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# Adsorption Equilibrium of Copper and Cadmium on Silica Gel from Ammoniacal Solutions

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## Abstract

The ion-exchange adsorption of copper and cadmium ions on silica gel from aqueous ammonium nitrate solution of various concentrations was investigated at 30°C. It was found that the surface of silica gel acts as an ion exchanger of the weakly acid type and that metal ions adsorbed on silica gel can be desorbed with dilute acid solutions. It was determined that copper and cadmium are adsorbed according to the cation-exchange reaction

$$GH_2 + MNH_3^{2+} \rightleftharpoons GMNH_3 + 2H^+ \qquad K_M$$

The apparent equilibrium constants for this reaction were evaluated as $K_{Cu} = 4.3 \times 10^{-13}$ mol/dm$^3$ and $K_{Cd} = 5.1 \times 10^{-20}$ mol/dm$^3$ for 1 mol/dm$^3$ ammonium nitrate solution. Based on these results, the selective separation of copper from cadmium on silica gel is considered to be possible.

## INTRODUCTION

Silica gel has been used as an adsorbent, particularly for hydrocarbons (*1*) and various kinds of poisonous gases. Silica gel is also well known as a useful inorganic cation exchanger for metal ions. The silanol group (≡SiOH) on the hydrated silica gel surface acts as a weak acid and therefore silica gel has some properties as a cation exchanger when it is contacted with an aqueous electrolyte solution (*2–7*). Recently wastewater containing metals as ammine complexes have been treated with organic cation-exchanger resins (*8*).

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Adsorption of heavy metal ions on silica gel from aqueous solutions which contain ligands comprising such nitrogen atoms as ammonia, ethylenediamine, and other amines has been studied by numerous authors (*9–15*) for the purpose of separating the metals. However, the adsorption mechanism has not been satisfactorily elucidated. In the present work the authors have studied the adsorption mechanism of heavy metal ions on silica gel from ammoniacal solutions, and examined its applicability as an adsorbent for wastewater containing metal–ammine complexes. The correlation between the amount of metal–ammine complexes, specifically those of copper and cadmium, and the pH were particularly investigated because this information would be very useful for the preparation of catalysts to cover the silica gel surface with a layer of metals.

## EXPERIMENTAL

The commercial adsorbent WAKO GEL (particle size 30-50 mesh, and BET area 494 $m^2/g$ for chromatographic use) was used as delivered from Wako Chemical Ltd. without further purification. This sample was dried at 110°C and was then stored in a desiccator.

First, the adsorption equilibrium relation of ammonia on silica gel was measured to determine the amount of silanol groups ($\equiv$SiOH). The initial concentration of ammonia in the aqueous solution ranged from $2 \times 10^{-3}$ to 3 $mol/dm^3$. The procedure was the same as the measurement of the adsorption of metals described later.

Second, the adsorption equilibrium relation of metals from the aqueous ammonium nitrate solutions was measured. The aqueous copper and cadmium solutions were prepared by dissolving GR grade copper nitrate and cadmium nitrate in 0.5, 1, and 3 $mol/dm^3$ aqueous ammonium nitrate solutions to maintain constant ionic strength of the solution during adsorption. The other reagents used were of GR grade. The initial concentration of copper or cadmium in the aqueous solution was $5 \times 10^{-3}$ $mol/dm^3$. The pH of the aqueous solution, which ranged from 5 to 9, was adjusted by adding small amounts of ammonia. A silica gel sample of 1.0 g was mixed with the aqueous solution in a 100-mL flask and allowed to attain equilibration in a water bath maintained at 30 ± 0.5°C. After about 24 h the sample was centrifuged and the supernatant solution was analyzed for metal ions by titrating with EDTA or by atomic absorption spectrochemical analysis with a Nippon Jarrell-Ash model AA-782 spectrophotometer in the case of low metal ion concentration. From the differences between the initial metal concentration and that at equilibration, the amount of metal ions adsorbed on the silica gel was calculated.

