

## Microphase Separation in Mixed Langmuir Monolayers

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The surface pressure-area ( $\Pi$ -A) isotherm curves of pure and mixed monolayers which have been reported by Mori and Imae[*Langmuir* **11**, 4799(1955)] were analyzed to get the molecular insight into mixed monolayers. The  $\Pi$ -A isotherm curves of the pure octadecyldimethylamine oxide {CH<sub>3</sub>(CH<sub>2</sub>)<sub>17</sub>NO(CH<sub>3</sub>)<sub>2</sub>, C<sub>18</sub>DAO} , the pure arachidic acid {CH<sub>3</sub>(CH<sub>2</sub>)<sub>18</sub>COOH, AA} monolayers and the mixed monolayers were analyzed to assume the mixed situation between C<sub>18</sub>DAO and AA at the air-water interface. As a result, it was assumed that part of C<sub>18</sub>DAO molecules forms mixed clusters with AA molecules and the residual C<sub>18</sub>DAO molecules exit individually without any formation of mixed clusters with AA in the mixed monolayer. Not only the ratio of the clustered C<sub>18</sub>DAO molecules to the total C<sub>18</sub>DAO molecules was estimated, but also the mixed cluster's composition in the mixed monolayers was deduced to be 2:1 for AA and C<sub>18</sub>DAO. The resultant  $\Pi$ -A curves well fitted with the observation.

It is concluded that the microphase separation occurs with the mixed clusters as well as free C<sub>18</sub>DAO molecules in the mixed monolayer.

Abbreviations used : C<sub>18</sub>DAO/octadecyldimethylamine oxide/AA; arachidic acid

Key words : mixed monolayer/cluster/octadecyldimethylamine oxide/arachidic acid/ $\Pi$ -A isotherm curve

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### Introduction

Mixed monolayers that consist of insoluble and soluble amphiphiles at the air-water interface are a kind of models for studying the penetration of a soluble amphiphile into an insoluble monolayer. The molecular arrangement of such monolayers at the air-water interface has been studied from the biophysical and biotechnological viewpoints<sup>1~8)</sup>. Mori and Imae<sup>1)</sup> studied the monolayers formed by octadecyldimethylamine oxide

{CH<sub>3</sub>(CH<sub>2</sub>)<sub>17</sub>NO(CH<sub>3</sub>)<sub>2</sub>, C<sub>18</sub>DAO} and arachidic acid {CH<sub>3</sub>(CH<sub>2</sub>)<sub>18</sub>COOH, AA} by atomic force microscopy (AFM) and  $\Pi$ -A isotherms. Both alkyl chain lengths are nearly equal each other and are sufficiently long to make a monolayer at the air-water interface. However, the hydrophilic groups of the amphiphiles are different, that is, one is easily hydrated and another is less hydrated. Although the respective molecular orderings in the pure monolayers of C<sub>18</sub>DAO and AA were proposed, the distribution of the components in the mixed monolayer has been still unclear. In this paper, we analyze the  $\Pi$ -A isotherm curves of respective pure and mixed monolayers to estimate the cluster composition in the mixed monolayer.

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## Model

The C<sub>18</sub>DAO, of which hydrophilic head, amine oxide, exists as either a non-ionic or cationic (protonated) species, depending on the pH of the aqueous solution<sup>9,10</sup>, is a weak-base amphiphile in pure water at room temperature. Another amphiphile, AA, is a typical fatty acid with a saturated hydrocarbon chain. The  $\Pi$ -A isotherm curves of AA, C<sub>18</sub>DAO, and their mixtures on water subphase of pH 6.5 at 25°C have been reported by Mori and Imae<sup>11</sup>. They suggested by AFM observation<sup>11</sup> that, while the pure monolayer of AA is in a compact packing state, hydrophilic groups of C<sub>18</sub>DAO are arranged loosely in the monolayer.

The poor packing of C<sub>18</sub>DAO monolayer is assumed to be due to the hydration around the amine oxide group; the head group is enveloped by eight hydrated water molecules. This was supported by comparison of the AFM images of an aged monolayer of C<sub>18</sub>DAO with the fresh one<sup>11</sup>. Kato and Imae found the short range-repulsion due to the hydration of the amine oxide head group facing the aqueous solution by measuring surface force between glass beads<sup>11</sup>. Therefore, the  $\Pi$ -A isotherm curve of the pure C<sub>18</sub>DAO monolayer was greatly expanded in comparisons with that of the pure AA. On the other hand, the AFM image of the mixed monolayer suggested that any phase separation into respective clusters of AA and C<sub>18</sub>DAO (1:1) in the mixed layer did not apparently occur, but the heterogeneous arrangement of the extended and poorly extended alkyl chains was observed<sup>11</sup>.

