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A Study of Surfactant Solutions Using the Liquid Membrane Electrode Selective to Alkyl Sulfate Ions

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Liquid membrane electrodes selective to alkyl sulfate ions were devised for octyl, decyl, and dodecyl sulfate ions, and employed in the study of micellar solutions. A nitrobenzene solution of hexadecyltrimethylammonium–alkyl sulfate complex was used as the liquid membrane. The membrane potential-logarithmic concentration showed a maximum at the critical micelle concentration (CMC), an increase with the Nernstian slope at the lower concentrations and a decrease at the higher concentrations. Below CMC, the presence of excess inorganic salt did not alter the Nernstian slope, *i.e.*, the liquid membrane was more highly permselective to alkyl sulfate ions than to inorganic anions. From a simple thermodynamic consideration of a micellar solution based on the pseudo phase model of the micelle, the change in the activity of alkyl sulfate ions and the dissociation of the micelle were discussed. It has been deduced that the concentration of the singly dispersed surfactant ions above CMC is reduced with concentration, except for the presence of a large excess of added electrolyte, and that the degree of dissociation of the micelle is unaltered even when the excess electrolyte is added.

The surfactant ion activity in surfactant solutions has been studied by using solid exchange membranes, including the cation-selective glass electrode.[1-6] Botré *et al.*[1] used the solid ion exchange membranes of both negative and positive types and evaluated the degree of association of the counterions with micelles in aqueous solutions of sodium laurate and dodecylamine hydrochloride. Satake *et al.*[2] used the sodium glass electrode for estimating the degree of association of Na ions in the micelles of sodium alkyl sulfates. Further, Sasaki *et al.*[3] determined the mean activity of sodium dodecyl sulfate in aqueous solutions by using both the sodium ion response glass electrode and the solid anion exchange membrane.

On the other hand, only a few studies[7-9] have been performed with a liquid membrane electrode with a response only for surfactant ions, although various ion-selective electrodes using liquid membranes have recently been devised.[10-13] By virtue of the response only for a particular ion, the use of the liquid membrane would be superior to the solid ion exchange membrane in the study of surfactant solutions. In this respect, new information can be obtained by applying the surfactant ion selective liquid membrane to the study of micellar solutions.

This paper is concerned with the study of the selective permeability coefficient of various surfactant ions as well as the states of surfactant ions in the solution.

Experimental

Materials. The surfactants used were sodium alkyl sulfate (SAS) with chain length C_8 to C_{12}, *i.e.*, sodium octyl sulfate (SOS), sodium decyl sulfate (SDeS), and sodium dodecyl sulfate (SDS). The purified alcohol was obtained by fractional distillation and sulfated with chlorosulfuric acid, then neutralized with sodium hydroxide solution and recrystallized from ethanol. The crystalline sodium alkyl sulfate was finally purified by the solvent extraction with diethyl ether for 48 h. The purity of specimen was confirmed by the absence of a minimum in the surface tension *vs.* concentration curve. Hexadecyltrimethylammonium bromide (HTAB) of guaranteed grade was used after recrystallization from redistilled water. The membrane material, hexadecyltrimethylammonium–alkyl sulfate complex (HTA–AS), was prepared by mixing HTAB solution with SAS solution and washing the precipitate with distilled water. The nitrobenzene solution of HTA–AS was used as the liquid membrane which is denoted as the AS membrane. All the other reagents were of guaranteed grade and used without further purification.

Membrane Potential Measurement. An Orion model 801A digital ion analyzer was used for measuring the membrane potential of the following concentration cell:

$$\text{Calomel}\left|\begin{array}{l}\text{Satd NH}_4\text{Cl}\\ \text{Agar}\end{array}\right|\begin{array}{l}10^{-3}\text{ mol dm}^{-3}\text{ SAS}\\ \text{Ref. Soln}\end{array}\right\|$$

$$\begin{array}{l}10^{-4}\text{ mol dm}^{-3}\text{ HTA–AS}\\ \text{in Nitrobenzene}\end{array}\left\|\begin{array}{l}\text{SAS Soln with}\\ \text{varying Concn}\end{array}\right|$$

