A Study of the Sorption of Metal Ions by Cotton Cloth

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(Received January 8, 1964)

The interactions of cellulose with metal ions in aqueous solutions have long been known. For example, cellulose can react with metal ions in such strong alkaline media as Schweizer's solution. In connection with the structure and the nature of cellulose, mechanisms for the sorptions of metal ions by cellulose have been discussed by various workers.[1-5] Some of them ascribe the sorption phenomena to an acidic action of hydroxyl groups and a complex formation,[4] and some, to an ion-exchange reaction of the carboxyl groups which exist in cellulose.[3,5]

The present paper will study, by means of the tracer technique, the sorption phenomena of metal ions by cotton cloth in the aqueous media. In the neutral and the acidic region, the exchange mechanism by the carboxyl groups has again been confirmed. Since it has been another object of this work to obtain information on the decontamination of metal ions from cotton cloth, the relative affinities of metal ions, i. e., Cu^{2+}, Co^{2+}, Zn^{2+}, Ca^{2+}, Sr^{2+}, Cs^{+}, K^{+} and Na^{+}, to cotton cloth have also been determined.

Experimental

Materials.—The cotton print cloth (Nitto Boseki K. K.) was purified by extracting it with hot ethanol and boiling for 2.5 hr. in a 1% sodium hydroxide solution. The residual sodium hydroxide was removed from the cotton by washing it with distilled water; it was then acidified with dilute acetic acid, again neutralized with dilute aqeous ammonia, and finally washed with deionized distilled water. The cotton thus obtained was dried and stored. The Cu-value was found to be 0.048.

Commercial metal salts (reagent grade) were used without further purification. The water employed was treated with ion exchange resin and distilled. Radioisotopes, ^{45}Ca, ^{60}Co and ^{137}Cs, were diluted to the proper activity level for use.

Procedures. — *The Determination of Uptake.* — Weighed samples of cotton cloth, about 4.5 cm² in apparent area (ca. 0.05 g.), were immersed into 20 ml. of a metal salt solution of a known concentration containing the radioisotope as a tracer and shaken for 2 hr. at a desired constant temperature (usually 25°C) in most cases. Then the cotton sample was taken out of the solution, pressed between two sheets of filter paper, and reweighed to determine the amount of the moisture retained in the sample. The activity of the air-dried sample was measured by a Geiger-Mueller counter or a scintillation counter, while the total number of metal ions taken up by the sample was calculated by means of the calibration curve which had been obtained in the preliminary experiment for the sample soaked with a known number of the metal ions. The real amount of sorbed metal ions was obtained by correcting for the moisture retained in the sample. In this correction it was assumed that the concentration of the metal ion in the retained moisture was the same as that in the bulk solution.

The Determination of Rates of Sorption. — The rates of the sorption of Co^{2+} were determined at 2, 4.7, 25 and 38°C by measuring the uptake at appropriate intervals by a method similar to that mentioned above until equilibrium was achieved.

pH Adjustment.—In the studies of the pH dependence, hydrogen ion concentrations were changed by adding hydrochloric acid to solutions while keeping the amount of metal hydroxide constant.

The Determination of Relative Affinities. — The maximum uptakes of Co^{2+} from mixed solutions of Co^{2+} and any one of the following ions, Cu^{2+}, Zn^{2+}, Ca^{2+}, Cs^{+}, K^{+} and Na^{+}, were determined. The initial concentrations of the two ions in the mixed solutions were the same (10^{-3} M). An affinity series was determined from the order of the maximum uptake of Co^{2+}. A similar experiment was undertaken for mixed solutions of Ca^{2+} and any one of the following ions, Cu^{2+}, Co^{2+}, Zn^{2+}, Cs^{+}, K^{+} and Na^{+}.

Results and Discussion

pH Dependence. — The equilibrium uptakes of Co^{2+}, Ca^{2+} and Cs^{+} by cotton cloth exhibit a marked dependence upon the hydrogen ion concentration of the media, as is shown, for instance, for Ca^{2+} in Fig. 1. The uptake becomes perceptible around pH 3 and increases rapidly with the increasing pH, with an intermediate approximate plateau in the neutral region. This suggests two mechanisms for the

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1) G. F. Davidson and T. P. Nevell, *Shirley Inst. Mem.*, **21**, 46 (1947).

2) H. F. Church, *J. Soc. Chem. Ind.* (*London*), **66**, 221 (1947).

