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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 (Cr^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ca^{2+}, Ni^{2+}, and 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 Å^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 developing the supramolecular systems as novel ion exchange devices and sensors.

EXPERIMENTAL SECTION

1. Materials

Stearic acid ($CH_3(CH)_{16}COOH$; 99+%), $CrCl_2$ (95+%), $PbCl_2$ (99.999 %), $CdCl_2$ (99.99 %), $NiCl_2$ (99+%), $CuCl_2$ (99.0+%), $ZnCl_2$ (98+%), $CaCl_2$ (99+%), and $BaCl_2$ (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 purifing system. The final deionized (DI) water had an initial resistivity of 18.2 MΩ·cm. The metal ionic concentration in aqueous sub-solution was 10^{-4} 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 ($CHCl_3$) solution (1 mM), by using microsyringes, on the air/water interface of the ionic sub-solution (at room temperature) in a precleaned Langmuir minitrough (75×270 mm; KSV, Finland). Platinum Wilhelmy plate (10×20 mm) was used to measure the interfacial tension (γ, mN/m), from which the surface pressure (Π, mN/m) is obtained as $\Pi=\gamma_0-\gamma$, where γ_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 CaF_2 plates (12×25×2 mm;

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Wilmad) by manual lifting method. Sampling was done several times carefully such that molecules in the deposited films do not possess the order as appearing in the Langmuir monolayer. In the FTIR analysis, the intensity of each IR band is influenced both by composition and amount of the sample and by molecular orientation of a specific group [Ahn and Franses, 1992, 1994]. The above sampling procedure gets rid of the contribution of molecular chain orientation with respect to the electrical field of the IR beam, so that the spectra reflect only the composition and the amount of the sample.

Before the spectroscopic measurements were made, the films on CaF_2 plates were dried with a nitrogen gas (99.99 %) stream. FTIR spectra were collected in the transmission mode (normal beam incidence) using Perkin-Elmer FTIR system 2000, Bio-Rad FTS-60, and Bomem DA-8 equipped with a KBr beam splitter and with DTGS (deuterated triglycin sulfate) or MCT (mercury cadmium telluride) detector. The spectral resolution was 8 cm^{-1} and 256 scans were accumulated for each sample. In order to enhance the signal-to-noise (S/N) ratio, the sample chamber was purged with nitrogen gas (Perkin-Elmer and Bio-Rad spectrometers) or was in vacuo (Bomem spectrometer).

RESULTS AND DISCUSSION

1. Surface Isotherms

Surface isotherms of the acidic Langmuir monolayers are known to be affected by the adsorption of metal ions at the surface [Yazdanian et al., 1992]. We have investigated the change in surface isotherms with pH of each ionic solution. Fig. 1 shows a typical surface isotherm of stearic acid Langmuir monolayer spread on pure DI water at pH=5.5 and at room temperature. At a large mean molecular area (MMA, $Å^2$/molecule), the monolayer is *gaseous*. As MMA decreases, the monolayer undergoes phase transitions to *liquid-expanded*, *liquid-condensed* and *solid-like* states [Gaines, 1966; Kim et al., 1996]. The transition from *gaseous* to *liquid-expanded* is not clearly observable in the isotherm, because the surface pressures of the two states do not differ much and the Wilhelmy plate method is not proper for the distinction of the two states. However, as the monolayer is in the *liquid-condensed* state, the surface pressure increases notably with decreasing MMA. Upon changing into *solid-like* state the surface pressure sharply increases. The surface isotherm on pure water changes little over a wide range of pH less than ca. 8.

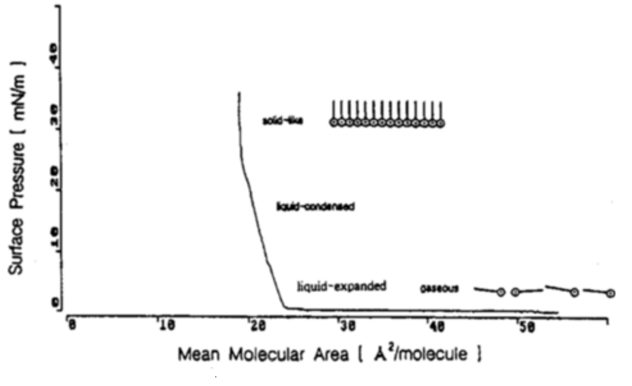

Fig. 1. The surface isotherm of stearic acid monolayer on pure water at pH=5.5.

