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Biionic Potential across Liquid Membranes with Some Anionic Surfactants

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The biionic membrane potential was measured with the system in which a solution of calcium chloride was separated by a liquid membrane from a solution of another metal chloride. Four kinds of liquid membranes were prepared by dissolving calcium hexadecyl sulfate, stearate, cholate or deoxycholate in aqueous 1-octanol. All of the membranes studied were nearly permselective to cation. The membrane potential was analysed according to the Goldman-type equation based on the irreversible thermodynamics. The slope of a linear portion of the biionic potential *vs.* logarithmic activity curve showed fairly good agreement with the theoretical slope, *i.e.*, $2.303\times 2RT/(Z_{Ca}+Z_M)F$ per a ten-fold increase in activity, where Z_{Ca} and Z_M were the valencies of calcium ion and another metal ion M existing across a membrane, respectively. The selective permeation coefficients of various metal ions were estimated for each membrane. The surprisingly small differences in the selective permeation coefficient between uni- and bi-valent cations were observed for the liquid membranes with calcium stearate, cholate or deoxycholate, while the about ten-fold increase in the coefficient per valency was observed for the liquid membrane with calcium hexadecyl sulfate. These results were discussed according to the theory previously presented.

The ion transport across membrane has usually been explained by the Goldman-type equation. The equation of this type has been presented for a fixed-site membrane as a limiting form of the general equation on the basis of the irreversible thermodynamics by Kimizuka *et al.*[1—3] In the theory, the general expression of multiionic membrane potential has been derived without any assumptions concerning the distribution of concentration as well as that of potential within membrane. The theory has successfully been applied to the biionic system in which different multivalent ions exist across the membranes of some permselective ion-exchangers.[4,5]

The equation of the membrane potential for a liquid membrane with mobile sites has been derived on the basis of the Nernst-Planck equation by Sandblom *et al.*[6] The equation is expressed as a sum of the two logarithmic terms in the case of strong association between counter ion and membrane site, while being expressed as the single logarithmic term in the case of complete dissociation. Only when the unlikely assumption that the mobility of free site is much larger than that of counter ion is made, the equation for strong association can be reduced to the familiar form with the single logarithmic term. On the other hand, it is well known facts that the membrane potentials measured with liquid membranes can be expressed by the equation with the single logarithmic term, even when liquid membranes are prepared from solvents of low dielectric constant.[7,8]

The total flux of a permeable ion across a liquid membrane can be expressed by the equation of the same form as that for a fixed-site membrane, although the physical contents of the permeability coefficients are somewhat modified.[9—11] Thus, the Goldman-type equation with the single logarithmic term can also be derived from the flux equation in the same way as described elsewhere,[1—3] and is equally applicable to the liquid membrane systems.[10,11]

In the present study, the membrane potential was measured in the biionic systems with four kinds of thin liquid membranes. The results were analysed and discussed according to the Goldman-type equation.

Experimental

Materials. Calcium hexadecyl sulfate, $Ca(HS)_2$, was prepared from sodium hexadecyl sulfate according to the method of Lottermoser and Püschel.[12] Sodium hexadecyl sulfate was prepared from purified 1-hexadecanol obtained by fractional distillation of a commercial sample, as stated elsewhere.[13] Stearic, cholic and deoxycholic acids from Merck were neutralized with sodium hydroxide to sodium salts, from which calcium stearate, cholate and deoxycholate, abbreviated as $Ca(ST)_2$, $Ca(CH)_2$, and $Ca(DC)_2$, respectively, were prepared by metathesis in aqueous ethanol with the same procedure as described elsewhere.[14] All other reagents were of guaranteed grade and used without further purification.

Liquid membrane was prepared by dissolving a site species in water-saturated 1-octanol. The concentration of the site species in liquid membranes was *ca.* 10^{-3} M (1 M= 1 mol dm^{-3}).

Procedure. The following cell assembly, connected to the Orion digital pH meter, Model 701, was used for the measurement of membrane potential.

$$\mathrm{Ag|AgCl|Internal\ Solution\ (1.10\times 10^{-2}\ M\ CaCl_2)|}$$
$$\mathrm{Liquid\ Membrane|External\ Solution|Calomel}$$

For the liquid membranes with $Ca(ST)_2$, $Ca(CH)_2$, and $Ca(DC)_2$, the internal and external solutions were adjusted to pH=8.5 with 2×10^{-3} M Tris buffer. A body of the Orion calcium ion selective electrode and a Teflon millipore film (Fluoro Pore, No. FP080, 0.8 μm of pore size, 50 μm in thickness, Sumitomo Electric Co. Ltd.) as an inert porous matrix for liquid membranes were employed for constructing the membrane electrode.

