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In-situ FTIR investigation of heterogeneous Langmuir monolayers at the air/water interface

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Abstract

In this study, we tried to measure ion reactivity at heterogeneous mixed Langmuir monolayers at the air/water interface by using in-situ near-normal external reflection FTIR spectroscopy. To achieve better spectral signals with less water vapor noise, close-packed monolayers of respective composition were chosen as backgrounds. Upon the adsorption of cadmium ions, the corresponding asymmetric carboxylate band clearly appeared. As the relative amount of non-reactive stearyl alcohols mixed with reactive stearic acids exceeded 15%, the adsorptivity of cadmium ions decreased nearly by half. The results have implications to molecular design of catalysts and biomineralization.

Keywords: In-situ FTIR; Heterogeneous monolayers; Metal ion adsorption

1. Introduction

Langmuir monolayer at the air/water interface is an interesting system out of many supramolecular assemblies. It enables one to conveniently investigate surface reactivity and molecular structure by varying packing density of constituent amphiphilic molecules. It has been used as one of the best model systems to study surface phenomena on the 2-D domains [1].

There have been plenty of works reported on FTIR spectroscopic studies for metal adsorption to Langmuir–Blodgett (LB) monolayer or multilayers sampled on solid substrates. However, ion adsorption to the LB films deposited on substrates does not necessarily reflect that to the Langmuir monolayer at the air/water interface. For the last decade, the techniques of in-situ FTIR spectroscopy have been advanced much especially for film systems on the air/water interfaces. Gericke and Hühnerfuss [2] reported for the first time that external reflection FTIR spectroscopy was useful to investigate in-situ metal ion adsorption to homogeneous acidic Langmuir monolayers. Berman et al. [3] and Ahn et al. [4] also probed in-situ the biomineralization of calcite crystals at the pure acidic Langmuir monolayer.

However, in materials aspect, investigation of chemical properties at the heterogeneous surfaces is more relevant to real catalytic or biological systems than at the homogeneous ones. For instance, Higashi et al. [5] found that the association constant of carbonic anhydrase reaches its maximum when the surface composition of benzenesulfonamide group is about $\sim$ 10%. In the present study, we tried to investigate in-situ ion adsorptivity on the heterogeneous Langmuir monolayers at the air/water interface, consisting of varying compositions of reactive and non-reactive molecules. By introducing a new measurement strategy, we could remarkably improve the spectral signals compared to previously reported methods, which leads us to substantiate the effect of surface heterogeneity on the ion adsorption. The new measurement strategy demonstrated in this study would directly reveal properties of heterogeneous surfaces in contact with water, which leads one to a better design of catalysis or biomineralization.

2. Experimental

2.1. Materials

Stearic acid (octadecanoic acid; $CH_3(CH_2)_{16}COOH$), stearyl alcohol (octadecanol; $CH_3(CH_2)_{16}OH$) and $CdCl_2$ used were purchased from Aldrich. Deionized (DI) water was purified with a Millipore water purifier and its resis-

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