Adsorption Equilibria of Silver(I) and Copper(II) Ions on *N*-(2-Hydroxybenzyl)chitosan Derivative

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N-(2-Hydroxybenzyl)chitosan (=HR) of an insoluble chitosan derivative was synthesized by reducing *N*-(2-hydroxybenzylidene)chitosan obtained from chitosan and 2-hydroxybenzaldehyde. We examined its adsorption selectivities for various metal ions in terms of the pH dependence of the distribution ratio of metal ions at 303 K. The chelating ability of *N*-(2-hydroxybenzyl)chitosan for various metal ions was measured by a batchwise operation from 1 mol dm⁻³ of ammonium nitrate solution. The separations of gallium and iron(III) from zinc, and nickel from cobalt were possible because of the high selectivity of the present derivative. Since *N*-(2-hydroxybenzyl)chitosan showed the high adsorption abilities for silver(I) and copper(II), the adsorption equilibria of both silver(I) and copper(II) were investigated in order to elucidate the adsorbed species by examining the concentration dependencies of hydrogen ion and ammonium nitrate. Silver(I) was adsorbed according to this adsorption reaction, accompanied by an ammonia molecule: $\text{AgNH}_3^+ + \text{HR} \rightleftharpoons \text{RAgNH}_3 + \text{H}^+$ while, copper(II) was adsorbed according to the following reactions: $\text{Cu}^{2+} + 2\text{HR} \rightleftharpoons \text{R}_2\text{Cu} + 2\text{H}^+$ and $\text{CuNH}_3^{2+} + 2\text{HR} \rightleftharpoons \text{R}_2\text{CuNH}_3 + 2\text{H}^+$.

Keywords Chitin, chitosan, chitosan derivative, chitosan-metal chelate, adsorption equilibrium, adsorbed species, silver(I), copper(II)

Since chitin and chitosan are structurally similar to cellulose^{1,2} and are quite abundant in nature, it is very important to conduct studies on their effective applications. Although they have so far been discarded as a raw waste material, recently they are attracting much attention as an unutilized resource. The chitosan which is obtained by the deacetylation of chitin has been used as an effective coagulating reagent in activated sludge plants and for recovering proteins from food processing factories. Chitosan can also act as an adsorbent for transition metal ions through a metal-chelate formation, in which the amino group of glucosamine unit acts as a coordination ligand. In addition, chitosan is considered to be an interesting raw material with high potentials for developing new functional materials through chemical modifications, owing to the presence of the reactive amino groups as well as the hydroxy groups. In contrast, the amino group is also responsible for the dissolution of chitosan in a dilute acidic media. This is one serious disadvantage when the chitosan is used as an adsorbent in the separation and purification process. Though an attempt of crosslinking chitosan was conducted^{3,4} using (chloromethyl)oxirane or glutaraldehyde, the cross-linking resulted in the lowering of the adsorption capacity for metal ions. Muzzarelli *et al.*⁵⁻¹⁰ syn-

thesized various types of chitosan derivatives and investigated their adsorption properties for various metal ions. These studies revealed the chitosan derivatives to be an effective adsorbent for metal ions, though most of its derivatives are soluble in acidic media.

In the present work, the authors synthesized a new chitosan derivative, *N*-(2-hydroxybenzyl)chitosan, by applying the reaction between the reactive first amine of chitosan with 2-hydroxybenzaldehyde *via* Schiff-base formation. The authors examined the pH dependencies of the distribution ratio of various metal ions to clarify the adsorption selectivity. Further, since the *N*-(2-hydroxybenzyl)chitosan revealed the high adsorption abilities for silver(I) and copper(II), the effect of the concentration of the aqueous ammonium nitrate solution on the distribution ratio of silver(I) and copper(II) was investigated in order to elucidate the metal species adsorbed.

