Study of Cationic Surfactant Ion Selective Poly(vinyl chloride) Membrane Electrode Containing Dibenzo-18-crown-6

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(Received July 15, 1980)

Study was made of the potentiometric selectivities of poly(vinyl chloride) membrane with and without dibenzo-18-crown-6. It was found that these membrane electrodes were highly selective for cationic surfactant ions and showed a Nernstian response to surfactant ion such as 1-dodecylpyridinium ion even in the concentration range as low as 10^{-6} mol/dm^3. The selectivity coefficients of inorganic cations, taken with respect to 1-dodecylpyridinium ion, were of the order of 10^{-5} or less, while that of surfactant ion was found to depend not only on hydrophobic alkyl chain length but also on the type of hydrophilic head group. For cationic surfactants with the same hydrocarbon chain length, the membrane without crown ether exhibited the order of selectivity: 1-alkylpyridinium ion>alkyltrimethylammonium ion>alkylammonium ion. In the case of the membrane with crown ether, the selectivity sequence became alkylammonium ion>1-alkylpyridinium ion>alkyltrimethylammonium ion. For a homologous series of cationic surfactants, the selectivity coefficient increased regularly with increasing alkyl chain length.

A recent study of a number of surfactant ion selective membrane electrodes$^{1-18)}$ has revealed the utility of such electrodes in the determination of critical micelle concentration$^{2-4,7,8,15,17,18)}$ as well as in potentiometric titration$^{1,2,9-14,16)}$ of ionic surfactant solutions. In addition, the use of surfactant ion electrode made it possible to obtain information regarding the surfactant ion activity in solution of ionic surfactant with$^{5,6)}$ and without$^{2-4,7,17)}$ interacting polymers.

With the exception of ionic polymer membrane,$^{17)}$ all of the surfactant ion sensitive membrane electrodes so far studied are composed of either liquid$^{1-13)}$ or plastic$^{14-18)}$ membrane, into which is dissolved an ion exchanger made up of a surfactant ion and an oppositely charged organic ion. An ion association complex between cationic and anionic surfactant ions has widely been used as an ion exchanger.$^{2-7,14,16,17)}$ These electrodes are found to be highly selective for surfactant ion over inorganic ions.$^{4,12,13)}$ On the other hand, the presence of an interfering surfactant ion is shown to affect appreciably the electrode response to a particular surfactant ion in such a way that the interference increases regularly with increasing hydrocarbon chain length of the interferent.$^{4,12,13,17)}$

So far as we know, however, little is known about the selective behavior of surfactant ion sensitive membrane electrode containing electroneutral carriers. It is well known that macrocyclic polyether such as dibenzo-18-crown-6 serves as an electroneutral carrier of membrane electrode sensitive to alkali metal cations, especially to potassium ion.$^{19-22)}$ Moreover, crown compounds have been found to form complexes with primary alkylammonium ions in aqueous$^{23)}$ and methanol$^{24,25)}$ media. It is thus interesting to study whether the crown compound-based membrane electrode responds selectively to cationic surfactant ions. In this paper is described the selective property of cationic surfactant ion sensitive poly(vinyl chloride) (PVC) membrane electrode with and without dibenzo-18-crown-6.

Experimental

Materials. Dibenzo-18-crown-6 (Nakarai Chemicals Ltd.) was recrystallized twice from benzene and dried *in vacuo*. Alkylammonium chlorides with 10, 12 and 14 carbon atoms were prepared from the corresponding alkylamines (purity>99%, Nakarai Chemicals Ltd.) according to the method of Kolthoff and Strickes.$^{26)}$ Alkyltrimethylammonium chlorides with 10, 12, and 16 carbon atoms (Tokyo Kasei Kogyo Co. Ltd.) were recrystallized twice from acetone. 1-dodecylpyridinium chloride (Wako Pure Chemical Industry Co. Ltd.) was purified by repeated recrystallization from acetone, then from isobutyl methyl ketone and finally by extraction with ether for 48 h. Tetraalkylammonium chlorides of guaranteed grade and other chemicals of reagent grade were used without further purifications.

