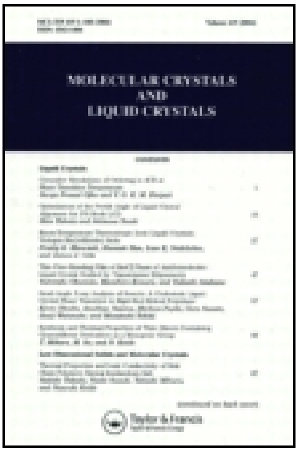

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Langmuir Monolayer Formation of Zinc Complex from 8-Hydroxyquinoline Amphiphilic Ligand

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Langmuir Monolayer Formation of Zinc Complex from 8-Hydroxyquinoline Amphiphilic Ligand

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The behavior of 2-octadecylcarbamoyl-8-hydroxyquinoline(HL) spreading monolayers was investigated as a function of the metal ion concentration and counterions of the subphase. Stable complex monolayers were formed when the subphase contained more than 0.1 mM Zn(II) ion. LB films transferred from subphase containing $ZnCl_2$ were characterized by XPS, UV-vis spectra and low-angle X-ray diffraction.

Keywords: Langmuir; zinc complex; 8-hydroxyquinoline amphiphilic ligand

INTRODUTION

The interactions between metal ions and the amphiphiles functionalized by chelating groups have intensively been studied[1]. 8-Hydroquinoline is known as good chelating reagent. It is very interesting that some complexes of 8-hydroxyquinoline (Hq) and its derivatives such as Alq_3, Znq_2, and Beq_2 can be used as emitting elements in electroluminescent (EL) devices[2]. These EL devices have a high external quantum efficiency and brightness at a driving low voltage below 10 V.

In order to increase the quantum efficiency and brightness of EL devices, we have synthesized a series of 8-hydroxyquinoline amphiphilic ligands and their complexes[3]. Their LB films were fabricated and used as emitters in EL devices[4]. In LB film layers, the presence of long aliphatic chains increases the resistance of the emitting layer better than that of the short chain 8-hydroxyquin-

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oline complexes. Under the same bias, the current passing through the LB films becomes smaller. Thus, the heat energy in the circuit is decreased and the life of the device lengthened.

In addition to the direct use of the amphiphilic complexes of 8-hydroxy quinoline, the complexes formed at the air-water interface by spreading the amphiphilic 8-hydroxyquinoline ligand on subphases containing metal ions may also be used as emitter. With this in mind, the metal ions complexation of an amphiphilic 8-hydroxyquinoline ligand at the air-water interface was investigated[5]. In order to find the optimal conditions for the fabrication of unique properties of LB films, in the present work, the monolayer formation of zinc complex from 8-hydroxyquinoline amphiphilic ligand was studied.

METHODS AND EXPERIMENTS

The amphiphilic ligand, 2-octadecylcarbamoyl-8-hydroxy-quinoline (HL), was synthesized following previous procedures.[3] All the other reagents were of A.R. grade. Formation of air-water monolayers and the deposition of the LB films have been outlined in another paper[5].

RESULTS AND DISCUSSION

HL Spreading Isotherms as a Function of Zinc Ion Concentration

Fig. 1 shows the surface pressure-area (π -A) isotherms of HL monolayers on different concentration of $ZnCl_2$ and pure water at 25 °C. Compared with pure water surface, the curve on 0.01 mM $ZnCl_2$ subphase shows much different characteristics, indicating that coordination between HL and zinc ion at the air-water interface has occurred. This coordination not only causes an increase of collapse pressure but also changes the area of HL. The area per HL molecule on Zn^{2+} ion subphase is around 0.28 nm^2 at the pressure of 30 mN/m (A_{30}) and is much larger than the A_{30} value of HL (0.21 nm^2) on pure water subphase.

The concentration of $ZnCl_2$ on subphase has an apparent effect on the isotherms. The isotherm on 1.0×10^{-7} M $ZnCl_2$ subphase is almost similar to that of HL on pure water subphase, suggesting that under this condition very little or no complexation took place at the air-water interface. When the concentration of $ZnCl_2$ increases to 0.1 mM, the π-A isotherms show different characteristics, indicating that under this condition complexation occurred. Further increment of $ZnCl_2$ in the

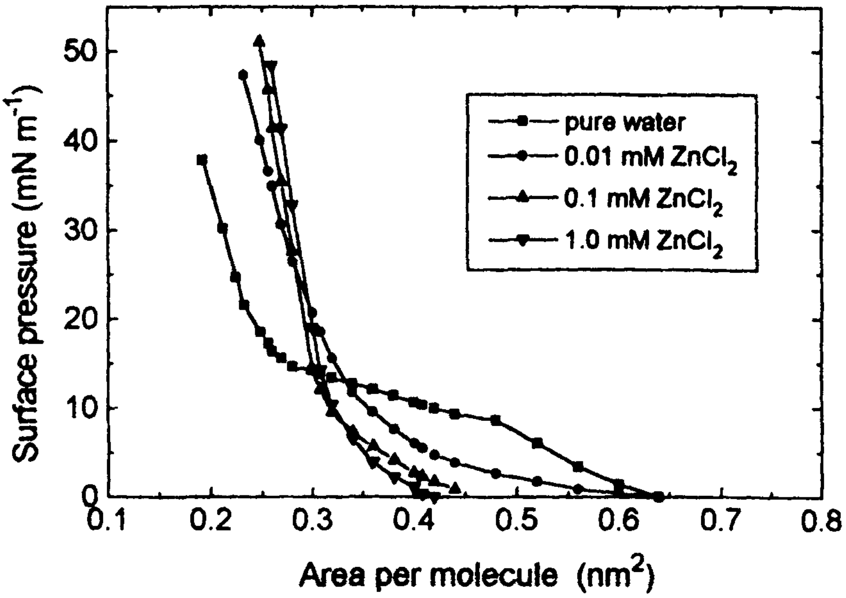

FIGURE 1 π-A curves of HL monolayer on subphases with different $ZnCl_2$ concentration

subphase did not change the π -A isotherms except for a slight "shift" to the larger molecular area with a slight decrease of the collapse pressure. That is, stable complex monolayers were formed when the subphase contained more than 0.1 mM Zn(II) ions.

