

## Nonaqueous Liquid-Liquid Extraction of Zinc, Cadmium and Cobaltous Ions from Ethylene Glycol and Propylene Glycol Solutions of Chloride by Long Chain Alkyl Amine and Alkyl Ammonium Compound

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The nonaqueous liquid-liquid extractions of zinc, cadmium and cobaltous ions were investigated between the chloride solution of ethylene and propylene glycols and the toluene phase having long chain alkyl amine or ammonium chloride. In the extraction of zinc, cadmium and cobaltous ions from hydrogen and lithium chloride solutions by tri-*n*-octylamine and Capriquat, 2:1 complex,  $R_3R'N^+Cl^-R_3R'N^+MCl_3^-$ , may be mainly extracted in the toluene phase except the extraction of cobaltous ion in ethylene glycol by Capriquat, where a mixture of 2:1 and 1:1 ( $R_4N^+CoCl_3^-$ ) complexes may be extracted into the toluene phase.

KEY WORDS: Nonaqueous Extraction/ Glycols/ Tertiary Amine/ Quaternary Ammonium Chloride/

### INTRODUCTION

In the solvent extraction of non-chelate system, the solutes which usually are electrolytes distribute between two liquid phases, generally an aqueous phase and an organic phase. However, there exist several polar organic solvents such as glycols, methanol, DMSO, *etc.* soluble sparingly with nonpolar organic solvents. Previously<sup>1~4)</sup> we have started to investigate the nonaqueous liquid-liquid extraction of metals between the nonpolar organic solvent having tri-*n*-octylphosphine oxide (TOPO) and the polar organic solvent described above.

On the other hand, high molecular amines have often been used in the solvent extraction of metals from mineral acid solutions. The object of the present work is to study the solvent extraction behavior of metals from glycolic solution of hydrogen or lithium chloride using high molecular weight amine and ammonium salts.

### EXPERIMENTAL

#### Materials

Radioisotopes, Zn-65, Co-60 and Cd-115 m, were obtained from New England Nuclear, Boston, Mass., U.S.A. as chloride in hydrochloric acid. The purification of ethylene glycol and propylene glycol and the preparation of their hydrochloric acid and lithium chloride solutions were as previously described.<sup>1~3)</sup> Stock solutions of zinc,

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cadmium and cobaltous ions were prepared by dissolving the corresponding purest metals or oxide with perchloric acid, evaporating to near dryness and diluting with glycols. The glycol solutions of the radioisotopes were also prepared by repeating the addition of perchloric acid to the isotopes and the fuming to almost dryness twice more and by diluting with the glycol to give a solution of about  $1 \mu\text{Ci/ml}$ .

High molecular weight tertiary amine were converted to the hydrochloride salt using the procedure of Kertes.<sup>5)</sup> Primary and secondary amines, and Capriquat (tri-*n*-octylmethylammonium chloride, Dojindo) were used without any treatment.

### Extraction procedure

Most of the experimental procedures were the same as those described in the previous study.<sup>1-3)</sup> Ten milliliters of the glycol phase containing metal ion with radiotracer and the hydrogen and/or lithium chlorides were placed in a 30 ml glass-stoppered centrifugal tube. The hydrogen ion concentration in the glycol phase was adjusted by adding the hydrogen chloride solution of the glycol. Ten milliliters of toluene was added, and the both phases were shaken for 30 min. at 20°C. After centrifugal separation, 2 ml of each phase were pipetted out, and the  $\gamma$ -activities were counted with the well-type NaI scintillation counter.

## RESULTS AND DISCUSSION

### Extraction of Zinc from Hydrogen or Lithium Chloride Solution

Figure 1 presents the extraction of zinc into a toluene phase containing high molecular weight amine or ammonium chloride as a function of hydrochloric acid concentration in the ethylene glycol phase. The curve for di-*n*-octylamine could

