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Amphiphilic Compounds Having Pyrazine Nucleus. Formation of Monolayer and Langmuir-Blodgett Film

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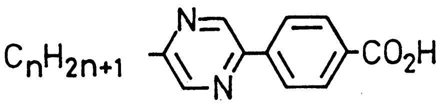
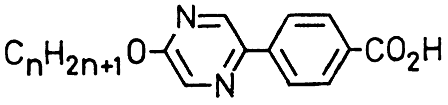
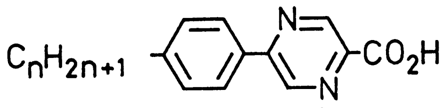
Among the all types of amphiphilic carboxylic acids, having phenylpyrazine as the chromophore and alkyl or alkoxy group as the hydrophobic part, 5-(4'-alkoxyphenyl)pyrazine-2-carboxylic acid formed the most stable and closely packed monolayer, which could be easily deposited to form a Y-type Langmuir-Blodgett film.

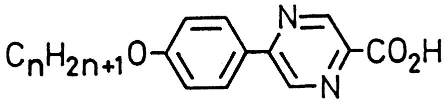
Many investigations on Langmuir-Blodgett (LB) films have been reported because of its enormous potential applicability.1) For preparation of high-performance LB films a stable and closely packed monolayer, containing appropriate chromophore, is required. We have been interested in the synthesis of series of pyrazine containing amphiphiles,2) as pyrazine, one of electron deficient hetero-aromatic rings, can enhance the polarity without destabilizing the molecule. Here, we report our investigation to explore the compounds containing pyrazine nucleus to get amphiphiles suitable for LB film preparation.

Four types of amphiphiles 1 - 4, having alkyl or alkoxy group on one side of phenylpyrazine and carboxyl group on the other side, were synthesized by base catalyzed hydrolysis of the corrsponding nitriles.3)


1 (n=12; C_n-1)


3 (n=12,14,16; C_nO-3)


2 (n=13; C_n-2)


4 (n=8,12,16; C_nO-4)

The π-A isotherms of these compounds on pure water subphase are shown in Fig. 1. Among the homologs of 4, $C_{16}O$-4 formed the most closely packed monolayer with the highest collapse pressure. Although the amphiphile $C_{12}O$-4 also formed a closely packed stable monolayer, the octyl derivative C_8O-4 seems to be dissolved into the subphase. In the case of the amphiphile C_{13}-2, having the phenylpyrazine chromophore in the same direction as 4, the limiting area was large and the collapse pressure was low. On the other hand the amphiphiles of the types 1 and 3, having reversely directed chromophore, showed worse behaviors at the air-water interface. The compound C_{12}-1 did not formed monolayer. And in the case of the homologs of 3, only the longest homolog C_{16}-3 formed a closely packed monolayer but the collapse pressure was low.

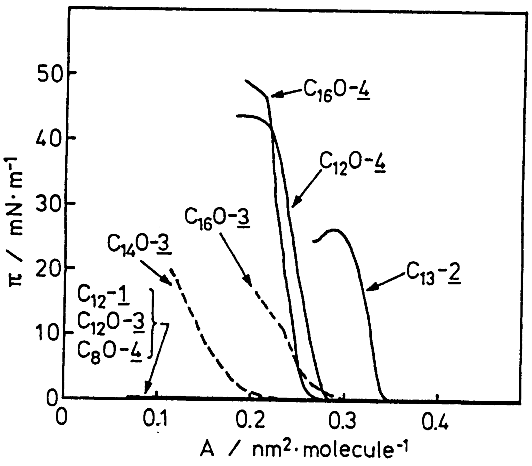


Fig. 1. π-A isotherms of amphiphiles on pure water (pH 6) at 15 - 18°C.

