Nonaqueous Extraction of Zinc from Diethylene Glycol Solution of Chloride by TOPO in Decaline

Yasumichi NAKAI*, Toru AOKI**, Hiroshi MUKAI*,
Sorin KIHARA*, and Masakazu MATSUI*

A Study has been made of the nonaqueous extraction of zinc from hydrogen chloride solution of diethylene glycol with TOPO in decaline. Zinc ion was extracted at three different hydrogen chloride regions. The first extraction occurred in the neutral region of pC_H. The second appeared between 4×10^{-5} and 4×10^{-2} M HCl, and the extracted species was found to be $ZnCl_2 \cdot 2TOPO$. The third showed a maximum distribution at 0.4 M HCl, and the species was mainly attributable to the extraction of $HZnCl_3 \cdot 4TOPO$.

KEY WORDS: Nonaqueous extraction/ Zinc chloride/ Diethylene glycol/ TOPO/

INTRODUCTION

In our previous papers the liquid-liquid extractions of metals from the polar organic phase such as glycols and aqueous methanol into an immiscible nonpolar organic phase were investigated[1~5]. In the zinc halide extraction the extraction curves, i.e., the distribution ratios of zinc as a function of halide concentration in glycols have a maximum value at 0.04 M of chloride and 0.1 M of bromide in ethylene glycol, respectively, and at 0.07 M of chloride in propylene glycol; the extracted species was $ZnX_2(TOPO)_2$ (X=Cl, Br) in each system. In the present work we extended our research to the extraction of zinc in diethylene glycol which has three solvating oxygen atoms in a molecule, and has a similar dielectric constant to propylene glycol and a lower one than ethylene glycol.

EXPERIMENTAL

Apparatus and Materials

Reagent grade diethylene glycol (DEG) was dried for several days with Molecular Sieves 3 A which was treated for 3 hrs at 270°C in vacuo and was distilled under reduced pressure. The glycol solution of hydrochloric acid was prepared by passing dry hydrogen chloride gas into the glycol and then standardized by titrating it with standard aqueous alkali after mixing with pure water.

The radioisotope, zinc-65 was supplied as the chloride in aqueous solution by New England Nuclear, Boston, Mass., U.S.A. The tracer was converted into per-

* 仲井 康通, 向井　浩, 木原 壯林, 松井 正和 : Laboratory of Radiochemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan
** 青木　達 : Radioisotope Center, Kyoto University, Kyoto 606, Japan

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chlorate by being repeated evaporation with perchloric acid, and diluted with the purified diethylene glycol. The stock zinc solution was prepared by dissolving dry zinc oxide with perchloric acid, evaporating to near dryness and diluting it with diethylene glycol. Tri-*n*-octylphosphine oxide (TOPO) was purchased from the Dojindo Co., Ltd., Research Laboratories. All other reagents were GR grade materials and were used without further purification.

Radioactivity countings were carried out with a Metro NaI(Tl) well-type scintillation counter, Model PbW-6 connected with a Metro single channel pulse height analyzer, Model SS-1061H.

Procedure

Ten milliliters of an diethylene glycol solution containing a radioactive tracer, a carrier, and various amounts of hydrogen chloride were placed in a 30 ml glass-stoppered centrifuge tube. Ten milliliters of decaline containing TOPO were added. Two phases in the tube were shaken for 30 min at 25° and centrifuged until they got clear. Two milliliters of each phase were pipetted out into test tubes, and γ-activities were measured with a NaI(Tl) scintillation counter.