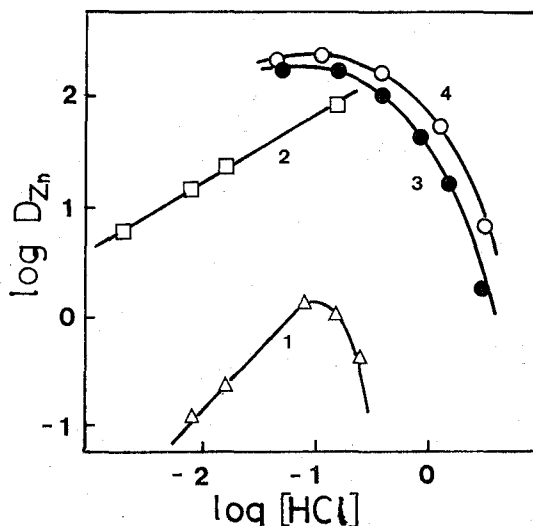


Fig. 1. Extraction of Zn from hydrochloric acid solution of ethylene glycol by various amines and ammonium chloride in toluene. Curve 1, 0.3 M mono-*n*-octylamine; 2, 0.3M di-*n*-octylamine; 3, 0.3M tri-*n*-octylamine; 4, 0.15 M Capriquat.

not be obtained owing to the formation of a precipitate on the treatment of the secondary amine by hydrochloric acid. And the curve for mono-*n*-octylamine is not be shown because the  $\log D$  values of zinc are less than  $-3$  over the entire range when the primary amine is treated by hydrochloric acid in ethylene glycol. Therefore, the primary and secondary amines in Fig. 1 were obtained without any treatment.

The increasing order of the extraction efficiency is as follows; primary < secondary < tertiary < quaternary, which is similar to that found in the extraction system from aqueous system.<sup>6)</sup> The curve for tri-*n*-octylamine is analogous to that for Capriquat; the extraction curves for zinc have a maximum around 0.1 M of hydrochloric acid, beyond which a rapid decrease in  $D_{Zn}$  values follows. The chloride ion concentration (0.1 M HCl) at the maximum value of  $D_{Zn}$  in the present system is appreciably lower than that in the aqueous solution system (2 M HCl)<sup>6)</sup> but is higher than that in the extraction system of ethylene glycol, where TOPO was used as an extractant (0.04 M HCl)<sup>1)</sup>; the former case indicates that the zinc chloride complexes in the ethylene glycol are rather more stable than those in aqueous solution, and the latter suggests that the more consecutive chloride complexes of zinc were also partly extracted by the tertiary amine and quaternary ammonium chloride.

To investigate the role of hydrogen ion in the extraction of zinc chloride complexes, the chloride source was exchanged from hydrochloric acid to lithium chloride solution. As seen in Fig. 2, the  $\log D_{Zn}$  values were determined at different con-

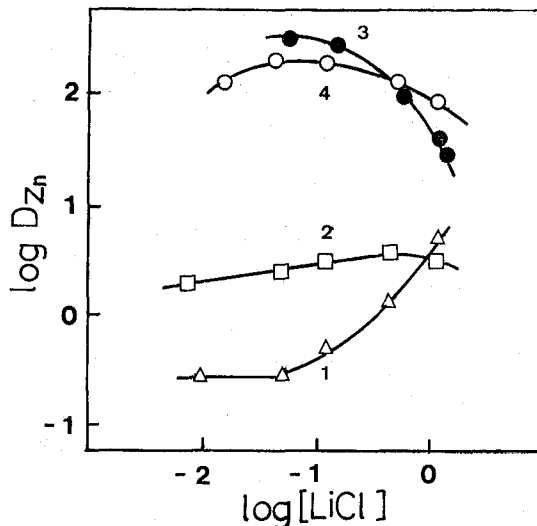


Fig. 2. Extraction of Zn from lithium chloride solution of ethylene glycol by various amines and ammonium chloride.  
Curve 1, 0.3 M mono-*n*-octylamine; 2, 0.3 M di-*n*-octylamine;  
3, 0.3 M tri-*n*-octylamine; 4, 0.15 M Capriquat.

centrations of lithium chloride solution. When tri-*n*-octylamine and Capriquat were used, the extraction curves thus extracted are considerably similar to those for extraction from hydrochloric acid, but slightly higher values in the high concentration range of lithium chloride were observed. The extraction behavior with lithium

chloride is different from that with hydrochloric acid in the extraction system by primary and secondary amines. Hence, subsequent experiments were mainly carried out using tertiary amine or quaternary ammonium salt.

