

# Ion Adsorption and Ion Exchange in Ultrathin Films of Fatty Acids

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*Ion exchange equilibria of ultrathin Langmuir and Langmuir-Blodgett films of stearic and arachidic acids in contact with aqueous electrolyte solutions were studied experimentally and theoretically. A model considering electrochemical and thermodynamic aspects of the adsorption of protons, calcium, and cadmium ions from solution to the film has been developed. Key parameters are the binding constants ( $K$ 's) of ions and the mixing characteristics (or Flory-Huggins interaction parameters  $\chi$ 's) of ions in the two-dimensional film lattice plane. The ternary system can be described by the parameter values determined with binary proton-calcium ion, proton-cadmium ion, and calcium-cadmium ion systems:  $K_{Ca} = 2.9 \times 10^2$ ,  $K_{Cd} = 8.6 \times 10^3$ ,  $K_H = 3.6 \times 10^6$ ,  $\chi_{H-Ca} = -0.76$ ,  $\chi_{H-Cd} = 0.13$ , and  $\chi_{Ca-Cd} = 1.0$ . Competitive ion adsorption was measured by FTIR ATR spectroscopy of either collapsed or ordered LB films. Data for the proton-calcium-cadmium ion system agreed well with the model predictions. The results show possible future applications of such thin films as ion sensors or ion exchange materials.*

## Introduction

Ultrathin films of organic materials have received much attention in several science and engineering fields (Swalen et al., 1987; Stroeve and Franses, 1987; Roberts, 1990; Ulman, 1991). During the last decade, many attempts have been made to develop engineering applications using thin films. Promising application areas are:

- Nonlinear optical and light-harvesting polymer systems (Swalen, 1986; Williams, 1988; Fox et al., 1993) utilizing oriented chromophores inducing directional electron transfer, for conversion of light energy into information and chemical energy
- Corrosion-barriers, passivating films, or membranes for separation or selective permeation of gas and liquid substances (Kuan et al., 1988; Bruinsma et al., 1992), since transport properties of such films are controlled by their thickness and micro (or nano) structure
- Sensors for detecting chemical and biological substances (Wohltjen et al., 1985; Moriizumi, 1988; Hua et al., 1990), since they use unique interactions of film materials with foreign species
- Molecularly engineered mono or multilayers for altering solid surfaces and controlling surface or interparticle forces (Whitesides and Laibinis, 1990; Chapman, 1993).

In this study, we report some interesting properties of thin films which may lead to ion exchange materials or better understanding of ion exchangers, with precise control of surface charge density.

When insoluble (Langmuir) monolayers of fatty or alkanolic acids are spread at the air/water interface, they interact strongly with bivalent or multivalent metal ions. Previous studies for binary ionic systems related certain ion adsorption characteristics only to the binding (or adsorption) constants of the ions. Yamauchi et al. (1968) and Petrov et al. (1982) used chemical equilibrium reaction models with the assumption that the Langmuir monolayer is neutral in charge. By contrast, McLaughlin et al. (1981), Löche et al. (1985), Pezron et al. (1990), and Bloch and Yun (1990) indicated that the Langmuir monolayer is electrically charged due to partial dissociation of the polar groups of the monolayer. They developed several electrochemical models that use a Langmuir isotherm for adsorption in the Stern layer and consider the electrical diffuse layer. Their models could account for ion binding of certain ions but not others. Experimental evidence amply indicated a need for improving the models (Deamer et al., 1967; Petrov et al., 1982; Kobayashi et al., 1988). Recently, it was found by Ahn and Franses (1991) that binary ion adsorption onto