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Electrical Double Layer Formed on the Monolayer of Crown Ether Compounds

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The binding behavior of metal ions to the monolayers of a crown ether compound has been studied by the surface potential measurements. The obtained data are analyzed from the viewpoint of interfacial electrochemistry, i.e., the electrical double layer theory at the interfaces. The analysis reveals that the generated double layer at a membrane-solution interface after the complexing of metal ions with crown ethers is well described by the Stern model for the electrical double layer; it shows that there exists a possibility to evaluate the binding constants of metal ions with crown ethers under interfacial circumstances.

The transport behavior across biological membranes or oil liquid film is one of the attractive problems in colloid and surface chemistry. A lot of compounds which mediate ion transport through membranes have been found in biological systems (e.g. antibiotics) and have been manufactured artificially.[1-3] These compounds are called "ionophores" and are classified approximately into two categories from their functional characteristics, (carrier type and channel type). Crown ethers are the most attractive synthetic ionophores, which can complex with various metal ions with a characteristic selectivity.[2,3] Since these complexes are lipophilic, arising from crown's hydrophobic rings, they can dissolve in nonaqueous media. Thus, the crown ether can transport metal ions through oil liquid films or lipid bilayer membranes. Despite the fact that a lot of studies have been performed on this subject, details concerning the transport mechanisms, whether carrier type or channel type, have been incompletely revealed. For the purpose of understanding the transport mechanism, it is desirable to clarify fundamental factors of the transport process, e.g. the binding characteristics of metal ions with crown ethers, the adsorption and desorption equilibrium between oily phase and aqueous phases, etc.[4,5] In the case of amphiphilic crown ethers, binding with metal ions can occur both in the bulk aqueous phase and at the interface of the membrane-aqueous phase. On the other hand, some lipophilic crown ethers hardly dissolve in the aqueous phase; therefore, they make complexes with metal ions only at the interface of the oil-aqueous phase or the membrane-aqueous phase. At such interfaces, the binding behavior of metal ions with crown ether are influenced by various interfacial properties, especially an electrical double layer at the interface.

In this work, the binding behavior of metal ions with a crown ether under interfacial circumstances has been studied from the viewpoint of interfacial electrochemistry. To find the fundamental feature of binding at the interface, simple systems have been employed, i.e., monolayers of a water-insoluble crown compound and the change in the surface potential of the monolayers caused by ion-binding to them has been studied.[6]

Experimental

Materials. To make a monolayer on a water surface, a crown ether which had a long hydrocarbon chain was prepared. The compound was octadecyloxymethyl 18-crown-6 (see Fig. 1) and is hereafter abbreviated as C18-18-crown-6.

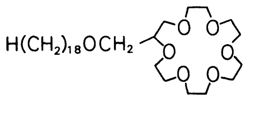

Fig. 1. Molecular structure of octadecyloxymethyl 18-crown-6.

C18-18-crown-6 was synthesized from octadecyl glycidyl ether and pentaethylene glycol by the same method as that reported in the literature.[7,8] The product was purified by column chromatography on silica gel or repeated Kugelrohr distillation (bp 230—235 °C/0.002 Torr (1 Torr=133.322 Pa)) and then recrystallized from methanol (mp 46—47 °C). The purity (>99%) was confirmed by GLC, TLC, NMR, IR, and elemental analyses. To make mixed monolayers with C18-18-crown-6, stearyl alcohol (Tokyo Kasei Kogyo Co.) was employed.

Surface Potential Measurement. A monolayer of C18-18-crown-6 was spread from a hexane solution on pure water. The packing density of the membrane was about 1/100 (molecule/Å^2). This value is comparable to the density of this compound in a close-packed state of a two-dimensional array. After the addition of a concentrated metal chloride aqueous solution to the subphase solution in a 80-ml Teflon trough, the solution was stirred for more than 30 min; the change in the surface potential ($\Delta\Delta V$) caused by a binding of the metal ions was measured by the vibrating-electrode method[9] at 23 °C. The 1 : 1 mixed monolayer of C18-18-crown-6 with stearyl alcohol was also employed and the experiment was carried out according to the same procedure as that for the pure monolayer, except for the packing density (in this case: ca. 1/100 molecular pair/Å^2).