Membrane Potential Measurements. The measurements were made with the membranes consisting of 20% PVC and 80% plasticizer, and of 1% dibenzo-18-crown-6, 20% PVC and 79% plasticizer by weight, (abbreviated hereinafter as carrier-free membrane and crown ether membrane). PVC (reported degree of polymerization is 1100) and bis(2-ethylhexyl) phthalate were dissolved into the least amount of tetrahydrofuran and mixed with a tetrahydrofuran solution of dibenzo-18-crown-6. The solution was poured onto a Petri's dish with a cover and allowed tetrahydrofuran to evaporate gradually at room temperature. A resulting membrane of 0.15 mm thickness was fixed to one end of PVC tube of 10 mm diameter by using a tetrahydrofuran solution of PVC as an adhesive. The preparation of carrier-free membrane is the same as that described above, except that dibenzo-18-crown-6 is omitted.

The electrode assembly is shown schematically in Fig. 1. In order to eliminate the leakage of ammonium ion from agar bridge, a double junction was constructed by inserting a small test tube with a pin-hole at the top into PVC electrode. The electrode was rinsed well with distilled water and stored in air when not in use. The selectivity coefficient was determined with the following cell by using the mixed solution method.$^{27)}$

Reference electrode (Ag–AgCl) | 1 mol/dm^3 NH_4NO_3 Agar bridge | Reference solution (DPC, 1×10^{-4} mol/dm^3) | PVC membrane | Sample solution (DPC, C_i; Interferent, C_j) | 1 mol/dm^3 NH_4NO_3 Agar bridge | Reference electrode (Ag–AgCl).

Here, C_i denotes the varying concentrations of 1-dodecylpyridinium chloride (DPC) and C_j the constant concentration of interfering ion, respectively. The electromotive force (EMF)(E) of the cell was measured with an accuracy of

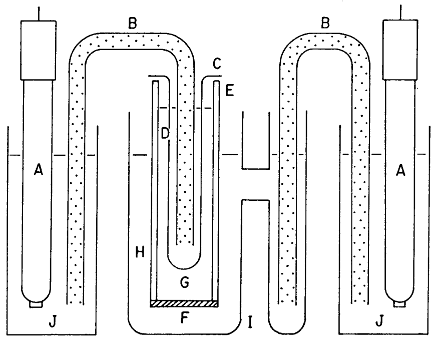

Fig. 1. Schematic diagram of PVC membrane electrode.
A: Reference electrode, B: agar bridge, C: small test tube, D: pin hole, E: PVC tube, F: PVC membrane, G: reference solution, H: sample solution, I: glass cell, J: saturated KCl solution.

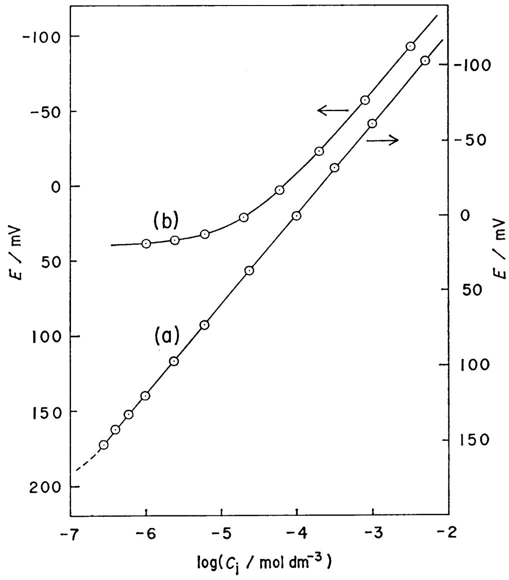

Fig. 2. Plots of EMF (E) of the cell *vs.* the logarithm of 1-dodecylpyridinium chloride concentration (C_i) at 25 °C.
(a): In the absence of interferent, (b): in the presence of 8.0×10^{-5} mol/dm^3 dodecyltrimethylammonium chloride. Arrows indicate the ordinate to be applied.

±0.1 mV, by using a Yokogawa Universal Digital Meter model 2502 connected to a voltage follower amplifier (input impedance $\approx 10^{13}\,\Omega$). All measurements were conducted at 25 °C. The PVC membrane was renewed after a series of experiments for a given kind of interferent.