Experimental

Reagents and procedures

N-(2-Hydroxybenzyl)chitosan was prepared by way of *N*-(2-hydroxybenzylidene)chitosan, the intermediate

product, obtained from the first amine of chitosan and 2-hydroxybenzaldehyde according to a conventional method. That is, *N*-(2-hydroxybenzylidene)chitosan was synthesized through the reaction of chitosan (degree of deacetylation, 100%) with a 5-fold excess 2-hydroxybenzaldehyde in a mixture of acetic acid and methanol at room temperature. The intermediate was obtained as the powdery precipitate from the mixture. It was filtered and washed with ethanol and diethyl ether to remove excess aldehyde and then with deionized water to neutrality. Thus, *N*-(2-hydroxybenzylidene)chitosan of the intermediate was obtained as a light yellow gel material. This was reduced with sodium borohydride for 24 h by stirring it in the aqueous solution. The final product, *N*-(2-hydroxybenzyl)chitosan, was washed with 0.1 mol dm⁻³ sulfuric acid and then with deionized water to neutrality. The product was dried *in vacuo* till its weight became constant. The intermediate and the product were identified by IR spectra. In the IR spectra, characteristic peaks appeared at around 1640 cm⁻¹ and 750 cm⁻¹ due to the resulting C=N linkage and substituted phenyl group, respectively. The reduction of the Shciff base was confirmed by the disappearance of the characteristic peak for C=N linkage. The degree of substitution was determined by elemental analysis, and calculated to be about 0.90 on the basis of the free amino groups in chitosan. The present chitosan derivative was insoluble in 0.1 mol dm⁻³ hydrochloric acid, due to the hydrophobicity of the phenyl group introduced into the chitosan.

The adsorption of metal ions was carried out batchwise as follows: about 100 mg of the dried gel and 15 ml of aqueous ammonium nitrate solution containing metal ions were shaken in a stoppered glass flask immersed in a thermostated water bath maintained at 303 K overnight to achieve equilibration. The 1 mol dm⁻³ aqueous ammonium nitrate solution containing 1 mmol dm⁻³ metal ion was used to prevent the formation of the metal hydrolyzed species in the higher pH region, except when the effect of the ammonium nitrate concentration on the distribution ratio of metal ions was investigated. Initial pH was adjusted by adding a small amount of aqueous ammonia or nitric acid. The initial and equilibrium concentrations of the metal ions in the aqueous solution were measured by titration with EDTA or by using a Nippon Jarrell-Ash Model AA-782 atomic absorption spectrophotometer. The amount of adsorbed metal ion was calculated from the concentration change in the aqueous solution before and after the equilibration.

Results and Discussion

Effect of pH on the distribution ratio of various metals

Figure 1 shows the relationship between the equilibrium pH of the aqueous solution and the distribution ratio ($D(\text{cm}^3 \text{g}^{-1})$) of the metal ion, which is defined as the ratio of concentration of the metal ion on the gel to that in the aqueous solution. It is clear from Fig. 1 that

Fig. 1 Effect of pH on the distribution ratio of various metals.

the plots for the trivalent metal ions, iron(III) and gallium(III), are lying on straight lines with the slope of 3. Those for divalent metal ions, except for cobalt(II), copper(II), nickel(II) and zinc(II), lie on the straight lines with the slope of 2, and that for the univalent metal ion, silver(I), lies on a straight line with the slope of 1. In the case of cobalt(II), the plots appear to lie on a straight line with the slope of 3 but not 2, which suggests that the divalent cobalt is oxidized to the trivalent state during adsorption, as is frequently observed in solvent extraction with chelating extractants from aqueous ammoniacal solutions, as in the present case. The order of selectivity for metal ions is as follows: $\text{Fe}^{III} > \text{Ga}^{III} \gg \text{Cu}^{II}$, $\text{Ag}^I > \text{Ni}^{II} > \text{Zn}^{II} > \text{Co}^{II}$. Compared with the crosslinked chitosan gel described previously¹¹, the order of adsorption of metal ions on the present gel nearly parallels that on the cross-linked chitosan. However, the adsorption with the present gel occurs at a lower pH by about 0.5 units for all metal ions except for iron(III). This may be attributed to the difference between the acid dissociation constant of the alcoholic hydroxy group in a glucosamine unit of the chitosan gel and the hydroxy group in the phenol functional groups of the present gel. As seen from Fig. 1, the present gel has a high adsorption properties for silver(I) and copper(II), while manganese(II) was not adsorbed with the present adsorbent in the pH region of 1–5.

