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Bilayer lipid membranes formed from thermotropic liquid crystals

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This paper reports a new type of bilayer lipid membrane (BLM) with aqueous interfaces which are formed from thermotropic liquid crystals (nematic–6CB, smectic–8CB, and cholesteric–cholesteryl palmitate, ChP). The electrical properties of these unmodified membranes have been investigated. We suggest that BLMs of this type in their 'black' states consist of two molecular layers with a smectic-like structure.

1. Introduction

As a result of the search for a more realistic model of biological membranes, the discovery of a method for forming black or bilayer lipid membranes of planar configuration in aqueous media, commonly referred to as BLM, has been made. During the past two decades bilayer lipid membranes of less than 100 Å thick, formed from a variety of compounds (including totally synthetic materials) have been extensively investigated, mainly from the viewpoint of membrane reconstitution [1, 2].

The research in membranes has two main objectives. The first is to obtain a better and more detailed understanding of biological membranes. The availability of artificially constituted bilayer lipid membranes of planar configuration (BLM) as models of biomembranes, has played an important role in providing insights into molecular processes which take place in natural membranes [3, 4]. The second objective of BLM studies has been to develop a novel photophysical chemistry based on membrane-mediated processes and its utilization for practical purposes. These studies are being undertaken primarily to mimic natural systems for possible uses of solar energy and membrane-based devices [5, 6]. The rational use of membrane mimetic systems however, requires a sufficient understanding of their physical and chemical properties [7–9]. Recently, all kinds of photophysicochemical investigations of such systems have been carried out [10, 11]. This line of investigation opens up yet a new field in which BLMs may be used. These new systems offer a potentially powerful experimental tool for the study of the physics of two-dimensional structures [12].

We have employed a simple approach to form the BLMs using thermotropic liquid crystals. It is thought that application of material with mesomorphic properties to BLM separating two aqueous phases will further enhance both research and utilization possibilities. In this paper we report that liquid crystal black lipid membranes (LC-BLM) can be formed. The basic electrical properties of membranes formed from three main types of thermotropic liquid crystals (nematic, smectic and cholesteric liquid crystals) are described.

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2. Materials and methods

In general, the liquid crystal BLMs should possess the following basic properties: they should be chemically stable, optically transparent and mechanically long-lasting. In order to obtain these properties cyanobiphenyl liquid crystals were chosen as a proper nematic (4′-hexyl-4-cyanobiphenyl-6CB) and smectic (4′-octyl-4-cyanobiphenyl-8CB) material. Cholesteryl palmitate (ChP) was used as a cholesteric liquid crystal. All of the liquid crystals were dissolved in decane with butanol (1 : 1 v/v) before the membrane formation in the following concentrations: 6CB–solvent (1 : 2 v/v), 8CB–solvent (1 : 3 v/v) and the solution of ChP was saturated with the liquid crystal. As a bathing solution, we used 0.1 M KCl saturated with appropriate liquid crystal materials.

BLMs were formed using a Hamilton microsyringe to eject a small amount of membrane forming solution over the 1·5 mm orifice in the wall of a Teflon cup separating two aqueous (bathing) solutions in a plexiglass chamber. Calomel electrodes with salt bridges were used in the usual manner for electrical contact [1]. A binocular microscope was used to observe the thinning of the membranes to the black state.

To keep the membrane for a longer period of time the liquid crystal molecules have to be strongly anchored (with a proper surface orientation) to the solid holder. Because in our case a homeotropic alignment at the surface is expected, the walls of the membrane holder were wetted prior to membrane formation with lecithin.

The electrical parameters; potential (E_m), current across the membrane (I_m) and capacitance (C_m) of BLMs have been measured as described previously [1] with a 610 Keithley electrometer, 417 Keithley picoammeter and low level ICE Electronics capacitance meter. The resistance of BLMs (R_m) was calculated from the experimentally determined values of I_m as a function of E_m. 6CB and 8CB (BDH Chemicals) and ChP (Eastman Organic Chemicals) were used without further purification.

3. Results and discussion

Different stages of the liquid crystal BLM formation have been observed both visually (using binocular microscope) and by measuring the electrical parameters (capacitance, and resistance). Typical changes of both parameters during the thinning process are shown in figures 1 and 2. From those curves it can be seen that capacitance of black membrane is quite stable whereas resistance is slightly but systematically dropping. The rate of drop depends on the material used. This process of R_m decreasing is always faster for the nematic liquid crystal (6CB) in comparison with smectic material (figure 2). The difference between absolute values of R_m for nematic and smectic liquid crystals at the black membrane stage (figure 2) is small and would fall well within the error bars of the experiment. But the difference in capacitance (figure 1) seems to be significant. All measured parameters are shown for comparison in the table. As can be seen from the table the capacitance of liquid crystal BLMs is much higher than unmodified lecithin BLM. Likewise, the resistance of cyanobiphenyl BLMs is several orders of magnitude smaller than that of lecithin BLM. Such large differences between those two types of membranes in both parameters (C_m and R_m) were expected on the basis of known properties of pure hydrocarbons (dielectric constant = 2·3 and R = 10^{15}–10^{19} ohm cm) in comparison to pure cyanobiphenyls (dielectric constant depends strongly on macroscopic orientation of molecules and in the most common cases $\varepsilon_{\parallel}$ = 14 [13], and R = 10^{10} ohm cm). The data shown in the table are within the experimental errors independent of the amount of liquid crystal