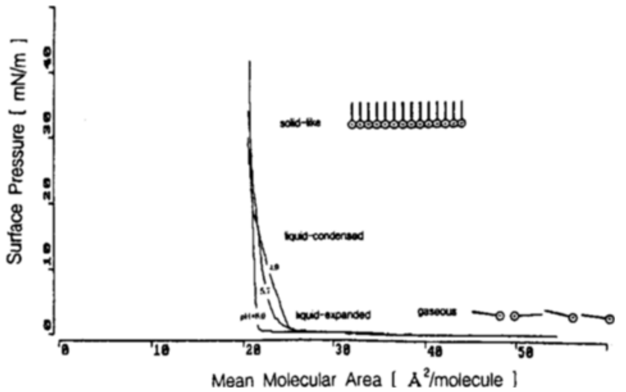

Fig. 2. The surface isotherm of stearic acid monolayer on aqueous zinc ionic sub-solution (10^{-4} M).

When the zinc ions are dissolved in the aqueous sub-solution, the surface isotherms are affected by pH, as shown in Fig. 2. In the case of pH=4.9, the isotherm is nearly identical to that on pure water, indirectly indicating the Langmuir monolayer is in acid form. As the pH increases to 6.0 the *liquid-condensed* region disappears and the monolayer under goes direct phase transition from *liquid-expanded* state to *solid-like* state. At the same surface pressure, say Π=10 mN/m, MMA is smaller as the pH increases. This implies that carboxylic head groups at the monolayer surface are deprotonated as zinc ions adsorb at the surface, which is evident in FTIR spectra (see next section). The isotherms at pH higher than 6.0 are identical to the one at pH=6.0, and those at pH lower than 4.9 are identical to the one at pH=4.9. Therefore, simply based on surface isotherms we can deduce that surface ion exchange of protons by zinc ions occurred in between pH=4.9-6.0.

Similar behaviors of surface isotherms are observable on aqueous sub-solutions containing other metal ions. The isotherms on sub-solutions containing chromium, copper, and nickel ions are given in Figs. 3 to 5, respectively. Depending on the identity of the metal ions, the surface ion exchange occurs in the different regions of pH values: 2.9-3.7 for chromium ions, 4.3-6.0 for copper ions, and 4.7-7.0 for nickel

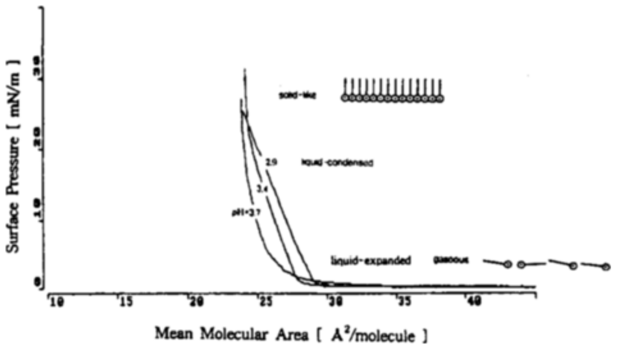

Fig. 3. The surface isotherm of stearic acid monolayer on aqueous chromium ionic sub-solution (10^{-4} M).

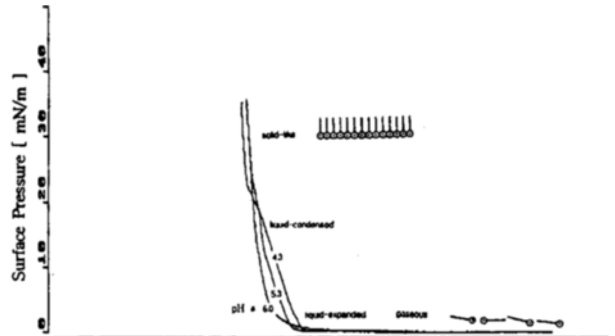

Fig. 4. The surface isotherm of stearic acid monolayer on aqueous copper ionic sub-solution (10^{-4} M).

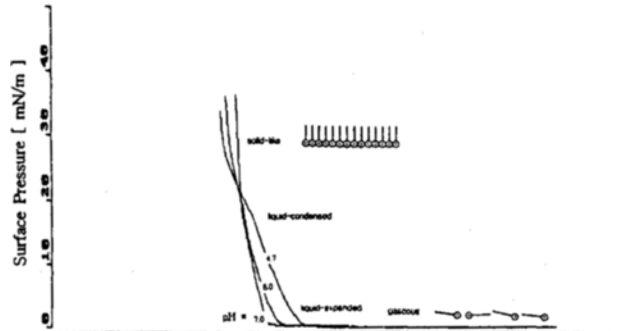

Fig. 5. The surface isotherm of stearic acid monolayer on aqueous nickel ionic sub-solution (10^{-4} M).

ions. It indicates that metal ions have different affinity to acidic Langmuir monolayers. Only with the isotherms it is difficult to estimate accurately the change in ionic composition of the monolayer in the ion exchange region, which is easily analyzable by using FTIR spectroscopy, as detailed in the subsequent section. It is noted that for the cases of copper and nickel ions the monolayers at lower pH are not stable enough so that the isotherms are distorted in the *liquid-condensed* to *solid-like* transition.

