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Amphiphilic Compounds Having Heterocycles. Effects of the Structure of Heterocycle on the Behavior of the Monolayer at the Air-Water Interface

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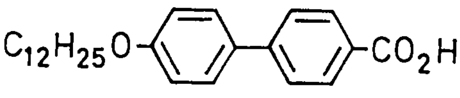
Surface pressure-area (π-A) isotherms of monolayers of amphiphilic compounds, in which one phenyl ring of 4'-dodecyloxybiphenyl-4-carboxylic acid was replaced by a pyrazine, pyridine, or pyrimidine nucleus, were measured. The difference of π-A isotherms depending on the structure of heterocycles can be understood in terms of interaction between chromophores.

In the previous paper, we have reported that among four types of amphiphilic carboxylic acids, having phenylpyrazine as the chromophore and alkyl or alkoxy group as the hydrophobic part, 5-(4'-dodecyloxyphenyl)pyrazine-2-carboxylic acid 2 formed the most stable and closely packed monolayer, which could be easily deposited to form a Y-type Langmuir-Blodgett film.$^{1)}$ Here, we report our investigation on the effects of heterocycles incorporated into amphiphilic compounds.

The amphiphiles 3 - 5, having a pyridine and pyrimidine ring, were newly synthesized by modification of the reported procedures$^{2)}$ and purified by the procedure reported in our previous report.$^{1)}$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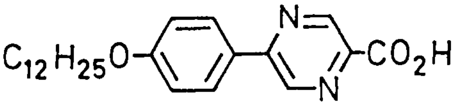
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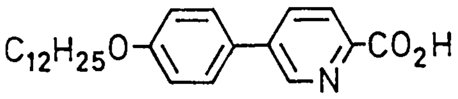
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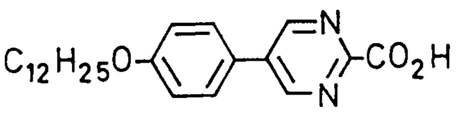
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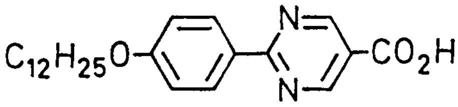
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The surface pressure-area (π-A) isotherms of amphiphiles 1 - 5 on pure water changed largely depending on the structure of heterocycles incorporated, as shown in Fig. 1. The amphiphiles 2, 3, and 5 formed closely packed monolayers with the collapse pressures much higher than that of 1, whereas the compound 4 formed expanded monolayer. Although the monolayers of 2 and 3 were stable, the monolayer of 5 having the smallest limiting area was fragile. The monolayer of 5 collapsed in a few minutes at the surface pressure of 20 mN/m, whereas the monolayers of 2 and 3 could be kept over hours under the same conditions.

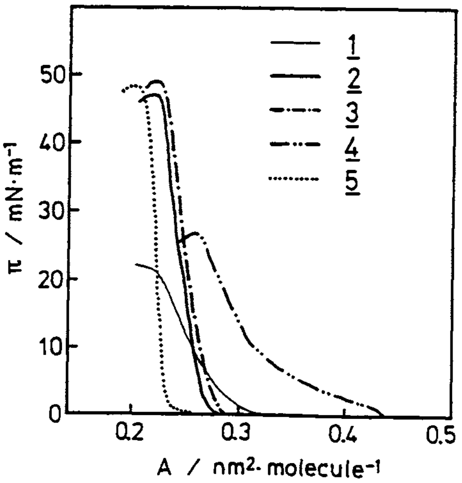


Fig. 1. π-A isotherms of 1 - 5 on pure water (pH 6) at 15 °C.

The large difference of the π-A isotherms depending on the structure of the heterocycles incorporated into amphiphilic molecules would be explained in terms of overall dipole moment of the amphiphilic molecules and electrostatic interaction between heterocycles.

The amphiphile 1 has large dipole moment because of the electron donating alkoxy group on one side of the chromophore and the electron withdrawing carboxyl group on the other side. By replacement of one benzene ring adjacent to carboxyl group with electron deficient heterocycles, such as pyrazine, pyridine, or pyrimidine, dipole moment from the benzene ring to the heterocycle would be induced. Furthermore, dipole moments of heterocycles must also be taken into account. According to the reported data,[3)] the dipole moment of pyrazine, pyridine, and pyrimidine along the molecular axes of 2 - 5 are 0, 1.1 and 2.4 D, respectively, which predicts the overall dipole moments of the amphiphiles along the molecular axes would be in the order 4 > 3 > 2 > 5.

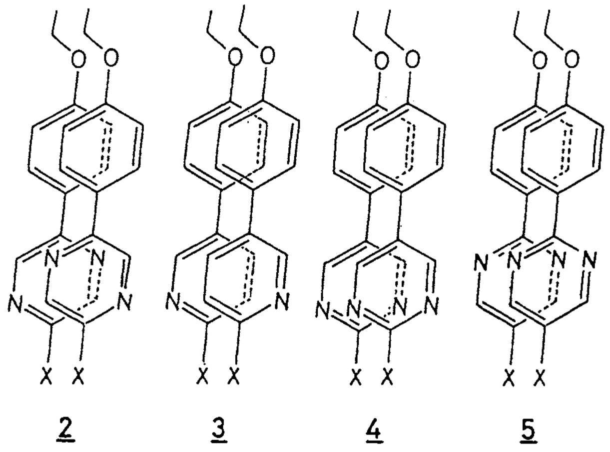
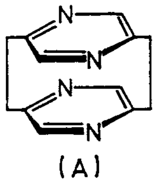


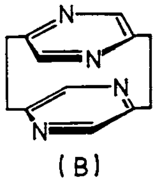
Fig. 2. Schematic representations of possible arrangement of 2, 3, 4, and 5.