Results and Discussion

The monolayer of C18-18-crown-6 has no electrical charges when it is spread on distilled water. The addition of metal ions to the subphase solution causes the formation of an electrical double layer at the membrane-water interface by binding to the crown rings, leaving counter ions (Cl^-) in the aqueous phase. The generation of the electrical double layer can be observed by measuring the surface potential of the monolayer. Strictly speaking, the surface potential of the monolayer is described as a combination of the potential arising from the oriented dipoles of polar head groups of crown ether molecules and the ionic double-layer potential. In the present analysis, the change in the surface potential is assumed to be caused by a structural change in the ionic double layer; this has no serious disadvantage judging from the following fact. The change in the molecular orientation of this type crown ether, caused by a variation in the molecular packing density in the monolayer, shows a rather drastic potential change (Details will be published elsewhere). In Fig. 2, the change in the surface potential is plotted against the concentration of several kinds of metal ions. As can be seen, the contribution of these ions to $\Delta\Delta V$ is of the order of $K^+ > Na^+$ for alkali ions and $Ba^{2+} > Ca^{2+}$ for alkaline earth ions. These orders are the same as those of the complexing stability constant of these ions with 18-crown-6 in water or methanol.[10] For a mixed monolayer of C18-18-crown-6 with steary alcohol (1 : 1 molar ratio), plots of $\Delta\Delta V$ vs. the concentrations of various metal ions are shown in Fig. 3. A similar tendency to those in Fig. 2 is observed regarding $\Delta\Delta V$; however, the apparent ion-selectivity is lower than that for the pure membrane. All these facts suggest that there exists the same ion-selectivity of crown ethers at the membrane-solution interface to that in the bulk phase.

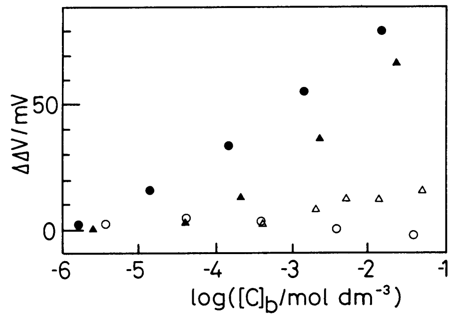

Fig. 2. Surface potential change of C18-18-crown-6 monolayer vs. concentration of various ions, (●) Ba^{2+}, (▲) K^+, (△) Na^+, (○) Ca^{2+}.

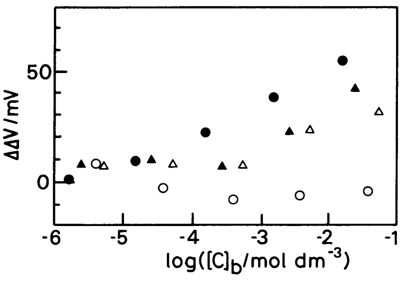

Fig. 3. Surface potential change of mixed monolayer of C18-18-crown-6 and stearyl alchol (molar ratio=1/1) vs. concentration of various ions, (●) Ba^{2+}, (▲) K^+, (△) Na^+, (○) Ca^{2+}.

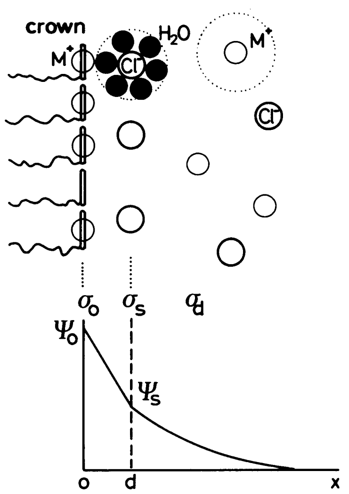

Fig. 4. Schematic representation of the distribution of ions and the profile of electrostatic potential across the double layer at the interface of crown ether monolayer and aqueous solution.

