Extraction and Separation of Zinc and Cadmium Chlorides by TOPO from Mixed Media

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Summary

The effect of water-miscible alcohols and acetone on the extraction and separation of Cd and Zn chlorides by TOPO was systematically investigated.

The maximum extraction of Zn chloride with 0.1 M TOPO decreases in the order: acetone > methanol > ethanol > 2-propanol > 2-butanol. For alcohols, the sequence of decreasing extractability is thus parallel to the order of their dielectric constants. This can be explained by the increase of HCl extraction by TOPO in the same direction. The presence of additives in the polar phase prevents the formation of a bulky white precipitate encountered during extraction of ZnCl₂ from pure aqueous solutions.

A decrease of Cd chloride extraction was generally noticed in presence of additives; this is more noticeable for the longer chain alcohols.

The highest separation factor (E) for ZnCl₂ and CdCl₂ in 0.48M HCl is obtained from 30% methanol (13.8 compared to about 3.8 in absence of methanol) and from 10-20% acetone where it reaches 30.

INTRODUCTION

Solvent extraction with tri-n-octylphosphine oxide (TOPO), from aqueous acidic solutions was reviewed by White and Ross. It was reported that a bulky white precipitate forms in zinc chloride-TOPO system during the extraction of 0.015M ZnCl₂ with 0.1M TOPO at >2M
HG1: In the present work, it has been found that such precipitate disappears in presence of organic additives such as water-miscible alcohols and acetone, thus demonstrating the favourable use of mixed aqueous-organic media instead of the pure aqueous medium. Since cadmium co-exists with zinc almost always in the concentrates of the latter, it seemed interesting to carry out a systematic study on the extraction and separation of the two metal chlorides by TOPO from mixed media. The physical chemistry of such systems was described by Corington and Dickinson (2). Liquid-liquid extraction from such media was introduced in 1967 (3) and extended in 1975 (4). Since that time many papers have been published on this field which was reviewed by Hala in 1977 and 1981 (5,6) and by Sukle and Subramanian in 1981 (7). Hala and Coworkers found that the organic additives influence the shape of extraction curves in case of extraction by tri-n-butyl-phosphate(TBP) (8,9). In 1987 a systematic study was published on thorium extraction from mixed organic-aqueous nitric acid media by TOPO (10).

EXPERIMENTAL

Reagents:

Solutions of ZnCl₂ and CdCl₂, both 0.1M, were prepared by dissolving the appropriate weight of the salts (Riedel de Haen, RDH, AG, Seelze Hanover, Germany) in distilled water and then completing to 1 liter by distilled water.

A 0.1M solution of EDTA (disodium salt of ethylene diamine tetraacetic acid) was prepared by dissolving exactly 7.444 g of EDTA (BDH) in distilled water and completing the solution to 2 liters by distilled water. The indicator was prepared by mixing 0.3 g Eriochrome black T with 100g of high purity (AR) sodium chloride salt, homogenization of the mixture through grinding in a mortar and keeping dry in tightly stoppered bottle. Under these conditions the indicator remains stable for quite longer periods of time.

Buffer 10 solution was prepared by carefully mixing together 568 ml concentrated ammonia and 70 grams solid NH₄Cl, dissolution both in distilled water and completing to 1 liter by distilled water. Both the two reagents used were AR grade from BDH.

Other reagents such as acids, etc. were highest purity available in this laboratory.
Radiozinc tracer

The isotope Zn-65 was prepared by dissolving ~50 mg of irradiated zinc metal in concentrated hydrochloric acid and dilution to 2M HCl with distilled water.

Organic Reagents

TOPO: (Tri-n-octylphosphine oxide), pure (RDH).
Cyclohexane was of an analytical grade reagent from RDH (min 99.5%).

Water-miscible organic additives: Methanol, reagent grade (RDH), ethanol, absolute (reinst from MERCK), 2-propanol 99% from Koch-Light laboratories Ltd., Colubrock Berbs, England, 2-butanol and acetone, 99.5% analytical reagent from BDH.