3) R. J. Demint and J. C. Arthur, Jr., *Textile Research J.*, **29**, 276 (1959).

4) D. S. Belford, A. Myers and R. D. Preston, *Biochim. Biophs. Acta*, **34**, 47 (1959).

5) R. I. C. Michie, *Nature*, **190**, 803 (1961).

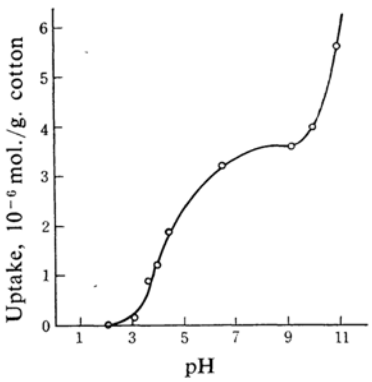

Fig. 1. pH dependence of Ca^{2+} uptake on cotton cloth.
$[Ca^{2+}]=1.1\times10^{-3}$ M, 25°C

sorption, one effective in the acidic and neutral regions, and the other only in the strongly alkaline region. The former is a cation exchange mechanism of the carboxyl groups, in accordance with Michie's[5] observation that the uptake of copper is proportional to the carboxyl content and with Demint and Arthur's[3] study of the exchanging properties of γ-ray irradiated cotton.

The latter mechanism is an acidic action of the hydroxyl groups in cellulose. Complex formations of this groups have long been known in strongly alkaline media, such as Schweizer's solution. In the strongly alkaline region, however, cotton shows a swelling which may increase the active sites. This renders the interpretation difficult. Therefore, the following experiments are restricted to the sorption in the acidic and neutral regions.

The Rate of Sorption. — The rates of the sorption of Co^{2+} were measured at various temperatures and at various concentrations of Co^{2+} at pH ca. 4.7. As is shown in Fig. 2, the uptakes increase with time approaching the equilibrium values.

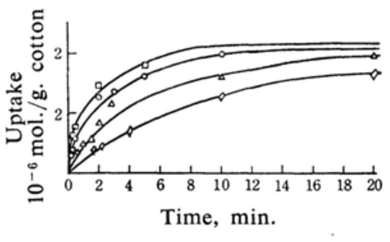

Fig. 2a. Uptake of Co^{2+} at various temperatures.
$([Co^{2+}]=1\times10^{-4}$ M)
2°C (◇), 4.7°C(△), 25°C (○), 38°C (□)

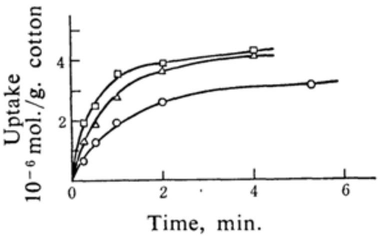

Fig. 2b. Uptake of Co^{2+} at various concentrations. (25°C)
4×10^{-4} M (□), 2×10^{-4} M (△), 1×10^{-4} M (○)

According to the mechanism of cation exchange between the hydrogen ion of the caboxyl groups, H^+, and the metal ions, M^+, the following rate expression may be expected to hold as a first approximation;

$$dx/dt=k_1(a-x)[M^+]-k_2x[H^+] \tag{1}$$

where x is the uptake at time t, a is the total number of sites available for ion exchange, and k_1 and k_2 are rate constants. Equation 1 was derived by assuming a hypothetical homogeneous solution. Further, it can be assumed that $[H^+]$ and $[M^+]$, practically speaking, do not change during the sorption under our experimental conditions. Thus, from Eq. 1, a linear relationship for $\ln(1-x/x_e)$ vs. t plots follows, where x_e is the equilibrium uptake. The experimental results under the various conditions are illustrated in Fig. 3. The deviation from linearity in Fig. 3 indicates that the simplified model mentioned above is not accurate. The actual process is a heterogeneous one. Possibly, delayed transporting phenomena of the metal ions from the surface into the inner sorption site of the cotton are responsible for the nonlinearity obtained.

Fig. 3. $\log(1-x/x_e)$ vs. t plots.
2°C (◇), 4.7°C (△), 25°C (○), 38°C (□)

However, as the limiting case of Eq. 1, the following relation may be applied for an initial stage of the sorption;

$$(dx/dt)_0=k_1a[M^+] \tag{2}$$

where $(dx/dt)_0$ means the initial velocity. $(dx/dt)_0$ can be obtained from the initial slopes of curves in Fig. 2. Equation 2 is satisfied as illustrated in Fig. 4, as far as the change of $[M^+]$ is concerned in the sorption of Co^{2+}. k_1 can be calculated from the slope of the straight line in Fig. 4, using the maximum uptake, a, obtained in the equilibrium experiments.