To know further details regarding the binding behavior, the obtained data are analyzed using the concepts of interfacial electrochemistry.[11] Figure 4 shows a schematic representation of an electrical double layer at the interface between the monolayer of a crown ether and aqueous salt solution. In this system, the charges on the membrane-surface arise from the binding of metal ions with crown rings after dehydration, while the hydrated chloride ions remaining in the solution become counter ions. Therefore, the Gouy-Chapman-Stern model may be adequate for describing this elctrical double layer. However, a slight modification is required to describe the feature of surface charges. That is, the charges are localized at each of the crown rings; then the number of binding sites for metal ions is limited. This corresponds to the number of crown ether molecules in the monolayer. Therefore, the Langmuir adsorption isotherm is adopted to represent the binding behavior of metal ions to the membrane. The relations between the potential and the charges are described in the following way.

(1) The electroneutrality requires the following relation:

$$\sigma_0 + \sigma_s + \sigma_d = 0, \tag{1}$$

where σ_0 is the charge density on the membrane surface, σ_s the charge density on the Stern plane, and σ_d the charge density in the diffuse double layer.

(2) σ_0 is represented by a Langmuir-type equation:

$$\sigma_0 = z|e|\frac{KC_0[M^+]_b\exp(-z|e|\Phi/kT)}{1+K[M^+]_b\exp(-z|e|\Phi/kT)} \tag{2}$$

where K is the binding constant, C_0 the density of crown ether on the monolayer (in the present experiment, C_0=1/100 number/Å^2), $[M^+]_b$ the concentration of metal ion in the bulk solution, z the valency of metal ions, and Φ the micropotential which influences the binding of metal ions.[12] Φ is represented by the following simple formula:

$$\Phi = \alpha \cdot \psi_0, \quad (3)$$

where ψ_0 is the surface potential of the membrane and α is a constant ($0<\alpha<1$).

(3) σ_s is also represented by a Langmuir-type equation:

$$\sigma_s = -|e|\frac{K^* C_0^* [\mathrm{Cl}^-]_b \exp(|e|\psi_s/kT)}{1+K^* C_0^* [\mathrm{Cl}^-]_b \exp(|e|\psi_s/kT)}, \quad (4)$$

where K^* is the binding constant of Cl^- to the Stern plane, C_0^* the maximum binding density of Cl^- ions, $[\mathrm{Cl}^-]_b$ the concentration of Cl^- ion in the bulk, and ψ_s the electrostatic potential at the Stern plane.

(4) The electrical charge density in a diffuse double layer is expressed by the Gouy-Chapman theory, as follows:

$$\sigma_d = -\left(\frac{2N[\mathrm{Cl}^-]_b \varepsilon kT}{\pi}\right)\sinh\left(\frac{\psi_s|e|}{2kT}\right), \quad (5)$$

where N is Avogadoro's number and ε is the dielectric constant of bulk water ($\varepsilon=80$).

(5) The potential at the Stern plane is related to the surface potential as

$$\psi_0 - \psi_s = \frac{4\pi d \sigma_0}{\varepsilon^*}, \quad (6)$$

where d is the distance between the membrane surface and the Stern plane and ε^* is the dielectric constant in the Stern layer.

When the counter ions are completely distributed in the diffuse double layer, i.e., when the existence of the Stern plane can be ignored, the relation $\sigma_0+\sigma_d=0$ can hold by replacing ψ_s in Eq. 5 by ψ_0. On the other hand, when the counter ions are completely localized on the Stern plane, the relation $\sigma_0+\sigma_s=0$ holds. For the intermediate states, K^* and C_0^* in Eq. 4 can be expressed by the following equations:

