ADSORPTION PROPERTIES OF METAL IONS ONTO HYDROLYZED POLYACRYLAMIDE GEL

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An experimental investigation of the adsorption properties of metal ions onto gel was carried out by using hydrolyzed polyacrylamide gel and copper sulphate, ferrous ammonium sulphate and ferrous sulphate solutions. Considering that carboxyl groups in the gel bond with the metal ions according to their electric charge number, the adsorption properties were examined on the basis of dissociation equilibria from monocarboxyl to dicarboxyl acid. From theoretical analyses, empirical equations that give the amount of metal ions adsorbed on the gel were obtained. For the adsorption equilibrium of copper and ferrous ions, the amount of ions adsorbed within the gel can be calculated well from the initial and equilibrium concentrations of the metal ions in aqueous phase, the concentrations of hydrogen ions, the weight of the gel and the volume of solution used.

Introduction

Polyelectrolyte gels have been attracting much attention as functional polymers that possess the properties of water absorption and molecular-sieving effect. At the same time, these gels have been expected to find use as functional polymers for collecting or separating metal ions, since a separation process using such gels has many advantages. Operations are simple and applicable to many cases, and the equipment used is rather cheap. Investigation of the functional properties of the gels is thus important for the chemical industry, which must place increasing importance on resource- and energy-saving.

For example, polyacrylamide gel can swell and shrink as much as several hundred times by altering the composition, *pH*, ionic strength, temperature or electric field of the solvent in which the gel is immersed.^{12,13,14} These varied responses of the gel can now be understood in the context of phase transition and critical phenomena.^{15,16,17} Also, the kinetic behavior of a temperature-sensitive water-absorbing gel has been analyzed experimentally.³ In the fields of chemistry and biochemistry, gels are employed in analytical methods of chromatography and electrophoresis. Furthermore, the gels can be utilized in the enriching separation of various alcohol-water solutions⁴ or polymer materials² and have been applied to a three-phase fluidized bed bioreactor.^{9,10}

On the other hand, it is thought to be a most effective

technique from the viewpoint of resource- and energy-saving to apply the function of absorbing and collecting the metal ions within the gel in enriching separation. For this reason, investigations and developments concerning the function of gels are needed. Yet no studies of the adsorption properties of metal ions onto the gel have been carried out, nor has the mechanism yet been resolved.

From the point of view mentioned above, the authors have investigated the adsorption mechanism of metal ions onto the gel, based on the adsorption equilibrium of divalent metal ions. The present paper reports the experimental results.

1. Experimental Method

1.1 Preparation of gel

The gel was made by hydrolyzing cross-linked polyacrylamide beads produced commercially (from Bio-Rad Laboratories, Richmond, CA, U.S.A. as Bio-Gel P-6 having particle size in water of $150\text{--}300 \times 10^{-6}$ m). It was hydrolyzed for 48 h at 323 K in 0.5 mol/dm^3 of Na_2CO_3 ⁵. The hydrolytic reaction is as follows.

This gel was purified fully with distilled water to exclude $(\text{NH}_4)_2\text{CO}_3$ and was used as Na^+ -type gel swelled by absorption of water. The total amount of

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monocarboxyl groups in the gel was measured by the back-titration method with 0.1 mol/dm³ (CH₃COO)₂-Ca,¹⁸⁾ and for the wet gel of Na⁺-type the value was $q_{1,0} = 2.78 \times 10^{-1}$ mol/kg-wet Na-gel. It is reported that the maximum hydrolysis transforms roughly one-fourth of the side chains.¹⁷⁾

1.2 Adsorption of metal ions

Metal salts used in the adsorption experiments were copper sulphate CuSO₄·5H₂O, ferrous ammonium sulphate FeSO₄(NH₄)₂SO₄·6H₂O and ferrous sulphate FeSO₄·7H₂O. Recrystallized CuSO₄·5H₂O was dissolved in distilled water to prepare 0.1 mol/dm³ solution. This solution was diluted suitably so as to contain 0.01 mol/dm³ in the experiments. FeSO₄(NH₄)₂SO₄·6H₂O was dissolved in distilled water by adding a few drops of concentrated sulphuric acid to prepare 0.01 mol/dm³ solution. This solution was also diluted to a suitable concentration. FeSO₄·7H₂O was dissolved in a sulphuric acid solution, because Fe [II] ions can easily be oxidized to Fe [III]. The pH of these solutions was adjusted using buffer solutions of 0.2 N HCl-0.2 N KCl to the range from pH=1 to 3 and those of 0.1 N CH₃COOH-0.1 N CH₃COONa to pH=3 to 6.

