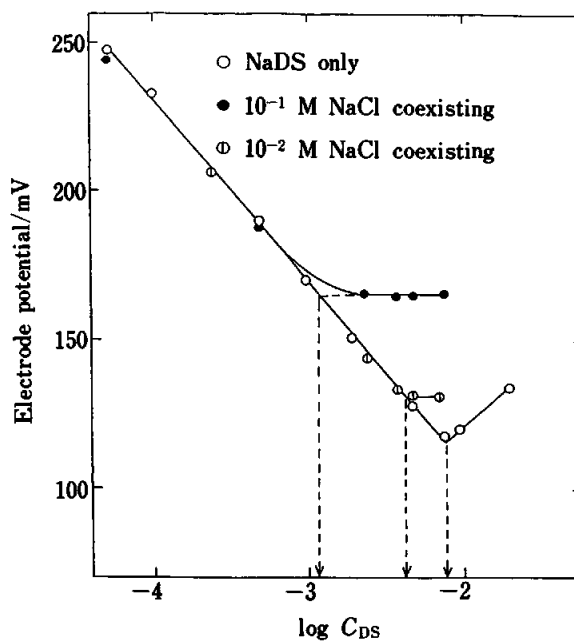


Fig. 3 Effect of coexisting NaCl on the C.M.C. of the DS<sup>-</sup> ion.

Table 1 Selectivity coefficients of the DS<sup>-</sup> ion selective electrode

Coexisting ion j	Concentration of coexisting ion/M	$K_{DS,j}^{pot}$
Cl <sup>-</sup>	0.5	<1×10 <sup>-5</sup>
Br <sup>-</sup>	0.5	<1×10 <sup>-5</sup>
I <sup>-</sup>	0.5	5×10 <sup>-5</sup>
NO <sub>3</sub> <sup>-</sup>	0.5	1×10 <sup>-5</sup>
ClO <sub>4</sub> <sup>-</sup>	0.05	3×10 <sup>-3</sup>
C <sub>14</sub> S <sup>-</sup> a	1×10 <sup>-4</sup>	6.4
DBS <sup>-</sup> b	1×10 <sup>-4</sup>	4.7

a. Tetradecylsulfate ion.

b. Dodecylbenzenesulfonate ion.

the DS<sup>-</sup> ion under the presence of inorganic electrolytes, since the electrode is highly selective for the DS<sup>-</sup> ion. Observed calibration curves of Fig. 3 for the DS<sup>-</sup> ion have break points, which correspond to the C.M.C. of the DS<sup>-</sup> ion. From Fig. 3, C.M.C. values are 8.0×10<sup>-3</sup> M, 5.5×10<sup>-3</sup> M, and 1.3×10<sup>-3</sup> M for pure DS<sup>-</sup> solution and two DS<sup>-</sup> solutions containing sodium chloride at 0.01 M and 0.1 M, respectively. These results agree well with reported C.M.C. values for the DS<sup>-</sup> ion.<sup>11,14</sup>

#### Application to HPLC detector

The electrode has no selectivity between anionic surfactants. However, this means that the separate determination of surfactants in their mixture can be possible with the electrode if they are separated by liquid chromatography. The water-methanol mixture containing an electrolyte such as NaCl, NaClO<sub>4</sub> is effective as an eluent for separation of the surfactants

by reversed phase high performance liquid chromatography. Therefore, the effect of alcohol concentration on the selectivity and the sensitivity of the detector electrode was examined by the flow injection technique, using an aqueous methanol solution as a carrier solution. Two hundreds microliters of surfactant solutions were injected into the stream of the carrier solution (methanol-water mixed solution containing  $5 \times 10^{-2}$  M sodium chloride) flowing at the flow rate 2.5 ml/min. The peak heights were linear against the  $DS^-$  concentrations from  $5 \times 10^{-6}$  to  $10^{-3}$  M in the carrier of a methanol content from 30% to 50%(v/v). For the methanol content of the carrier higher than 50%(v/v), the selectivity for the  $DS^-$  ion obtained by the matched potential method<sup>15</sup> was lower and the linear response range of the peak height against the  $DS^-$  concentration became much narrower. These results show that the ion selective electrode detector can be used in the methanol content less than 50%(v/v). As shown in Fig. 1, the effluent was mixed with a water stream in order to decrease an alcohol content at the detector position. Nakamura *et al.*<sup>16</sup> succeeded in separation of several ionic and nonionic surfactants by reversed phase high performance liquid chromatography using an octadecyl-silica column and a water/methanol eluent (85/15, v/v) containing 0.4 M sodium chloride at a column temperature of 50°C. The condition for separation of surfactants under room temperature was examined here. The retention time of the cetylsulfate

ion was examined by HPLC system as shown in Fig. 1, using the methanol/water mixture (85/15, v/v or 90/10, v/v) containing  $5 \times 10^{-2}$  M NaCl as an eluent. A flow rate of the eluent was 0.7 ml/min. The flow rate of the water stream added to the effluent was 1.6 ml/min. The retention time of the cetylsulfate ion with the methanol/water eluent (90/10, v/v) containing  $5 \times 10^{-2}$  M NaCl was about 30 min shorter than that of the cetylsulfate ion with the methanol/water (85/15, v/v) eluent containing  $5 \times 10^{-2}$  M NaCl. Figure 4 shows a typical chromatogram of alkylsulfates detected by the PVC membrane electrode. The four alkylsulfate ions have been simultaneously detected well. The reproducibility of peak heights was examined by six times of injections of the alkylsulfate mixed solution. The relative standard deviations for peak heights were 1.2% for the  $DS^-$  ion, 2.8% for the tetradecylsulfate ion, 4.6% for the cetylsulfate ion, 8.8% for the octadecylsulfate ion. The result shows that the electrode detector has a quite good reproducibility.

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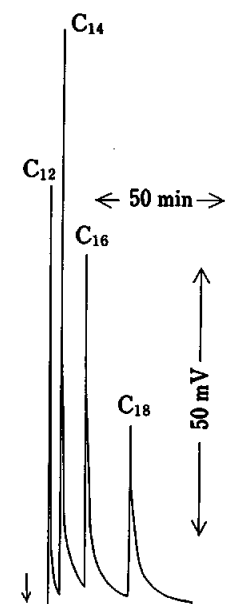


Fig. 4 Chromatogram of alkylsulfates observed with PVC membrane electrode detector. Eluent, methanol-water (90/10, v/v) containing  $5 \times 10^{-2}$  M NaCl; flow rate of eluent, 0.7 ml/min; flow rate of water, 1.6 ml/min; sample, mixed solution of  $10^{-4}$  M alkylsulfates, 200  $\mu$ l; C<sub>12</sub>, dodecylsulfate ion; C<sub>14</sub>, tetradecylsulfate ion; C<sub>16</sub>, cetylsulfate ion; C<sub>18</sub>, octadecylsulfate ion.

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