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Ion Sensitive Tin Oxide Electrodes Carrying Amphiphilic Crown Ether Langmuir-Blodgett Films

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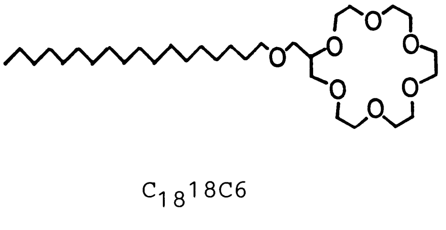
Langmuir-Blodgett films of octadecyloxymethyl-18-crown-6 or 6-[bis(tetradecyloxymethyl)methoxyethanoylamino]hexanoylaminomethyl-18-crown-6 were deposited onto an SnO_2 electrode to give depletion-mode field-effect semiconductor sensors based on the surface conductance change upon ionic incorporation.

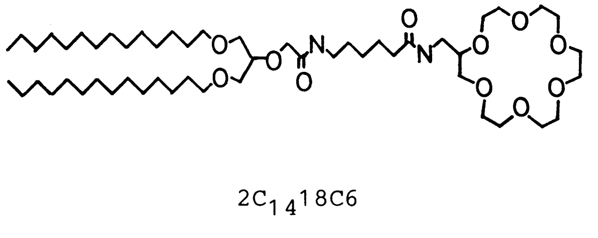
Crown ethers are capable of highly selective complexation with metal ions, particularly with alkali and alkaline-earth metal ions.1) Combination of this trait with the Langmuir-Blodgett (LB) technique, which yields a highly ordered assembly of amphiphilic molecules on a solid electrode, would be promising for fabrication of ion sensitive devices. However, except for a few works on an amphiphilic β-cyclodextrin2) and a mixture of crown ether and stearic acid,3) no attempt has been made to use LB films capable of host-guest complexation in sensor fabrication. In this letter we report the ion recognition by LB films of amphiphilic crown ethers.

Octadecyloxymethyl-18-crown-6 ($C_{18}18C6$) was prepared from octadecylglycidyl ether and pentaethylene glycol by a method reported in the literature.4) 6-[Bis(tetradecyloxymethyl)methoxyethanoylamino]hexanoylaminomethyl-18-crown-6 ($2C_{14}18C6$) was synthesized from aminomethyl-18-crown-6,5) 1,3-ditetradecyl-2-carboxymethylglycerylether,6) and 6-aminohexanoic acid. The purities of $C_{18}18C6$ and $2C_{14}18C6$ were evaluated to be 99.9% and 98%, respectively, by TLC, NMR, IR, and elemental analyses.

A benzene solution of these compounds was spread on water which had been purified with Milli Q-II (Millipore Ltd.). Surface pressure-area (F-A) isotherms were measured at a compression speed of 3.5×10^{-4} nm^2 $molecule^{-1}$ s^{-1} by the Wilhelmy method on a Kyowa Kaimenkagaku surface tensiometer Model AP-2. The monolayers were



$C_{18}18C6$



$2C_{14}18C6$

deposited onto SnO_2-coated glass plates (Stanley Electric Co., Ltd.) pretreated with a 10% toluene solution of octadecyltriethoxysilane for hydrophobication.

Ion sensing electrodes, or the depletion-mode field-effect semiconductor sensors, were constructed as described in a previous paper,7) in which two terminals were placed on the SnO_2 layer with indium ohmic contacts. The surface conductance (G_S) of the LB film-deposited SnO_2 electrode at controlled electrode potential (V_W) was determined from a small voltage (10-20 mV), V_D, applied between the two terminals and the current (I_D) flowing between the two terminals as follows: $G_S = \partial I_D/\partial V_D$. All measurements were carried out at room temperature and in a supporting electrolyte solution (0.1 M LiCl; 1 M = 1 mol dm^{-3}) flushed with nitrogen.