The external solution was stirred and all measurements were carried out at 25±0.02 °C.

Results and Discussion

For the liquid membranes with $Ca(ST)_2$, $Ca(CH)_2$, or $Ca(DC)_2$, the pH dependence of the membrane electrode potential, V, was studied at constant calcium ion concentration, as shown in Fig. 1. The potential for the liquid membrane with $Ca(ST)_2$ was independent of pH in the alkaline region of pH>8.5. A similar pH dependence was also observed with the calcium ion selective liquid membrane electrode using didecyl hydrogenphosphate site.[15] The potentials for the liquid membranes with $Ca(CH)_2$ or $Ca(DC)_2$ were unstable below pH 7, possibly being due to the dissolution of membrane site into aqueous phase.

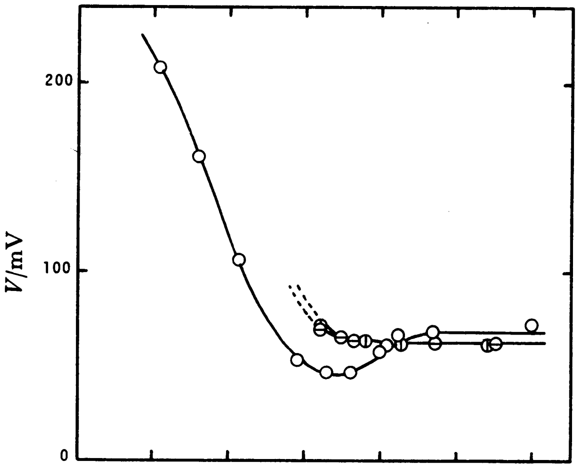

Fig. 1. Membrane electrode potential *vs.* pH curves. Liquid membranes with $Ca(ST)_2$, ○; $Ca(CH)_2$, ⦶; $Ca(DC)_2$, ⊖. $C_{Ca(i)} = C_{Ca(e)} = 1.10 \times 10^{-2}$ M.

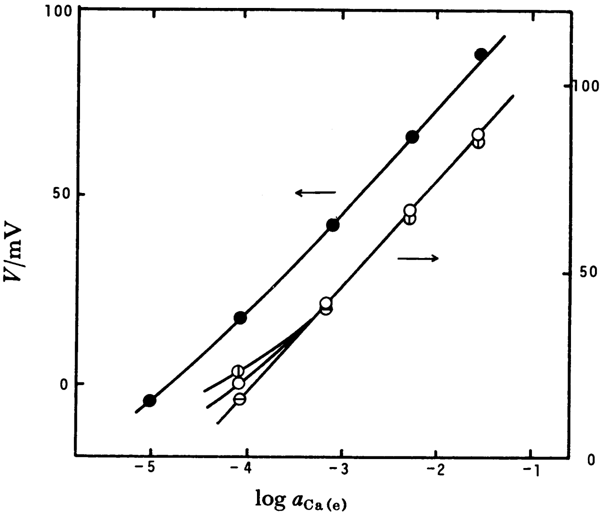

Fig. 2. Membrane electrode potential *vs.* logarithmic activity curves for the single electrolyte system of $CaCl_2$. Liquid membranes with $Ca(HS)_2$, ●; $Ca(ST)_2$, ○; $Ca(CH)_2$, ⦶; $Ca(DC)_2$, ⊖. $C_{Ca(i)} = 1.10 \times 10^{-2}$ M. The pH's of aqueous phases were 5.6 for liquid membrane with sulfate site and 8.5 for those with carboxylate site.

The membrane electrode potential for the liquid membrane with $Ca(HS)_2$, measured at 10^{-1} M $CaCl_2$, was independent of pH in the range of pH>3.3.

The potentials of the membrane electrodes for all of liquid membranes studied were found to be linear against the logarithm of external calcium ion activity, as shown in Fig. 2. The values of ion activity were calculated according to the extended Debye-Hückel equation. Assuming that a membrane is ideally permselective to cation, the potential of the membrane electrode for the single electrolyte system of $CaCl_2$ is given as

$$V = V_{Ca} + V_o = \frac{RT}{Z_{Ca}F} \ln \frac{a_{Ca(e)}}{a_{Ca(i)}} + V_o, \qquad (1)$$

where V_{Ca} is the membrane potential in the present system: $a_{Ca(e)}$ and $a_{Ca(i)}$, the activities of calcium ion in the external and internal solutions, respectively; R, gas constant: T, absolute temperature: F, Faraday constant: Z, valency; and V_o, the potential difference between the internal and external electrodes, including the liquid junction potential. Since the same internal solution was used throughout the experiment and the liquid junction potential is negligibly small, V_o can be regarded as constant. Therefore, the slope of the V *vs.* log $a_{Ca(e)}$ curve is approximately the same as that of the V_{Ca} *vs.* log $a_{Ca(e)}$ curve. The slopes of the linear portions shown in Fig. 2 are *ca.* 29 mV per decade for all of the liquid membranes studied, agreeing well with the theoretical slope predicted by Eq. 1. This indicates that these liquid membranes are ideally permselective to cation.

