The Ion-exchange Equilibrium between Cesium and Phenol-sulfonic-acid-type Cation Exchange Resin[*]

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Many researchers have investigated the specific adsorption of cesium on the phenol-sulfonic-acid-type cation exchange resin as a technique for analyzing cesium in various materials[1-4]. However, studies of the ion-exchange equilibrium with the resin have not yet been carried out, with the exception of one of the Cs^+-Na^+ exchange in a sodium hydroxide solution[5]. In this paper, the distribution coefficients of cesium between several basic solutions and the resin as measured by the batch method are reported. In addition, the phenomenon of the specific adsorption of cesium on the resin from an ammoniacal solution as compared to sodium hydroxide and potassium hydroxide solutions will be discussed.

Experimental

Chemicals.—Diaion BK (phenol-sulfonic-acid-type cation exchange resin) and Duolite C-3 of 60∼80 mesh were used[**]. They were prepared as ammonium, sodium and potassium forms using basic solution of ammonium, sodium and potassium salts respectively. It was confirmed that about 90%, or more, of the phenolic-active groups were in NH_4^+-, Na^+- or K^+-forms. The exchange capacity of the active sulfonic group was 2.0 meq., and that of the phenolic group was 2.2 meq. for 1 g. of air-dried resin. The exchange capacities were determined by measuring the salt-splitting capacities and the exchange capacity in the basic solution.

Solutions of the following composition were used. Various amounts of cesium, with cesium-137 as the tracer, were added to ammoniacal solutions of various concentrations and pH values. The pH value was adjusted by adding ammonium formate. They were prepared in the range of 0.5∼7.5 M of total concentration, a pH value of 10∼12, and 0∼100 mg. of cesium carrier for 50 ml. of solution. Sodium hydroxide plus sodium chloride and potassium hydroxide solutions were prepared in similar ways. All alkaline solutions were kept in CO_2-free air as far as possible.

Instruments.—The pH value of the ammoniacal solution was determined by a glass electrode pH-meter.

The β-activity was measured by a G. M. counter connected with an automatic sample changer. The γ-activity was measured for the photo-peak of 0.66 MeV. by using a well-type NaI(Tl) scintillation counter connected with a single-channel pulse height analyzer.

Measurements.—For each run, 50 ml. of the solution were shaken for 24 hr. with 0.500 g. of the dried ion-exchange resin in a constant temperature bath at 25°C. After an exchange equilibrium had been attained, 5 ml. of the solution were pipetted out, and the radioactivity or cesium concentration of the solution phase (C) was measured. From the C values and the cesium concentration in the initial solution (C_0), the distribution coefficients of cesium (K_d) under various conditions were obtained from the following equation. (Here, the volume decrease of the solution caused by the swelling of the ion exchanger is disregarded).

$$K_d=\{(C_0-C)/C\}\{50/0.5\}$$
$$=100\cdot(C_0-C)/C \qquad \text{(ml./g.)}$$

In the case of ammoniacal solutions, 2 ml. of the solution were put into a stainless steel counting dish, and the β-activity was measured after drying it under an infrared lamp. In the case of sodium or potassium solutions, 5 ml. of the solution were placed in a capsule and the γ-activity was measured. All measurements were made twice.

Results

$Cs^+-(NH_4^++NH_3)$ Exchange System.—The values of the distribution coefficients of cesium when the pH value of the outer solution was varied and the total concentration of the outer solution was kept constant are shown in Fig. 1. Straight lines, the slopes of which were nearly constant for various concentrations, were obtained, although they deviated slightly at both ends. The slopes are expressed as follows:

$$\left(\frac{\partial \log K_d}{\partial \mathrm{pH}}\right)_{[NH_4^++NH_3]}=1.0 \qquad (1)$$

Figure 2 shows the relationship between the distribution coefficients of cesium and the total

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[*] A part of this work was read at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

[**] Similar results for distribution coefficients were obtained. The results for Diaion BK will be reported here.

1) H. S. Miller and G. E. Kline, *J. Am. Chem. Soc.*, **73**, 2741 (1951).

2) W. F. Merritt, *Can. J. Chem.*, **36**, 425 (1958).