These results indicate that the *n*-valent metal ions are adsorbed on the gel as metal-chelates of the composition of metal:glucosamine unit in the ratio of 1:*n*¹² by releasing "*n*" hydrogens of the phenol group per one metal ion, as expressed by Eq. (1):

The bar indicates the species in the *N*-(2-hydroxybenzyl)-chitosan. The equilibrium constant K_{0M} , for the above reaction can be described as

$$K_{0M} = \frac{[\overline{\text{HR}_n}][\text{H}^+]^n}{[\text{M}^{n+}][\overline{\text{HR}}]^n} \quad (2)$$

In the regions of low pH, the concentration of free metal ions ($[M^{n+}]$) in Eq. (2) can be approximated by the total concentration of metal ions in the aqueous phase (C_{MW}), because the formation of metal-ammine complexes, $M(NH_3)_i^{n+}$, as well as the hydrolyzed species, $M(OH)_j^{n-s}$, should be negligible. In addition, the concentration of the unreacted adsorbent, $[HR]$, is approximated to its initial concentration (C_{HRO}), since the initial concentration of the adsorbent is much higher than that of metal ion. The logarithm of the distribution ratio, D , can be expressed by Eq. (3) in this region:

$$\log D = npH + n \log C_{HRO} + \log K_{OM} \quad (3)$$

$$= npH + \log K'_{OM} \quad (K'_{OM} = K_{OM} C_{HRO}^n) \quad (4)$$

where K'_{OM} represents the apparent equilibrium constant.

Equation (4) suggests that the relationship between the logarithm of the distribution ratio and pH gives a straight line with a slope which is equal to the valency of the metal ion. This equation explains well the experimental results shown in Fig. 1, therefore, the stoichiometric relation of adsorption for metal ions on the *N*-(2-hydroxybenzyl)chitosan is expressed by Eq. (1). These results suggest that the *N*-(2-hydroxybenzyl)chitosan behave as a chelating adsorbent for these metal ions.

Effect of the ammonium nitrate concentration on the distribution ratio of silver(I) and copper(II)

In order to elucidate the reason why the distribution ratio of silver(I) and copper(II) is much higher than that of other metals, further examination was carried out in detail to clarify the adsorption mechanism of silver(I) and copper(II).

Figures 2 and 3 show the effect of ammonium nitrate concentration in the aqueous solution on the distribution ratios of silver(I) and copper(II), respectively. In both figures, the distribution ratio increases with an increase of pH in the lower pH region. This is due to a cation exchange between the hydrogen ions of the gel and the metal ions, as mentioned above. On the other hand, the distribution ratio decreases with an increase of pH in the higher pH region. This is due to the formation of higher-ammine complexes, $M(NH_3)_i^{n+}$, in the aqueous phase, which are unlikely to be adsorbed by the present derivative. This is also supported by the fact that the distribution ratio decreases with an increase in the ammonium nitrate concentration.

Therefore, in the high pH region, it is necessary to take into account the formation of the ammine complexes of silver(I) and copper(II), described as follows:

where β_i denotes the stability constants^{13,14} of the ammine complexes; these values are $\beta_1 = 1.35 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$, $\beta_2 = 4.1 \times 10^7 \text{ (dm}^3 \text{ mol}^{-2})^2$, $\beta_3 = 3.0 \times 10^{10} \text{ (dm}^3 \text{ mol}^{-1})^3$, $\beta_4 = 3.9 \times 10^{12} \text{ (dm}^3 \text{ mol}^{-1})^4$ for copper(II), and $\beta_1 = 2.09 \times 10^3 \text{ dm}^3$

Fig. 2 Effect of ammonium nitrate concentration on the distribution ratio of silver(I).

Fig. 3 Effect of ammonium nitrate concentration on the distribution ratio of copper(II).

mol^{-1} , $\beta_2 = 1.74 \times 10^7 \text{ (dm}^3 \text{ mol}^{-1})^2$ for silver(I).

Since the hydrolyzed species, $M(OH)_j^{n-s}$, should be negligible under the conditions of a large excess of ammonia¹⁵, the concentration of free metal cations can be expressed by Eq. (6):

$$[M^{n+}] = \frac{C_{MW}}{1 + \sum \beta_i [NH_3]^i} \quad (6)$$

In addition, the concentration of free ammonia is related to that of ammonium ion through this equilibrium relation:

where $K_A = 5.5 \times 10^{-10} \text{ mol dm}^{-3}$.¹⁴ The concentration of

ammonium ions under the present experimental conditions, where the concentration of metal ions is much less than that of ammonium ions, can be approximated from the electroneutrality in the aqueous phase as follows:

