Korean J. Chem. Eng., **18**(6), 977-985 (2001)

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

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(*Received 5 March 2001 • accepted 16 July 2001*)

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}, [illegible] 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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[‡] Presented at the Int'l Symp. on Chem. Eng. (Cheju, Feb. 8-10, 2001), dedicated to Prof. H. S. Chun on the occasion of his retirement from Korea University.

Then the monolayers were carefully skimmed with a CaF_2 plate (Wilmad, 12×25×2 mm) so that the absorption intensities of the signature bands in FTIR (Fourier transform infrared) spectra depended only on the number density rather than the molecular orientation of the functional groups [Vijendra, 1988]. Samples were analyzed with an FTIR spectrometer (Bio-Rad FTS 60). The transmission spectra were collected at the resolution of 8 cm^{-1} by adding 256 scans. All experiments were done at the temperature of 25 °C.

EXPERIMENTAL RESULTS AND ANALYSES

1. Surface Isotherms

The relations between the surface pressure (Π) and the mean molecular area (MMA, $Å^2$/molecule) indicate the progress of monolayer phase on the air/water interface as the monolayer is compressed by the barriers. The surface isotherm provides useful information as follows: First, it enables one to implicitly understand if the stearic acid molecules on the air/water interface are in gaseous, liquid-expanded, liquid-condensed, or solid-like state with decreasing MMA as shown in Fig. 1 [Shin et al., 1990]. In the solid-like state, the stearic acid monolayer is known to organize in a close-packed fashion and its MMA is about 20 $Å^2$/molecule [Vogel, 1986]. Second, the adsorption of metallic ions to the surface of the stearic acid monolayer can be deduced. Ion adsorption occurs at the terminal carboxylic acid groups of the monolayer as protons are dissociated, depending on the surrounding conditions like ionic concentrations. When the bivalent metallic ions are adsorbed, the 2 : 1 complexation with acidic molecules is known to be favored (Fig. 2). The 2 : 1 complexation makes the intermolecular distance a bit shorter and consequently the MMAs at the same surface pressures become reduced compared to those of purely or less acidic monolayer as demonstrated in Figs. 1, 3-5. The surface isotherms of binary systems such as calcium-lead, calcium-chromium, calcium-copper, and calcium-zinc are shown in Figs. 1, 3-5. When the surface pressure is higher than 20 mM/m in these Figures, MMAs are ca. 20 $Å^2$/molecule. Therefore, it can be inferred that the monolayers are closely packed in the solid-like state. In Fig. 1, when the lead concentration is 10^{-7} M, the isotherm is nearly identical to that of the purely acidic monolayer on deionized water, even if the calcium concentration is present as much as 10^{-4} M. This implies that no metallic ions are adsorbed to the stearic acid monolayer. As the lead concentration increases, the liquid-condensed state disappears and the monolayer undergoes a direct transition from the liquid-expanded state to the solid-like state, which indicates that metallic ions are adsorbed. It is most probable that lead ions, not calcium ions, are adsorbed because calcium ions were barely adsorbed even when the lead concentration was smaller at 10^{-7} M. When the lead concentration was increased to 10^{-6} M, the liquid-condensed states com-

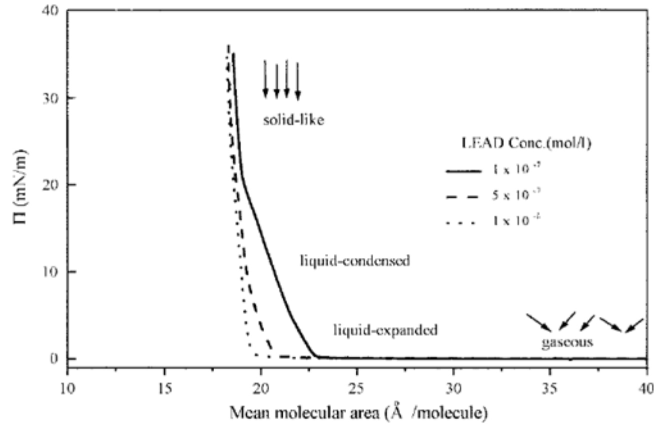

Fig. 1. Surface isotherms of stearic acid monolayers on calcium-lead aqueous sub-solution (pH=5.5, Ca=10^{-4} mol/*l*).

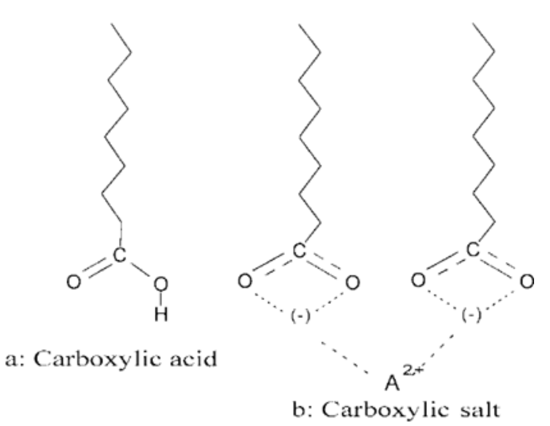

Fig. 2. Complexation of bivalent ions with stearate molecules.

