

Electron Microscopic Evidence
for Thermally Induced Phase Separation
in a Monolayer Containing Dye-Surfactant and Fatty Acid

Keiji IRIYAMA, Toshinari ARAKI,⁺ and Takashi IWASAKI⁺⁺
Institute of Medical Science,
The Jikei University School of Medicine,
Nishi-Shinbashi, Minato-ku, Tokyo 105
⁺Frontier Technology Research Institute,
Tokyo Gas Co. Ltd., Shibaura, Minato-ku, Tokyo 105
⁺⁺Department of Physics, Faculty of Science and Engineering,
Chuo University, Kasuga, Bunkyo-ku, Tokyo 112

An evidence for the thermally induced phase separation
in a mixed monolayer on an aqueous subphase was electron
microscopically visualized.

As reviewed by Kato,¹⁾ the dynamic properties of a monolayer at an air-water interface has gradually been accumulated, especially for preparing a Langmuir-Blodgett (LB) film system of high quality. Kato et al.²⁾ suggested the usefulness of the isobaric thermal treatment of a monolayer on an aqueous subphase to reduce defect in monolayers. To our knowledge, however, there was no appropriate method for the determination of an LB-film structure on the molecular scale.³⁾ Progress in almost any area of chemistry and physics depends on reliable methods. Recently, Inoue *et al.*⁴⁾ succeeded in the direct observaiton of lattice images of cadmium arachidate (CdA) in LB-films. We also could add a replica technique for electron microscopic observation of LB-film surface structure.⁵⁾ When a morphological change in a mixed monolayer system was investigated as a function of aqueous subphase temperature, the thermally induced two-dimensional phase separation in the film system was able to be visualized by using the replica technique coupled with transmission electron microscopy.

The chemical structure of a surface-active spiropyran (SP-98) used in this study is shown in Fig. 1. An aliquot of a mixed solution containing 1×10^{-4} mol \cdot l $^{-1}$ SP-98 and arachidic acid (AA) with a molar ratio of [SP-98] : [AA] = 1 : 2 in chloroform was carefully delivered onto an aqueous subphase containing 1×10^{-4} mol \cdot l $^{-1}$ CdCl₂, whose pH was adjusted to 6.0 by the addition of Na₂CO₃, to allow the formation of a mixed monolayer. Figure 2 shows a surface pressure-area isotherm of the mixed monolayer

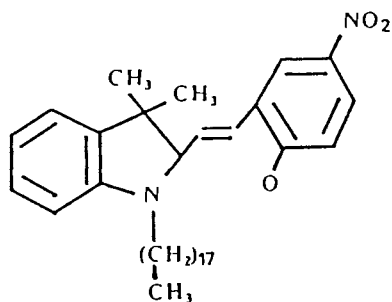


Fig. 1. Chemical structure of a surface-active spiropyran (SP-98).

formed on the aqueous subphase at 18 °C. Each monolayer was deposited onto a glass plate at a surface pressure of 30 mN/m. A constant surface pressure given to a monolayer was automatically monitored. A replica film of each monolayer-coated glass plate was prepared according

to the same procedure as employed in our previous report.⁵⁾ Each replica film was examined with a JEM 100 S or EX 1200 electron microscope (JEOL).

Figure 3 shows a replica image of the mixed monolayer. Numerous micro-structural patterns are visualized. We assumed that the thermal treatment of the monolayer on the aqueous subphase might be able to diminish the micro-structural pattern as shown in Fig. 3. After the monolayer preparation at 18 °C and 30 mN/m, the subphase temperature was raised up to 40 °C and then lowered to the original value. The monolayer treated thermally was deposited onto a glass plate. Figure 4 shows a replica image of the thermally treated monolayer. The replica image shown in Fig. 4 suggests that the thermal treatment of the mixed monolayer induces two-dimensional phase separation between the monolayer components on the electron microscopic scale (see the