Adsorption experiments with the gel were carried out by placing 0.001 kg of the Na⁺-type gel and 0.01 dm³ of CuSO₄, FeSO₄(NH₄)₂SO₄ and FeSO₄ solution respectively in test tubes. The tubes were shaken mechanically for 4 h in a thermostated bath at 298 K. After equilibrium was attained, the gel was centrifuged and the concentrations of Cu²⁺ and Fe²⁺ in aqueous solution were measured by atomic absorption spectrophotometry. At the same time, pH of the aqueous solutions was measured by a pH meter. From these measured values the concentrations of metal salts per unit weight of the Na⁺-type gel, q_{RM} , were calculated as follows. When the Na⁺-type gel adsorbs the metal ions, the gel releases water and shrinks. However, as the volume change in the aqueous phase caused by the shrinking of the gel was 8% at the maximum, it was concluded to be negligibly small. So, q_{RM} is approximately given by

$$q_{RM} = \frac{V(C_i - C_M)}{m} \quad (2)$$

where V is the volume of solution used, C_i and C_M are the initial and equilibrium concentrations of the metal ions, respectively, and m is the weight of the wet Na⁺-type gel.

2. Adsorption Equilibrium of Divalent Metal Ions onto Gel

Applying a fundamental theory of separation of metal ions by use of chelate resin,¹⁾ the adsorption equilibrium of the divalent metal ions onto the gel can be expressed as follows. In cases where carboxyl

groups fixed in the gel take up the divalent metal ions, it can be considered that the combination ratio of the carboxyl groups to a divalent metal ion is 2:1 stoichiometry. Accordingly, if it is assumed that two carboxyl groups fixed in Na⁺-type gel dissociate completely as a dicarboxyl group with a divalent anion, the equilibrium relation between the ionized gel, R²⁻, and the metal ions of M²⁺ is given by

where K_{M_2} is a formation constant of metal complexes and q_R^{2-} is the concentration of the dicarboxyl groups fixed in the gel. When dicarboxyl acid in the H⁺-type gel dissociates in the aqueous phase, the following equilibrium relations at two steps are obtained.

where K_{d_1} and K_{d_2} are the first- and second-order dissociation constants, respectively, and q and C_H are the concentrations of subscript components in the gel and hydrogen ions in the aqueous phase.

The values of C_H may be assumed to be the same as the concentrations of hydrogen ions in the gel, and Eqs. (4) and (5) are summarized as follows.

As can be seen from Eqs. (3)–(6), the fixed dicarboxyl group species exist as RH₂, RH⁻, R²⁻ and RM in the gel. Therefore, when M²⁺ ions are adsorbed from acidic solution, a mass balance for these species is given by

$$q_{2,0} = q_{RH_2} + q_{RH^-} + q_R^{2-} + q_{RM} \quad (7)$$

where $q_{2,0}$ is the total concentration of the fixed dicarboxyl groups, that is, $q_{2,0} = q_{1,0}/2 = 1.39 \times 10^{-1}$ mol/kg-wet Na-gel from the total amount of monocarboxyl groups given before. Substituting Eqs. (5) and (6) in Eq. (7), Eq. (8) can be obtained.

$$q_{2,0} - q_{RM} = q_R^{2-} \left(1 + \frac{C_H}{K_{d_2}} + \frac{C_H^2}{K_{d_1} \cdot K_{d_2}} \right) \quad (8)$$

Combining Eqs. (3) and (8), Eq. (9) can be obtained.

$$\frac{C_M(q_{2,0} - q_{RM})}{q_{RM}} = \frac{1}{K_{M_2}} \left(1 + \frac{C_H}{K_{d_2}} + \frac{C_H^2}{K_{d_1} \cdot K_{d_2}} \right) \quad (9)$$

The values of K_{d_1} , K_{d_2} and K_{M_2} can be estimated by use of the curve-fitting method^{7,8)} as follows. Setting as experimental variables

$$x = \log C_H; \quad y = \log \{C_M(q_{2,0} - q_{RM})/q_{RM}\} \quad (10)$$

the following normalization may be used.

$$\left. \begin{aligned} X &= x + p_1 = \log v \\ Y &= y + p_2 = \log(1 + p_3 v + v^2) \end{aligned} \right\} \quad (11)$$

Figure 1 gives a family of normalized curves $Y(X)_{p_3}$ calculated from Eq. (11). The curves have two common asymptotes:

$$\left. \begin{aligned} v \rightarrow 0 \quad Y &= 0 \\ v \rightarrow \infty \quad Y &= 2X \end{aligned} \right\} \quad (12)$$