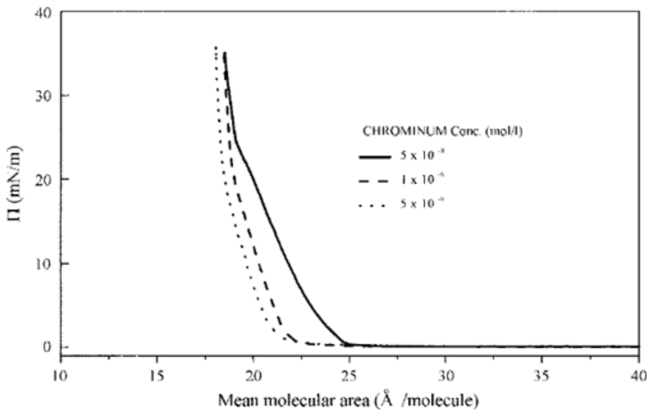

Fig. 3. Surface isotherms of stearic acid monolayers on calcium-chromium aqueous sub-solution (pH=5.5, Ca=10^{-4} mol/*l*).

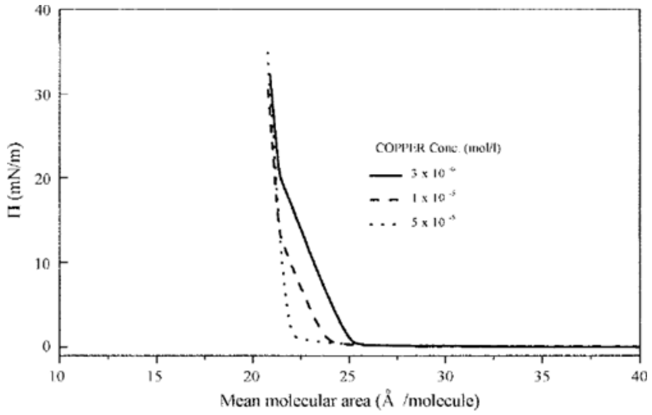

Fig. 4. Surface isotherms of stearic acid monolayers on calcium-copper aqueous sub-solution (pH=5.5, Ca=10^{-4} mol/*l*).

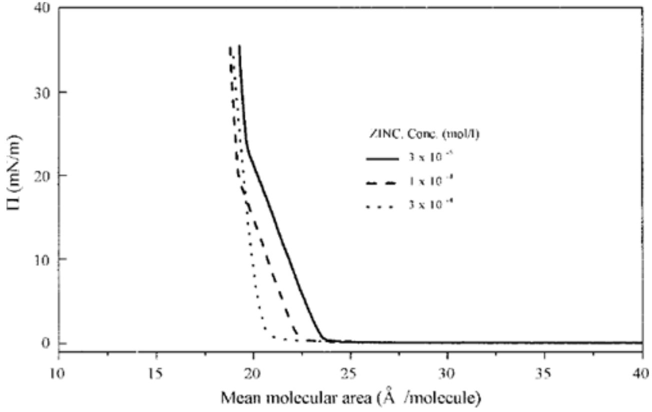

Fig. 5. Surface isotherms of stearic acid monolayers on calcium-zinc ionic aqueous sub-solution (pH=5.5, Ca=10^{-4} mol/*l*).

pletely disappeared, from which one could infer that the adsorption of lead ions was saturated and the monolayer was in the form of pure salt. Similar behaviors of the surface isotherms were also observed for other binary mixture solutions such as calcium-chromium (Fig. 3), calcium-copper (Fig. 4), and calcium-zinc systems (Fig. 5).

2. FTIR Results

Quantitative information on how much ions are adsorbed on the stearic acid monolayer is not possible to obtain from the surface isotherm measurements. The FTIR spectra can provide one with such quantitative information. The FTIR spectra obtained for each binary metallic ionic system with varying ionic concentration are given in Figs. 6-9.

The spectra contain asymmetric methyl stretching ($\nu_a CH_3$), asymmetric methylene stretching ($\nu_a CH_2$), symmetric methylene stretching ($\nu_s CH_2$), carbonyl stretching ($\nu C=O$), asymmetric carboxylate stretching ($\nu_a COO^-$), and methylene scissoring stretching (δCH_2) bands [Colthup et al., 1990; Kimura et al., 1986; Marshbanks et al., 1994]. The band assignments and the corresponding peak positions are summarized in Table 1.

The signature bands useful for identifying the adsorbed ions and their amounts are carbonyl and carboxylate stretching bands ranging from ca. 1,700 cm^{-1} to 1,500 cm^{-1}. The carbonyl band stands for protonated carboxylic acids and the carboxylate band for carboxyl salts. Especially, the latter band is found to be different in its peak position depending on the nature of adsorbed ion species as shown in the figures and the table. For the calcium-lead system (Fig. 6), the peak intensity of the asymmetric carboxylate stretching band (1,512 cm^{-1}) increases with the lead concentration in the sub-solution [Yamauchi et al., 1968]. The carbonyl stretching band shows a simultaneous decrease. When the lead concentration is very low, there exist a large carbonyl stretching band and a small carboxylate stretching band for calcium, indicating that the monolayer is mostly acidic with small portion of calcium salt. When the lead ion concentration is 3×10^{-7} M, the carboxylate stretching band for lead appears, indicating the adsorption of lead ions begins to occur. The complexation of the monolayer with lead ions is completed when their concentration reaches 3×10^{-6} M.

