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Preorganization of the Salicylideneaniline Ligand by Means of Bilayer Membrane[1)]

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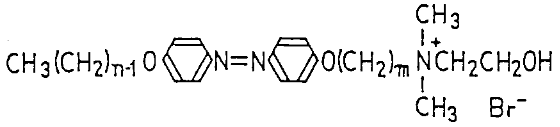
Single-chain ammonium amphiphiles which contain the salicylideneaniline unit formed stable bilayer membranes in water. The component orientation is either parallel or tilted depending on the alkyl chain length, as inferred from X-ray diffraction patterns and absorption spectral shifts.

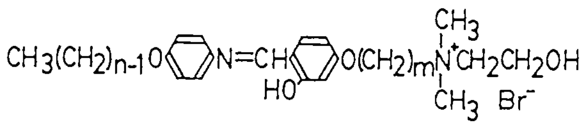
We have shown that some single-chain amphiphiles produce stable bilayer membranes in water.[2)] These amphiphiles contain aromatic units whose orientations in bilayer are extensively varied. In particular, the aggregation structure of azobenzene-containing ammonium amphiphiles has been studied by absorption spectral changes,[3)] differential scanning calorimetry,[3)] and X-ray diffraction.[4-6)] Figure 1 shows schematic illustrations of the representative aggregation structures. The azobenzene-containing bilayer **1** may assume the tilted component arrangement, the parallel stacking, or the interdigitated structure. These characteristic modes of molecular packing arise mainly from the difference in the length of the methylene chain.

we can take advantage of these aggregation rules for organizing other functional units. The salicylideneaniline unit is geometrically analogous to the



$CH_3(CH_2)_{n-1}O-C_6H_4-N=N-C_6H_4-O(CH_2)_m\overset{+}{N}(CH_3)_2CH_2CH_2OH\ Br^-$

1: $C_nAzoC_mN^+$



$CH_3(CH_2)_{n-1}O-C_6H_4-N=CH-C_6H_3(HO)-O(CH_2)_m\overset{+}{N}(CH_3)_2CH_2CH_2OH\ Br^-$

2: $C_n{\cdot}Salan{\cdot}C_m{\cdot}N^+$

(n,m) = (8,10), (12,5), (12,10)

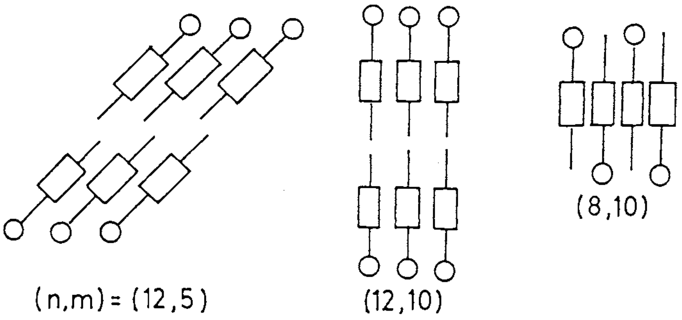


Fig. 1. The mode of molecular assembly of $C_nAzoC_mN^+$ bilayers.

azobenzene unit and forms stable metal chelates. In order to prepare bilayer matrices that are effective for specific assembly of metal ions, we studied in this paper the aggregation behavior of a new series of ammonium amphiphiles **2**,7) which are expected to display different modes of aggregation like those of the azobenzene bilayers. The chelating characteristics of these new amphiphiles and the resulting bilayers will be described in a subsequent paper.

Powdery **2**(8, 10) and **2**(12, 10) were dissolved in warm deionized water to give transparent 10-mM dispersions. **2**(12, 5) dissolved readily in water without warming. The results of differential scanning calorimetry (Seiko Instrument, SSC/560) of these dispersions are summarized in Fig. 2. They all show sharp, single peaks. The peak for **2**(12, 5) is much larger than the other two. A systematic investigation of the bilayer phase transition indicated that its ΔS values are in the range of 25-75 J/K mol for single-chain amphiphiles.8) The ΔS values for **2**(12, 10) and **2**(8, 10) are within this standard range, but ΔS for **2**(12, 5) is much larger. The observed endothermic peak of the latter may not be attributed to a typical gel-to-liquid crystal phase transition of bilayer.

