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The Selectivity Characteristics of Surfactant Ion-sensitive Nitrobenzene-membrane Electrode

Iwao Satake,* Shun-ichi Noda, and Tamaki Maeda

Department of Chemistry, Faculty of Science, Kagoshima University, Korimoto, Kagoshima 890

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The selectivity coefficients of nitrobenzene-membrane electrode containing dodecyltrimethylammonium dodecyl sulfate as an ion exchanger were determined. For a homologous series of surfactant ions, the logarithm of the selectivity coefficient was found to increase linearly with increasing hydrocarbon chain length. The selectivity sequence for anionic surfactant ions with the same alkyl chain length became alkylbenzenesulfonate ion > alkyl sulfate ion ≫ alkanesulfonate ion, while that for cationic ones became alkyltrimethylammonium ion ≈ 1-alkylpyridinium ion ≫ alkylammonium ion. These results can reasonably be interpreted in terms of the partition coefficient of surfactant ion between aqueous and membrane phases. A tentative estimation based on the theory of liquid-membrane electrode led to $-2900\,\mathrm{J\,mol^{-1}}$ for the standard free energy of transfer of a methylene group from water to nitrobenzene.

The utility of the liquid-membrane electrode sensitive to a surfactant ion both in analytical and physicochemical studies of ionic surfactant solutions is now well recognized. However, only a few works[1–4] have been concerned with the determination of the selectivity coefficients of these electrodes for various interferents. It has been found that *o*-dichlorobenzene-membrane electrodes[1–3] with an appropriate ion exchanger are highly selective for a surfactant ion over common inorganic ions but subject to serious interference from surfactant ions with longer alkyl chain length than the measuring ion. For a homologous series of surfactant such as sodium alkyl sulfates[1–3] and sodium alkanoates,[2,3] the selectivity coefficient was found to increase regularly with increasing hydrocarbon chain length. A similar result, though confined to sodium alkyl sulfates, was also obtained for a nitrobenzene-membrane electrode[4] which is an another typical liquid-membrane electrode sensitive to the surfactant ion. So far as we know, however, the selectivity characteristics of nitrobenzene-membrane electrode have yet not been fully elucidated. In this work, we investigated the effects of the nature of ionic head group as well as the alkyl chain length of interfering surfactant ion on the selectivity coefficient of nitrobenzene-membrane electrode which contains dodecyltrimethylammonium dodecyl sulfate as an ion exchanger.

Experimental

Materials. Sodium alkyl sulfates with 8, 10, and 12 carbon atoms were synthesized by esterification of the corresponding long-chain alcohols which had been purified by vacuum distillation. Sodium alkanesulfonates with 9, 11, and 13 carbon atoms (Tokyo Kasei Kogyo Co. Ltd.) were further extracted with petroleum ether for 40 h and recrystallized twice from ethanol. Dodecylammonium chloride was prepared from dodecylamine according to the method of Kolthoff and Stricks.[5] 1-Dodecylpyridinium chloride (Wako Pure Chemical Industry Co. Ltd.) was dissolved in ethanol and refluxed overnight with active carbon. After removal of the active carbon, the precipitate was purified further by repeated recrystallization from acetone. Dodecyltrimethylammonium chloride (DTAC, Tokyo Kasei Kogyo Co. Ltd.) was recrystallized twice from acetone. Sodium dodecylbenzenesulfonate (purity >99%, Wako Pure Chemical Industry Co. Ltd.) and tetraalkylammonium chlorides of guaranteed grade were used without further purifications. An ion exchanger, dodecyltrimethylammonium dodecyl sulfate (DTADS) was prepared by mixing the dilute solutions of DTAC and sodium dodecyl sulfate (SDS). The resulting complex was recrystallized twice from acetone and dissolved in nitrobenzene in a concentration of about $5\times10^{-4}\,\mathrm{mol\,dm^{-3}}$.