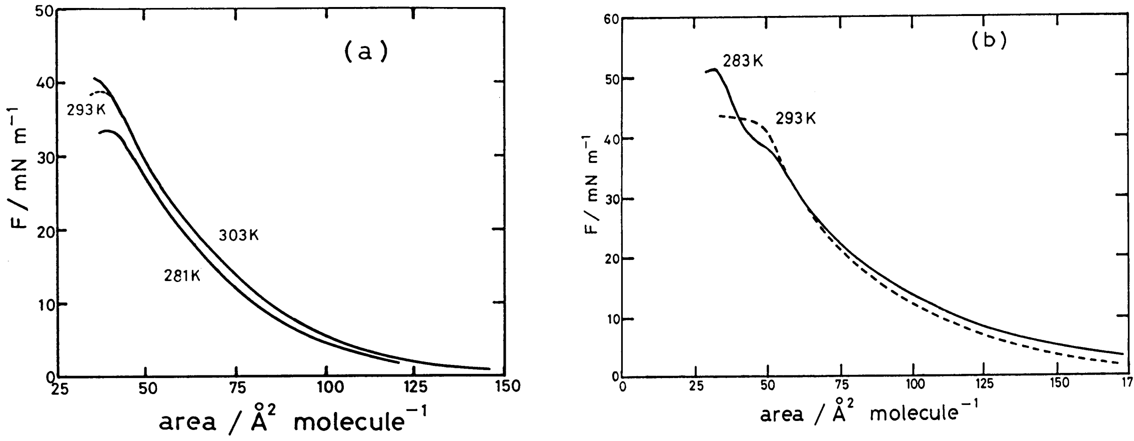


Fig. 1. Surface pressure-area isotherms for (a) C_{18}18C6 and (b) $2C_{14}$18C6.

Figure 1(a) shows the F-A isotherms for C_{18}18C6 at three temperatures. The monolayers are stable up to 34-40 mN m^{-1}. At 281 K the isotherm lies on a smaller area side and hence the packing density of the monolayer is slightly higher, than at 293 and 303 K. C_{18}18C6 was deposited onto a hydrophobic SnO_2 surface at 30 mN m^{-1} at 283 K up to 4 layers by a vertical dipping method. Figure 1(b) depicts the F-A isotherms for $2C_{14}$18C6. The compression curve obtained at 283 K shows inflection at 40 mN m^{-1} and the monolayers are stable up to 50 mN m^{-1}, while no inflection was observed on the compression curve obtained at 293 K. This inflection at low temperature is similar to the phase transition behavior which is usually observed for the monolayers of phospholipids having two fatty acid chains.8) Consequently, the first and second rises in the isotherm shown in Fig. 1(b) correspond to the liquid-expanded and liquid-condensed phases, respectively. The amphiphile $2C_{14}$18C6 has a hydrophobic aliphatic double-chain and contains an amino acid residue in the connecting portion between hydrophobic region and crown ring. The existence of the phase transition in the monolayer of $2C_{14}$18C6 could be explained through the action of Van der Waals forces between the methylene groups of the hydrocarbon chains of neighboring molecules. The intermolecular attraction due to hydrogen bonding of the amino acid residues is also anticipated to contribute to the formation of liquid-condensed film.9) The monolayer of $2C_{14}$18C6 in a liquid-condensed phase was transferred onto an SnO_2 surface at 42 mN m^{-1} at 283 K by a horizontal lifting method.

The formation of cation-crown ether complexes in the LB film on the SnO_2 surface has been examined by measuring the surface conductance change of SnO_2 electrode. When an anodic bias is applied to an n-type semiconductor in contact with an electrolyte solution, the conduction electrons are driven away from the surface region leading to the buildup of a depletion layer in the semiconductor. Under such conditions, when a cation adsorbs to the LB film in contact with the semiconductor surface, the depletion layer becomes thinner at a constant electrode potential and hence the surface conductance of the semiconductor increases.[7)]

Figure 2 depicts a typical dependence of the surface conductance (G_S) of the $2C_{14}18C6$ LB film-deposited SnO_2 electrodes on the electrode potential (V_W). The addition of potassium ion to the supporting electrolyte solution causes an increase in the surface conductance, indicating that the ion is indeed incorporated into the crown ring in the LB film.