2. FTIR Spectroscopic Results

FTIR spectroscopy is useful for examining the ionic composition of the sampled films, because it can differ protonated stearic acid molecules from deprotonated molecules with metal ions bound. Exemplary FTIR transmission spectra, obtained from monolayer samples taken from aqueous chromium ionic solutions of different pH, are given in Fig. 6. The spectra have asymmetric methyl stretching (ν_aCH_3), asymmetric methylene stretching (ν_aCH_2, peak A), symmetric methylene stretching (ν_sCH_2, peak B), carbonyl stretching ($\nu C=O$, peak C), asymmetric carboxylate stretching (ν_aCOO^-, peak D), methylene scissoring (δCH_2, peak E), and symmetric carboxylate stretching (ν_sCOO^-, peak F) bands [Colthup et al., 1990; Kimura et al., 1986; Marshbanks et al., 1994]. Band assignments and corresponding peak positions are summarized in Table 1. At pH=2.9 the carboxylate stretching band (peak D; 1,543 cm^{-1}) is completely absent while the carbonyl band (peak C; 1,701 cm^{-1}) is strong, indicating that carboxylic head groups are in protonated state without chromium ions adsorbed at the head groups. This spectrum is identical to that for the monolayer on pure water (not shown). When the pH increases to 3.4, the carboxylate band appears and the carbonyl band intensity is weakened relatively. At pH=3.7 the carboxylate band is relatively stronger than the other. This clearly indicates that chromium ions replace protons at the head groups as the pH of the sub-solution increases. Hence, FTIR analyses enable one to estimate ionic composition accurately, in addition to qualitative results inferred from the surface isotherms in the previous section.

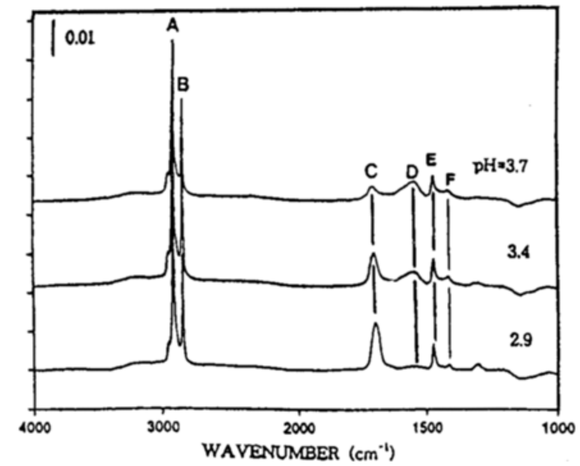

Fig. 6. FTIR transmission spectra for chromium ion adsorption.

Table 1. FTIR band assignments (for chromium ion adsorption)

Peak	Notation	Peak position (cm^{-1})
Asymmetric methyl stretching	ν_aCH_3	2,956.0
Asymmetric methylene stretching	ν_aCH_2	2,917.1
Symmetric methylene stretching	ν_sCH_2	2,850.0
Carbonyl stretching	$\nu C=O$	1,701.2
Asymmetric carboxylate stretching	ν_aCOO^-	1,542.8*
Methylene scissoring	δCH_2	1,469.8
Symmetric carboxylate stretching	ν_sCOO^-	1,400.3
COOH bending	bCOOH	1,301.9

*Peak position is different depending on metal ion species (zinc: 1,538 cm^{-1}, copper: 1,591 cm^{-1}, nickel: 1,553 cm^{-1})

FTIR results for zinc, copper, and nickel ions are presented in Figs. 7 to 9, respectively. In Fig. 7, at pH=4.9 the spectrum resembles those of stearic acid on pure water and on aqueous chromium solution at pH=2.9, indicating the sample is nearly in acid form. As pH increases to 6.0, there appears a huge asymmetric carboxylate band (peak D) at 1,538 cm^{-1}. Accordingly, a symmetric carboxylate band (peak F) at 1,395 cm^{-1} is clearly observable. As seen in the chromium ion case, the relative intensity ratio of the carboxylate band

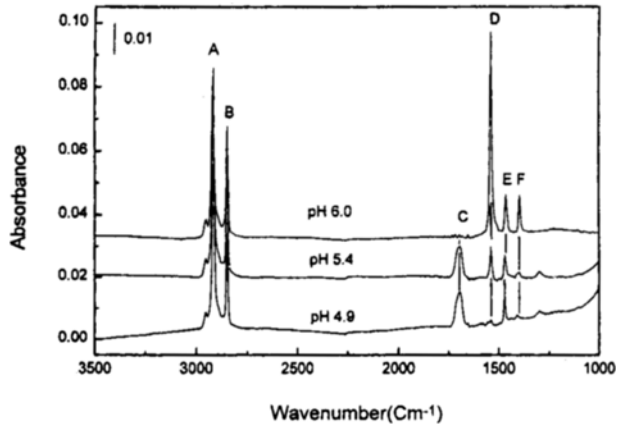

Fig. 7. FTIR transmission spectra for zinc ion adsorption.