<div align="center">RESULTS AND DISCUSSION</div>

The results for the extractions of zinc chloride with decaline solution of 0.1 M TOPO from hydrogen chloride solution of diethylene glycol at 25°C are illustrated in Fig. 1 and compared with those from lithium chloride solution at different concentrations. As shown in the figure, zinc was extracted at three different hydrogen chloride concentration regions. The distribution coefficients of zinc in the presence of hydrogen chloride firstly rise steeply below about 3×10^{-5} M (or below 4.5 of
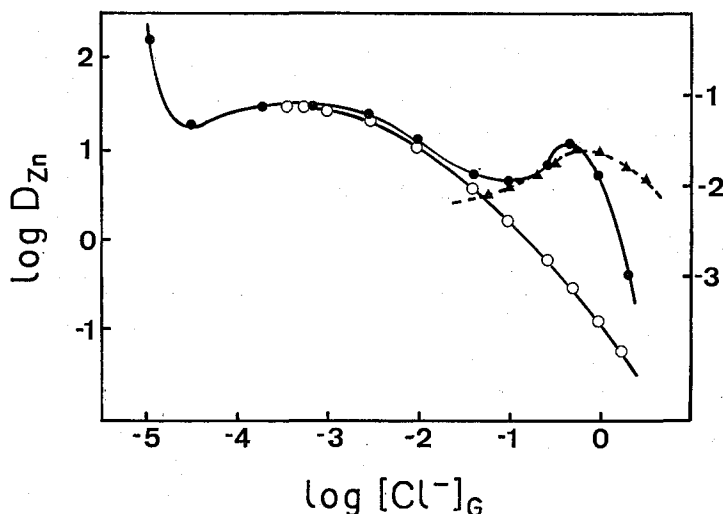

Fig. 1. Distribution of zinc as a function of chloride concentration.
Zn^{2+}; 10^{-6}M, TOPO; 0.1M in decaline, temp.; 25°C
●; HCl in diethylene glycol, ○; LiCl ([H$^+$]=4×10^{-4} M),
▲; distribution of HCl.

pC_H), secondly pass through gently a maximum at around 2.5×10^{-4} M as the hydrogen chloride increases, thirdly reach another maximum at about 0.5 M of HCl, and then decrease rapidly.

The first extraction in the neutral region of pC_H can be also observed in the extraction systems from ethylene glycol and propylene glycol solutions of zinc[4] and from ethylene glycol solution of manganese[6]. In the present extraction the species of $Zn(deprotonated\ diethylene\ glycol)_2 \cdot nTOPO$ is presumed to be extracted into decaline, where diethylene glycol probably behaves as a tridentate or bidentate ligand and the extracted species may be solvated moderately by TOPO in the decaline phase.

The second extraction curve which is found between 4×10^{-5} and 4×10^{-2} M hydrogen chloride concentrations is probably attributable to the extraction of $ZnCl_2 \cdot nTOPO$. Almost the same curve is also observed in the extraction system of zinc from lithium chloride solution having a constant concentration of hydrogen chloride, 4×10^{-4} M (Fig. 1).

The third curve having a maximum at 0.4 M of hydrogen chloride is observed for the first time in the analogous nonaqueous extraction equilibria, and the curve vanishes in the extraction of zinc from the decaline solution of lithium chloride. Then the extraction species in this region of HCl are expected to be $H_{n-2}ZnCl_n \cdot mTOPO$.
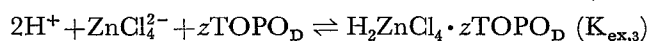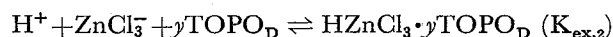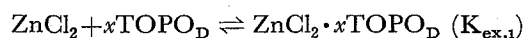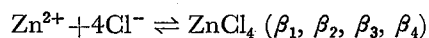
Figure 2 shows the extraction curve of zinc with 0.1 M TOPO in decaline from diethylene glycol solutions having different concentrations of chloride ion in the presence of a constant hydrogen ion concentration (upper curve 3×10^{-4} M, lower curve 0.18 M) keeping the ion concentration a constant, 0.18 M, using sodium chloride and sodium perchlorate.

The distribution ratio of zinc may be written as follows, when the effect of perchlorate ion is ignored,

$$D_{Zn} = \frac{[ZnCl_2 \cdot xTOPO]_D + [HZnCl_3 \cdot yTOPO]_D + [H_2ZnCl_4 \cdot zTOPO]_D}{[Zn^{2+}]_G + [ZnCl^+]_G + [ZnCl_2]_G + [ZnCl_3^-]_G + [ZnCl_4^{2-}]_G} \quad (1)$$

where the subscripts D and G refer to the decaline and diethylene glycol phases, respectively.

