The Distribution of Zinc Chloride and Bromide between Cation Exchanger and Methanol-Water Solution

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A cation-exchange resin employed for the forced-flow liquid chromatography was used in an investigation of the aqueous methanol solution containing zinc chloride and bromide complexes. The distribution of zinc was measured between the cation exchanger and water-methanol mixture using zinc-65 as a tracer, and the formation constants for the zinc complexes were calculated.

INTRODUCTION

In the previous papers, authors have investigated the liquid-liquid extractions of metals from the polar organic phase into the nonpolar organic phase to gain knowledge of the metal ion equilibrium in nonaqueous solvents.[1-5] However, only the several polar organic solvents such as glycols, methanol and DMSO are immiscible with the nonpolar organic solvents such as decaline and cyclohexane. In contrast, some of the ion exchange resins for the forced flow liquid chromatography can withstand most of the polar organic solvents for considerably long hours and attain equilibrium rapidly with the ions in the polar solvent phase.

The aim of the present research as well as the previous one is to gain knowledge of the equilibrium of chemical species in the nonaqueous solution phase, though a few investigations were already performed by the ion exchange method[6].

EXPERIMENTAL

Materials and Apparatus

The cation exchange resin, Hitachi custom ion exchange resin 2611, was employed in the Na⁺ form. The resin was soaked in 1 N hydrochloric acid four times and washed with pure water until the aqueous phase was neutral. And 0.2 M sodium chloride was added to the resin to make it Na⁺ form. The resin was washed with pure water and dried.

Zinc-65 was supplied as the chloride in aqueous solution by New England Nuclear, Boston, Mass., U.S.A. The tracer was converted into perchlorate by repeated evaporation with perchloric acid and diluted with methanol-water mixture.

The stock zinc solution was also prepared by dissolving dry zinc oxide with perchloric acid, evaporating to near dryness and diluting it with methanol-water.

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Reagent grade methanol was dried with anhydrous sodium sulfate for several days and distilled. Methanol-water mixture was prepared from the distilled methanol and the redistilled water. Methanolic solution of hydrochloric acid was prepared by passing dry hydrogen chloride through the mixture and standardized by titration with alkali.

Radioactivity countings were made with a Metro Electronics NaI (Tl) (44.5 mm in dia. × 50.8 mm) well type scintillation counter, PbW-6, connected with a Metro automatic scaler, SS-1060H.

Procedure

A batch procedure was adopted for the measurement of distribution coefficient, D, which is defined as the ratio of γ-activity countings per gram of the dry resin to γ-activity countings per milliliter of the solution phase at equilibrium. Twenty milliliters of the methanol-water mixture of sodium halide containing zinc perchlorate with radioactivities and perchloric acid $(1.0 \times 10^{-4}$ M) were stirred together with portions (50 mg) of the dry resin in 30 ml glass stoppered centrifuge tube by using a magnetic stirrer for 1 hr. All experiments were performed at 25 ± 0.1°C. After equilibration, the solution and resin phases were separated by centrifugation. Two milliliters of the solution phase and a total amount of the resin were taken out of the tube, and the γ-activities were counted with a NaI (Tl) scintillation counter.

RESULTS AND DISCUSSION

Zinc Concentration and Cation Exchange Resin

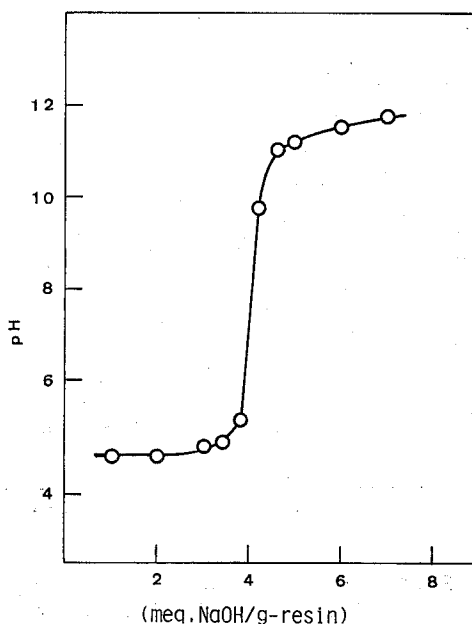The exchange capacity of the cation exchange resin was found to be about

Fig. 1. Ion-exchange capacity.

