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# Ion Exchange from a Nonaqueous Solution. Zinc (II) Bromide and Iodide in Ethylene Glycol

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The distribution behavior of the zinc ion in sodium bromide and iodide solutions between the cation-exchange resin for forced-flow liquid chromatography and the absolute or aqueous ethylene-glycol phase was investigated radiometrically. From the experimental data, consecutive complex formation constants for zinc bromide and iodide in the glycol have been calculated by the nonlinear least-squares method. The results are as follows: in absolute glycol $\beta_1^{Br}$=2.60 and $\beta_2^{Br}$=3.91 for zinc bromide, $\beta_1^{I}$=2.36 and $\beta_2^{I}$=3.04 for zinc iodide; in 5 wt% aqueous glycol $\beta_1^{Br}$=2.30, $\beta_2^{Br}$=3.32, and in 10 wt% aqueous glycol, $\beta_1^{Br}$=1.87, $\beta_2^{Br}$=2.78, respectively.

There have been many investigations of the complex formation of metal ions in a pure or aqueous organic solvent, especially using such electrochemical methods as the emf, electric conductivity, and ion-selective electrode techniques. However only a little work seems to have been done on complex formation in a nonaqueous solution using a distribution method between the two phases, for example, the solvent-extraction and ion-exchange techniques. Previously, the solvent-extraction method between the polar organic and nonpolar organic phases has been studied in order to gain knowledge that the metal-ion equilibrium in a nonaqueous system.[1—6] However there are not many polar solvents immiscible with the nonpolar solvents. In contrast to the solvent extraction, the ion-exchange method seems to be hopeful because some of the exchange resins for the forced-flow liquid chromatography can resist many of the organic solvents and so the distribution equilibrium can be easily reached between the resin and the metal ions.

In previous papers,[7,8] the present author and his co-workers have reported data on the formation constants of zinc chloride in pure and aqueous ethylene glycol, and in aqueous methanol, obtained using the ion-exchange method. The aim of the present work is to extend our research to bromide and iodide complexes of zinc in pure and aqueous ethylene glycol using the ion-exchange method.

## Experimental

*Materials and Apparatus.* Zinc-65 was supplied as the chloride in hydrochloric acid by New England Nuclear, Boston, Mass., U. S. A. The radioactive tracer was converted into perchlorate by the addition of perchloric acid, followed by repeated evaporation. It was dissolved with ethylene glycol. Reagent-grade ethylene glycol was dried on zeolite and distilled under reduced pressure.

The cation-exchange resin, Hitachi custom ion-exchange resin 2611, for the liquid chromatograph was washed with 1 mol dm$^{-3}$ hydrochloric acid and converted into the Na$^+$ form by the use of a 0.2 mol dm$^{-3}$ sodium-chloride solution. After having been washed with pure water and dried in a vacuum, the resin was stored over phosphorus pentaoxide in a desiccator. The stock zinc solution was prepared by dissolving dry zinc oxide with perchloric acid, evaporating to near dryness, and diluting it with ethylene glycol.

The procedure of ion-exchange was essentially the same as that described in a previous paper.[8] Sixteen milliliters of an ethylene-glycol solution of sodium halide containing sodium perchlorate, zinc perchlorate (1×10$^{-6}$ mol dm$^{-3}$) with radioactivities, and perchloric acid (1×10$^{-5}$ mol dm$^{-3}$) were stirred together with portions (10—50 mg) of the dry resin, in a 30-cm$^3$ centrifugal tube equipped with a grass stopper by using a magnetic stirrer for 12 h in a thermostat at 25 °C. After the equilibrium had been attained, the solution and the resin phase were separated by centrifugation. Two milliliters of the solution phase were pipetted out, and the $\gamma$-activities were counted with a well-type scintillation counter, Metro Electronics Model PBW-6.

## Results and Discussion

The distribution of zinc in present system was practically independent of the range of zinc perchlorate (5×10$^{-7}$—1×10$^{-4}$ mol dm$^{-3}$). Therefore in subsequent studies, 1×10$^{-6}$ mol dm$^{-3}$ of zinc perchlorate in an ethylene-glycol solution was used.

Even stirring for 30 min was found to be enough for the attainment of the distribution equilibrium. In the present studies, however stirring for 12 h was adopted, because ethylene glycol has a somewhat high viscosity and the resin was a little difficult to disperse in the glycolic solution. The influence of the cation-exchange resin on the distribution of zinc was examined with regard to resin amounts of 1.25, 2.5, and 5.0 g dm$^{-3}$, while keeping the other variables constant. As is to be expected from Eq. 10, a linear relationship between log $D^*$ and the resin amount was observed, with a slope of about 1, in various bromide concentrations (Fig. 1).