The dependence of extraction of zinc from hydrochloric acid on the concentration of tri-*n*-octylamine or Capriquat was presented in Fig. 3. The log  $D_{Zn}$  vs. log

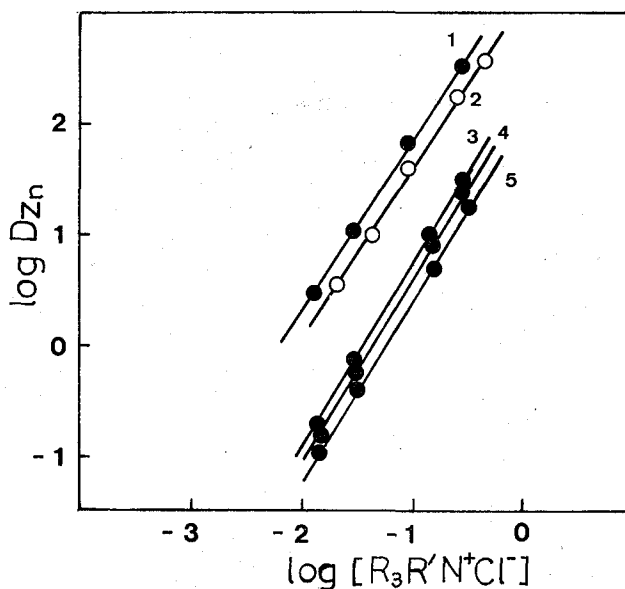
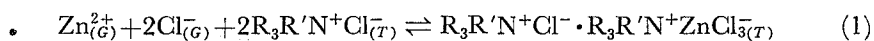


Fig. 3. Distribution ratio of Zn as a function of amine and ammonium chloride.

Toluene: Curve 1, tri-*n*-octylamine, 0.15 M HCl; 2, Capriquat, 0.2 M HCl; 3, tri-*n*-octylamine, 0.17 M HCl; 4, carbon tetrachloride, 0.17 M HCl; 5, tri-*n*-octylamine, 0.17 M HCl.

( $R_3R'_N^+Cl^-$ ) ( $R_3R'_N^+Cl^-$  denotes tertiary or quaternary ammonium chloride) plot in the figure gave an almost straight line with a slope of 1.9. Taking into consideration the formation only of 2:1 complex and neglecting association and hydration of the species in the nonpolar solvent phase, the extraction of zinc from chloride medium by a salt of a tertiary amine or by a quaternary ammonium salt may be described by the following equation.



where the subscripts G and T indicate the ethylene glycol phase and the toluene or other non-polar solvent phase, respectively.

#### Extraction of Cadmium and Cobaltous Ions from Hydrogen or Lithium Chloride Solution

The extraction curves of cadmium with alkylamine or alkylammonium chloride in toluene at different concentrations of hydrogen or lithium chloride are shown in Fig. 4. The curve in the lithium chloride system is almost the same to the curve in the hydrogen chloride system for tri-*n*-octylamine or for Capriquat, respectively.

These curves show a maximum around 0.05 M hydrogen or lithium chloride, beyond which  $\log D_{Cd}$  decreases with increasing chloride concentration. This behavior is analogous to that of zinc extraction. The extraction lowering in higher chloride concentration range as well as the case in hydrogen chloride in Fig. 4 may attribute to the higher complex formation of cadmium chloride.

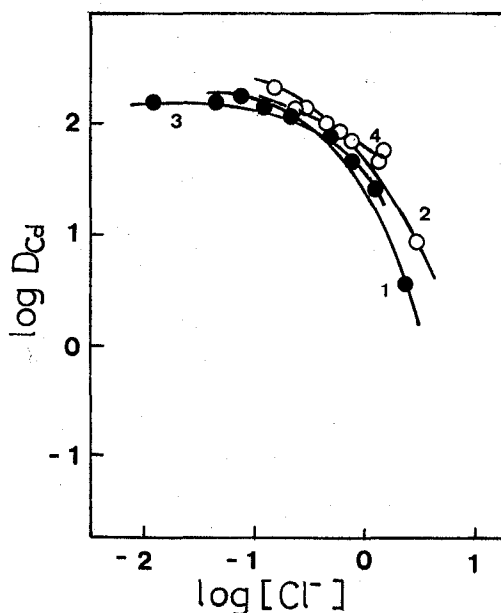


Fig. 4. Extraction of Cd from hydrogen or lithium chloride solutions of ethylene glycol.

