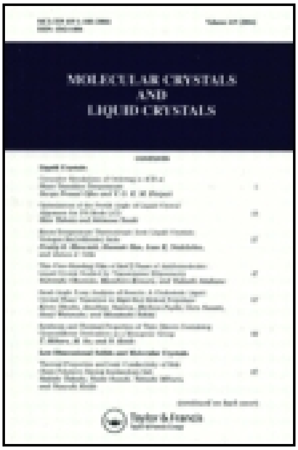

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MONOLAYER PROPERTIES OF 4,5-IMIDAZOLEDICARBOXYLIC ACID MONOSTEARYL ESTER AT THE AIR-WATER INTERFACE

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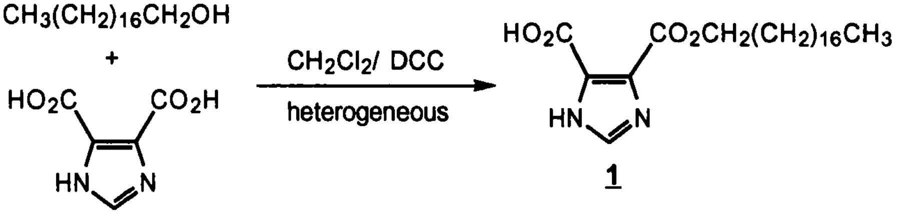
Abstract An imidazole-containing amphiphile, 4,5-imidazoledicarboxylic acid monostearyl ester (1), was synthesized *via* esterification of 4,5-imidazoledicarboxylic acid with stearyl alcohol. Monolayer properties of 1 at the air-water interface were studied by measuring surface pressure-area isotherms. The molecular surface area of the monolayers were expanded at acidic or basic subphases compared with that on pure water subphase. The monolayers on subphases containing metal ions showed increased stability against surface pressure and rather expanded molecular area than on pure water subphase. The monolayers were poorly transferred on quartz and calcium fluoride plates as Z type. UV-visible and FT-IR spectra were used to characterize the LB film.

INTRODUCTION

Molecular recognition by the monolayer on water and the Langmuir-Blodgett (LB) film has characteristics different from the homogeneous systems. Firstly, the host monolayer molecules can be arranged with an orientation on water and substrate surfaces. That gives concentration effect and sensitivity. Second, the two-dimensional arrangement of the molecules can make the cooperative active site, that is, the control of active site for multi-point interaction is possible. However, although many works have been made about the interaction between the host monolayers and guest molecules, the employment of imidazole group as an active component was not reported.[1] The imidazole group, which is usually found as a moiety of histidine or histamine in nature, plays various roles in the living system.[2] For examples, a zinc ion at the active site of carboxypeptidase A is coordinated to two histidine imidazoles and a glutamate carboxylate. Meanwhile, in the another proteolytic enzyme of α-chymotrypsin, the imidazole group constitutes a charge relay network together with aspartic acid and serine. In cytochrome C of an electron transport protein, the iron atom of the heme is bonded to a methionine and a histidine side chain. And, the iron atom in prosthetic groups of myoglobin and hemoglobin is coordinated to imidazole group of histidine, and the another distal histidine prevents CO from binding linearly and so the affinity for CO is markedly reduced. Besides the roles as ligands, imidazole groups gives significant buffering capacity at pH 7, and act as nucleophile to yield a histidine-aldol cross-link in collagen. And, a phosphorylated intermediate of histidine is formed in the active site of succinyl-CoA synthetase in citric acid cycle.

The aims of the present work are to study the mechanism of the formation of a complex structure between the metal ion in the subphase and the ligand in the monolayer and to explore the possibility of obtaining chemical sensors using the LB technique. As an example of the use of imidazole-containing molecule for monolayer spreading , 2-heptadecylimidazole was only found to be employed to fabricate a LB film for the photoinduced proton transfer.[3] In the present work, we have focused on the various roles of imidazole group in the living system as stated above, specifically, on the role as ligands to metal ions. Thus, as the first step to imidazole-containing functional LB films, we synthesized an imidazole derivative, 4,5-imidazoledicarboxylic acid monostearyl ester (1), and report the preliminary results obtained of studying monolayers of 1 and its interactions with metal ions in the subphase. The investigation was carried out by means of surface pressure-area isotherms and spectroscopic techniques such as UV-visible and FT-IR absorption.