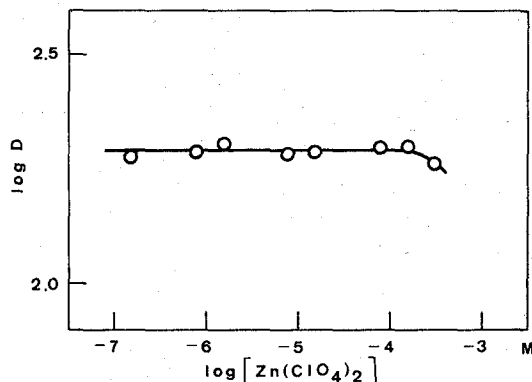S. IWASAKI, M. SUGIYAMA, M. MATSUI and T. KUMAGAI

Fig. 2. Effect of $Zn(ClO_4)_2$ concentration.
NaCl 2.0×10^{-2} M
$HClO_4$ 1.0×10^{-4} M

4 milliequivalent per gram of the dried resin as calculated from the titration curve in Fig. 1.   As shown in Fig. 2, the distribution of zinc is practically independent of its concentration in the range of $1.5 \times 10^{-7} \sim 1.5 \times 10^{-4}$ M zinc perchlorate, which is predictable from the exchange capacity of the resin.   This also shows that there occurs no adsorption of radiozinc on the walls of the tubes.   In subsequent studies, 1.5×10^{-6} M zinc perchlorate in the methanol-water mixture was used.

The effect of the cation exchange resin on the distribution of zinc ion was ex-
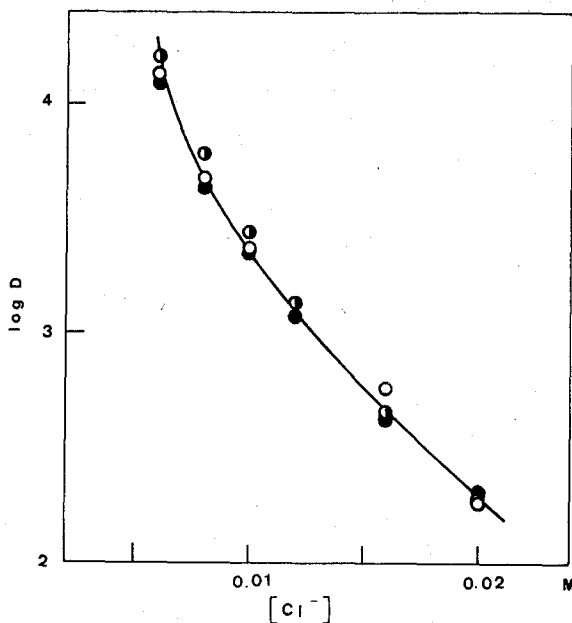

Fig. 3. Effect of resin weight.
○: 25 mg   ●: 50 mg   ◑: 100 mg
$Zn(ClO_4)_2$ 1.5×10^{-6} M
$HClO_4$ 1.0×10^{-3} M