The equilibria in the diethylene glycol phase and the extraction equilibria are

$$Zn^{2+} + 4Cl^- \rightleftharpoons ZnCl_4 \ (\beta_1,\ \beta_2,\ \beta_3,\ \beta_4)$$
$$ZnCl_2 + xTOPO_D \rightleftharpoons ZnCl_2 \cdot xTOPO_D \ (K_{ex,1})$$
$$H^+ + ZnCl_3^- + yTOPO_D \rightleftharpoons HZnCl_3 \cdot yTOPO_D \ (K_{ex,2})$$
$$2H^+ + ZnCl_4^{2-} + zTOPO_D \rightleftharpoons H_2ZnCl_4 \cdot zTOPO_D \ (K_{ex,3})$$

Substituting the above expressions in Eq. 1 yields the following equation.

$$D_{Zn} =$$
$$\frac{K_1\beta_2[Cl^-]_G^2[TOPO]_D^x + K_2\beta_3[H^+]_G[Cl^-]_G^3[TOPO]_D^y + K_3\beta_4[H^+]_G^2[Cl^-]_G^4[TOPO]_D^z}{1 + \beta_1[Cl^-]_G + \beta_2[Cl^-]_G^2 + \beta_3[Cl^-]_G^3 + \beta_4[Cl^-]_G^4}$$
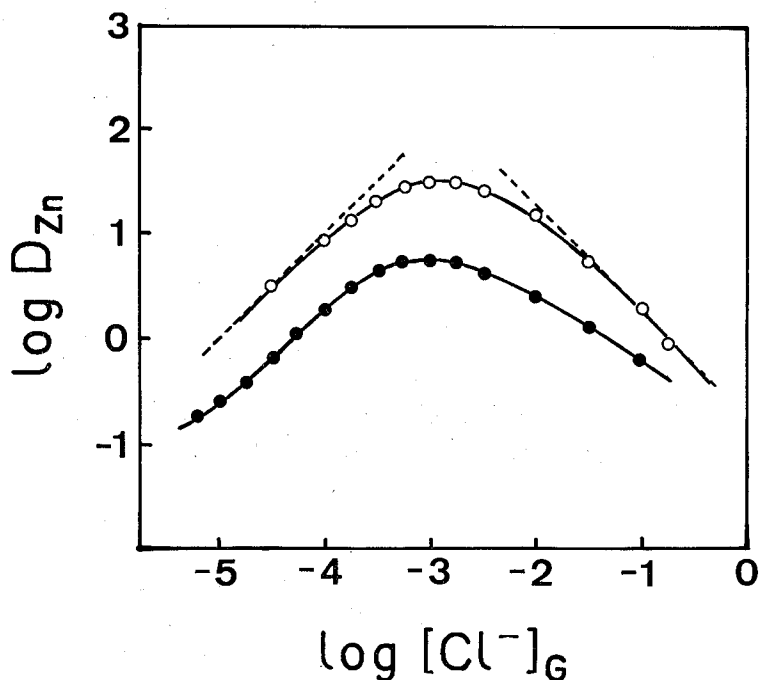$$(2)$$

Fig. 2. Log D_{Zn} vs. log $[Cl^-]_G$ plots at a constant hydrogen ion concentration. $[H^+]$; $\bigcirc$ 3.0×10^{-4} M, $\bullet$ 0.18M, ionic strength; 0.18, H_2O; 0.7 V% in diethylene glycol. Others are the same to those in the Fig. 1.

When $[H^+] = 4 \times 10^{-4}$ M, the extraction of the acido-complexes such as $HZnCl_3 \cdot$ yTOPO and $H_2ZnCl_4 \cdot z$TOPO into decaline is negligible, then Eq. 2 can be expressed as follows.

$$D_{Zn} = \frac{K_1 \beta_2 [Cl^-]_G^2 [TOPO]_D^x}{1 + \beta_1 [Cl^-]_G + \beta_2 [Cl^-]_G^2 + \beta_3 [Cl^-]_G^3 + \beta_4 [Cl^{-4}]_G}$$

$$\text{or} \quad \frac{K_1 \beta_2 [TOPO]_D^x}{[Cl^-]_G^{-2} + \beta_1 [Cl^-]_G^{-1} + \beta_2 + \beta_3 [Cl^-]_G + \beta_4 [Cl^-]_G^2} \quad (3)$$

Equation 3 indicates that in a log-log plot of D_{Zn} against chloride ion concentration of diethylene glycol phase, $[Cl^-]_G$, the slope is 2 at low $[Cl^-]_G$ and -2 at high $[Cl^-]_G$. However the upper curve in Fig. 2 has a slope of $+1$ at around 3×10^{-5} M, 0 at 1.3×10^{-3} M and -1 at around 6.3×10^{-2} M of $[Cl^-]_G$, respectively. As the formation between Zn^{2+} and Cl^- in diethylene glycol is considerably stable, $ZnCl^+$ may predominantly be formed around $+1$ of the slope, and $ZnCl_4^{2-}$ may partly exist at more than 0.1 M of $[Cl^-]_G$.