3) J. B. Niday, *Phys. Rev.*, **98**, 42 (1955).

4) T. T. Sugihara, H. I. James, E. J. Troianello and V. T. Bowen, *Anal. Chem.*, **31**, 44 (1959).

5) H. Kakihana, T. Murase and M. Nakagawa, The 12th Annual Meeting of the Chemical Socity of Japan, Kyoto, April, 1959.

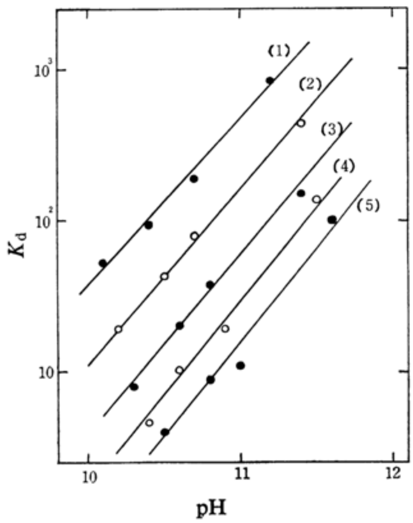

Fig. 1. Distribution coefficients of cesium in $Cs^+-(NH_4^++NH_3)$ exchange system.

Total concn. of ammonia, mol./l.
(1) 0.5, (2) 1, (3) 2, (4) 3, (5) 5

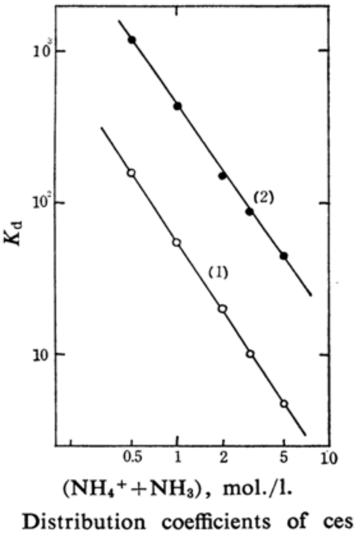

Fig. 2. Distribution coefficients of cesium in $Cs^+-(NH_4^++NH_3)$ exchange system.

(1) pH 10.6 (2) pH 11.4

concentration of the outer solution when the pH value of the outer solution was kept constant. They are expressed approximately by the following equation:

$$\left(\frac{\partial \log K_d}{\partial \log [NH_4^+ + NH_3]}\right)_{pH} = -1.6 \qquad (2)$$

where $[NH_4^+ + NH_3]$ denotes the total concentration of the solution.

From Eqs. 1 and 2, the following equation is obtained:

$$\log K_d = pH - 1.6 \log [NH_4^+ + NH_3] + C_1 \qquad (3)$$

where C_1 is the constant for the $Cs^+-(NH_4^+ + NH_3)$ exchange system.

The value when the salt-splitting capacity is 2.0 meq./g.* is as follows:

$$C_1 = -8.8$$

The Cs^+-Na^+ and Cs^+-K^+ Exchange Systems.—The relationship between the distribution coefficients of cesium and the pH value or the concentration of sodium hydroxide when the total sodium concentration in the outer solution was kept constant is shown in Fig. 3. The relation is expressed as follows:

$$\left(\frac{\partial \log K_d}{\partial \log [OH^-]}\right)_{[Na^+]} = 0.25 \qquad (4)$$

or

$$\left(\frac{\partial \log K_d}{\partial pH}\right)_{[Na^+]} = 0.25 \qquad (4')$$

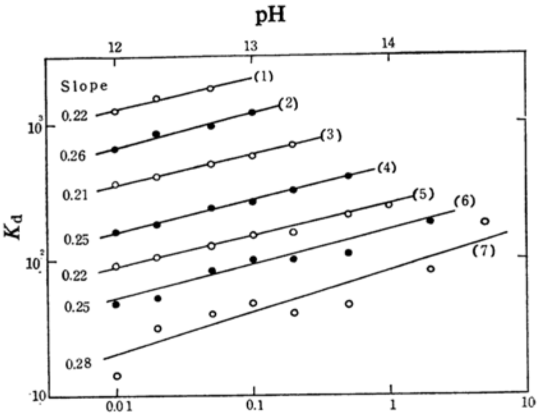

Fig. 3. Distribution coefficients of cesium in Cs^+-Na^+ exchange system.

