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Infrared reflection absorption spectroscopy study of smectite clay monolayers

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Abstract

Infrared reflection absorption spectroscopy (IRRAS), also called infrared external reflection spectroscopy, is used for studying ultrathin hybrid clay films prepared by the Langmuir–Blodgett (LB) method. Infrared spectra of the hybrid films have been obtained at the air–water and air–solid (gold) interface. The presence of a smectite monolayer is observed when cationic surfactants are spread over the surface of a dilute aqueous smectite clay suspension. The in-plane ν(Si–O) band of saponite is observed in IRRAS spectra of saponite clay monolayers at the air–water interface. In contrast, the out-of-plane ν(Si–O) band at 1063 cm^{-1} is the dominant band in the p-polarized IRRAS spectra of a saponite monolayer deposited on a gold surface. These data correspond to the first-reported infrared spectra of clay minerals showing the enhancement of the out-of-plane vibrational modes and the nearly complete suppression of the in-plane vibrational modes. The results provide direct spectroscopic evidence confirming the orientation of the smectite particles parallel to the substrate.

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1. Introduction

The Langmuir–Blodgett (LB) method allows the preparation of hybrid clay films consisting of single layered clay particles [1–6]. The procedure consists of spreading cationic surfactants over a clay suspension, compression of the monolayer and transfer of the hybrid monolayer to solid substrates. It is believed that the negatively charged clay particles are attracted to the cationic surfactant monolayer. Most of the studies on hybrid clay films deal with films deposited on solid substrates [1–6]. Measurements of the film on water are limited to surface pressure versus molecular area (Π-a) isotherms and Brewster angle microscopy. The Π-a isotherms of the monolayer on suspensions with varying clay concentration resulted in varying lift-off areas and compressibilities [2–5]. Brewster angle microscopy images showed the appearance of bright spots, even at zero surface pressure [1]. The observations of the film at the surface of a clay suspension were attributed to adsorbed clay particles; however, they do not prove that clay is present in the monolayer. In this paper, we show that IRRAS can detect the presence of clay in the film at the surface of a clay suspension.

Recently, we performed polarized attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy on hybrid monolayers of clay [6]. Highly resolved clay bands were seen, confirming their in-plane and out-of-plane character and the orientation of the clay layer parallel to the substrate. ATR-FTIR spectra made with s-polarized light were shown to effectively suppress the out-of-plane ν(Si–O) band whereas p-polarized ATR-FTIR spectra show both in-plane and out-of-plane ν(Si–O) bands. IRRAS of the hybrid clay–organic LB films on a substrate of ZnSe enhanced the intensity of the out-of-plane ν(Si–O) band rela-

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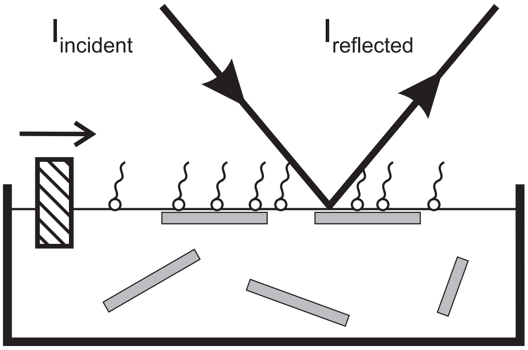

Fig. 1. Schematic representation of the IRRAS set-up for measurements at the liquid surface.

tive to the in-plane bands. Here we present a method to suppress the in-plane bands giving nearly completely resolved out-of-plane bands of clay.

2. Experimental details

The clay used in this study was the SapCa-1 saponite specimen obtained from the Source Clays Repository of the Clay Minerals Society. Saponite is a trioctahedral 2:1 phyllosilicate member of the smectite group [7,8]. The clay was Na^+-saturated by repeated (three times) exchange with one molar NaCl solutions followed by dialysis with water until a negative Cl^- test was obtained using $AgNO_3$. The particle size fraction between 0.5 and 2.0 μm was obtained by centrifugation and freeze-drying of a salt-free, Na-exchanged clay suspension.

Monolayers were prepared on 50 mg dm^{-3} clay suspensions stirred for 24 h in Milli-Q water. The LB film on gold was prepared on a NIMA Technology model 611 LB trough at a temperature of 23±1 °C. A microsyringe was used to spread 40 μl of octadecyl rhodamine B chloride (RhB18; Molecular Probes) dissolved in chloroform (9.1×10^{-4} mol dm^{-3}). After 15 min, the film was compressed at a rate of 30 cm^2 min^{-1}. The film was deposited in upstroke (lifting speed of 5 mm min^{-1}) on a gold substrate at a surface pressure of 15 mN m^{-1}. The gold substrate was prepared by sputtering a 25-nm-thick gold layer on a Si wafer. The films for measurements at the liquid surface were prepared in a PTFE trough (area=17.6 cm^2) with one manually controlled barrier. A schematic representation of the IRRAS set-up for measurements at the liquid surface is shown in Fig. 1. A microsyringe was used to spread 1 μl of 3,3′ -dioctadecyl oxacarbocyanine perchlorate (OXA18; Fluka) dissolved in chloroform (10^{-3} mol dm^{-3}). After 15 min, the film was compressed to an area of 13.2 cm^2.

