

Direct Evidence for Two Interaction Modes in Adsorption of Divalent Metal Ions to Iminodiacetate-Type Chelating Resins

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The adsorption curves of divalent metal ions (M^{2+}) to an iminodiacetate(IDA)-type chelating resin ($-L^{2-}$) under the condition of metal ions in excess against IDA groups clearly indicated the difference in contribution between two species. Copper and nickel are adsorbed only as $[(-L)M^{II}]$, while cadmium and calcium are adsorbed as $[(-L)M^{II}]$ and $[(-LH)_2M^{II}]$. Addition of salts may enhance the deprotonation of IDA groups, interfere with the adsorption as $[(-LH)_2M^{II}]$, and yield remarkable changes in adsorption curves, depending on the metal ions.

(Received January 7, 2002; Accepted March 18, 2002)

Adsorption to chelating resins is efficient for separation and concentration of metal ions prior to their determination.¹ Iminodiacetate(IDA)-type chelating resins ($-L^{2-}$) are commercially available and widely used. It is also well known that the adsorption curves of Co^{2+} , Zn^{2+} , and especially Mn^{2+} , Cd^{2+} , and Pb^{2+} are shifted to a higher pH region in the application to seawater, compared with freshwater.²

Recently, based on a Gibbs-Donnan model, the adsorption equilibria of divalent metal ions (M^{2+}) to IDA-type resins have been studied intensively.³ A competition method with protonation was adopted under the condition of the total amount of functional groups in excess against that of metal ions ($TA_L > TA_M$). The deviation of the observed adsorption capacities from those calculated using the adsorption constants of $[(-L)M^{II}]$ was assigned to the adsorption as $[(-LH)_2M^{II}]$, for which the adsorption constants were evaluated; the adsorption constants of $[(-L)M^{II}]$ were assumed to be the same as the stability constants of metal complexes with methyliminodiacetate in an aqueous solution. The effects of salts on the adsorption have also been described quantitatively, but the presentation is rather complicated.⁴

In contrast, we have proposed a competition method with protonation under a reversed condition of the total amount of metal ions in excess against that of functional groups ($TA_M > TA_L$), and have applied it to analyses of the adsorption equilibria of trivalent and tetravalent metal ions to an IDA-type chelating resin; the presence of $[(-LH)_3M^{III}]$ (M^{III} : Sc, Y, La) and $[(-LH)_4Th^{IV}]$ was reflected in the adsorption curves.^{5,6} In this study, we applied this type of analysis to the adsorption of divalent metal ions to directly demonstrate the presence of $[(-LH)_2M^{II}]$ as well as $[(-L)M^{II}]$ and also give a rather qualitative, but intuitive, explanation for the effects of salts on the adsorption equilibria.

Experimental

Stock solutions of metal ions were prepared from reagent-grade

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nitrate. The IDA-resin used was Amberlite IRC-718 (Rohm and Haas; particle size of 0.40 – 0.56 mm, Na-form, IDA density of 2.0 mmol g^{-1}). Adsorption experiments were carried out under two different conditions. One condition was a total amount of metal ions in excess against that of IDA, $TA_M > TA_L$; a 50 cm^3 -portion of 10^{-3} mol dm^{-3} solution (0.05 mmol metal) was added to 0.0125 g of the resin (0.025 mmol IDA). The other condition was a total amount of IDA in excess against that of metal ions, $TA_L > TA_M$; a 50 cm^3 -portion of 10^{-4} mol dm^{-3} solution (0.005 mmol metal) was added to 0.2 g of the resin (0.4 mmol IDA). The pH values were adjusted by addition of an acid or a base, and were measured on an activity scale using standard buffer solutions. After adjustment of the ionic strength with NaCl and of the total volume, the resulting solutions were shaken with an IDA-resin for two days at 25°C. Equilibration required longer time for $TA_M > TA_L$ than for $TA_L > TA_M$. The supernatants were subjected to the pH measurement and to the determination of metal ions by EDTA titrimetry or atomic absorption spectrometry. The equilibrium adsorption capacities were expressed in terms of mmol g^{-1} .