Other binary metallic solutions of calcium-chromium (Fig. 7), calcium-copper (Fig. 8), and calcium-zinc (Fig. 9) systems show basically similar trends in spectral change with increasing concentration of the counterpart ion. These FTIR results prove that the above-mentioned inferences from the surface isotherms are qualitatively valid.

Table 1. Band assignments of FTIR spectra

Peak	Notation	Peak position (cm^{-1})
Asymmetric methyl stretching	$\nu_a CH_3$	2956.0
Asymmetric methylene stretching	$\nu_s CH_2$	2917.1
Aymmetric methylene stretching	$\nu_s CH_2$	2850.0
Carbonyl stretching	$\nu C=O$	1701.2
Asymmetric carboxylate stretching	$\nu_a COO^-$	$-(COO)_2Pb$: 1512 $-(COO)_2Cr$: 1536 $-(COO)_2Cu$: 1587 $-(COO)_2Zn$: 1536 $-(COO)_2Ca$: 1578, : 1538
Symmetric carboxylate stretching	$\nu_s COO^-$	1440-1380
Methylene scissoring	δCH_2	1473-1465
$-CH_2$ - progression		1400-1180
COOH bending	bCOOH	1301.9

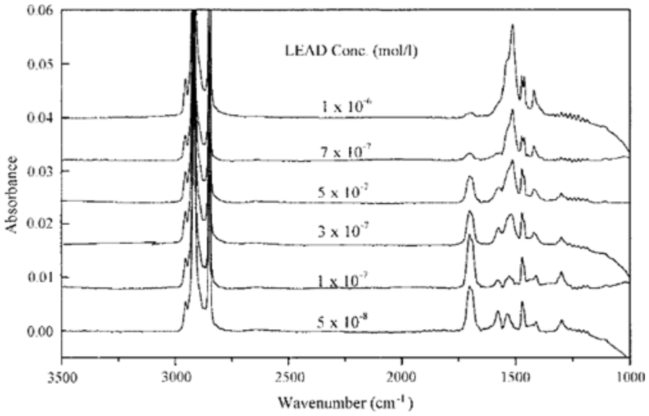

Fig. 6. FTIR transmission spectra for calcium-lead ion adsorption (pH=5.5, Ca=10^{-4} mol/*l*).

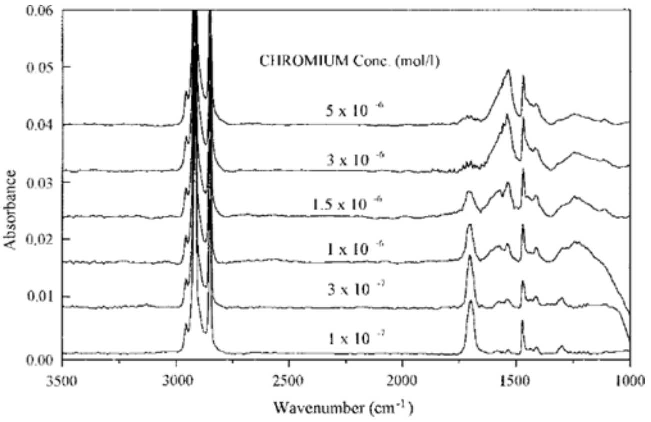

Fig. 7. FTIR transmission spectra for calcium-chromium ion adsorption (pH=5.5, Ca=10^{-4} mol/*l*).

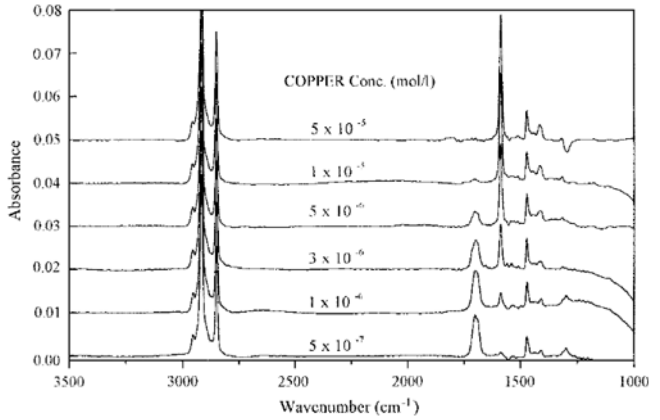

Fig. 8. FTIR transmission spectra for calcium-copper ion adsorption (pH=5.5, Ca=10^{-4} mol/*l*).

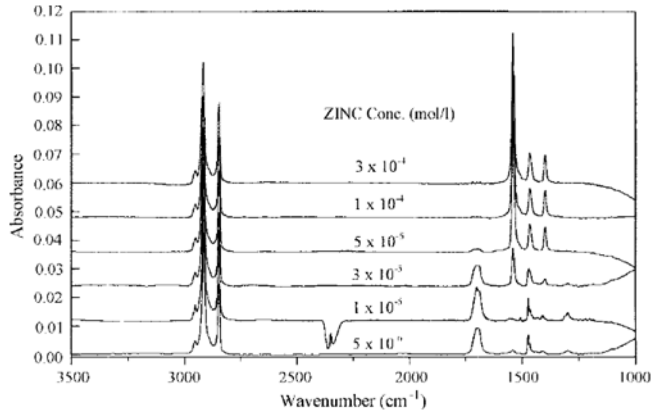

Fig. 9. FTIR transmission spectra for calcium-zinc ion adsorption (pH=5.5, Ca=10^{-4} mol/*l*).