The films were measured in a monolayer/grazing incidence angle accessory P/N 19650 Series (Specac). The gold substrate was measured at grazing incidence (80° with respect to the normal) using a Bruker IFS 66/v FTIR spectrometer. The background was the gold substrate before LB deposition. Polarized IR light was obtained using a wire-grid polarizer. A total of 512 scans were signal averaged using an optical resolution of 2 cm^{-1}. The films on the liquid surface were measured at 40° incidence using a Nicolet Protege FTIR spectrometer. The background for the film on water was the water surface before spreading. The background for the film on a clay suspension was the liquid surface 15 min after spreading. A total of 512 scans were signal averaged using an optical resolution of 4 cm^{-1}. Both FTIR spectrometers used in this study were equipped with a liquid nitrogen cooled MCT detector and a KBr beam splitter. Spectra were analyzed with Grams/32 AI version 6.00 software.

3. Results and discussion

3.1. Clay at the liquid surface

The unpolarized infrared reflection absorption spectra (IRRAS) of an OXA18 monolayer on water and on a saponite clay suspension are shown in Fig. 2. The absorp-

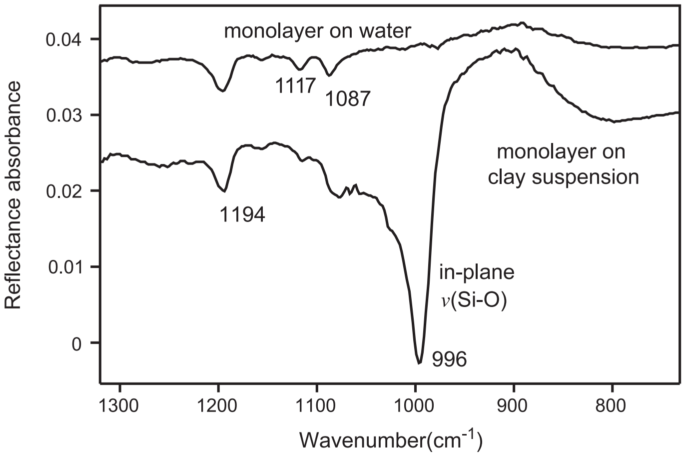

Fig. 2. Infrared reflection absorption spectra (IRRAS) of an OXA18 surfactant monolayer on water and on a saponite clay suspension.

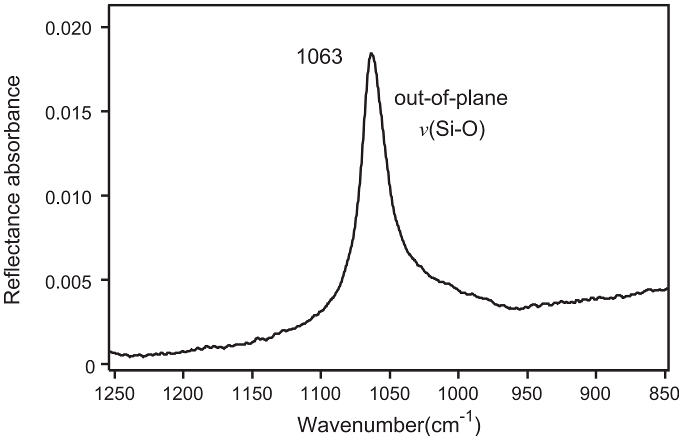

Fig. 3. p-Polarized grazing angle IRRAS spectrum of an LB monolayer containing RhB18 and saponite clay deposited on gold at a surface pressure of 15 mN m^{-1}.

tion bands are negative, which is typical for IRRAS at dielectric surfaces [9]. Both spectra have bands at 1087, 1117 and 1194 cm^{-1}, thus showing the presence of OXA18 surfactant [10]. The IRRAS spectrum created at the air–water interface has an additional strong band at 996 cm^{-1} corresponding to the in-plane Si–O stretching vibration, ν(Si–O), of saponite [6,11]. This is direct evidence that clay particles are present at the surface of the aqueous clay suspension after spreading of the surfactant. It verifies that the hybrid film is formed at the air–water interface by adsorption of the clay particles from suspension onto the surfactant monolayer.

3.2. Clay at the gold surface

The p-polarized grazing angle IRRAS spectrum of the hybrid LB film containing RhB18 and saponite clay deposited on gold is shown in Fig. 3. To the best of our knowledge, this is the first reported IRRAS spectrum of a clay monolayer deposited on a metallic substrate.

The band at 1063 cm^{-1} is the out-of-plane Si–O stretching vibration of saponite [6,11]. The band width at half-height is 22.8 cm^{-1}. The in-plane Si–O stretching vibration (996 cm^{-1}) is greatly reduced to a weak shoulder. The suppression of the in-plane clay bands results from the so-called “metal surface selection rule”, which states that only vibrational transition dipole moments oriented normal to the surface will absorb light [12]. It shows that the clay layer is oriented parallel to the substrate, and the corresponding IRRAS spectrum is completely dominated by the out-of-plane Si–O stretching band at 1063 cm^{-1}. Infrared spectra of clay minerals measured in transmission [11], in ATR [6] or in IRRAS on a ZnSe surface [6] have intense in-plane bands. Grazing angle IRRAS of a thin clay film on gold can effectively suppress the in-plane bands resulting in highly resolved out-of-plane clay bands. The enhancement of the out-of-plane ν(Si–O) band is significant and IRRAS on gold may provide a novel method to observe the structure and properties of guest molecules/sorbed species on clay surfaces.

4. Conclusions

Infrared reflection absorption spectroscopy (IRRAS) is an analytical technique that can yield valuable information on the formation and structure of hybrid LB films. IRRAS spectra have been obtained of hybrid clay films at the water surface. It is confirmed that clay particles are adsorbed at the air–water interface when surfactant molecules are spread on a clay suspension. Grazing angle IRRAS is measured of the clay film deposited at the gold surface. The spectrum shows a nearly completely resolved out-of-plane ν(Si–O) band, confirming the orientation of the clay layer parallel to the substrate.

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