The measurements of the biionic potential were carried out on the systems in which the internal solution containing a constant concentration of $CaCl_2$ was separated by a liquid membrane from an external solution containing varying concentrations of another metal chloride. Typical results are shown in Figs. 3—5. When the membrane is ideally permselective to cation, the potential of the membrane electrode for the biionic system of Ca^{2+} and M^{Z_M+}, V', can be written as[4]

$$V' = V_{Ca,M} + V_o = \frac{2RT}{(Z_{Ca}+Z_M)F} \ln \frac{Z_M P_M a_{M(e)}}{Z_{Ca} P_{Ca} a_{Ca(i)}} + V_o, \qquad (2)$$

where $V_{Ca,M}$ is the membrane potential in the biionic system; and P, the membrane permeability. Assuming that the permeability ratio, P_M/P_{Ca}, and the concentration of $CaCl_2$ in the internal solution are constant, Eq. 2 becomes

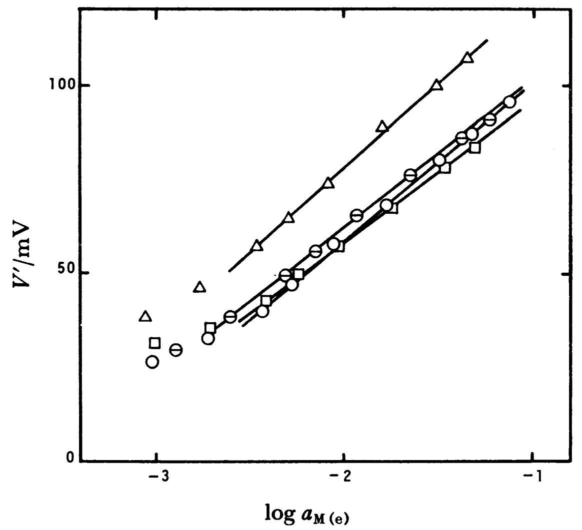

Fig. 3. Membrane electrode potential *vs.* logarithmic activity curves for the system Ca^{2+}(i)–M^{+}(e). Liquid membrane with $Ca(CH)_2$. $M^{+}=Li^{+}$, △; Na^{+}, ○; K^{+}, □; Cs^{+}, ⊖. $C_{Ca(i)}=1.10\times10^{-2}$ M. pH=8.5.

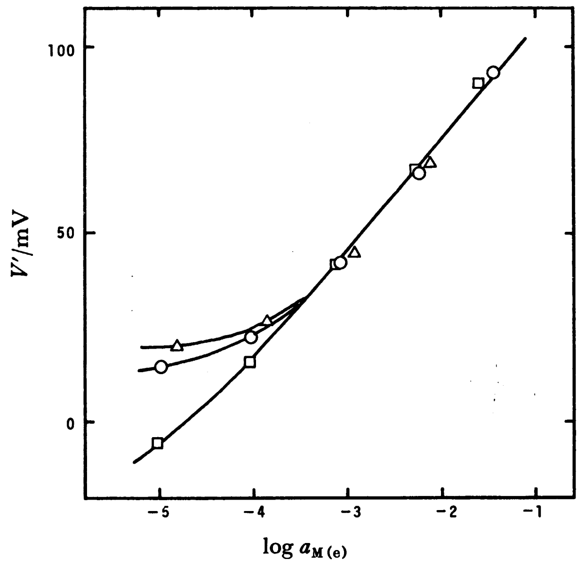

Fig. 4. Membrane electrode potential *vs.* logarithmic activity curves for the system Ca^{2+}(i)–M^{2+}(e). Liquid membrane with $Ca(HS)_2$. $M^{2+}=Mg^{2+}$, ○; Sr^{2+}, △; Ba^{2+}, □. $C_{Ca(i)}=1.10\times10^{-2}$ M. pH=5.6.

$$V' = \frac{2RT}{(Z_{Ca}+Z_{M})F}\ln a_{M(e)} + \text{const.}, \tag{3}$$

where

$$\text{const.} = \frac{2RT}{(Z_{Ca}+Z_{M})F}\ln\frac{Z_{M}P_{M}}{Z_{Ca}P_{Ca}a_{Ca(i)}} + V_{o}, \tag{4}$$

The slopes of linear portions in Figs. 3—5 were 37—41 (except 45 for the Ca^{2+}-Li^{+} system), 30 and 21—22 mV per decade for the 2—1, 2—2, and 2—3 valent biionic systems, respectively, agreeing approximately with the theoretical slope predicted by Eq. 3, *i.e.*, 118/ $(Z_{Ca}+Z_{M})$ mV per decade.