It should be noted that the peak intensity and the shape of the corresponding carboxylate band are quite different for the cases studied. In order to get quantitative amounts of adsorbed species we need to deconvolute the overlapped peaks through the spectral analyses, as shown in Fig. 10, so that sound values of individual peak areas are obtained for further compositional analyses as detailed in the next section.

3. Compositional Analyses of Adsorbed Ions

The intensity ratio of the asymmetric carboxylate stretching band to the carbonyl stretching band indicates the adsorbed amount of the specific ion. However, since the sensitivity of the individual band to the IR beam varies, the ratio itself is not a sound value of the ionic composition [Colthup et al., 1990; Ahn et al., 1992]. Thus one needs to normalize each band intensity with its IR sensitivity.

Whether the molecules in the sample are in acid form or in salt form, each stearic molecule has 16 methylene (-CH_2-) units. Therefore, one can use the methylene stretching band as an internal reference for the calibration. Here we introduce the relative sensitivity α_i of each band i to the methylene stretching band, as follows:

$$\alpha_i = \frac{A_i}{A_{CH_2}} \tag{1}$$

where A_i is the intensity area of the carbonyl band when the sample is in pure acid form (i=1) and that of the asymmetric carboxylate band when pure calcium salt (i=2) or other metal's pure salt (i=3). A_{CH_2} is that of the asymmetric methylene stretching band (2,917 cm^{-1}). As a reference, we choose this asymmetric methylene stretching band, the largest band in the spectra, in order to minimize the influence of peaks noises. The calculated values of α_i are given in

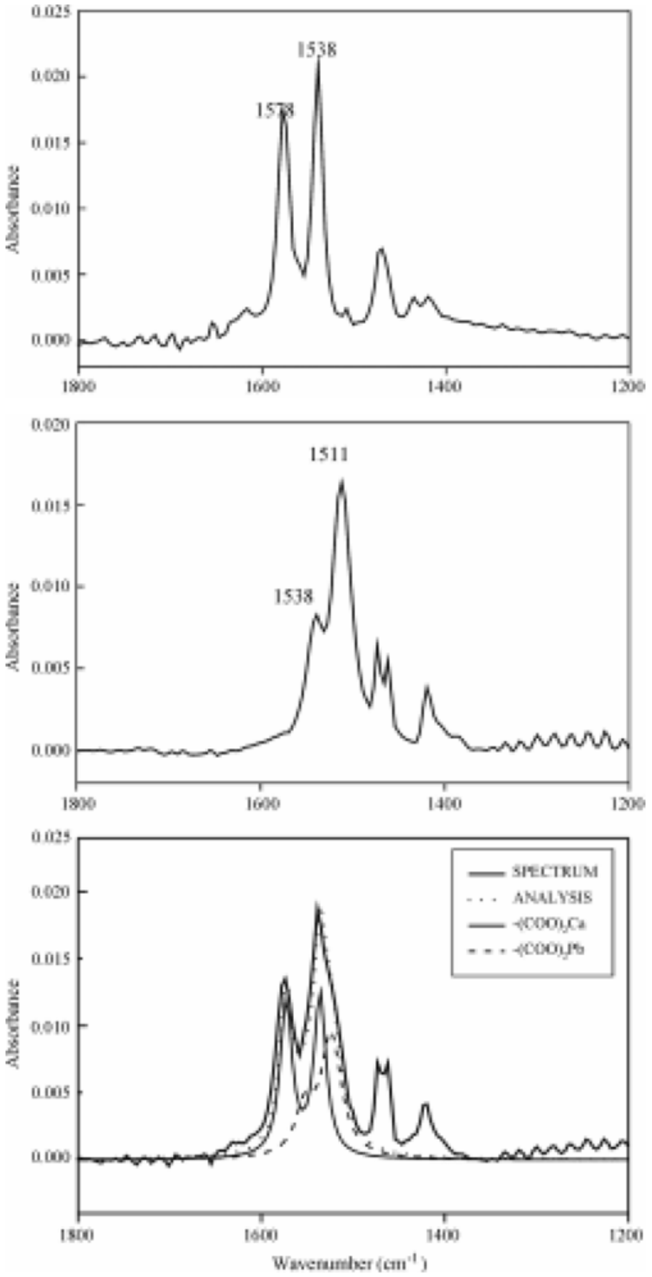

Fig. 10. Peak deconvolution of FTIR spectra.

Table 2. Relative sensitivity to IR beam

Ion	α_1 (acid)	α_2 (salt)
Pb^{2+}	0.247	0.396
Cu^{2+}	0.244	0.628
Ca^{2+}	0.247	0.412
Cr^{2+}	0.245	0.277
Zn^{2+}	0.255	1.230

Table 2. The value of α_1 is 0.250±0.005, regardless of metal ion species present in the sub-solution. By contrast, the value of $\alpha_{i\neq 1}$ is different depending on metal ion species: that is, 0.396 for lead ions, 0.277 for chromium ions, 0.412 for calcium ions, 0.629 for copper ions, and 1.230 for zinc ions (Table 2). Thereby, the ionic composition in the sample Φ_i is related to the relative sensitivity α_i as follows:

$$\Phi_i = \frac{\alpha_i^{-1} A_i}{\sum \alpha_i^{-1} A_i} \tag{2}$$

Here, we assumed that the relative sensitivity obtained from pure samples (acid or salt) preserve its values in the mixture samples. A_i in the numerator is the corresponding peak intensity in the mixture, that is, the carbonyl band intensity (indicative of acid form) when i=1 and the asymmetric carboxylate band intensity (indicative of salt form) when i=2 and 3.

