

## Organophosphorus reagents as extractants: Part 2—Synergic effect of triphenylphosphine oxide on the extraction of Co(II)/Zn(II) from binary mixtures with Cr(III), Ag(I), Hg(II), Mg(II) or Al(III) using 8-hydroxyquinoline

Tarlok S Lobana\* & Pushvinder K Bhatia

Department of Chemistry, Guru Nanak Dev University,  
Amritsar 143 005

Received 3 November 1989;  
revised and accepted 5 January 1990

Suitable combinations of 8-hydroxyquinoline (HQ) and triphenylphosphine oxide ( $\text{Ph}_3\text{PO}$ ) show synergism of 10-12% in the extraction of Co(II) and Zn(II) compared to the use of HQ alone. At the synergic points, Co(II)/Zn(II) are separated from their binary mixtures with Cr(III), Ag(I), Hg(II), Mg(II) or Al(III). The recovery is 95-97% and the nature of the species is  $\text{CoQ}_2(\text{Ph}_3\text{PO})$  and  $\text{ZnQ}_2(\text{Ph}_3\text{PO})_2$  respectively for Co(II) and Zn(II). The effects of pH of solutions, dilution of the phases and various anions are studied.

Organophosphorus reagents like trioctylphosphine oxide (TOPO) and tributylphosphine oxide (TBPO) have been reported to act as synergists in the extraction of Co(II) or Zn(II) using  $\beta$ -diketones, 1-phenyl-3-methyl-4-(trifluoroacetyl)pyrazol-5-one and 8-hydroxyquinoline<sup>1-8</sup>. However, separations of Co(II) or Zn(II) from binary or ternary mixtures have not been attempted. Since the aryl substituents show higher extractions<sup>9</sup>, we decided to use  $\text{Ph}_3\text{PO}$  along with HQ for liquid-liquid extraction studies of Co(II) and Zn(II).

### Experimental

Stock solutions of HQ(0.1 M) and  $\text{Ph}_3\text{PO}$ <sup>10</sup> (0.2 M) were made in  $\text{CHCl}_3$ ; those of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.01 M) and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (0.01 M) were made in water. For studying the effect of other metal ions, solutions of different molarities were prepared. Each solution was standardised using 0.01 M EDTA with xylenol orange as the indicator<sup>11</sup>. A stock solution of *o*-phenanthroline (0.05 M) was also prepared. All the solvents and materials were of reagent grade and purified before use.

### Procedure for extraction

*With HQ:* To a 0.01 M solution of  $\text{Co}^{2+}$  (1 ml), 4 ml of distilled water was added and the resulting mixture

was equilibrated (15 min) with 5 ml of HQ. For the  $\text{Zn}^{2+}$  system, the quantities used were: 1 ml of 0.01 M  $\text{Zn}^{2+}$  solution, 7 ml of distilled water, 5 ml of HQ and 3 ml of *o*-phenanthroline (*o*-phenanthroline avoids precipitation of HQ as its hydrate in  $\text{CHCl}_3$  layer). The metal contents were determined from the organic and aqueous layers. For the organic layer, stripping with 1 ml of conc. HCl and 5 ml of distilled water transferred the metal ions to the aqueous phase.

*With  $\text{Ph}_3\text{PO}$ :* Co(II) showed no extraction, while for Zn(II) the procedure was the same as above except that no addition of *o*-phenanthroline was required.

*With  $\text{Ph}_3\text{PO}$  and HQ:* The following solutions were used: (i)  $\text{Co}^{2+}$  (1 ml), HQ (5 ml),  $\text{Ph}_3\text{PO}$  (5 ml) and distilled water (9 ml) (ii)  $\text{Zn}^{2+}$  (1 ml), HQ (5 ml),  $\text{Ph}_3\text{PO}$  (5 ml), *o*-phenanthroline (3 ml) and distilled water (12 ml). Rest of the procedure was the same as indicated above. For the separation of Co(II)/Zn(II) from binary mixtures, the volumes used were: (i)  $\text{Co}^{2+}$  solution (1 ml), metal salt solution (1 ml), HQ (5 ml, 0.09 M),  $\text{Ph}_3\text{PO}$  (5 ml, 0.05 M), distilled water (9 ml).

(ii)  $\text{Zn}^{2+}$  solution (1 ml), metal salt solution (1 ml), HQ (5 ml, 0.09 M),  $\text{Ph}_3\text{PO}$  (5 ml, 0.01 M), *o*-phen (3 ml) and distilled water (12 ml).