## EXPERIMENTAL RESULTS

### The Adsorption of Ammonia

Although metal ions existing as aqua-ions in the aqueous solution are not significantly adsorbed on silica gel, substitution of hydrated water molecules for ammonia caused considerable adsorption of the metal ions (*16–18*). Hence, the adsorption of ammonia was investigated to measure the adsorption capacity on silica gel prior to the measurement of the adsorption of metal ions. The adsorption of ammonia is supposed to be expressed as

$$\mathrm{RH} + \mathrm{NH_3} \rightleftharpoons \mathrm{RNH_4} \qquad K \tag{1}$$

Accordingly, the total concentration of the silanol groups is expressed as

$$[\mathrm{RH}]_0 = [\mathrm{RH}] + [\mathrm{RNH_4}] \tag{2}$$

Substitution of Eq. (1) into Eq. (2) gives

$$\frac{[\mathrm{NH_3}]}{[\mathrm{RNH_4}]} = \frac{[\mathrm{NH_3}]}{[\mathrm{RH}]_0} + \frac{1}{K[\mathrm{RH}]_0} \tag{3}$$

Figure 1 shows experimental results according to Eq. (3). The results evidently demonstrate a high affinity of ammonia for the surface of silica gel and good agreement with the adsorption model based on Eq. (1). The constants $K$ and $[\mathrm{RH}]_0$ in Eq. (3) were evaluated as 13.2 $\mathrm{dm^3/mol}$ and 3.03 mol/kg from the intercept of the ordinate and the slope of the straight line in Fig. 1, respectively.

### pH Dependency of the Adsorption of Metal Ions

Figures 2 and 3 show the effect of pH on the amount of adsorption of copper and cadmium, respectively, on silica gel from the aqueous ammonium nitrate solutions of 0.5, 1.0, and 3.0 $\mathrm{mol/dm^3}$. In both figures the amount of adsorption increases remarkably with an increase of pH in the lower pH region, which is considered to be due to cation exchange between the hydrogen ion of silica gel and the metal ions.

On the other hand, adsorption decreases with an increase of pH in the higher pH region, which suggests the formation of higher metal–ammine

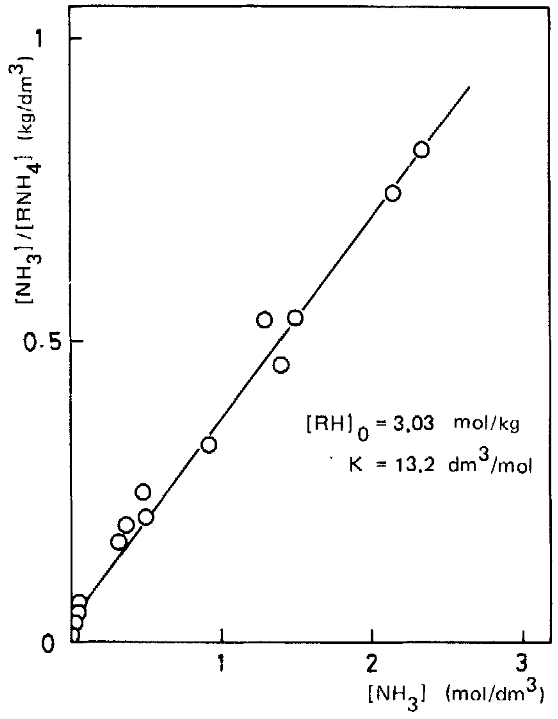

FIG. 1. Adsorption equilibrium of ammonia on silica gel.

complexes which are hardly adsorbed on silica gel. This is also supported by the fact that adsorption decreases with an increase of ammonium nitrate concentration.

## DISCUSSION

From the fact that silica gel does not adsorb metals existing as aqua ions in aqueous solution, and that addition of ammonia causes the adsorption of these metals, it is believed that metals adsorbed on silica gel exist as metal–ammine complexes, $M(NH_3)_j^{n+}$, on its surface. Therefore, the adsorption of divalent metal ions such as copper(II) and cadmium(II) on silica gel is described by a general stoichiometric relation:

$$GH_2 + M(NH_3)_j^{2+} \rightleftharpoons GM(NH_3)_j + 2H^+ \qquad K_e$$

where $j$ denotes the number of ammonium molecules coordinated in the metal–ammine complexes which can be adsorbed on silica gel. $GH_2$ denotes the silanol acid of silica gel. The equilibrium constant $K_e$ for the above reaction is described as

$$K_e = \frac{[GM(NH_3)_j][H^+]^2}{[M(NH_3)_j^{2+}][GH_2]} \qquad (4)$$

The formation of the metal–ammine complexes is described as

$$M^{2+} + iNH_3 \rightleftharpoons M(NH_3)_i^{2+} \qquad \beta_i$$

The stability constants, $\beta_i$, for copper and cadmium are listed in Table 1.