Surface ion adsorption to the stearic acid monolayer is presented in Fig. 11 against the lead concentration with a fixed calcium concentration (10^{-4} M) at pH=5.5. At lower lead concentrations the monolayer is largely in acidic form, partly with calcium salt. As the lead concentration increases, calcium ions are desorbed first from the monolayer and then protons while lead ions start to adsorb. The half surface coverage of lead ions is at the concentration of ca. 3×10^{-7} M and the full coverage is at the concentration of 3×10^{-6} M.

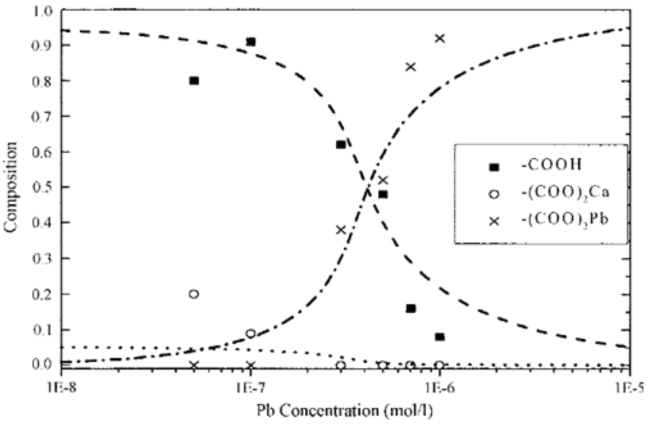

Fig. 11. Ion adsorption data (symbols) compared to model calculations (lines) for the calcium-lead binary system.

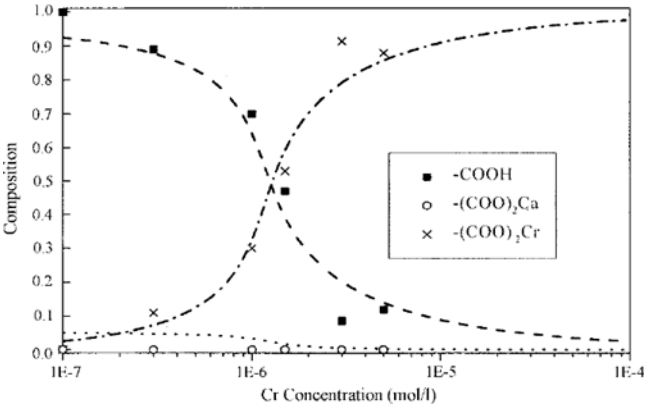

Fig. 12. Ion adsorption data (symbols) compared to model calculations (lines) for the calcium-chromium binary system.

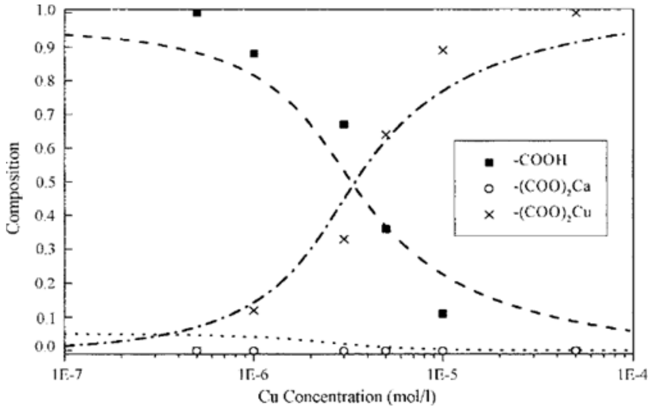

Fig. 13. Ion adsorption data (symbols) compared to model calculations (lines) for the calcium-copper binary system.

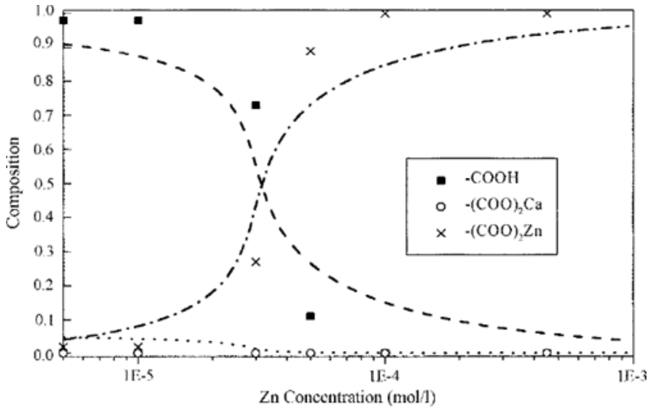

Fig. 14. Ion adsorption data (symbols) compared to model calculations (lines) for the calcium-zinc binary system.