Co(II) was estimated spectrophotometrically using sodium N, N-diethyldithiocarbamate<sup>12</sup>; Zn(II) by EDTA<sup>11</sup>, Hg(II) and Ag(I) by  $\text{KSCN}$ <sup>11</sup> and other metal ions by 0.1 M EDTA (xylenol orange indicator)<sup>11</sup>.

The distribution coefficient ( $K_d$ ) was calculated using the relation:

$$K_d = \frac{\text{Amount of Co(II)/Zn(II) in organic layer per ml}}{\text{Amount of Co(II)/Zn(II) in aqueous layer per ml}}$$

### Results and discussion

The extraction of Co(II)/Zn(II) into  $\text{CHCl}_3$  by HQ increased with the increase in molarity of HQ [for Co(II), increase in [HQ] from 0.01 to 0.10 M increased % E from 11.7 to 97.4 and  $K_d$  from 0.13 to 32.63; for Zn(II), increase in [HQ] from 0.01 to 0.15 M increased % E from 14.9 to 96.3 and  $K_d$  from 0.17 to 25.75]. From the plots of  $\log K_d$  versus  $\log [\text{HQ}]$ , the nature of the extracted species was found to be  $\text{CoQ}_2$  in the 0.09-0.10 M concentration range and  $\text{ZnQ}_2 \cdot \text{HQ}$  in 0.09-0.15 M concentration range.

There was no extraction of Co(II) with  $\text{Ph}_3\text{PO}$  under the experimental conditions, while Zn(II) showed poor extraction (~40% at 0.2 M  $\text{Ph}_3\text{PO}$ ) ( $\text{Ph}_3\text{PO}$ , 0.05-0.20 M;  $K_d$ , 0.07 to 0.67; %E, 6.7-39.9). The nat-

ure of the species was found to be  $ZnSO_4(Ph_3PO)_2$  on the basis of  $\log K_d$  versus  $\log[Ph_3PO]$  plot. Due to the unequal sizes of P and O in PO, the  $\pi$ -bonding is weak and thus greater charge density concentration on oxygen enhances its affinity for relatively softer Zn(II) as compared to Co(II).

Significantly, when a combination of 0.09M HQ and 0.05M  $Ph_3PO$  was used, Co(II) showed 97.5% extraction, registering a synergism of 10% (for 0.09M HQ alone, % E was 86.9) (Table 1). Whereas increase in concentration of HQ from 0.080 to 0.090M led to an increase in the extraction of Co(II), there was no effect on the extraction of Co(II) when concentration of  $Ph_3PO$  was varied in the vicinity of 0.05M at constant HQ concentration (0.09M). The nature of the extracted species is believed to be  $CoQ_2(Ph_3PO)$ .

Table 1-- Extraction of Co(II)/Zn(II) into  $CHCl_3$  by the synergic combination (HQ +  $Ph_3PO$ )  
[pH of the aqueous phase = 6.0]

Co(II) <sup>a</sup> : Keeping [ $Ph_3PO$ ] constant at 0.05 M		
[HQ] (M)	$K_d$	%E
0.080	7.90	88.6
0.082	8.98	89.9
0.084	11.27	91.7
0.086	14.47	93.2
0.088	23.54	95.9
0.090	32.63	97.5
Zn(II) (i): Keeping [ $Ph_3PO$ ] constant at 0.01M		
0.080	6.62	86.9
0.082	7.56	88.0
0.084	8.57	89.3
0.086	10.03	90.6
0.088	15.25	93.4
0.089	17.60	94.5
0.090	19.38	95.0
0.091	31.60	98.5
0.092	92.25	98.9
Zn(II) (ii): Keeping [HQ] constant at 0.09M		
0.0090	5.35	83.6
0.0092	5.49	84.0
0.0094	6.00	85.5
0.0096	6.31	86.0
0.0098	9.67	90.3
0.0099	13.10	92.4
0.01	19.37	95.2

(a) Variation of  $Ph_3PO$  concentration in the vicinity of 0.05M caused no effect on extraction.