The change in the distribution ratio of zinc as a function of the concentration of TOPO at low concentration of $[H^+]$ is presented by the upper curve in Fig. 3. The slope of the plot log D_{Zn} against log $[TOPO]_D$ at the constant chloride concentration shows the number of TOPO associated with the zinc species extracted. The slope is nearly 2, indicating that the species extracted is $ZnCl_2 \cdot 2TOPO$ in the lower range of $[Cl^-]_G$.
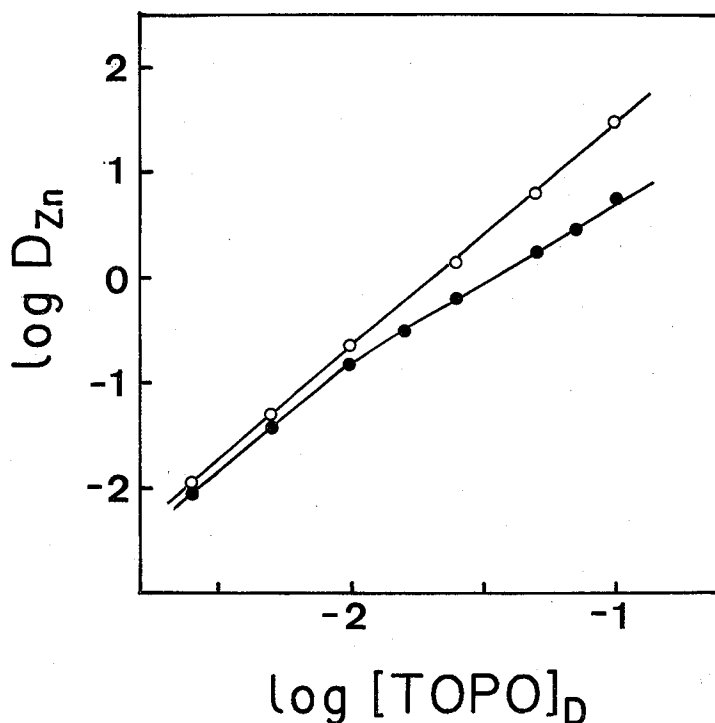
Fig. 3. Distribution of zinc as a function of TOPO concentration.
[H$^+$]; ○ 3.0×10^{-4} M, ● 0.18M,
initial chloride concentration; 9.7×10^{-4} M.

The lower curves in Figs. 2 and 3 present the log-log plots of D_{Zn} against [Cl$^-$]$_G$ and [TOPO]$_D$, respectively, when [H$^+$]$_G$=0.18 M. The decrease of D_{Zn} owing to the increase of hydrogen ion concentration may be attributed to the lowering of TOPO concentration which is consumed by the extraction of hydrochloric acid.

As shown in Fig. 1, the log D_{Zn} curve based on the extracted species, ZnCl$_2$· 2TOPO has a maximum value at around 0.002 M of chloride. When H$_2$O (ε=80), ethylene glycol ($\varepsilon=37.7$) and propylene glycol ($\varepsilon=32.0$) were used as a polar solvating medium, the extraction curves of zinc had a maximam at 2.0[8], 0.03[1] and 0.007[4] M of chloride, respectively. The zinc chloride complexes in diethylene glycol are more stable than those in propylene glycol, though both the solvents have almost the same dielectric constant. This may be caused by the fact that diethylene glycol having ether linkage has weaker solvating ability for zinc ion than α-diol, propylene glycol.

