

## SELECTIVITY OF HEAVY METAL IONS AT ACIDIC SUPRAMOLECULAR SURFACES

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**Abstract** – Langmuir monolayers containing surface carboxylic acid head groups were examined in order to characterize their selectivity to metal ion adsorption. Experimental data of ion adsorption obtained by surface isotherms and FTIR spectroscopy were analyzed using a thermodynamic-and-electrochemical model. Among bivalent ions examined ( $\text{Cr}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Ba}^{2+}$ ), Langmuir monolayers showed the highest selectivity to chromium ions. In addition, it was found that adsorption constants of the surface ions are quite different from binding constants of the bulk ions. The results show important implications to sensing and separating metal ions by the use of acidic supramolecular materials.

**Key words:** Supramolecules, Langmuir Monolayers, Interfaces, Metal Ion Adsorption, FTIR Spectroscopy

### INTRODUCTION

Supramolecular systems are self-organizing structures including natural cells, liposomes, micelles, monolayers, multilayers, and liquid crystals [Ringsdorf et al., 1988]. They show unique properties in order and function that other bulk materials lack. Based on these facts, various attempts have recently been made to develop engineering applications using supramolecular systems. Molecularly engineered materials can be used as chemical and biological sensors, highly selective membranes, photoresist films in the semiconductor process, molecular sieves, surface coatings, etc. [Stroeve and Franses, 1987; Ulman, 1991; Roberts, 1990; Tredgold, 1994; Choi et al., 1997].

In this study, we are interested in the surface functions of a supramolecular system, Langmuir monolayer. Langmuir monolayer can be easily formed by spreading amphiphilic molecules at the air/water interface. Simply by moving the barriers that enclose the active interfacial area, we can change the density of radicals up to ca.  $20 \text{ \AA}^2$  per radical. In addition, we can enhance the affinity of the surface to a certain target, by employing proper molecules out of ample library of amphiphilic molecules.

Such affinity is known to be different from that in the bulk [Ahn and Franses, 1991], and currently under investigation. We have chosen a carboxylated Langmuir monolayer to examine its selectivity to heavy metal ions which are harmful to environments and various life forms, and hence need to be monitored or effectively separated. The ion affinities of the films to chromium, copper, zinc, and nickel were analyzed by using Fourier transform infrared (FTIR) spectroscopy. Then, a model incorporating both electrochemical and thermodynamic aspects was applied to quantify the surface ion affinity. The results deliver important data useful for devel-

oping the supramolecular systems as novel ion exchange devices and sensors.

### EXPERIMENTAL SECTION

#### 1. Materials

Stearic acid ( $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ ; 99+%),  $\text{CrCl}_2$  (95+%),  $\text{PbCl}_2$  (99.999%),  $\text{CdCl}_2$  (99.99%),  $\text{NiCl}_2$  (99+%),  $\text{CuCl}_2$  (99.0+%),  $\text{ZnCl}_2$  (98+%),  $\text{CaCl}_2$  (99+%), and  $\text{BaCl}_2$  (98+%) were purchased from Fluka and Aldrich and were used without further purification. Water used in experiments as a subphase liquid (sub-solution) was first distilled and then purified with a Millipore-Q water purifying system. The final deionized (DI) water had an initial resistivity of  $18.2 \text{ M}\Omega \cdot \text{cm}$ . The metal ionic concentration in aqueous sub-solution was  $10^{-4} \text{ M}$ . The pH of the sub-solution was adjusted by adding diluted 1 N HCl and 1 N NaOH aqueous solutions.

#### 2. Langmuir Monolayer Formation

Stearic acid monolayers were spread from chloroform ( $\text{CHCl}_3$ ) solution (1 mM), by using microsyringes, on the air/water interface of the ionic sub-solution (at room temperature) in a pre-cleaned Langmuir minitrough ( $75 \times 270 \text{ mm}$ ; KSV, Finland). Platinum Wilhelmy plate ( $10 \times 20 \text{ mm}$ ) was used to measure the interfacial tension ( $\gamma$ , mN/m), from which the surface pressure ( $\Pi$ , mN/m) is obtained as  $\Pi = \gamma_0 - \gamma$ , where  $\gamma_0$  is the surface tension of pure water [Gaines, 1966]. 10 min was allowed until the chloroform evaporates. The air/water interface was then compressed symmetrically with barriers, at a speed of 10 mm/min. When the surface pressure approached 35 mN/m, ca. 15 min was allowed for the system to reach chemical equilibrium.

#### 3. FTIR Spectroscopy

After reaching equilibrium, the Langmuir monolayer was over-compressed with barriers beyond the collapse surface pressure and then deposited on the  $\text{CaF}_2$  plates ( $12 \times 25 \times 2 \text{ mm}$ ;

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