Total sodium concn., mol./l.
(1) 0.05 (2) 0.1 (3) 0.2 (4) 0.5
(5) 1 (6) 2 (7) 5

Equation 5, which is obtained by rearranging the results shown in Fig. 3, gives the relationship between the distribution coefficients of cesium and the total sodium concentration when the pH value or the concentration of sodium hydroxide in the outer solution is kept constant.

$$\left(\frac{\partial \log K_d}{\partial \log [Na^+]}\right)_{pH} = -0.90 \qquad (5)$$

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* Equations 1 and 2 can be formulated even when the quantities of the ion exchnger or the exchange capacities are varied because of the drying state of the resin. However, the value of C_1 in Eq. 3 changes. Therefore, all values of K_d and the constant C_1 are normalized when the salt-splitting capacity, which can be easily determined, is 2.0 meq./g.

From Eqs. 4 and 5, a formula for the Cs^+-Na^+ exchange system may be given with a good approximation as follows:

$$\log K_d = 0.25 \log [OH^-] - 0.90 \log [Na^+] + C_2 \quad (6)$$

where C_2 is the constant for the system, and

$$C_2 = 2.4$$

when the salt-splitting capacity is 2.0 meq./g.

Figure 4 shows the relations between the distribution coefficients of cesium and the concentration of the outer solution when the outer solution contained only sodium hydroxide or potassium hydroxide, and neither sodium chloride nor potassium chloride. The following equation holds when the outer solution was a sodium hydroxide solution:

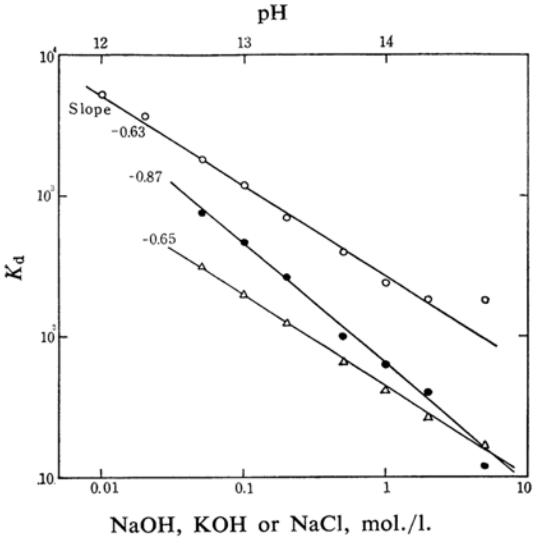

Fig. 4. Distribution coefficients of cesium in Cs^+-Na^+ and Cs^+-K^+ exchange system.
The outer solution:
○ Sodium hydroxide solution
● Sodium chloride solution
△ Potassium hydroxide solution

$$\log K_d = -0.63 \log [NaOH]_T + C_3 \quad (7)$$

where C_3 is a constant, and

$$C_3 = 2.4 = C_2$$

A similar equation is found when the outer solution was a potassium hydroxide solution:

$$\log K_d = -0.65 \log [KOH]_T + C_4 \quad (8)$$

where C_4 is a constant, and

$$C_4 = 1.7$$

When the outer solution is neutral, i. e., a sodium chloride solution, the distribution coefficients of cesium can be expressed by the following equation:

$$\log K_d = -0.87 \log [NaCl]_T + C_5 \quad (9)$$

where C_5 is a constant, and

$$C_5 = 1.8$$

The $Cs^+-NH_4^+$ Exchange System.—It was very difficult to estimate the ammonium ion concentration in the outer solution exactly, but it was necessary for the rearrangement of the relation expressed by the Eq. 3 for the $Cs^+-(NH_4^+ + NH_3)$ exchange system to provide for the relation of the distribution coefficients of cesium to the ammonium ion concentration. Two ways were tried for the estimation of the ammonium ion concentration in the outer solution, 1) assuming that the ammonium ion concentration is equivalent to the quantities of ammonium formate added to the system, and 2) assuming that the ammonium ion concentration can be calculated by using the dissociation constant of ammonia water $pK = 4.74$ at 25°C[6]. When the ammonium ion concentration was kept constant, the relation between the distribution coefficients of cesium and the pH value of the outer solution can be expressed by the following equation:

$$\left(\frac{\partial \log K_d}{\partial \text{pH}}\right)_{[NH_4^+]} = 0 \quad (10)$$

