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Synthetic chiral chromophoric bilayer membranes as chemical transducers: effect of alcohols on enhanced circular dichroism

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A bilayer-forming synthetic lipid containing a chiral centre and a chromophoric group was investigated as a spectroscopic transducer, based on its enhanced circular dichroism (CD). The CD intensity of chiral bilayers was reduced with addition of alcohol. For ten additives tested, a linear correlation was observed between the CD spectral response to the alcohols and their partition coefficient (log *P*) in octanol/water system. By use of an immobilization technique, the bilayer film was obtained on a quartz plate, and a possible application as a solid-phase assay of methanol was demonstrated.

1. Introduction

Bilayer formation has been observed for a number of synthetic amphiphiles. These synthetic bilayers possess physicochemical properties fundamentally similar to those of natural lipid membranes [1]. Thus they are of interest in the construction of molecular transduction devices to mimic biological membranes [2–7].

Some synthetic double-chain amphiphiles containing a chiral centre and a chromophoric group show marked enhancement of circular dichroism (CD) in aqueous bilayer dispersion [8, 9]. The CD intensity reduces when the ordered configuration of the chromophores in chiral bilayers is disturbed by phase transition (Fig. 1). This phenomenon should offer a possible application of these bilayers as a spectroscopic transducer for a variety of chemicals which interact with the oriented bilayer assemblies and change their organized structure.

In the present study, the effect of alcohols on the CD intensity of $2C_{12}GluphC_4N^+$ bilayer was studied. The immobilization of aqueous bilayer assemblies is possible using some recently developed techniques [10–12]. By taking advantage of the formation of a polyion complex [12] of $2C_{12}GluphC_4N^+$ with poly(styrenesulphonate) anion, a water-insoluble, chiral bilayer film was fabricated on a quartz plate, and a possible application for a solid-phase assay of methanol was investigated.

2. Experimental procedure

A bilayer-forming amphiphile, $2C_{12}GluphC_4N^+$ and its polyion complex, $2C_{12}GluphC_4N^+PSS^-$ were synthesized according to the literature [8, 12].

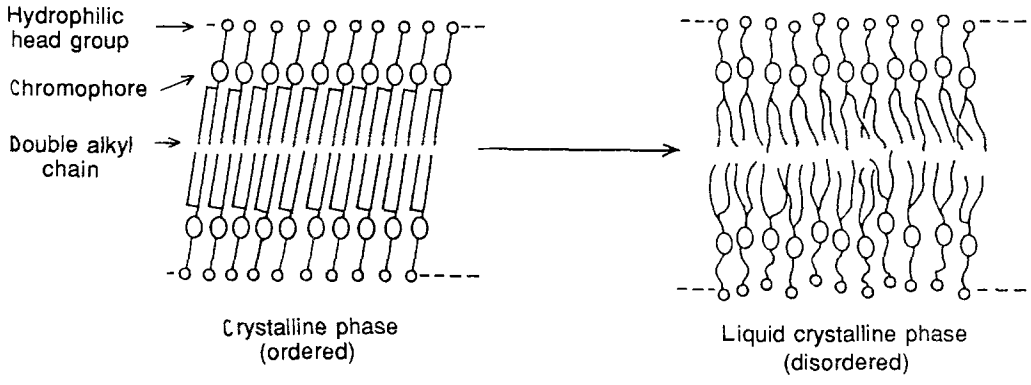

Figure 1 Schematic illustration of bilayer phase transition.

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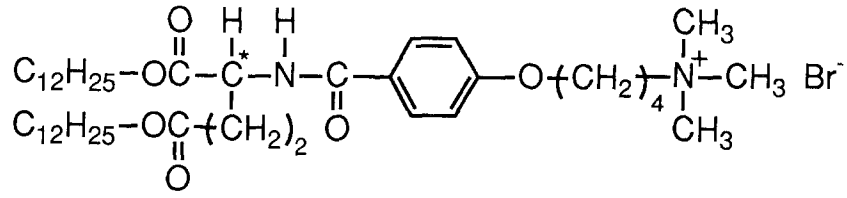
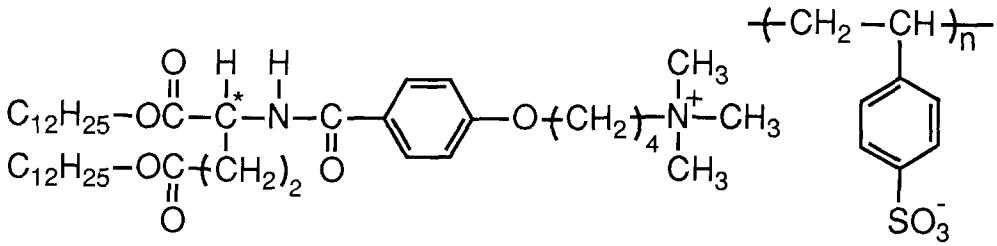


