분자공학적으로 제어된 고밀도 산성표면에서의 이온흡착 및 교환

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# Ion Adsorption and Ion Exchange at Acidic Supramolecular Surfaces

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## Introduction

Supramolecular materials are molecularly-engineered, novel organic materials that possess unique properties distinguishing themselves from bulk materials [1]. Such properties include well-defined structures and taylored chemical interactions. Supramolecular materials consist of closed-packed individual molecules. The structures vary from monolayer and multilayers to liposomes and vesicles. Dimensional size lies usually in the range from a few nanometers to less than a micrometer. Chemical properties depend not only upon those of individual organic molecules, but upon assembled final architecture. Molecules are amphiphilic such that one end group is hydrophilic (so-called head group) and the other is hydrophobic. Therefore, they tend to self-organize as molecular films or membranes at interfaces such as liquid/gas, liquid/solid, and liquid/liquid interfaces. Supramolecular technologies or nano-technologies are the processes that capture the essential properties of these molecular films and convert them into structures showing unique collective properties. Optical, electrical, transport, and specific chemical properties have been invoked for various engineering applications including nonlinear optics, energy conversion of light into electrical current, photolithographic films, membranes, and chemical/biosensors. From the series of studies, we suggest the application of supramolecular materials for ion exchange and removal of heavy metallic ions [2,3].

Alkanoic acid molecules, of which head group is carboxylic acid, are molecularly-engineered to form highly-densed molecular films at the air/water interface (Langmuir monolayer). Thus, in the interfacial region, a two-dimensional acidic plane faces an aqueous subphase. Dissolved cationic ions, for example, calcium, cadmium, lead ions, etc. react and adsorb at acidic head groups by replacing protons. Present paper focuses specifically on revealing thermodynamic features which govern ion adsorption and ion exchange at these acidic supramolecular surfaces. Not only binding capacities but nonideal mixing behavior of ions at the acidic plane are found to be important. A model considering both the electrochemical and thermodynamic aspects is constructed

rigorously and its calculations are compared to experimental data
obtained with Fourier Transform Infrared (FTIR) spectroscopy.

## Results and Discussion

Compositional analyses of the interfacial films equilibrated after
ion adsorption for binary systems, for example protons and cadmium
ions, have been reported after proper sampling of the films [4,5].
Figure 1 shows example data indicating, at least, two distinct
characteristics of ion adsorption.  Firstly, the compositional transition
(say, mid-point where both ion concentrations are the same) occurs at
different pH values for different metallic ions.  Secondly, the slope of
the compositional transition curve differs significantly depending on the
kind of ions.

To accomodate both of these trends, a lattice model is invoked
in this study.  The interfacial acidic head groups form a lattice plane,
upon which adsorbed ions locate and mix.  The mixing behavior of ions
is, in general, nonideal, which is addressed by introducing the
Flory-Huggins interaction parameter ($\chi_{ij}$) in the model.  Then, the
generalized Flory-Huggins equation can be rephrased in terms of the
adsorbed ion activity ($a_i$) as follows:

$$\ln a_i = \ln \phi_i + \sum_{j \neq i} \left(1 - \frac{p_i}{p_j}\right) \phi_j + p_i \left[ (1 - \phi_i) \sum_{j \neq k} \chi_{ij}\phi_j - \frac{1}{2} \sum_{j \neq i} \sum_{k \neq i} \chi_{jk}\phi_j\phi_k \right]$$

where, $\phi_i$ and $p_i$ are the area fraction (or surface fraction) of i
component and the number of lattice sites occupied by each of i ions,
respectively.  Hence, $\phi_i$ is a measure of ionic composition.  After
combining with the Gouy-Chapman theory to account for the electrical
diffuse layer in the lquid interfacial region, the elementary surface
reaction equations result in a novel adsorption isotherm, which leads us
to calculations of surface ion compositions.

For the binary systems, the model calculations are fitted quite well
with the available experimental data, as shown in Figure 1.  For the
lead-proton system, the interaction parameter deviates positively from
the ideal case.  By contrast, the barium-proton system is negatively
nonideal, indicating two ions mix well each other.  This is a reason for
a smaller slope of the composition curve for the barium-proton system.
Nearly ideal mixing behavior is preserved for both the cadmium-proton
and the calcium-proton systems, for which other suggested models are
adequate [6,7].  It should be noted that lead ions bind to the acidic
supramolecular surface much more strongly than calcium ions (about
10,000 times stronger).

