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Nonaqueous Extraction of Zinc from Ethylene Glycol Solution of Lithium Perchlorate and/or Chloride

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The nonaqueous liquid-liquid extraction of zinc from the lithium perchlorate solution of ethylene glycol into the toluene phase was firstly studied by using Zn-65. The complex, $Zn(ClO_4)_2 \cdot 2TOPO$ was mainly extracted in the toluene phase, but it was difficult to calculate the formation constants of zinc perchlorate using this extraction system, because it was attended by "salting out effect". Therefore, the extractions of zinc chloride and perchlorate between the ethylene glycol and toluene phases were secondly examined. A perchlorate ion, which was added in the glycol phase to keep the ionic strength constant, lowered the distribution ratio of zinc. This can be explained by the formation of such unextractable species as $ZnClO_4^+$ and $ZnCl \cdot ClO_4$ in the glycol phase. From the extraction data, the consecutive stability constants of zinc chloride and perchlorate in the glycol phase were calculated by trial and error method using a computer.

INTRODUCTION

Authors have been investigating the nonaqueous solvent extraction of metals[1-4] in order to gain knowledge of the metal ion equilibrium in nonaqueous solvents.

In the previous papers authors reported the nonaqueous extraction of zinc chloride from ethylene glycol with tri-*n*-octylphosphine oxide (TOPO) in toluene, where it was found that only the complex $ZnCl_2 \cdot 2TOPO$ was extracted into the toluene phase as a mono-nuclear complex[1] and the formation constants of zinc with chloride and perchlorate were calculated when the maximum value of the distribution ratio for zinc was adopted as the value of the distribution coefficient for zinc chloride, D_0.[4] In the present work, firstly the nonaqueous extraction behavior of zinc perchlorate between the ethylene glycol and toluene phases was examined and secondly the consecutive formation constnts of zinc with chloride and perchlorate in pure ethylene glycol, E. G., and ethylene glycol-water (9:1), 10% H_2O-E. G., were calculated by the nonaqueous extraction technique using a computer.

EXPERIMENTAL

Reagents.

A zinc-65 tracer was supplied as chloride from New England Nuclear, Boston,

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Mass., U.S.A. TOPO was obtained from the Dojindo Co., Ltd., Research Laboratories.

Reagent grade ethylene glycol was purified by drying with anhydrous sodium sulfate for several days, followed by distilling under reduced pressure over anhydrous sodium sulfate. Ethylene glycol solution of hydrogen chloride was prepared by passing dry hydrogen chloride and determined by titration with alkali after mixing with pure water. Lithium perchlorate solution was prepared by dissolving lithium perchlorate dried in vacuum. A zinc-65 tracer solution was made free from chloride by repeating the adding perchloric acid and the fuming to almost dryness. A zinc stock solution was prepared by dissolving dry zinc oxide with perchloric acid, evaporating to near dryness and diluting with ethylene glycol.

All chemicals were reagent grade materials and were used without further purification.

Procedure.

Extraction procedure was almost the same as previously described.[1-4]

We carried out all the extraction experiments at 20°C. The distribution ratio, D, is defined as the ratio of the molar concentration in the organic phase to that in the ethylene glycol phase. The distribution ratio of zinc, D_{Zn}, was measured by counting the γ-activities with a NaI (Tl) scintillation counter. The distribution ratio of lithium, D_{Li}, was obtained by determining the lithium concentration in each phase using the atomic absorption method. The following procedure was adopted for the measurement of the distribution ratio of TOPO, D_L. Ten milliliters of pure ethylene glycol were shaken with the same volume of toluene containing 0.1 M of TOPO for 30 min. An aliquot of the glycol phase after equilibration was taken into a tube. To the glycol phase the equal volume of toluene and, if necessary, a known amount of TOPO were added, and the distribution of zinc was measured after shaking. The concentration of TOPO in the glycol phase was then obtained from the calibration curve of the D_{Zn} vs. log [TOPO] plot. The TOPO concentration in the toluene phase was also determined similarly. The value of D_L was found to be about 200.

