Nonaqueous Liquid-Liquid Extraction: Solvent Extraction Studies of Zinc Chloride and Perchlorate Complexes in Glycols

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The nonaqueous liquid-liquid extraction of zinc was investigated between the toluene phase having tri-*n*-octylphosphine oxide and the glycol phase (ethylene glycol, 9:1 ethylene glycol-water and propylene glycol) having chloride and perchlorate ions. Perchlorate ion in the glycol solvent influenced the distribution ratio of zinc, which is due to the formation reaction between zinc and perchlorate ions. The formation constants of zinc with chloride and perchlorate ions were determined by using the nonaqueous solvent extraction technique. The decreasing order of the formation constants in the glycol solvents is as follows; propylene glycol > ethylene glycol > 9:1 ethylene glycol-water, which is the reverse order in the dielectric constant of the glycol solvents.

INTRODUCTION

Authors have investigated the liquid-liquid extraction of metals in a nonaqueous system,[1~3] because no attempt had been made to study the solvent extraction chemistry in the nonaqueous system and the information on the chemical equilibria of metal ions in the nonaqueous system was expected to be obtained from the data of the extraction.

In the previous paper, the nonaqueous extraction of zinc chloride from ethylene glycol with trioctylphosphine oxide was investigated[1] by using zinc-65. In the zinc chloride system, it was found that the complex $ZnCl_2 \cdot 2TOPO$ was predominantly extracted into the toluene phase and only mononuclear zinc complex existed in the two phases. In the present work the consecutive complex formation constants of zinc chloride and perchlorate in ethylene glycol and propylene glycol were estimated by using the nonaqeuous solvent extraction technique.

EXPERIMENTAL

Apparatus and Materials

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

Radioisotope, zinc-65 was supplied from New England Nuclear, Boston, Mass.,

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U.S.A., as chloride in hydrochloric acid. The chloride-free solution of zinc-65 was prepared by repeating the adding perchloric acid and the fuming to almost dryness twice more and by diluting with ethylene glycol or propylene glycol to give a solution of about 1 μCi/ml.

Reagent grade ethylene glycol or propylene glycol was dried with anhydrous sodium sulfate for several days and distilled under reduced pressure (25 mmHg) over anhydrous sodium sulfate.

Hydrochloric acid in ethylene glycol or propylene glycol was prepared by passing dry hydrogen chloride through the solvent and then standardized by titration with alkali after mixing with water.

A zinc stock solution was prepared by dissolving dry zinc oxide with the hydrogen perchlorate solution of glycol, evaporating to near dryness and diluting with 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.

Procedure

Experimental procedure was almost the same as described in the previous paper.[1] Ten milliliters of the glycol phase containing zinc ion with radiotracer and the hydrogen and lithium chlorides were placed in a 30 ml glass-stoppered vessel. The hydrogen ion concentration in the glycol phase was adjusted to a desired value by adding the hydrogen chloride solution of glycol. Ten milliliters of toluene containing TOPO were added. Two phases in the vessel were shaken for one hour in a thermostat regulated at 20°C and centrifuged until they got clear. Two milliliters of each phase were pipetted out in a polyethylene tube, and gamma-activities were counted with the NaI scintillation counter.

RESULTS AND DISCUSSION

Figure 1 shows the distribution ratio of zinc with 0.1 M TOPO solution of toluene as a function of the hydrogen or hydroxy ion concentration in the ethylene glycol phase. The hydrogen or hydroxy ion concentration was controlled by adding hydrogen chloride or potassium hydroxide. As seen in the figure, the distribution ratio of zinc decreased at first as the hydrogen chloride in ethylene glycol decreased. This is caused by the dissociation of zinc chloride. Subsequently, the distribution ratio of zinc suddenly increased, as the hydrogen ion concentration decreased, where the minimum distribution occurred around -3.7 of log C_H. The second increase of the distribution ratio appeared between -4 and -5 of log C_{OH}. Though the species of Zn (deprotonated ethylene glycol)$_2 \cdot n$TOPO is expected to be extracted in the toluene phase, there needs a more detailed investigation to make the extraction mechanism clear.