Because Fainerman *et al.*<sup>12</sup> have demonstrated in the AA monolayer of pH 11 at 25°C that the clusters are already formed even in the region of  $\Pi = 0$ , the clusters are considered to be not almost responsible for surface pressure. Therefore, it is assumed that C<sub>18</sub>DAO molecules which exist individually without any formation of mixed clusters with AA in the mixed monolayer are only responsible for the surface pressure, but the residual C<sub>18</sub>DAO molecules which form mixed clusters

with AA molecules are not responsible.

Based upon this assumption, we estimated the ratio of free C<sub>18</sub>DAO molecules to the total C<sub>18</sub>DAO molecules and the mixed cluster's composition in the mixed monolayers by analysis of the  $\Pi$ -A isotherm curves of the pure C<sub>18</sub>DAO, AA and mixed monolayers.

## Results and Discussion

The  $\Pi$ -A isotherm curve was expanded as the mixed ratio of C<sub>18</sub>DAO increased, but the shape of the curve came to be similar to that of the pure C<sub>18</sub>DAO monolayer. This tendency has been observed for the mixed monolayers of docosyldimethylamine oxide and stearic acid<sup>12</sup>, where stearic acid is very condensed and is seen to affect markedly the mixed monolayers.

The empirical equations were numerically estimated for the  $\Pi$ -A isotherm curves of the pure C<sub>18</sub>DAO and pure AA monolayers, separately. It was found that the exponential equations as a function of A, occupied surface area/molecule, were best fitted on the curve of Eq. [1], as shown in Fig. 1.

$$\Pi = B/\exp \{ (A/C)^D \} \quad [1]$$

where B, C, and D are arbitral coefficients. The regression analysis curve gave the coefficients of the empirical equations, shown as follows, respectively. C<sub>18</sub>DAO; B = 517 (mN/m), C = 9.47 ( $\text{\AA}^2$ ), and D = -1.94, and AA ; B =  $1.31 \times 10^6$  (mN/m), C = 1.81 ( $\text{\AA}^2$ ), and D = 1.0. This indicates that the surface pressures for C<sub>18</sub>DAO and AA exponentially decrease, though the coefficients are significantly different between them.

Because the shapes of the mixed monolayers curves for AA: C<sub>18</sub>DAO = 1 : 2 and 1 : 4 are very similar to the pure C<sub>18</sub>DAO curve, but different from the pure AA one (Fig. 1), they can be scaled along to the pure C<sub>18</sub>DAO curve. When the pure C<sub>18</sub>DAO curve is represented as  $\Pi = f(A)$ , the mixed layer curves can be drawn as  $\Pi = f(kA)$ , using a scale factor, k.