The experimental data $y(x)$, Eq. (10), are moved so as to best fit. Then the shape of the curve gives p_3 , and the coordinates (x_0, y_0) coinciding with $(X=0, Y=0)$ give $-p_1$ and $-p_2$. The required constants are calculated from Eqs. (9), (10) and (11):

$$\left. \begin{aligned} \log K_{M_2} &= p_2 \\ \log K_{d_2} \cdot K_{M_2} &= -p_1 + p_2 - \log p_3 \\ \log K_{d_1} \cdot K_{d_2} \cdot K_{M_2} &= -2p_1 + p_2 \end{aligned} \right\} \quad (13)$$

3. Experimental Results and Discussion

3.1 Adsorption of divalent metal ions onto gel

The variations of q_{RM} with pH were obtained experimentally by use of Eq. (2). The results are shown in **Fig. 2**. In the low pH region, q_{RM} is equal to zero; over some intermediate pH range, it increases sharply; and it approaches a constant value at high pH . **Figure 3** shows the relation between $\log \{C_M(q_{2,0} - q_{RM})/q_{RM}\}$ and $\log C_H$ based on Eq. (10). The constants of K_{d_1} , K_{d_2} and K_{M_2} for Cu[II] and Fe[II], respectively, were calculated by the curve-fitting method mentioned above. The constants thus determined are shown in **Table 1**. The calculated curves, obtained by substituting these values in Eq. (9), are shown by solid lines in **Fig. 3**. They satisfy the experimental values, confirming that the correlation of Eq. (9) was valid.

Further, K_{d_1} and K_{d_2} were estimated by the identical values for Cu[II] and Fe[II] and the relation of $K_{d_1} > K_{d_2}$ was obtained and was found to be the same order as that in successive formation constants of general polycarboxyl acid. From the above results, it is known that the difference in amount of metal ions adsorbed against the concentration of hydrogen ions depends only on the formation constant of K_{M_2} between the metal ions and dicarboxyl groups fixed in the gel, because the dissociation constants of K_{d_1} and K_{d_2} for Cu[II] and Fe[II] are nearly equal.

Fig. 1. Normalized curves used for graphical determination of K_{d_1} , K_{d_2} and K_{M_2}

Fig. 2. Correlation q_{RM} for CuSO_4 or $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$ against pH

Table 1. Values of K_{d_1} , K_{d_2} and K_{M_2}

Metal	K_{d_1}	K_{d_2}	K_{M_2}
Cu [II]	6.31×10^{-3}	3.31×10^{-6}	7.94×10^3
Fe [II]	6.76×10^{-3}	3.55×10^{-6}	2.51×10^3

Combining Eqs. (2) and (9), the following equations can be derived.

$$\left. \begin{aligned} \frac{m}{V} q_{RM}^2 - \left(\frac{m}{V} q_{2,0} + C_i + \frac{Z}{K_{M_2}} \right) q_{RM} + C_i q_{2,0} &= 0 \\ Z &= 1 + \frac{C_H}{K_{d_2}} + \frac{C_H^2}{K_{d_1} \cdot K_{d_2}} \end{aligned} \right\} \quad (14)$$

Fig. 3. Correlation $y = \log\{C_M(q_{2,0} - q_{RM})/q_{RM}\}$ against $x = \log C_H$

Solving Eq. (14) for q_{RM} , one can obtain

$$\frac{q_{RM}}{q_{2,0}} = \frac{1}{2} \left\{ 1 + \frac{C_i V}{m q_{2,0}} + \frac{V Z}{K_{M_2} m q_{2,0}} - \sqrt{\left(1 + \frac{C_i V}{m q_{2,0}} + \frac{V Z}{K_{M_2} m q_{2,0}} \right)^2 - \frac{4 C_i V}{m q_{2,0}}} \right\} \quad (15)$$

Using $C_i = 0.01 \text{ mol/dm}^3$, $V = 0.01 \text{ dm}^3$ and $m = 0.001 \text{ kg}$ in Eq. (15), the ratio of metal ions adsorbed to total change capacity, $q_{RM}/q_{2,0}$, was calculated. The results are shown with the experimental values in Fig. 4. The ratio, $q_{RM}/q_{2,0}$, against the concentration of hydrogen ions in the outer aqueous phase could be correlated also by Eq. (15). Namely, in the adsorption equilibrium of the divalent metal ions, the ratio of metal ions adsorbed on the gel can be represented by experimental conditions of C_i , C_H , m and V .