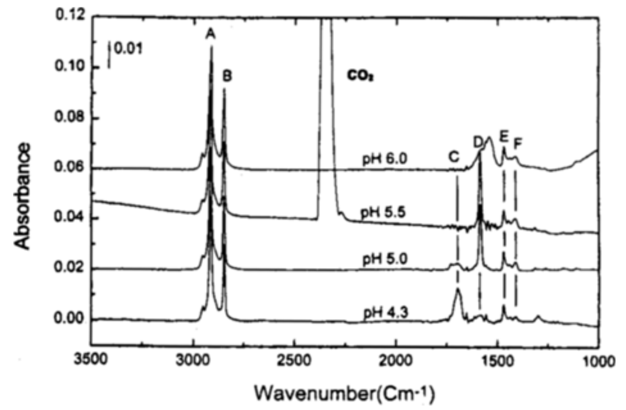

Fig. 8. FTIR transmission spectra for zinc ion adsorption.

to the carbonyl band (peak C) increases with increasing pH. The increase of this ratio indicates the increase of the surface ion exchange of protons by zinc ions. In Fig. 8, as pH increases from 4.3 to 5.5 the intensity ratio of the peak D (1,591 cm^{-1}) to the peak C becomes larger, again indicating the adsorption of copper ions. As the pH increases to 6.0, another broad band centered at 1,542 cm^{-1} appears. At present, the assignment for this band is not clear. However, this opens the possibility that another form of complex between the surface head groups and copper ions might exist. A thorough analysis of this band is beyond the scope of the present study, and will be described elsewhere in the future. In Fig. 9, the intensity ratio of the peak D (1,553 cm^{-1}) to the peak C becomes larger as the pH changes from 3.3 to 8.0, showing that nickel ions adsorb at the surface head groups.

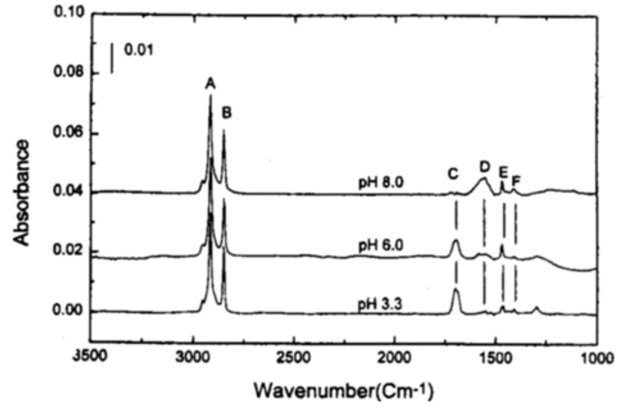

Fig. 9. FTIR transmission spectra for nickel ion adsorption.

3. Ionic Composition Analysis of FTIR Results

The intensity ratio of the asymmetric carboxylate band (peak D) to the carbonyl band (peak C) is clearly indicative of ion adsorption. However, the ratio itself is not the value of the ionic composition because the sensitivity of the individual band to the IR beam varies [Colthup et al., 1990; Ahn and Franses, 1992]. Thus, one needs to normalize each peak intensity with its IR sensitivity. Whether the molecules in the sample are in acid form or in salt form, each stearic acid molecule has 16 methylene (-CH_2-) units. Therefore, one can use the methylene stretching band as an internal reference for the calibration. We introduce the relative sensitivity α_i of each band i to the methylene stretching band, as follows:

$$\alpha_i = \frac{A_i}{A_{CH}} \tag{1}$$

where A_i is the carbonyl band (peak C) intensity when the sample is in pure acid form (i=1) or the asymmetric carboxylate band (peak D) intensity when pure salt (i=2). A_{CH} is the asymmetric methylene stretching band (peak A; 2,917 cm^{-1}) intensity. As a reference, we choose this asymmetric methylene stretching band, the largest band in the spectra, in order to minimize the influence of peak noise.

The calculated values of α_i are given in Table 2. The value of α_1 is nearly constant at 0.250±0.005, regardless of metal ion species present in the sub-solution. By contrast, as one might expect, the value of α_2 is different depending on metal ion species; 0.277 for chromium ion, 0.720 for zinc ions, 0.628 for copper ions, and 0.182 for nickel ions. Thereby, the ionic composition in the sample Φ_i is related to the relative sensitivity α_i as follows:

$$\Phi_i = \frac{\alpha_i^{-1}A_i}{\alpha_1^{-1}A_1 + \alpha_2^{-1}A_2} \tag{2}$$

Here, we presumed that the relative sensitivity obtained from pure samples (acid or salt) preserves its value in the mixture samples. A_i in the numerator is the corresponding peak intensity in the mixture, i.e., the carbonyl band intensity (indicative of acid form) when i=1 and the asymmetric carboxylate band intensity (indicative of salt form) when i=2.