EXPERIMENTAL

Materials

An imidazole derivative, 4,5-imidazoledicarboxylic acid monostearyl ester (1), was prepared by esterification of 4,5-imidazoledicarboxylic acid with stearyl alcohol using dicyclohexylcarbodiimide (DCC) as coupling agent. The reaction proceeded heterogeneously for 3 days. After filtration of the reaction mixture, the product was purified by column chromatography: white powder; FT-IR (KBr, cm^{-1}) 2917, 2850 (C-H), 1685 (C=O), 1630, 1575 (carboxylate), 1467 (CH_2), 1375 (CH_3), 1270, 1159 (C-O), 825, 720 (imidazole ring); ^{1}H-NMR(chloroform-d, ppm) 0.92 (t, 3H), 1.11-1.70 (broad s, 32H), 4.35 (t, 2H), 7.65 (s, 1H), 10.20 (broad s, 2H). NaCl (Junsei), KCl (Sigma), $CaCl_2$ (Sigma), $MgCl_2$ (Junsei), $AlCl_3$ (Junsei), and $FeCl_3$ (Katayama) were used as obtained.

Surface Pressure-Area (π-A) Isotherm and LB Transfer

A film balance system HBM-SS (Kyowa Interface Science) was used for measuring surface pressure as a function of molecular area (trough size, 150 x 600 mm). Isotherms were taken at a compression rate of 0.5 mm/sec and at ambient temperature. Chloroform was employed as spreading solvent. Monolayers were spread on pure water or on aqueous metal ions (1.0 x 10^{-4} N) and incubated for 30 min before starting the compression.

The deposition of monolayer was performed in the vertical mode. The transfer onto solid substrates was carried out at a surface pressure of 20 mN/m and at a lifter speed of 5 mm/min. The employed substrates were quartz plate and CaF_2 plate (GL Sciences) for the UV-Vis and the transmission FT-IR measurements, respectively.

Measurements

FT-IR measurement was carried out on a Perkin-Elmer FT-IR spectrometer by the transmission method. UV-vis spectra were obtained by using KONTRON UVIKON 860 spectrophotometer.

RESULTS AND DISCUSSION

Monolayer Formation and Its Transfer on Solid Substrates

Monolayers of 1 were spread with chloroform solution on various aqueous subphases with different pHs or metal ions. π-A isotherms of Figure 1 were obtained from the

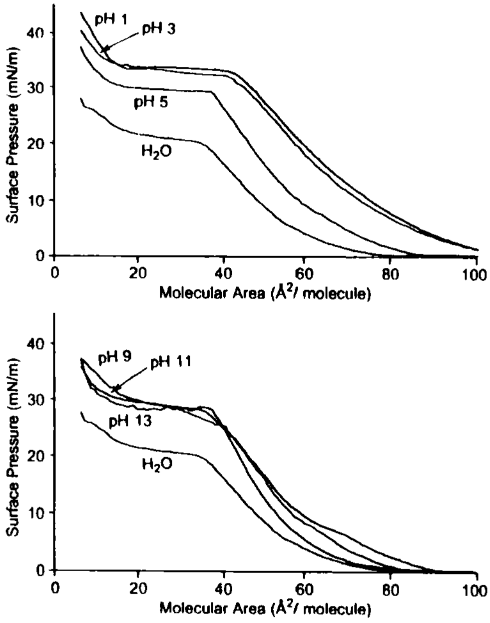


FIGURE 1 π-A isotherms of 1 monolayers at different subphase pH.