amined with regard to resin amounts of 25, 50 and 100 mg, keeping the other variables constant. The effect was found to be negligible within the range investigated, as shown in Figs. 3 and 4. In the figures, the distribution coefficients of zinc were plotted as a function of chloride and perchlorate concentrations, respectively. In this experiment 50 mg of the resin was used.
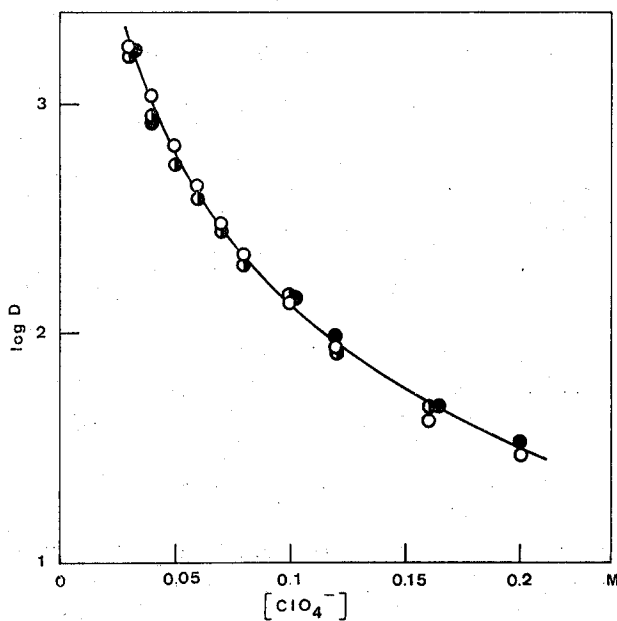

Fig. 4. Effect of resin weight.
○: 25 mg ◑: 50 mg ●: 100 mg
Zn(ClO$_4$)$_2$ 1.5 × 10^{-6} M
HClO$_4$ 1.0 × 10^{-4} M

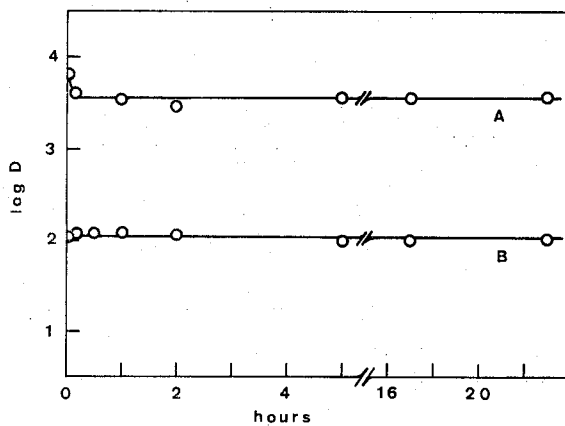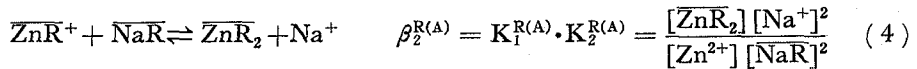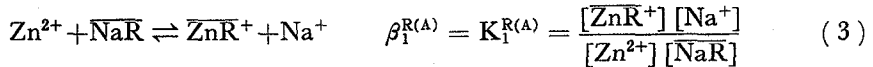

Fig. 5. Effect of stirring time.
Zn(ClO$_4$)$_2$ 1.5 × 10^{-6} M
HClO$_4$ 1.0 × 10^{-4} M
A: NaCl 1.0 × 10^{-1} M   B: NaCl 2.5 × 10^{-2} M

A 10 min. stirring period was found to be adequate for reaching equilibrium as indicated in Fig. 5.

Zinc Chloride System

The equilibria in the methanol-water phase are

$$Zn^{2+} + A^- \rightleftharpoons ZnA^+ \qquad (\beta_1^A = K_1^A) \tag{1}$$

$$ZnA^+ + A^- \rightleftharpoons ZnA_2 \qquad (\beta_2^A = K_1^A \cdot K_2^A) \tag{2}$$

$$Zn^{2+} + \overline{NaR} \rightleftharpoons \overline{ZnR^+} + Na^+ \qquad \beta_1^{R(A)} = K_1^{R(A)} = \frac{[\overline{ZnR^+}][Na^+]}{[Zn^{2+}][\overline{NaR}]} \tag{3}$$