Surface ion adsorption to acidic Langmuir monolayers is

Table 2. Relative IR sensitivity

Ion	α_1*	α_2**
Cr^{2+}	0.245	0.277
Zn^{2+}	0.255	0.720
Cu^{2+}	0.244	0.628
Ni^{2+}	0.248	0.182

*Calculated when the samples are pure acids. Average value is 0.250±0.005.

**Calculated when the samples are pure salts. The sensitivity is different depending on metal ion species.

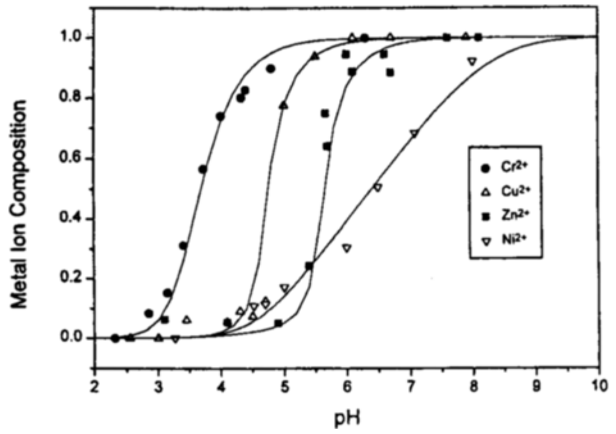

Fig. 10. Metal ion adsorption to stearic acid monolayers with pH. Bulk ionic concentration is 10^{-4} M. Solid lines are the model fittings.

presented against pH in Fig. 10. In general, at lower pH the monolayers are acidic, i.e., surface coverage of metal ions equals zero, while at higher pH they become salts, i.e., the surface coverage approaches unity. Interestingly, metal ion species differ in the adsorption characteristics, i.e., the characteristics of ion exchange breakthrough. Firstly, the value of pH where the compositional change occurs depends on ion species. For example, the pH at half coverage is ca. 3.6 for chromium ions, 4.7 for copper ions, 5.7 for zinc ions, and 6.4 for nickel ions. Secondly, the range of pH for ion exchange varies. The ion exchange of copper or zinc ions occurs in a narrow region of pH (ca. 1 pH unit), whereas it occurs in a wide region (ca. 4 pH units) for the case of nickel ions. A model to assess these characteristics is described in detail in the subsequent section.

4. Modelling of Surface Ion Adsorption to Langmuir Monolayers

To describe surface ion adsorption, we apply a model that considers competitive ion adsorption to a 2-dimensional charged monolayer surface. The reaction of competitive ion adsorption can be depicted by the following equilibria containing fatty acid and its complex with bivalent metal ions:

$$R^- + H^+ \xleftrightarrow{K_1} RH \tag{3}$$

$$2R^- + A^{2+} \xleftrightarrow{K_2} R_2A \tag{4}$$

where H^+ denotes protons and A^{2+} denotes metal ions. K_1 and K_2 indicate corresponding surface adsorption constants. The system contains three different components in the monolayer; R^- (deprotonated stearic acid), RH (stearic acid), and R_2A (metal complex). Here, we assume that there exists 2 : 1 metal complex only. Recent synchrotron X-ray study [Bloch et al., 1988] suggests that the number ratio of adsorbed manganese ions to stearate molecules is 0.5 at maximum. Thus, even if one presumes 1 : 1 complexation, the number of stearate molecules is twice the number of metal ions at complete surface metal ion coverage. Hence, we consider 2 : 1 complexation plausible. Once empirical evidence for 1 : 1 complexation is given, the model can be extended in the future.

The above reaction equilibria correspond to the following equations using surface ion activities:

$$a_1 = K_1 a_0 a_1^S \tag{5}$$

$$a_2 = K_2 a_0^2 a_2^S \tag{6}$$

where a_1 and a_2 denote, respectively, the surface ion activity of protons and metal ions adsorbed at surface lattice sites (R^-); a_0 denotes that of empty sites; a_1^s and a_2^s represent the sub-surface ion activities at the outer Helmholtz plane, which differ from the bulk ion activities due to electrostatic interaction of charged monolayers with dissolved ions. Here, we make use of activities instead of mole fractions, in order to assess nonideality in ion adsorption [Bloch and Yun, 1990; Ahn and Franses, 1991].