$$[\text{NH}_4^+] \approx [\text{NO}_3^-]. \quad (8)$$

Consequently, Eq. (6) can be rewritten as Eq. (9) by taking Eqs. (7) and (8) into account:

$$[\text{M}^{n+}] = \frac{C_{\text{MW}}}{1 + \sum \beta'_i / [\text{H}^+]^i} = \alpha_0 C_{\text{MW}} \quad (9)$$

where $\beta'_i = \beta_i (K_A [\text{NO}_3^-])^i$ and $\alpha_0 = 1 / (1 + \sum \beta'_i / [\text{H}^+]^i)$. Accordingly, the logarithm of the distribution ratio, D , is expressed by Eq. (10) using Eqs. (2) and (9), since the concentration of the unreacted adsorbent, $[\overline{\text{HR}}]$, is nearly equal to its initial concentration, C_{HRO} :

$$\log D = 2\text{pH} + \log \alpha_0 + \log K'_{0\text{M}}. \quad (10)$$

Now, when the formation of ammine complexes is negligible, *i.e.* $\alpha_0 = 1$ in Eq. (10), the apparent equilibrium constants for silver(I) and copper(II) were evaluated based on Eq. (4) from the intercept of the straight line with the ordinate in the low pH region as $K'_{0\text{Ag}} = 1.1 \times 10^{-2} \text{ mol g}^{-1}$ and $K'_{0\text{Cu}} = 3.2 \times 10^{-7} \text{ mol}^2 \text{ g}^{-1} \text{ dm}^{-3}$, respectively.

The dashed lines in Figs. 2 and 3 are the theoretical lines which are calculated using the stability constants and the adsorption equilibrium constants for silver(I) and copper(II), respectively, based on Eq. (10). Only the line calculated for copper(II) adsorption from 1 mol dm^{-3} aqueous ammonium nitrate solution fully agrees with the experimental results. Accordingly, the adsorption reaction of copper(II) in this system may be expressed as follows:

On the other hand, the calculated line for copper(II) adsorption from 3 mol dm^{-3} was not in agreement with the experimental results in the high pH region. Further, the other calculated results also are not in good agreement with the experimental ones, these curves deviate downward from the plotted points in the high pH region. This suggests that an ammine complex of silver(I) or copper(II) is adsorbed according to the following reaction proposed in the place of Eq. (1) for the adsorption of silver(I) or copper(II) for 3 mol dm^{-3} aqueous ammonium nitrate solution:

The concentration of MNH_3^{n+} participating in the reaction can be expressed as follows:

$$[\text{MNH}_3^{n+}] = \frac{\beta'_i / [\text{H}^+]^i}{1 + \sum \beta'_i / [\text{H}^+]^i} C_{\text{MW}} = \alpha_1 C_{\text{MW}} \quad (13)$$

where $\beta'_i = \beta_i K_A [\text{NO}_3^-]$

On the basis of the adsorption reaction expressed by Eq. (12), the distribution ratio, D , was derived using Eq. (13) instead of Eq. (9) in a similar manner to that mentioned above as Eq. (14).

$$\log D = n\text{pH} + \log \alpha_1 + \log K'_{\text{IM}} \quad (K'_{\text{IM}} = K_{\text{IM}} C_{\text{HRO}}^n). \quad (14)$$

The solid lines in Fig. 2 are the theoretical lines, which are calculated using the stability constants and the adsorption equilibrium constants for silver(I), based on Eq. (14) derived by assuming that the silver-ammine complexes with one ammonia molecule per metal ion are adsorbed on the present gel. The theoretical lines for silver(I) are in good agreement with the experimental results for both concentration of ammonium nitrate. Therefore, the adsorption equilibrium for silver(I) is expressed by the following equation for both concentrations of aqueous ammonium nitrate solution:

Here, the adsorption equilibrium constants were obtained as $K'_{\text{IAG}} = 5.0 \times 10^{-2}$ for silver(I) by method of least squares.

On the other hand, the theoretical line denoted by a dot and dashed line, which was calculated on the basis of Eq. (14) using $K'_{\text{ICu}} = 8.9 \times 10^{-8}$ obtained for copper(II) similarly to silver(I), is not in good agreement with the experimental results in the low pH region.