Subsequently, electron microscopic observations (instrument, Hitachi H-600) were carried out. The 10-mM dispersions were applied to carbon-coated Cu grids, dried, and stained by aqueous uranyl acetate. A dispersion of **2**(8, 10) gave flexible fibrous aggregates with diameters of ca. 150 Å. **2**(12, 10) also displayed a fibrous morphology which is made of interconnected particles (diameter ca. 150 Å). However, **2**(12, 5) gave less developed, fragmented fibers.

Absorption spectral characteristics are useful for examining chromophore orientations in the bilayer aggregate. All the salicylideneaniline units in **2** give absorption maxima at 345 nm in methanol. The corresponding spectra in water showed a large variation, depending on the component structure and temperature. Figure 3a gives the temperature dependence of the absorption spectrum of the bilayer of **2**(8, 10). The absorption maximum is located at 290 nm at temperatures of 20-30 °C, but shifts to 345 nm at 50-60 °C with an isosbestic point at 318 nm. Since T_c (DSC peak top) of this bilayer is 48.5 °C, this spectral change must reflect the change in the bilayer physical state. The large blue shift observed in the gel state is indicative of parallel packing of the chromophore, which, however is lost in the liquid-crystalline state. A very similar temperature dependence has been found for absorption spectra of the azobenzene bilayer of **1**(8, 10). The pH change of the aqueous medium from 5.2 to 9.0 did not affect the spectrum : therefore, the salicylideneaniline group must remain undissociated in this pH range. The same results were obtained for the other bilayers. The spectral shift for **2**(12, 10) as shown in Fig. 3b is much less pronounced, and a slight shift is observed at 25-30 °C, in agreement with its T_c value of 29 °C. In contrast, aqueous **2**(12, 5) gives spectra which are identical to that in methanol and are not affected by temperature at 20-60 °C. These spectral data suggest that **2**(12, 5) does not form organized aggregates in water at the concentration employed(below 10 mM).9)

The mode of molecular assembly can be unequivocally determined by X-ray diffraction. The electron density matching has been used to determine the molecular packing in cast films of synthetic bilayers, when single crystals are not

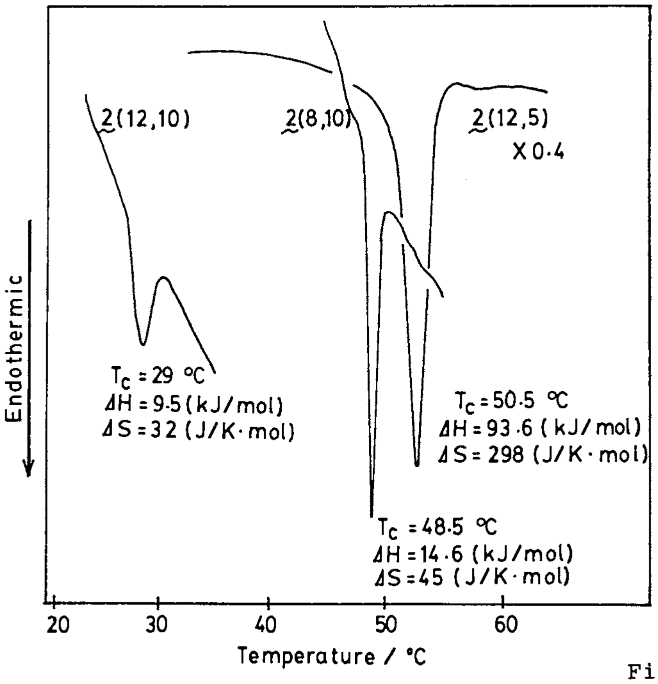


Fig. 2. DSC thermograms of aqueous dispersions. 10 mM, heating scan at 1 °C/min.