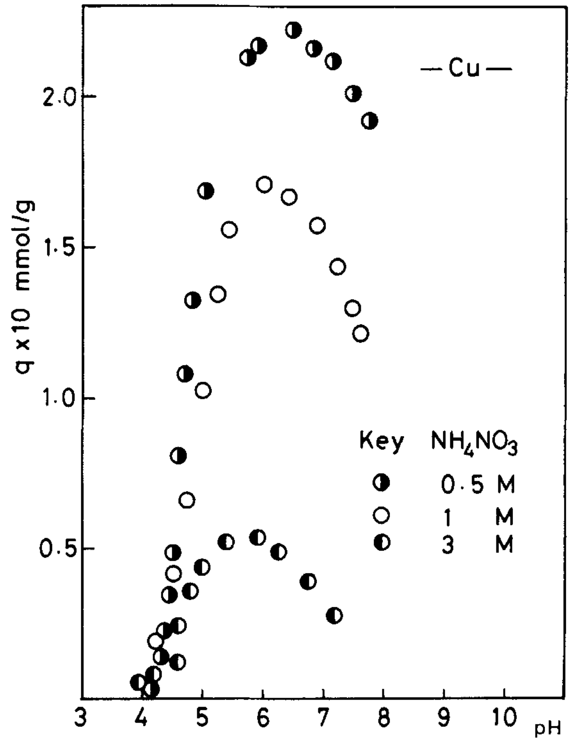

FIG. 2. Effects of the concentration of ammonium nitrate and pH of the solution on the amount of copper adsorbed.

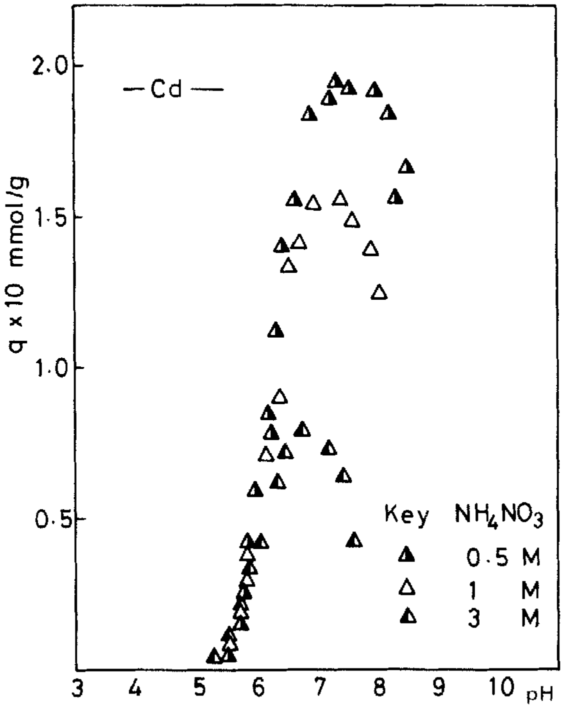

FIG. 3. Effects of the concentration of ammonium nitrate and pH of the solution on the amount of cadmium adsorbed.

If hydrolysis of metals can be ignored, as is the case for ammoniacal media, the concentration of $M(NH_3)_j^{2+}$ is described by the total metal concentration in the aqueous solution, $C_{MW}$ and the concentration of free ammonia as

$$[M(NH_3)_j^{2+}] = \frac{\beta_j[NH_3]^j}{1 + \sum_{1}^{i} \beta_i[NH_3]^i} C_{MW} \qquad (5)$$

Furthermore, the concentration of free ammonia is related to that of ammonium ion by the equilibrium relation

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \qquad K_A \qquad (6)$$

where

$$K_A = 5.5 \times 10^{-10} \text{ mol/dm}^3$$

Electroneutrality in the aqueous phase provides

$$2C_{\mathrm{MW}} + [\mathrm{H}^+] + [\mathrm{NH}_4^+] = [\mathrm{OH}^-] + [\mathrm{NO}_3^-] \tag{7}$$

