

The Effect of Chain Length of Hydrophilic Group on the Langmuir-
Blodgett Films Containing Perfluoroalkyl Groups

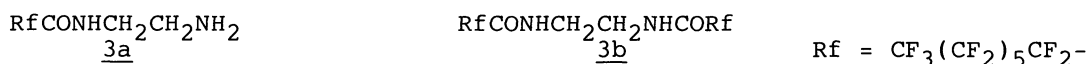
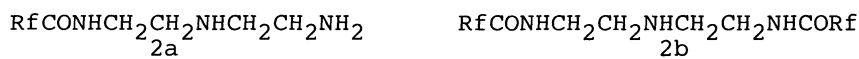
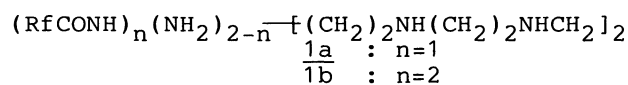
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Long chain perfluoroalkyl groups were introduced to polyamine derivatives which had different chain length and Langmuir-Blodgett films of these amphiphiles were prepared. When pentaethylenhexamine was used as polyamine derivative, stable surface monolayers were formed and properties of the LB films were similar to the polymer LB films, however, less stable surface monolayer was formed as chain length became shorter.

Long chain perfluoroalkyl (Rf) groups show excellent surface properties, such as low surface energy, oxygen affinity, and insulation, etc., so that the thin film containing long chain perfluoroalkyl groups is expected to be useful material for surface coating and film separation, etc. Recently we have demonstrated that new type Langmuir-Blodgett (LB) films of polymers modified with Rf groups by covalent bonds are successfully prepared, and that molecular ordering and surface energy can be controlled by slight change of chemical structure of the polymer.¹⁻⁶⁾ On the other hand, it has been reported that low molecular-weight amphiphiles containing Rf groups are difficult to be deposited onto substrates without any support of metal ions⁷⁾ or polyion complex.^{8,9)} These facts suggest that polymer chain contributes to formation of stable LB films in the case of polymer LB films containing Rf groups. In this paper we wish to report that chain length of hydrophilic groups has an influence on formation of the LB films, and that more stable surface monolayer is formed as hydrophilic groups chain becomes longer.

Perfluoroalkyl group was introduced to pentaethylenhexamine, which has 16 membered chain, by reaction with ethyl perfluorooctanoate,¹⁾ and two amphiphiles which had different ratio of perfluoroalkyl groups to amino groups (see next formula 1a, 1b) were prepared. And 2a, 2b, 3a,¹⁰⁾

and 3b¹⁰⁾ were prepared as amphiphiles which have much shorter hydrophilic chains.¹¹⁾



The benzene / methanol (2 : 1 - 1 : 1) solutions of 1a, 1b, 2a, 2b, and 3a ($0.5 - 1.1 \times 10^{-3} \text{ mol dm}^{-3}$) and ethyl acetate solution of 3b ($0.25 \times 10^{-3} \text{ mol dm}^{-3}$) were spread on the water surface at 290 K, and the surface pressure - surface area (F-A) isotherms were measured. The F-A isotherms are shown in Fig. 1. 1a and 1b, which have longer hydrophilic chains, formed stable surface monolayers with collapse pressures at more than 55 mN m^{-1} . On the other hand, the amphiphiles which have shorter hydrophilic chain, 2a, 2b, and 3a showed lower collapse pressure, less than 50 mN m^{-1} .

The limiting areas (A_0) of perfluoroalkyl unit at zero pressure are summarized in Table 1. The amphiphiles 1a and 1b, which have the longest hydrophilic chains, show the A_0 values larger than the section area of Rf group (28 \AA^2),¹⁾ being similar to polymer LB films containing Rf groups, for example, 69 \AA^2 for PAAF5,¹⁾ 49 \AA^2 for PVAF39,³⁾ 40 \AA^2 for PAAURF12,⁴⁾ and so on. This result indicated that the hydrophilic part of these amphiphiles becomes in a condensed state in the monolayers because of long hydrophilic chain, and that Rf groups are oriented in lying or leaning position. On the other hand, the A_0 value decreases as the hydrophilic chain length becomes shorter. 2a and 3a show the A_0 values smaller than 28 \AA^2 , which indicates that the molecules are put one on another. In the case of 2a and 3a, it is assumed

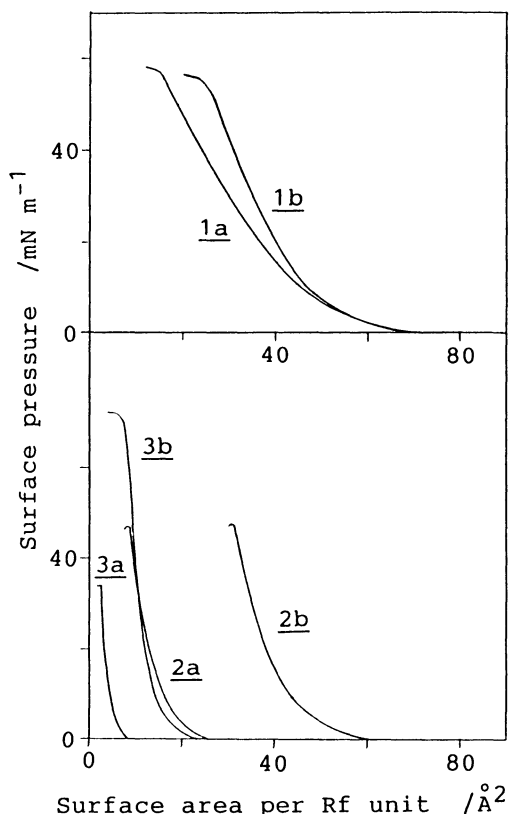


Fig. 1. F-A isotherms.