As the zinc acido-complexes form in the high concentration of hydrogen chloride, the terms, [Zn^{2+}]$_G$ and [ZnCl$^+$]$_G$, are negligible from Eq. 2, and D_{Zn} is introduced as follows.

$$D_{Zn} = \frac{K_1\beta_2[\text{TOPO}]_D^2+K_2\beta_3[\text{H}^+]_G[\text{Cl}^-]_G[\text{TOPO}]_D^y+K_3\beta_4[\text{H}^+]_G^2[\text{Cl}^-]_G^2[\text{TOPO}]_D^z}{\beta_2+\beta_3[\text{Cl}^-]_G+\beta_4[\text{Cl}^-]_G^2} \quad (4)$$

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When $[Cl^-]_G$ and $[TOPO]_D$ are considered constant, D_{Zn} is given by

$$D_{Zn} = \frac{a+b[H^+]_G+c[H^+]_G^2}{d}$$

where $a=K_1\beta_2[TOPO]_D^2$
$b=K_2\beta_3[Cl^-]_G[TOPO]_D^y$
$c=K_3\beta_4[Cl^-]_G^2[TOPO]_D^z$
$d=\beta_2+\beta_3[Cl^-]_G+\beta_4[Cl^-]_G^2$

The variation of the distribution ratio of zinc as a function of hydrogen ion concentration at the constant concentrations of chloride ion (0.32 M) and TOPO (0.1 M) was shown in Fig. 4; the log D_{Zn} values show a constnat value, -0.30, in the lower concentration range of hydrogen ion, where $ZnCl_2(TOPO)_2$ alone is extracted and such acido-complexes as $HZnCl_3 \cdot n TOPO$ are not extracted. The log D_{Zn} increases as the hydrogen ion increases, and the plot has a slope of 0.9. This indicates the extracted species are effectively $ZnCl_2(TOPO)_2$ and $HZnCl_3(TOPO)_y$, and the extraction of a higher acido-complex, $H_2ZnCl_4(TOPO)_z$, is negligible.

Figure 5 shows the log-log plots of D_{Zn} vs. $[TOPO]_D$ at 0.25 M of $[HCl]_G$. As the extracted species in this HCl concentration are considered to be $ZnCl_2(TOPO)_2$ and $HZnCl_3(TOPO)_y$, Eq. 4 can be rewritten as follows.

$$\log D_{Zn} = \log ([TOPO]_D^2 + A[TOPO]_D^y) + \log B \qquad (5)$$

where $A=K_2\beta_3[H^+]_G[Cl^-]_G/K_1\beta_2$ and $B=K_1\beta_2/(\beta_2+\beta_3[Cl^-]_G+\beta_4[Cl^-]_G^2)$. Open circles in the figure indicate the experimental points, and the slope of the plot varies from 2.5 to 4.0. From the slope and the plots calculated from Eq. 4, the number of
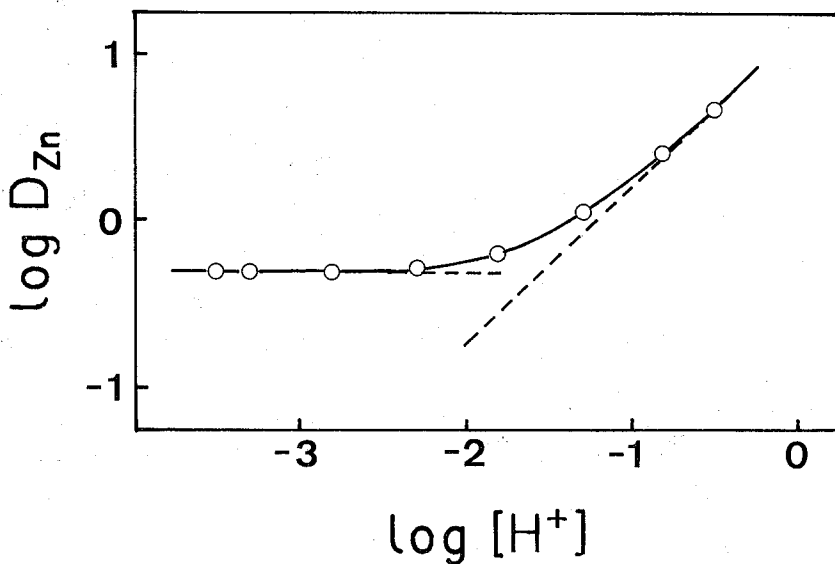