The increase of the distribution ratio in the range of more than -3.7 of log C_H is caused by the extraction of the monomeric species, ZnCl$_2 \cdot$2TOPO, as described in detail in the previous paper.[1] In the following experiment, the hydrogen chloride concentration in ethylene glycol was kept at 3.45×10^{-4} M (pC_H=3.5) and the chloride
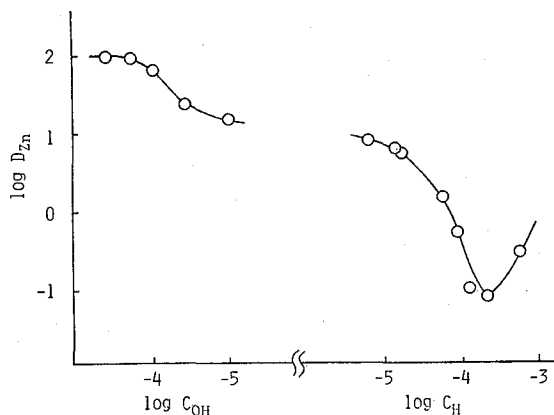
Fig. 1. The distribution of zinc between the ethylene glycol and
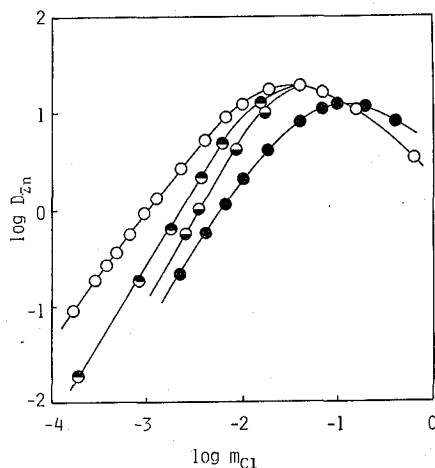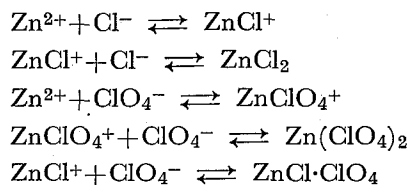toluene phases in the pC_H region.
TOPO; 0.1 M in toluene, temp.; 20°C

Fig. 2. The plots of log D_{Zn} vs. log m_{Cl} at different perchlorate concentrations.
m_{ClO_4}; ○ 0 M, ◕ 2×10^{-2} M, ◔ 5×10^{-2} M, in ethylene glycol, ● 0 M
in 9:1 ethylene glycol-water
TOPO; 0.1 M in toluene, temp., 20°C

concentration was controlled by the addition of lithium chloride.

Lithium perchlorate was added in the ethylene glycol solution in order to keep
the ionic strength constant. However, perchlorate ion influenced the distribution
ratio of zinc as shown in Fig. 2. This influence is evidently due to the interaction
between zinc and perchlorate ions. Taking into account the following formation
reactions in the ethylene glycol phase,

$$Zn^{2+} + Cl^- \rightleftharpoons ZnCl^+$$
$$ZnCl^+ + Cl^- \rightleftharpoons ZnCl_2$$
$$Zn^{2+} + ClO_4^- \rightleftharpoons ZnClO_4^+$$
$$ZnClO_4^+ + ClO_4^- \rightleftharpoons Zn(ClO_4)_2$$
$$ZnCl^+ + ClO_4^- \rightleftharpoons ZnCl \cdot ClO_4$$

the corresponding consecutive equilibrium constants are given by:

$$K_1 = \frac{[ZnCl^+]_G}{[Zn^{2+}]_G[Cl^-]_G} \tag{1}$$

$$K_2 = \frac{[ZnCl_2]_G}{[ZnCl^+]_G[Cl^-]_G} \tag{2}$$

$$K_1{}^A = \frac{[ZnClO_4{}^+]_G}{[Zn^{2+}]_G[ClO_4{}^-]_G} \tag{3}$$

$$K_2{}^A = \frac{[Zn(ClO_4)_2]_G}{[ZnClO_4{}^+]_G[ClO_4{}^-]_G} \tag{4}$$

$$K_m = \frac{[ZnCl \cdot ClO_4]_G}{[ZnCl^+]_G[ClO_4{}^-]_G} \tag{5}$$

where $[\ ]_G$ denotes the concentration of the species in ethylene glycol.