The relationship between the distribution coefficients and the ammonium ion concentration is shown in Fig. 5. The relationship

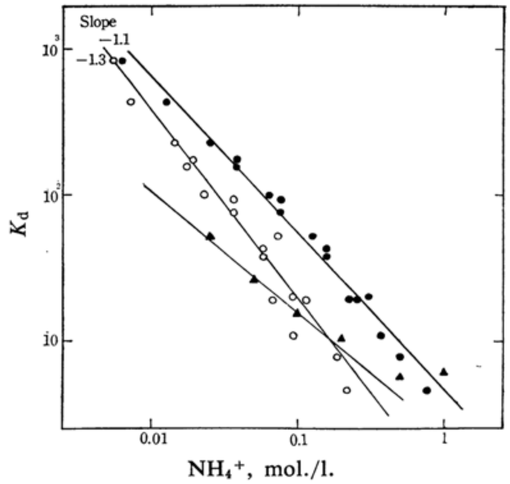

Fig. 5. Distribution coefficients of cesium in $Cs^+-NH_4^+$ exchange system.

- ● When NH_4^+ is equivalent to the quantities of ammonium formate added.
- ○ When NH_4^+ is calculated using the dissociation constant of ammonia water.
- ▲ When the outer solution is ammonium chloride solution.

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[6] B. E. Conway, "Electrochemical Data", Elsevier Pub., Amsterdam (1952).

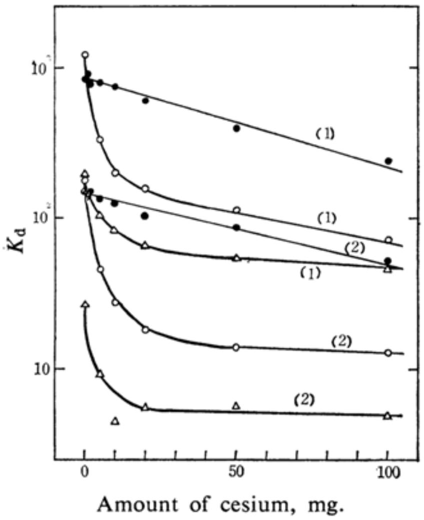
is independent of the pH value and of the total concentration of outer solution, and can be expressed as follows:

$$\log K_d = -1.1 \log[NH_4^+] + C_6 \qquad (11)$$

where C_6 is a constant, and

$$C_6 = 0.62$$

The Variation of the Distribution Coefficients of Cesium with Variation in the Cesium Quantities. — The distribution coefficients of cesium when the cesium quantities in the exchange system were changed are shown in Fig. 6. No simple formula could be found for these variations.



Fg. 6. Relation between distribution coefficients of cesium and amounts of cesium.

● $Cs^+ - (NH_4^+ + NH_3)$ exchange system
  (1) Total concn. 0.5 mol./l., pH 11.2 (NH_4^+ 0.006)
  (2) Total concn. 2 mol./l., pH 11.4 (NH_4^+ 0.03)
○ $Cs^+ - Na^+$ exchange system
  (1) 0.1 mol./l. NaOH
  (2) 2 mol./l. NaOH
△ $Cs^+ - K^+$ exchange system
  (1) 0.1 mol./l. KOH
  (2) 2 mol./l. KOH

Discussion

The observed values of the distribution coefficient of cesium are due to both the sulfonic group and the phenolic group of the resin. Therefore, the adsorption of cesium must be discussed by separating K_d into two functions: K_{d_p}, which is due to the phenolic group, and K_{d_s}, which is due to the sulfonic group.

$$K_d = K_{d_p} + K_{d_s} \qquad (12)$$

As the sulfonic acid group is strongly acidic, K_{d_s} is probably a function only of the cation concentration in the outer solution $[M^+]$:

$$K_{d_s} = B_s[M^+]^{m_s} \qquad (13)$$

where B_s and m_s are constants. Since the phenolic acid group is weakly acidic, however, K_{d_p} may be a function of both the cation concentration and the pH value, or $[OH^-]$, of the outer solution:

$$K_{d_p} = B_p[M^+]^{m_p}[OH^-]^{n_p} \qquad (14)$$

where B_p, m_p and n_p are constants.