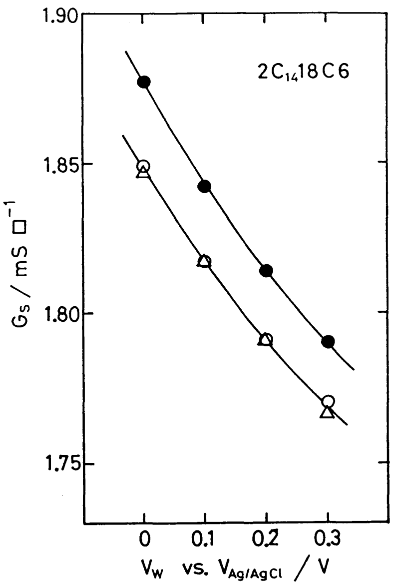


Fig. 2. Plot of G_s vs. V_w.
○: 0.1 M LiCl
●: 0.1 M LiCl + 10 mM KCl
△: 0.1 M LiCl + 10 mM NaCl

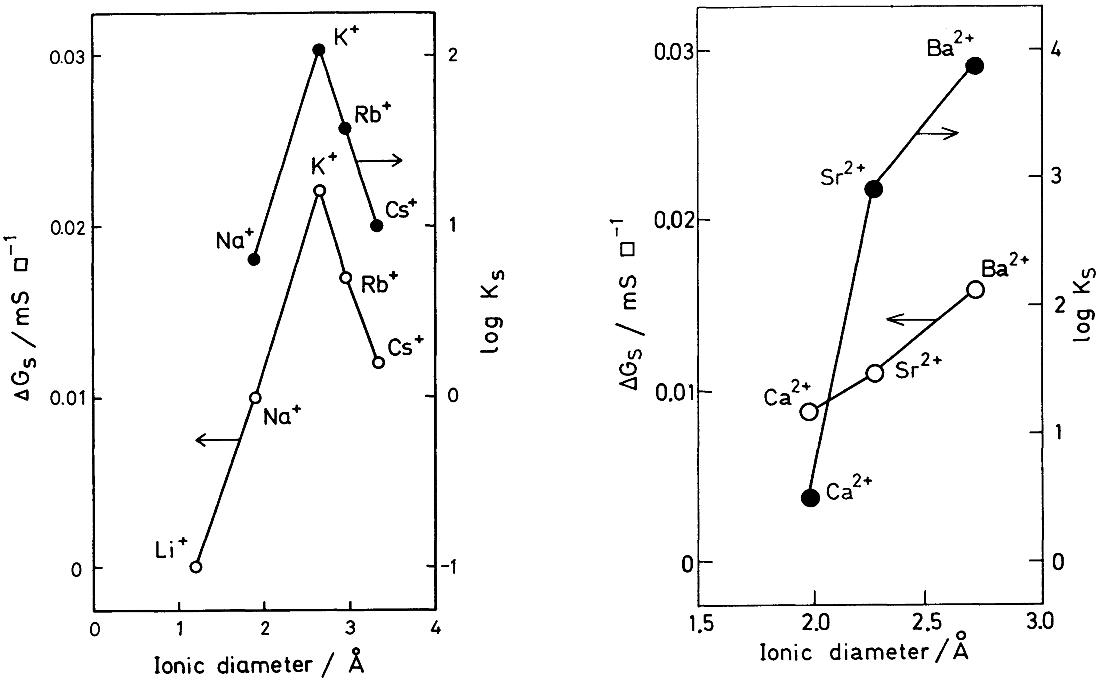


Fig. 3. Relationship between surface conductance change (ΔG_S) or stability constant of complex (K_S) and ionic diameter. Solution: 0.1 M LiCl + 10 mM alkali or alkaline-earth metal chloride. Electrode: $C_{18}18C6$ LB film-deposited SnO_2 electrode. V_W: 0.1 V vs. Ag/AgCl.

The surface conductance change upon ionic incorporation to the C_{18}18C6 LB film is compared in Fig. 3 with the stability constant of the 18-crown-6/metal ion complexes as a function of ionic diameter. The decreasing order of the surface conductance change is $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$ for alkali metal ions and $Ba^{2+} > Sr^{2+} > Ca^{2+}$ for alkaline-earth metal ions. As seen in Fig. 3, these orders are the same as those of the complexing stability constant of 18-crown-6 with these ions in water. In the case of $2C_{14}$18C6, the surface conductance is also increased by the addition of potassium ion, while by the addition of sodium ion it is little affected, as shown in Fig. 2. Thus, it is confirmed that the crown ether in the LB films recognizes a specific metal cation.

The ion selectivity of an amphiphilic crown ether monolayer spread at an air-water interface has been suggested through surface potential measurements by Matsumura et al.$^{10)}$ Our results demonstrate for the first time that ion sensitive solid electrodes can be fabricated by combining the ion-recognizing property of crown ethers and the LB technique applied to their amphiphilic derivatives.

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