If $C_{\mathrm{MW}}$ is low enough compared to ammonium nitrate concentration, and where pH is neither too low nor too high, Eq. (7) can be approximated as

$$[\mathrm{NH}_4^+] \cong [\mathrm{NO}_3^-] \tag{8}$$

Equation (5) is reduced to Eq. (9) from Eqs. (6) and (8):

$$[\mathrm{M(NH_3)}_j^{2+}] = \frac{\beta_j'/[\mathrm{H}^+]^j}{1 + \sum_1^i \beta_i'/[\mathrm{H}^+]^i} C_{\mathrm{MW}} \tag{9}$$

where

$$\beta_i' = \beta_i(K_A[\mathrm{NO}_3^-])^i \tag{10}$$

$$\beta_j' = \beta_j(K_A[\mathrm{NO}_3^-])^j \tag{11}$$

Substitution of Eq. (9) into Eq. (4) followed by rearrangement provides the distribution ratio of metal, $D$:

TABLE 1
Stability Constants

| Metal | $\beta_1$ | $\beta_2$ | $\beta_3$ | $\beta_4$ |
|---|---|---|---|---|
| Copper[a] | $1.35 \times 10^4$ | $4.1 \times 10^7$ | $3.0 \times 10^{10}$ | — |
| Cadmium[b] | $3.98 \times 10^2$ | $4.47 \times 10^4$ | $1.10 \times 10^6$ | $8.32 \times 10^6$ |

[a] A. J. Bard, *Yōekinai Ion Heikō*, translated by Y. Matsuda and K. Ogura, Kagaku Dōjin, Kyoto, 1975.

[b] A. Ringbom, *Sakukeisei Hannō, (Complexation in Analytical Chemistry)* (in Japanese), Sangyo Tosho, Tokyo, 1965.

$$\log D = 2\text{pH} + \log K_e + \log[\text{GH}_2] + \log \frac{\beta_j'/[\text{H}^+]^j}{1 + \sum_1^i \beta_i'/[\text{H}^+]^i} \qquad (12)$$

where distribution ratio $D$ is defined as

$$D = \frac{\text{moles of metal per gram of silica gel}}{\text{moles per milliliter of solution}}$$

In the lower pH region, where $1 \gg \Sigma_1^i \, \beta_i'/[\text{H}^+]^i$, Eq. (12) can be approximated as

$$\begin{aligned} \log D &\cong (2+j)\text{pH} + \log[\text{GH}_2] + \log K_e \, \beta_j(K_A[\text{NO}_3^-])^j \\ &= (2+j)\text{pH} + \log K_M \end{aligned} \qquad (13)$$

where the apparent equilibrium constant, $K_M$, is defined as

$$K_M = K_e\beta_j(K_A[\text{NO}_3^-])^j[\text{GH}_2]$$

Figure 4 shows plots of the experimental results based on Eq. (12). The plotted points in Fig. 4 lie on straight lines in the lower pH region as expected from Eq. (13). The slopes of the straight lines are about 3 for both metals, which indicates that $j \cong 1$ for both metals from Eq. (13). Therefore, the adsorbed species is considered to be $\text{MNH}_3^{2+}$ for both metals. From the above results, the stoichiometric relation for the adsorption of these metals in expressed as

$$\text{GH}_2 + \text{CuNH}_3^{2+} \rightleftharpoons \text{GCuNH}_3 + 2\text{H}^+ \qquad K_{\text{Cu}}$$

$$\text{GH}_2 + \text{CdNH}_3^{+} \rightleftharpoons \text{GCdNH}_3 + 2\text{H}^+ \qquad K_{\text{Cd}}$$

where

$$K_{\text{Cu}} = 4.3 \times 10^{-13} \text{ mol/dm}^3$$

$$K_{\text{Cd}} = 5.1 \times 10^{-20} \text{ mol/dm}^3$$

These results coincide with those reported for the adsorption of copper from ammonia solution by Tominaga (*21*) who indicated that the adsorbed species are neither $\text{Cu}^{2+}$ nor $\text{Cu(NH}_3)_4^{2+}$ but $\text{Cu(NH}_3)_n^{2+}$ ($n$ = 1–3) from observations with ESR and electronic specta. Burwell (*22*) also predicted the same adsorbed species of adsorbed cupric ions. Kolthoff et al. (*23*)