The large difference depending on the direction of phenylpyrazine chromophore could be explained in terms of hydrophilicity of the pyrazine ring. In the cases of 2 and 4, the pyrazine ring and carboxyl group as a whole act as the hydrophilic part. On the other hand, the pyrazine ring in 1 and 3 separated from carboxyl

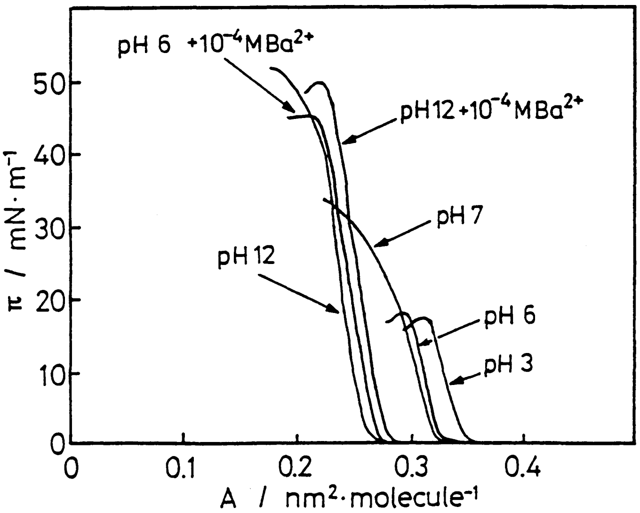


Fig. 2. π-A isotherms of C_{13}-2 depending on the conditions of subphase.

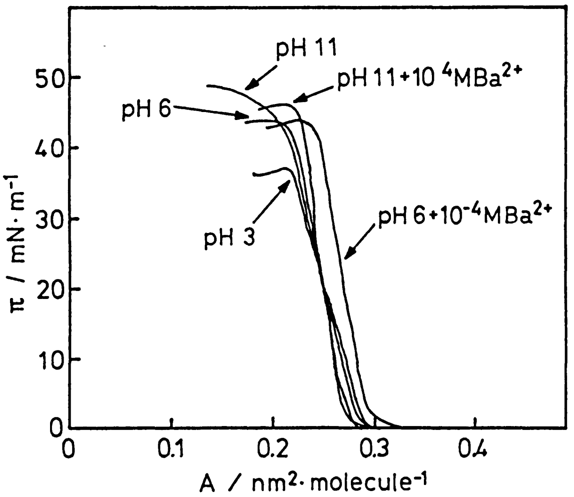


Fig. 3. π-A isotherms of $C_{12}O$-4 depending on the conditions of subphase.

group by benzene ring destroys the balance of hydrophilicity and hydrophobicity necessary for the formation of stable monolayer.

In order to get more insight into marked difference in π-A isotherms between C_{13}-2 and $C_{12}O$-4, which was caused by small difference of the structure, alkyl vs. alkoxy group, the π-A isotherms of these two compounds were measured under several conditions of the subphase. When the subphase was basic or contained Ba^{2+} the limiting area of C_{13}-2 became smaller and collapse pressure higher, as shown in Fig. 2. But as shown in Fig. 3, a small change was observed in the π-A profiles of $C_{12}O$-4. This suggests that $C_{12}O$-4 can form a closely packed stable monolayer without assistance by base or Ba^{2+} in the subphase.

Formation of the stable monolayer of $C_{12}O$-4 would be ascribed to the presence of the ether linkage. The attractive interaction between dipoles of the ether linkages, as shown by arrows in Fig. 4, would be the reason to combine the amphiphilic molecules 4.