$2C_{12}GluphC_4N^+$ (L)



$2C_{12}GluphC_4N^+$ PSS^-

Methanol and ethanol were used as spectroscopic grade and other solvents were used as extra-pure grade. CD spectra and absorption spectra of the chiral bilayer membranes were measured with a JASCO J-40AS spectropolarimeter and a Hitachi 556 spectrophotometer, respectively. The temperature was controlled with a Haake F-3 constant-temperature bath.

For CD measurements of aqueous bilayers, a weighed amount of $2C_{12}GluphC_4N^+$ was taken in a flask and dissolved in a small portion of chloroform. After evaporation of the solvent, the lipid was dispersed in 0.1 M aqueous tetramethylammonium chloride (TMACl) solution by warming and gently shaking. The resulting transparent solution of $2C_{12}GluphC_4N^+$ (10^{-4} M) was stored at 5 °C for 1 h, then 3 cm^3 portions of the solution was taken to a quartz cuvette (optical path length, 10 mm) and alcohol addition experiments were conducted. Added alcohol concentration was calculated by density data [13] of aqueous organic solution.

A 50-μl portion of chloroform solution of $2C_{12}GluphC_4N^+PSS^-$ (0.1 M) was dropped onto a quartz plate and the solvent evaporated under constant temperature (20 °C) and constant relative humidity (40%). The obtained membrane-immobilized plate was then immersed in water (5 °C) for 1 h. Absorption spectra were measured for several spots of the resulting film and the uniformity was checked. The lipid films which showed less than 10% of deviation in absorbance at 254 nm were used for the following study. The plate was immersed in a quartz cuvette filled with aqueous alcohol solutions containing 0.1 M aqueous TMACl, and CD spectra were measured.

3. Results and discussion

3.1. Effect of alcohol concentration in aqueous system

As reported before, the bilayer assembly of $2C_{12}GluphC_4N^+$ formed in aqueous solution shows

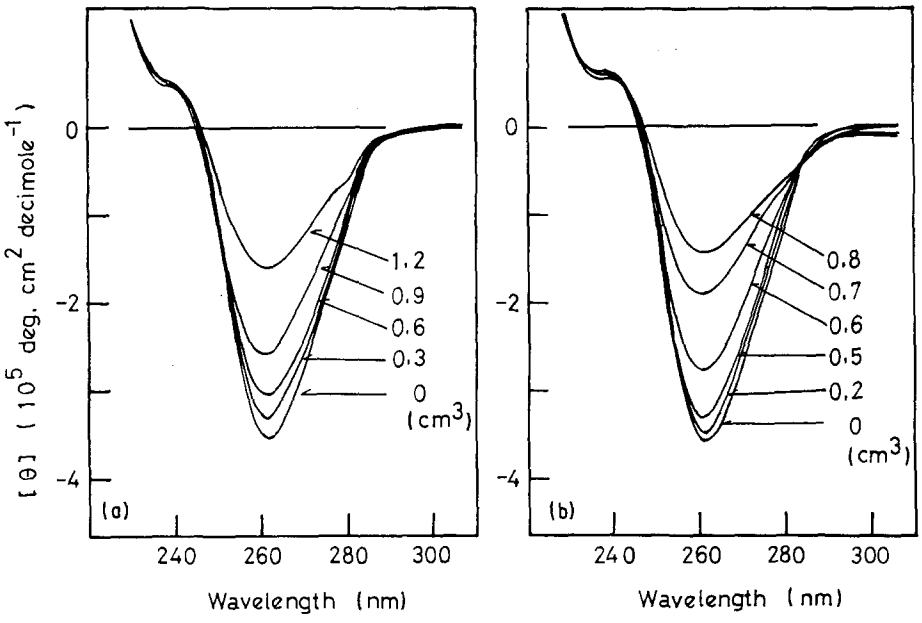


Figure 2 CD spectra of the $2C_{12}GluphC_4N^+$ bilayer in the presence of (a) methanol and (b) ethanol. Numerical values: added volume of alcohol. Experimental conditions: $[2C_{12}GluphC_4N^+] = 10^{-4}$ M; temperature, 15 °C; ionic strength, 0.1 (TMACl).

