Nonaqueous Liquid-Liquid Extraction. Extraction of Zinc and Cadmium from Ethylene Glycol Solution of Bromide by Trioctylphosphine Oxide

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The distribution of zinc between toluene phase containing trioctylphosphine oxide (TOPO) and nonaqueous ethylene glycol phase containing either hydrogen or alkali bromide has been investigated by using zinc-65 and cadmium-115 m. The distribution ratio, D from ethylene glycol phase reached a maximum value at about 0.1 N of hydrogen bromide for zinc and at about 0.4 N for cadmium. This shows that zinc bromide complexes are considerably more stable in ethylene glycol phase than in aqueous phase. In the zinc-hydrogen or alkali bromide-TOPO system, the complex $ZnBr_2 \cdot 2TOPO$ may occur in toluene phase, while in the cadmium-hydrogen bromide-TOPO system, such acid complexes as $HCdBr_3 \cdot lTOPO$ and $H_2CdBr_4 \cdot mTOPO$ are probably formed in the toluene phase. Under the conditions of the experiment, only mononuclear zinc and cadmium complexes appear to exist in the two phases.

INTRODUCTION

Glycolic solvents such as ethylene glycol and propylene glycol have extensively been used as media for acid-base titration, but no attempt has been made to study liquid-liquid extractions of metal ions in such nonaqueous systems. It is an interesting problem to study liquid-liquid extraction in nonaqueous system, because the information on the chemical equilibria of metal ions in nonaqueous system may be obtained from the data of the extraction. As a prelude to such studies, authors have been investigating nonaqueous liquid-liquid extraction of metal ions by trioctylphosphine oxide from glycolic solvents of halide. Of course, the several works on the extraction of metal ions by tributyl phosphate or trioctylphosphine oxide from aqueous halide solutions have been reported.[1] For example, the extraction of zinc into tributyl phosphate from aqueous hydrochloric acid or hydrobromic acid has been reported by Morris and Short.[2]

The present paper reports on the nonaqueous liquid-liquid extraction of zinc and cadmium by trioctylphosphine oxide from the ethylene glycol solution of bromide.

EXPERIMENTAL

Apparatus and Reagents

Radioactivity countings were made with a TEN NaI (Tl) (44.5 mm in dia. ×

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50.8 mm) well type scintillation counter, EA-14, connected with a Metro dekatron scaler, Model MCL-6B.

The radioisotope, zinc-65 was supplied by the Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A. and cadmium-115 m was supplied by the New England Nuclear, Boston, Mass., U.S.A., as chloride in hydrochloric acid solution. They were dried on a hot plate and was dissolved in ethylene glycol.

Reagent grade ethylene glycol was refluxed with 2% sodium hydroxide for a few hours and distilled. The distilled solvent was dried with anhydrous sodium sulfate for several days and distilled under reduced pressure (25 mmHg) over anhydrous sodium sulfate.

Hydrogen bromide in ethylene glycol was prepared by saturation with dry hydrogen bromide. Hydrogen bromide gas was generated by dropping bromine on tetraline and dried by passing through a U-tube filled with fused calcium bromide. The ethylene glycol solutions of hydrogen bromide were standardized by titrating it with standard aqueous alkali after mixing with water.

Zinc and cadmium stock solutions were prepared by dissolving their dry oxide with hydrogen bromide solution of ethylene glycol, evaporating to near dryness and diluting it with pure ethylene 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

Ten milliliters of an ethylene glycol solution containing a radioactive tracer, a carrier, and various bromides were placed in a 30 ml glass-stoppered centrifuge tube. Ten milliliters of toluene containing TOPO were added. Two phases in the tube were shaken for 30 minutes at about 25°C 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.

The ethylene bromide concentration of each phase after equilibria was determined with the titration of standard aqueous alkali with phenolphthalein.

RESULTS AND DISCUSSION

Extraction of Hydrogen Bromide

The distribution of hydrogen bromide between toluene and ethylene glycol phases was investigated in order to know the concentrations of hydrogen bromide in both the phases after equilibration. The distribution ratio of hydrogen bromide is given by

$$D_{HBr} = \frac{\text{total concentration of hydrogen bromide in toluene phase}}{\text{total concentration of hydrogen bromide in ethylene glycol phase}} \quad (1)$$

As shown in Fig. 1 the log D_{HBr} between 0.13 M TOPO toluene solution and
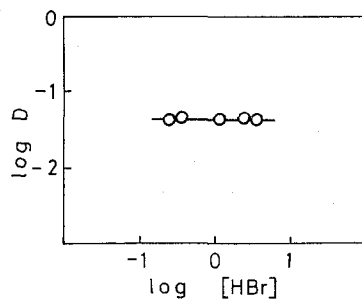
M. Matsui, T. Aoki, O. Inoue, and T. Shigematsu

Fig. 1. The distribution ratio of hydrogen bromide between ethylene glycol and 0.13 M TOPO toluene phase.

ethylene glycol is not so high and the value is about -1.35. Hydrogen bromide is slightly more extractable than hydrogen chloride ($\log D = -1.5$).