Results and Discussion

It has already been found by Higuchi *et al.*[28] that PVC membrane plasticized with *N*,*N*-dimethyloleamide or dioctyl phthalate shows a Nernstian response to tetraalkylammonium ions. One might, thus, expect that the carrier-free membrane would also response to cationic surfactant ions. Curve (a) in Fig. 2 shows the typical semilogarithmic plots of EMF of the carrier-free membrane electrode *vs.* DPC concentration in the absence of interferent. In the concentration range below the critical micelle concentration (1.7×10^{-2} mol/dm^3), a linear relation with a slope of 59.6 mV per decade change in DPC concentration was found to hold down to 3×10^{-7} mol/dm^3. The observed slope agrees well with an ideal Nernst slope (59.2 mV at 25 °C), suggesting that the membrane is completely permselective to surfactant ion and 1-dodecylpyridinium ion behaves almost ideally in this concentration range. Similar Nernstian response was also obtained for the crown ether membrane, though a linear relation was confined to the range above 2×10^{-6} mol/dm^3. These electrodes are stable and permit the replicate measurements with surfactant solutions. For example, with the crown ether membrane, the observed slope of 59.3 mV/decade was reproducible to ±0.1 mV over a period of 47 d.

The presence of an interfering ion other than 1-dodecylpyridinium ion, particularly of surfactant ion, affects appreciably the membrane potential. A typical example is given in Fig. 2 by curve (b), which shows the change in EMF of the carrier-free membrane electrode with DPC concentration under constant concentration of dodecyltrimethylammonium chloride. Below a certain DPC concentration, the EMF of the cell tends to deviate gradually from a straight line with a Nernst slope and eventually to level off.

According to the common practice in describing the selectivity of membrane electrode, we calculated the selectivity coefficient, K_{ij}^{pot}, from the following equation,

$$E = E_a - \frac{RT}{F} \ln \frac{a_i + K_{ij}^{pot} a_j}{a_i^\circ}, \tag{1}$$

where subscript i refers to the primary ion to which the membrane is selective, j to the interfering ion and superscript ° to the reference solution, respectively. E_a is the asymmetric potential of overall cell system and other symbols have their usual meanings. As is shown in Fig. 2, the measurements were made by applying the mixed solution method, *i.e.*, E was followed as a function of the primary ion concentration under the conditions where the concentration of the interfering ion was kept constant. For simplicity, the activity coefficients in Eq. 1 were ignored in the following estimation of K_{ij}^{pot}. In order to estimate the most reliable value of selectivity coefficient, we used a slight modification of graphical curve-fitting method devised by Sillén[29] in the determination of equilibrium constants. Denoting $2.303RT/F$ by S and introducing new variables,

$$X = \frac{C_i}{K_{ij}^{pot} C_j} \tag{2}$$

and

$$Y = -S \log(1+X), \tag{3}$$

Eq. 1 may be written as

$$E = E_a + Y - S \log \frac{K_{ij}^{pot} C_j}{C_i^\circ} = Y + D_1. \tag{4}$$

Furthermore, it follows from Eq. 2 that

$$\log C_i = \log X + \log K_{ij}^{pot} C_j = \log X + D_2. \tag{5}$$

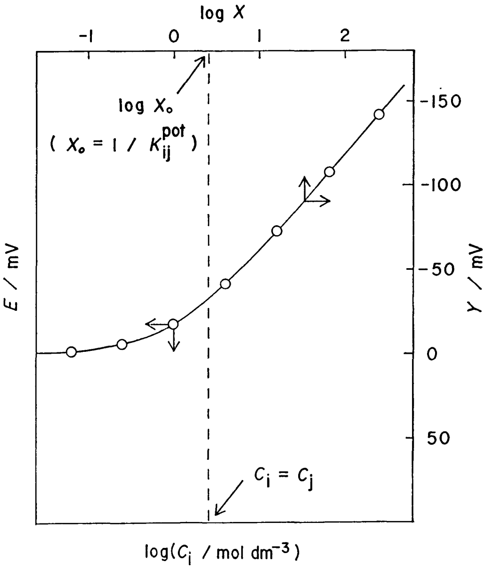

Fig. 3. Determination of the selectivity coefficient by graphical curve-fitting method.
Solid line: Normalizing curve, ○: experimental plots of E *vs.* $\log C_i$. Arrows indicate the coordinates to be applied.

