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STUDIES ON FORMATION AND ION SELECTIVITY OF MESOMORPHIC CROWN ETHER-MODIFIED SOLID SUPPORTED BILAYER LIPID MEMBRANES

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ABSTRACT When metalic wire has heen cut in a organic phase saturated with cholesterol and crown ether compounds, and then put into a suitable aqueous phase, the orientable adsorption of the amphiphilic lipid molecules at the interfaces of metal/organic and organic/aqueous phases resulted in a formation of the solid supported bilayer lipid membranes (S-BLMs) modified with mesomorphic crown ethers. The membrane potentials show Nernst response to the concentration of metal cations M^+ in the aqueous solution at the concentration range of 10^{-4}-10^{-1} mol • dm^{-3}. The response to K^+ is more significant than that to Rb^+ and Na^+. The responses to Li^+, Cs^+ and Mg^{2+} have not been observed. Trace amounts of Fe^{2+} and Fe^{3+} interferes with the determination.

Key words: bilayer lipid membranes, mesomorphic crown ethers, ion complex selectivity, chemical sensor.

INTRODUCTION

Both the lipids and the crown ether compounds studied in this paper are amphiphilic which resulted in the formation of the self-assembled membranes at the interfaces of metal/organic and organic/aqueous phases[1-2]. Due to this thermodynamic character, crown ether-modified solid supported bilayer lipid membranes have been prepared at the surfaces of freshly cut wires. The S-BLMs modified with crown ether compounds, within which the crown ether rings could selectively form some complexes with metal cations M^+[3], show Nernst response to the concentration of M^+ present in aqueous solutions. This made it possible to differentiate different ions. In this paper, the influences of mesomorphic crown ethers used as modifiers on the stability and the Nernst response to different M^+ of S-BLMs are reported. A possible path to prepare new ion

sensors by self-assembly technology is put forward.

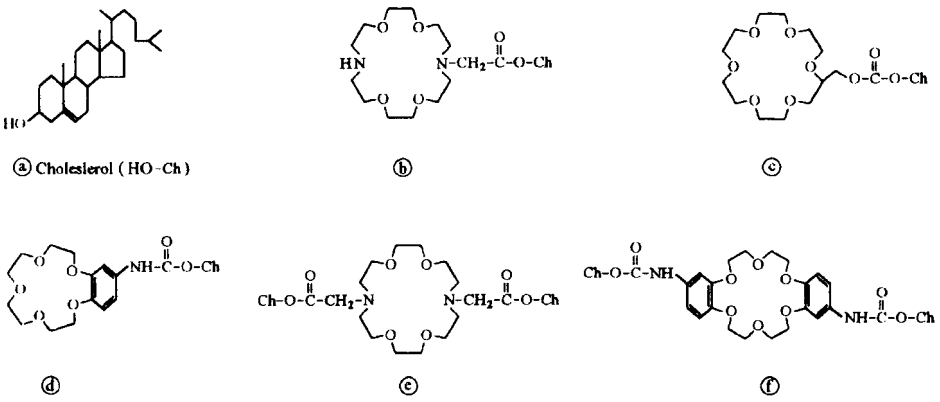
EXPERIMENT

Stainless steel wires, 0.2～0.5mm in diameter and covered with Teflon tubing, were used as solid supporter. They were supplied by H. T. Tien from Department of physiology, Michigan State University, USA.

Lipids and crown ethers were used as shown in Figure 1 ⓐ～ⓕ. The mixed solution of squalane or squalene saturated with cholesterol and crown ether compound in chloroform (V : V=2 : 1) was used as the organic phase.

Solution of MCl with concentration in the range of 10^{-4}-10^{-1} mol • dm^{-3} was used as the aqueous phase.

S-BLMs were prepared and the membrane potentials were measured following the procedure previously described by ref. [4], at 22-25℃.



ⓐ Cholesterol (HO-Ch) ⓑ ⓒ ⓓ ⓔ ⓕ

FIGURE 1 Structures of lipids ⓐ and modifiers ⓑ～ⓕ used in S-BLMs experiments.

RESULTS AND DISCUSSION

Formation of S-BLMs

Cholesterol ⓐ, with hydrophilic hydroxy and hydrophobic hydrocarbon groups, and modifying crown ethers ⓑ～ⓕ, with hydrophilic crown ether rings and hydrophobic hydrocarbon groups, are all amphiphilic lipid molecules which are able to self-assemble

at the interfaces of metal/organic and organic/aqueous phases in a strictly oriented fashion. The crown ether compounds, having a hydrophobic stucture similar to that of cholesterol molecules, could be "drawn" into the S-BLMs by intermolecular forces.

Stability of S-BLMs

The compounds ⓑ~ⓕrepresent the mesomorphic derivatives of 15-crown-5 and 18-crown-6. All the S-BLMs modified with ⓑ~ⓔhave proven stable and ⓑ, ⓔshown good reproducibility of membrane potentials in repeated experiments. The compounds ⓑ, ⓒand ⓓare monosubstituted, that mean they are more similar to cholesterol in structure and easier to parallely arrange in the membranes.