Extraction of Zinc Bromide

The distribution ratio of zinc is given by

$$D = \frac{\text{total concentration of zinc in toluene phase}}{\text{total concentration of zinc in ethylene glycol phase}} \qquad (2)$$

It may be written as

$$D = ([ZnBr_2 \cdot kTOPO]_{(t)} + [HZnBr_3 \cdot lTOPO]_{(t)} + [H_2ZnBr_4 \cdot mTOPO]_{(t)})/[Zn]_{(e)}$$

Figure 2 presents the change in the distribution ratio of zinc as a function of the concentration of TOPO. The number of molecules of TOPO directly associated with the extracted zinc species may be deduced from the results in Fig. 2. In the constant concentrations of zinc, bromide, H^+ and ethylene glycol, if the acid complexes are not formed, we have
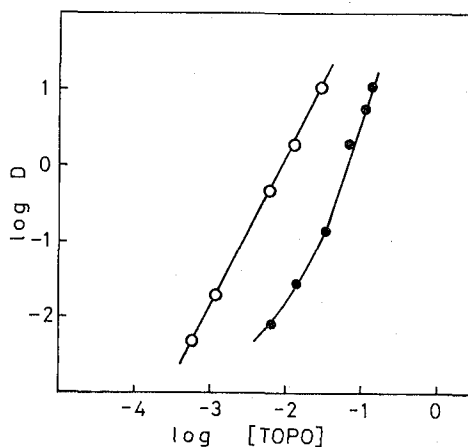

Fig. 2. The distribution ratio of zinc (—○—) and cadmium (—●—) as a function of TOPO concentration. Ethylen glycol phase: 0.1 N HBr
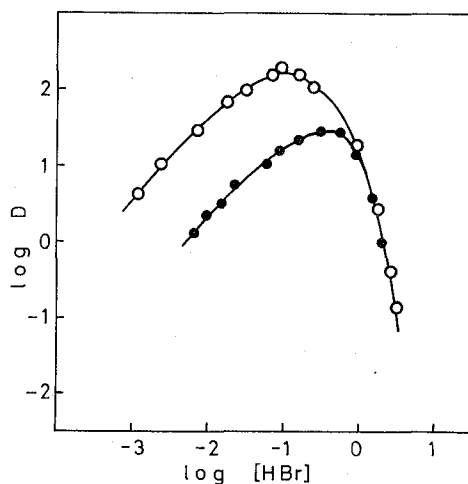
Fig. 3. The distribution ratio of zinc (—◯—) and cadmium
(—●—) as a function of hydrogen bromide concent-
ration.
Toluene phase: 0.13 M TOPO

$$\partial \log D/\partial \log [\text{TOPO}] = \bar{S}_t - \bar{S}_e$$

where the symbol $\bar{S}$ represents the average number of molecule of TOPO directly associated with zinc complexes in a given phase; subscript t and e refer to the toluene and ethylene glycol phases respectively. Since the solubility of the TOPO in the ethylene glycol phase is small, $\bar{S}_e$ may be taken as zero. Therefore, $\bar{S}_t$ is equal to 2.

Figure 3 shows the distribution of zinc in TOPO toluene solution as a function of hydrogen bromide concentration in the ethylene glycol phase. The maximum value of log D occurs when hydrogen bromide concentration is about 0.1 N, and the concentration is lower than the value from aqueous solution (ca. 2.6 N).[2]

It is found that zinc bromide complex in ethylene glycol is considerably more stable than the complex in aqueous solution. The distribution of zinc decreases as the concentration of hydrogen bromide increases at more than 0.1 N. This may be caused by the fact that free TOPO concentration decreases as hydrogen bromide increases, owing to transfer of hydrogen bromide into the toluene phase. The distribution ratio of zinc decreases as the hydrogen bromide concentration decreases from the maximum value of log D, and the slope is about 1. ZnBr$^+$ may occur predominantly in ethylene glycol within a low hydrogen bromide concentration, and the following equilibria is proposed:

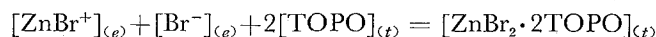$$[\text{ZnBr}^+]_{(e)} + [\text{Br}^-]_{(e)} + 2[\text{TOPO}]_{(t)} = [\text{ZnBr}_2 \cdot 2\text{TOPO}]_{(t)}$$

Figure 4 shows the extraction of zinc as a function of lithium bromide concentration.