Table 1. The selectivity coefficients (K_{ij}^{pot}) for various interferents at 25 °C

Interferent (j)	Carrier-free membrane	Crown ether membrane
$C_nH_{2n+1}NH_3^+Cl^-$		
$n=10$	2.2×10^{-3}	2.5×10^{-1}
$n=12$	2.2×10^{-2}	3.3
$n=14$	2.9×10^{-1}	3.6×10
$C_nH_{2n+1}N^+(CH_3)_3Cl^-$		
$n=10$	2.0×10^{-2}	1.7×10^{-2}
$n=12$	2.4×10^{-1}	2.3×10^{-1}
$n=16$	4.2×10	2.2×10
$C_{16}H_{33}N^+C_5H_5Cl^-$	2.1×10^{2}	1.7×10^{2}
$(C_nH_{2n+1})_4N^+Cl^-$		
$n=1$	$<10^{-6}$	$<10^{-6}$
$n=2$	9×10^{-6}	7×10^{-6}
$n=3$	8×10^{-4}	5×10^{-4}
Inorganic salts		
NaCl	$<10^{-6}$	2×10^{-5}
KCl	$<10^{-6}$	1×10^{-5}
NH_4Cl	$<10^{-6}$	2×10^{-6}
HCl	$<10^{-6}$	$<10^{-5}$

Under our experimental conditions, both D_1 and D_2 are constant. The comparison of Eq. 4 with Eq. 5 leads immediately to the conclusion that the experimental plot of E against $\log C_i$ is shifted by constant D_1 in the ordinate and by D_2 in the abscissa from a plot of Y against $\log X$. As is schematically shown in Fig. 3, therefore, the normalizing curve, in which Y is plotted as a function of $\log X$ for the given value of S, may easily be superimposable on the experimental plot of E against $\log C_i$ by sliding it both along ordinate and abscissa. The curve-fitting should be made so as to give the best fit of experimental data over the concentration range of C_i studied. This can usually be attained without difficulty. Then one may read the value of $\log X_0$ which corresponds to $C_i=C_j$. According to Eq. 5, the value of X_0 thus determined is equal to the reciprocal of K_{ij}^{pot}.

The estimated values of selectivity coefficients for various interfering ions are summarized in Table 1, where 1-dodecylpyridinium ion is conventionally taken as the primary ion, i. In some cases in which K_{ij}^{pot} defined above is much larger than unity, the determination of it suffers some experimental limitations, since the presence of even the trace amounts of interfering ion affects significantly the electrode response to 1-dodecylpyridinium ion. For instance with 1-hexadecylpyridinium ion and hexadecyltrimethylammonium ion, the presence of these ions as low as 10^{-6} mol/dm³ was sufficient to interfere the electrode response to 1-dodecylpyridinium ion. In such cases, therefore, we determined K_{ji}^{pot} and converted it to K_{ij}^{pot} on the basis of the relationship, $K_{ij}^{pot}\cdot K_{ji}^{pot}=1$, which is confirmed to hold for surfactant solutions.[17] It should be noted that inorganic cations and tetraalkylammonium ions with shorter alkyl chain length do not affect appreciably the electrode response to 1-dodecylpyridinium ion. An interesting feature of Table 1 is a marked difference in selectivity sequence for surfactant ions with the same alkyl chain length. The carrier-free membrane gives the selectivity sequence as 1-alkylpyridinium ion>alkyltrimethylammonium ion>alkylammonium ion. In the case of the crown ether membrane, however, the selectivity sequence becomes alkylammonium ion>1-alkylpyridinium ion>alkyltrimethylammonium ion. In fact, the selectivity coefficients of the crown ether membrane for alkylammonium ions are greater than those of the carrier-free membrane by a factor of about 100. This result may reasonably be interpreted in terms of the selective interaction of dibenzo-18-crown-6 with primary alkylammonium ion in membrane phase, since dibenzo-18-crown-6 has been found to form complex in methanol only with primary alkylammonium ion among various organic ammonium ions.[24]

Another important aspect of Table 1 is the regular increase in selectivity coefficient for a homologous series of interfering surfactant ions with respect to the hydrocarbon chain length. A similar trend was already noted both for liquid and plastic membrane electrodes containing an ion association complex.[4,12,13,17] On the basis of an assumption that the mobilities of ions of similar size in membrane phase are comparable with each other, Cutler *et al.*[17] attributed the regular change in selectivity coefficient for a homologous series of surfactant ions to the regular change in partition coefficient of surfactant ion between membrane and aqueous phases.