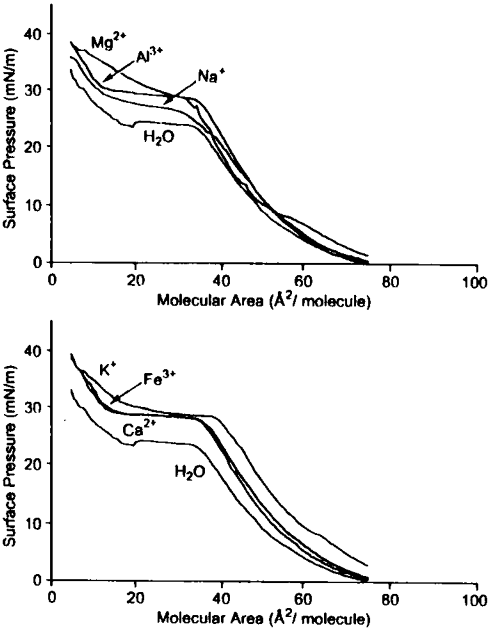
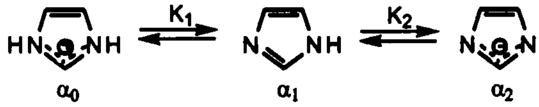


FIGURE 2 π-A isotherms of 1 monolayers on aqueous metal halides.

subphases of different pHs which were adjusted by using aqueous HCl and NaOH. The isotherms show that 1 forms more stable monolayers on acidic or babic pH subphase than on pure water. When compared with the isotherm on pure water, the monolayers give more expanded phases and increased collapse pressures at acidic and basic pHs. Besides the ionization of carboxyl group at basic pH, the imidazole group of 1 can take the three forms according to the pH as shown below.[4] In acidic condition, the imidazole



group is protonated and the positive charges act as repuslive force between the molecules. This is supposed to be a reason of expanded monolayer area. The opposite case can be considered in basic condition. At pH of over 10, the imidazole groups begin to lose the nitrogen proton and become also negatively charged together with carboxylate ion. The major intermolecular force operating at the neutral imidazole groups is probably the hydrogen bond. This attracting force makes the monolayer condensed. The change of

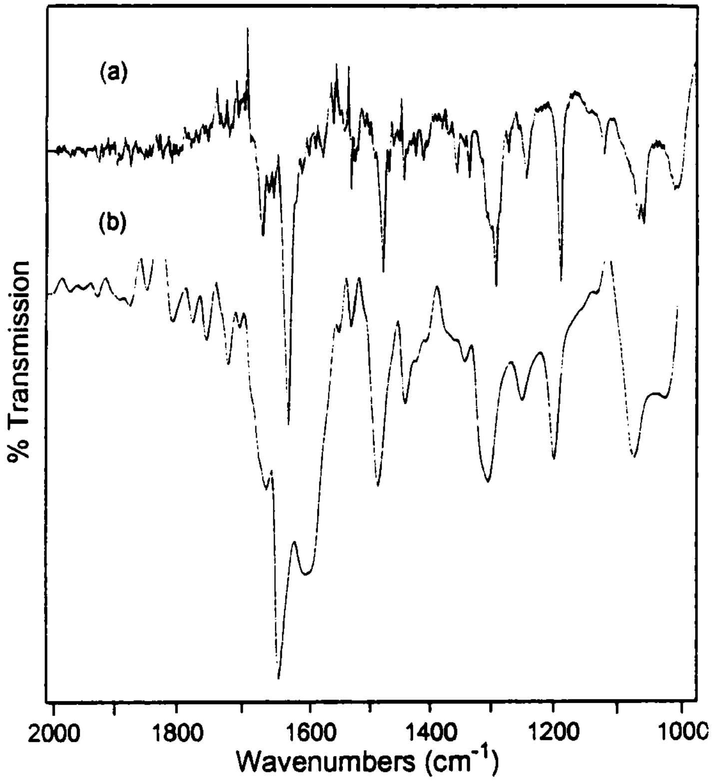


FIGURE 3 FT-IR spectra of 1 LB films on CaF_2 substrates deposited from (a) pure water and (b) aq. $FeCl_3$ subphases.

surface molecular area according to the pH was noticeable at surface pressure of below 20 mN/m. The molecular area of 75 Å^2 at pH 1 was reduced to 48 Å^2 at pure water at the surface pressure of 10 mN/m. The external compressional force operating on monolayer is certainly believed to suppress the area expansion. The change of the molecular area with increasing the pH was slower at basic conditions than at the acidic conditions. A characteristic of the π-A isotherms of 1 monolayers is the plateau occuring about 40 Å^2 of molecular area. The plateau isotherm again begin to arise about 15 Å^2 of molecular area which is below the theoretical cross section area of about 20 Å^2 of hydrocarbon chain, that is, the latter increase of surface pressure is supposed to happen together with monolayer collapse. Therefore, it is thought that monolayer reorganization occur during the area reduction at fixed surface pressure. Direct observation of the monolayers at the air-water interface by Brewster angle or fluorescence microscopy, however, was not applied at this point.