$$\begin{array}{l}\text{Satd NH}_4\text{Cl}\\ \text{Agar}\end{array}\Big|\,\text{Calomel} \qquad \text{(A)}$$

where the left half cell including the AS membrane may be termed the AS ion selective electrode. For the study of the selectivity of some inorganic and alkyl sulfates (AS) ions to the dodecyl sulfate (DS) ion electrode, the following cell was used:

$$\begin{array}{l}10^{-3}\text{ mol dm}^{-3}\text{ SDS}\\ \text{Ref. Soln}\end{array}\left\|\begin{array}{l}10^{-4}\text{ mol dm}^{-3}\text{ HTA–DS}\\ \text{in Nitrobenzene}\end{array}\right\|$$

$$\begin{array}{l}10^{-3}\text{ mol dm}^{-3}\text{ SAS or}\\ 10^{-3}\text{ mol dm}^{-3}\text{ Inorganic Anion}\end{array} \qquad \text{(B)}$$

For the study of the effect of electrolyte, a constant concentration of NaCl was added to the test solution with varying concentrations of surfactant. The potential reached a steady value (±0.2 mV) within 10 min. The measurements were carried out at 25.0±0.1 °C.

Results and Discussion

In Fig. 1, typical response curves for the AS electrodes are shown for SOS, SDeS, and SDS. The kink point in the response curve agreed with the values of CMC in the literature.[14] The values of CMC observed were: SDS, 8.0×10^{-3} mol dm^{-3}; SDeS, 3.3×10^{-2} mol dm^{-3}; SOS, 1.2×10^{-1} mol dm^{-3}. Below CMC, the membrane potential V obeyed the Nernst equation,

$$V = \frac{RT}{F}\ln\frac{C_{\text{AS}}}{C_{\text{AS}}{}^{\circ}}, \qquad (1)$$

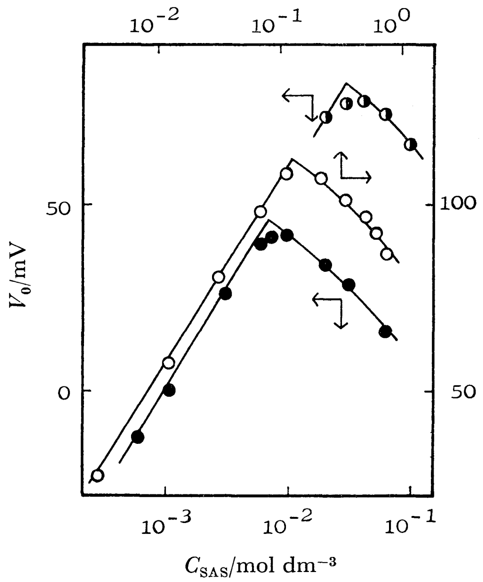

Fig. 1. Response curves of HTA–DS and HTA–DeS and HTA–OS liquid membrane for SDS, SDeS, and SOS solutions with 10^{-3} mol dm^{-3} SDS, SDeS, and SOS reference solutions, respectively.
●: SDS, ◑: SDeS, ○: SOS.

where C_{AS}° and C_{AS} denote the concentration of AS ion in the reference solution and the test solution, respectively. This indicates that the AS electrode is ideally permselective to AS ions and the change in the activity coefficient of AS ions as well as the interference by Na ions may be ignored. Above CMC, the decrease in the potential with increasing SAS concentration, an indicative of the decrease in the apparent surfactant ion activity, was observed.