Thus copper(II) is thought to be adsorbed from 3 mol dm^{-3} aqueous ammonium nitrate solution by the following two reactions:

and

By considering the mass balance of copper(II), the distribution ratio of copper(II) can be expressed as follows:

$$\log D = 2\text{pH} + \log(K'_{0\text{Cu}} + \beta_1 K'_{\text{ICu}} K_A / [\text{H}^+]) + \log \alpha_0. \quad (18)$$

The solid line for 3 mol dm^{-3} aqueous ammonium nitrate solution in Fig. 3 is the theoretical one which was calculated using the stability constants and $K'_{0\text{Cu}} = 3.2 \times 10^{-7}$, $K'_{\text{ICu}} = 8.9 \times 10^{-8}$ for copper(II) obtained from the reaction mentioned above, based on Eq. (18). The calculated line for copper(II) adsorption from 3 mol dm^{-3} ammonium nitrate solution is in good agreement with the experimental result.

Figure 4 shows the adsorption isotherms of copper(II)

Fig. 4 Adsorption isotherms of copper(II) ion on crosslinked chitosan and *N*-(2-hydroxybenzyl)chitosan at 303 K

ion on the two kinds of adsorbents. The ordinate stands for the amounts of copper(II) adsorbed, q , and the abscissa stands for the equilibrium concentration of copper(II), C . This result indicates that *N*-(2-hydroxybenzyl)chitosan newly synthesized in this study possesses a high adsorption capacity for copper(II), compared with crosslinked copper-complexed chitosan described earlier.¹¹ Their adsorption capacities are about 2.0 mmol g⁻¹ and 1.4 mmol g⁻¹, respectively. The value of *N*-(2-hydroxybenzyl)chitosan was comparable to 1.9 mmol g⁻¹ of the iminodiacetic acid type of chelating resin, PT-207, reported earlier.¹¹ In addition, the desorption of metal ions from *N*-(2-hydroxybenzyl)chitosan was completely performed in 0.1 mol dm⁻³ hydrochloric acid. Thus, the chitosan derivative hardly solubilized at all in the hydrochloric acid, and was stable under the present experimental conditions. Therefore, *N*-(2-hydroxybenzyl)chitosan is expected to be applicable to the separation and purification of metal ions in analytical chemistry.

References

1. R. A. A. Muzzarelli, "Chitin and Chitosan", Pergamon, London, 1977.
2. K. Takemoto, *Gendai Kagaku*, No. 6, 57 (1981).
3. K. Kurita, Y. Koyama and A. Taniguchi, *J. Appl. Polym. Sci.*, **31**, 1169 (1986).
4. K. Ohga, Y. Kurauchi and H. Yanase, *Bull. Chem. Soc. Jpn.*, **60**, 444 (1987).
5. R. A. A. Muzzarelli, "Natural Chelating Polymers", Pergamon, Oxford, 1973.
6. R. A. A. Muzzarelli and F. Tanfani, *Pure Appl. Chem.*, **54**, 2141 (1982).
7. R. A. A. Muzzarelli, F. Tanfani, M. Emanuelli and S. Mariotti, *Carbohydr. Res.*, **107**, 199 (1982).
8. R. A. A. Muzzarelli, F. Tanfani, S. Mariotti and M. Emanuelli, *Carbohydr. Polymers*, **2**, 145 (1982).
9. R. A. A. Muzzarelli, F. Tanfani, S. Mariotti and M. Emanuelli, *Carbohydr. Res.*, **104**, 235 (1982).
10. R. A. A. Muzzarelli and A. Zattoni, *Int. J. Biol. Macromol.*, **8**, 137 (1986).
11. K. Inoue, Y. Baba, K. Yoshizuka, *Bull. Chem. Soc. Jpn.*, **66**, 2915 (1993).
12. Y. Inaki, M. Otsuru, K. Takemoto, *J. Macromol. Sci.-Chem.*, **A12**, 953 (1978).
13. H. Freiser and Q. Fernando, "Ionic Equilibria in Analytical Chemistry", John Wiley and Sons, Inc., New York, 1963; "Ion Heiko", translated by T. Fujinaga and E. Sekido, Kagaku Dojin, Kyoto, 1975.
14. A. J. Bard, "Chemical Equilibrium", Harper & Row Publishers, Inc., New York, 1966; "Yoekinai Ion Heiko", translated by Y. Matsuda and K. Ogura, Kagaku Dojin, Kyoto, 1975.
15. V. B. Spivakovskii and G. V. Makovskaya, *Zhur. Neorg. Khim.*, **13**, 1555 (1968).

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