The equilibria in the ethylene glycol phase are expressed as follows:

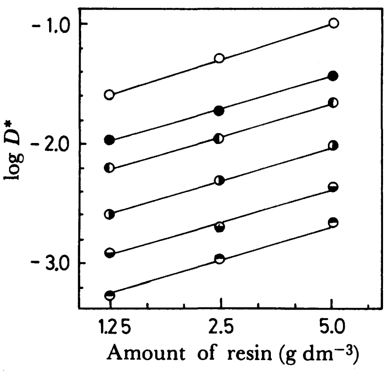

Fig. 1. Influence of resin amount in sodium bromide system (pure ethylene glycol).
Concentration of sodium bromide; ○: 0.03 mol dm$^{-3}$, ●: 0.05 mol dm$^{-3}$, ◐: 0.07 mol dm$^{-3}$, ◑: 0.10 mol dm$^{-3}$, ◒: 0.15 mol dm$^{-3}$, ⊖: 0.20 mol dm$^{-3}$,

$$Zn^{2+} + 2X^- = ZnX_2 \qquad (\beta_n^X), \qquad (1)$$

$$Zn^{2+} + 2Y^- = ZnY_2 \qquad (\beta_n^Y), \qquad (2)$$

$$ZnX^+ + Y^- = ZnXY \qquad (K_m^Y), \qquad (3)$$

$$ZnY^+ + X^- = ZnXY \qquad (K_m^X), \qquad (4)$$

$$Zn^{2+} + Na_2R = ZnR + 2Na^+ \qquad (\beta_n^R), \qquad (5)$$

$$ZnX^+ + Na_2R = ZnXNaR + Na^+ \ (K_m^{RX}), \qquad (6)$$

$$ZnY^+ + Na_2R = ZnYNaR + Na^+ \ (K_m^{RY}). \qquad (7)$$

Here, $X^-$ denotes the halide ion, $Y^-$ shows $ClO_4^-$, and R stands for the two functional groups in the resin.

The total concentration of zinc in the resin phase, $(C_{Zn})_R$, is defined as follows:

$$(C_{Zn})_R = m_{ZnR} + m_{ZnXNaR} + m_{ZnYNaR}. \qquad (8)$$

Here $m$ stands for the weight molarity.

The total zinc concentration in the glycol phase at equilibrium, $(C_{Zn})_E$, is given by:

$$\begin{aligned}(C_{Zn})_E &= C_{Zn}+C_{ZnX}+C_{ZnX_2}+C_{ZnY}+C_{ZnY_2}+C_{ZnXY} \\ &= (m_{Zn}+m_{ZnX}+m_{ZnX_2}+m_{ZnY}+m_{ZnY_2}+m_{ZnXY})/\rho. \qquad (9)\end{aligned}$$

Here $\rho$ is the density of the glycolic solution.

The distribution coefficient, $D$, is defined as:

$$D = (C_{Zn})_R/(C_{Zn})_E. \qquad (10)$$

Equations 8—10 are rewritten using Eqs. 1—7 as follows:

$$\begin{aligned}(C_{Zn})_R = \Bigg(&\frac{\gamma_{Zn}\cdot\gamma_{Na_2R}\cdot m_{Zn}}{\gamma_{ZnR}\cdot\gamma_{Na}^2\cdot m_{Na}^2}\cdot\beta_2^R+\frac{\gamma_{Zn}\cdot\gamma_X\cdot\gamma_{Na_2R}\cdot m_{7n}\cdot m_X}{\gamma_{Na}\cdot\gamma_{ZnXNaR}\cdot m_{Na}}\cdot K_m^{RX}\cdot\beta_1^X \\ &+\frac{\gamma_{Zn}\cdot\gamma_Y\cdot\gamma_{Na_2R}\cdot m_{Zn}\cdot m_Y}{\gamma_{Na}\cdot\gamma_{ZnYNaR}\cdot m_{Na}}\cdot K_m^{RY}\cdot\beta_1^Y\Bigg)\cdot m_{Na_2R}, \qquad (8')\end{aligned}$$