$$\overline{ZnR^+} + \overline{NaR} \rightleftharpoons \overline{ZnR_2} + Na^+ \qquad \beta_2^{R(A)} = K_1^{R(A)} \cdot K_2^{R(A)} = \frac{[\overline{ZnR_2}][Na^+]^2}{[Zn^{2+}][\overline{NaR}]^2} \tag{4}$$

$$ZnA^+ + \overline{NaR} \rightleftharpoons \overline{ZnAR_2} + Na^+ \qquad K_m^{AR} = \frac{[\overline{ZnAR}][Na^+]}{[ZnA^+][\overline{NaR}]} \tag{5}$$

where A^- denotes anion, R stands for the functional group in the resin and MR shows the chemical species attached to the functional group in the resin.

Total concentration of zinc in the resin phase, $[\overline{Zn}]_{R,total}$ is given by the following equation:

$$[\overline{Zn}]_{R,total} = [\overline{ZnR_2}] + [\overline{ZnRA}] \tag{6}$$

When the concentration of chloride ion was not so high as to form anion complexes, total concentration of zinc in the solution phase is expressed as:

$$[Zn]_{S,total} = [Zn^{2+}] + [ZnA^+] + [ZnA_2] \tag{7}$$

Then, the distribution coefficient, D, is defined:

$$D = \frac{[\overline{Zn}]_{R,total}}{[Zn]_{S,total}} = \frac{[\overline{ZnR_2}] + [\overline{ZnAR}]}{[Zn^{2+}] + [ZnA^+] + [ZnA_2]} \tag{8}$$

From Eqs. (1)~(6), the distribution coefficient is given by

$$D = \frac{1}{[Na^{+2}]} \cdot \frac{\beta_2^{R(A)}[\overline{NaR}]^2 + K_m^{AR}\beta_1^A[\overline{NaR}][A^-][Na^+]}{1 + \beta_1^A[A^-] + \beta_2^A[A^-]^2} \tag{9}$$

The concentration of functional group in the resin phase, $[\overline{NaR}]$, is constant before the addition of zinc to the resin and after equilibration of zinc with the resin, because zinc is negligible for $[\overline{NaR}]$. Similarly, the sodium ion concentration in the solution phase after equilibration with the resin is considered to be equal to the initial one, which is derived from the complete dissociation of NaA.

Hence Eq. (9) is reduced to

$$F = \frac{P(1) + P(2)[A^-]^2}{1 + P(3)[A^-] + P(4)[A^-]^2} \tag{10}$$

where $F = D \cdot [A^-]^2 = D \cdot [Na^+]^2$, $P(1) = \beta_2^{R(A)}[\overline{NaR}]^2$, $P(2) = K_m^{AR}\beta_1^A[\overline{NaR}]$, $P(3) = \beta_1^A$

and $P(4) = \beta_2^A$.

To solve Eq. (10), we have used the computer program of "Statistical Analysis with Least-Squares Fitting (SALS)" by T. Nakagawa and Y. Oyanagi[7].

The dependence of $D \cdot [Na^+]^2$ and $\log(D \cdot [Na^+]^2)$ on the chloride concentration in the methanol-water is shown in Figs. 6 and 7: As the concentration of chloride