Fig. 4. Distribution of zinc as a function of hydrogen ion concentration.
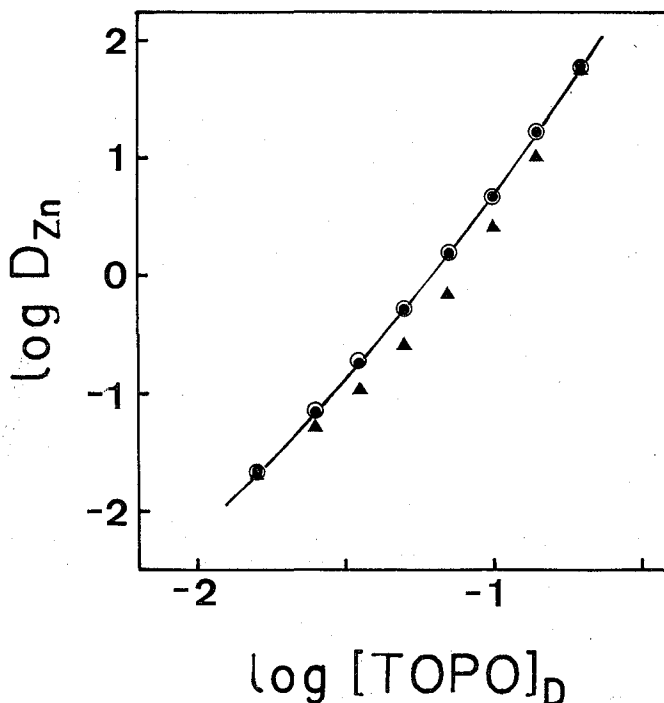Chloride ion; 0.32M, TOPO; 0.1M.

Fig. 5. Log D_{Zn} vs. log $[TOPO]_D$ plots.
○; observed, ●; calculated from Eq. 5 as $y=4$,
▲; calculated as $y=5$.

y is anticipated to be 4 or above. As seen in Fig. 5 the calculated data when $y=4$ (where $A=500$ and log $B=1.90$) are in fair agreement with the observed ones. The plots when $y=5$ (where $A=2000$ and log $B=1.92$) deviate from the observed data, and the plots when $y=6$ further deviate. Therefore, the extracted species as an acido-complex turns out to be $HZnCl_3(TOPO)_4$. The log D_{Zn} value when the acido-complex is not extracted is calculated to be -0.1 from Eq. 5, which is very closely agreed with the value (log $D_{Zn}=-0.2$) read off from the curve of Fig. 1 at 0.25 M LiCl.

Figure 6 indicates the dependence of log D_{Zn} on the hydrochloric acid concentration in the extraction from pure and aqueous diethylene glycol (1.0 and 15 wt% H_2O-DEG). By adding small amount of water (1.0 wt%, 0.05 mole fraction) into diethylene glycol, the extraction curve of zinc acido-complexes is sensitively shifted to higher chloride concentration, though the curve of zinc chloride, $ZnCl_2$, is scarcely moved. On the other hand, by mixing moderate quantity of water (15 wt%, 1.08 mole fraction) both the extraction peaks attributable to $ZnCl_2$ and zinc acido-complexes are considerably shifted to higher chloride concentration.