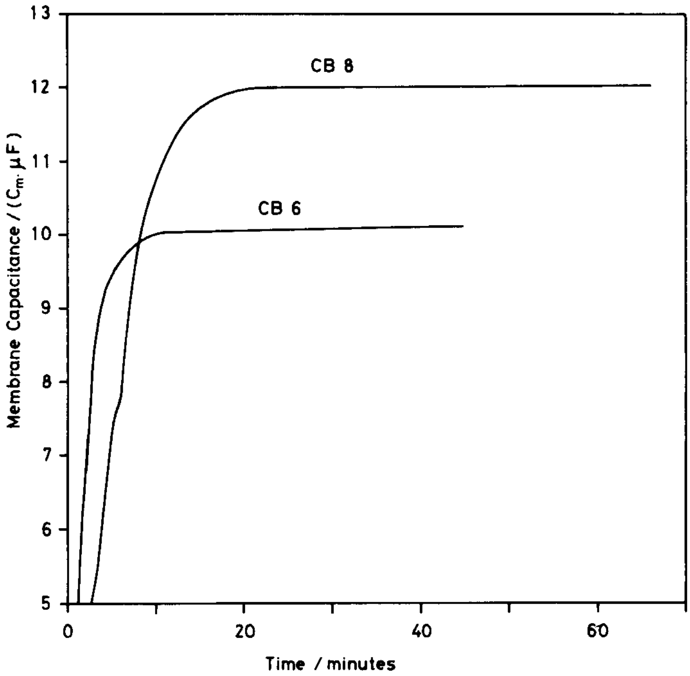

Figure 1. Time course of the capacitance changes during the thinning process of liquid crystal membranes.

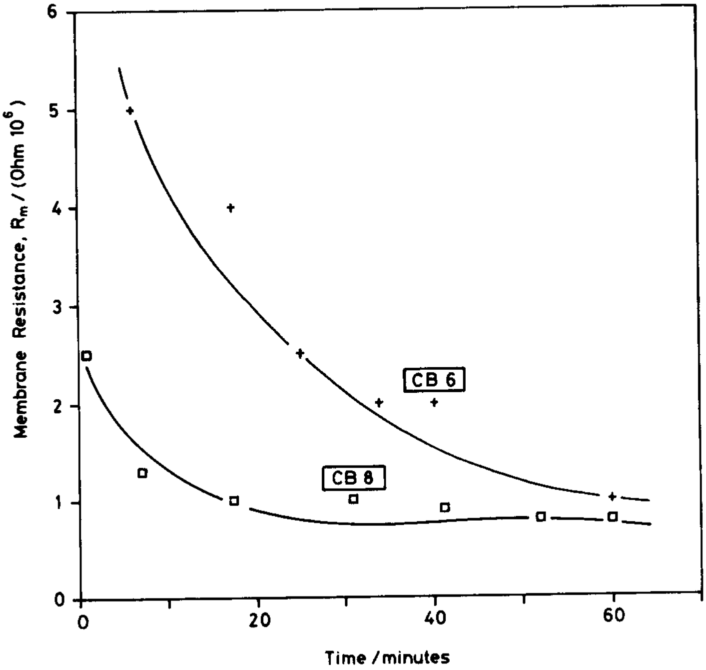

Figure 2. Plot of the time course of resistance changes during the liquid crystal membrane thinning process.

Electrical properties of liquid crystal bilayer lipid membranes.

Sample	R_m ohm cm^2	C_m μF/cm^2	Breakdown voltage/mV	Lifetime/ min
6CB	10^4	0·80	80–120	30–60
8CB	10^4	1·0	90–120	40–80
ChP	10^8–10^9	0·70	150	
BLM† (lecithin)	10^7–10^9	0·35	200	

† From [1].

material ejected into the hole for membrane formation. This observation indicates that the final stage of liquid crystal membranes (black state) is independent of amount of material used, suggesting that this stage always has the same structure.

