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Selective ion-sensing based on Langmuir-Blodgett films having potential sensitive dyes. Effect of monolayer matrix on host-guest interaction of valinomycin with potassium ion

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Surface pressure-area isotherms of anionic monolayers, arachidic acid and didodecylphosphate, containing valinomycin and a potential sensitive dye were measured on both KCl and NaCl subphases. The isotherm indicated that a phase separated cluster of valinomycin was formed in the arachidic acid monolayer. Fluorescence imaging of the surface monolayer with a newly constructed fluorescence microscope attached to a Langmuir film balance proved phase separation in the arachidic acid monolayer. The isotherm of arachidic acid on a KCl subphase was very similar to that on the NaCl subphase, but a small contraction was found on the KCl subphase. An isotherm of a valinomycin monolayer complexed with potassium ion, however, was more expansive than that for pure valinomycin. A large expansion in the isotherm observed in a mixed monolayer with didodecylphosphate suggested that valinomycin was homogeneously distributed in the fluid monolayer matrix. The isotherm on the KCl subphase was very different from that on the NaCl subphase. Based on results of fluorescence imaging, conditions for preparation of an optical ion-sensor using a Langmuir-Blodgett film which detects potassium ions as fluorescence change of the potential probe are discussed.

INTRODUCTION

Potassium ion sensors using valinomycin incorporated in Langmuir-Blodgett (LB) films have been previously reported. Petty *et al.* found that valinomycin in LB films could not capture potassium ion in the absence of a secondary component such as arachidic acid[1] or phosphatidic acid.[2] Umezawa *et al.* reported that the surface charge of a matrix monolayer in which valinomycin was embedded strongly affected inclusion of potassium ion.[3] A surface pressure-area (π-A) isotherm of dioctadecyldimethylammonium monolayer containing valinomycin was not affected by the presence of potassium, sodium, or lithium dissolved in the water subphase. On the other hand, owing to specific host-guest interactions at the air water interface, a small condensation effect on the π-A isotherm of a didodecyl phosphate monolayer containing valinomycin was observed when the monolayer was spread on a KCl subphase.

Wolfbeis and Schaffer have proposed a new type of optical ion-sensor specific to potassium ions.[4,5] The ions were detected by the fluorescence change of a potential-sensitive dye incorporated into a Langmuir-Blodgett film made from arachidic acid and deposited on a glass slide. The fluorescence change of the probe, octadecylrhodamine B, was ascribed to a potential change induced by the host-guest interaction that occurred at the lipid-water interface. Non-specific response in the fluorescence intensity was observed, however, when the LB film lacking valinomycin was exposed to aqueous solutions of alkali metal ions. In order to exclude a non-specific response, a reference LB film without valinomycin was required in their sensing system.

By using a newly constructed fluorescence microscope attached to a Langmuir film balance,[6] we have determined the factors that influence octadecylrhodamine B fluorescence intensity in the surface monolayer of didodecyl phosphate.[7] The fluorescence image and intensity of the didodecyl phosphate monolayer were found to be strongly affected by lateral-compression-induced phase transition of the monolayer. Fluorescence properties of the potential probe were also

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affected by a non-specific interaction with alkali metal ions (so-called salt effect based on ionic strength change) as well as by a specific host-guest interaction between valinomycin and potassium ion.

In this article, the effect of the matrix monolayer on the host-guest interaction of valinomycin at the air-water interface is investigated by measuring surface pressure-area isotherms and fluorescence imaging. Based on the results of the monolayer studies, preperative conditions for an optical ion sensor based on LB film are discussed.

