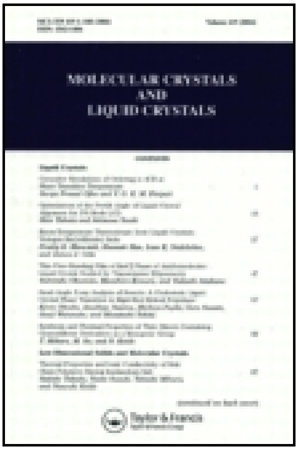

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Spectroscopic Probe of Metal Complexation of Imidazole in the Langmuir Monolayer

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Spectroscopic Probe of Metal Complexation of Imidazole in the Langmuir Monolayer

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An imidazole ring containing amphiphilic molecule, N-[2-(4-imidazolyl) ethyl] 11-mercaptoundecanamide (IMA) was synthesized and constructed into a Langmuir monolayer at the air-water interface to monitor the specific interaction of imidazole residue with metal ions in the subphase.

Keywords: imidazole; surface enhanced Raman spectroscopy; atomic force microscopy; metal complex; Langmuir monolayer

INTRODUCTION

Imidazole is a biologically important residue because imidazole in the various proteins can coordinate to metal ions via the lone pair of electrons on nitrogen atoms[1-2]. In this study, Langmuir monolayers at the air-water interface were constructed by using the Langmuir-Blodgett (LB) technique and characterized by atomic force microscopy (AFM) and surface enhanced Raman spectroscopy (SERS).

EXPERIMENTS

IMA was synthesized as previously reported[3]. A multicompartment circular trough was used to measure the Π-A isotherm and to prepare

Langmuir films at the air-water interface. AFM images were obtained by using the normal contact mode measurement with V-shaped silicon nitride cantilevers (spring constant : 0.067 N/m, SPM-LS, Park scientific instruments, USA). The electrode surface was successively polished with aqueous suspensions of 5 μm, 0.3 μm and 0.05 μm alumina and roughened by an oxidation reduction cycle. The SERS spectra were obtained in the air with 514.5 nm excitation from an argon ion laser source with the output power of 10 mW at the sample. SERS spectra were collected using a triple monochromator coupled with a blue intensified CCD array detector (SPEX Industries, Edison, NJ, USA).

RESULTS AND DISCUSSION

Π-A isotherms of IMA on pH 2, pH 7 and pH 12 subphases were shown in Figure 1. On basic subphase, molecular area at the surface pressure developing point was increased from 46 Å^2 to 61 Å^2 compared with that on neutral subphase. This indicates less aggregation of the molecules due to deprotonation of imidazole and thiol group of IMA on basic subphase. Figure 2 depicts SERS spectra of IMA films on roughened Ag electrodes. In the basic condition, 216 cm^{-1} band appears very weak. When the molecule has a flat orientation on the metal surface, the intensity of the metal - nitrogen stretching mode is decreased[4-5]. Thus, it appeared that the imidazole ring of IMA was oriented flat on the electrode surface when it

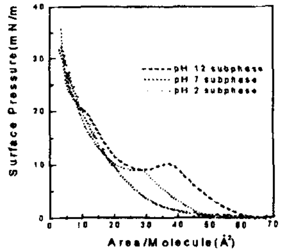


FIGURE 1. Π-A Isotherm of pure IMA on pH 2, pH 7 and pH12 subphases.