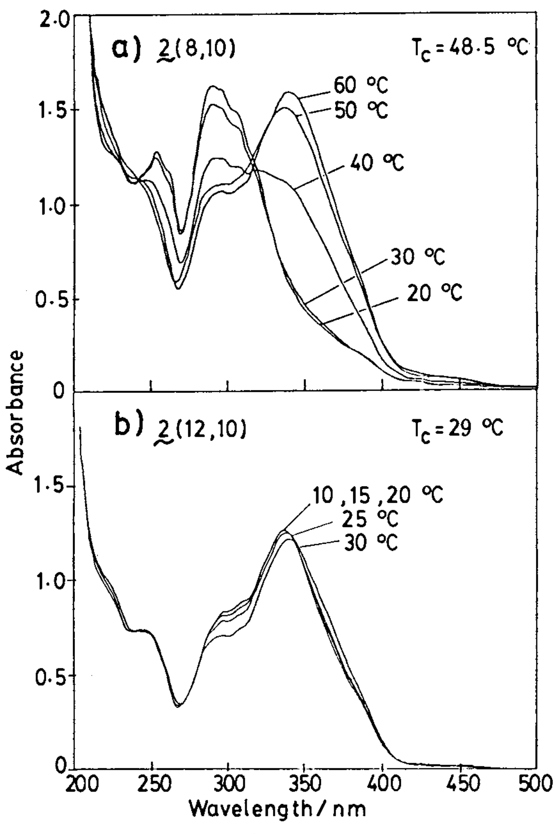


Fig. 3. Absorption spectra of aqueous bilayers of **2**. 1 mM acetate buffer, pH 5.2, μ=0.01(CH_3COOK)

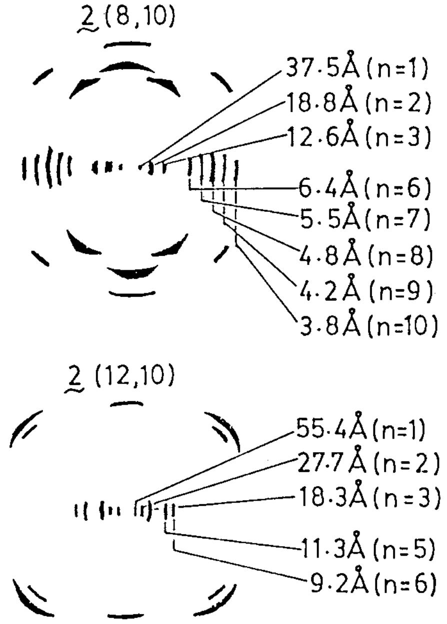


Fig. 4. X-Ray diffraction patterns of cast films of **2**. X-Ray beam is directed toward the edge of vertically-positioned cast films.