The selectivities of some inorganic and alkyl sulfate ions to the DS electrode were examined by using the cell systems (B). The selectivity was calculated according to the following equation for the membrane potential V:

$$V = \frac{RT}{F} \ln K^{\mathrm{pot.}}_{\mathrm{DS.X}} \frac{a_{\mathrm{X}}}{a_{\mathrm{DS}}}, \qquad (2)$$

where a_{X} and a_{DS} denote the activity of X ion and that of DS ion, respectively, and $K^{\mathrm{pot.}}_{\mathrm{DS.X}}$, the selectivity of X ion to DS ion. In estimating the selectivities, the activity coefficients were assumed to be unity, since the concentrations of sodium alkyl sulfates and inorganic salts were low. The selectivities are summarized in Table 1. It is seen in Table 1 that chloride and bromide ions hardly interfere with the response of the DS electrode to DS ions. On the other hand, the responses of the DS electrode to perchlorate and thiocyanate ions are more or less greater than those to halide anions. Thus, these inorganic anions may interfere with DS ions in the response to the DS electrode. It is known that the perchlorate and thiocyanate ions dissolve considerably in the organic solvent.[15] This may be responsible for the higher selectivities of these inorganic ions, since the selectivity is given by the product of the ratio of transport coefficients and that of partition coefficients. The selective permeability coefficients of the homologous alkyl sulfate ions increased by a factor of about 10 with the increase in alkyl chain length by two methylene groups.

Table 1. Selective permeability coefficients

Examined salt	$K^{\mathrm{pot.}}_{\mathrm{DS.J}}$
STS(C_{14})	10
SDS(C_{12})	1
SDeS(C_{10})	2.8×10^{-1}
SOS(C_8)	1.2×10^{-2}
$NaClO_4$	4.4×10^{-2}
KSCN	2.8×10^{-2}
KBr	1.1×10^{-3}
NaCl	6.0×10^{-4}

This agrees with the Traube rule and reflects the greater partition coefficient of a surfactant of longer chain length in the organic solvent. The longer the chain length, the greater the selectivity; thus tetradecyl sulfate (TS) ion, which has more carbon atoms than DS ion, exhibited greater response to the DS electrode, as shown in Table 1.

The selective permeability coefficient of Cl ion is of the order of 10^{-4}. This implies that even though Cl ions coexist in the test solutions of cell system (B), there would be little influence on the response of the AS electrode to AS ions. Thus, using the cell system (B), the study of the effect of added electrolytes in aqueous SAS solutions was performed. In Figs. 2 to 4, the response curves for SAS solutions in the presence of 0.1 and 0.01 mol dm^{-3} NaCl are shown together with those for the salt-free systems. For all the cases of the surfactants with alkyl chain length from C_8 to C_{12}, CMC of each surfactant solution in the presence of NaCl agreed well with that in the literature.[14] It is also shown in these figures that the presence of inorganic salt more or less decreased the membrane potential below CMC. Furthermore, the longer the chain length, the greater the decrease in the potential. This tendency was also enhanced as the added amount of electrolytes increased. This may reflect a decrease in the activity

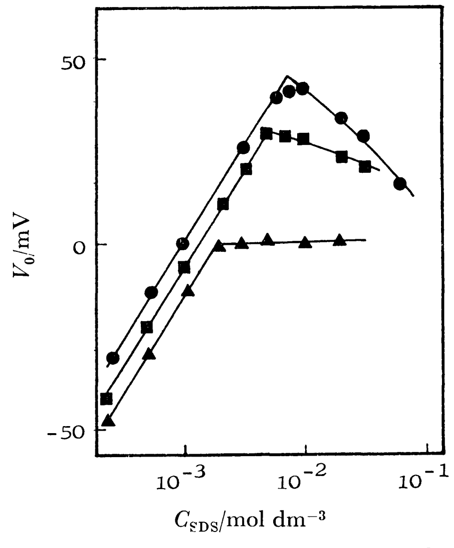

Fig. 2. Membrane potential as a function of concentration of SDS in test solution in the presence of added electrolytes.
●: No NaCl, ■: 0.01 mol dm^{-3} NaCl, ▲: 0.1 mol dm^{-3} NaCl.