In the extraction of Zn(II), a combination of HQ (0.09M) and  $Ph_3PO$  (0.01M) showed synergism of about 12% (% E, 95.0). There was no measurable extraction of Zn(II) with 0.01M  $Ph_3PO$  when used alone, and extraction with HQ (0.09M) alone was 83.6%. The nature of the species is suggested to be  $ZnQ_2(Ph_3PO)_2$ . The higher slopes of 2.5 for HQ (at constant concentration of  $Ph_3PO$ ) and 3 for  $Ph_3PO$  (at constant HQ concentration) might be due to the presence of the excess reagents in the organic phase.

Co(II)/Zn(II) was separated from the binary mixtures M(II)-Cr(III), M(II)-Mg(II), M(II)-Al(III), M(II)-Ag(I) and M(II)-Hg(II) (M = Co, Zn) at the synergic points using combinations of 0.09M HQ and 0.05M  $Ph_3PO$  for Co(II) and 0.09M HQ and 0.01M  $Ph_3PO$  for Zn(II). On adding the following salts (mg/ml), the  $K_d$  and % E values (single extraction) for Co(II) and Zn(II) were found to be ~32 (~97) and ~19 (~95) respectively:  $CrCl_3 \cdot 6H_2O$  (5.20);  $MgSO_4 \cdot 7H_2O$  (2.43);  $AlCl_3 \cdot 6H_2O$  (5.38);  $AgNO_3$  (10.78) and  $HgCl_2$  (20.06). Co(II) interfered in the extraction of Zn(II) and vice-versa; a ten-fold increase in the concentration of the metal salt added had the same effect. The extraction became quantitative when slightly higher HQ concentration (i.e. 0.092M) was used. Hg(II) and Ag(I) got transferred to the organic layer alongwith Co(II)/Zn(II). The stripping of the organic layer with conc. HCl released Co(II) to the aqueous phase, while Hg(II)/Ag(I) remained in the organic phase. Further stripping of the organic layer with conc.  $HNO_3$  facilitated release of Hg(II)/Ag(I) to the aqueous layer.

The anions tested ( $NO_3^-$ ,  $CH_3COO^-$ ,  $SO_4^{2-}$  and  $Cl^-$ ) caused no interference. Further, there was no effect of dilution on the extraction, even when organic to aqueous phase ratio was 1:80. The extraction was maximum in the pH range 4.0-10.0 and poor at pH = 2.0 [22.4%, Co(II); 15.3%, Zn(II)]. Here the pH of the solution was varied by using Robinson-Britton buffer ( $CH_3COOH-NaOH$ ).

#### Acknowledgement

Financial assistance from the CSIR, New Delhi (Scheme No. 1(1095/87-EMR.II) and research facilities to (PVKB) by the Guru Nanak Dev University, Amritsar are gratefully acknowledged.

#### References

- 1 Wang S M & Li N C, *J inorg nucl Chem*, 31 (1969) 755.
- 2 Wang S M & Walker W R, *J inorg nucl Chem*, 28 (1966) 875.
- 3 Casey R J & Faraday M, *J inorg nucl Chem*, 29 (1967) 1139.
- 4 Walker W R & Farrell M S, *J inorg nucl Chem*, 28 (1966) 1485.
- 5 Shigematsu T, *Bull chem Soc Japan*, 43 (1970) 793.
- 6 Umetani S, Matsui M, Kuzunishi T & Nishikawa Y, *Bull Inst Chem Res, Kyoto Univ*, 60 (1982) 254; *Chem Abstr*, 129940j (1983).

## NOTES

- 7 Shigematsu T, *Bull Inst Chem Res, Kyoto Univ*, 45 (1967) 2908; *Chem Abstr*, 69 (1968) 70584s.
- 8 Akawa H & Kawamoto H, *Nippon Kagaku Zasshi*, 92 (1971) 1156; *Chem Abstr*, 76 (1972) 104508g.
- 9 (a) Lobana T S & Sandhu S S, *Coord Chem Rev*, 42 (1982) 283.  
(b) Lobana T S & Bhatia P V K, *Indian J Chem*, 29A (1990) 93.
- 10 Lobana T S, *Nat Acad Sci Lett (Allahabad)*, 8 (1985) 271; *Chem Abstr*, 106 (1987) 196510r.
- 11 Basette J, Denny R C, Jeffery G H & Mendham J, *Vogel's text book of quantitative inorganic analysis ELBS and Longman, London* 1978, 265.
- 12 Sandell E B & Onishi H (eds), *Photometric determination of traces of metal*, Vol. 3, Part 1, 4th Edn (John Wiley, NY) 1978, 420.