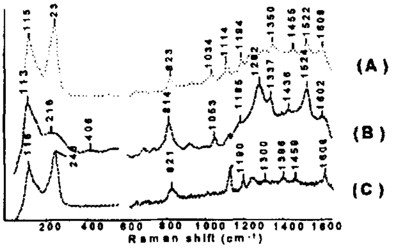
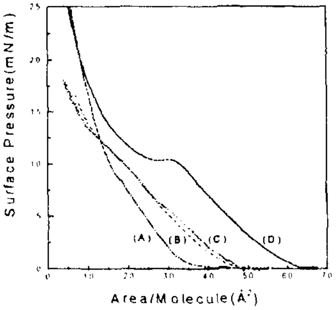


FIGURE 2. SERS spectra of IMA on roughened Ag electrode. IMA films were transferred from;(A) neutral (B) basic (C) acidic subphases.

was transferred from the basic subphase. In the basic condition, the relatively high intensity of the out of plane band at 815 cm^{-1} and decrease in the intensity of in plane band at 1601 cm^{-1} of the ring also suggests that the imidazole ring had parallel orientation to the Ag surface.

Figure 3 illustrates Π-A isotherms of the monolayers of pure IMA on the subphase containing different metal ions(5×10^{-4} M). In the case of Mg^{2+} contained subphase, area/molecule at a surface pressure started to develop was around 65 Å^2 whereas it was decreased to 32 Å^2 on Fe^{3+} contained subphase. When Fe^{3+} ion was contained, the relative intensity of the band at 821 cm^{-1} was lower than that of 1609 cm^{-1} as shown in Figure 4. This indicated that imidazole ring had a highly tilted orientation to the surface. The opposite result was observed in case of Mg^{2+}.

AFM studies of LB monolayers prepared from subphase containing different metal ions also revealed a consistent result as shown in Figure 5. The difference in the molecular packing is interpreted in terms of characteristics of imidazole interaction with metal ion. Due to the strong chelating effect of Fe^{3+}, Cd^{2+} ions to the nitrogen atom in imidazole and to the oxygen atom in amide residue, these ions tend to form "a pseudo ring" type structure as evidenced in SERS spectra. On the other hand, Mg^{2+} ions form simple ionic complexes by electrostatic attraction both with a lone



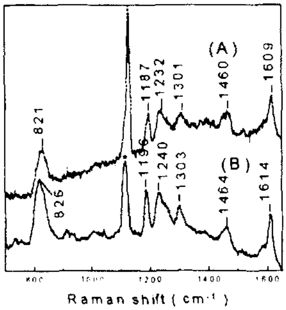


FIGURE 3. Π-A isotherms of IMA on subphase containing metal ions (A) $FeCl_3$, (B) $CdCl_2$, (C) KCl and (D) $MgCl_2$

FIGURE 4. SERS spectra of IMA films transferred from metal ion contained subphase (A) $FeCl_3$, (B) $MgCl_2$

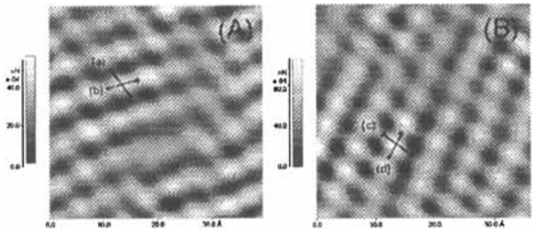


FIGURE 5. AFM images of IMA LB monolayers transferred from (A) $MgCl_2$ and (B) $FeCl_3$ contained subphase. Lattice parameters are (a) 6.9 ± 0.5 Å, (b) 5.3 ± 0.5 Å, (c) 5.8 ± 0.5 Å and (d) 4.4 ± 0.5 Å

pair of electrons of oxygen and nitrogen atoms respectively. That induced a linear complex formation and larger molecular area at the complexed state of the monolayers. AFM data indicated the larger lattice parameter in the case of Mg^{2+} ion, which was consistent with above observation.

CONCLUSION

On a basic subphase, aggregation of IMA was significantly reduced by minimizing the inter-molecular interaction of IMA and by enhancing interaction between IMA and subphase. Simple electrostatic interaction between Mg^{2+} ion with imidazole residue resulted in a linear shape complex formation and larger molecular area, whereas with Fe^{3+} or Cd^{2+}, imidazole formed "a pseudo ring" type structures and consequently IMA monolayers were more compacted at the air-water interface.

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