Loose packing of 4 in monolayer would be ascribed to repulsion caused by its largest dipole moment.

However, consideration of overall dipole moment cannot explain the formation of closely packed stable monolayers of 2 and 3 and the instability of the monolayer of 5. If we consider the electrostatic interaction between the heterocycles arranged in the monolayer, the behaviors of 2, 3, and 5 would be recognized. The dipole-dipole interaction between pyrazine rings could not be expected, because the pyrazine nucleus has no dipole. However, if we consider the electrostatic interaction between pyrazine rings as that between multipoles, with negatively charged nitrogen atoms and positively charged carbon atoms, attractive interaction can be recognized in the monolayer of 2, arranged as shown in Fig. 2.

It was recently reported that among two isomers of pyrazinophane (A) and (B), the UV absorption of (B) is observed at longer wave length than (A).[3)] This indicates the isomer (B) is stabilized compared to (A) and supports our consideration.

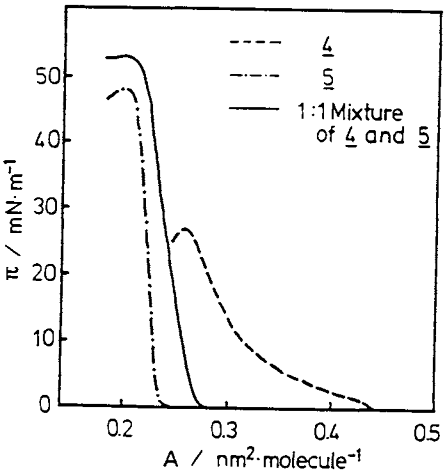

(A)

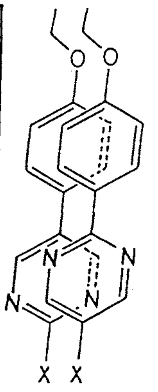

(B)

By considering the same attractive interaction in the arrangement as shown in Fig. 2, the formation of closely packed stable monolayer of 3 can be recognized.

In the case of 5, formation of closely packed monolayer is possible because of smallest overall dipole moment, but close packing of 5 brings about large multipole-multipole repulsion between pyrimidine nuclei, which makes the monolayer fragile.

If such multipole-multipole interaction is effective, the mixture of 4 and 5 must form closely packed stable monolayer. This was proved to be the case by the fact that the 1 : 1 mixture of 4 and 5 showed smaller limiting area than the average of each component and showed higher collapse pressure, as shown by the π-A isotherms in Fig. 3. Dependence of the limiting area on the composition of the mixture of 4 and and 5 is shown in Fig. 4. In all range





1:1 Mixture of 4 and 5

Fig. 3. π-A isotherm of the 1 : 1 mixture of 4 and 5 on pure water (pH 6) at 15 °C.

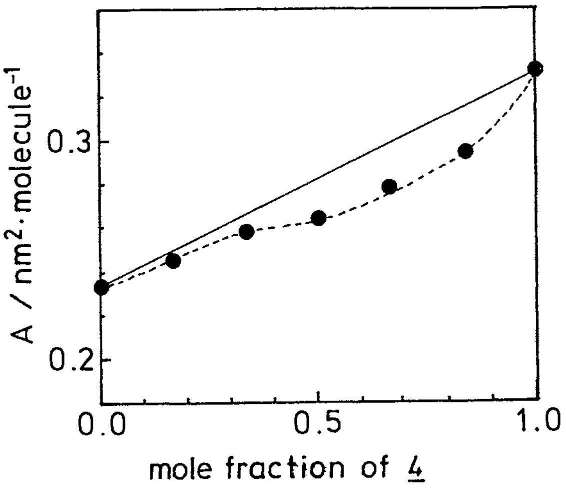


Fig. 4. Dependence of limiting area on the mole fraction in the mixture of 4 and 5 on pure water (pH 6) at 15 °C.

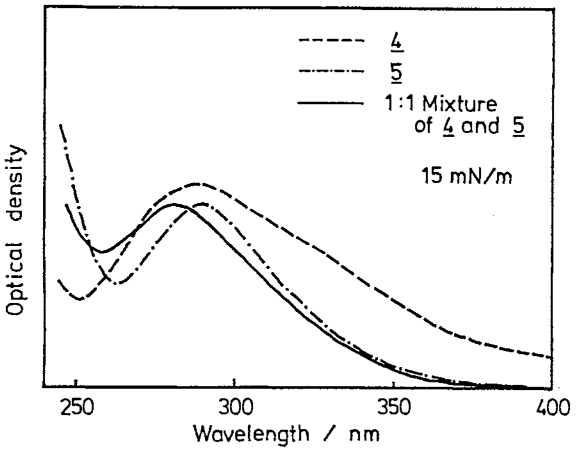


Fig. 5. UV spectra of the monolayers of 4, 5, and 1 : 1 mixture of 4 and 5 on pure water (pH 6) at 15 °C.

of the composition, limiting area was below the ideal mixing line which suggests the mixing of the two components occurred at molecular level, caused by attractive interaction between reversely oriented pyrimidine rings in 4 and 5. This was further substantiated by the fact that UV spectrum of the monolayer of the 1 : 1 mixture of 4 and 5, as shown in Fig. 5, cannot be reproduced by addition of those of 4 and 5.

Results in this paper demonstrate the importance of multipole-multipole interaction as a guideline for the molecular design of amphiphiles and their mixing in the preparation of stable and closely packed monolayers.

References

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