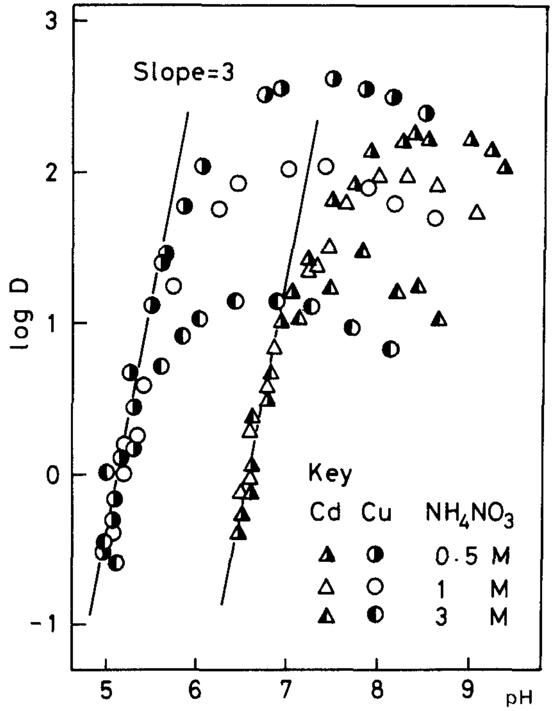

FIG. 4. Determination of the number of ammonia molecules in the adsorption species, $M(NH_3)_j^{2+}$.

inferred that the copper–ammine complex, $Cu(NH_3)_2^{2+}$, undergoes reaction with silicate to produce $Cu(NH_3)_2(H_2O)_3SiO_3$, which transforms into $Cu(NH_3)(H_2O)_3SiO_3$ when it is allowed to stand. The solid lines in Fig. 5 represent the calculated results from Eq. (12) using the value of $K_M$ evaluated and the stability constants listed in Table 1. The experimental results are in good agreements with the calculated lines for each metal.

## CONCLUSION

The adsorption equilibrium of copper and cadmium from an aqueous ammonium nitrate–ammonia mixture on silica gel was studied, and the effects of the concentrations of ammonium nitrate and hydrogen ion in aqueous solution were elucidated. It was concluded that copper and

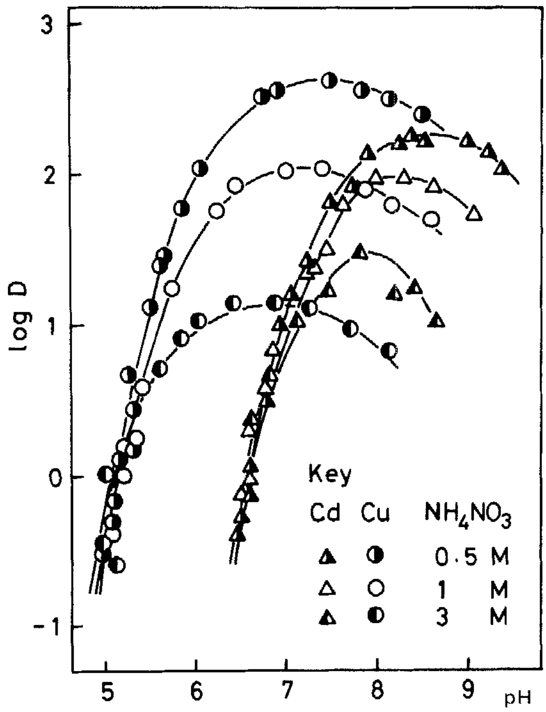

FIG. 5. Comparison of experimental results with calculated results for the relation between distribution ratio and pH.

cadmium ions are adsorbed on silica gel according to the following stoichiometric relations:

$$GH_2 + CuNH_3^{2+}(H_2O)_3 \rightleftharpoons GCuNH_3(H_2O) + 2H^+ \qquad K_{Cu}$$

$$GH_2 + CdNH_3^{2+}(H_2O)_5 \rightleftharpoons GCdNH_3(H_2O)_3 + 2H^+ \qquad K_{Cd}$$

The adsorption equilibrium constants were evaluated as $K_{Cu} = 4.3 \times 10^{-13}$ mol/dm$^3$ and $K_{Cd} = 5.1 \times 10^{-20}$ mol/dm$^3$. Because of the large difference between these adsorption equilibrium constants, it is believed that silica gel can be successfully used for the separation of copper from cadmium in ammoniacal solutions.

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