Results on the extraction of zinc with 0.1 M TOPO in decaline from diethylene glycol solution of hydrochloric acid at different temperatures are presented in Fig. 7. Each extraction peak assigned to $ZnCl_2$ and zinc acido-complexes decreases with the increase in temperature, and the latter is affected more strongly than the
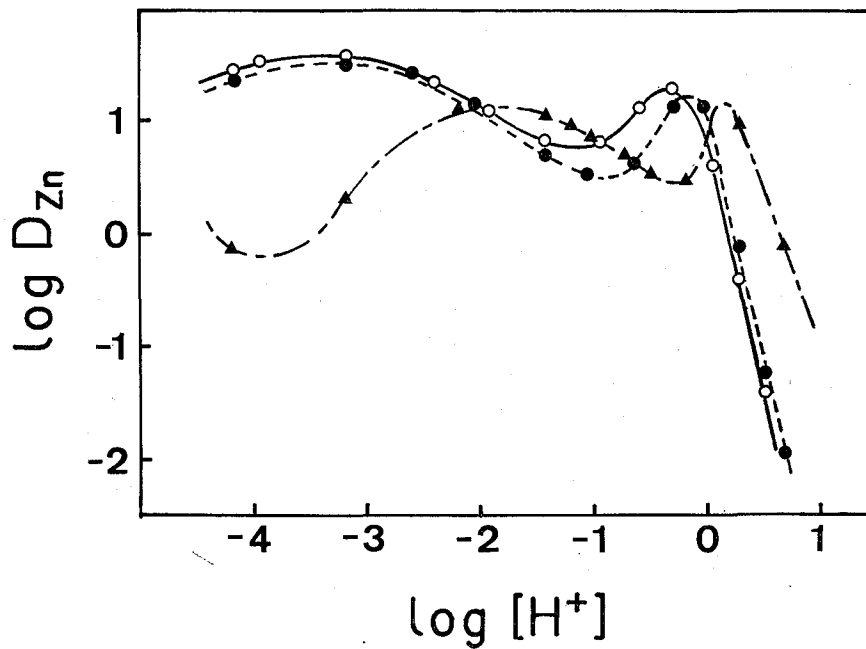
Fig. 6.   Distribution of zinc from aqueous diethylene glycol.
Water content; ○ almost nil,
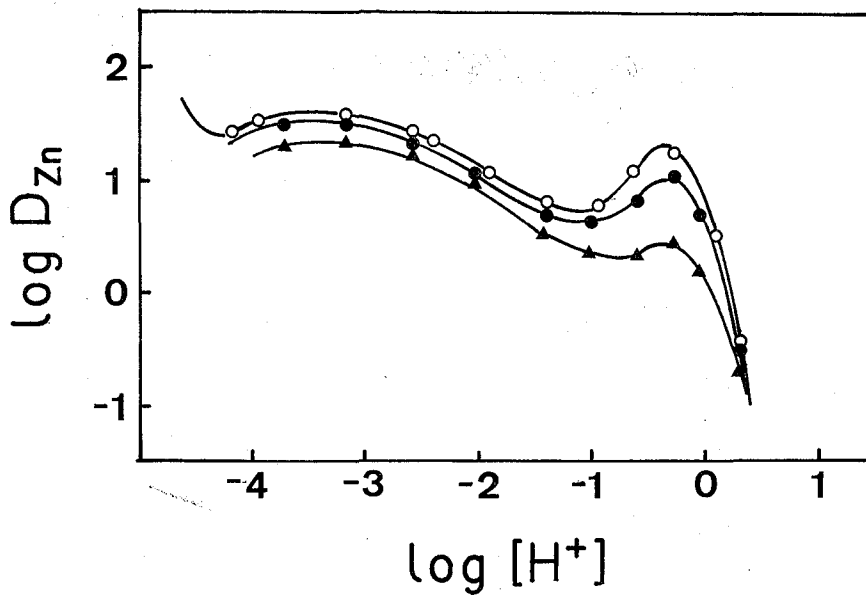● 1.0 V%,   ▲ 15.0 V%.

Fig. 7.   Effect of temperature.
Temperature; ○ 10°C,   ● 23°C,   ▲ 43°C.

former.

Clear and isolated extraction curve of the acido-complexes was found in the diethylene glycol system, despite no extraction of zinc acido-complexes from hydrochloric acid solution of ethylene glycol. Diethylene glycol reacts with the hydrogen ion in strongly acidic medium to form protonated cation, H^+DEG, in which the ethereal oxygen atom binds to the hydrogen ion. Then, as the hydrochloric acid increases in diethylene glycol, the species, protonated diethylene glycol and zinc chloride complexes, increase, and the acido complexes should be extracted in the form of $H^+DEG\ ZnCl_3^-(TOPO)_4$ and probably $(H^+DEG)_2ZnCl_4^{2-}(TOPO)_y$.

According to Moriya and Sekine,[7] it was concluded that the extracted species were $Zn(ClO_4)_2(TOPO)_4$, $ZnCl(ClO_4)(TOPO)_3$ and $ZnCl_2(TOPO)_2$ in the extraction of zinc from aqueous perchlorate-chloride solution with TOPO, and hence their solvation numbers were four. When this solvation number is applied to the present extracted species, the extracted species are realized to be $ZnCl_2(TOPO)_2$, $[H^+(DEG)(TOPO)_3ZnCl_3(TOPO)^-]$ and probably $[H^+(DEG)(TOPO)_{z/2}]_2ZnCl_4^{2-}$.

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