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An infrared study on Langmuir–Blodgett films of 14,15-bis(hydroxyimino)-13-thiaoctacosane

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Abstract

The Langmuir–Blodgett (LB) films of 14,15-bis(hydroxyimino)-13-thiaoctacosane (TOC) on aluminium plated substrates were investigated using Fourier transform infrared (FTIR), grazing angle (GAIR) and horizontal attenuated total reflectance (HATR) techniques. The LB films of TOC can be transferred onto the solid substrate successfully. The molecular structure of LB films was analysis by comparing the GAIR and HTAR spectra. The intense bands at 2848 and 2918 cm^{-1} are assigned to symmetric $\nu_s(CH_2)$ and asymmetric $\nu_a(CH_2)$ stretching vibrations of methylene groups. These peaks suggest that the alkyl chains in TOC are nearly in all-trans conformational state. The presence in the infrared spectra of several bands due to the methylene wagging and twisting modes and of the splitting of the bands due to the methylene scissoring mode at 1467 and 1459 cm^{-1} and the CH_2 rocking mode at 720 and 731 cm^{-1} also indicates that in films of TOC alkyl chains are in the all-trans conformation and packed in either an orthorhombic or a monoclinic structure with an orthorhombic subcell containing two mutually orthogonal molecules. Another conclusion presented in this paper that the alkyl chain tilt, which is the angle between the axis, which bisects the C–C bonds and the surface normal, was quite large by comparing the GAIR and HATR spectra.

Keywords: *vic*-Dioxime; Langmuir–Blodgett; FTIR spectra

1. Introduction

The Langmuir–Blodgett (LB) technique offers an efficient method for preparing well-ordered organic ultra-thin films on suitable substrates. Ordered monolayer films transferred from a water surface onto a solid substrate by the LB technique have drawn growing interest for a recent few years. This is because the LB films have a good possibility to be artificial molecular assemblies with planed structure and properties. Furthermore, they form well-defined molecular organizates, which can be externally handled and controlled [1,2]. In our previous work [3], the formation of Langmuir monolayer of 14,15-bis(hydroxyimino)-13-thiaoctacosane (TOC) molecule at the air–water interface, π–A isotherm and stability of this monolayer has been investigated as a function of pH of subphase. Due to the structure of containing long alkyl chains, expectational stability and unique electronic properties, *vic*-dioximes gain importance in LB films. The expectational stability and unique electronic properties of these complexes can be attributed to their planar structure, which is stabilized by hydrogen bonding. The most exciting feature of these complexes is their solubility in common organic solvents [4]. These very soluble complexes were investigated as sensitive materials for the detection of organic solvents vapours by utilizing a quartz crystal microbalance and inter digital capacitors as sensor transducers [5,6]. We also studied the monolayer properties of this ligand spread on a subphase containing different metal ions. The optimal conditions for the

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formation of stable, metal complex containing monolayers and transfer as their LB films have been determined.

In this research, we have studied the structural and conformational characterization of LB films of TOC molecule deposited on aluminium substrate by using infrared spectroscopy. It has been expected that infrared spectra of LB films could afford an excellent insight into the structure–function relationship of these molecular systems. In addition to these, infrared spectroscopy has the advantage of being easy to use, non-destructive against to samples and sensitive to changes in the molecular conformation [7]. However, the sensitivity of infrared transmission method by usual dispersion-type spectrophotometers was influenced to record spectra of very thin films. Infrared measurements of LB films became possible only by using novel reflection techniques such as GAIR and HATR. These techniques with their associated surface selection rule are of great value for the characterization of thin LB films [8]. Fourier transform infrared (FTIR) spectrophotometer with these reflection techniques made possible to investigate LB films and determined the molecular orientations of films more clearly. Especially, changes in frequency and intensity of the $\nu(CH_2)$ symmetric and asymmetric vibrations in the alkyl chain of TOC molecule and the splitting of the band due to the methylene scissoring mode can be used to characterize film ordering and preferential molecular packing by a comparison of GAIR and HATR spectra.

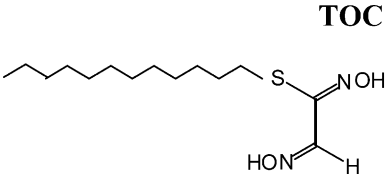
2. Experimental details

2.1. Materials

The thioglyoxime ligand (TOC) was synthesized according to the literature [6] and its structure is given in Scheme 1. Chloroform and KOH were purchased from Merck, and they were used without further purification. Water used in the subphase was purified by Elga UPH water purification system to have a resistance 18 MΩ cm.

2.2. Langmuir–Blodgett film deposition

Floating Langmuir monolayer of TOC were prepared using a solution of concentration 0.5 mg ml^{-1} in which the solvent was chloroform. This solution was applied drop wise (200 μl) using a Hamilton micro syringe on to subphase, allowing 10 min for solvent evaporation. A subphase, whose pH was adjusted to the 7.75 pH value by adding dilute solution of KOH were used. TOC multilayers were deposited using a constant perimeter single-compartment Langmuir trough. The substrate was a glass slide coated with a 50 nm film of thermally evaporated aluminium. The deposition pressure of TOC was 23 mN m^{-1}. Five multilayered LB films of TOC with thicknesses of 11, 15, 21, 25 and 31 monolayers were prepared. The upstroke deposition speed for the first layer was 6 mm min^{-1} and both the upstroke and downstroke deposition speeds for the other layers were 9 mm min^{-1}.



Scheme 1.

2.3. Fourier transform infrared measurements

Transmittance at normal incidence, grazing angle, and horizontal attenuated total reflectance spectra were recorded using Perkin-Elmer Spectrum One Fourier Transform Infrared Spectrometer equipped with deuterated triglycine sulfate (DGTS) detector. A rotating ZnSe wire-grid polarizer was positioned in front of the sample to obtained p-polarized spectra. To obtain HTAR spectra, Perkin-Elmer HATR accessory with ZnSe (45° edges) crystal was used. Transmittance spectra at normal incidence and p-polarized GAIR spectra at an incidence angle of 86° were recorded by co-adding 1000 scans. All spectra were obtained at a resolution of 4 cm^{-1}.

3. Results and discussion

IR spectroscopy has proved to be a powerful tool to investigate changes in molecular aggregation, orientation, and structure at the level of functional groups in LB films [9–11]. Fig. 1 shows the IR spectrum of TOC in a KBr pellet by transmission. The spectrum provides a useful basis with which to assign the spectra of LB films containing TOC. The wavenumbers and assignments of the major IR bands are summarized in Table 1. In Fig. 1, there is a strong band at

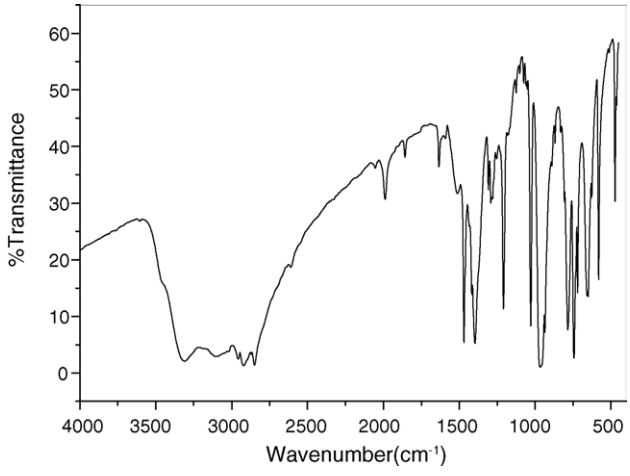


Fig. 1. Infrared spectrum of TOC in a KBr pellet by transmission.