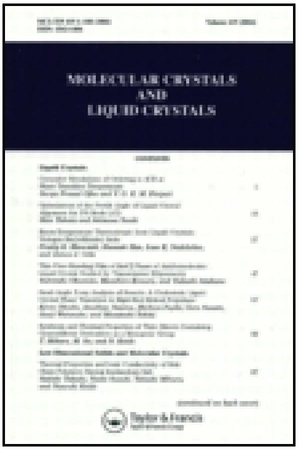

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Studies on Preparation of Composite Films by Adsorption of Methyl Orange Molecules onto the Interface of Tetracationic Porphyrazine Monolayer

Xu-Sheng Feng [a], Mei-Xiang Yu [a], Hong-Guo Liu [a] & Jin Mu [a]

[a] Laboratory for Colloid and Interface Chemistry of State Education Ministry, Shandong University, Jinan, 250100, P. R. China

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Studies on Preparation of Composite Films by Adsorption of Methyl Orange Molecules onto the Interface of Tetracationic Porphyrazine Monolayer

XU-SHENG FENG, MEI-XIANG YU, HONG-GUO LIU and JIN MU

Laboratory for Colloid and Interface Chemistry of State Education Ministry, Shandong University, Jinan 250100, P. R. China

The composite monolayer and Langmuir-Blodgett (LB) films of cobalt tetrahexadecyl tetrapyridino porphyrazinium bromide (TA16PyPzCo) / methyl orange (MO) were characterized by surface pressure-area (π-A) isotherm, UV-VIS spectra, polarized UV-VIS spectra, TEM and SAXD. The MO molecules were arranged with a special orientation in the composite films. The composite films have an ordered lamellar structure.

Keywords: tetracationic porphyrazine; adsorption; Langmuir-Blodgett films

INTRODUCTION

In recent years, a great deal of investigations has been devoted to Langmuir - Blodgett (LB) films of azobenzene derivatives due to their potential applications in optical, electrical and switching devices [1-3]. The methyl orange (MO) molecules containing an azobenzene group have been adsorbed onto the dicationic LB films [4]. An important problem is to give adequate free volume for the trans-cis isomerization of azobenzene to occur reversibly in these LB films. TA16PyPzCo, which have a large macrocycle [5], can solve this problem if introducing azobenzene groups into the molecules. In this paper, the TA16PyPzCo monolayer was used as the template to adsorb

MO molecules in the subphase. The structure and properties of the composite LB films were characterized.

EXPERIMENTAL DETAILS

The π-A isotherms of monolayers and deposition of LB films were performed on the Model MW-II LB system (Southeast Univ. China). The monolayers of TA16PyPzCo (shown in Fig.1) were spread from a chloroform solution onto the surface of distilled water or aqueous solution of MO. The compression speed is 20 cm^2/min. The monolayers were transferred by the vertical dipping method at 25 mN/m. The quartz plates and glass slides were used as substrates for UV-VIS spectra (UV-240 spectrometer, Shimadzu, Japan) and SAXD (D/Max-γB X-ray diffractometer, Rigaku, Japan), respectively. The monolayers transferred onto Formvar-covered copper grids (230 mesh) by the method of dropping subphase were used for TEM experiments (JEM-100CXII electron microscope, Japan).

RESULTS AND DISCUSSION

The adsorption of MO on the TA16PyPzCo monolayer

Fig.1 shows the π-A isotherms of TA16PyPzCo monolayers on the surfaces of distilled water and aqueous solution of MO (2×10^{-4}mol dm^{-3}). As can be seen from Fig.1, on the surface of distilled water the TA16PyPzCo molecules formed an expanded monolayer even at higher surface pressure, while on the surface of aqueous MO solution more condensed monolayer was formed. This can be attributed to the ionic repulsion between pyridinium groups of TA16PyPzCo reduced by the adsorption of MO due to the electrostatic interaction [6]. This result is coincident to the TEM observations of TA16PyPzCo monolayers. The TEM image of TA16PyPzCo monolayer transferred at 20 mN/m from the surface of distilled water shows a uniform morphology. But on the surface of MO aqueous solution, the image shows some domains separated by some silk-like bands. This results show that the monolayer on the MO aqueous solution surface is more condensed than that on pure water, indicating the interactions between MO anions and TA16PyPzCo molecules.

An Absorption peak appears at 429.0 nm in the UV-VIS spectrum of TA16PyPzCo LB films transferred from the surface of aqueous solution of MO. This peak is attributed to the absorption of MO molecules, indicating that the MO molecules were incorporated into the TA16PyPzCo monolayer.

The structure of TA16PyPzCo / MO composite LB films

Fig.2 shows the polarized UV-VIS absorption spectra of TA16PyPzCo / MO composite LB films (26 layers). The transition moment of the chromophore of MO molecules is considered to be almost parallel to the long axis of the molecules. The tilt angle of MO molecules could be estimated to be 46.2° from the dichromic ratio according to Chollet et al [7,8]. This indicates that the molecules in the TA16PyPzCo / MO composite LB films were arranged with a special orientation with its long axis.

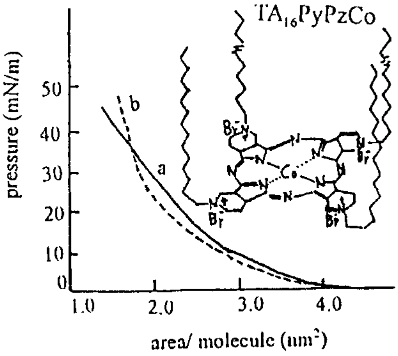

FIGURE 1 π-A isotherms of TA16PyPzCo monolayers on pure water (a) and aqueous solution of MO (b).

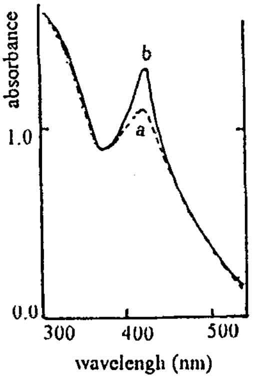

FIGURE 2 Polarized UV-VIS spectra (a, s-; b, p-) of the composite LB films at an incidence of 45°.

The layer dependence on the adsorption of MO molecules was investigated for 1 to 17 layers of TA16PyPzCo / MO composite LB films. The linear relationship between the absorbance at 429.0 nm and the number of layers was obtained, suggesting that TA16PyPzCo monolayer adsorbed MO molecules quantitatively.

The SAXD patterns for pure TA16PyPzCo and TA16PyPzCo / MO composite LB films were measured. The first order Bragg peak was found in the both pictures, showing the lamellar structure of these LB films. The spacing distances were calculated to be 3.84 nm for TA16PyPzCo LB films and 6.04 nm for TA16PyPzCo / MO composite LB films, respectively. The later was longer than the former, suggesting that the incorporated MO molecules were under the macrocycle of TA16PyPzCo at the air/liquid interface. The thickness of one layer of MO in the LB films can be evaluated to ca 1.1nm.

CONCLUSION

The TA16PyPzCo / MO composite LB films were fabricated by means of adsorption at the air/liquid interface. The MO molecules were adsorbed under the plane of TA16PyPzCo. This structure may give sufficient free volume for the isomerization of the azobezene group in MO molecules.

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