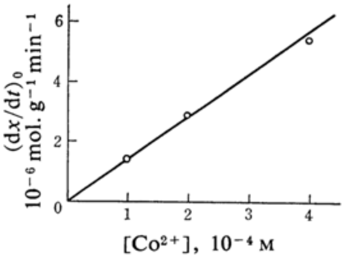

Fig. 4. Initial rates of Co^{2+} uptake at various concentrations (25°C).

An activation energy for the sorption of Co^{2+} was calculated from k_1 values at various temperatures (Fig. 5) to be 7.6 kcal./mol. It is interesting to note that this value is of the same order as the activation energies of the diffusion of metal ions in aqueous solutions.[6,7]

The facts may indicate that the diffusion of Co^{2+} to the cotton surface is the rate-determining step in the early stage of the sorption of the ion.

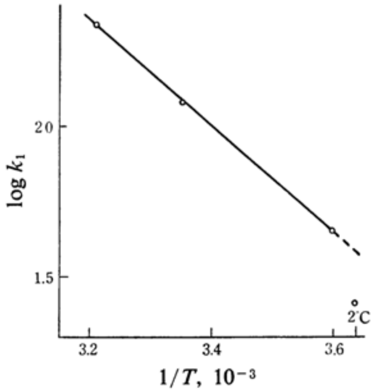

Fig. 5. Temperature dependence of initial rate constants of uptake of Co^{2+}.

The Concentration Dependence of the Uptake. —The equilibrium uptakes at various concentrations of Co^{2+} are expressed as a Langmuir-type sorption isotherm (Fig. 6).

Assuming a cation exchange mechanism,

$$RH + M^+ \rightleftharpoons RM + H^+$$

a Langmuir-type isotherm (Eq. 5) is derived as follows:

$$\frac{(RM)\,[H^+]}{(RH)\,[M^+]} = K_H^M \tag{3}$$

$$(RH) + (RM) = a \tag{4}$$

$$a = \frac{(RM)\,[H^+]}{K_H^M\,[M^+]} + (RM)$$

$$\frac{[M^+]}{(RM)} = \frac{[H^+]}{aK_H^M} + \frac{[M^+]}{a} \tag{5}$$

where (RH) and (RM) are the total number of sites per gram of cotton occupied by H^+ and M^+ respectively, and $[H^+]$ and $[M^+]$ are the concentrations of H^+ and M^+ respectively in the solution.

The total amount of available sites a mol. per gram of cotton can be obtained as the maximum uptake experimentally. The value, 4.2×10^{-6} mol./g. cotton, calculated for a from Fig. 6 is about 10^{-3} times the number of hydroxyl groups in cellulose. These results seem to indicate that some special group, possibly a carboxyl group, is responsible for the sorption phenomena in the acidic region.

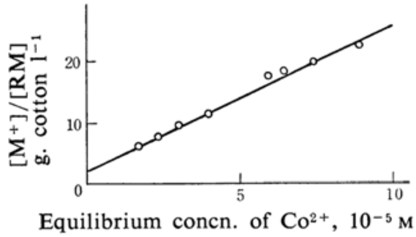

Fig. 6. Langmuir absorption isotherm of Co^{2+} (25°C).

The Heat of Sorption. — The heat of the sorption of Co^{2+} was determined to be ca. -2 kcal./mol. from the variation of uptake with temperature. Because of the small effect of the temperature on the uptake, it was difficult to ascertain the heat of sorption accurately. The low value of the heat of sorption may be an evidence for the exchange mechanism of the sorption.

The Affinities of Various Metal Ions.—When two kinds of metal ions, M_1^+ and M_2^+, coexist in the sorption system, the following exchange equilibria are to be expected;

$$RH + M_1^+ \rightleftharpoons RM_1 + H^+$$

$$RH + M_2^+ \rightleftharpoons RM_2 + H^+$$

$$RM_1 + M_2^+ \rightleftharpoons RM_2 + M_1^+$$

The relative affinity of these metal ions to the cotton can be given as;

$$K_{M_1}^{M_2} = \frac{K_H^{M_2}}{K_H^{M_1}} = \frac{\dfrac{(RM_2)\,[H^+]}{(RH)\,[M_2^+]}}{\dfrac{(RM_1)\,[H^+]}{(RH)\,[M_1^+]}} = \frac{(RM_2)\,[M_1^+]}{(RM_1)\,[M_2^+]} \tag{6}$$

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[6] J. H. Wang, *J. Phys. Chem.*, **58**, 686 (1952).