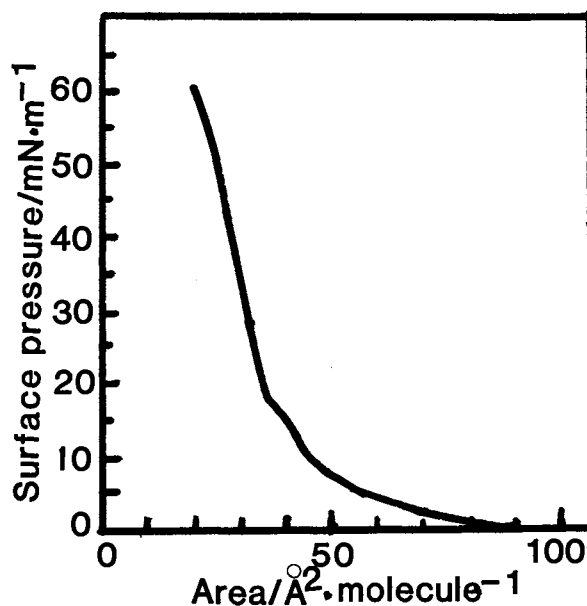


Fig. 2. A typical surface pressure-area curve of a mixed monolayer containing SP-98 and AA. For explanations, see the text.

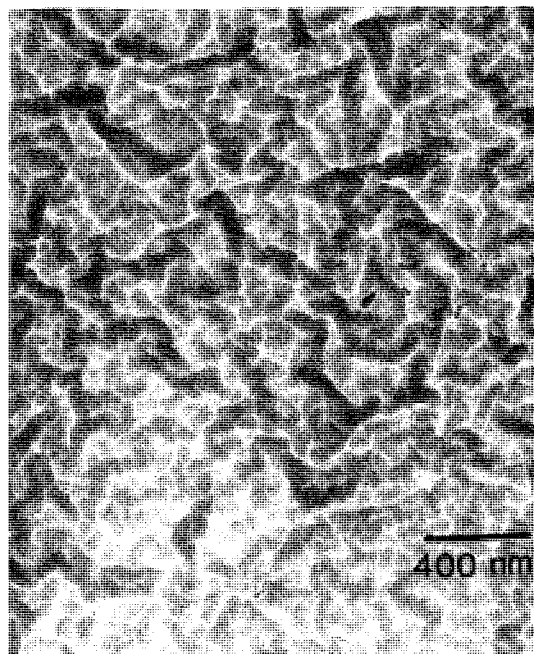


Fig. 3. A typical replica image of a mixed monolayer deposited onto a glass plate at 18 °C under a constant surface pressure controlled at 30 mN/m.

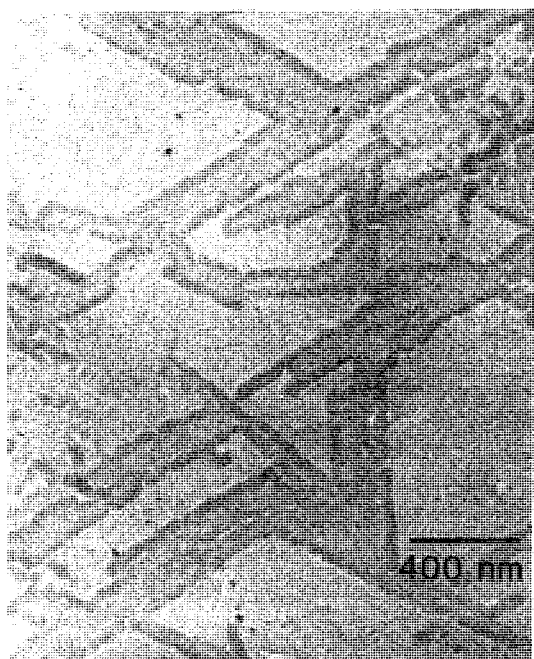


Fig. 4. A typical replica image of the thermally treated mixed monolayer. For explanations, see the text.

scale bars in Figs. 3 and 4).