marked enhancement of CD at temperatures below phase transition (maximum at 260 nm: $[\theta] = -400\,000$) [9]. This is induced by a strong exciton coupling between the adjacent chromophores which align in a highly ordered configuration in the chiral bilayers. The enhancement disappears according to the phase transition (T_c, 31 °C) of the organizates (maximum at 245 nm: $[\theta] = 6000$) [9].

CD spectra of water-dispersed $2C_{12}GluphC_4N^+$ in the presence of methanol and ethanol at 15 °C are shown in Fig. 2. The CD intensity decreased with addition of alcohol and became constant after a few minutes. Fig. 3 demonstrates suppression of CD intensity at 260 nm against alcohol concentration. A slight deviation in the initial $[\theta]_{260}$ value (less than ±5%) was observed depending on the preparation of bilayers. Thus the initial $[\theta]_{260}$ value was chosen as a standard, and the relative molar ellipticities at added alcohol concentration were plotted.

As can be seen in Fig. 3, the degree of CD suppression increased with the increase of each added alcohol. In the present study, alcohol concentrations at the relative molar ellipticity of 0.5, $C_{0.5}$, were used as a measure of the degree of CD suppression and were plotted against their partition coefficient, P, in an octanol/water system [14] (Fig. 4). Although the plots are relatively scattered, they are correlated by a straight line with a slope of 1. Thus the two-phase partition phenomena between the aqueous and bilayer phases seems to be the cause of CD suppression. Added alcohols are extracted to the bilayer phase, and this leads to disintegration of the ordered configuration of chromophores. The decrease in dielectric constant of the bulk medium accompanied by alcohol addition is also expected to suppress the CD intensity. However, the plot with dielectric data [15] of water/alcohol mixed solvent systems instead of with log P does not give such major dependence of the CD response.

3.2. Application as solid-phase assay

Fig. 5a shows CD spectra of $2C_{12}GluphC_4N^+PSS^-$ films on a quartz plate at various temperatures. The molar absorption coefficient of $2C_{12}GluphC_4N^+$ in

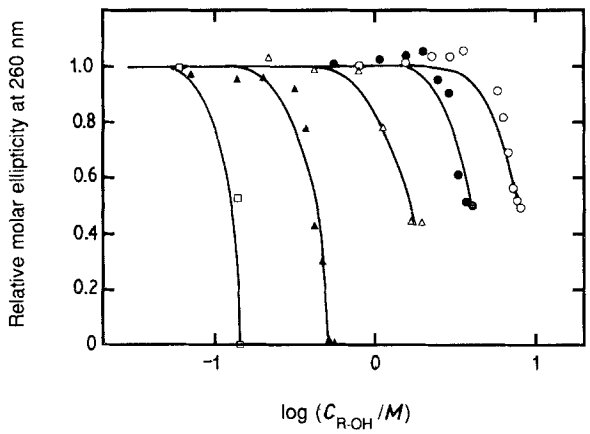


Figure 3 CD spectral response of $2C_{12}GluphC_4N^+$ bilayer to various alcohol. ○, Methanol; ●, ethanol; △, propanol; ▲, butanol; □, pentanol. Experimental conditions as in Fig. 2.