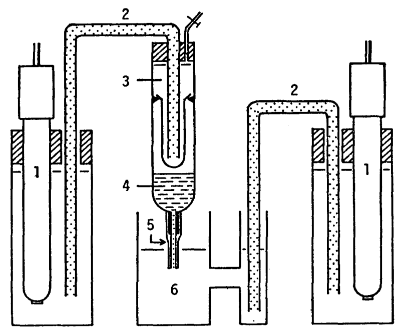

Fig. 1. The experimental setup of the nitrobenzene membrane electrode.
1; Reference electrode, 2; agar bridge, 3; reference solution, 4; nitrobenzene, 5; Teflon tube, 6; sample solution.

Membrane Potential Measurements. Since the nitrobenzene-membrane electrode containing DTADS as an ion exchanger responds both to anionic and cationic surfactant ions, the measurements were made with the following cells which have the experimental setup shown in Fig. 1.

Reference electrode (Ag-AgCl) | 1 mol dm^{-3} NH_4Cl agar bridge | Reference solution (SDS or DTAC, 5×10^{-4} mol dm^{-3}) | Nitrobenzene (5×10^{-4} mol dm^{-3} DTADS) | Sample solution (SDS or DTAC, C_i; Interferent, C_j) | 1 mol dm^{-3} NH_4Cl agar bridge | Reference electrode (Ag-AgCl).

The electromotive force (E) of the cell was measured with an accuracy of ±0.1 mV at 25 °C, by using a digital voltmeter connected to a voltage follower amplifier (input impedance $\approx 10^{13}\,\Omega$). The selectivity coefficient was determined by the mixed solution method,[6] *i.e.*, E was followed as a function of the measuring ion concentration, C_i, under the conditions of a constant interferent concentration, C_j.

Results and Discussion

In Fig. 2 is shown the typical semilogarithmic plots of E *vs.* SDS concentration in the presence and

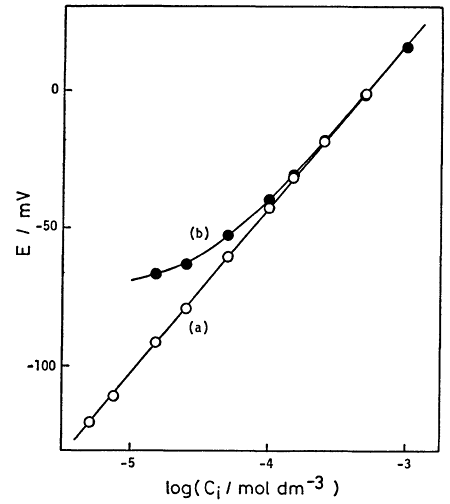

Fig. 2. Plots of the electromotive force (E) of the cell *vs.* the logarithm of SDS concentration (C_i) at 25 °C.

(a); In the absence of interferent, (b); in the presence of 1.5×10^{-4} mol dm^{-3} SDeS.

TABLE 1. THE SELECTIVITY COEFFICIENTS OF NITROBENZENE MEMBRANE ELECTRODE FOR VARIOUS INTERFERENTS AT 25 °C

Measuring ion (i)	Interferent (j)	K_{ij}
Dodecyl sulfate ion	$C_nH_{2n+1}SO_4Na$	
	$n=10$	9.0×10^{-2}
	$n=8$	9.3×10^{-3}
	$C_nH_{2n+1}SO_3Na$	
	$n=13$	6.3×10^{-2}
	$n=12$	$(1.8\times10^{-2})^{a)}$
	$n=11$	5.3×10^{-3}
	$n=9$	5.9×10^{-4}
	$C_{12}H_{25}C_6H_4SO_3Na$	8.9
Dodecyltrimethyl ammonium ion	$C_{12}H_{25}C_5H_5N^+Cl^-$	9.3×10^{-1}
	$C_{12}H_{25}NH_3^+Cl^-$	2.5×10^{-2}
	$(C_nH_{2n+1})_4N^+Cl^-$	
	$n=1$	2.0×10^{-5}
	$n=2$	2.0×10^{-4}
	$n=3$	1.0×10^{-2}

a) Estimated from Fig. 3.