Fig. 6. Distribution coefficient of Zn.
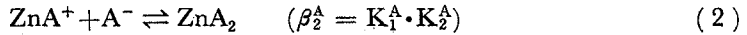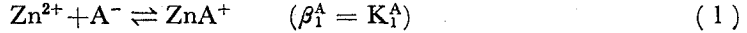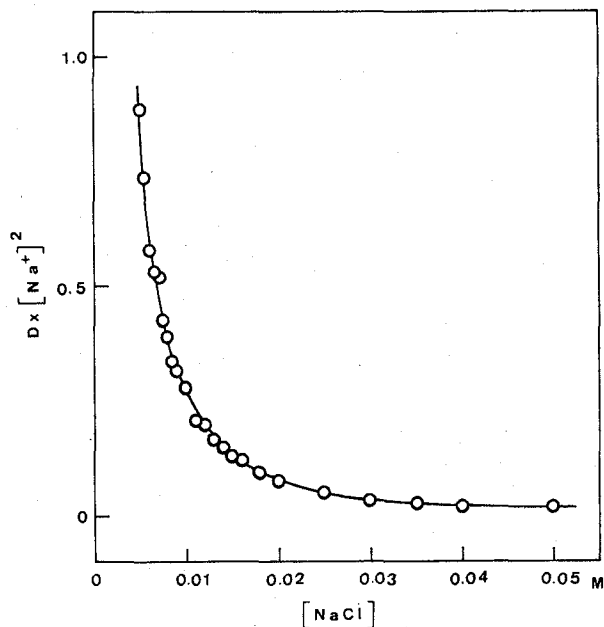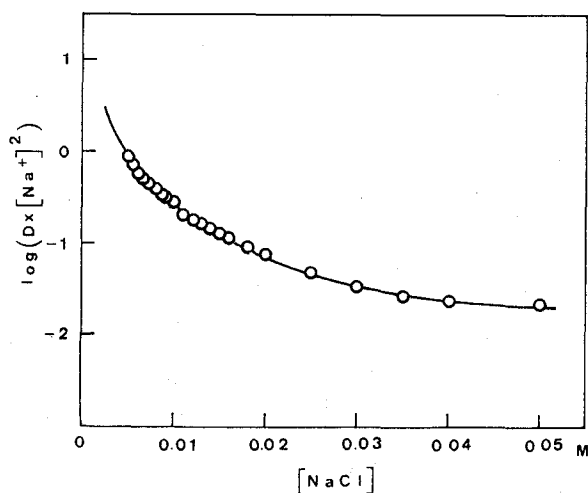Zn(ClO₄)₂ 1.5×10^{-6} M
HClO₄ 1.0×10^{-4} M

Fig. 7. Distribution coefficient of Zn.
Zn(ClO₄)₂ 1.5×10^{-6} M
HClO₄ 1.0×10^{-4} M

Table I. Equilibrium constants.

	Zn-Cl	Zn-Br	Zn-ClO$_4$	Zn-Cl-ClO$_4$
β_1^A	$1.0_2 \times 10^4$	$1.0_6 \times 10^3$	$2.2_1 \times 10$	5.0×10^3(Cl)
β_2^A	$3.4_3 \times 10^6$	$1.0_6 \times 10^4$	—	2.5×10^6(Cl)
$K_m^{AR}[\overline{NaR}]$	1.2_3	1.4_3	5.1_3	2.5×10 (Cl)
$\beta_2^{R(A)}[\overline{NaR}]^2$	$1.1_7 \times 10^2$	8.8_0	2.2_4	1.2×10^2

ion increases, the distribution of zinc decreases precipitously. The values obtained by using the above program are listed in Table I.

Zinc Bromide and Zinc Perchlorate Systems.

The distribution measurements of zinc with cation exchange resin were performed between 8×10^{-3} and 1.0×10^{-1} M in bromide concentration. The zinc distribution $(D \cdot [Na^+]^2)$ as a function of bromide ligand concentration is shown in Fig. 8: The distribution of zinc decreases suddenly as the concentration of bromide as well as that of chloride increases. The slope of the reducing curve is steeper in the case of chloride than in that of bromide. This indicates that zinc chloride complexes are more stable than the corresponding bromide complexes.