Table 1. The limiting area of Rf unit A_0 / \AA^2

Amphiphiles	A_0
<u>1a</u>	44
<u>1b</u>	48
<u>2a</u>	15
<u>2b</u>	41
<u>3a</u>	5
<u>3b</u>	13

Table 2. The γ_c values of the LB films /dyn cm^{-1}

Amphiphiles	1Lay	3Lay
<u>1a</u>	16.1	14.5 ^{a)}
<u>1b</u>	11.8	9.3 ^{a)}
<u>2a</u>	11.5	10.5
<u>2b</u>	9.4	9.2
<u>3a</u>	17.0	16.0
<u>3b</u>	— ^{b)}	— ^{b)}

a) 5 layers.

b) Zisman plot was not on a line.

that hydrophilic group does not balance with hydrophobic group resulting that the molecules are overlapped one another. And since the hydrophilic chain length is short, the surface monolayers of 2a and 3a would be less stable against surface pressure and show lower collapse pressure than 1a and 1b. In the case of 3b no hydrophilic group is in the molecule, so that the stable monolayers could not be formed and the molecules would be overlapped one another. In the case of 2b the A_0 value is larger than 28\AA^2 , which indicated that the molecules are not overlapped. 2b has two Rf groups at both end of diethylenetriamine and one secondary amino group at the center of the molecule. It is assumed that this symmetrical structure of 2b makes the balance between hydrophilic group and hydrophobic group better to afford the monolayer, however, collapse pressure of the monolayer is lower and the monolayer is less stable than 1a and 1b.

Deposition of these surface films was attempted under surface pressure of 20 mN m^{-1} on slide glasses. Y type multilayers were obtained for 1a and 1b, and Z type multilayers were obtained for 2a, 2b, 3a, and 3b.

The γ_c values of Zisman plot were measured with n-alkanes on the LB films (1 and 5 layers for Y type films, 1 and 3 layers for Z type films) in usual manner.¹⁾ The results are summarized in Table 2. These LB films show smaller γ_c values than polytetrafluoroethylene (18.5 dyn cm^{-1}), indicating that Rf groups are arranged and that CF_3 groups exist on the surface of the LB film.¹⁾ The smaller γ_c value of the multilayer film than the monolayer film indicates that glass surface has an effect on the γ_c value.¹²⁾

The γ_c value of 1a is close to that of polymer LB films containing Rf groups, such as PAAF,¹⁾ PVAf,³⁾ PAAURF,⁴⁾ and so on. In the case of polymer LB films, Rf groups are arranged on a condensed hydrophilic part as shown by large A_0 values,^{1,4)} so that Rf groups can not be closely ordered, resulting that γ_c values are not very low, about 15 dyn cm^{-1} . The γ_c value of 1a close to that of polymer LB films and large A_0 value like

polymer suggests that the molecular ordering in the LB film of 1a is close to that of polymer LB films, that is, Rf groups are arranged on a condensed hydrophilic part. On the other hand, 1b, 2a, and 2b show much smaller γ_c value than 1a. In the case of 1b, it is considered that higher ratio of Rf groups to amino groups make the γ_c value smaller than 1a. Concerning 2a and 2b, it is assumed that arrangement of Rf groups easily be well-ordered compared with 1a and 1b because these amphiphiles have short hydrophilic chains. Furthermore, since Rf groups are put one upon another in the LB film of 2a due to the small value of A_0 as shown in Table 2, the γ_c value becomes very low. In the case of 2b, it is assumed that excellent low surface energy is obtained because the ratio of Rf groups to amino groups is high and Rf groups are ordered more vertically than 2a. Concerning 3a and 3b, although Rf groups are put one upon another, the γ_c values of 3a are not very low. And in the case of 3b, the γ_c value could not be measured because Zisman plot was not on a line. These results indicate that the arrangement of Rf groups is disordered because the molecules which have too short chain length to make stable LB films are put one upon another.

In conclusion, when the hydrophilic chain of the amphiphile containing Rf groups is sufficiently long, the stable surface monolayer is formed, and the LB films show similar properties to polymer LB films. On the other hand, when the hydrophilic chain is short, the stable surface monolayer is not stably formed and the molecules are apt to be put one on another. However, if Rf groups are easy to be well-ordered in the LB films, so that excellent low γ_c value can be obtained in the case that the amphiphile has suitable structure.

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