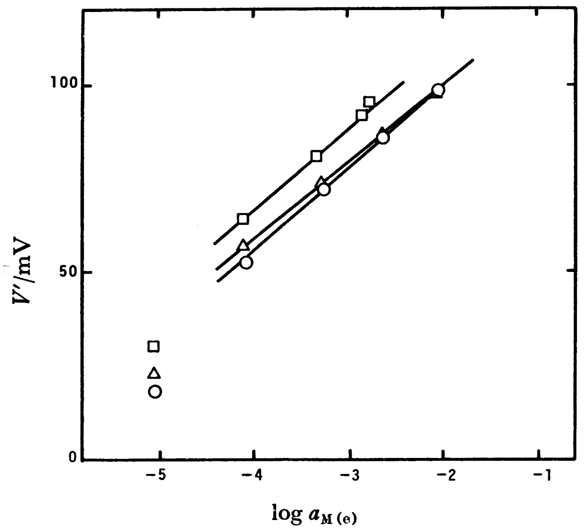

Fig. 5. Membrane electrode potential *vs.* logarithmic activity curves for the system Ca^{2+}(i)–M^{3+}(e). Liquid membrane with $Ca(HS)_2$. $M^{3+}=Al^{3+}$, ○; La^{3+}, △; $[Co(NH_3)_6]^{3+}$, □. $C_{Ca(i)}=1.10\times10^{-2}$ M. pH(i)=5.6. The pH's of external solutions of Al^{3+}, La^{3+} and $[Co(NH_3)_6]^{3+}$ were 3.4—5.4, 5.2—5.5, and 5.5—5.4 depending upon the concentrations, respectively, where the electrode potential was independent of pH.

TABLE 1. SELECTIVE PERMEATION COEFFICIENTS, $K_{Ca,M}$

Ion, M	Liquid Membranes			
	$Ca(HS)_2$	$Ca(ST)_2$	$Ca(CH)_2$	$Ca(DC)_2$
Li^{+}	0.16	0.40	1.1	1.0
Na^{+}	0.06	0.18	0.37	0.41
K^{+}	0.07	0.19	0.37	0.38
Rb^{+}	0.07	—	—	—
Cs^{+}	0.09	0.20	0.44	0.39
Mg^{2+}	1.0	0.79	0.86	0.93
Sr^{2+}	1.0	0.46	0.50	0.55
Ba^{2+}	1.0	0.46	0.43	0.43
Cu^{2+}	1.3	—	—	—
Ni^{2+}	1.2	3.5	2.3	—
Co^{2+}	1.3	—	—	—
Al^{3+}	9.3	—	—	—
La^{3+}	10	—	—	—
$[Co(NH_3)_6]^{3+}$	17	—	—	—

The selective permeation coefficients of Z_M valent cation M, relative to Ca^{2+} ion, $K_{Ca,M}=Z_MP_M/Z_{Ca}P_{Ca}$, were estimated from the potential difference, $V'-V$, by using Eqs. 1 and 2. The results are shown in Table 1.

According to the previous theory,[11] the membrane permeability to cation M, P_M, can be expressed as

$$P_{M} = RT\bar{u}_{M}C_{M}^{to}/\{a_{M(e)}a_{M(i)}\}^{1/2}d, \tag{5}$$

where

$$\bar{u}_{M} = \alpha_{M}u_{M} + (1-\alpha_{M})u_{I}, \tag{6}$$

and C_{M}^{to} denotes the mean total concentration of cation

M: d, the membrane thickness: u_M and u_I, the mean mobilities of cation M and ion pair I formed between cation M and site anion, respectively; and α_M, the dissociated fraction of cation M ($\alpha_M = C_M/C_M^{to} = 1 - \nu_M C_I/C_M^{to}$, where ν_M is the stoichiometric coefficient of cation M in the ion-pair formation), all referred to the values within membrane. Inserting the following relation for the site species[11]