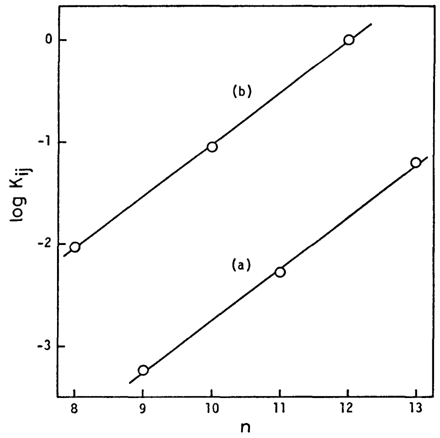

Fig. 3. The semilogarithmic plots of the selectivity coefficients for the homologous series surfactant ions *vs.* the number of carbon atoms in the alkyl chain at 25 °C.

(a); Sodium alkanesulfonate, (b); sodium alkyl sulfate.

absence of sodium decyl sulfate(SDeS). In the absence of interfering ion, the electrode responds to the dodecyl sulfate ion down to 5×10^{-6} mol dm^{-3} with a slope of 59.7 mV per decade change in SDS concentration. This is also the case for the cationic surfactant ion sensitive electrode in which SDS is replaced by DTAC. An excellent agreement between the observed slope and an ideal Nernst slope (59.2 mV at 25 °C) suggests that the inorganic counterions such as Na$^+$ and Cl$^-$ do not interfere appreciably with the electrode response to the surfactant ion. As is shown in Fig. 2 by the curve(b), however, the presence of a surfactant ion other than the dodecyl sulfate ion causes a remarkable interference. Under constant concentration of SDeS, the deviation from Nernstian response becomes progressively greater as SDS concentration decreases. Similar results were also obtained for all the interferents studied.

On the basis of these experimental results, we estimated the selectivity coefficient, K_{ij}, defined by

$$E = E_a + (RT/F)\ln[(C_i+K_{ij}C_j)/C_i^\circ], \tag{1}$$

where the subscript i refers to the measuring ion, *i.e.*, dodecyl sulfate ion or dodecyltrimethylammonium ion, j to the interfering ion, superscript ° to the reference solution, and E_a to the asymmetric potential of overall cell system, respectively; other symbols have their usual meanings. Under our experimental conditions, the activity coefficients can be ignored without loss of accuracy. The calculation was made by applying the graphical curve-fitting method described elsewhere.[7)] The selectivity coefficients for various interferents, taken with respect to the dodecyl sulfate ion or the dodecyltrimethylammonium ion, are summarized in Table 1. In conformity with the results obtained both for liquid[1–4)] and plastic[7,8)] membrane electrodes, the selectivity coefficient for a homologous series of surfactant ions increases quite regularly with increasing alkyl chain length. As is shown in Fig. 3, the semilogarithmic plot of K_{ij} *versus* the number of carbon atoms, n, in the alkyl chain gives the straight line with a slope virtually independent of the nature of ionic head group. This fact leads immediately to the selectivity coefficient of 1.8×10^{-2} for sodium dodecanesulfonate. Thus the present electrode gives the selective sequence for anionic surfactant ions with the same alkyl chain length as alkylbenzenesulfonate ion>alkyl sulfate ion≫alkanesulfonate ion. In the case of cationic surfactant ions, the selective sequence becomes alkyltrimethylammonium ion≈1-alkylpyridinium ion≫alkylammonium ion. The interference of the tetraalkyl ammonium ion with shorter chain length is negligibly small.

According to the theory[9)] of liquid-membrane electrode in which the dissolved ion exchanger is completely dissociated, the selectivity coefficient is described in terms of the mobility, u^*, in the membrane phase and the partition coefficient, k, as

$$K_{ij} = u_j^*k_j/u_i^*k_i. \tag{2}$$

It is somewhat doubtful whether DTADS is completely dissociated in such medium as nitrobenzene having comparatively low relative permittivity of 34.8 at 25 °C. However, the use of Eq. 2 still shed light on the fundamental factors which determine the selectivity sequence shown in Table 1. Substituting the thermodynamic expression for the partition coefficient in Eq. 2, we have