RESULTS AND DISCUSSION

Figure 1 shows surface pressure-area isotherms for arachidic acid containing 10 mol-% valinomycin on various subphases, on pure water, 10^{-2} M aq. KCl, and 10^{-2} M aq. NaCl at 20°C. A wide plateau in the π-A isotherm at *ca.* 30 mN m^{-1} corresponding to that found for a pure valinomycin forms phase separated clusters in the monolayer matrix of arachidic acid. Fluorescence images of the arachidic acid monolayer on various subphases are shown in Figure 2. Dark patches suggest that crystalline clusters of arachidic acid are formed in the mixed monolayer.[9] The fluorescence imaging is consistent with the result of π-A isotherm measurements. When the concentration of NaCl in the water subphase was increased, the dark domains increased in size and fused together to form a large dark field. Similar morphological changes were observed for the KCl subphase. Due to the self-quenching effect of the potential probe concentrated in a similar area of the fluid monolayer, the fluorescence intensity strongly decreases with crystallization of the monolayer induced by the salt effect. The fluorescence change caused purely by a potential change resulted from a specific host-guest interaction is much smaller than that caused by the morphological change. This is the reason that the reference LB film is required in the sensing system prepared from arachidic acid.

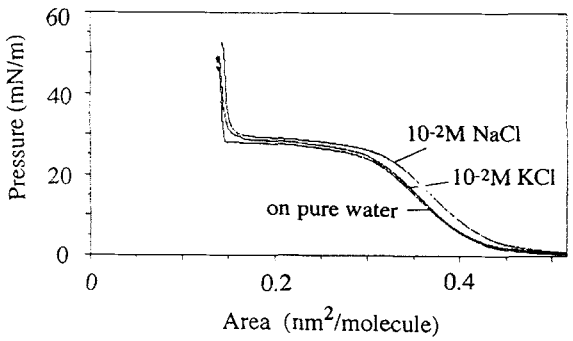


Figure 1 Surface pressure-area isotherms of arachidic acid containing 10 mol % valinomycin at 20°C on various subphases.

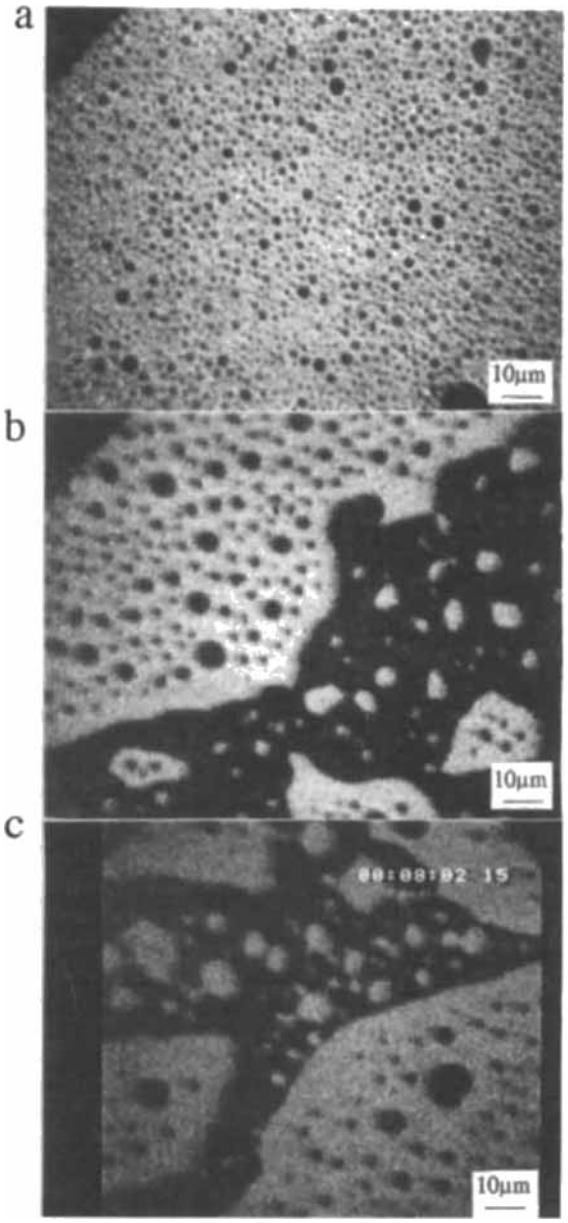


Figure 2 Fluorescence images of the valinomycin-containing arachidic acid monolayer at the air-water interface (23 mN m^{-1}). (a) On pure water subphase, (b) on 10^{-2} M NaCl, (c) on 10^{-2} M KCl.