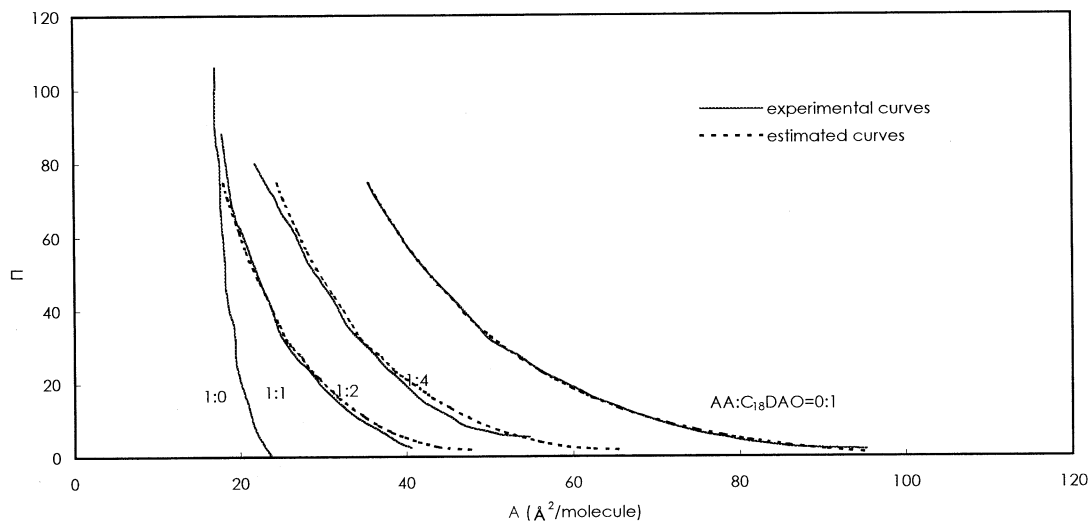


Fig. 1 The experimental curves of  $\Pi$ -A isotherms of AA,  $C_{18}DAO$ , and their mixtures and fitting curves redrawn based upon the molar ratio of AA:  $C_{18}DAO = 2 : 1$  in the complex cluster

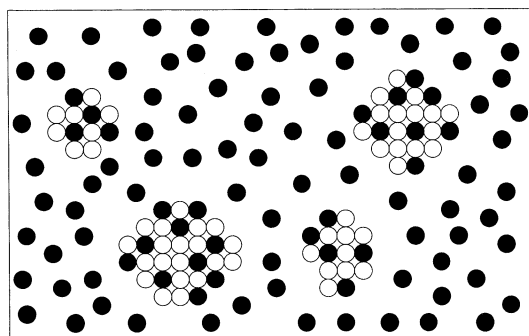


Fig. 2 Phase separation model in the mixed langmuir monolayer of AA :  $C_{18}DAO = 1 : 2$   
AA ; ○,  $C_{18}DAO$  ; ●

According to this procedure, the scaling factors for the curves were estimated to be 1.45 for AA :  $C_{18}DAO = 1 : 4$  and 1.96 for 1 : 2, respectively. Because 80% of the total molecules is  $C_{18}DAO$  molecules for the AA:  $C_{18}DAO = 1 : 4$  in the mixed layer, it is calculated that free  $C_{18}DAO$  molecules exist in 69% and the residual 11%  $C_{18}DAO$  molecules form the complex clusters with AA. Consequently, the ratio in the complex cluster could be deduced to AA :  $C_{18}DAO = 1 : 0.55$ .

For the 1 : 2 curve, free  $C_{18}DAO$  molecules exist in 51 % of the total molecules and the residual 16%  $C_{18}DAO$  molecules form the complex clusters, and accordingly the ratio in the complex cluster is deduced to AA :  $C_{18}DAO = 1 : 0.48$ . Therefore, the molar ratio of the clustered complex corresponds approximately to AA :  $C_{18}DAO = 2 : 1$ . The calculated curves were redrawn based upon the molar ratio (2 : 1), as shown in Fig. 1 and fitted well to the observed ones. The curves calculated by Eq.[1] were nearly equal to those calculated from the data points of the experimental curves, and the estimated curves shown in Fig. 1 were also calculated directly from the experimental points.

On the other hand, the curve of AA:  $C_{18}DAO = 1 : 1$  comes close to the pure AA one, though the surface pressure is slightly observed above  $A = ca.24 \text{ \AA}^2/\text{molecule}$  in the curve of 1 : 1. It is considered that the mixed clusters approach each other closely due to increase of the number of the mixed clusters below  $A = ca.20 \text{ \AA}^2/\text{molecule}$ , bringing about strong repulsion. This is assumed to cause such steep rise of the surface pressure of the curve (1 : 1).

In this study, based upon the assumption that free

C<sub>18</sub>DAO molecules without complex formation are responsible for the surface pressure, but the clusters are not, it was assumed by scaling the curves of the mixed monolayer to the pure C<sub>18</sub>DAO that free C<sub>18</sub>DAO molecules as well as the mixed clusters exist in the mixed monolayer, in which the molar ratio of the cluster is 2 : 1 for AA and C<sub>18</sub>DAO. Therefore, it is concluded that the microphase separation occurs with mixed clusters as well as free C<sub>18</sub>DAO molecules in the Langmuir mixed monolayer, as shown in Fig. 2. This model seems to be not incompatible with the picture observed by the AFM<sup>1)</sup>. Our result suggests that such analysis of the  $\Pi$ -A isotherm curves might enable to estimate the complex composition in the mixed Langmuir monolayers, where one surfactant can form easily clusters and another can form scarcely clusters.

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