Extraction Procedure

The polar phases (5 ml each) were prepared by mixing the appropriate volumes of the various reagents in 100 ml conical flasks having tight glass stoppers. Equal volumes of the organic phases were then introduced to the flasks. The two phases were then mixed on a "Gallenkamp" mechanical shaker for 40 minutes at room temperature (25±4°C); preliminary experiments have shown that this time is sufficient for reaching extraction equilibrium and that changes of temperature within the given range have negligible effects on extraction. The contents were then transferred to 150 ml pear shaped separatory funnels to separate the phases. The lower phases (polar phases) were discarded, 5 ml of buffer 10 were transferred to each organic phase that has been taken into another similar and clean conical flask and the two phases were subsequently mixed as before. The contents of the flasks were then transferred to separatory funnels as those used in the first extraction step, the phases separated and each polar phase was taken into a clean 500 ml conical flask for analysis of zinc or cadmium, using complexometric titration with 0.01M EDTA.

Each polar phase from the reextraction step with buffer 10 was diluted with 50 ml distilled water, a small amount of Erichrome black T indicator was then added to the solution, whereby the colour of the solution becomes light pink. Titration was then performed by adding EDTA solution using an automatic burette. The end point was indicated by a colour change from pink to blue.
The distribution ratio (D) can be evaluated as the ratio of the metal concentration in the organic phase (C_{org}) to its concentration in the polar phase. The percentage extraction (E%) was calculated with the help of the relation.

\[
E\% = \frac{C_{org} \times 100}{C_{original}} = \frac{100}{1 + D}
\]

The metal concentration in the polar phase was calculated as the difference between initial metal concentration and its concentration in the organic phase (that was stripped by a buffer 10 solution). However, a second extraction or stripping step was sometimes applied to check the completeness of extraction or stripping. The D values for zinc were also determined using the radioactive tracer technique as described before (11). The D values determined by the radioactive tracer technique were very close to the corresponding values obtained from titration with EDTA.

RESULTS AND DISCUSSION

Extraction of ZnCl\textsubscript{2} with 0.1M TOPO

Fig.(1), shows the effect of hydrochloric acid concentration on the extraction percent (E%) of zinc chloride (0.02M initial concentration) for distribution between the polar phase containing 20% (V/V) of a water-miscible alcohol or acetone and the organic phase (0.1M TOPO in cyclohexane).

It can be noticed from Fig.(1), that the percentage extraction of zinc increases with the increase of hydrochloric acid concentration till a certain molarity beyond which extraction decreases with acidity except for the propanol and butanol systems. The maximum extractability decreases in the order:

Acetone > methanol > ethanol > 2-propanol > 2-butanol.

For acetone, for example, Zn extraction reaches 95%. In case of alcohols the sequence of decreasing extractability is parallel to the order of the values of the dielectric constant of these alcohols (32.7, 24.6, 19.9 and 16.6, respectively), which decreases with increase of the chain length of the alcohol.

The decrease of extractability of zinc with the decrease of the polarity of the alcohol (decrease of the value of the dielectric constant), can be explained to be the result of the increase of hydrochloric acid extraction by TOPO in the same direction. Such extraction takes place as follows:
The addition of a low-polarity organic substance to the polar phase enhances the association of H\(^+\) and Cl\(^-\) ions and hence promotes acid extraction. This view is supported by the fact that the extraction of zinc decreases with the increase of hydrochloric acid concentration beyond a certain acidity in absence of additives or in their presence except in case of 2-butanol. Thus it has been shown that zinc is extracted with neutral organophosphorous solvents such as tri-n-butyl phosphate (TBP) and TOPO according to the following reaction (5):

\[
\text{Zn}^{2+} + 2\text{Cl}^- + 2S \leftrightarrow \text{ZnCl}_2 . 2S,
\]

where S stands for TBP or TOPO. From the above relation it follows that the distribution ratio (D) is given by:

\[
D = \frac{K[\text{Cl}^-]^2 [S]^2}{1 + \sum \beta_j [\text{Cl}^-]^j}
\]

where,

- \(K\) is the equilibrium constant.
- \(\beta_j\) is the stability constant of (ZnCl\(_2\))\(^{2-j}\).