Similar trends are also observable for other systems as shown in Figs. 12-14. However, the characteristic values are quite different, that is, the concentrations for half and full coverages of the counterpart ions are, respectively, ca. 1.5×10^{-6} M and 10^{-5} M for the calcium-chromium system, 4×10^{-6} M and 5×10^{-5} M for the calcium-copper system, and 3×10^{-5} M and 10^{-4} M for the calcium-zinc system.

THEORETICAL MODELLING FOR SURFACE ION ADSORPTION

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:

$$R^- + H^+ \xrightleftharpoons{K_H} RH$$

$$2R^- + A^{2+} \xrightleftharpoons{K_A} R_2A$$

$$2R^- + B^{2+} \xrightleftharpoons{K_B} R_2B \tag{3}$$

where H^+ denotes protons, and A^{2+} and B^{2+} denote metal ions. K_H,

K_A, and K_B indicate the corresponding surface binding constants. The system contains four different components in the monolayers: R^- (deprotonated stearic acid), RH (stearic acid), R_2A (calcium salt), and R_2B (other metal salt). Here we assume that there exists the 2 : 1 metal complex only. The 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 complex, the number of stearate molecules is twice the number of metal ions at the complete surface coverage of bivalent ions. We also considered the 1 : 1 complexation into this model, but its effect was negligible. Hence, we consider the 2 : 1 complexation plausible as far as the model fitting is in need. The above reaction equilibria correspond to the following equations using surface ion activities:

$$\begin{aligned} a_H &= K_H \cdot a_o \cdot a_H^s \\ a_A &= K_A \cdot a_o^2 \cdot a_A^s \\ a_B &= K_B \cdot a_o^2 \cdot a_B^s \end{aligned} \tag{4}$$

where a_H denotes the surface ion activity of protons. a_A and a_B denote those of calcium and other metal ion species adsorbed at surface lattice sites (R^-), respectively. a_o denotes that of empty sites. a_H^s, a_A^s, and a_B^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. Hence, we make use of activities instead of mole fractions in order to access nonideality in ion adsorption [Bloch et al., 1990; Ahn et al., 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 monolayers is defined as follows:

$$\phi_i \equiv \frac{p_i n_i}{\sum_{i=0}^{r} p_i n_i} \quad \text{or} \quad \phi_i = \frac{p_i y_i}{\sum_{i=0}^{r} p_i y_i} \tag{5}$$

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 $p_o=p_H=1$ and $p_A=p_B=2$ because bivalent metal ions occupy two stearate lattices. By introducing the Flory-Huggins binary interaction parameter χ_{ij}, we can describe the interaction between adsorbed ions, hence the nonideal ion mixing behaviors. The Gibbs energy of mixing ΔG_m considering the entropy of mixing and the energetic interaction is derived as follows [Kurata, 1982]:

$$\frac{\Delta G_m}{RT} = \sum_{i=0}^{r} n_i \ln\phi_i + \left(\sum_{i=0}^{r} p_i n_i\right) \sum_{i=0}^{r-1} \sum_{j=i+1}^{r} \chi_{ij}\phi_i\phi_j \tag{6}$$

where R is gas 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. (6) for the activities is given in Eq. (7).

$$\ln a_i = \frac{\Delta\mu_i^m}{RT} = \ln\phi_i + \sum_{j\neq i}\left(1-\frac{p_i}{p_j}\right)\phi_j + p_i\left[(1-\phi_i)\sum_{j\neq i}\chi_{ij}\phi_j - \frac{1}{2}\sum_{j\neq i}\sum_{k\neq i}\chi_{jk}\phi_j\phi_k\right] \tag{7}$$

Among χ_{OH}, χ_{OA}, χ_{OB}, and χ_{AB}, those which define interactions of H^+, A^{2+}, and B^{2+} with unoccupied lattice sites (χ_{OH}, χ_{OA}, and χ_{OB}) are assumed to be negligible for simplification. With this assumption the activities a_o, a_H, a_A, and a_B are as follows:

$$\ln a_o = \ln\phi_o - \ln\gamma_o + \frac{1}{2}(\phi_A+\phi_B) - \chi_{HA}\phi_H\phi_A - \chi_{HB}\phi_H\phi_B - \chi_{AB}\phi_A\phi_B \tag{8}$$

$$\ln a_H = \ln\phi_H + \frac{1}{2}(\phi_A+\phi_B) + \chi_{HA}(1-\phi_H)\phi_A + \chi_{HB}(1-\phi_H)\phi_B - \chi_{AB}\phi_A\phi_B \tag{9}$$

$$\ln a_A = \ln\phi_A - (\phi_o+\phi_H) + 2[\chi_{AH}\phi_H(1-\phi_A) - \chi_{HB}\phi_H\phi_B + \chi_{AB}(1-\phi_A)\phi_B] \tag{10}$$

$$\ln a_B = \ln\phi_B - (\phi_o+\phi_H) + 2[-\chi_{AH}\phi_H\phi_A - \chi_{HB}\phi_H(1-\phi_B) + \chi_{AB}\phi_A(1-\phi_B)] \tag{11}$$

where γ_i indicates the surface ion activity coefficient of component i.