The surface ion activities are obtained by applying the Flory-Huggins model to the surface lattices. The area fraction ϕ_i of the component i in the Langmuir monolayer is defined as follows:

$$\phi_i \equiv \frac{p_i n_i}{\sum_{i=0}^{r} p_i n_i} = \frac{p_i y_i}{\sum_{i=0}^{r} p_i y_i} \tag{7}$$

where n_i and y_i indicate, respectively, the number of surface ion species i and the surface mole fraction of i; p_i is the parameter of surface aggregation; here $p_0=p_1=1$, and $p_2=2$ because bivalent metal ions occupy two stearate lattices. By introducing Flory-Huggins binary interation parameter χ_{ij}, we can describe the interaction between adsorbed ions, hence the nonideal ion mixing behavior. The Gibbs energy of mixing ΔG_m considering the entropy of mixing and the energetic interaction is derived as follows [Kurata, 1982]:

$$\frac{\Delta G_m}{k_B T} = \sum_{i=0}^{r} n_i \ln \phi_i + \left(\sum_{i=0}^{r} p_i n_i \right) \sum_{i=0}^{r-1} \sum_{j=i+1}^{r} \chi_{ij} \phi_i \phi_j \tag{8}$$

where k_B is Boltzmann's constant and T is the absolute temperature. When the Flory-Huggins binary interaction parameter χ_{ij} is positive, it implies de-mixing of the two components. By contrast, negative nonideality implies well-mixing. An equivalent expression of Eq. (8) for the activities is given in Eq. (9).

$$\ln a_i = \ln \phi_i + \sum_{j \neq i} \left(1 - \frac{p_i}{p_j} \right) \phi_j + p_i \left[(1 - \phi_j) \sum_{j \neq i} \chi_{ij} \phi_j - \frac{1}{2} \sum_{j \neq i} \sum_{k \neq i,j} \chi_{jk} \phi_j \phi_k \right] \tag{9}$$

Among χ_{01}, χ_{02} and χ_{12}, those which define interactions of H^+ and A^{2+} with unoccupied lattice sites (χ_{01} and χ_{02}) are assumed to be negligible, for simplification. With this assumption the activities a_0, a_1 and a_2 are as follows:

$$\ln a_0 = \ln(\gamma_0 y_0) = \ln \phi_0 + \frac{\phi_2}{2} - \chi_{12} \phi_1 \phi_2 \tag{10}$$

$$\ln a_1 = \ln(\gamma_1 y_1) = \ln \phi_1 + \frac{\phi_2}{2} + \chi_{12}(1 - \phi_1) \phi_2 \tag{11}$$

$$\ln a_2 = \ln(\gamma_2 y_2) = \ln \phi_2 - (\phi_0 + \phi_1) + 2\chi_{12} \phi_1 (1 - \phi_2) \tag{12}$$

where γ_i indicates the surface ion activity coefficient of component i. By rearranging Eqs. (5), (6), (10)-(12), one can obtain the following modified Langmuir isotherms for surface ion adsorption:

$$\phi_0 = \frac{1}{1+K_1 a_1^S e^{-\chi_{12}\phi_2} + K_2 a_2^S \phi_0 e^{(1-\chi_{12}\phi_1)}} \tag{13}$$

$$\phi_1 = \frac{K_1 a_1^S e^{-\chi_{12}\phi_2}}{1+K_1 a_1^S e^{-\chi_{12}\phi_2} + K_2 a_2^S \phi_0 e^{(1-\chi_{12}\phi_1)}} \tag{14}$$

$$\phi_2 = \frac{K_2 a_2^S \phi_0 e^{(1-\chi_{12}\phi_1)}}{1+K_1 a_1^S e^{-\chi_{12}\phi_2} + K_2 a_2^S \phi_0 e^{(1-\chi_{12}\phi_1)}} \tag{15}$$

Here, ϕ_i indicates the surface coverage of the component i in the Langmuir monolayer.

The sub-surface ion concentrations, and hence the sub-surface ion activities, are dependent upon electrostatic interactions exerted by the charged portion (ϕ_0) of the monolayer. To accommodate this effect the Gouy-Chapman diffuse layer equation [Adamson, 1990] for the asymmetric 2 : 1 electrolyte solution is solved analytically with one dimensional electrical potential $\psi(z)$ in the z-direction.

$$\frac{\psi(z)}{k_B T/q} = \ln\left[I \cdot \tanh^2\left(\frac{\kappa z}{2} + \beta\right) - C_2\right] - \ln C_N \tag{16}$$

$$\beta = \tanh^{-1}\left(\frac{C_2 + C_N\, e^{\frac{F\psi_0}{RT}}}{I}\right)^{1/2} \tag{17}$$