$$\begin{aligned}(C_{Zn})_R = \Bigg(&\gamma_{Zn}\cdot m_{Zn}+\frac{\gamma_{Zn}\cdot\gamma_X\cdot m_{Zn}\cdot m_X}{\gamma_{ZnX}}\cdot\beta_1^X+\frac{\gamma_{Zn}\cdot\gamma_X\cdot m_{Zn}^2\cdot m_X^2}{\gamma_{ZnX_2}}\cdot\beta_2^X \\ &+\frac{\gamma_{Zn}\cdot\gamma_Y\cdot m_{Zn}\cdot m_Y}{\gamma_{ZnY}}\cdot\beta_1^Y+\frac{\gamma_{Zn}\cdot\gamma_Y^2\cdot m_{Zn}\cdot m_Y^2}{\gamma_{ZnY_2}}\cdot\beta_2^Y \\ &+\frac{\gamma_{Zn}\cdot\gamma_X\cdot\gamma_Y\cdot m_{Zn}\cdot m_X\cdot m_Y}{\gamma_{ZnXY}}\cdot\beta_1^X\cdot K_m^Y\Bigg)\Big/\rho, \qquad (9')\end{aligned}$$

$$\begin{aligned}D = m_{Na_2R}\cdot\rho\cdot\Bigg(&\frac{\beta_2^R}{\gamma_{Na}^2\cdot m_{Na}^2}+\frac{\gamma_X\cdot m_X}{\gamma_{Na}\cdot m_{Na}}\cdot K_m^{RX}\cdot\beta_1^X \\ &+\frac{\gamma_Y\cdot m_Y}{\gamma_{Na}\cdot m_{Na}}\cdot K_m^{RY}\cdot\beta_1^Y\Bigg)\Big/(1+\sum\gamma_X^n\cdot m_X^n\cdot\beta_n^X/\gamma_{ZnX_n} \\ &+\sum\gamma_Y^n\cdot m_Y^n\cdot\beta_n^Y/\gamma_{ZnY_n}+\gamma_X\cdot\gamma_Y\cdot m_X\cdot m_Y\cdot\beta_1^X\cdot K_m^Y/\gamma_{ZnXY}). \qquad (10')\end{aligned}$$

Here, $\gamma$ stands for the activity coefficient of each ion, $\gamma_{Na_2R}$, $\gamma_{ZnR}$, $\gamma_{ZnXR}$, and $\gamma_{ZnYR}$ can be regarded as 1, and $\gamma_{ZnX}=\gamma_{ZnY}$, $\gamma_{ZnX_2}=\gamma_{ZnY_2}=\gamma_{ZnXY}$. $\gamma_X$, $\gamma_Y$, $\gamma_{Zn}$, and $\gamma_{Na}$ are calculated, on the basis of Debye-Hückel's theory, as;

$$\ln\gamma_X = \ln\gamma_\pm^{1/2} = -\left(\frac{A|Z^+Z^-|I^{1/2}}{1+BdI^{1/2}}\right)^{1/2}, \qquad (11)$$

$$A = 8.1622\times\frac{\rho}{\varepsilon^{3/2}}\times 10^2 \quad B=2.9127\times\left(\frac{\rho}{\varepsilon}\right) \text{ at } 25\ ^\circ\text{C}. \qquad (12)$$

Here, $d$ denotes the parameter of the ionic radius (Å unit), $I$ represents the ionic strength; $m_{Na_2R}$ is expressed as g resin (Na-form)/dm³ ethylene glycol, and $\varepsilon$ is the dielectric constant of ethylene glycol. The dielectric constant of 5% aqueous ethylene glycol was obtained by the interpolation of the constants of 100, 90, and 80% ethylene glycol.[9] In the $Zn^{2+}$–X–Y system, the sum of $m_X$ and $m_Y$ was kept constant, and sodium halide and sodium perchlorate are assumed to dissociate perfectly into ions in the glycolic solution. Therefore ,the $m_{Na}=m_X+m_Y$ holds good. Hence, Eq. 10′ can be transformed as a function of the halide-ion weigth molarity, $m_X$. As it is assumed that $\beta_2^R$ is much greater than $\beta_1^R$, $\beta_1^R$ can be disregarded.

In the zinc halide system, Eq. 10′ can be converted into the following fractional functions:

$$D^* = \frac{P_{(1)}+P_{(2)}L^2}{1+P_{(3)}L+P_{(4)}L^2}. \qquad (13)$$

Here, $L=\gamma_X\cdot m_X$, $D^*=D\cdot\gamma_{Na}^2\cdot m_{Na}^2/\rho$, $P_{(1)}=\beta_2^R\cdot m_{Na_2R}$,
$P_{(2)}=\beta_1^X\cdot K_m^{RX}\cdot m_{Na_2R}$, $P_{(3)}=\beta_1^X/\gamma_{ZnX}$ and $P_{(4)}=\beta_2^R$.