By rearranging Eqs. (4) and (8)-(11), one can obtain the following modified Langmuir isotherms for surface ion adsorption:

$$\phi_o = \frac{1}{D} \tag{12}$$

$$\phi_H = \frac{K_H a_H^s \exp(1-\chi_{HA}\phi_A-\chi_{HB}\phi_B)}{D} \tag{13}$$

$$\phi_A = \frac{K_A a_A^s \phi_o \exp[1-2(\chi_{HA}\phi_H+\chi_{AB}\phi_B)]}{D} \tag{14}$$

$$\phi_B = \frac{K_B a_B^s \phi_o \exp[1-2(\chi_{HB}\phi_H+\chi_{AB}\phi_A)]}{D} \tag{15}$$

where

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

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

The sub-surface ion concentrations, and hence the sub-surface ion activities, are dependent upon electrostatic interaction exerted by the charged portion (ϕ_o) of the monolayer. To accommodate this effect the Gouy-Chapman diffuse layer equation [Shrauner, 1975; Adamson, 1990] for the asymmetric 2 : 1 electrolyte solution is solved analytically with one dimensional electrical potential $\Psi(x)$ in the x-direction.

$$\frac{F\Psi(x)}{RT} = \ln\left[I\tanh^2\left(\frac{\kappa x}{2}+\beta\right) - (C_A+C_B)\right] - \ln C_N \tag{16}$$

$$\beta = \tanh^{-1}\left[C_N\exp\left(\frac{F\Psi(x)}{RT}\right) + C_A + C_B\right]^{1/2} \tag{17}$$

Here, C_H, C_A, C_B, and C_N denote the bulk molar concentration of protons, calcium, other metal ion species, and anions ($C_N=C_H+2C_A+2C_B$) in the sub-solution, I is the ionic strength of the aqueous sub-solution ($C_I=C_H+2C_A+2C_B$), κ is the inverse Debye length as defined by $\chi^2=(2F^2I/\varepsilon\varepsilon_o RT)$ where F is Faraday constant, ε is the dielectric constant of water, and ε_o is the permittivity of vacuum space. $\Psi(0)$ is the surface potential at x=0, i.e., the outer Helmholtz plane. Then the sub-surface ion concentrations are described as follows:

$$C_H^S = C_{H0} e^{-\frac{F\Psi(0)}{RT}} \tag{18}$$

$$C_A^S = C_{A0} e^{-\frac{2F\Psi(0)}{RT}} \tag{19}$$

Table 3. Parameter values of ion species

Ion	Electro-negativity	Bulk	Binary solution			Pure solution	
		Binding constant K_B	Binding constant K_B	Mixing parameter χ_{HB}	Mixing parameter χ_{CaB}	Binding constant K_B	Mixing parameter χ_{HB}
Pb^{2+}	1.8	4.36×10^7	4.5×10^6	1.1	0.9	8.5×10^6	0.78
Cr^{2+}	1.6	2.57×10^6	1.5×10^5	1.2	0.9	7.5×10^7	0.14
Cu^{2+}	1.9	1.32×10^7	5.5×10^5	0.85	0.9	5.5×10^5	0.85
Zn^{2+}	1.6	2.45×10^5	6.0×10^4	1.3	0.9	8.5×10^5	0.9
Ca^{2+}	1.0	9.0×10^2	1.5×10^2	−0.76	-	1.5×10^2	−0.76
H^+	2.1	3.63×10^6	-	-	-	-	-

(1) Parameters for calcium are predetermined from pure solution and used for model calculations for binary solutions.
(2) Bulk binding constant of protons K_H is used for further calculations.

$$C_B^S = C_{B0}e^{-\frac{2F\Psi(0)}{RT}} \tag{20}$$

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

$$a_i^s = x_i^s = \frac{C_i^s}{C_{water} + \sum_i C_i^s} \tag{21}$$

$\Psi(0)$ can be solved by using the surface charge density $\sigma = \varepsilon\varepsilon_0(d\Psi/dx)|_{x=0}$ that is related to ϕ_0 by the Graham equation which is $\sigma = -q\Gamma\phi_0$ [Bloch and Yun, 1990], where $\Gamma^{-1}=20$ Å^2/molecule, i.e., the MMA of the close-packed stearate molecules at $\Pi=35$ mN/m.

$$\sigma = -q\Gamma\phi_0 = -\sqrt{2\varepsilon\varepsilon_0 RT}\left(e^{-\frac{F\Psi(0)}{RT}} - 1\right)\sqrt{C_B e^{-\frac{F\Psi(0)}{RT}} + C_A + C_H} \tag{22}$$

By solving coupled Eqs. (12)-(15), (22) and the Graham equation by an iterative method, one can obtain ϕ_0, ϕ_H, ϕ_A, ϕ_B, $\Psi(0)$, and σ with parameters K_H, K_A, K_B, χ_{HA}, χ_{HB}, and χ_{AB}.