$$K^* = AK\exp(-z|e|(\Phi+\psi_s)/kT) \quad (7a)$$

$$C_0^* = C_0, \quad (7b)$$

where A is a parameter representing the mixed ratio of Stern model and Gouy-Chapman model ($0<A<1$). For monovalent ions, the potential change ($\Delta\Delta V=\psi_0$) is calculated using the above equations; the results are drawn against the concentration of metal ions in Fig. 5. In these calculations, several parameters are assumed to be consistent with the physical meaning. That is, $\varepsilon^*=32$, which corresponds to a partially immobilized water layer and $d=7$ Å, which is calculated from $d=r_M+\phi_w+r_{Cl}$, where r_M is the radius of metal ions (for K^+ $r_M \simeq 1.3$, for Ba^{2+} $r_M \simeq 1.4$ Å), ϕ_w is the diameter of a water molecule ($\phi_w=3$—4 Å), and r_{Cl} is the radius of a chloride ion ($r_{Cl}=1.8$ Å). In Fig. 5, the experimental data of $\Delta\Delta V$ for K^+ are also plotted. As can be seen from the figure, the data are fit the Stern model better than the Gouy-Chapman model. That is, a condenser-type double layer is adequate for describing the present double layer. Next, the same analysis is carried out for divalent ions. In Fig. 6, analytical curves are presented together with experimental data for Ba^{2+}. As can be seen, the Stern model is more suitable for describing the double layer on the membrane of crown ethers than the Gouy-Chapman model. Further, in Figs. 7 and 8, the experimental data for K^+ and Ba^{2+} are plotted along with the analytical curves from the Stern model calculated using "α" as a parameter. In these calculations, we assumed that α is a parameter which correlates the micropotential (Φ) with macropotential ($\Delta\Delta V=\psi_0$) and takes a value between 0 and 1, where $\alpha=0$ indicates that the adsorbing ions are not influenced by electrostatic potential generated by the already adsorbed ions, while $\alpha=1$ indicates that the electrostatic potential influences the adsorption of next adsorbing ions completely. As can

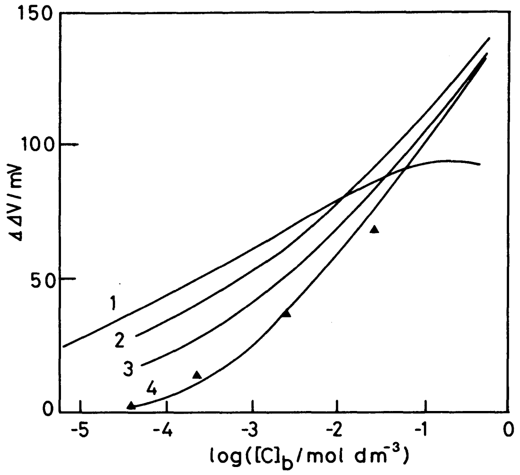

Fig. 5. Calculated curves from Eqs. 1—6 for the change of surface potential caused by mono-valent metal ions in various cases: (1) Gouy-Chapman model, (2) $A=0.5$, (3) $A=0.8$, and (4) Stern model; $\log K=2.3$, $\alpha=1$. Experimental data (▲) of KCl are also plotted as to fit to one of these curves.

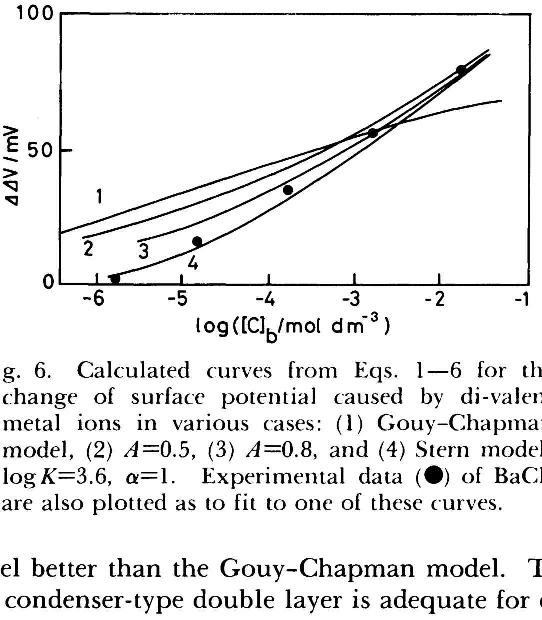

Fig. 6. Calculated curves from Eqs. 1—6 for the change of surface potential caused by di-valent metal ions in various cases: (1) Gouy-Chapman model, (2) $A=0.5$, (3) $A=0.8$, and (4) Stern model; $\log K=3.6$, $\alpha=1$. Experimental data (●) of $BaCl_2$ are also plotted as to fit to one of these curves.