In the presence of an excess plasticizer, which is the case for the present experiment, the selectivity characteristics of PVC membrane will presumably be described by the theory of liquid membrane electrode. Ciani *et al.*[30] derived the following expression for the selectivity coefficient of liquid membrane with electrically neutral ligand.

$$K_{ij}^{\mathrm{pot}} = \frac{u_{jx}^{*} k_{jx} K_{jx}}{u_{ix}^{*} k_{ix} K_{ix}} = \frac{u_{jx}^{*} k_{j} K_{jx}^{*}}{u_{ix}^{*} k_{i} K_{ix}^{*}} \tag{6}$$

In Eq. 6, u represents the mobility, k the partition coefficient and K the association constant. The asterisk refers to the membrane phase and subscript ix to the complexed cation formed between cation i and electrically neutral ligand x.

For a homologous series of surfactant ions, it seems reasonable to assume that the association constant of the complexed cation is independent of hydrocarbon chain length. Moreover, the mobilities of complexed cations will probably be comparable with each other so long as the difference in hydrocarbon chain length remains small. In such cases, therefore, the selectivity coefficient will depend only on the partition coefficient of surfactant ion, and Eq. 6 reduces to

$$\frac{K_{ij}^{\mathrm{pot}}}{K_{il}^{\mathrm{pot}}} \approx \frac{k_j}{k_l}. \tag{7}$$

The same relationship has already been noted for PVC membrane containing an ion association complex.[17] Equation 7 provides a reasonable explanation for the regular change in K_{ij}^{pot} of the crown ether membrane shown in Table 1, since k is the increasing function of hydrocarbon chain length. In order to check the validity of Eq. 7, we made a tentative calculation of the free energy change, w, for transferring one methylene group from an aqueous medium to the membrane phase. Denoting the number of methylene groups of surfactant ion by n, Eq. 7 can be rewritten as

$$\frac{K_{ij}^{\mathrm{pot}}}{K_{il}^{\mathrm{pot}}} = \exp \frac{w(n_l - n_j)}{RT}. \tag{8}$$

In Table 2 are given the values of w calculated from Eq. 8 with the data for the crown ether membrane. It is worth noting that the values of w are all similar in magnitude regardless of the type of ionic head group and are close to the free energy change of -3400 J mol^{-1} for transferring one methylene group from an aqueous medium to pure long chain aliphatic alcohols.[31] This observation seems to support the validity of the foregoing treatment based on the theory of liquid membrane.

Examination of Table 1 also shed light on factors which determine the selectivity coefficient of the carrier-free membrane. It can immediately be seen that the quotients of the selectivity coefficients of the carrier-free membrane for a homologous series of surfactant ions are comparable to those of the crown ether membrane. This fact implies that Eq. 7 must also hold, at least experimentally, for the carrier-free membrane. Indeed, the substitution of the selectivity coefficients of the carrier-free membrane into Eq. 8 gives w of $-(2900$—$3300)$ J mol^{-1} which is in good agreement with those in Table 2. So far as a homologous series of surfactant ions is concerned, therefore, the presence of the electroneutral ligand seems to play a minor role in determining the selectivity characteristics of PVC membrane electrode.

TABLE 2. THE CALCULATED VALUES OF w FROM Eq. 8 WITH THE DATA FOR THE CROWN ETHER MEMBRANE AT 25 °C

Surfactant	n_j	n_l	$-w$/J mol^{-1}
Alkylammonium ion	12	10	3200
	14	12	3000
	14	10	3100
Alkyltrimethylammonium ion	12	10	3200
	16	12	2800
	16	10	3000
1-Alkylpyridinium ion	16	12	3200
			av. 3100

These membrane electrodes provide a simple means of determining a cationic surfactant ion activity even in the presence of added salts. Under appropriate conditions, it is also possible to estimate the activity of a particular surfactant ion in mixed surfactant solution. Details of the determination of the surfactant ion activity in micellar solution will be reported in a separate paper.

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