The monolayers were also spread on subphases containing metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, and Fe^{3+}. When compared with the cases in the absence of the metal ions at the same pH, all the monolayers showed more expanded phases in the presence of metal ions as shown in Figure 2. The changes of the molecular areas, however, are not noticeable compared with that of pH changes. This change between the two surface molecular areas is attributed to the interaction of 1 with metal ions at the air-water interface and the consequent change of the monolayer organization. This phenomena have also been observed in the cases of the polymers containing pendants of carboxyls and oligoethyleneglycols.[5,6] The repulsion between ionized carboxylates and the resulting decrease of hydrogen bonding, and decrease of hydration of oligoethyleneglycols and the resulting replacement of pendant oligoethyleneglycol group from the inside of the subphase on to the water surface by the increase of ionic strength were together considered as the reasons of area expansion. In present system, however, the hydrogen bonding is considered to be loosened along with the increase of ionic strength, i.e., the relatively tightened hydrogen bonding of the monolayer on pure water is weakened by the addition of ionic salts. The difference of π-A isotherms according to the ionic species was, however, not remarkable. The coordination of imidazole nitrogen to ferric ion as a ligand is also supposed to be a reason of the additional area change. Further investigation to explore the interaction mechanism is in progress.

The monolayers interacting with metal ions at the air-water interface were transferred onto solid substrates such as a CaF_2 plate and a quartz plate. In all cases, the Z type deposition occurred at a surface pressure of 20 mN/m and a lifter speed of 5 mm/min. A rapid downward dipping speed of 50 mm/min was necessary in order for the deposited films not to be lost during the downward dipping run with slow lifter speed. The transfer ratio was very poor to 0.3-0.6.

Characterization of LB Film

The molecular structures of LB films were investigated by means of FT-IR and UV-Vis spectra. Figure 3 shows two absorption peaks at 1677 cm^{-1} and 1640 cm^{-1}, which are attributed to carbonyl and imidazole ring vinyl groups, respectively. It means the presence of imidazole moiety in the LB film. However, all the LB films obtained from pure water and metal ion-containing subphases gave similar peak patterns. The peaks below 800 cm^{-1} could not be obtained by FT-IR spectra, which are the range of stretching vibrations of coordination bonds due to imidazole-metal ion complex. Further investigations will be performed by means of Raman spectroscopy.

The UV-Vis spectra (not shown here) of **1** obtained from a chloroform solution and LB films on quartz plates. When we observed the absorption phenomena of **1** in the chloroform solution, the typical band due to conjugate structure of imidazole and carbonyl groups revealed at 280 nm. This band have changed to two characteristic bands in the LB films, which had λ_{max} at 197 and 295 nm. The band due to conjugate structure was red-shifted in the LB film compared with the band in chloroform solution. This bathochromic shift can be understood owing to the close stacking of chromophores in the LB films.

ACKNOWLEDGMENT

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REFERENCES

1. G. Roberts, Langmuir-Blodgett Films (Plenum Press, New York, 1990).
2. L. Stryer, Biochemistry (W.H. Freeman and Company, San Francisco, 1981), p. 163 et al.
3. M. Fujihira and Y. Niidome, Thin Solid Films, 210/211, 378 (1992).
4. C.G. Overberger, T. St. Pierre, N. Vorchheimer, J. Lee, and S. Yaroslavsky, J. Am. Chem. Soc., 87, 296 (1965).
5. H. Jeong, J. H. Son, B.-J. Lee, and Y.-S. Kwon, Synthetic Metals, 71, 2021 (1995).
6. J. H. Son, G. Choi, B.-J. Lee, and K. Kurihara, Bull. Korean Chem. Soc., 16, 316 (1995).