RESULTS AND DISCUSSION

Extraction of Zinc from Lithium Perchlorate Solution

Figure 1 shows the extraction of zinc as a function of the lithium perchlorate concentration; the hydrogen ion concentration in the ethylene glycol phase was kept at 3.45×10^{-4} M, because the minimum distribution ratio of zinc occurred around -3.7 of log C_H.[4] As shown in the figure the steep increase of the distribution ratio of zinc occurred at more than 0.5 M of lithium perchlorate. This may be caused by the extraction of zinc perchlorate.

The dependence of extraction of zinc (from 2.69 M of LiClO$_4$) on the concentration of TOPO in pure ethylene glycol was presented in Fig. 2. The log D_{Zn} vs. log [TOPO] plot in the figure gave an almost straight line with a slope of 2, indicating that the extraction equilibrium of zinc may be written as follows:

$$Zn_{(G)}^{2+} + 2ClO_{4(G)}^{-} + 2TOPO_{(T)} \rightleftharpoons Zn(ClO_4)_2(TOPO)_{2(T)}$$
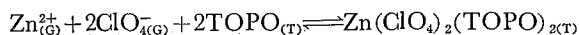
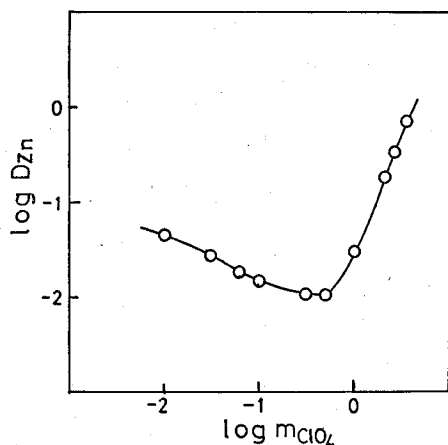where the subscripts G and T indicate the ethylene glycol phase and the tolune phase,

Fig. 1. The plot of log D_{Zn} vs. log m_{ClO_4} in E. G.-toluene system.
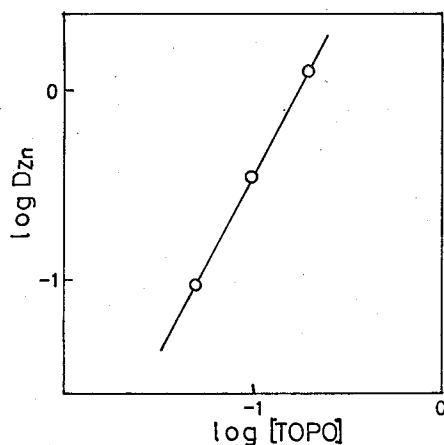HCl : $3.45 \times 10^{-4}M$

Fig. 2. The plot of log D_{Zn} vs. log [TOPO] in E. G.-toluene system.
HCl ; $3.45 \times 10^{-4}M$, LiClO$_4$; $2.69M$
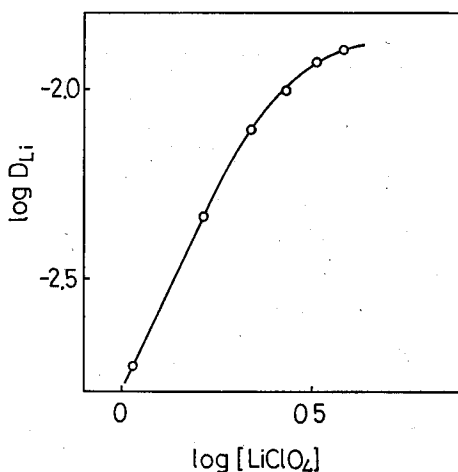
Fig. 3. The plot of log D_{Li} vs. log [LiClO$_4$] in E. G.-toluene system.

respectively.

The extraction of lithium between the ethylene glycol and toluene phases was investigated in order to know the concentration of lithium perchlorate in both the phases after equilibration. The distribution ratio of lithium increased remarkably as the concentration of lithium perchlorate increased as shown in Fig. 3. This may be explained in terms of the change of solvent properties based on the increase of lithium perchlorate in the ethylene glycol phase, that is, salting-out effect. The slope of the plot in Fig. 1 was about 3, which was a considerably high value compared with the theoretical value, 2. This may be also caused by the salting-out effect of lithium perchlorate.