Here, C_1, C_2, and C_N denote the bulk molar concentrations of protons, metal ions, and anions ($C_N=2C_2+C_1$). I is the ionic strength of the aqueous sub-solution ($I=3C_2+C_1$), k_B is the Boltzmann's constant, T is the absolute temperature of the system, and q is the electron charge. κ is the inverse Debye length as defined by $\kappa^2 = \frac{2F^2 I}{\varepsilon\varepsilon_0 RT}$ where F is Faraday's constant, R is the gas constant, ε is the dielectric constant of water, and ε_0 is the permittivity of vacuum space. ψ_0 is the surface potential at z=0, i.e., the outer Helmholtz plane. Then, the sub-surface ion concentrations are described as follows:

$$C_1^S = C_1 \cdot e^{-\frac{q\psi_0}{k_B T}} \tag{18}$$

$$C_2^S = C_2 \cdot e^{-\frac{2q\psi_0}{k_B T}} \tag{19}$$

Therefore, when the solution is dilute, the sub-surface ion activities are

$$a_1^S \cong x_1^S \cong \frac{C_1^S}{C_{water} + C_1^S + C_2^S} \tag{20}$$

$$a_2^S \cong x_2^S \cong \frac{C_2^S}{C_{water} + C_1^S + C_2^S} \tag{21}$$

ψ_0 can be solved by using the surface charge density $\sigma=\varepsilon\varepsilon_0 (d\psi/dz)|_{z=0}$ that is related to ϕ_0 by the Grahame equation ($\sigma=-q\Gamma\phi_0$ [Bloch and Yun, 1990], where $\Gamma^{-1}=20\text{Å}^2$/molecule, i.e., the mean molecular area of the stearate molecules at $\Pi=$ 35 mN/m).

$$\sigma = -\left(e^{-\frac{F\psi_0}{RT}} - 1\right)\left[2\varepsilon\varepsilon_0 RT\left(C_N e^{-\frac{F\psi_0}{RT}} + C_2\right)\right]^{1/2} \tag{22}$$

By solving coupled Eqs. (13)-(15), (22) and the Grahame equation by iterative method, one can obtain ϕ_0, ϕ_1, ϕ_2, ψ_0, and σ with parameters K_1, K_2, and χ_{12}.

Whereas Langmuir monolayers are partially charged (ϕ_0 is less than ca. 0.1), collapsed film samples are completely neutralized during the sampling procedure. Hence, we made a plausible correction by introducing the assumption that the additional ion adsorption is determined by relative ion concentration in the diffuse layer. Then, the metal ion surface coverage Φ_2 of the sampled films can be given:

$$\Phi_2 = \phi_2 + \frac{2\Gamma_2}{\Gamma_1 + 2\Gamma_2}\phi_0 \tag{23}$$

where ϕ_i is the surface ion coverage in the Langmuir monolayer. Γ_i is the integrated ion density in the diffuse layer from z=0 to $10\kappa^{-1}$.

$$\Gamma_1 = \int_0^z C_1 e^{-\frac{q\psi(z)}{k_B T}}\, dz \tag{24}$$

$$\Gamma_2 = \int_0^z C_2 e^{-\frac{2q\psi(z)}{k_B T}}\, dz \tag{25}$$

Metal ion composition in the sampled film as calculated by Eq. (23) is now compared to that obtained by Eq. (2) through FTIR analyses.

5. Adsorption Selectivity of Acidic Langmuir Monolayers to Metal Ions

Model fitting results with experimental data are shown in Fig. 10. In the course of fitting data, two parameters K_2 and χ_{12} were optimized with K_1 fixed at a literature value of 3.63 × 10^6 [Bloch and Yun, 1990]. The model depicts very well the surface ion adsorption characteristics: the location and the range of ion exchange breakthrough. The values of fitting parameters are listed in Table 3 for the metal ions studied in the present study (chromium, copper, zinc, and nickel ions) along with other ions (lead, cadmium, calcium, and barium

Table 3. The values of fitting parameters*

Ion	Surface ion adsorption constant K_2	Flory-Huggins mixing parameter χ_{12}	pK_a	Bulk ion binding constant**
Cr^{2+}	7.5×10^7	0.14	3.6	2.6×10^6
Pb^{2+}	8.5×10^6	0.78	4.1	4.4×10^7
Cu^{2+}	5.5×10^5	0.85	4.7	1.3×10^7
Cd^{2+}	2.1×10^4	0.13	5.4	4.4×10^6
Zn^{2+}	8.5×10^3	0.90	5.7	2.5×10^5
Ca^{2+}	9.0×10^2	−0.76	6.2	–
Ni^{2+}	1.6×10^2	−3.00	6.4	3.9×10^4
Ba^{2+}	8.9×10^0	−4.10	7.0	–

*K_1 is fixed at 3.36 × 10^6 [Bloch and Yun, 1990]. Data of lead, cadmium, calcium, and barium are cited from the literature [Kobayashi et al., 1988; Ahn and Franses, 1991].