Results and Discussion

Acid-base equilibria of IDA resin

The acid-base equilibria of IDA resins were previously studied.^{3,7} The intrinsic protonation constants, which refer to the activity of proton in a resin phase, were as follows: $\log K_1 = 9.12$, $\log K_2 = 3.10$, $\log K_3 = 1.44$. The observed protonation constants, which refer to the activity of proton in an aqueous phase, on the other hand, depended on the ionic strength (I); e.g., ($\log K_2$, $I/mol\ kg^{-1}$): (4.5, 0.013), (3.9, 0.1), (3.1, 1.0).³ The deprotonation of $(-LH_2)$ is enhanced by cations in supporting electrolytes, as given by



Thus, the pH range for $(-LH_2)$ to be a major species is relatively wide (1.4 – 4.5) at $I = 0.01$, while being narrow (1.4 – 3.1) at $I = 1.0$.

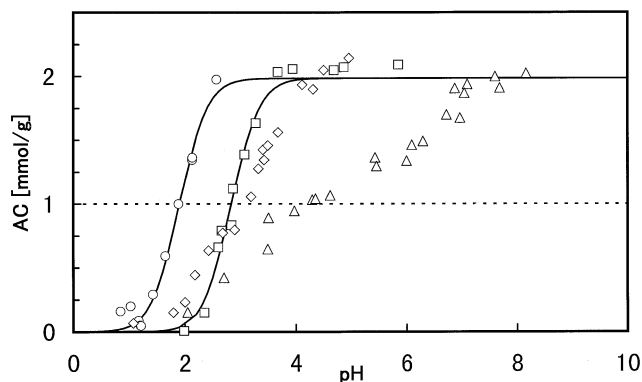
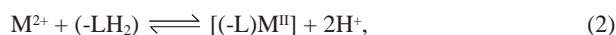


Fig. 1 Adsorption curves of divalent metal ions under the condition $TA_M > TA_L$. Resin, 0.0125 g; aqueous phase, 50 ml of 10^{-3} mol dm^{-3} metal solution; metals: (○) Cu^{2+} ; (□) Ni^{2+} ; (◇) Cd^{2+} ; (△) Ca^{2+} . The solid lines were calculated using K_{10} for Cu^{2+} and Ni^{2+} . The dotted line indicates half occupation of IDA groups.

Adsorption curves under the condition $TA_M > TA_L$

The adsorption of divalent metal ions to an IDA-resin is generally expressed by



Since the concentrations of hydrogen ions were measured on an activity scale, mixed constants were used to define these adsorption equilibria:

$$K_{10} = \frac{[(-L)M^{II}]a_{H^+}^2}{[M^{2+}][(-LH_2)]},$$

$$K_{22} = \frac{[(-LH)_2M^{II}]a_{H^+}^2}{[M^{2+}][(-LH_2)]^2}.$$

Under the condition of $TA_M > TA_L$, the distribution ratio of IDA between free and complexed states is expressed by

$$D_L = \frac{[(-L)M^{II}] + 2[(-LH)_2M^{II}]}{[(-LH_2)]}.$$

A simulation indicates that the adsorption curve would be simple in the unique formation of $[(-L)M^{II}]$, but would become more stepwise with an increase in contribution of $[(-LH)_2M^{II}]$. Thus, the contribution of $[(-LH)_2M^{II}]$ is judged from the shape of the curve.

The adsorption curves of four divalent metal ions at $I = 0.01$ are shown in Fig. 1. Simple sigmoidal curves for Cu^{2+} between pH 1 – 2.5 and for Ni^{2+} between pH 2 – 3.5 indicate the unique formation of $[(-L)M^{II}]$. The plots of $\log D_L$ vs. pH according to

$$\log D_L = 2pH + \log K_{10} + \log[M^{2+}]$$

actually gave straight lines with a slope of two (not shown) and the adsorption constants were obtained from the intercepts, K_{10} : $10^{-0.67}$ for Cu^{2+} , $10^{-2.52}$ for Ni^{2+} . The curves calculated with these constants well reproduce the experimental points, as shown in Fig. 1. On the other hand, the curves for Cd^{2+} and Ca^{2+} are spread over pH ranges of 1.5 – 4 and 2 – 7, respectively. The inflection points observed at half occupation of the IDA groups ($AC = 1.0$) for Ca^{2+} definitely indicate the presence of $[(-LH)_2M^{II}]$, just as the inflection points at one third for M^{3+} (Sc^{3+} , Y^{3+} , La^{3+}) had indicated the presence of $[(-LH)_3M^{III}]$ in a previous study.⁵ Since the formation of $[(-LH)_2M^{II}]$ was