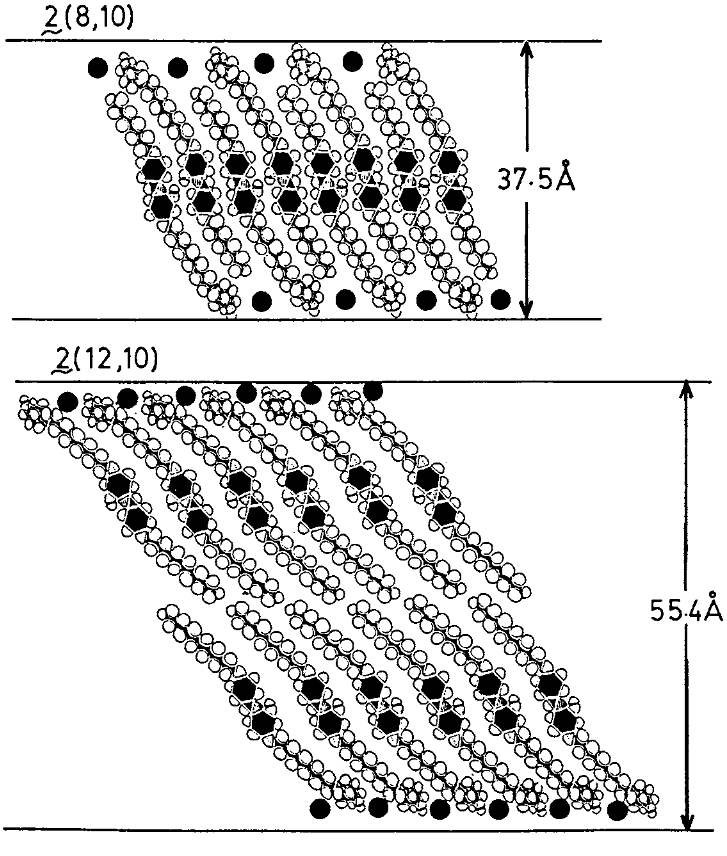


Fig. 5. Plausible models for bilayers of **2**(8, 10) and **2**(12, 10).

available.4,10) Self-supporting films are obtainable from **2** by slow casting of the aqueous dispersions on Teflon films at room temperature. The diffraction patterns of Fig. 4 suggest the formation of highly regular multilayers, which are very similar to those of the corresponding azobenzene bilayers. **2**(8, 10) gave a long spacing of 37.5 Å, as against 39 Å for **1**(8, 10), and **2**(12, 10) gave a long spacing of 55 Å, compared with 58 Å for **1**(12, 10). The extended molecular length of **2**(8, 10) is 39 Å. This figure implies the formation of the interdigitated structure, together with the blue shift which indicates the parallel chromophore stacking. In the case of **2**(12, 10), the bilayer structure is assumed since its long spacing is larger than the molecular length (44 Å).

Plausible structure models for **2**(12, 10) and **2**(8, 10) are shown in Fig. 5. They were constructed by taking into consideration their structural similarities to the corresponding azobenzene bilayers. The model is not given for **2**(12, 5), since its aggregation in water appears too weak to form a regular bilayer structure, although a tilted chromophore packing is assumed in a cast film. The observed variation in molecular assemblage indicates that bilayer formation is an effective way to preorganize ligand units in desired manners. The subsequent chelation could produce unique metal complexes which are not favored under the unorganized conditions.11) This system may also be applied to photoreaction control of the salicylideneaniline group.12,13)

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7) **2**'s were synthesized by condensation of 4-(ω-bromoalkyloxy)salicyl aldehydes and 4-alkyloxyanilines, followed by quaternization with N,N-dimethylaminoethanol. The final products were identified by NMR and IR spectroscopies. **2**(8, 10), yellow powder, mp 145→220 °C(the arrow indicates the liquid crystalline region). Found : C, 64.32; H, 8.78; N, 4.34%. Calcd for $C_{35}H_{57}N_2O_4Br$: C, 64.70; H, 8.84; N, 4.31%. **2**(12,10), pale yellow powder, mp 113→249 °C, Found : C, 66.09; H, 9.21; N, 3.90%. Calcd for $C_{39}H_{65}N_2O_4Br$: C, 66.36; H, 9.28; N, 3.97%. **2**(12, 5), yellow powder, mp 126→263 °C. Found : C, 64.10; H, 8.66; N, 4.46%. Calcd for $C_{34}H_{55}N_2O_4Br$: C, 64.24; H, 8.72; N, 4.41%.
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9) A yellow cast film of **2**(12, 5) gave a broad λ_{max} at 350-360 nm and a long spacing of ca. 44 Å by X-ray diffraction. These data suggest a tilted stacking of the component in a concentrated dispersion.
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