When the distribution ratio of zinc in the range of a comparatively low concentration of chloride $(5 \times 10^{-4} \sim 5 \times 10^{-3}$ M) was used for determining the formation constants, there was no necessity for taking account of higher chloride complexes of zinc, such as $ZnCl_3{}^-$ and $ZnCl_4{}^{2-}$. The distribution ratio of zinc chloride was defined as follows.

$$D_0 = \frac{[ZnCl_2 \cdot 2TOPO]_T}{[ZnCl_2]_G} \tag{6}$$

where $[\ ]_T$ stands for the concentration in the toluene phase. The overall distribution ratio is then given by

$$D_{Zn} = \frac{[ZnCl_2 \cdot 2TOPO]_T + [ZnCl \cdot ClO_4 \cdot mTOPO]_T +}{[Zn^{2+}]_G + [ZnCl^+]_G + [ZnCl_2]_G + [ZnClO_4{}^+]_G +}$$
$$\frac{[Zn(ClO_4)_2 \cdot nTOPO]_T}{[ZnCl \cdot ClO_4]_G + [Zn(ClO_4)_2]_G} \tag{7}$$

In the toluene phase, $[ZnCl \cdot ClO_4 \cdot mTOPO]_T$ and $[Zn(ClO_4)_2 \cdot nTOPO]_T$ may be almost neglected compared with $[ZnCl_2 \cdot 2TOPO]_T$, because the addition of perchlorate ion in the ethylene glycol phase lowered the distribution ratio of zinc and zinc ion was scarcely extracted by the perchlorate ion within the range used in the experiment. Hence, from Eqs. (1)~(5) and the reduction of Eq. (7), the overall distribution ratio can be expressed as follows.

$$D_{Zn} = \frac{D_0 K_1 K_2 m_{Cl}{}^2}{1 + K_1 m_{Cl} + K_1 K_2 m_{Cl}{}^2 + K_1{}^A m_{ClO_4} + K_1{}^A K_2{}^A m_{ClO_4}{}^2 + K_1 K_m m_{Cl} m_{ClO_4}} \tag{8}$$

where m_{Cl} and m_{ClO_4} indicate $[Cl^-]_G$ and $[ClO_4{}^-]_G$, respectively. The equation is transformed into:

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

or

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

$$+ \frac{K_1^A K_2^A}{K_1 K_2 m_{Cl}^2} m_{ClO_4}^2 \tag{10}$$

The formation constants, K_1 and K_2 can be obtained graphically from the slope and intercept of the $(D_o/D_{Zn}-1)m_{Cl}$ vs. $1/m_{Cl}$ plot as seen in Eq. (9) when $m_{ClO_4}=0$ and the maximum value of the distribution ratio was adopted as the value of D_o. And the formation constants regarding perchlorate ion, K_1^A and K_m can also be calculated from the various slopes of the D_o/D_{Zn} vs. m_{ClO_4} plots in the concentration range of perchlorate ion as low as the $m_{ClO_4}^2$ term is negligible.

Figure 3 shows the plot of $m_{Cl}(D_o/D_{Zn}-1)$ vs. $1/m_{Cl}$ in the ethylene glycol-toluene system when $[TOPO]_T$ and D_o are 0.1 M and 19, respectively. The values of K_1 and K_2 were calculated from the figure. These values in ethylene glycol, water–ethylene glycol (1:9 ratio in volume) and propylene glycol are listed in Table I.