The extraction of lithium perchlorate in ethylene glycol with TOPO increased with the neutral ligand as shown in Fig. 4. The slope of the plot log D_{Li} against total log [TOPO]$_T$ (Curve I) had a value of 1.83. On the other hand, taking account of the decrease of TOPO concentration in the toluene phase due to the association between
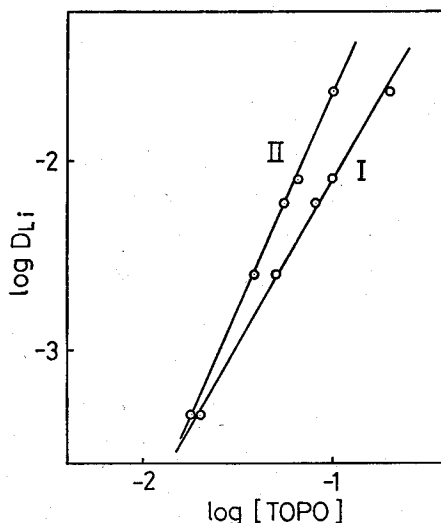
Fig. 4. The plot of log D_{Li} vs. log [TOPO] in E. G.-toluene system.

LiClO$_4$ and TOPO (calculated as LiClO$_4\cdot$2TOPO), the slope of the plot log D_{Li} against free log [TOPO]$_T$ (Curve II) became a value of 2.25. These suggest that the species extracted is LiClO$_4\cdot$2TOPO.

We found it difficult to calculate the formation constants between zinc and perchlorate ions by using the solvent extraction of zinc perchlorate as described above. Therefore, the formation constants of zinc with chloride and perchlorate in the glycol were tried to be calculated by trial and error method using a computer described below.

Extraction of Zinc from Lithium Perchlorate and Chloride Solution

Lithium ion can be scarcely extracted in the toluene phase below 0.1 M of lithium, as expected from Fig. 3. Therefore, the TOPO concetration in the toluene phase was not affected by lithium ion in the present work. The extraction experiments were performed in the area of lower concentration of chloride ion in which the formation of higher complexes such as ZnCl$_3^-$ and ZnCl$_4^{2-}$ was neglected.

The equilibria in the ethylene glycol phase are

$$Zn^{2+}+2Cl^- \rightleftharpoons ZnCl_2 \quad (K_1, K_2) \tag{1}$$

$$Zn^{2+}+2ClO_4^- \rightleftharpoons Zn(ClO_4)_2 \quad (K_1^A, K_2^A) \tag{2}$$

$$ZnCl^+ +ClO_4^- \rightleftharpoons ZnCl \cdot ClO_4 \quad (K_m) \tag{3}$$

The distribution ratios of zinc chloride and TOPO were defined as

$$D_O = \frac{[ZnCl_2 \cdot 2TOPO]_T}{[ZnCl_2]_G} \tag{4}$$

$$D_L = \frac{[TOPO]_T}{[TOPO]_G} \tag{5}$$

As Fig. 4 indicates, TOPO complexes of Zn(ClO$_4$)$_2$ and ZnCl$\cdot$ClO$_4$ were little extracted compared with ZnCl$_2$ (TOPO)$_2$ in the area of ClO$_4^-$ concentration, m_{ClO_4}, used for this analysis ($m_{ClO_4} \simeq 10^{-3} \sim 10^{-2}$ M).

The overall distribution ratio of zinc is then

$$D_{Zn} = \frac{[ZnCl_2(TOPO)_2]_T}{[Zn^{2+}]_G + [ZnCl^+]_G + [ZnCl_2]_G + [ZnClO_4^+]_G + [Zn(ClO_4)_2]_G + [ZnCl \cdot ClO_4]_G} \qquad (6)$$

From the formation constants of Eqs. (1)~(3), Eq. (6) can be expressed as follows:

$$D_{Zn} = \frac{D_0 K_1 K_2 m_{Cl}^2}{1 + K_1 m_{Cl} + K_1 K_2 m_{Cl}^2 + K_1^A m_{ClO_4} + K_1^A K_2^A m_{ClO_4}^2 + K_1 K_m m_{Cl} m_{ClO_4}} \qquad (7)$$

where m_{Cl} and m_{ClO_4} indicate the concentrations of the chloride and perchlorate ions in the glycol phase, respectively.