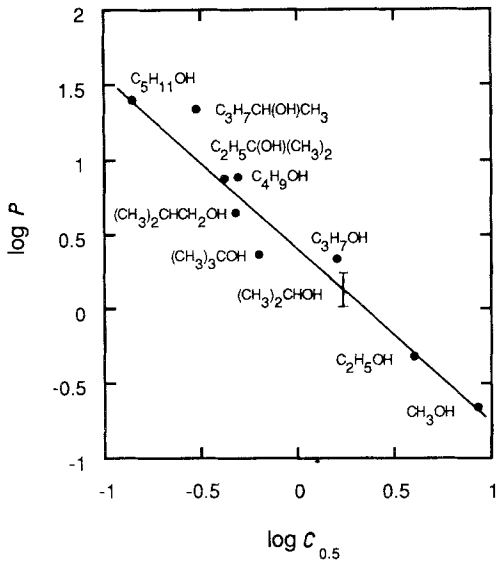
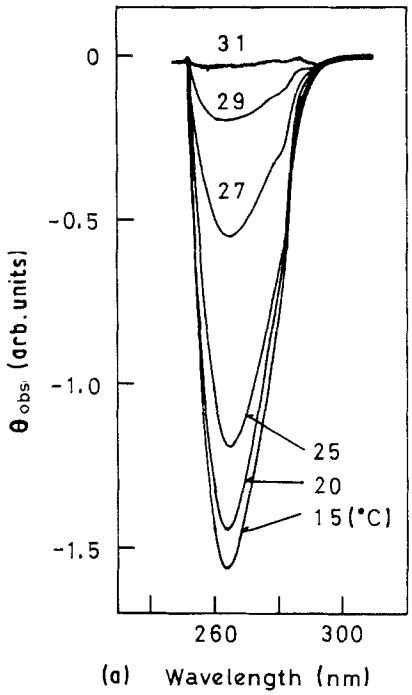


Figure 4 Log P against log $C_{0.5}$. Bar, expected value of P in [10]. Experimental conditions as in Fig. 2.



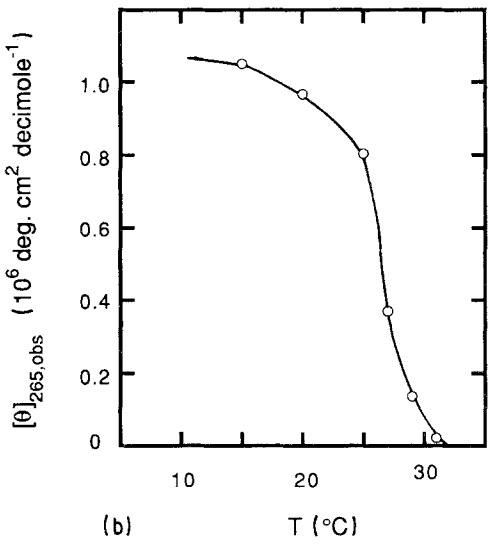


Figure 5 (a) Temperature dependence of CD spectra of $2C_{12}GluphC_4N^+PSS^-$ bilayer film on a quartz plate. Ionic strength, 0.1 (TMACl). (b) Plots of $[\theta]_{265,obs}$ against temperature.

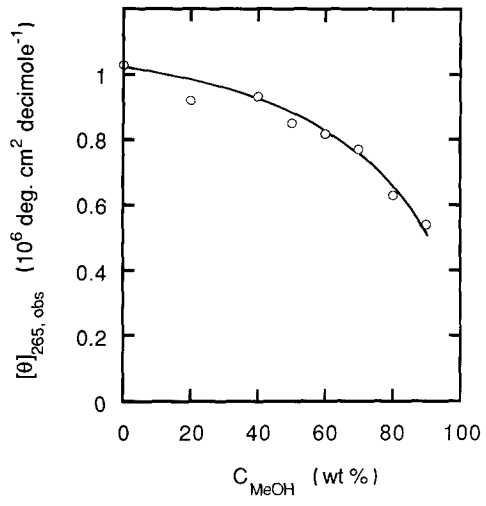


Figure 6 CD spectral response of $2C_{12}GluphC_4N^+PSS^-$ bilayer film to methanol. 15 °C; ionic strength, 0.1 (TMACl).

aqueous solution at 254 nm (1.26×10^4 mol^{-1} dm^3) was used for the sake of convenience in calculating the apparent molar ellipticity of the film at 265 nm, $[\theta]_{265,obs}$. Fig. 5b shows its temperature dependence. The immobilized film also shows a drastic temperature dependence of CD spectra due to phase transition. The CD intensity of the film was twice that of the aqueous dispersion. This is probably due to the contribution of linear dichroism which appears sensitively in oriented solid crystal [16], but we do not discuss this topic in detail here. The CD spectral response of the bilayer film to methanol is shown in Fig. 6. The gradual decrease of $[\theta]_{265,obs}$ was observed according to the increase in methanol concentration. The response time was several minutes after immersion into the sample solution.

4. Conclusion

A potential use of synthetic chiral bilayer membrane as a spectroscopic transducer has been demonstrated in both aqueous and solid-phase systems. The present technique is applicable to a wide variety of chemicals which interact with the organizates and change their ordered structures. The basic idea described here is important to analytical aspects of utilizing organized bilayer assemblies.

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