CHEMISTRY LETTERS, pp. 1577-1580, 1983.

CASTING OF SYNTHETIC BILAYER MEMBRANES ON GLASS AND SPECTRAL VARIATION OF MEMBRANE-BOUND CYANINE AND MEROCYANINE DYES[1)]

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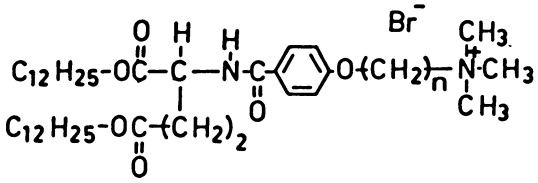
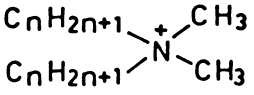
Cast films were prepared on glass from aqueous dispersions of double-chain ammonium amphiphiles. The bilayer characteristics were preserved and specific spectral variations were observed for film-bound cyanine and merocyanine dyes.

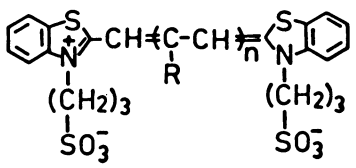
The synthetic bilayer membrane possesses unique characteristics common to those of the biomembrane,[2-4)] and is considered promising as novel functional materials. Immobilization is a necessary process for this purpose, since the bilayer membrane is usually obtained as aqueous dispersions. Although polymer blends[5,6)] and microcapsules[7,8)] that contain dialkylammonium salts have been shown to retain the bilayer characteristics, more general ways to immobilize the bilayer is desired. The spectral property of cyanine(3) and merocyanine(4) dyes bound to aqueous bilayers of double-chain ammonium salts(1 and 2) are highly sensitive to the chemical structure and physical state of the bilayers.[9)] Therefore, these dyes are used as probes suitable for examination of bilayer characteristics, apart from the interest in the dye-bilayer complex as a photoelectric material. In the present study, we describe that cast films are readily formed on glass plates from synthetic bilayer membranes and that film-bound dyes show spectral properties which indicate retention of the bilayer characteristics.



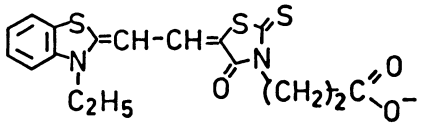
1 (n= 2, 3, 4, 5, 6, and 10)



2 (n=14, 16)



3a (R=CH_3, n=1)
3b (R=H, n=2)



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Aqueous dispersions(5×10^{-3} mol dm^{-3}) of the bilayer aggregate of double-chain salts 1(n = 2,3,4,5,6, and 10) and 2 were prepared by sonication, as described previously.[2,3] A few drops of the clear dispersion were spread on glass or quartz plates, and water was removed by one of the three methods: 1, keeping the plate in vacuo(ca. 20 mmHg) at room temperature ; 2, heating at 50 - 60°C ; 3, allowing to stand at room temperature(ca. 30°C). Transparent films were obtainable from 1 by either of these methods, but only method 2 was effective for 2(n = 14,16). These films were aged in a refrigerator for several hours. Maintenance of the bilayer characteristics is confirmed by the presence of the crystal-to-liquid crystal phase transition.[10] For example, cast film obtained from 1(n = 4) was peeled off, cut into pieces and placed directly in a sample pan of differential scanning calorimetry(DSC): instrument, Daini-Seikosha SSC-560. A sharp endothermic peak was observed at 38°C(peak top) in the heating scan. Although this is 7°C higher than the phase transition temperature(T_c) observed for the corresponding aqueous dispersion,[3] the differance may be explained by the decrease in free water.[5] Transparent films were similarly obtainable from mixtures of 1 and the dyes up to the 1 : 1 mole ratio by methods 2 or 3. Cast films were not transparent enough for the combinations of the dyes and membrane 2. On the other hand, crystallization prevented formation of a transparent film when dyes are used without the membrane.

Figure 1A shows the spectral change with temperature of the cast film of a 3b/1(n = 4) mixture. The film was cast in this case on one surface of a uv cell, and the maintenance of a given temperature was confirmed by measuring the temperature of water in the cell. The cell was usually kept in the water-circulated cell compartment at the given temperature for ca. 30 min in order to assure thermal equilibration. A sharp peak is present at 722 nm at 15°C. With rising temperature, this peak diminishes and a new peak appears at 667 nm. The reversible change occurs when the temperature is lowered. The temperature-dependent spectral change is very similar to that observed for the aqueous bilayer dispersion shown in Fig. 1B.[9]

Figure 2 illustrates the change with temperature of the relative absorbance at 722 and 667 nm. The A_{722}/A_{667} value changes drastically at 38°C(dotted line), which agrees with T_c of the film determined by DSC. Similarly, the spectral change of Fig. 1B is drastic at 29 - 30°C, in agreement with T_c(31°C) of the aqueous dispersion.