The isotherms on both the KCl and NaCl subphases are similar and a little more expansive than that on the pure water subphase. The isotherm on the KCl subphase is slightly more condensed than that in the NaCl case. The host-guest interaction of valinomycin with potassium ion is represented as a very small change in the isotherm. A similar condensation effect

of potassium ions on a π-A isotherm has been reported by Umezawa[3] for a didodecyl phosphate monolayer measured at 5°C. They attributed the condensation effect either to the diminution of repulsive membranous negative charge by potassium ion capture or to conformational changes in valinomycin due to host-guest interactions.

The effect of pure valinomycin in the membrane system is observed as a small change in the surface chemistry. Surface pressure-area isotherms for pure valinomycin either with or without potassium ion were measured. Since the pure valinomycin monolayer cannot capture potassium ion,[1] the π-A isotherm 10^{-2} M KCl subphase is exactly the same as that on a pure water subphase (Figure 3). A host-guest complex was prepared by mixing valinomycin and KOH in chloroform. Spectral shifts (from 1753 cm^{-1} to 1741 cm^{-1} for ester carbonyl, from 1654 cm^{-1} to 1650 cm^{-1} for amide I) caused by complex formation[1] were clearly observed by infrared spectroscopy (Figure 4). Expansion in the isotherm was found when the host-guest complex was spread as a monolayer on 10^{-2} M KCl subphase (Figure 3).

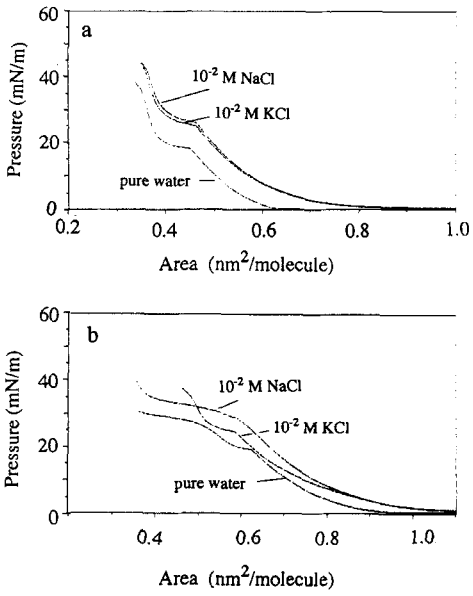


Figure 5 Surface pressure-area isotherms of didodecylphosphate monolayer at 20°C on various subphases. (a) Without valinomycin, (b) with 10 mol % valinomycin.

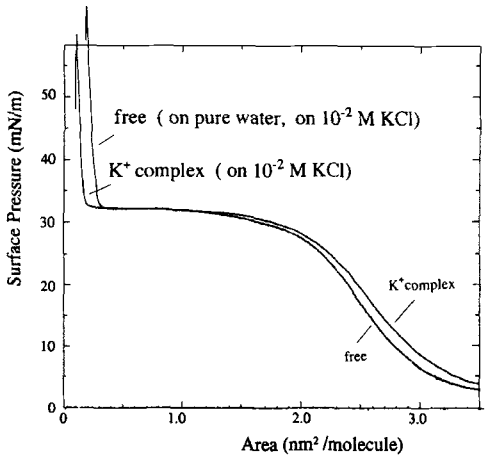


Figure 3 Surface pressure-area isotherms of valinomycin and its potassium ion complex at 20°C.