The dependence of the zinc distribution at 25°C on the concentration of perchlorate ion is shown in Fig. 9. From Figs. 8 and 9, the formation constants of zinc in bromide and perchlorate solutions can be calculated by the same procedure as in the case of zinc chloride, except that $\beta_1^{ClO_4}$ is neglected in the perchlorate system. The results are listed in Table I.
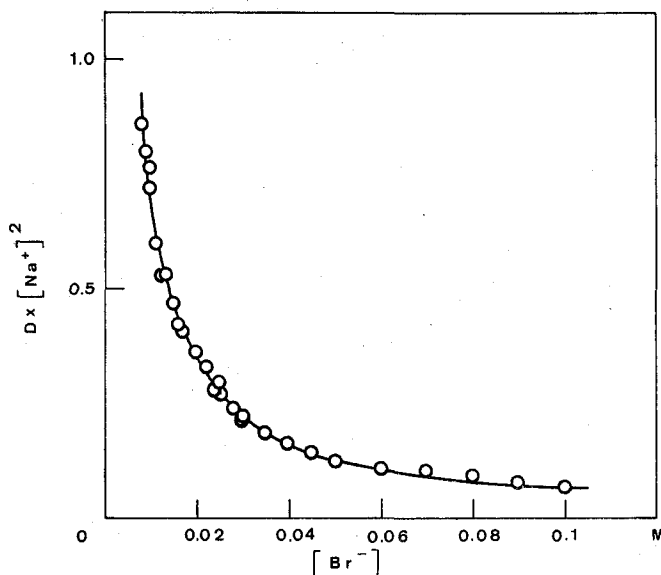

Fig. 8. Distribution coefficient of Zn.
Zn(ClO$_4$)$_2$ 1.5×10^{-6} M
HClO$_4$ 1.0×10^{-4} M
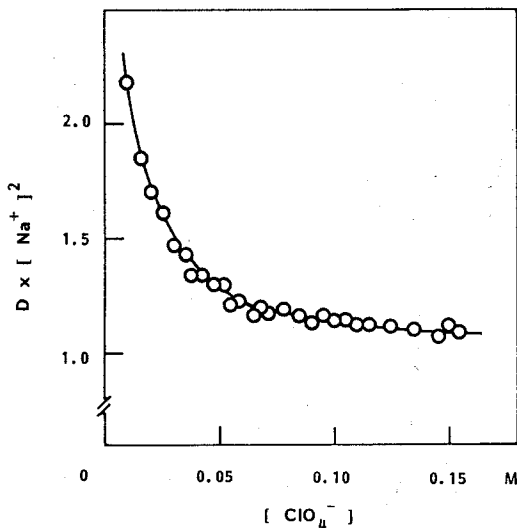
Fig. 9.   Distribution coefficient of Zn.
Zn(ClO₄)₂ 1.5×10⁻⁶ M
HClO₄   1.0×10⁻⁴ M

Zinc Chloride and Perchlorate System

In order to keep the ionic strength of the solution phase constant, it is necessary to examine the variation of the zinc distribution in the presence of both chloride and perchlorate ions. The following equilibrium should be considered in this system in addition to the equilibria already described:

$$Zn^{2+}+Cl^-+ClO_4^- \rightleftharpoons ZnCl \cdot ClO_4 \qquad K_m^{Cl \cdot ClO_4} = \frac{[ZnCl \cdot ClO_4]}{[Zn^{2+}][Cl^-][ClO_4]} \qquad (11)$$

Then the distribution coefficient is represented by the following equation:

$$D = \frac{\beta_2^R[\overline{NaR}]^2/[Na^+]^2+[\overline{NaR}](\beta_1^{Cl}K_m^{ClR}[Cl^-]+\beta_1^{ClO_4}K_m^{ClO_4R}[ClO_4^-])/[Na^+]}{1+\beta_1^{Cl}[Cl^-]+\beta_2^{Cl}[Cl^-]^2+\beta_1^{ClO_4}[ClO_4^-]+\beta_2^{ClO_4}[ClO_4^-]^2+K_m[Cl^-][ClO_4^-]} \qquad (12)$$

When $[ClO_4^-]=0.05-[Cl^-]$, this equation can be expressed as:

$$D = \frac{P(1)+P(2)[Cl^-]}{P(3)+P(4)[Cl^-]+P(5)[Cl^-]^2} \qquad (13)$$

where

$P(1) = [\overline{NaR}](\beta_2^R[\overline{NaR}]/[Na^+]+0.05\beta_1^{ClO_4}K_m^{ClO_4R})/[Na^+]$,