Combining Eqs. 12, 13 and 14,

$$K_d = B_s[M^+]^{m_s} + B_p[M^+]^{m_p}[OH^-]^{n_p} \qquad (15)$$

Differentiating Eq. 15 with respect to $[M^+]$, when $m_s = m_p$,

$$\left(\frac{\partial \log K_d}{\partial \log[M^+]}\right)_{[OH^-]} = \text{const.} \qquad (16)$$

except when $B_s = 0$.

However, differentiating it with respect to $[OH^-]$, for every value of constants, B_s, B_p, B_s, m_p and n_p:

$$\left(\frac{\partial \log K_d}{\partial \log[OH^-]}\right)_{[M^+]} \neq \text{const.} \qquad (17)$$

Moreover, it should be considered that some of the metal ions are associated in the resin phase.

Thus, the results of the experiments cannot be generally expressed by the straight lines shown in Figs. 1—5, but they should be shown according to Eq. 15.

Because Eq. 15 cannot be generally solved, it has to be numerically evaluated. The variation of distribution coefficients, however, may be empirically discussed by assuming that the results are expressed by the straight lines in a limited range, even though it must be discussed more generally using Eq. 15.

The $Cs^+ - Na^+$ Exchange System.—Equation 7, obtained when the outer solution is sodium hydroxide, can be derived from Eq. 6. Sodium hydroxide is almost completely dissociated in an aqueous solution, so that:

$$[Na^+] = [OH^-] \simeq [NaOH]_T \qquad (18)$$

Substituting Eq. 18 in Eq. 6,

$$\log K_d = -0.65 \log[NaOH]_T + C_2 \qquad (6')$$

which is the same as Eq. 7. In the same manner, Eq. 8, obtained for the $Cs^+ - K^+$ exchange system, may be reduced as follows:

$$\log K_d = 0.25 \log[OH^-] - 0.90 \log[K^+] + C_4 \qquad (19)$$

Putting the condition of pH=7, or $\log[OH^-] = -7$, into Eq. 6,

$$\log K_d = -0.90 \log[Na^+] + 0.65 \qquad (20)$$

The constant term of Eq. 20 is evidently different from that of Eq. 9, obtained when the outer solution is a sodium chloride solution. This fact shows that Eq. 6, which was obtained in the high pH range, cannot be applied in the neutral range[*]. K_d calculated with Eq. 6 must be larger than K_d calculated by Eq. 9, where the phenolic group plays a part in adsorbing the cesium: therefore,

$$\log K_d\ (6) > \log K_d\ (9)$$

Resolving the equation,

$$[\mathrm{OH}^-] > 4.0\times10^{-3}$$

or

$$\mathrm{pH} > 11.6 \qquad \text{(21)**}$$

This shows that the specific adsorption of cesium caused by the phenolic group of the resin may be effective in the range of the pH value over 11.6 for Cs^+-Na^+ exchange system. To increase the specific adsorption of cesium, the concentration of sodium hydroxide must be increased. Consequently, the total adsorption of cesium and K_d will decrease.