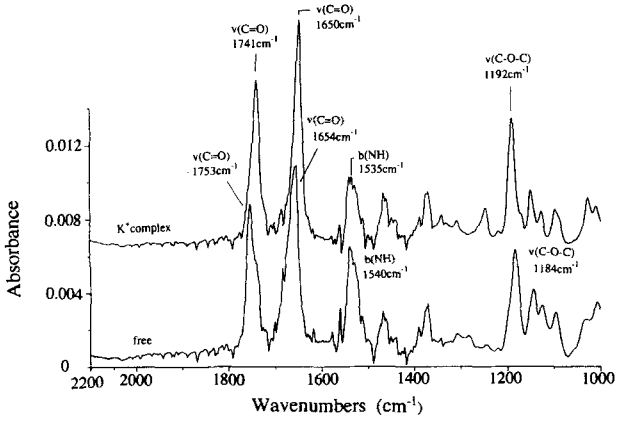


Figure 4 Infrared spectra of valinomycin and its potassium ion complex.

The surface pressure-area isotherm of a didodecyl phosphate monolayer without valinomycin was also found to be affected by the ionic strength of the subphase. The isotherm expanded with increasing sodium ion concentration (Figure 5a). The size of the crystalline domains at the plateau region of the pressure-area isotherm decreased with increasing sodium ion concentration. Addition of potassium chloride to the water subphase leads to a similar change in the pressure-area isotherm and in the crystallization process.[7] The non-specific salt effect is represented as an expansion of the isotherm.

The expanding nature of the mixed monolayer's isotherm on the pure water subphase indicates that valinomycin is homogeneously distributed in the fluid didodecyl phosphate matrix. A different effect of potassium chloride, distinguishable from that of sodium chloride, was found in the pressure-area isotherm (Figure 5b). Although both the host-guest interaction and the salt effect made the isotherm more expansive (see Figure 3 and Figure 5a), the isotherm on the KCl subphase was more contracted than that on the NaCl subphase. The condensation effect may be ascribed to the phase change of the matrix monolayer triggered by the host-guest interaction of valinomycin at the air-water interface. Clusterization of the didodecyl phosphate monolayer is expected to be enhanced by the host-guest interaction.

A remarkable effect of the potassium ion on the domain size was clearly observed in the fluorescence