[7] F. Fukuoka, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **56**, 51 (1953).

where $K_{M_1}^{M_2}$ denotes the relative affinity of M_2^+ with respect to M_1^+. The uptake of the metal ions of 10^{-3} M on a RH ion exchanger was found to be almost equal the maximum uptake, *a*. Therefore, in this case the following relation holds.

$$a = (RM_1) + (RM_2) \tag{7}$$

Therefore, Eq. 6 can be written;

$$K_{M_1}^{M_2} = \frac{(a - (RM_1))\,[M_1^+]}{(RM_1)\,[M_2^+]} \tag{8}$$

Using ^{45}Ca or ^{60}Co as a tracer, K_{Ca}^{M} or K_{Co}^{M} were determined experimentally using Eq. 8, and then K_{H}^{M} was calculated using the value of K_{H}^{Ca} ($=0.26$) obtained from the studies of pH dependence. The results are given in Table I. This order nearly parallels that of the stabilities of metal complexes[8] and that of the catalytic activities of metal ions in the oxygen exchange reaction between lactose and water.[9]

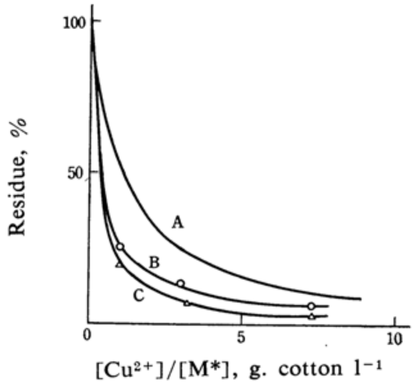

Fig. 7. Decontamination efficiency of Cu^{2+}.
Decontamination of Co
Decontamination of Ca
Solid lines show calculated values.
A, decontamination by the same ion $K_{M}^{M}=1$
B, decontamination by the same ion $K_{Co}^{Cu}=3.6$
C, decontamination by the same ion $K_{Ca}^{Cu}=5.3$

TABLE I. RELATIVE AFFINITIES

Ion	Cu^{2+}	Zn^{2+}	Co^{2+}	Ca^{2+}	Sr^{2+}	Cs^+	K^+	Na^+
K_{H}^{M}	1.4	0.54	0.36	0.26	0.11	0.03	0.03	~0

The Decontamination of Radioactive Metal Ions from Cotton.—It can be expected that metal ions sorbed by cotton cloth may be effectively replaced by an ion which has a much stronger affinity to cotton. This was ascertained by the following experiments. Cotton cloth which had been contaminated by ions, ^{60}Co or ^{45}Ca, was immersed in a solution of Cu^{2+}. After the solution had been shaken for 2 hr., the residual contamination was measured. As Fig. 7 shows, of ^{60}Co or ^{45}Ca can be decontaminated very efficiently by using a Cu^{2+} solution. The solid lines show the theoretical values calculated by using these relative affinities; A : $K_{M}^{M}=1$, B : $K_{Co}^{Cu}=3.6$, and C : $K_{Ca}^{Cu}=5.3$. Thus, the order of relative affinities in Table I turns out to be useful as a guide for the decontamination problems.

Summary

The uptakes of the metal ions, Co^{2+}, Ca^{2+} and Cs^+, by cotton cloth have been determined by using the tracer technique. In the acidic and the neutral media, the isotherms were the Langmuir type, and the cation exchange mechanism of the special groups (probably the carboxyl group) has been confirmed. The heat and the activation energy for the sorption of Co^{2+} were -2 kcal./mol. and 7.6 kcal./mol. respectively (at pH ca. 4.7). In the alkaline media, the cotton cloth showed marked uptakes. The order of the affinity of various metal ions to cotton cloth was also determined as follows:

$$Cu^{2+} > Zn^{2+} > Co^{2+} > Ca^{2+} > Sr^{2+} > Cs^+, K^+ > Na^+$$

The order is useful for the purpose of decontamination.

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[8] M. Yasuda, K. Yamasaki and H. Ohtaki, This Bulletin, 33, 1067 (1960).

[9] T. Titani and K. Goto, *Catalysis* (*Shokubai*), 3, 123 (1948).