In the zinc halide perchlorate system, Eq. 10′ can be reduced to:

$$D^*=\frac{(P_{(1)}+P_{(2)}m_X+P_{(3)}m_Y)}{1+P_{(4)}m_X+P_{(5)}m_X^2+P_{(6)}m_Y+P_{(7)}m_2^Y+P_{(8)}m_X\cdot m_Y}. \qquad (14)$$

Here $D^*=D\cdot\gamma_{Na}^2\cdot m_{Na}^2/\rho$, $P_{(1)}=m_{Na_2R}\cdot\beta_2^R$,
$P_{(2)}=m_{Na_2R}\cdot\beta_1^X\cdot K_m^{RY}\cdot\gamma_X\cdot\gamma_{Na}\cdot m_X\cdot m_{Na}$,
$P_{(3)}=m_{Na_2R}\cdot\beta_1^Y\cdot K_m^{RY}\cdot\gamma_{Na}\cdot\gamma_Y\cdot m_{Na}\cdot m_Y$,
$P_{(4)}=\gamma_X\cdot\beta_1^X/\gamma_{ZnX}$, $P_{(5)}=\gamma_X^2\cdot\beta_2^X$, $P_{(6)}=\gamma_Y\cdot\beta_1^Y/\gamma_{ZnY}$,
$P_{(7)}=\gamma_Y^2\cdot\beta_2^Y$, and $P_{(8)}=\gamma_X\cdot\gamma_Y\cdot m_X\cdot m_Y\cdot\beta_1^X\cdot K_m^Y$.

Each activity coefficient, $\gamma$, was calculated from Eqs. 11 and 12 as a function of the ionic strength. These coefficients have a constant ionic strength.

To obtain the parameters, $P_{(i)}$, of Eqs. 13 and 14, we used the computer program of the nonlinear least-squares method, a modified Gauss-Newton method; the valuses obtained by this procedure were then tested by the aid of the curve-fitting method using computer graphics.

The dependence of log $D^*$ on the bromide activity calculated using Eq. 11 in pure and aqueous ethylene glycol is shown in Figs. 2—4. The figures show that the distribution of zinc decreases precipitiously in the lower activity range of bromide and gradually in the higher range. The stability constants obtained by using the program described above are listed in Table 1.

Figure 5 indicates the dependence of the zinc distribution on the iodide activity in pure ethylene glycol in 1.25, 2.5, and 3.75 g resin per 1 dm³ glycol. Though the zinc distribution decreases abruptly with the increase in the iodide activity, much as in the case of the bromide system, the magnitude of the decrease in the iodide system is somewhat less than that in the bromide one. This means that zinc-iodide complexes are less stable than the corresponding bromide complexes. This results are listed in Table 1. The blending of water for pure ethylene glycol leads to considerably large errors in the calculations of the stability constants of zinc iodide because of a lowering of the stability.

The variation in the zinc distribution in the presence of both bromide and perchlorate ions was examined in order to make the ionic strength in the glycol solution constant. The distribution coefficient of zinc is plotted

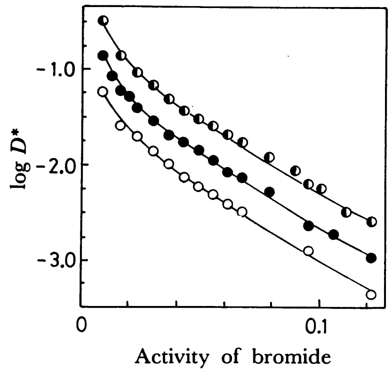

Fig. 2. Distribution coefficients of zinc bromide system in the pure glycolic solution.
amount of resin; ○: 1.25 g dm$^{-3}$, ●: 2.50 g dm$^{-3}$, ◐: 5.00 g dm$^{-3}$.

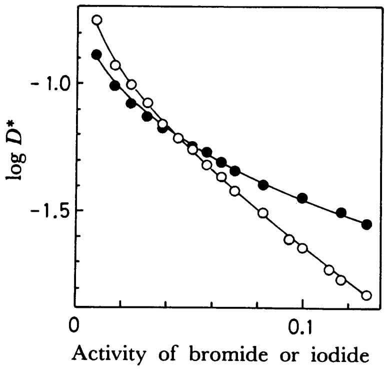

Fig. 3. Distribution of zinc bromide and zinc iodide system in the 5% aqueous glycolic solution.
○: NaBr, resin 1.36 g dm$^{-3}$, ●: NaI, resin 0.91 g dm$^{-3}$.