The influence of perchlorate ion on the distribution ratio of zinc was examined at different concentrations of chloride, 4.88×10^{-4} and 1.27×10^{-3} M. As shown in Fig. 4, an increase of perchlorate ion in the glycol phase results in a decrease in the distribution ratio of zinc.

Typical plots of D_o/D_{Zn} vs. m_{ClO_4} at 4.88×10^{-4} and 1.27×10^{-3} M of chloride ion in the ethylene glycol-toluene system were indicated in Fig. 5. The formation constants K_1^A and K_m, were calculated from the slopes of the D_o/D_{Zn} vs. m_{ClO_4} plots at different chloride concentration, and these values are also listed in Table I: The decreasing
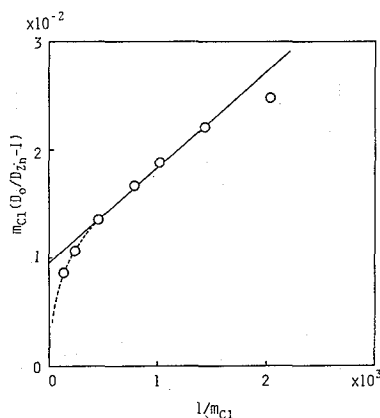

Fig. 3. The plot of m_{Cl} $(D_o/D_{Zn}-1)$ vs. $1/m_{Cl}$ in the ethylene glycol toluene system.
D$_o$; 19, TOPO; 0.1 M in toluene

Table I. Formation Constants of Zinc Chlorides and Perchlorate in Glycols

solvent	D_o	K_1	K_2	K_1^A	K_m
ethylene glycol	19	1100	100	150	93
ethylene glycol-water (9:1)	13	130	29	0.62	—
propylene glycol	19	7700	870	1200	230
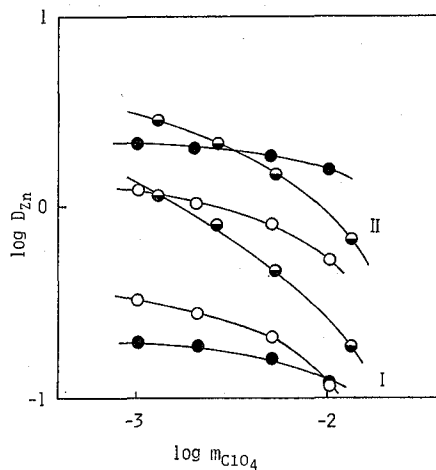
Fig. 4. The plots of log D_{Zn} vs. log. m_{ClO_4} in glycols.
m_{Cl}; I; 4.88×10^{-4} M, II; 1.27×10^{-3} M
○; ethylene glycol, ◐; propylene glycol, ●; 9:1
ethylene glycol-water
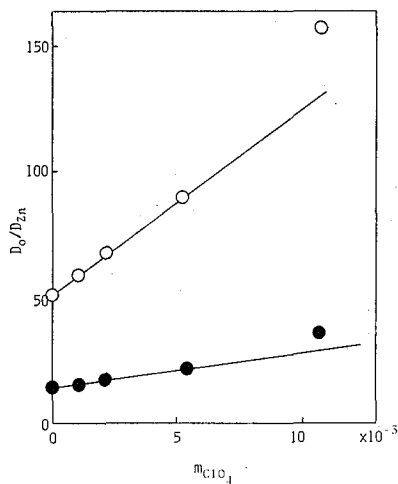
Fig. 5. The plots of D_o/D_{Zn} vs. m_{ClO_4}.
m_{Cl}; ○ 4.88×10^{-4} M, ● 1.27×10^{-3} M in ethylene
glycol, TOPO; 0.1 M in toluene

order of the formation constants of zinc ion with chloride and/or perchlorate in the glycol solvent is as follows; propylene glycol>ethylene glycol>ethylene glycol-water (9:1), which is the reverse order of dielectric constant of the glycol solvents.

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