The same situations(drastic spectral change near T_c of the matrix membrane and agreement of the spectral behavior between the cast film and the aqueous dispersion) were found for other combinations: 3b/1(n = 3,6,10) and 3a/1(n = 2,3,6,10). Some of the results are summarized in Table 1. Except for the matrix of 1(n = 2), absorption spectra(λ_{max}) of the aqueous bilayer and the corresponding cast film agree well, including the T_c dependence. In the case of 1(n = 2), the characteristic red shift is not observed for the crystalline ($T < T_c$) bilayer in water. The spectrum of the cast film in this case is very broad with λ_{max} at 690 nm. The red shifts observed at $T < T_c$ have been attributed to the J-like aggregate,[9] and, in fact, it is lessened when the

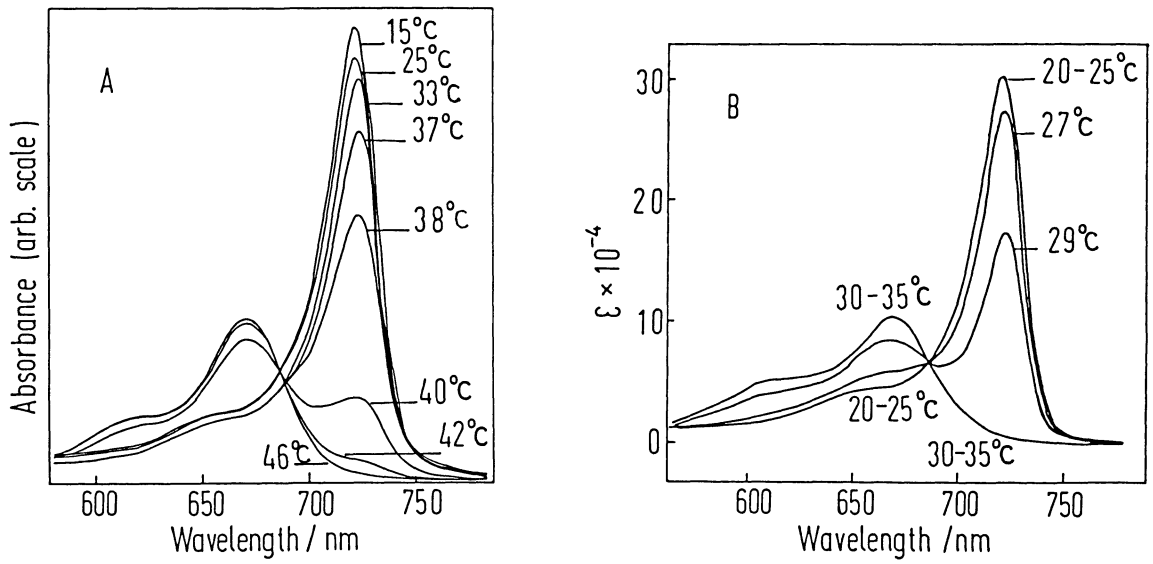

Fig. 1. Temperature dependence of visible absorption spectra of the membrane-bound cyanine dye(3b).
A: cast film on glass plate(3b, 2 x 10^{-8} mol/cm^2; 1(n = 4), 2 x 10^{-7}mol/cm^2).
B: aqueous bilayer solution (3b, 5 x 10^{-6} M; 1(n = 4), 2,5 x 10^{-6} M).

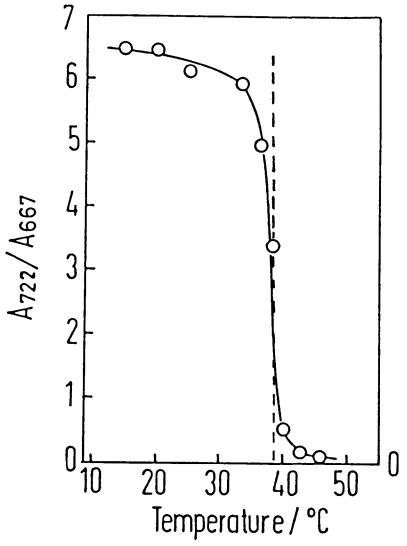

Fig. 2. Plots of A_{722}/A_{667} (Fig. 1A) vs. temperature. The dotted line indicates T_c of the cast film as determined by DSC.

Table 1. λ_{max} (nm) of cyanine dye(3b) in various media[a)]

Amphiphiles	Media	λ_{max} below T_c	λ_{max} above T_c
1 (n=2)	cast film	690(broad)	667
〃	aqueous bilayer	666	667
1 (n=3,4)	cast film	722	666
〃	aqueous bilayer	720	667
1 (n=4)[b)]	cast film	695	666
〃	aqueous bilayer	693	666
1 (n=6)	cast film	705	666
〃	aqueous bilayer	706	666
2 (n=16)	cast film	500-800	500-800
〃	aqueous bilayer	500-800	500-800
	in H_2O	580,648	
	in MeOH	653	

a) [3b]/[Amphiphiles] = 1/10 .
b) [3b]/[1(n = 4)] =1/1000 .

dye/membrane ratio is diminished. The extent of the red shift is highly sensitive to the minor structural change(different spacer length,n) in the aqueous dispersion as well as in the cast film. In contrast, the spectrum in the 2 (n = 16) matrix is very broad in the two systems and there is no T_c dependence.

Cast films obtained from bilayer 1 and merocyanine dye 4 gave generally the same spectral results as those for cyanine dyes 3, and a red shift observed at low temperatures was lost upon phase transition.

In conclusion, it is established that aqueous bilayer dispersions can be immobilized by casting on solid plates without losing the bilayer characteristics.

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(Received July 1, 1983)