$$(\nu_M/\nu_S)\alpha_M u_S - (1-\alpha_M)u_I = 0 \tag{7}$$

into Eq. 6, we have

$$\bar{u}_M = \alpha_M\{u_M + (\nu_M/\nu_S)u_S\} \tag{8}$$

where ν_S is the stoichiometric coefficient of site anion S in the ion-pair formation; and u_S, the mean mobility of site anion. Assuming that the selective permeation coefficient, $K_{Ca,M}$, can be expressed as the ratio of $Z_M P_M$'s in the single electrolyte system, we have from Eqs. 5 and 8

$$\begin{aligned} K_{Ca,M} &= Z_M P_M / Z_{Ca} P_{Ca} \\ &= Z_M \bar{u}_M C_M^{to}\{a_{Ca(e)} a_{Ca(i)}\}^{1/2} / Z_{Ca} \bar{u}_{Ca} C_{Ca}^{to}\{a_{M(e)} a_{M(i)}\}^{1/2} \\ &= Z_M \alpha_M\{u_M + (\nu_M/\nu_S)u_S\} K_M / Z_{Ca}\alpha_{Ca} \\ &\quad \times \{u_{Ca} + (\nu_{Ca}/\nu_S)u_S\} K_{Ca} \end{aligned} \tag{9}$$

where K_{Ca} and K_M are the apparent partition coefficients of cations Ca^{2+} and M between the membrane and aqueous phases. This expression of the selective permeation coefficient has the same form as that for a fixed-site membrane,[3] except that u_M and C_M are replaced by $\bar{u}_M$ and C_M^{to}. Considering Eq. 7, Eq. 9 is reduced to the same limiting form as that derived by Sandblom *et al.* in the case of complete dissociation.

The noticeable feature seen among the estimated values of $K_{Ca,M}$ is the surprisingly small differences in the $K_{Ca,M}$ value between uni- and bivalent cations for the membranes with $Ca(ST)_2$, $Ca(CH)_2$, and $Ca(DC)_2$. Let us consider the case of $M = Na^+$ for the liquid membrane with $Ca(ST)_2$. Assuming that the mobility ratio, $\{u_{Na} + (\nu_{Na}/\nu_S)u_S\}/\{u_{Ca} + (\nu_{Ca}/\nu_S)u_S\}$, can be replaced by that in aqueous solution and using 50.15, 119.0[16], and 19.95 (extrapolated from the values for fatty acid anions of C_1—C_{14})[17] $ohm^{-1}\,cm^2\,mol^{-1}$ for the values of the limiting molar conductances of Na^+, Ca^{2+}, and stearate ions, respectively, Eq. 9 can be rewritten as

$$K_{Ca,Na} = 0.504(\alpha_{Na}/\alpha_{Ca})(K_{Na}/K_{Ca}) \tag{10}$$

According to Eq. 10, the $K_{Ca,Na}$ value is governed by the two ratios, *i.e.*, α_{Na}/α_{Ca} and K_{Na}/K_{Ca}. In the case of complete dissociation, the selective permeation coefficient is solely determined by the partition ratio. Experimental results with liquid membranes formed from solvents of high dielectric constant can be explained according to this reasoning.[8] However, in the case of partial dissociation, these two ratios usually exert the opposite effects on the selective permeation coefficient, *i.e.*, the strong affinity of an ion to the membrane site is favorable to the partition ratio, but not to the dissociation ratio.

The very small value of K_{Na}/K_{Ca} can be expected from the partition data of metal ions between the aqueous and the water-saturated 1-octanol phase with a partially neutralized polycarboxylic acid,[18] while the large value of α_{Na}/α_{Ca} can be expected from the conductance data for metal salts of the above polycarboxylic acid in water-saturated 1-octanol.[19] Thus, the partial cancellation of the K_{Na}/K_{Ca} value by the α_{Na}/α_{Ca} value seems to bring the $K_{Ca,Na}$ value close to those for bivalent cations, leading to the diminished valency effect on the selective permeation coefficient.

Contrary to the above membranes, the about tenfold increase in the $K_{Ca,M}$ value per valency were observed for the liquid membrane with $Ca(HS)_2$, as seen in Table 1. Because of the dissociable sulfate site, the α_{Ca} value of $Ca(HS)_2$ reachs 0.25 at the concentration of 2.5×10^{-3} M even in aqueous 1-octanol.[11] On the other hand, the association constant of sodium dodecyl sulfate in the dioxan-water mixture of the same dielectric constant as that of aqueous 1-octanol, *i.e.*, 8.92,[19] was obtained by the extrapolation, from which the α_{Na} value was estimated to be *ca.* 0.25 at the concentration of 2.5×10^{-3} M.[20] It is obvious from the estimated values of the dissociated fraction that the observed valency effect on the selective permeation coefficient can primarily be attributed to the partition ratio.

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