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Ion Separation of Binary Metallic Aqueous Solutions at Acidic Langmuir Monolayer Surfaces

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Abstract–We focused on analyzing the capability of the acidic monolayer surfaces for separation of toxic metal ions out of house-prepared binary inorganic ionic solutions such as calcium-lead, calcium-chromium, calcium-copper, and calcium-zinc aqueous systems. The affinities of the films to toxic metal ions were analyzed by using Fourier transform infrared spectroscopy. A model considering both the electrochemical and thermodynamic aspects was also applied to quantify the surface ion affinities. It is noted that surface ion binding capability for binary ionic solutions can be much different from that for pure ionic solutions. As a result, surface binding constants were found to be 4.5×10^6, $^{++}$ for lead ions, 1.5×10^6 for chromium ions, 5.5×10^5 for copper ions, and 6×10^4 for zinc ions, respectively, at pH=5.5. For the separation experiments done at pH=5.5, lead, copper, zinc ions were separated more efficiently from the mixed ionic solutions by the factors of ca. 30,000, 10,000, 3,700, and 400, respectively, compared to calcium ions of which binding constant is 1.5×10^2. Interestingly, when compared to corresponding pure ionic systems, copper and lead ions were separated as much, while chromium and zinc ions were less by the factor of 500 and 50, respectively.

Key words: Langmuir Monolayer, Binary, Ion Adsorption, Surface, FTIR, Modelling

INTRODUCTION

A Langmuir monolayer on an air/water interface is an interesting system out of many supramolecular assemblies in the sense that it enables one to conveniently investigate surface reactivity and molecular structure by varying packing density of constituent amphiphilic molecules [Kim et al., 1996]. Such properties are essential information in order to harvest useful functions from more complex supramolecular systems having molecular arrays in 3-dimensions. Functional and stable Langmuir monolayers can be directly deposited into multilayered Langmuir-Blodgett (LB) films, which have been investigated extensively for potential applications to chemical and biological sensors, photon or electron devices, selective membranes, and reaction or immobilization substrates [Swalen, 1986; Vijendra, 1988].

Properties of Langmuir monolayers are in general dependent upon the physicochemical nature of constituent molecules of which the library includes lipids, synthetic polymers, and biological macromolecules [Choi et al., 2000]. Other key factors are order and organization in 2-dimensional surfaces which often differentiate properties of the surfaces from those of bulk structures made of identical materials [Pezron et al., 1990; Whitesides et al., 1991]. One can easily form close-packed molecular structures of appropriate molecules that are sometimes impossible to achieve by other techniques.

We have been interested in surface reactivity of close-packed acidic Langmuir monolayers with toxic bivalent metallic species [Petrov et al., 1982; Ahn et al., 1991, 1994; Hyun et al., 1997]. Surface adsorptivity of many metallic ions was found to deviate much from bulk adsorptivity [Kim, 2000]. In this study, we present new results on ion separation out of aqueous solutions containing binary metallic ion species, which is more meaningful for real processes involving multicomponents. Results show that ion adsorption in binary systems can be much different from that in pure systems previously studied, depending on the nature of metallic species.

EXPERIMENTAL PROCEDURES

The preparation of Langmuir monolayers was done on KSV-minitrough (Finland) made of teflon. Stearic acids [$CH_3(CH_2)_{16}COOH$; Aldrich, 99.9%] dissolved in chloroform at the concentration of 10^{-3} M were dispersed on the air/water interface of the trough by using a microsyringe. Close-packed Langmuir monolayers were obtained by compressing the barriers symmetrically until the surface pressure (Π, mN/m) measured with a Wilhelmy plate approached 35 mN/m. Carboxylic acid groups exposed at the monolayer surface were the adsorption sites avaliable to metallic ions for further experiments.

The sub-solution contains binary heavy metallic components of which one cationic component is from $CaCl_2$, and the other is from $PbCl_2$, $CuCl_2$, $CrCl_2$, or $ZnCl_2$ (purchasedfrom Fluka, 99.999%). Solvent used was deionized water distilled and filtered by a Mill-Q water purifier and its initial resistivity was 18 MΩ·cm. The concentration of calcium ions was held at 10^{-4} M and that of the other component was varied. The pH of the mixture sub-solution was adjusted by adding 1 mM aqueous solution of HCl or NaOH at 5.5 throughout the experiments. We waited ca. 15 min until the equilibrium between the Langmuir monolayers and the binary metallic sub-solutions was attained.

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