**The values are cited from the literature [Smith and Martell, 1989] for 2 : 1 complexation.

ions) from the literature [Kobayashi et al., 1988].

Among these ions, the surface ion adsorption constants are, in descending order, 7.5×10^7 for chromium, 8.5×10^6 for lead, 5.5×10^5 for copper, 2.1×10^4 for cadmium, 8.5×10^3 for zinc, 9.0×10^2 for calcium, 1.6×10^2 for nickel, and 8.8×10^0 for barium ions. Accordingly, the pK_a increases in a reverse manner. It should be noted that the surface ion adsorption constants do not relate to the literature bulk ion binding constants [Smith and Martell, 1989]. For example, chromium and cadmium ions have the same order of bulk ion binding constant around 3×10^6. However, the surface ion adsorption constant of chromium ions is ca. 4,000 times higher than that of cadmium ions. The reason for this difference is not clear at present. The ion binding might be altered probably due to extremely high density of surface head groups (ca. 20 Å^2 per group) in the Langmuir monolayer. Clarifying the cause for this effect is a subject of future study. In general, bulk binding constants are not valid when one deals with supramolecular surfaces.

The values of the Flory-Huggins mixing parameter are positively deviated (de-mixing) for lead, copper, and zinc ions; close to zero (athermal) for chromium and cadmium ions; and negatively deviated (well-mixing) for calcium, nickel, and barium ions. Positively-deviated ions show steep slopes in the ion exchange curve in Fig. 10, while negatively-deviated ions show sluggish slopes. Hence, the range of breakthrough for the latter ions is wider than that for the former ions. This implies that when one swings the pH to separate ions from an aqueous solution, the latter ions cannot be chelated efficiently within a small range of pH.

Acidic Langmuir monolayers are found to certainly have the selectivity in ion adsorption. Among the ions studied, chromium and lead ions strongly adsorb to the surface carboxylic head groups. The results are useful in developing supramolecular materials for sensing and separating metal ions from aqueous solutions.

CONCLUSIONS

Adsorption of metal ions to acidic Langmuir monolayers were analyzed by investigating surface isotherms and FTIR spectroscopy. The adsorption characteristics of surface ions was revealed quantitatively by applying the model incorporating both electrochemical and thermodynamic features. Selectivity of surface carboxylic acid groups of the Langmuir monolayer becomes higher in the order of barium, nickel, calcium, zinc, cadmium, copper, lead, and chromium ions. Interestingly, the adsorption constants of surface ions are found to be different from the bulk binding constants, in general. Therefore, the surface ion adsorption constants should be used for chemical processes where ion adsorption to supramolecular surfaces is involved. Ion selectivity information newly eatablished in the present study is useful in sensors and ion chelators using supramolecular materials.

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NOMENCLATURE

a_0 : surface activity of vacant lattice site
a_i : surface activity of component i in the monolayer (i=1, 2)
a_i^s : solution ion activity at sub-surface (outer Helmholtz plane)
C_i : bulk ion concentration, M [mol/L]
C_i^s : surface ion concentration at sub-surface (z=0) [M]
C_N : total bulk concentration of anions [M]
ΔG_m : Gibbs free energy of mixing per molecule [J]
F : Faraday's constant=96500 C/mol
I : ionic strength of aqueous sub-solution [M]
k_B : Boltzmann's constant=1.381×10^{-23}J/K
K_i : surface ion adsorption constant, dimensionless
n_i : number of molecules of component i in the monolayer
p_i : degree of aggregation of component i in the monolayer
q : electron charge=1.602×10^{-19}C
R : gas constant=8.314 J/(K·mol)
R^- : stearate molecules, $CH_3(CH_2)_{16}COO^-$
T : absolute temperature [K]
x_i^s : mole fraction of ion i at sub-surface
y_i : mole fraction of component i at monolayer surface
z : coordinate of one-dimensional diffuse layer

Greek Letters

α_i : relative sensitivity of IR band i
β : function defined in Eq. (17)
Γ : surface density of stearate molecules in *solid-like* monolayer, Γ^{-1}=20 Å^2/molecule
Γ_i : integrated density of ion i in the diffuse layer [mol/m^2]
γ_i : activity coefficient of component i in the monolayer
ε : dielectric constant of water=80
ε_0 : permitivity of vacuum=8.854×10^{-12} [F/m]
κ : inverse Debye length [m^{-1}]
σ : surface charge density of the monolayer [C/m^2]
Φ_i : surface coverage of component i in sampled films
ϕ_i : surface coverage of component i in Langmuir monolayers
χ_{ij} : Flory-Huggins binary interaction parameter or mixing parameter
$\psi(z)$: surface potential due to electrostatic interaction [V]
ψ_0 : surface potential at z=0 [V]

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