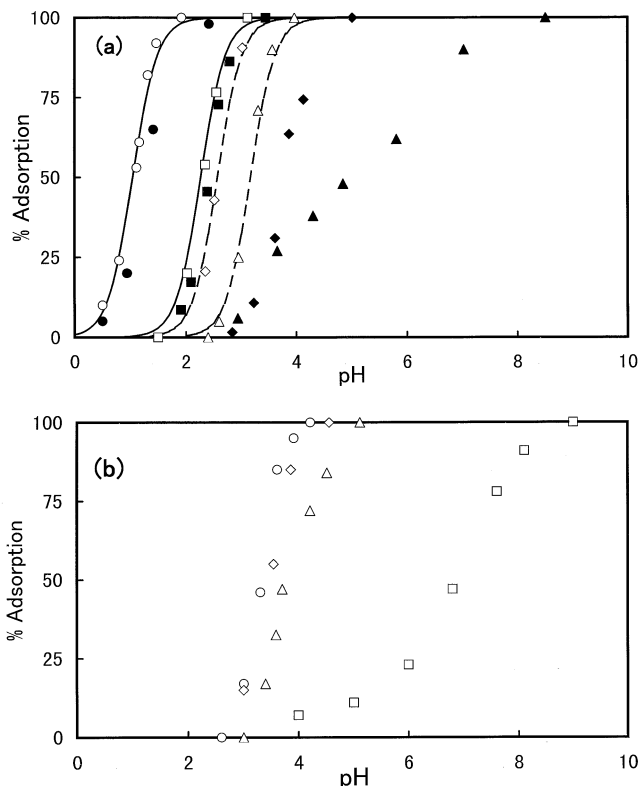


Fig. 2 Adsorption curves of divalent metal ions under the condition $TA_L > TA_M$. Resin, 0.2 g; aqueous phase, 50 ml of 10^{-4} mol dm^{-3} metal solution. (a) Effects of 1 mol dm^{-3} NaCl on the adsorption of four metal ions. Metals: (○, ●) Cu^{2+} ; (□, ■) Ni^{2+} ; (◇, ◆) Cd^{2+} ; (△, ▲) Ca^{2+} . Supporting electrolyte/mol dm^{-3} NaCl: (○, □, ◇, △) 0.01; (●, ■, ◆, ▲) 1. The solid curves were calculated using K_{10} for Cu^{2+} and Ni^{2+} . The broken curves were calculated using K_{22} for Cd^{2+} and Ca^{2+} . (b) Effects of the NaCl concentration on the adsorption of Mg^{2+} . Concentrations of NaCl/mol dm^{-3} : (○) 0; (◇) 10^{-2} ; (△) 10^{-1} ; (□) 1.

recognized even under the condition of $TA_M > TA_L$, which favors the 1:1 species, the 1:2 species would be more predominant under the reversed condition of $TA_L > TA_M$.

Adsorption curves under the condition $TA_L > TA_M$

Under the condition of $TA_L > TA_M$, a distribution ratio of a metal ion between resin and aqueous phases is expressed by

$$D_M = \frac{[(-L)M^{II}] + [(-LH)_2M^{II}]}{[M^{2+}]V_{aq}},$$

where W_r denotes the mass of the resin and V_{aq} the volume of an aqueous solution. A simulation indicates that the adsorption curve shifts to a lower pH region with an increase in K_{22} value or in contribution of $[(-LH)_2M^{II}]$ without changing the shape. The logarithmic expression suggests that a plot of $\log D_M$ vs. pH will yield a straight line with a slope of two, since $[(-LH_2)]$ is practically constant under these conditions,

$$\log D_M = 2pH + \log(K_{10}[(-LH_2)] + K_{22}[(-LH_2)]^2) + \log W_r/V_{aq}.$$

The intercept, however, generally consists of two terms.

