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Complete Mixing of Two Amphiphilic Compounds at Air-Water Interface

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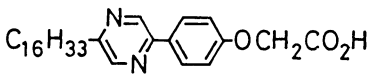
Two amphiphilic compounds, 5-(p-hexadecylphenyl)pyrazin-2-oxyacetic acid (1) and p-(5-hexadecylpyrazin-2-yl)phenoxyacetic acid (2), were newly synthesized. The mixture of 1 and 2 formed more closely packed monolayer than pure 1 or 2 did. This phenomenon was revealed to be caused by complete mixing due to the attractive interaction between reversely oriented chromophores of 1 and 2.

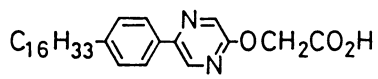
Multilayers of amphiphilic compounds, Langmuir-Blodgett Films, have been focusing much attention.[1] To obtain high-performance films, a closely packed monolayer of molecules having an appropriate chromophore is required. However, a large chromophore sometimes interferes with the close packing. Hence, to attain close packing, long hydrocarbon chains are introduced or close packing molecules, such as fatty acid, are occasionally mixed.[2]

Here, we report the characteristics of mixed monolayers, composed of two amphiphilic compounds, which were designed to obtain a closely packed monolayer by attractive interaction between reversely oriented polar phenylpyrazine chromophores.

Two amphiphilic compounds, p-(5-hexadecylpyrazin-2-yl)phenoxyacetic acid 1 and 5-(p-hexadecylphenyl)pyrazin-2-oxyacetic acid 2, were synthesized by the newly developed method.[3] The corresponding non-polar biphenyl analogue, p-(p'-hexadecylphenyl)phenyloxyacetic acid (3), was also synthesized for comparison.



1



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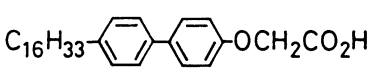

3

The π-A isotherms for the monolayers of 1, 2, 3, and the 1 : 1 mixture of 1 and 2 on pure water surface (pH 6) are shown in Fig. 1. Although the monolayers were stable up to about 25 mN/m, the limiting areas of 1 and 2 were considerably larger than that of 3, suggesting the packing of monolayers of 1 and 2 are looser than that of 3. These phenomena would be ascribed to intermolecular dipole-dipole repulsion in the monolayers of 1 and 2, whereas the polarity of the chromophore is small in 3. On the other hand, the mixture of 1 and 2 assembled into closely packed monolayer having nearly equal limiting area to that of 3.

In order to know the origin of the close packing in the mixed monolayer, the π-A isotherms of mixtures of 1 and 2 at different mole ratio were studied. The variation of the limiting areas (A_0) and the molecular areas at the surface pressure of 10 mN/m (A_{10}) are shown in Fig. 2. Both of the concaves show minimum at the center, where 1 and 2 are mixed in 1 : 1 molar ratio. From these results, two components are considered to be completely miscible with each other.

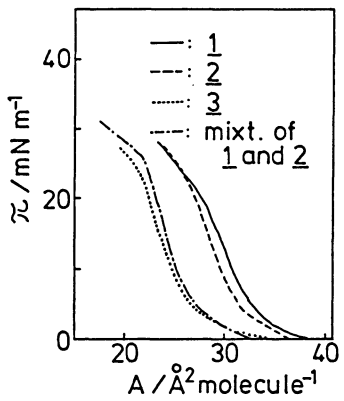

Fig. 1. π-A isotherms of monolayers at 20°C.

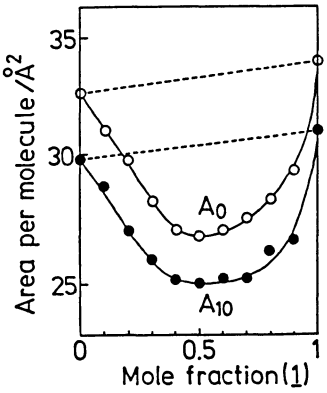

Fig. 2. Dependence of A_0 and A_{10} on mole ratio.

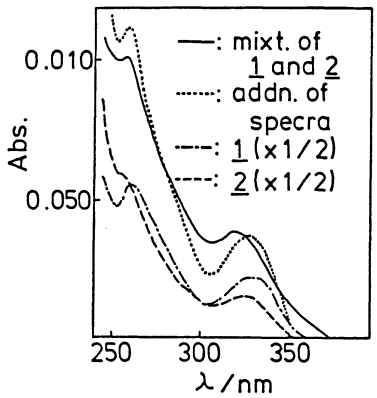

Fig. 3. UV spectrum of mixed monolayer (15 mN/m).

The UV spectrum of monolayer at the air-water interface for the 1 : 1 mixture was different from the shape of the spectrum obtained by addition of those for 1 and 2, as shown in Fig. 3, which also supported complete mixing. Although mixing of two components to improve the stability of monolayers has been reported by many workers,[4] the miscibility of components in molecular level has been scarcely examined. The results in this paper provided one of the typical examples of completely miscible systems. The complete miscibility of 1 and 2 would be caused by dipole-dipole attraction between the reversely oriented chromophores of 1 and 2, as shown in Fig. 4.

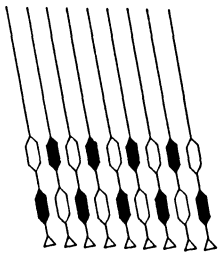

Fig. 4. Schematic representation of 1 : 1 mixture of 1 and 2.

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References

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2) H. Nakahara and K. Fukuda, J. Colloid Interface Sci., 69, 24 (1979); 93, 530 (1983); K. Fukuda, H. Nakahara, and T. Kato, ibid., 54, 430 (1976).
3) M. Matsumoto, H. Souda, M. Ogasawara, T. Nagaishi, S. Yosinaga, K. Isomura, and and H. Taniguchi, Chem. Express, 2, 109 (1987)
4) For example; I. S. Costin and G. T. Barnes, J. Colloid Interface Sci., 51, 94, (1975).

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