The compound ⓑhas a naked secondary N atom, that increased the hydrophilicity of one end of the molecule and makes it a good modifying crown ether.

The compound ⓔis a disubstitued diaza-18-crown-6 at N atoms. When the membrane has been formed, the two substitute arms must stretch to the same side and crown ether ring was naked. The compound ⓕis trans-disubstituted DB-18-C-6. Because of the existance of phenyl, it was difficult for the two substitute arms stretch to the same side. Instead of phenyl in ⓕ, the $-CH_2-$ group in compound ⓔmade the substitute arms more flexible and improved the orientation effect of the crown ether molecules on the membrane. The interaction between cholesteryl groups in ⓔand cholesterol made the ⓔmolecules easier to insert into the membrane and form stable S-BLMs.

According to LB experiments and the results calculated by CPK atom model[5-6], the monomolecular areas of compounds ⓑ(0.8nm^2) and ⓔ(0.9nm^2) are similar. This means the crown ether compounds orient at the interfaces in such a way that the hydrophilic crown ether rings lied anchored into the polar metal and aqueous phases and the hydrophobic groups were stretched far away into the organic solution. This scheme is shown in Figure 2.

Because preparation and purification of disubstituted crown ethers are simplier than that of monosubstitute ones, the formers are more practicable.

Selectivity of S-BLMs forming complexes with M^+ ions

Exeperimental results have shown that all the S-BLMs modified with crown ether ⓑ~ⓔhave Nernst response to the concentration of M^+ present in the aqueous phase. S-BLMs modified by ⓑand ⓔhave provided the fastest response to K^+, a good linear relationship between membrane potential and $\log[M^+]$, good stability and good repro-

ducibility of membrane potentials in repeated experiments. Next to the fastest response to K^+ have been Rb^+ and Na^+. The response to Li^+, Cs^+ and Mg^{2+} have not been observed. The S-BLMs modified by ⓒ, ⓓ have shown no difference of response to K^+, Rb^+ and Na^+ but the results were not ideal. The existance of trace amounts of Fe^{2+} and Fe^{3+} has a disturbance on the tests. Figure 3 shows the Nernst response curves of S-BLMs modified by ⓑ and ⓔ.

The ring size of Diaza-18-crown-6 rings in ⓑ, ⓔ fit well with K^+ ions. Furthermore, the strong ability of atom N to form a complex with M^+ makes the complexes more stable. Diaza crown ethers could complex with Rb^+ ions due to the similar diameters of ions to that of crown ether rings.

Because crown ethers could not build complexes with Li^+ and Mg^{2+} ions, that have smaller diameters, high charge density, high hydration energy, easy to form hydrated ions and difficult to dehydrate, and Cs^+, that have bigger diameters[7], the S-BLMs have provided no response to these ions.

The compound ⓓ could not form complexes with M^+ effectively. The reason is that the diameters of crown ether rings are smaller in addition to the fact that aryl and amide moieties in the molecule reduce the charge density of the crown ether rings.

Squalane and squalene not only increased the solubility of lipids but also improved the stability of the S-BLMs formed due to the higher boiling point to reduce the evaporation of the solvents in the self-assemble process.

This paper suggests further studies and applications of S-BLMs in the field of membrane biophysics and electrochemistry.

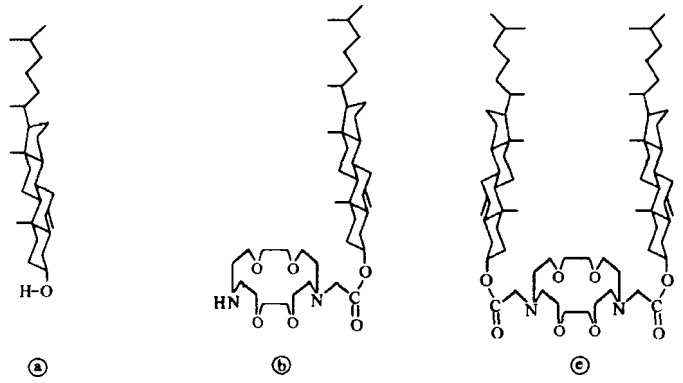


FIGURE 2 Schematic drawing of amphiphilic molecular orientation in S-BLM.

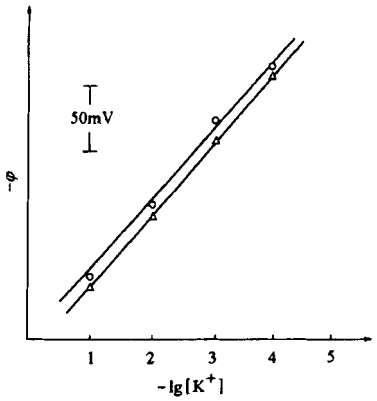


FIGURE 3 Nernst response curves of S-BLMs modified by crown ether ⓑ and ⓒ.

△: 0.5% Cholesterol in squalane + ⓑ in $CHCl_3$

○: 0.5% Cholesterol in squalene + ⓒ in $CHCl_3$

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