CHEMISTRY LETTERS, pp. 453-454, 1986.

SURFACE POTENTIAL STUDIES ON CATION BINDING CHARACTERISTICS OF THE MONOLAYER OF CROWN ETHER HAVING A LONG HYDROCARBON CHAIN

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The surface potential measurement of monolayer showed that there exists a possibility for determining binding constants of several metal cations with 18-crown-6 when they exist in interfacial circumstances by introducing a long hydrocarbon chain to the crown ether.

Crown ethers are synthetic macrocyclic ligands which can bind alkali and alkaline-earth cations. As the crown ether complexes of cations are lipophilic, they have been used as ion-carriers for transport of metal cation across bilayer membranes[1)] or oil phase[2)] with high selectivity and also utilized in the field of phase transfer catalysis.[3)] The binding characteristics of metal ions with crown ethers in water and methanol have been studied using several methods, e.g. calorimetric titration[4)] or potentiometric titration[5)] with ion-selective electrodes, and comparison of cloud point.[6)] However, some lipophilic crown ethers hardly dissolve in water. These compounds dissolve in oily phase and make complexes with metal cations at the oil-water or membrane-water interface. So, it is very important to know the binding constant of the cations with these crown ethers at such interfaces to understand the transport process and the catalytic behavior in phase-transfer-reactions.

In this communication, we report a method using monolayers to investigate the binding characteristics of metal ions with a crown ether at interfacial circumstances. As a model system, the monolayer of octadecyloxymethyl-18-crown-6 (Fig.1) on aqueous salt solutions was used and the interaction of this membrane with various metal cations was investigated by surface potential measurement. Octadecyloxymethyl-18-crown-6 was prepared from octadecylglycidyl ether and pentaethylene glycol by the method as reported in the literatue.[7,8)] The product was purified by column chromatography on

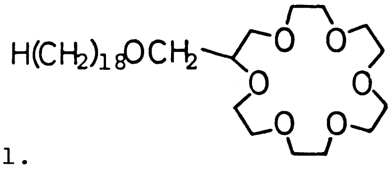

Fig. 1.

silica gel and recrystallized from methanol (mp 35-36 °C). The purity was confirmed by TLC, NMR, IR, and elemental analyses. The monolayer of this compound was spread from hexane solution on pure water, which was deionized (Barnstead NANO pure system) and doubly distilled. The monolayer used for measurement of surface potential had a packing density of ca. 1/100 (molecule/$Å^2$). This value is comparable to the density of this compound in close-packed state of two dimensional array. The change in surface potential ($\Delta\Delta V = \Delta V(\text{salt}) - \Delta V(\text{salt free})$) caused by the addition of metal cations to the subphase solution was measured by the vibrating electrode method.[9] $\Delta\Delta V$ can be caused by the binding of metal cations to crown ether membrane leaving counter ions (Cl^-) in the solution.

Figure 2a shows the surface potential change of monolayer ($\Delta\Delta V$) with an increasing concentration of KCl, CsCl, and NaCl, respectively in the subphase solution. As may be seen, the contribution of these alkali ions to $\Delta\Delta V$ is in the order of $K^+ > Cs^+ > Na^+$. This order is the same as that of the stability constant with 18-crown-6 in water. Figure 2b is the relation between $\Delta\Delta V$ and the concentration of some alkali-earth chloride, and reveals that the crown ether binds Ba^{2+} more strongly than Ca^{2+}. This feature is indeed identical with the results of stability constants obtained from the calorimetric titration. All these results indicate that the present method is useful to investigate the binding characteristics of metal ions with crown ether at the interface.

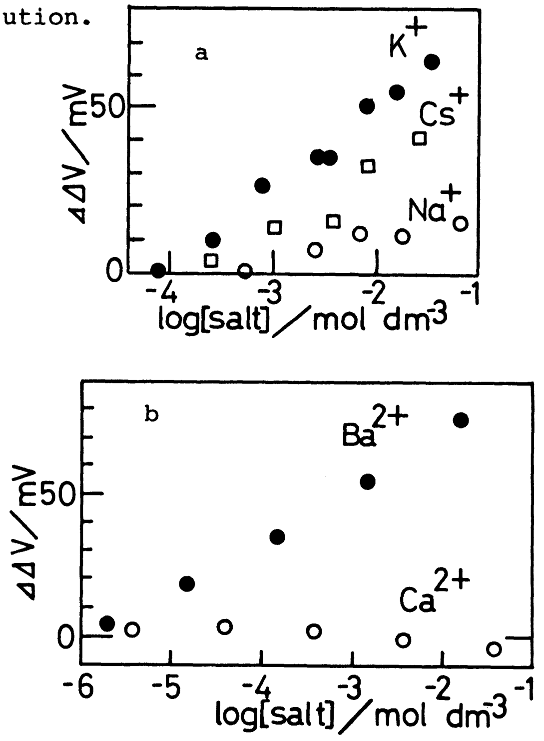

Fig. 2. Surface potential change.

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(Received December 12, 1985)