It is well known that molecules with a polar head and a hydrophobic tail are commonly used for the bimolecular (bilayer) formation in the aqueous solution. This process of lipid bilayer-like structure formation involves essentially the creation of two coexisting hydrophilic (water)/hydrophobic (organic solutions) interfaces, or biface. This spontaneous orientation of amphipathic molecules at the interface leads to a reduction of interfacial free energy, and is of fundamental importance in the formation of membranes composed from two separate monolayers [1]. The thickness (or bilayer spacing) of such kinds of membranes is usually larger than two lengths of the membrane formed molecules. This model of bilayer is essentially different in comparison to the usual bilayer models proposed for a smectic A phase [14]. The molecules in a smectic layer should pack so that on average the 'polar part' comprised of the benzene rings and cyano-groups are in lateral proximity to each other and the non-polar chains are in the same configuration with other aliphatic chains comprising the next-nearest neighbours laterally [14]. In such case the bilayer spacing is equal to cyano-aromatic head length plus two lengths of aliphatic chain [14]. For the molecules of 8CB the measured bilayer spacing is 32 Å as reported by Davidov *et al.* [15] which is of the order of $1\frac{1}{2}$ times the molecular length and agrees very well with the bilayer model proposed by Cladis *et al.* [14].

On the basis of Kunitake's observations that many different synthetic amphiles can produce the lipid-like bilayers in aqueous solutions [16], it is very reasonable to assume that black state in our case means the bilayer lipid membrane. If we present the phenyl rings of cyanobiphenyl molecules as a rectangle the structure of the liquid crystal bilayer can be visualized as shown in figure 3. Such a model is supported by the results with freely suspended liquid crystal films which are formed from one or more molecular layers [18] and above all by the recent results reported by Shen *et al.* [19]. They have shown that 8CB molecules spread uniformly as a monolayer on water. The molecules tend to have their CN group in water and the hydrophobic hydrocarbon tail up in air. Such a behaviour is characteristic for molecules with strong amphiphilic properties.

For the integrity of the liquid crystal BLM structue it seems to be essential that the molecular order of liquid crystal at the edges where it is terminated (in the BLM it is called the Plateau Gibbs border) have strong anchoring forces [2].

Taking into consideration the picture of liquid crystal BLM (figure 3) one can view the data (figures 1, 2 and the table) as follows: (i) either from the standpoint of $\varepsilon_{\parallel}$ being the same in both macroscopically ordered liquid crystal films [13] and our

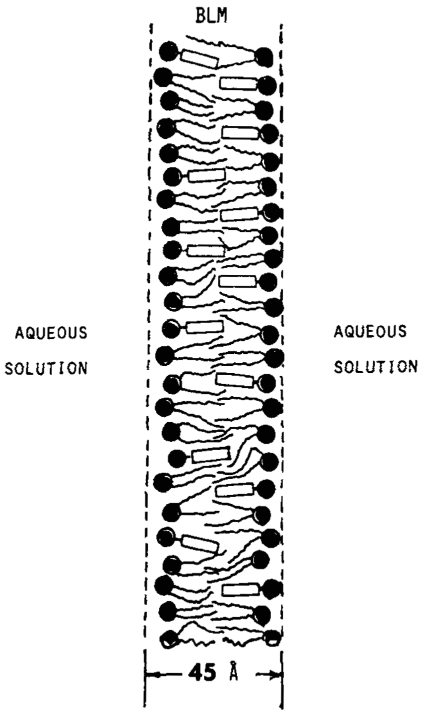

Figure 3. Schematic model of the molecular alignment of liquid crystal bilayer with aqueous interfaces (modified and adapted from [17]).

membranes which allows us to estimate a thickness of the black liquid crystal membrane, or (ii) from the assumed value of BLM thickness which allows us to estimate the average value of $\varepsilon_{||}$. In our experimental conditions it is a rather great possibility that $\varepsilon_{||}$ is decreased (in comparison to liquid crystal films) by some amount of solvent and lecithin molecules which might be present in the BLM. Therefore we try to estimate $\varepsilon_{||}$ on the basis of the assumed value of BLM thickness.

The sample pictured in figure 3 constitutes a parallel plate capacitor with area A and thickness t_m with a homeotropic alignment of 8CB molecules. The capacitance is

$$C_m = \varepsilon_{||}\varepsilon_0 A/t_m, \tag{1}$$

where ε_0 is the vacuum dielectric constant. Using the above equation we have evaluated the $\varepsilon_{||}$ value for the 8CB bilayer by comparison with the experimental values of membrane capacitance obtained for the pure lecithin and the liquid crystal BLM. To calculate this we have assumed the values of $\varepsilon_{||}$ and t_m for pure lecithin to be 2·3 and 50 Å respectively [1]. Taking $t_m \geqq 45$ Å [14] for 8CB bilayer (t_m = two lengths of liquid crystal molecule), we get $\varepsilon_{||} = 5{\cdot}5$.

The estimated value of $\varepsilon_{||}$ is consistently smaller than its corresponding value obtained for the macroscopically oriented liquid crystal films [13]. The difference might be partly due to real physical effects such as a slightly decreased $\varepsilon_{||}$ value by solvent and lecithin molecules of which can be present in a small amount inside the membrane. It can also be due to an uncertain value of layer spacing. In our experimental situation the layer spacing may be changed both by the aqueous environment near the surfaces and also by the presence of solvent within the membrane.

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