The $Cs^+-(NH_4^++NH_3)$ Exchange System.— Equation 11, obtained for the $Cs^+-NH_4^+$ exchange system, seemed to be inconsistent with the formula obtained for the Cs^+-Na^+ and Cs^+-K^+ exchange systems. This inconsistency can be interpreted as follows. The quantity of cesium A adsorbed on resin is a function of the concentration of the dissociated phenolic groups and of the cation concentration of the solution:

$$A=f\{[\mathrm{OH}^-],\ \ [\mathrm{M}^+]\} \tag{22}$$

From the experimental results mentioned above, function f may be expressed by a power function:

$$A=k_1[\mathrm{OH}^-]^{n_1}[\mathrm{M}^+]^{m_1}$$

or

$$K_d=k_2[\mathrm{OH}^-]^{n}[\mathrm{M}^+]^{m} \tag{23}$$

Equation 23 can be expressed in a logarithmic form:

$$\log K_d=n\log[\mathrm{OH}^-]+m\log[\mathrm{M}^+]+k_3 \tag{24}$$

and for a $Cs^+-NH_4^+$ exchange system, Eq. 24 is reduced to:

$$\log K_d=n\log[\mathrm{OH}^-]+m\log[\mathrm{NH_4}^+]+k_3' \tag{24'}$$

On the other hand, in an ammoniacal solution the following relation can be obtained:

$$\frac{[\mathrm{NH_4}^+]\,[\mathrm{OH}^-]}{[\mathrm{NH_3}]}=K_b \tag{25}$$

where K_b is the dissociation constant of ammonia water. Rearranging Eq. 25,

$$[\mathrm{OH}^-]=K_b[\mathrm{NH_3}]/[\mathrm{NH_4}^+] \tag{26}$$

As NH_3 may be kept constant before and after the exchange reaction,

$$[\mathrm{OH}^-]=K'/[\mathrm{NH_4}^+] \tag{27}$$

Substituting Eq. 27 into Eq. 24′,

$$\begin{aligned}\log K_d &= -n\log[\mathrm{NH_4}^+]+m\log[\mathrm{NH_4}^+]+k_3'\\ &\quad +n\log K'=(m-n)\log[\mathrm{NH_4}^+]+k_4 \end{aligned}\tag{28}$$

Substituting the values of n and m ($n=0.25$, $m=-0.90$) which were obtained for the Cs^+-Na^+ and Cs^+-K^+ exchange systems for n and m in Eq. 28 or 24, Eq. 29 can be obtained:

$$\begin{aligned}\log K_d &= (-0.90-0.25)\log[\mathrm{NH_4}^+]+k_4\\ &= -1.15\log[\mathrm{NH_4}^+]+k_4\end{aligned}\tag{29}$$

Substituting C_6 for the k_4 of Eq. 29, we can obtain Eq. 11 again. Thus, the tangent of Eq. 29 coincides with that of Eq. 11. This shows that the $Cs^+-NH_4^+$ exchange is not different from the Cs^+-Na^+ or Cs^+-K^+ exchange.

Because in the $Cs^+-(NH_4^++NH_3)$ exchange system the pH value of the outer solution is less than 11.6, which is the lower limit of pH value for a solution to adsorb cesium specifically with the phenolic group, it is necessary to verify whether or not the specific adsorption of cesium occurs. The distribution coefficients of cesium against NH_4^+ in the ammonium chloride solution shown in Fig. 5 can be attributed to the distribution coefficients caused by the sulfonic group. Because the estimated concentrations of NH_4^+ needed to plot Fig. 5 are uncertain, the results in an ammoniacal solution cannot be quantitatively compared with those in an ammonium chloride solution. The specific adsorption of Cs^+ by the phenolic group may occur in the pH range over 10.5∼11, or in the concentration range of $[NH_4^+]<0.1$ mol./l. In the $Cs^+-(NH_4^++NH_3)$ exchange system, to increase total adsorption of cesium the concentration of NH_4^+ must be kept low and the pH value of the solution must be raised; consequently, the specific adsorption of cesium increases. This characteristic, which is different from that of the Cs^+-Na^+ or Cs^++K^+ exchange system, is very

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[*] This is evident from Eq. 15. Substituting $m_s=m_p=m$ in Eq. 15, the following equation can be obtained:

$$\log K_d=m\log[\mathrm{M}^+]+\log\left\{1+\frac{B_p}{B_s}[\mathrm{OH}^-]^{n_p}\right\}+\log B_s$$

When

$$\frac{B_p}{B_s}[\mathrm{OH}^-]^{n_p}\gg1 \quad \text{(in high pH range)}$$

$$\log K_d\simeq m\log[\mathrm{M}^+]+n_p\log[\mathrm{OH}^-]+\log B_p$$

and when

$$\frac{B_p}{B_s}[\mathrm{OH}^-]^{n_p}\ll1 \quad \text{(in low pH range)}$$

$$\log K_d\simeq m\log[\mathrm{M}^+]+\log B_s$$

[**] It was solved by substituting Eq. 9 as follows:

$$\log K_d=-0.90\log[\mathrm{NaCl}]_T+C_5$$

important in the application of ion exchange to the analysis of cesium.