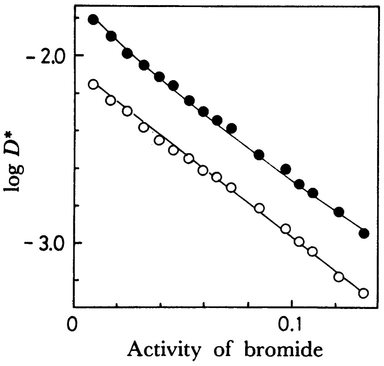

Fig. 4. Distribution coefficients of zinc bromide in the 10% aqueous ethylene glycol.
amount of resin; ○: 1.0 g dm$^{-3}$, ●: 2.0 g dm$^{-3}$.

TABLE 1. STABILITY CONSTANTS OF ZINC BROMIDE AND ZINC IODIDE

| log $\beta$ | $\beta_1^X$ | $\beta_2^X$ | $K_m^X$ |
|---|---|---|---|
| X=Br, pure E.G. | 2.60±0.06 | 3.91±0.06 | — |
| X=Br, 5% aqueous E.G. | 2.30±0.06 | 3.32±0.06 | — |
| X=Br, 10% aqueous E.G. | 1.87±0.07 | 2.78±0.07 | — |
| X=I, pure E.G. | 2.36±0.06 | 3.04±0.06 | — |
| Ionic strength 0.1, 0.2 | — | — | 0.3±0.1 |

E.G.=Ethylene glycol.

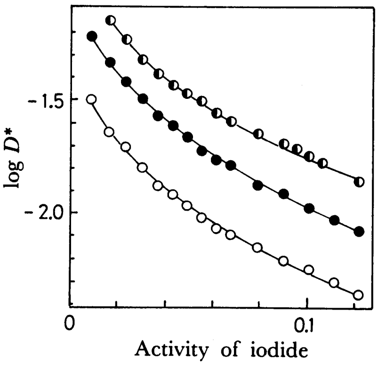

Fig. 5. Distribution coefficients variation *vs.* activity of iodide in the pure glycolic solution.
amount of resin; ○: 1.25 g dm$^{-3}$, ●: 2.50 g dm$^{-3}$, ◐: 3.75 g dm$^{-3}$.

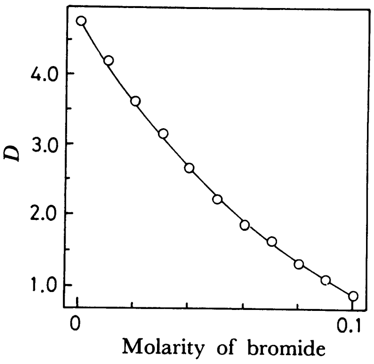

Fig. 6. Distribution coefficients variation *vs.* molarity of sodium bromide in the pure ethylene glycol at constant ionic strength (0.1).
Amount of resin 2.50 g dm$^{-3}$, (NaBr)+(NaClO$_4$)=0.1.

in Fig. 6 as a function of the concentration of bromide and perchlorate ions. As there exist 8 parameters in Eq. 14 in the present system, it is very difficult to obtain exact values. Only the value of $K_m$ can be calculated; it is listed in Table 1. Similally, in the zinc iodide-perchlorate system, exact results were not obtained.

The decreasing order of stability of zinc halide complexes in ethylene glycol is as follows; Cl>Br>I≃ ClO$_4$. Also the stability constants in ethylene glycol are somewhat smaller than those in methanol.

## References

1) M. Matsui, T. Aoki, O. Inoue, and T. Shigematsu, *Bull. Inst. Chem. Res. Kyoto Univ.*, **52**, 652 (1974).

2) M. Matsui, T. Aoki, H. Enomoto, and T. Shigematsu, *Anal. Lett.*, **8** (4), 247 (1975).

3) M. Matsui, H. Doe, T. Hirade, and T. Shigematsu, *Anal. Lett.*, **12** (A13), 1385 (1979).

4) H. Doe, M. Matsui, and T. Shigematsu, *Bull. Inst. Chem. Res. Kyoto Univ.*, **57**, 343 (1979).

5) H. Doe, M. Matsui, and T. Shigematsu, *Bull. Inst. Chem. Res. Kyoto Univ.*, **58**, 133 (1980).

6) T. Aoki, *Bull. Inst. Chem. Res. Kyoto Univ.*, **59**, 191 (1981).

7) S. Iwasaki, M. Sugiyama, M. Matsui, and T. Kumagai, *Bull. Inst. Chem. Res. Kyoto Univ.*, **61**, 340 (1983).

8) T. Kumagai, *Bull. Chem. Soc. Jpn.*, **57**, 1348 (1984).

9) T. F. Humbel and J. P. Scherrer, *Helv. Phys. Acta*, **26**, 17 (1953).