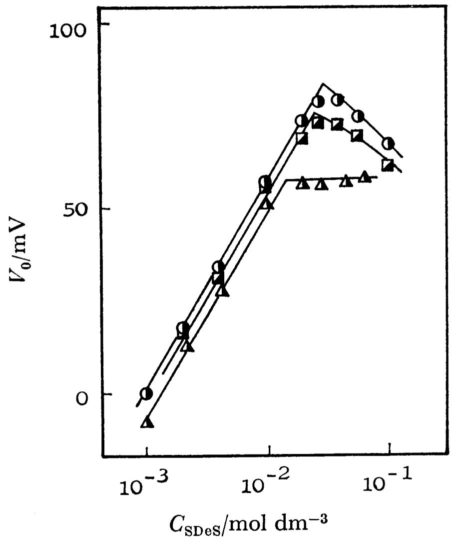

Fig. 3. Membrane potential as a function of concentration of SDeS in test solution in the presence of added electrolytes.
◐: No NaCl, ◪: 0.01 mol dm^{-3} NaCl, ◭: 0.1 mol dm^{-3} NaCl.

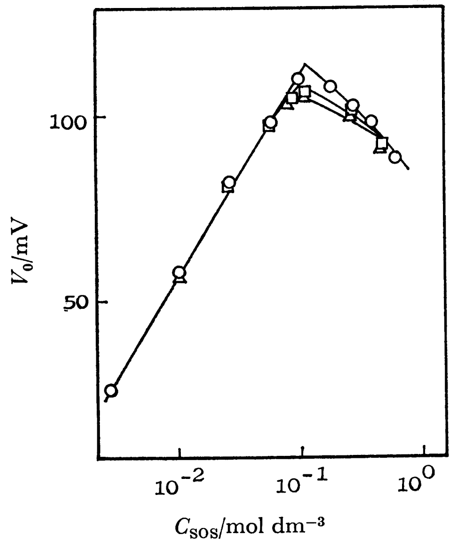

Fig. 4. Membrane potential as a function of concentration of SOS in test solution in the presence of added electrolytes.
○: No NaCl, □: 0.01 mol dm^{-3} NaCl, △: 0.1 mol dm^{-3} NaCl.

of surfactant ion caused by the added electrolyte. Mukerjee *et al.*[16,17] suggested the existence of a detergent dimer below CMC, on the basis of conductivity measurements of the SDS solution. In the present study, however, there was no sign of the dimerization of surfactant ions, because the concentration dependence of the membrane potential possessed the Nernstian slopes. The potential equation may be given by

$$V = \frac{RT}{F} \ln \frac{a_{AS}}{a_{AS}{}^{\circ}}, \tag{3}$$

where a_{AS} denotes the activity of AS ions in the presence of NaCl, and $a_{AS}{}^{\circ}$, the activity of AS ions in the 10^{-3} mol dm^{-3} SAS solution without added electrolyte. Equation 3 becomes

$$V = \frac{RT}{F} \ln \frac{C_{AS}}{C_{AS}{}^{\circ}} + \frac{RT}{F} \ln \frac{\gamma_{AS}}{\gamma_{AS}{}^{\circ}}, \tag{4}$$

where γ_{AS} and $\gamma_{AS}{}^{\circ}$ denote the activity coefficients of AS ions in the presence and the absence of NaCl, respectively. Thus, the decrement due to the added electrolyte may be ascribed to the decrease in the activity coefficient of AS ions caused by the added electrolyte. Since the Nernstian slope was unaltered even in the presence of the added electrolyte, the AS electrode may be regarded as ideally permselective to singly dispersed AS ions. In the absence of electrolyte, Eq. 4 is reduced to Eq. 1.

Above CMC, a decrease of the membrane potential was observed; this tendency was accelerated by increasing the amount of the added electrolyte or the chain length. These phenomena may be attributed to the change in the activity of surfactant ions.