The adsorption curves at $I = 0.01$ mol dm^{-3} are shown by open symbols in Fig. 2(a). The logarithmic plots were linear, and the slopes were actually two for all the metal ions (not shown). Since the term $K_{22}[(-LH_2)]^2$ is negligible for Cu^{2+} and Ni^{2+} , the K_{10} values were obtained to be $10^{-0.35}$ for Cu^{2+} and $10^{-2.52}$ for

Ni²⁺, which agree well with those obtained under the condition $TA_M > TA_L$. In the case of Cd²⁺ and Ca²⁺, the $K_{10}[(-LH)_2]$ term is rather negligible, and the K_{22} values were obtained to be $10^{-3.1}$ for Cd²⁺ and $10^{-4.0}$ for Ca²⁺. Taking the difference in concentration of a supporting electrolyte into account, these agree well with the constants obtained by Pesavento ($10^{-3.4}$ for Cd²⁺ and $10^{-5.1}$ for Ca²⁺). The calculated curves using these constants again agree well with the experimental points in Fig. 2(a) for both types of adsorbed species (solid curves for $[-LM^{II}]$ (M^{II} : Cu, Ni) and broken curves for $[(-LH)_2M^{II}]$ (M^{II} : Cd, Ca)).

Effects of supporting electrolyte

The adsorption curves at $I = 1.0 \text{ mol dm}^{-3}$ are shown by the closed symbols in Fig. 2(a). The curves for Cu²⁺ and Ni²⁺ at $I = 0.01 \text{ mol dm}^{-3}$ are only slightly shifted to higher pH regions at $I = 1.0 \text{ mol dm}^{-3}$ (○ and □ to ● and ■, respectively, by 0.1 - 0.2 pH unit). The free IDA mainly exists as $(-LH)_2$ in this pH range, irrespective of the concentration of a supporting electrolyte, and the metal ions are adsorbed only as $[-LM^{II}]$ according to Eq. (2). Thus, a decrease in activity coefficient of ions in an aqueous phase is responsible for the slight shift.

The curve for Cd²⁺ at $I = 0.01 \text{ mol dm}^{-3}$, on the other hand, is shifted by as much as 1.5 pH unit at $I = 1.0 \text{ mol dm}^{-3}$ without changing the shape. At $I = 0.01 \text{ mol dm}^{-3}$, an increase in adsorption of Cd²⁺ between pH 1.5 - 3 (◇) is expressed by Eq. (3). With an increase in pH, the resulting 1:2 species is converted to the 1:1 species as given by the following equation, but this change is not reflected in the adsorption curves because of saturation:

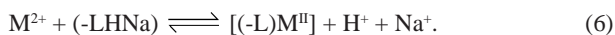


At $I = 1.0 \text{ mol dm}^{-3}$, on the other hand, the adsorption as $[(-LH)_2M^{II}]$ is strongly interfered by Na⁺ as given by



As a result, an increase in adsorption according to Eq. (2) was observed at higher pH values of 3 - 4.5 (◆).

The curve for Ca²⁺ at $I = 0.01 \text{ mol dm}^{-3}$ has both shifted to a higher pH region and spread over a wider pH range at $I = 1.0 \text{ mol dm}^{-3}$. An increase in adsorption of Ca²⁺ between pH 2.5 - 4 at $I = 0.01 \text{ mol dm}^{-3}$ (△) is also expressed by Eq. (3). The adsorption as $[(-LH)_2M^{II}]$ is similarly interfered by Na⁺. In contrast to Cd²⁺, however, the increase in adsorption observed between pH 3 - 8 (▲) at $I = 1.0 \text{ mol dm}^{-3}$ is ascribed to



Since only one proton is expelled by this reaction, the adsorption curve is spread over a wider pH range.

The effects of the NaCl concentration on the adsorption of Mg²⁺ are shown in Fig. 2(b). The addition of a supporting electrolyte up to 0.1 mol dm^{-3} NaCl only shifted the adsorption curve, while the addition of 1 mol dm^{-3} NaCl spread the adsorption curve.

Properties of protonated higher species

In a previous study,⁸ we synthesized a series of polymer complexes with an IDA-resin, and studied their hydration states. The average number of water molecules bound to $[(-LH)_mM]$ ($m = 2, M = \text{Ca}; m = 3, M = \text{Sc, Y, La}$) were practically the same as those of their aqua ions, except for Sc (Ca: 5.9; Sc: 4.2; Y: 7.2; La: 8.0). The aqua ions penetrate into the resin phase, and the charges are neutralized by two or three carboxylates without extensive dehydration just as simple ion-exchange reactions;⁹ a direct contact of the aqua ions with carboxylates is not a prerequisite. Thus, the adsorption as $[(-LH)_2M^{II}]$ is significantly interfered by cations in salts (Eq. (5)).

Acknowledgements

This research was financially supported by an NIT research promotion program.

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