Salt Formation in the Langmuir-Blodgett Films of Arachidic Acid Mixed with Amphiphilic Ammonium Ions and an Amphiphilic Amine

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In the Langmuir-Blodgett (LB) films of arachidic acid (AA) mixed with amphiphilic ammonium ions or an amphiphilic amine, AA was mixed with the second component at the molecular level and formed salt when the fraction of AA was not larger than 0.5. Further the fraction of the second component in the mixed LB films was smaller than that in the spreading solution with the fraction of the second component larger than 0.5.

The LB technique has been used to fabricate supramolecular structures with multiple components.[1] One of the problems is that the different components are not easily mixed at the molecular level due to the phase separation often observed in the mixed LB films.[2,3] To suppress the phase separation, the usage of salt formation between different species is promising. Salt formation in the monolayer at the air-water interface has been concluded, though indirectly, using grazing incidence X-ray diffraction measurements.[4] Deprotonation of octadecanoic acid and protonation of 1-octadecylamine (OA) in the mixed LB films have been shown using IR spectroscopy.[5] However, it is unknown whether an amphiphilic fatty acid, when mixed with a cationic amphiphile or an amphiphilic amine in the spreading solution, is mixed at the molecular level with the second component in the LB films. Further, it has not been investigated whether the mixing ratio in the LB film is the same with that in the spreading solution for these systems. This is also important since the mixing ratio in the LB film will provide us with valuable information on the structure of the film.

In this study, we will report on the salt formation of AA (or dAA: deuterated arachidic acid) with 1-docosyltrimethylammonium bromide (DAB), 1-docosylpyridinium bromide (DPB) or OA, focussing both on the molecular mixing state and on the mixing ratio in the LB films.

A chloroform solution containing mixture of AA/DAB, AA/DPB, or AA/OA was spread onto pure water. Figure 1 shows the π-A isotherms of AA/DAB system. It is clear that the Raoult's law or the additivity rule does not hold in this case, indicating that the two components are mixed at the molecular level.

IR transmission and reflection-absorption spectra of the dAA/DAB mixed LB films can be used to obtain information on the dissociation of dAA and the packing of each component.[6] The usage of dAA enables us to observe the vibration bands due to CD_2 (CD_3) of dAA and CH_2 (CH_3) of DAB separately.[7]

Figure 2(a) shows the IR spectra in the region of C=O stretching of dAA/DAB mixed LB films. At the mixing ratio (dAA/DAB) of 8/2, a band is seen at around 1720 cm^{-1} assigned to the C=O stretching vibration of COOH, whereas this band is almost missing when the mixing ratio is 5/5 and 2/8. On the other hand, two bands assigned to the C=O antisymmetric stretching (ca. 1570 cm^{-1}) and symmetric stretching (ca. 1390 cm^{-1}) vibration of COO^- are recognized except when the mixing ratio is 8/2. This shows that dAA is deprotonated when the fraction of dAA is not larger than 0.5. This suggests that the deprotonated dAA forms salt with DAB and is mixed at the molecular level due to electrostatic interaction.

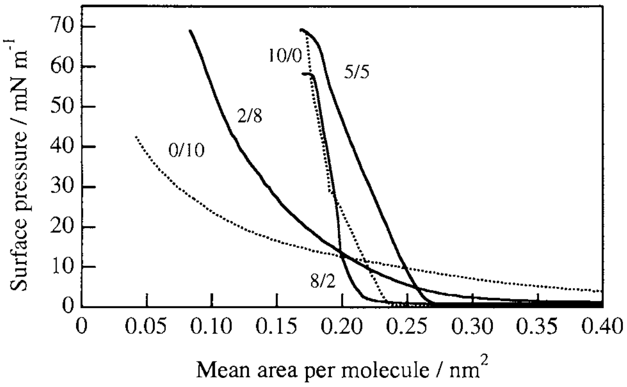

Figure 1. π-A isotherms of AA/DAB mixed monolayers at the air-water interface at 290 K. Mixing ratio AA/DAB is shown in the figure.

Figure 2(b) shows the IR spectra in the region of CD_2 bending vibration of dAA/DAB mixed LB films. This vibration mode is a doublet, as shown in the spectrum of a dAA single-component LB film, when the alkyl chains crystallize with the orthorhombic subcell packing.[8,9] However, this band is a singlet for all the mixing ratios investigated in this study. This indicates that the packing of dAA suffers significant modification by the introduction of DAB. Possible modification mechanisms are (1) a significant number of dAA molecules in the orthorhombic subcell are replaced by DAB molecules, (2) replacement of dAA by DAB is accompanied by the change in the packing mode, and (3) the packing mode of dAA is changed by the surrounding DAB molecules without penetration of DAB into the dAA lattice. Considering that dAA is deprotonated, the mechanism (1) or (2) should be responsible for the present phenomena.