The curve of log D vs. bromide concentration in the lithium bromide system is similar to the curve in the hydrogen bromide system. This suggests that the extracted species are not such acid complexes as HZnBr$_3 \cdot l$TOPO and H$_2$ZnBr$_4 \cdot$

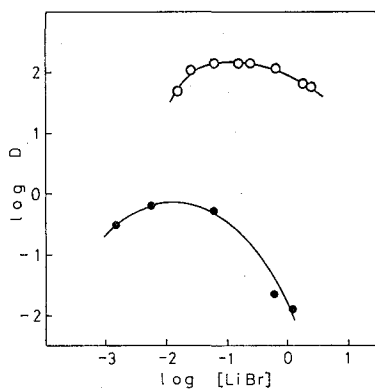M. Matsui, T. Aoki, O. Inoue, and T. Shigematsu

Fig. 4. The distribution ratio of zinc (—○—) and cadmium
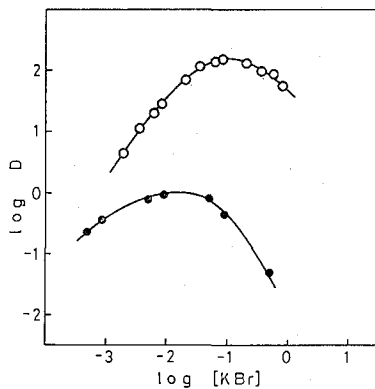(—●—) as a function of lithium bromide.
Toluene phase: 0.13 M TOPO

Fig. 5. The distribution ratio of zinc (—○—) and cadmium
(—●—)as a function of potassium bromide.
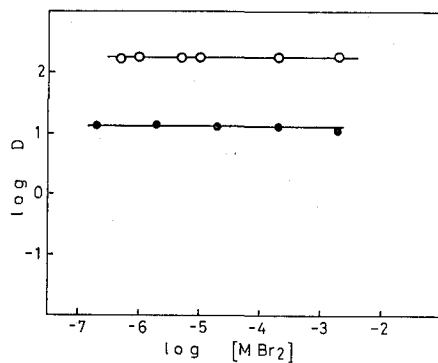Toluene phase: 0.13 M TOPO

Fig. 6. The distribution ratio of zinc (—○—) and cadmium
(—●—) as a function of metal concentration.
Toluene phase: 0.13 M TOPO
Ethylene glycol phase: 0.1 N HBr

mTOPO but $ZnBr_2 \cdot 2TOPO$. Despite the increase of lithium bromide concentration, the distribution ratio of zinc is not so decreased as that from hydrogen bromide. This may be due to almost no influence of the lithium bromide in the glycol phase on the free TOPO concentration in the toluene phase.

Figure 5 shows the extraction of zinc as a function of potassium bromide concentration. The distribution curve is similar to the curve obtained from lithium bromide.

Figure 6 shows the effect of the concentration of zinc on the distribution ratio D in the range [Zn] 2×10^{-3} to 5×10^{-7} M. The value D at given values of the hydrogen bromide concentration is found to be independent of the metal concentration, and this indicates that zinc complexes in both the ethylene glycol and the toluene phase are mononuclear. It is concluded that zinc occurs in the toluene phase predominantly as the complex $ZnBr_2 \cdot 2TOPO$.

Extraction of Cadmium Bromide

The distribution ratio of cadmium may be also written as

$$D = ([CdBr_2 \cdot kTOPO]_{(t)} + [HCdBr_3 \cdot lTOPO]_{(t)} + [H_2CdBr_4 \cdot mTOPO]_{(t)})/[Cd]_{(e)}$$

It is found from Fig. 2 that TOPO molecules associated with the extracted cadmium species change from 2 to 3 as TOPO concentration in toluene increases. Figures 3, 4, and 5 show that cadmium complex is more extractable from hydrogen bromide than from lithium bromide.

It may be that the extracted cadmium species from lithium bromide or potassium bromide is cadmium bromide, $CdBr_2$ and the extracted cadmium species from hydrogen bromide are $CdBr_2 \cdot kTOPO$ and such acid complexes as $HCdBr_3 \cdot lTOPO$ and $H_2CdBr_4 \cdot mTOPO$. The acid complexes are more extractable than cadmium bromide. Figure 6 shows that cadmium complexes in both the ethylene glycol and the toluene phases are mononuclear at 0.1 N hydrogen bromide concentration.

REFERENCES

(1) Y. Marcus and A. S. Kertes, "Ion Exchange and Solvent Extraction of Metal Complexes", Wiley-Interscience, London (1969), p. 694.
(2) D. F. C. Morris and E. L. Short, *J. Chem. Soc.*, 2662 (1962).