The complexation of HL with Zn^{2+} ion was conformed by XPS. We can clearly see the zinc peaks (1045.1 and 1022.6 eV) in HL multilayer built up from a 1.0 mM $ZnCl_2$ subphase. That is, a complexation of HL with Zn^{2+} ion was formed at the air-water interface and the complex monolayers were transferred onto quartz plates. The information on stoichiometry provided by XPS indicates that the elemental C/Zn ratio amounts to 27.2, which is good consistent with the theoretical C/Zn ratio of 28.0. That is, a zinc ion is coordinated by one HL molecule.

HL Spreading Isotherms as a Function of Counterions

The isothermal compression curves for HL monolayers with different zinc salts added in the subphase are shown in Fig. 2. It clearly shows that the counterions have an effect on HL-Zn monolayers. From the values of area per molecule at 30 mN/m (A_{30}), the condensibility of HL-Zn monolayers increases in the order: $ZnSO_4$(0.35) < $Zn(OAc)_2$ (0.33) < $Zn(NO_3)_2$ (0.31) < $ZnCl_2$ (0.29)

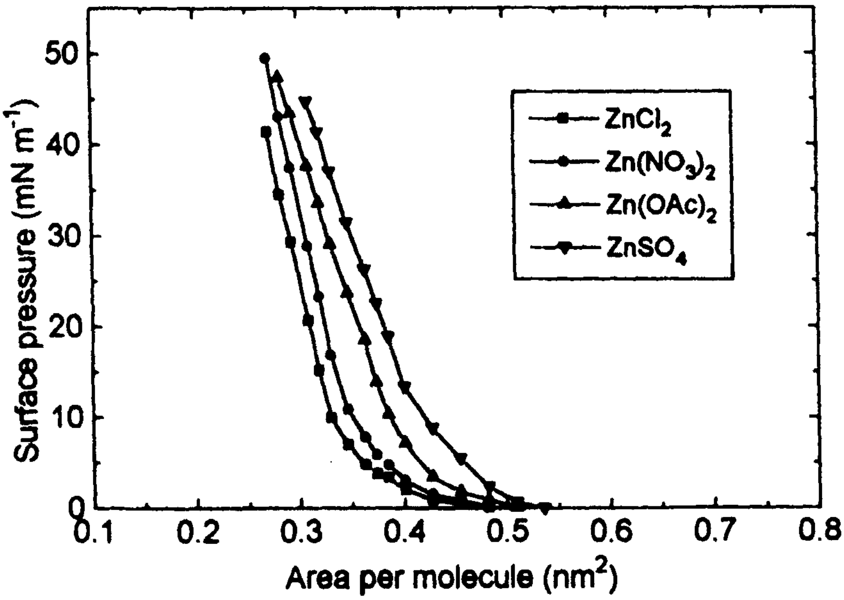

FIGURE 2 Influence of anions on π-A isotherms of HL-Zn. All salts are at a concentration of 1.0 mM

Langmuir-Blodgett Films

The UV-vis absorption spectra of the LB films of HL deposited from subphases containing different concentrations of $ZnCl_2$ were determined. Two peaks at 260 and 362 nm are observed in spectra for 11-layer HL LB films on 1.0 × 10^{-7}M $ZnCl_2$ subphase. This is the same as that of HL on pure water subphase, suggesting that under this condition no complexation occurred. When the concentration of $ZnCl_2$ reaches 0.01 mM, a new peak appears at 485 nm, which is ascribed to the complexation between the HL and Zn^{2+} ion at the air-water interface. This peak becomes stronger on subphase containing 0.1 mM $ZnCl_2$. Further increment of $ZnCl_2$ in the subphase did not change the spectrum any more. These results indicate that a stable complex can be partially formed even at low ion concentrations, while the maximum equilibrium concentration of the complex is achieved at about 0.1 mM of $ZnCl_2$.

Low-angle X-ray diffraction measurement was made with 29 layers of HL transferred from 1.0 mM $ZnCl_2$ subphase at 30 mN/m. Two broad Bragg peaks

($2\theta = 0.804$ and $1.591°$) were observed. The derived *d*-spacing by Bragg's law, $n\lambda = 2d\sin\theta$, is 5.529 ± 0.018 nm, which are near the thickness of 2-layer long side-chain (-$CONHC_{18}H_{37}$). It is clear that a Y-type bilayer structure was formed during the deposition process. Since the thickness of one single monolayer of HL estimated by the C.P.K. model is ca. 2.55 nm and 2.81 nm for HL orienting with face and side touching water respectively[3], we can deduce that at the air-water interface HL orients with its hydrophilic side touching water and forms 1:1 complex with Zn ion in the subphase, while its hydrophobic aliphatic chain localized perpendicularly above the air-water interface. Since the transfer ratio was 1.0 ± 0.1 for the up- and down-strokes, the complex monolayer at the air-water interface was transferred onto substrate without structural change.

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