The monolayer of $C_{12}O$-4 was spread on the subphase containing Ba^{2+} (1×10^{-4} M) and deposited by the vertical dipping method on a quartz plate and a polystyrene film at the surface pressure of 30 mN/m for optical measurements and X-ray diffraction analysis, respectively. A Y-type deposition was observed on both substrates with transfer ratio of unity. The UV spectrum of the LB film showed a blue shift compared with that of $C_{12}O$-4 in dichloromethane, as shown in Fig. 5, which indicated the formation of H-aggregate. The UV spectra using polarized light showed the angular dependence on the incident angle θ, as shown in Table 1

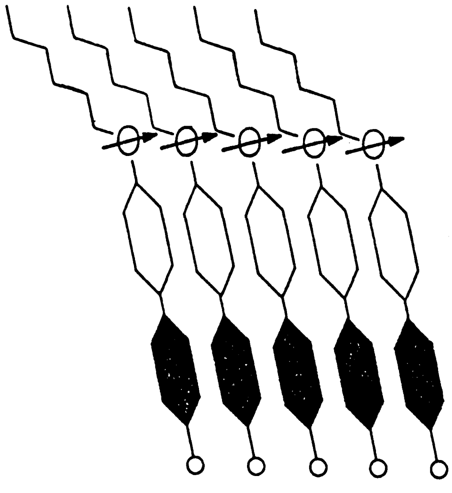


Fig. 4. Schematic representation of the monolayer of 4.

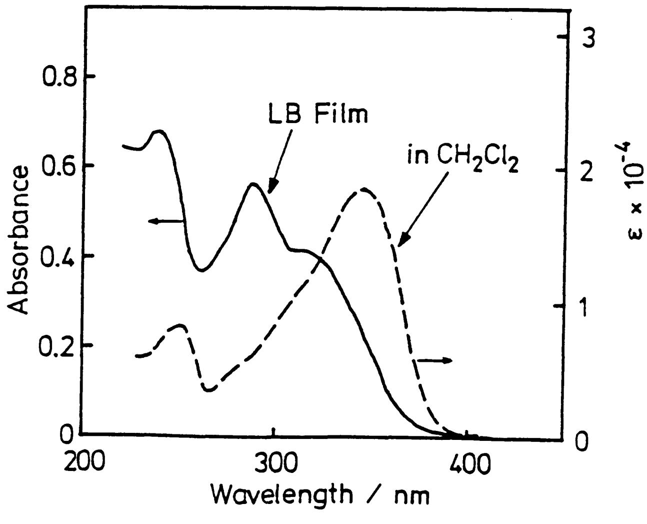


Fig. 5. UV spectra of $C_{12}O$-4 in CH_2Cl_2 and its LB film (29 layers) on quartz.

Table 1. The angular dependence of the dichroic ratio for the film obtained by deposition of Ba salt of $C_{12}O$-4

θ (deg)	0	15	45
Ap/As	0.72	0.85	0.95

(where Ap and As are absorbance of p- and s-polarized light at 290 nm, respectively, and the axis of p-polarization coincides with the dipping direction at θ=0°.)6) Increasing value of Ap/As with the angle θ suggests the average direction of the choromophore are oriented perpendicularly to the surface of the film. The X-ray diffraction of the LB film on polystyrene showing up to 5th diffraction revealed that the d spacing was 4.7 nm.7) These results show that 4 can be deposited into a regularly assembled Y-type LB film.

References

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2) H. Niino, K. Takehara, K. Isomura, H. Taniguchi, M. Era, T. Tsutsui, and S. Saito, Chem. Lett., 1988, 785.

3) The amphiphile 1 was prepared by the reported method.4) Other compounds were synthesized by modification of the reported procedures.5) The amphiphiles 1 - 4 used in this paper were purified by repeated recrystallization. Correct analyses were obtained and no impurity was detected in 400 MHz NMR specta.

4) M. Matsumoto, H. Souda, M. Ogasawara, T. Nagaishi, S. Yoshinaga, K. Isomura, and H. Taniguchi, Chem. Express, 2, 109 (1987).

5) K. Yoshimoto, T. Shimomura, K. Okimoto, and K. Kashiwagi, Kokai Tokkyo Koho (Japan Patent), 59(1984), 144770, 144772.

6) T. Sakuhara, H. Nakahara, and K. Fukuda, Thin Solid Films, 159, 345 (1988).

7) The molecular length of the carboxylate anion of $C_{12}O$-4 is estimated to be 2.78 nm using CPK model.

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