Because Eq. 15 cannot be generally solved, it has to be numerically evaluated. The results of the numerical calculation of distribution coefficients caused by the adsorption of cesium by phenolic group (K_{d_p}) for the Cs^+-Na^+ exchange system, using the results shown in Figs. 3 and 4, are shown in Fig. 7. The K_{d_p} values for the $Cs^+-(NH_4^++NH_3)$ excange system are shown in Fig. 8.

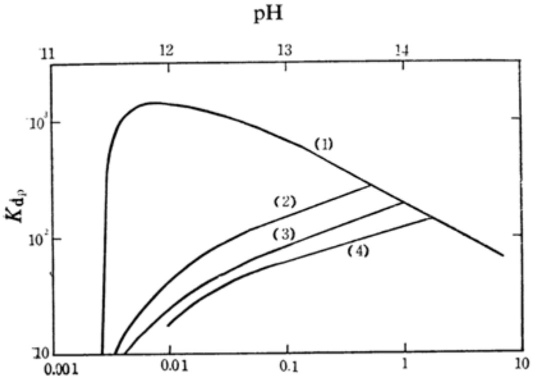

Fig. 7. Distribution coefficients of cesium due to phenolic group of the resin in Cs^+-Na^+ exchange system.

(1) NaOH
(2) $Na^+=0.5$ mol./l.
(3) $Na^+=1$ mol./l.
(4) $Na^+=2$ mol./l.

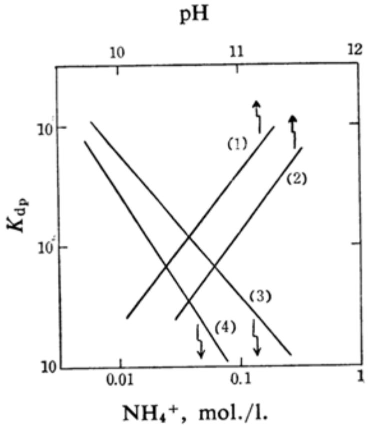

Fig. 8. Distribution coefficients of cesium due to phenolic group of the resin in $Cs^+-(NH_4^++NH_3)$ exchange system.

(1) Total concn., 0.5 mol./l.
(2) Total concn., 1 mol./l.
(3) When NH_4^+ is equivalent to the quantities of ammonium formate added.
(4) When NH_4^+ calculated using the dissociation constant of ammonia water.

Summary

1) In the $Cs^+-(NH_4^++NH_3)$ exchange system, the distribution coefficients of cesium can be approximately expressed as follows:

$$\log K_d = pH - 1.6 \log [NH_4^+ + NH_3] - 8.8$$

2) In the Cs^+-Na^+ and Cs^+-K^+ exchange systems, the distribution coefficients of cesium can be expressed with a good approximation by:

$$\log K_d = 0.25 \log [OH^-] - 0.90 \log [Na^+] + 2.4$$

and

$$\log K_d = 0.25 \log [OH^-] - 0.90 \log [K^+] + 1.7$$

In the $Cs^+-NH_4^+$ exchange system, the distribution coefficients of cesium can be expressed by:

$$\log K_d = -1.1 \log [NH_4^+] + 0.62$$

3) The specific adsorption of cesium by the active phenolic groups is observed when the pH value of the outer solution is above 12, and high selectivity is obtained above 13 for the Cs^+-Na^+ exchange system. For the $Cs^+-(NH_4^++NH_3)$ exchange system, the specific adsorption of cesium is observed above pH 11, and an extremely high selectivity can be obtained when the total concentration of the outer solution is below 1 mol./l.

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