The equation is transformed into:

$$\left(\frac{D_0}{D_{Zn}} - 1\right) m_{Cl} = \left(\frac{1}{K_1 K_2} + \frac{K_1^A m_{ClO_4}}{K_1 K_2} + \frac{K_1^A K_2^A m_{ClO_4}^2}{K_1 K_2}\right)\frac{1}{m_{Cl}} + \left(\frac{1}{K_2} + \frac{K_m \cdot m_{ClO_4}}{K_2}\right) \qquad (8)$$

or

$$\frac{D_0}{D_{Zn}} = \left(1 + \frac{1}{K_2 m_{Cl}} + \frac{1}{K_1 K_2 m_{Cl}^2}\right) + \left(\frac{K_1^A}{K_1 K_2 m_{Cl}^2} + \frac{K_m}{K_2 m_{Cl}}\right) m_{ClO_4} + \frac{K_1^A K_2^A}{K_1 K_2 m_{Cl}^2} m_{ClO_4}^2 \qquad (9)$$

In our previous paper,[4] the formation constants in the present system (K_1, K_2, K_1^A and K_m) were calculated by assuming that the maximum value of the distribution ratio was equal to the value of D_0. In the present work the estimation of these formation constants was carried out by fitting Eq. (8) to the extraction data changing the D_0 value, which was not able to be got from the extraction experiment. A computer was used for this calculation.

Figure 5 indicates the dependence of log D_{Zn} on the chloride concentration at different concentrations of perchlorate from 0 to $1.07 \times 10^{-2} M$. As shown in the figure, an increase of perchlorate ion in the glycol phase results in a decrease in the distribu-
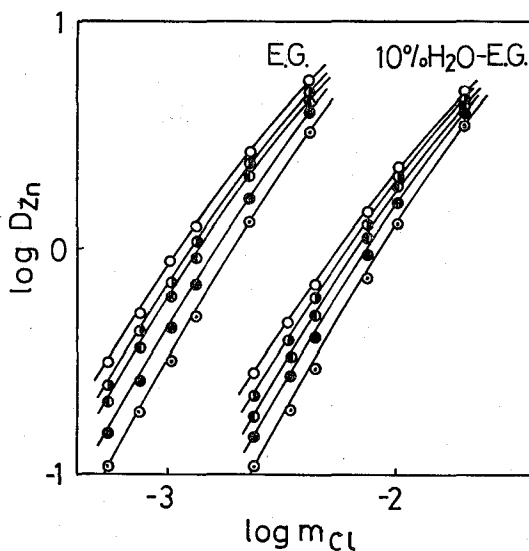

Fig. 5. The plots of log D_{Zn} vs. log m_{Cl} in E. G.-toluene and (10% H_2O-E. G.)-toluene systems.
m_{ClO_4} ; ○ $0 M$, ◑ $1.07 \times 10^{-3} M$, ◐ $2.14 \times 10^{-3} M$,
● $5.35 \times 10^{-3} M$, ◉ $1.07 \times 10^{-2} M$
TOPO ; $0.1 M$.

Table I Some Constants Calculated by Trial and Error Method

	E. G.	10% H_2O–E. G.
D_0	40 ~ 50	45 ~ 60
K_1	900 ± 35	220 ± 15
K_2	42 ± 7	6.5 ± 1.5
K_1^A	390 ± 10	130 ± 20
K_2^A	——	<4
K_m	15 ± 7	<3

Temp: 20 ± 0.1 °C

tion ratio of zinc. Such unknown constants as D_0, K_1, K_2, K_1^A, K_2^A and K_m were calculated from Eq. (9) and the data in Fig. 5. The values in water–ethylent glycol (1:9 ratio in volume) are listed in Table I together with those in ethylene glycol. Such a treatment for the solvent extraction has enabled the calculation of the formation constants in the mixed ligand complex system. However, the values of K_2^A and K_m in table I are not very reliable as understandable from Eq. (8) or (9).

The D_0 values by the present trial and error method were considerably higher than those by the method described in our previous paper.[4] Therefore K_2 values in the former became higher than those in the latter.