$$RT\ln K_{ij} = RT\ln(u_j^*/u_i^*) + (\Delta\mu_i^{\ominus} - \Delta\mu_j^{\ominus}), \tag{3}$$

where, $\Delta\mu^{\ominus}$ denotes the standard free energy of transfer of surfactant ion from aqueous medium to membrane phase. If, therefore, the mobilities of surfactant ions of similar size are comparable to each other in nitrobenzene phase, $\ln K_{ij}$ for a homologous series of the surfactant ions should be linearly dependent on n, since $\Delta\mu_j^{\ominus}$ is known to be a linear function of n.[10] This is exactly what was found with sodium alkyl sulfates and alkanesulfonates. We can thus expect that the slope of the straight lines in Fig. 3 represents the increment of $\Delta\mu_j^{\ominus}$ per methylene group, *i.e.*, the free energy change, w, for transfering a methylene group from aqueous medium to organic phase. A tentative estimation based on the result in Fig. 3 leads to -2900 J mol^{-1} for w from water to nitrobenzene at 25 °C. This figure is in good agreement with the value of -3100 J mol^{-1} for w from water to *bis*(2-ethylhexyl) phthalate estimated in a previous study of cationic surfactant ion-sensitive poly(vinyl chloride)-membrane electrode containing a neutral carrier[7]. It is also worth noting that the value of w estimated above is close to the free energy change of about -2700 J mol^{-1} associated with the transfer process of a methylene group from water to the hydrophobic interior of surfactant micelle at 25 °C.[11] Apart from the underlying assumptions, therefore, Eq. 2 seems to explain reasonably the observed selectivity characteristics of nitrobenzene-membrane electrode. It has already been pointed out by several authors[1–4,7,8] that the partition coefficient plays the most important role in determining the selectivity sequence of liquid and plastic membrane electrodes for the homologous series surfactant ions.

An interesting comparison may also be made between the selectivity coefficients for surfactant ions with the same alkyl chain length. If we denote the contribution of the head group to the transfer free energy of the surfactant ion by w^h, Eq. 3 can be rewritten as follows.

$$RT\ln(K_{ij}/K_{ii}) \approx w_i^h - w_j^h \tag{4}$$

In Table 2 are given the values of $w_i^h - w_j^h$ estimated for various combinations of surfactant ions with dodecyl chain at 25 °C. Since dodecanesulfonate and dodecylbenzenesulfonate have the same ionic group, the estimated value for these ions is presumed to be close to the transfer free energy of phenylene group from water to nitrobenzene. Indeed, the numerical value in Table 2 is comparable with the free energy change of -1.9×10^4 J mol^{-1} for transfering benzene molecule from water to pure liquid benzene.[12] This fact not only supports the validity of Eq. 4 but suggests that the marked difference in the selectivity coefficients for dodecylbenzenesulfonate and dodecanesulfonate comes virtually from the difference in their partition coefficients. In view of the fact that the value of $w_i^h - w_j^h$ for dodecyltrimethylammonium ion and 1-dodecylpyridinium ion is negligibly small, the hydrophobicity of trimethylammonium group is considered to be nearly identical with that of pyridinium ring. The lack of the hydrophobic part in the ionic head group will probably be responsible for the pronounced decrease in the selectivity coefficient for dodecylammonium ion. Unfortunately, we are unable to give any reasonable account of the observed value of $w_i^h - w_j^h$ for dodecyl sulfate and dodecanesulfonate, since an information about the free energy change associated with the dehydration process of ionic group in nitrobenzene phase is unavailable at the present stage.

TABLE 2. THE CALCULATED VALUES OF $w_i^h - w_j^h$ FOR VARIOUS SURFACTANT IONS WITH A DODECYL CHAIN AT 25 °C

Surfactant ion		$(w_i^h - w_j^h)$/J mol^{-1}
i	j	
$-C_6H_4SO_3^-$	$-SO_3^-$	-1.5×10^4
$-SO_3^-$	$-SO_4^-$	9.9×10^3
$-N^+C_5H_5$	$-N^+(CH_3)_3$	180
$-NH_3^+$	$-N^+(CH_3)_3$	9.1×10^3

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