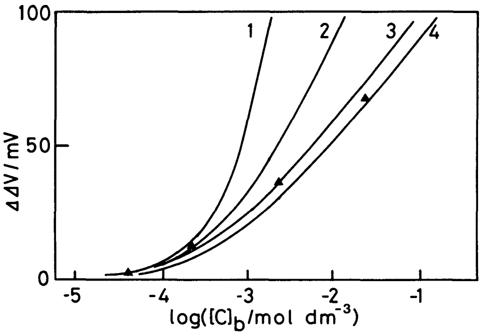

Fig. 7. Calculated curves of the change of surface potential for mono-valent ions from the Stern model with various values of parameters: (1) α=0, (2) α=0.5, (3) α=1, (d=7 Å); and (4) α=1, (d=5 Å). Experimental data (▲) of KCl are also plotted as to fit to one of the curves.

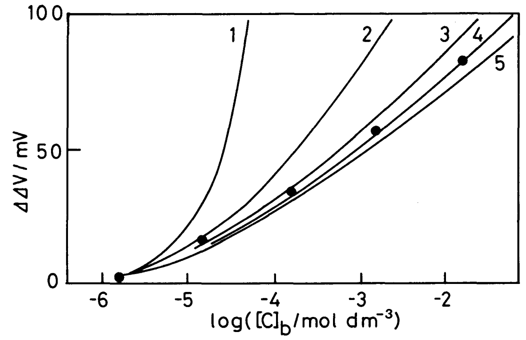

Fig. 8. Calculated curves of the change of surface potential for di-valent ions from the Stern model with various values of parameters: (1) α=0, (2) α=0.5, (3) α=0.8, (4) α=0.9, and (5) α=1. Experimental data (●) of $BaCl_2$ are also plotted as to fit to one of the curves.

be seen in Fig. 7, the experimental data for K^+ are well fitted to the analytical curve of α=1, in the range of low salt concentration. However, in the range of high salt concentration, $\Delta\Delta V$ changes more slowly than the analytical curve against the salt concentration. This phenomenon may arise from the fact that either the thickness of the Stern layer is smaller than that of this model (7 Å); in Fig. 7 the analytical curve of $\Delta\Delta V$ (assuming d=5 Å) is also drawn; or the diffuse double layer may be combined with the Stern layer to some extent in the high salt concentration range, i.e., an incomplete condenser type-double layer is formed and some counter ions are distributed over the diffuse double layer. The experimental data for Ba^{2+}, on the contrary, are well fitted to the theoretical curve for α=0.9—1. These results indicate that the mutual electrostatic repulsion among adsorbed metal ions is stronger for K^+ than for Ba^{2+}. This difference may arise from a difference in the discreteness of the charge distribution on the membrane surface. That is, the charges on di-valent metal ions are more localized than those on mono-valent ions on the membrane surface. In the case of di-valent ions, the one site for adsorption on the membrane can carry two electrical charges, while the site for mono-valent ions can carry only one charge.

Also, it is possible to obtain the value of the binding constant (K) in Eq. 2 by fitting the data to analytical curves. The estimated values for K^+ and Ba^{2+} are log $K \simeq 2$ and log $K \simeq 4$, respectively. These values are compared with the ones of 18-crown-6 appearing in the literatures, which were obtained by various kinds of experiments in the bulk liquid phase. Some typical examples are as follows: for K^+, log K=2.03—2.15 in H_2O and log K=5.93—6.20 in MeOH, while for Ba^{2+}, log K=3.87 in H_2O and log K=7.04 in MeOH.[10] As can be seen from these data, the estimated values of K in the present study are not so different from the values determined experimentally in bulk water.

In the present study, we can indicate that the electrical double layer generated by the complex-formation of a crown ether membrane with metal ions is of the type of the Stern model and that the binding constants of metal ions with the crown ethers under the interfacial circumstances can be evaluated by a simple electrical double layer theory.

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