Curve, 1, 0.15 M tri-*n*-octylamine, HCl; 2, 0.075 M Capriquat, HCl; 3, 0.15 M tri-*n*-octylamine, LiCl; 4, 0.075 M Capriquat, LiCl.

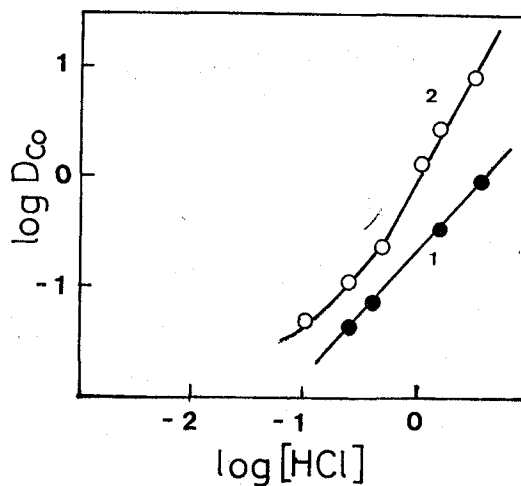


Fig. 5. Extraction of Co(II) from hydrochloric acid solution. Curve 1, 0.3 M tri-*n*-octylamine; 2, 0.3 M Capriquat.

The dependence of the cobalt distribution coefficient on the hydrogen chloride and lithium chloride concentrations is shown in Figs. 5 and 6. The extraction curves from hydrogen chloride in ethylene glycol are similar to those for extraction from lithium chloride.

Some plots of  $\log [\text{extractant}]$  vs.  $\log D$  of cadmium and cobaltous ions at constant hydrogen chloride concentration were drawn to determine the dependence of

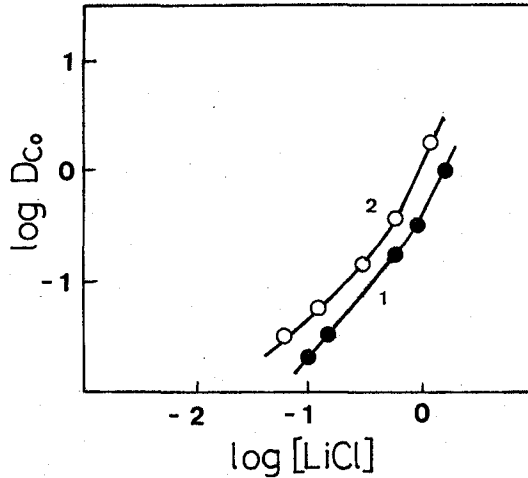


Fig. 6. Extraction of Co(II) from lithium chloride. Curve 1, 0.3 M tri-*n*-octylamine; 2, 0.3 M Capriquat.

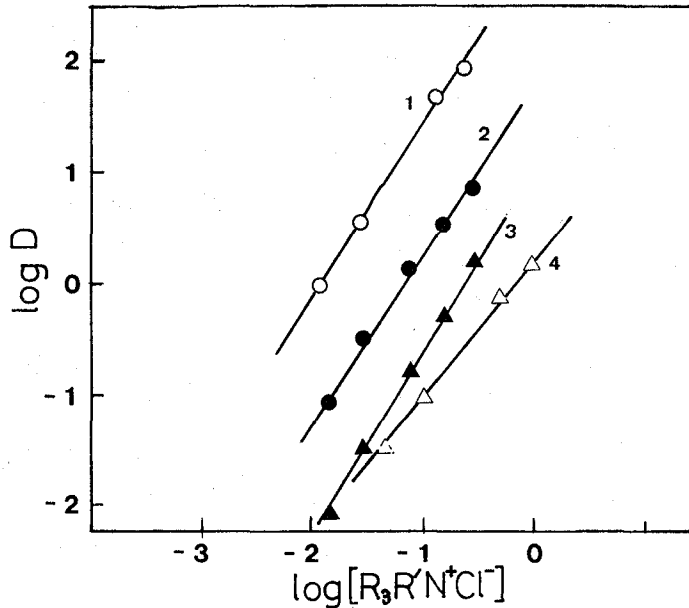


Fig. 7. Distribution ratio of Cd and Co(II) as a function of amine and ammonium chloride. Curve 1, Capriquat, 0.63 M HCl; 2, tri-*n*-octylamine, 2.73 M HCl; 3, tri-*n*-octylamine, 4.4 M HCl; 4, Capriquat, 1.25 M HCl.

the latter on the former (Fig. 7).