$P(2) = [\overline{NaR}](\beta_1^{Cl}K_m^{ClR}-\beta_1^{ClO_4}K_m^{ClO_4R})/[Na^+]$,

$P(3) = 1+0.05\beta_1^{ClO_4}+0.05^2\beta_2^{ClO_4}$,

$P(4) = \beta_1^{Cl}+0.05\beta_1^{ClO_4}-\beta_2^{ClO_4}-0.1\beta_2^{ClO_4}$,

$P(5) = \beta_2^{Cl}+\beta_2^{ClO_4}-K_m^{Cl \cdot ClO_4}$ and
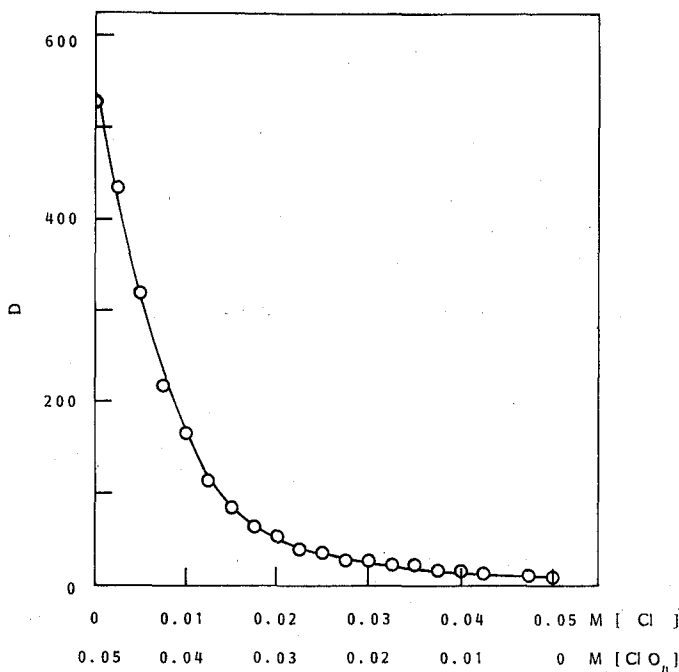
$[Na^+] = 0.05$

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Fig. 10. Distribution coefficient of Zn.
$Zn(ClO_4)_2$ 1.5×10^{-6} M
$HClO_4$ 1.0×10^{-4} M

The plot of D $vs.$ $[ClO_4^-]+[Cl^-]=0.05$ M is shown in Fig. 10. As this equation contains five parameters and eight unknown constants, it is difficult to obtain the constant values. And though the values ($\beta_1^{ClO_4}$, $K_m^{Cl \cdot ClO_4}[\overline{NaR}]$) calculated in the zinc perchlorate system were used to calculate the other unknown constants in Eq. 13, the exact results were not obtained. Therefore further attempts have not been made to calculate these constants.

REFERENCES

(1) M. Matsui, T. Aoki, H. Enomoto. and T. Shigematsu, *Anal. Lett.*, **8**, 247 (1975).
(2) M. Matsui, T. Aoki, O. Inoue, and T. Shigematsu, This Bulletin **52**, 652 (1974).
(3) M. Matsui, H. Doe, T. Hirade, and T. Shigematsu, *Anal. Lett.*, **12** (A13), 1385 (1979).
(4) H. Doe, M. Matsui, and T. Shigematsu, This Bulletin, **57**, 343 (1979).
(5) H. Doe, M. Matsui, and T. Shigematsu, This Bulletin, **58**, 133 (1980).
(6) Y. Marcus and E. Eyal, *J. Inorg. Nucl. Chem.*, **32**, 2045, (1970).
(7) T. Nakagawa and Y. Oyanagi, "Statistical Analysis with Least-Squares Fitting", Tokyo Daigaku Shuppankai (Tokyo Univ. Press), Tokyo (1982).