3.2 Effect of ionic strength

Divalent metal ions are adsorbed by accompanying the ion-exchange reaction with Na^+ -type gel as follows.

where $\text{R}(\text{Na})_2$ denotes the Na^+ -type gel. During the course of this ion exchange, the ionic strength in the outer aqueous phase ranges from 2×10^{-2} to $4 \times 10^{-2} \text{ mol/dm}^3$ in the case of CuSO_4 and from 5×10^{-2} to $7 \times 10^{-2} \text{ mol/dm}^3$ in $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$. Since the changes in activity due to this ionic strength may be estimated to be within about 10%,¹¹⁾ it is presumed that effect of ionic strength on K_{d_1} , K_{d_2} and K_{M_2} is negligible small.

Fig. 4. Correlation $q_{RM}/q_{2,0}$ for CuSO_4 or $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$ against pH

Fig. 5. Correlation $q_{RM}/q_{2,0}$ for FeSO_4 against pH

3.3 Effect of $(\text{NH}_4)_2\text{SO}_4$

$\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$ was used as a standard solution, because $\text{Fe}[\text{II}]$ can scarcely be oxidized to $\text{Fe}[\text{III}]$ and itself is a fairly stable salt. But, in the case where $\text{Fe}[\text{II}]$ ions are adsorbed on the gel, it can be presumed that there is an effect of $(\text{NH}_4)_2\text{SO}_4$ based on the formation of $\text{R}(\text{NH}_4)_2$ in the gel or metal complexes with SO_4^{2-} such as FeSO_4 in the aqueous solution.⁶⁾ To clarify this effect, adsorption experiments of FeSO_4 within the Na^+ -type gel were performed. The results are shown in Fig. 5 along with the calculated curve for $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$ based on Eq. (15). Similarly to the case of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$, the correlation of Eq. (15) is valid for the FeSO_4 system and it is obvious that the effect of $(\text{NH}_4)_2\text{SO}_4$ is negligible.

Conclusion

An experimental investigation of the adsorption properties of metal ions within a gel was carried out, using hydrolyzed polyacrylamide gel and copper sulphate, ferrous ammonium sulphate or ferrous sulphate. As a result of theoretical and experimental analyses, the equilibrium relationship between the

amount of metal ions adsorbed on the gel and the concentrations of hydrogen ions in the outer aqueous phase could be correlated by Eq. (9) or (15). Also, in the equilibrium state at required pH , little change of ionic strength in the outer aqueous phase was found. Further, the effect of $(NH_4)_2SO_4$ was clearly negligible. The analytical method developed here is expected to be applicable to the adsorption enrichment of other ions, especially those of rare metals.

Nomenclature

C_H	= concentration of hydrogen ions in aqueous phase	[mol/dm ³]
C_i	= initial concentration of metal ions in aqueous phase	[mol/dm ³]
C_M	= equilibrium concentration of metal ions in aqueous phase	[mol/dm ³]
K_{d1}	= first-order dissociation constant	[mol/dm ³]
K_{d2}	= second-order dissociation constant	[mol/dm ³]
K_{M2}	= formation constant of metal complexes	[dm ³ /mol]
M^{2+}	= divalent metal ions	
m	= weight of Na ⁺ -type gel	[kg]
p_1, p_2, p_3	= unknown parameters to be determined	
$q_{1,0}$	= total concentration of fixed monocarboxyl groups in unit Na ⁺ -type gel	[mol/kg-wet Na ⁺ ·gel]
$q_{2,0}$	= total concentration of fixed dicarboxyl groups in unit Na ⁺ -type gel	[mol/kg-wet Na ⁺ ·gel]
q_R^{2-}	= concentration of R ²⁻ ions in unit Na ⁺ -type gel	[mol/kg-wet Na ⁺ ·gel]
q_{RH}^-	= concentration of RH ⁻ ions in unit Na ⁺ -type gel	[mol/kg-wet Na ⁺ ·gel]
q_{RH_2}	= concentration of RH ₂ species in unit Na ⁺ -type gel	[mol/kg-wet Na ⁺ ·gel]
q_{RM}	= concentration of metal complexes in unit Na ⁺ -type gel	[mol/kg-wet Na ⁺ ·gel]
V	= volume of solution used	[dm ³]

v	= auxiliary variable	
X	= normalized values for x	
x	= variables determined experimentally	
x_0	= values of x coinciding with $X=0$	
Y	= normalized values for y	
y	= variables determined experimentally	
y_0	= values of y coinciding with $Y=0$	
Z	= $1 + C_H/K_{d2} + C_H^2/K_{d1} \cdot K_{d2}$	[—]

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