When the system is expanded to ternary ionic systems, one can
address ion exchange behavior among metallic ions.  The ionic
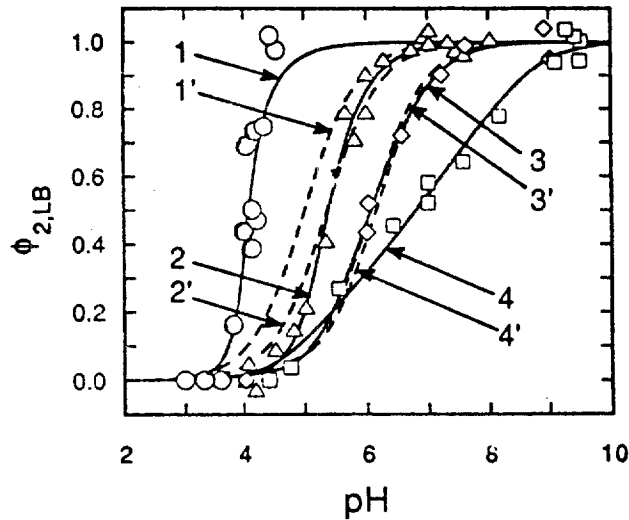compositions for this system are reduced to the following equations:

Figure 1. Comparision of compositional data [4] to model calculations: lead (O, 1, 1'), cadmium (△, 2, 2'), calcium (◇, 3, 3'), and barium ions (□, 4, 4'). Solid lines (1, 2, 3, 4) indicate the present model and broken lines (1', 2', 3', 4') indicate Bloch and Yun's model [6]. Bulk metallic ion concentration is $3 \times 10^{-4}$M.
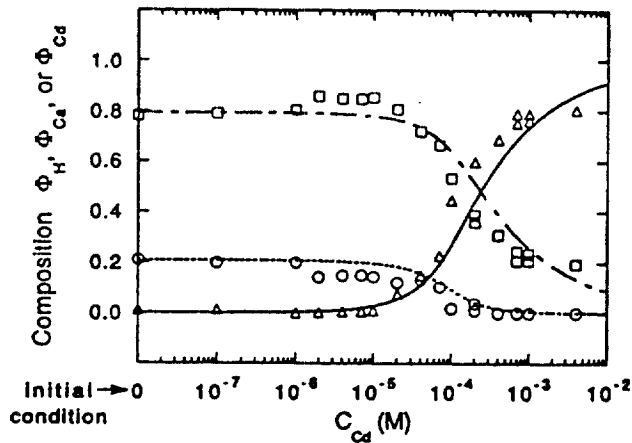


Figure 2. Ion exchange for a ternary ionic system: calcium salt (O, dotted line), cadmium salt (△, solid line), and acid (□, broken line). Lines are the model predictions. Bulk concentration of calcium ions is $5 \times 10^{-4}$M and pH=5.5.

$$
\begin{bmatrix} \phi_o \\ \phi_H \\ \phi_A \\ \phi_B \end{bmatrix} = D^{-1} \begin{bmatrix} 1 \\ K_H a_H' \exp(-\chi_{HA}\phi_A - \chi_{HB}\phi_B) \\ K_A a_A' \phi_o \exp\{1 - 2(\chi_{HA}\phi_H + \chi_{AB}\phi_B)\} \\ K_B a_B' \phi_o \exp\{1 - 2(\chi_{HB}\phi_H + \chi_{AB}\phi_A)\} \end{bmatrix}
$$

where

$$D = 1 + K_H a_H' \exp(-\chi_{HA}\phi_A - \chi_{HB}\phi_B)$$
$$+ K_A a_A' \phi_o \exp\{1 - 2(\chi_{HA}\phi_H + \chi_{AB}\phi_B)\} + K_B a_B' \phi_o \exp\{1 - 2(\chi_{HB}\phi_H + \chi_{AB}\phi_A)\}$$

Since dilute solutions are involved, the ideal solution equation is used for obtaining solution ion activity $a_i^s$. As a model case, the ternary system involving protons, cadmium and calcium ions is investigated. We have already determined from the binary systems the necessary parameters that are needed to calculate compositions; thus, calculations for the ternary system do not include any adjustable parameters. Figure 2 indicates that model predictions agree well with data obtained using FTIR analyses. Ion exchange characteristics is that as concentration of cadmium ions increases calcium ions desorb completely before protons become a minor component.

Current study reveals for the first time, to author's knowledge, the capability of supramolecular surfaces as an ion exchanger. Both the electrochemical and thermodynamic effects on ion adsorption were characterized successfully with a novel model. By using proper supramolecular techniques, surfaces exposing highly-densed radicals can be constructed on resins, which are processible better than the Langmuir monolayers. Supramolecular surfaces are readily taylored and functionalized by using molecules with different head groups. The technique is expected to open production of novel ion exchange resins.

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