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 the relative ion concentration in the diffuse layer. Then, the metal ion surface coverage Φ_i of the sampled films can be given:

$$\Phi_i = \phi_i + \frac{n_i K_i \Gamma_i}{\sum_i n_i K_i \Gamma_i}\phi_0 \tag{23}$$

where Γ_i is the integrated ion density in the diffuse layer from $x=0$ to $10\kappa^{-1}$

$$\Gamma_i = \int_0^{10\kappa^{-1}} C_{i0}\exp\left(-n_i\frac{q\Psi(0)}{k_B T}\right)dx \tag{24}$$

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

DISCUSSION

Fitted results of this electrochemical-thermodynamic model to the experiment data are indicated by lines in Figs. 11-14. The model includes six parameters K_H, K_A (or K_{Ca}), K_B, χ_{HA} (or χ_{HCa}), χ_{HB}, and χ_{AB} (or χ_{CaB}). Among these we choose K_B and χ_{HB} as control parameters by considering the following aspects: All systems studied commonly contain protons and calcium ions and hence their characteristic values can be fixed plausibly for simplicity. Thus, the value of K_H is fixed at a literature value of 3.63×10^6 for the bulk due to lack of data for the 2-dimensional surfaces [Bloch and Yun, 1990]. K_A (or K_{Ca}) and χ_{HA} (or χ_{HCa}) were predetermined through separate experiments for the proton-calcium system and they are fixed at 1.5×10^2 and −0.76, respectively [Hyun et al., 1997]. Among the remaining three parameters χ_{AB} (or χ_{CaB}) is found to be little important for model calculations. This is reasonable because calcium ions are merely adsorbed for the systems investigated as the FTIR results manifest and the mixing characteristics of calcium ions with other metallic ion species are minimally influential. χ_{CaPb} is determined to be 0.9 through separate experiments for the calclum-lead system at a higher pH of 8.9 at which protons are negligibly adsorbed. Then this value (0.9) is also applied to other χ_{CaB} parameters.

Model calculations are strongly dependent upon changes in K_B and χ_{HB}. The former parameter determines the breakthrough point and the latter does the slope of the curve. The model fittings are in reasonable agreement with the experimental composition data. The results of fitting are summarized in Table 3. In the case of the calcium-lead system, the value of lead ion binding constant (K_{Pb}) is 4.5×10^6 that is in the same order to that for the pure lead solution (8.5×10^6). The value of binary interaction parameter χ_{HPb} is 1.1; that is somewhat increased from 0.78 for the pure solution, indicating de-mixing is slightly enhanced in the presence of calcium ions though merely adsorbed. The calcium-copper system shows the identical characteristics as the pure copper system. By contrast, the calcium-chromium system shows K_{Cr} of 1.5×10^5 reduced much by a factor of 500, compared to the pure chromium system. χ_{HCr} is incredibly increased to 1.2 (de-mixing) from 0.14 (nearly ideal mixing). The calcium-zinc system similarly shows K_{Zn} of 6.0×10^4 reduced by a factor of ca. 10 and increased χ_{HZn} of 1.30 from 0.90. As a result, by adding merely adsorbing calcium ions into the subsolution, surface ion binding is increasingly suppressed in the order of lead, zinc, and chromium. Interestingly, copper and lead of which bindings are less affected have higher Pauling electronegativities of 1.9 and 1.8, respectively, while zinc and chromium of which binding is much suppressed have a lower electronegativity of 1.6, which is closer to 1.0 for calcium. It might be inferred that the addition of low electronegative calcium makes protons more strongly bound to the surface when low electronegative metallic ionic species are competing. Although rigorous chemical analyses need to be done further, ion adsorption from multicomponent ionic solutions to acidic Langmuir monolayers can be quite different from the case of pure ionic solutions and the electronegativities of the metallic species involved play a role, at least for the systems investigated.

CONCLUSIONS

The capability of the closely packed stearic acid monolayer surfaces for separation of toxic metal ions out of binary ionic solutions such as calcium-lead, calcium-chromium, calcium-copper, and calcium-zinc aqueous systems was evaluated both empirically and theoretically. The affinities of the monolayer 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. 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. Lead, chromium, 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. It can be concluded that surface ion binding capability for binary ionic solutions can be much different from that for pure ionic solutions.

ACKNOWLEDGEMENT

This work was supported by the Korea Science and Engineering Foundation (961-1107-045-2).

NOMENCLATURE

a_0 : activity of vacant lattice site
a_i : 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 interfacial diffuse layer (x=0), [M]
C_N : total bulk concentration of anions [M]
ΔG_m : Gibbs free energy of mixing per molecule [J]
F : faraday constant [96,500 C/mol]
I : ionic strength of aqueous sub-solution [M]
K_i : ion adsorption (or binding) 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 : $CH_3(CH_2)nCOO^-$
T : absolute temperature [K]
x : coordinate of one-dimensional diffuse layer
x_i^s : mole fraction of i ion at sub-surface
y_i : mole fraction of component i at monolayer surface
z : valency of ion

Greek Letters

α : relative sensitivity
β : function definition
Γ : surface density of the surfactant monolayer in the liquid condensed state; Γ^{-1}=0.2 nm^2/molecule
Γ_i : surface density of i ion in the diffuse layer [mol/m^2]
γ_i : activity coefficient of component i in the monolayer
ε : dielectric constant of water
ε_0 : permitivity of vacuum
κ^{-1} : Debye length [m]
μ : contribution from dipolar orientation to the measured surface potential
ν : number of the nearest neighbors to a give lattice
σ : surface charge density of the monolayer
Φ_i : area fraction of component i in the LB film
ϕ_i : area fraction of component i in the Langmuir monolayer
χ_{ij} : Flory-Huggins binary interaction parameter
$\Psi(x)$: surface potential due to electrostatic interaction [V]
Ψ_0 : surface potential at x=0

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