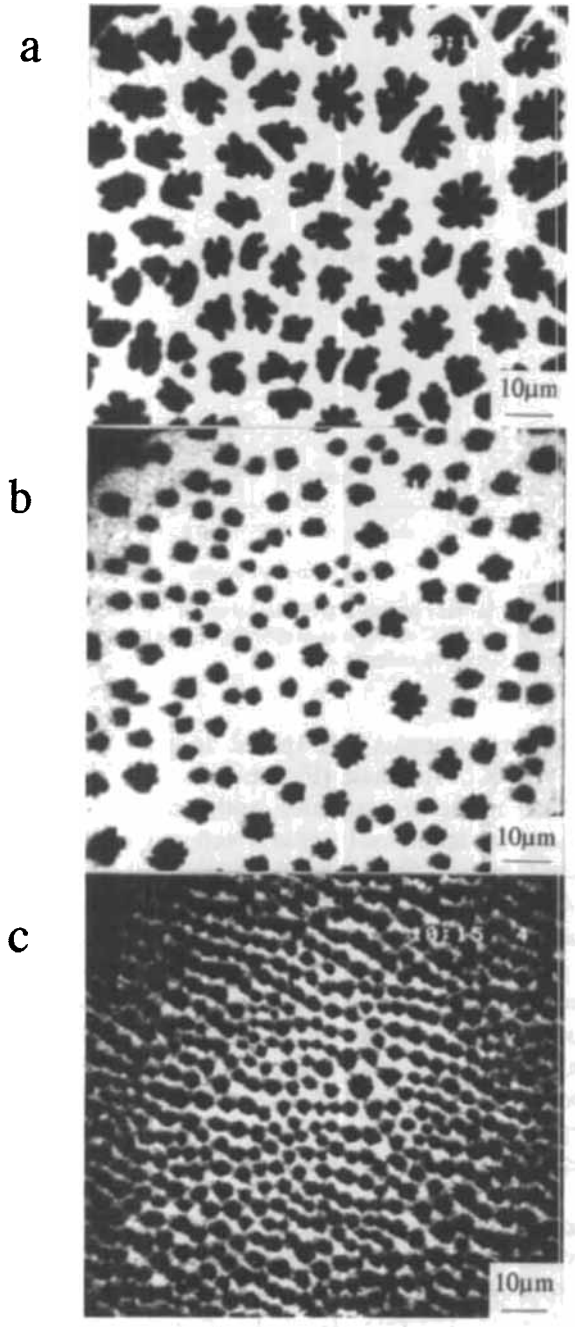


Figure 6 Fluorescence images of the valinomycin-containing didodecylphosphate monolayer at the air-water interface (0.56 nm^2 $molecule^{-1}$). (a) On pure water, (b) on 10^{-2} M NaCl, (c) on 10^{-2} M KCl.

imaging (Figure 6). Formation of very small crystalline clusters densely packed on the surface of the aqueous potassium chloride strongly suggests that the host-guest interaction induces the clusterization of the matrix monolayer. Unfortunately, interpretations of the isotherm change are not so simple at this stage because the π-A isotherm is affected by many closely related factors (physical and chemical, micro and macroscopic, etc.). Details of the host-guest interaction

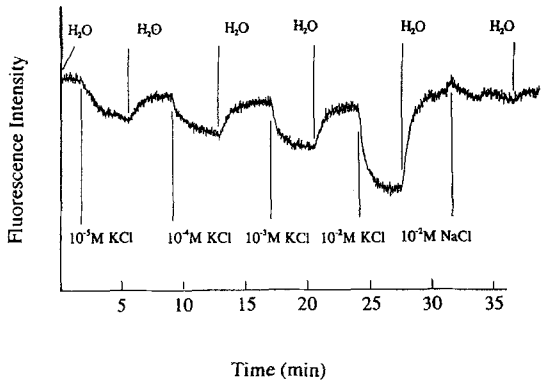


Figure 7 Fluorescence response of the valinomycin-containing LB film to alkali metal ions monitored at 585 nm.

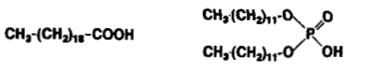
cannot, therefore, be clearly extracted from the change of the π-A isotherm.

From the viewpoint of optical sensing based on host-guest-interaction-induced fluorescence change in the potential probe, a large effect of cluster formation on fluorescence intensity must be excluded. Phase separation in the arachidic acid monolayer decreases the fluorescence selectivity, because the fluorescence intensity of the potential probe is non-specifically diminished by cluster formation. In order to suppress the non-specific response of the salt effect, conditions for preparation of the sensing film must be carefully chosen. If no cluster formation occurs when the monolayer is exposed to potassium ions, the fluorescence response could detect only host-guest interaction.

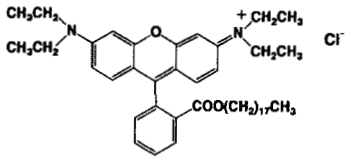
Four monolayers were deposited on a silylated quartz plate as a Y-type LB film by a vertical dipping method at 17 mN/m on a pure water subphase since no crystalline cluster is formed below phase transition (*ca.* 20 mN m^{-1}). The fluorescence response of the LB film to electrolyte solution introduced into the fluorescence flow-cell system is shown in Figure 7. Fluorescence intensity of the potential probe monitored at 585 nm decreases with increasing concentration of potassium ions. Fluorescence response against sodium chloride (10^{-2} M) is very small. Since the crystalline cluster is not formed during exposure of the LB film to the electrolyte solution in the flow-cell, any change in the fluorescence intensity is assumed to represent only the specific host-guest-induced fluorescence response at the monolayer-water interface.