In the extraction of cadmium by tri-*n*-octylamine and Capriquat diluted in toluene, the slopes of the extraction curves correspond to 1.8, and this suggests mainly the formation of the 2:1 complex of cadmium as well as that of zinc indicated in Eq. 1. As shown in Fig. 7, the extraction curve has the slope of 1.8 in the extraction of cobaltous ion by tri-*n*-octylamine. On the other hand, the curve by Capriquat denotes the slope of 1.3. This probably means the formation of the two complexes

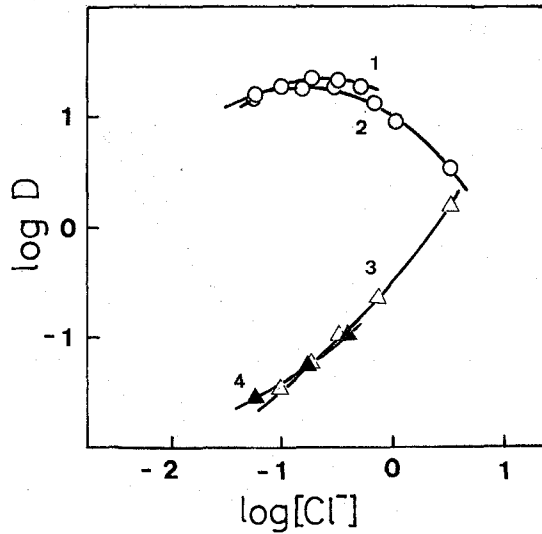


Fig. 8. Extraction of Zn and Co(II) from hydrogen or lithium chloride solution of propylene glycol.  
Curve 1, Zn, LiCl; 2, Zn, HCl; 3, Co(II), LiCl; 4, Co (II), HCl.

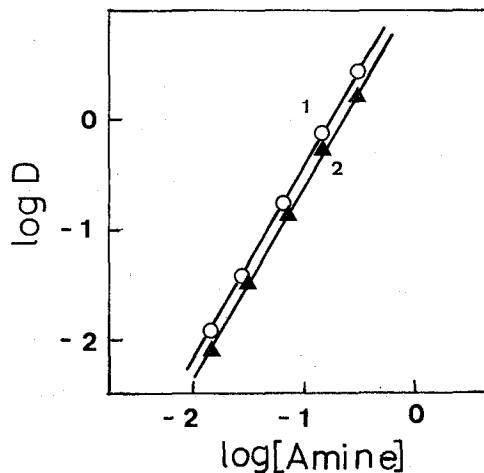


Fig. 9. Distribution ratio of Zn and Co(II) in hydrochloric acid solution of propylene glycol as a function of tri-*n*-octylamine.  
Curve 1, Zn, 3.2 M HCl; 2, Co(II), 4.4 M HCl.

2:1 ( $R_4N^+Cl^- \cdot R_4N^+CoCl_3^-$ ) and 1:1 ( $R_4N^+CoCl_3^-$ ) in the toluene phase.

### Extraction of Zinc and Cobaltous Ions from Chloride Solutions of Propylene Glycol

Results on the extraction of zinc and cobaltous ions by 0.3 M tri-*n*-octylamine in toluene at different concentration of hydrogen and lithium chlorides in the propylene glycol are presented in Fig. 8. Similarly to the extraction system in ethylene glycol, the extraction curve of zinc chloride from propylene glycol has a maximum around 0.1 M in the chloride concentration, and the extraction of cobaltous ion increases with the increase of the chloride concentration. Figure 9 show the change in the distribution ratio of zinc and cobaltous ions as a function of tri-*n*-octylamine concentration. In the constant concentrations of zinc and cobaltous ions, chloride and  $H^+$ , the slope of the plot  $\log D$  against  $\log [R_3HN^+Cl^-]$  gives the number of the ligand in toluene phase. Hence, the extracted species is supposed to be  $R_3HN^+Cl^- \cdot R_3HN^+MCl_3^-$  as the slopes are about 2.0.

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