Assuming the formation reaction in the glycol, $ZnCl_2 + n\,TOPO \rightleftharpoons ZnCl_2 \cdot n\,TOPO$, the formation constant, K_L, of the reaction is given by:

$$K_L = [ZnCl_2 \cdot 2TOPO]_G / [ZnCl_2]_G [TOPO]_G^n \tag{10}$$

Therefore the overall distribution coefficient, D_{Zn}, can be rewritten as:

$$D_{Zn} \doteqdot \frac{[ZnCl_2 \cdot 2TOPO]_T}{(1+\alpha)[ZnCl_2]_G + [ZnCl_2 \cdot 2TOPO]_G} \tag{11}$$

where $\alpha = \left(\dfrac{1}{K_1 K_2 m_{Cl}^2} + \dfrac{1}{K_1 m_{Cl}}\right)$

The distribution coefficient of the $ZnCl_2 \cdot 2TOPO$ species, D_0^0 was defined:

$$D_0^0 = \frac{[ZnCl_2 \cdot 2TOPO]_T}{[ZnCl_2 \cdot 2TOPO]_G} = \frac{[ZnCl_2 \cdot 2TOPO]_T}{K_L [ZnCl_2]_G [TOPO]_G^n} \tag{12}$$

From Eqs. (11) and (12), the following function of the TOPO concentration is obtained:

$$\frac{1}{D_{Zn}} = \frac{1+\alpha}{D_0^0 K_L}\left(\frac{1}{[TOPO]_G}\right) + \frac{1}{D_0^0}$$

$$= \frac{D_L^n}{D_0^0 K_L}(1+\alpha)\left(\frac{1}{[TOPO]_T}\right)^n + \frac{1}{D_0^0} \tag{13}$$

In the present system the value of n is equal to 2 ideally, but the value of 1.9 was used for the calculation as the slope of the log D_{Zn} vs. log [TOPO] plot in Fig. 6 had 1.9. The plot of $1/D_{Zn}$ vs. $(1/[TOPO]_T)^{1.9}$ is shown in Fig. 7. As indicated in Eq. (13), D_0^0 and K_L can be obtained from the intercept and slope of the plot in Fig. 7. However, the value of D_0^0, which is equal to the reciprocal of the intercept, was too high to be obtained graphically. The product of D_0^0 and K_L was able to be obtained from the slope ($D_0^0 K_L = 7.9 \times 10^7$). The calculation value of D_0, which is equal to $D_0^0 K_L [TOPO]^{1.9}$, was 42, and this roughly agreed with the value ($D_0 = 40 \sim 50$) was determined by the trial and error method described above.
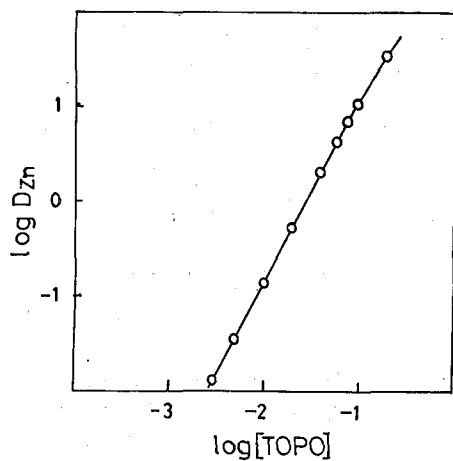
Fig. 6. The plot of log D_{Zn} vs. log [TOPO] in E.G.-toluene system.
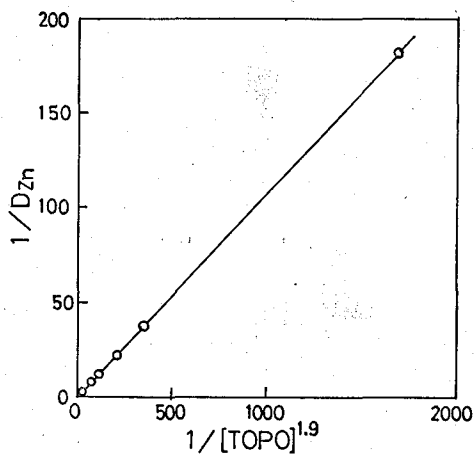

Fig. 7. The plot of $1/D_{Zn}$ vs. $1/[TOPO]^{1.9}$ in E.G.-toluene system.

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