Fig. (2). Shows the extraction behaviour of Zn in presence of 40% additives in the polar phase.

The maximum and minimum on the methanol curve are less prominent here.

**Extraction of CdCl\(_2\) with 0.1M TOPO and separation from ZnCl\(_2\)**

In this section the extraction data of zinc and cadmium are contrasted at constant hydrochloric acid concentration and varying additives percent in the polar phase.

In Fig.(3) is shown the effect of methanol content on the percentage extraction of 0.02M ZnCl\(_2\) and 0.02M CdCl\(_2\) at a constant initial hydrochloric acid concentration of 0.48M, using 0.1M TOPO in cyclohexane as the organic phase. It can be shown that the separation factor for zinc and cadmium (\(e_i\)) is given by the following equation:
\[
    \varepsilon = \frac{D_{\text{Zn}}}{D_{\text{Cd}}} = \frac{E_{\text{Zn}} (100-E_{\text{Cd}})}{E_{\text{Cd}} (100-E_{\text{Zn}})}
\]

Thus the highest \( \varepsilon \) value is obtained clearly at 30% methanol and is evaluated from the given data to be about 13.8 compared to about 3.8 in the absence of methanol.

The effect of the ethanol content at similar conditions is shown in Fig.4. Best separation of the two metallic species can clearly be achieved in the presence of 20% ethanol in the polar phase.

The presence of 2-propanol in the polar phase leads to a considerable decrease of the extraction of both ZnCl\(_2\) and CdCl\(_2\) from 0.48M HCl (Fig.5), although the extraction curve for the latter chloride exhibits a maximum at 40% propanol. Only at this propanol content the extraction of CdCl\(_2\) at the given acidity exceeds that of ZnCl\(_2\).

Like the propanol system, the extraction decreases at 0.48M HCl with the butanol content in the polar phase (Fig.6). The separation of the two metallic species is less effective in presence of this alcohol.

The results of the effect of the acetone content in the polar phase on the extraction of ZnCl\(_2\) and CdCl\(_2\) are shown in Fig.7. A separation improvement can clearly be realized upon introducing 10-20% acetone to the polar phase. Thus while the separation factor is 3.8 for the pure aqueous system, it rises to above 30 in presence of 10-20 acetone in the polar phase.

The present work shows many advantages of using aqueous organic media instead of the strictly aqueous medium. The discussion of the mechanism of extraction from mixed media has been reported by many authors (3-6).
References


**Figures Captions**

Fig.1. Effect of HCl concentration on extraction of ZnCl$_2$ by 0.1M TOPO in presence of 20% additives.  
(1) Water, (2) Acetone, (3) Methanol,  

Fig.2. Effect of HCl concentration on extraction of ZnCl$_2$ by 0.1M TOPO in presence of 40% additives.  
(1) Water, (2) Acetone, (3) Methanol,  

Fig.3. Effect of methanol content on extraction of ZnCl$_2$ and CdCl$_2$ from 0.48M HCl by 0.1M TOPO.  
(1) ZnCl$_2$, (2) CdCl$_2$

Fig.4. Effect of ethanol content on extraction of ZnCl$_2$ and CdCl$_2$ from 0.48M HCl by 0.1M TOPO.  
(1) ZnCl$_2$, (2) CdCl$_2$

Fig.5. Effect of 2-propanol content on extraction of ZnCl$_2$ and CdCl$_2$ from 0.48M HCl by 0.1M TOPO.  
(1) ZnCl$_2$, (2) CdCl$_2$

Fig.6. Effect of 2-butanol content on extraction of ZnCl$_2$ and CdCl$_2$ from 0.48M HCl by 0.1M TOPO.  
(1) ZnCl$_2$, (2) CdCl$_2$

Fig.7. Effect of acetone content on extraction of ZnCl$_2$ and CdCl$_2$ from 0.48M HCl by 0.1M TOPO.