Fraction of DAB in the LB films can be estimated by the IR and XPS measurements. Comparison of the intensity of antisymmetic stretching band of CD_2 of dAA and that of CH_2 of DAB in the IR spectra of the mixed LB films gives us information on the ratio of dAA to DAB. It is to be noted that the molar absorptivity of the antisymmetic stretching band of CD_2 differs from that of CH_2. Further the dAA and DAB chain axes were found to have virtually the same tilt angle using the

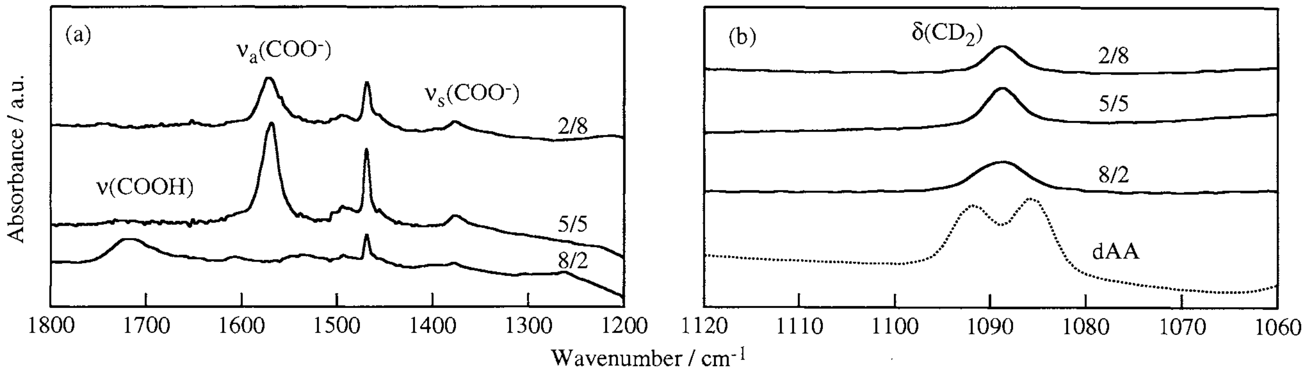

Figure 2. IR transmission spectra in C=O stretching (a) and CD_2 bending regions (b) of the dAA/DAB mixed LB films. Mixing ratio dAA/DAB is shown on the right of each spectrum. In part b, the spectrum of dAA LB film is also shown.

calculations employed by Umemura et al.,[7,10] indicating the validity of the above treatment. XPS measurements yields the atomic ratio of C to N, which can be reduced to the molar ratio of dAA to DAB.

The fraction of DAB of the dAA/DAB mixed LB films obtained from the measurements of IR and XPS is plotted against that in the spreading solution in Figure 3. If the composition of the LB film is the same with that in the spreading solution, a straight line passing through the origin with a slope of unity should be obtained. It is clear that the above assumption does not hold when the fraction of DAB in the spreading solution is larger than 0.5, whereas the composition of the LB film is similar to that in the spreading solution with the fraction of DAB not larger than 0.5. In other words, when the number of DAB is smaller than that of dAA in the spreading solution, the mixing ratio does not change on transfer to solid substrates, whereas some of the DAB molecules are not readily transferred onto solid substrates when the number of DAB is larger than that of dAA. This suggests that some of the DAB molecules which do not form salt with dAA are not deposited on solid substrates probably due to the solubility of DAB or to the scarcity of intermolecular interaction with the surrounding molecules.

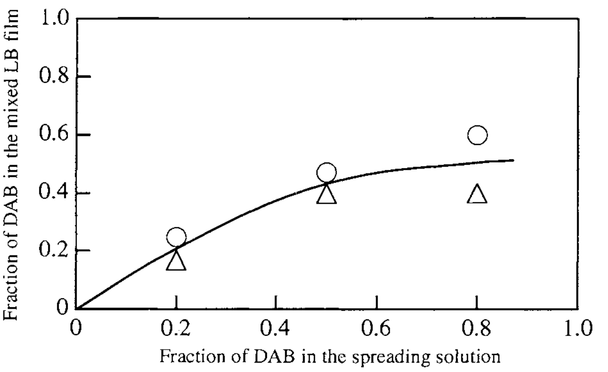

Figure 3. Composition of the dAA/DAB mixed LB films obtained from IR (○) and XPS (△) measurements as a function of the composition of the spreading solution. The curve is to guide the eye.

Similar results were obtained for the dAA/DPB and dAA/OA mixed LB films: (1) Raoult's law did not apply to the π-A isotherms, (2) dAA was deprotonated in the mixed LB films when the fraction of dAA was not larger than 0.5, which was concluded from the appearance of 1570-cm^{-1} and 1390-cm^{-1} bands, (3) the orthorhombic subcell packing of dAA was not maintained in the mixed LB films, judging from the fact that the CD_2 bending vibration mode of dAA was a singlet, and (4) the fraction of DPB or OA in the mixed LB film was smaller than that in the spreading solution on the basis of analyses of IR and XPS spectra when the fraction of dAA was smaller than 0.5.

The results indicate that dAA is mixed with DAB, DPB, and OA at the molecular level in the mixed LB films and forms salt with the second component when the fraction of dAA is not larger than 0.5. Further the fraction of the second component in the mixed LB films was smaller than that in the spreading solution with the fraction of the second component larger than 0.5. This study suggests that the phase separation often observed in mixed LB films can be suppressed by mixing the two components at the molecular level using the electrostatic interaction between the component molecules, providing a means to control the film structures precisely.

References and Notes

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