The chemical potential of the surfactants in the bulk phase μ_b and that, μ_m, in the micellar phase are described as follows:

$$\mu_b = \mu_b{}^{\circ} + RT \ln a_{Na} a_{AS}, \quad \mu_m = \mu_m{}^{\circ} + RT \ln a_m, \tag{5}$$

where a_{AS}, a_{Na}, and a_m denote the activity of the surfactant ion, Na ion, and NaAS in the micelle, respectively; $\mu_b{}^{\circ}$ and $\mu_m{}^{\circ}$ are the standard chemical potential for the dissociated surfactant and the micelle. Taking the micelle as a pseudo phase, the activity of the micelle may be set at unity. Since the singly dispersed surfactants are equilibrated with the micelles, we have from Eq. 5,[18,19)]

$$a_{Na} a_{AS} = \text{const.} \tag{6}$$

We may conclude that the response of the AS electrode to the micellar AS ions can be ignored, since the potentials never increase with surfactant concentrations. The potential should increase if the AS electrode responds to the micellar AS ions. The fact that the potential is kept constant in the large excess of added electrolyte, as shown in Figs. 2 and 3, supports this view.

Below CMC, the activity coefficient of AS ions may be regarded as a constant. Thus, the potential decrease above CMC implies the decrease in the concentration of singly dispersed surfactant ion providing that the activity coefficient does not change appreciably above CMC. On the other hand, since the potential remains constant in the presence of a large excess of electrolyte, a_{AS} as well as C_{AS} remains constant in this region. This can be deduced from Eq. 6, *i.e.*, in the presence of a large excess of electrolyte, a_{Na} may be regarded as a constant and hence a_{AS} becomes constant. Furthermore the activity coefficient of singly dispersed surfactant ions may be regarded as a constant due to the large excess of inorganic electrolyte, and thus C_{AS} might be constant. These conclusions agree with those obtained by Sasaki *et al.*[3,4] from the gel filtration data.

It is usually assumed that above CMC the concentration of singly dispersed surfactant ions is kept constant even though the total analytical concentration of surfactant increases. This hypothesis should be true only in the presence of a large excess of added electrolyte.

On the other hand, the activity of Na ions in the bulk phase may be expressed by

$$a_{\mathrm{Na}} = \gamma_{\mathrm{Na}}[C_{\mathrm{s}}+C_{\mathrm{AS}}+\alpha(C-C_{\mathrm{AS}})], \qquad (7)$$

where C_{S}, C_{AS}, and C denote the concentration of the added NaCl, that of the singly dispersed surfactant ions, and the total analytical concentration of surfactant, respectively; γ_{Na} is the activity coefficient of Na ions, and α, the degree of dissociation of the micelle. A similar relation is proposed by Botré *et al.*,[1] for a system with no added salt. Subtracting the potential at CMC, V^*, from V by the use of Eq. 3, we have

$$V-V^* = \frac{RT}{F}\ln\frac{a_{\mathrm{AS}}}{a_{\mathrm{AS}}{}^*}, \qquad (8)$$

where the asterisk refers to CMC.

Comparing this with Eq. 6, we obtain

$$V-V^* = \frac{RT}{F}\ln\frac{a_{\mathrm{Na}}{}^*}{a_{\mathrm{Na}}}. \qquad (9)$$

Assuming that γ_{Na} does not change appreciably above CMC, we have, from Eqs. 7 and 9,

$$V-V^* = \frac{RT}{F}\ln\frac{C_{\mathrm{s}}+C_{\mathrm{AS}}{}^*}{C_{\mathrm{s}}+C_{\mathrm{AS}}+\alpha(C-C_{\mathrm{AS}})}, \qquad (10)$$

where $C_{\mathrm{AS}}{}^*$ denotes CMC.

In the presence of a large excess of added salt, $C_{\mathrm{AS}}{}^*$, C_{AS}, and $(C-C_{\mathrm{AS}})$ can be ignored as compared with C_{S}, and thus $V=V^*$, which agrees with the experimental results.

Table 2. Degree of dissociation of micelle calculated according to Eqs. 8 and 10

SAS	SDS	SDeS	SOS
α	0.20	0.23	0.27

For other cases, the potential decreases with concentration above CMC. As pointed out previously, C_{AS} can be evaluated according to Eq. 8, if γ_{AS} is assumed to be constant. Table 2 shows the values of α calculated according to Eqs. 8 and 10 by assuming a constant activity coefficient of AS ions. This table indicates that the value of α is approximately constant for a given surfactant. This coincides with the additivity rule for the counterions of the polyelectrolyte in the presence of added electrolyte.[20]

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