EXPERIMENTAL SECTION

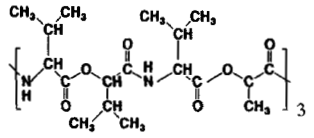
The didodecylphosphate is supplied from Sogo Pharmaceutical Company. Arachidic acid (Serdary Research Lab.) is analytical grade for gas chromato-



arachidic acid didodecylphosphate



octadecylrhodamine B



valinomycin

graphy. Valinomycin (Calbiochem-Behring Co.) and octadecylrhodamine B (Molecular Probes, Inc.) are used without further purification. Chloroform, used as a spreading solvent is of spectroscopic grade (Merk Uvasole). The inorganic salts used are of analytical grade (Wako Chemical Co.). Chloroform solutions of the amphiphiles containing 2 mol% octadecylrhodamine B with 10 mol% of the valinomycin are spread on either pure water or aqueous electrolyte solutions at 20°C. Water (18 MΩ cm) is purified by a Millipore system (Milli-R/Q and Milli-QII).

A fluorescence microscope attached to a Langmuir film balance (USI System Co., FSD-50) is newly constructed.[6] For scanning of a wide area on the water surface, a dichroic mirror and an ocular lens of an epifluorescence microscope (Olympus BHS-RFK) are mounted on a microprocessor-controlled X-Y-Z stage. The fluorescence image of the surface monolayer is monitored by a SIT camera-image processor system (Hamamatsu, C2741 and DVS-1000). A G-excitation filter (546 nm) is used with a dichroic mirror.

Fluorescence imaging of the surface monolayer is a powerful and direct method for proving the phase change of the monolayer. The bright image indicates that the fluorescence molecule, the octadecylrhodamine B, is homogeneously distributed in the fluid monolayer matrix. A dark domain is formed in the crystalline monolayer because the fluorescence molecule is squeezed out as an impurity from the crystalline matrix to the fluid monolayer.

Transmission Fourier transform infrared spectra of pure and potassium complex of valinomycin are measured by JEOL JIR-5500 infrared spectrometer. A thin film of valinomycin is cast from chloroform on a calcium fluoride plate. Potassium complex is prepared by extraction of potassium ion from KOH particles suspended in chloroform solution of valinomycin.[1]

The monolayer is transferred by a vertical dipping method on a quartz plate (1.25 cm × 4.5 cm) silylated with vinyltrichlorosilane (Wako Chemical Co.). A fluorescence flow-cell system for a JASCO FP-700 fluorimeter is assembled using a flow-cell unit (Nippon Sekiei Glass, T-49-UV-0.5) and a quartz plate. One side of the quartz plate is carefully wiped with chloroform to remove the LB film. Sensing film on the other side of the plate is exposed to the aqueous electrolyte solutions pumped into the flow cell by a peristaltic pump (Tokyo Rikakikai Co.). Time courses of the emission intensity at 585 nm of the LB film excited by monochromatic light of 520 nm are recorded. A color filter (O570) transparent above 570 nm is used to remove scattering of the excitation beam.

CONCLUDING REMARKS

The π-A isotherm measurement indicates that phase separated cluster of valinomycin is formed in the arachidic acid monolayer. The isotherm of arachidic acid both on KCl and NaCl subphases are very similar but a small contraction is found on the KCl subphase. While in the fluid monolayer matrix of didodecylphosphate, valinomycin is assumed to be homogeneously mixed in the monolayer. The isotherm on the KCl subphase is quite different from that on the NaCl subphase. The p-A isotherm is found to be affected not only by the specific host-guest interaction of valinomycin but also by the non-specific physicochemical change of the monolayer matrix.

Fluorescence imaging strongly indicates that phase separated cluster of arachidic acid is formed even at low surface pressure both on KCl and NaCl subphase. Fluorescence image and intensity of the didodecylphosphate monolayer are also found to be affected by the non-specific interaction, so-called salt effect, as well as by the specific host-guest interaction of valinomycin with potassium ion. The non-specific effect on the fluorescence change is alsmost excluded when the monolayer is compressed below phase transition. Fluorescence intensity of the LB film specifically responses to potassium ions. A reference LB film without valinomycin is not required in our experiment because our LB film does not response to sodium ions.

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