However, we were unable to determine the two-dimensional distribution of the film components due to the lack of an appropriate technique. To our knowledge, there has been no report on the two-dimensional phase separation in a monolayer system on the electron microscopic scale, although this event has been indirectly suggested in the literatures.⁶⁾

As pointed out by Kato et al.,²⁾ monolayers compressed to a certain high surface pressure show area relaxations with time under constant pressure. The relaxations take a very long time to be completed, especially at low temperatures in a condensed state, and part of some bulk quasi-stable states of film molecules

cannot be relaxed in practice within common experimental time scale. Fortunately, it can be completed in a relatively short time by raising the subphase temperature under constant surface pressure. In this study, we employed the so-called isobaric thermal treatment technique²⁾ in order to diminish not the structural defect but the micro-structural pattern (see Fig. 3). As demonstrated in Fig. 4, however, the isobaric thermal treatment induced the two-dimensional phase separation between the film components. On the basis of our finding, the thermal treatment seems to be useful in preparing a defect-free pure monolayer. In addition, the rate for temperature decrease as well as for temperature increase will influence the micro-structure of a thermally treated monolayer system on an aqueous subphase, since it has generally been recognized that the rate for temperature decrease in preparing a single three-dimensional crystal can strongly influence its size and shape.

If the thermally induced two-dimensional phase separation in a mixed monolayer is purposefully controlled, numerous functional units will be systematically arranged after the thermal treatment. The two-dimensional phase separation between the functional units and their matrix is schematically illustrated in Fig. 5. In Fig. 5 (b), the squares are symbolized as the thermally induced functional units in a mixed monolayer. In our previous report,⁷⁾ we aimed to regulate the size and distribution of the so-called J-aggregate as a functional unit such as a reaction center in

plant photosynthesis. However, we were unable to carry it out. Recently, we found that (unpublished result) that an appropriate thermal treatment could induce the enhanced formation of the two-dimensionally granulated J-aggregate particles in a pure monolayer of

another surface-active spiropyran

accompanied with an increase of a new electron spin resonance (ESR) signal.

Without any formation of the granules, no visible absorption and ESR signal

corresponding to the J-aggregate formation could be observed. The thermally induced two-dimensional phase separation in a mixed monolayer system will be applicable for preparing an ultra-thin film of functional interest, in which thermally induced functional units is purposefully arranged. Further effort along with the direction of this study will allow the construction of opto-electronic devices.

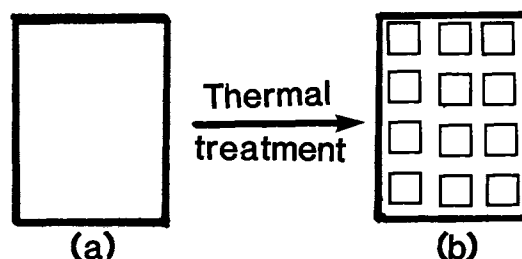


Fig. 5. A schematic illustration of the thermally induced functional unit formation in a mixed monolayer. For explanations, see the text.

References

- 1) T. Kato, Yukagaku, 11, 141 (1990).
- 2) T. Kato, K. Ohshima, and K. Suzuki, Thin Solid Films, 178, 37 (1989).
- 3) K. Iriyama and T. Araki, Chem. Lett., 1990, 1189, and references cited therein.
- 4) T. Inoue, K. Yase, M. Okada, S. Okada, H. Matsuda, H. Nakanishi, and M. Kato, Jpn. J. Appl. Phys., 28, L 2037 (1989).
- 5) A. Tanaka, M. Yamaguchi, T. Iwasaki, and K. Iriyama, Chem. Lett., 1989, 1219.
- 6) See, e.g., G.L. Gains, Jr., "Insoluble Monolayers at Liquid-Gas Interfaces," Interscience Publishers (1966).
- 7) K. Iriyama, M. Yoshiura, Y. Ozaki, T. Ishii, and S. Yasui, Thin Solid Films, 132, 229 (1985).

(Received May 7, 1990)