J. Serb. Chem. Soc. 67 (1) 41–51(2002)
JSCS – 2922

UDC 546.56,546.47:66.061+620.168.3
Original scientific paper

Extraction and separation studies of zinc(II) and copper(II) with D2EHPA and PC-88A from perchlorate media

RAJEEV K. SINGH and PURSHOTTAM M. DHADKE*

Department of Chemical Technology, University of Mumbai, Mumbai – 400 019, India

(Received 4 April, revised 17 July 2001)

The extraction behaviours of Zn(II) and Cu(II) from perchlorate media have been investigated using bis-2-ethylhexyl phosphoric acid (D2EHPA) and 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester, (PC-88A) in toluene. The extraction of Zn(II) was found to be quantitative in the pH range 2.5 to 3.0 and 3.0 to 4.0 using 1.0×10^{-1} mol dm^{-3} D2EHPA and 1.0×10^{-2} mol dm^{-3} PC-88A in toluene, respectively, while Cu(II) was extracted quantitatively in the pH range 6.0 to 8.0 and 5.5 to 7.0 with 1.0×10^{-2} mol dm^{-3} and 1.0×10^{-3} mol dm^{-3} D2EHPA and PC-88A in toluene, respectively. Zn(II) was stripped with 4.0 mol dm^{-3} HCl, while Cu(II) with 2.0 mol dm^{-3} H_2SO_4 and 3.0 mol dm^{-3} HNO_3 from the organic phase containing D2EHPA and PC-88A, respectively. The probable extracted species were ascertained by log *D vs*. log [HR] plot to be $ZnR_2 \cdot 2HR$ and $CuR_2 \cdot 2HR$ for both the reagents. These methods were used for the determination of Zn(II) and Cu(II) in real samples. The separation of Zn(II) and Cu(II) were carried out from each other and with associated metals.

Keywords: zinc, copper, D2EHPA, PC-88A, extraction, stripping, separation.

INTRODUCTION

Zinc and copper are essential elements in various biological and enzymatic reactions. Though they form desired constituents of various alloys and pharmaceutical preparations, their larger concentrations in the environment can severely effect aquatic as well as human life. In view of this, the separation and determination of zinc and copper are of great importance.

Numerous extractants, such as tributylphosphate,[1,2] trioctylphosphine oxide,[3,4] tri-*n*-butoxyetylphosphate,[5] (carboxy-2-ethyl)diphenylphosphine oxide,[6] triphenylphosphine oxide,[7] have been used for the liquid-liquid extraction of Zn(II). Extractants such as tributylphosphate,[8] methylisobutyl ketone,[9–11] mesityl oxide,[12,13] and trioctyl phosphine oxide[14] have been reported for the extraction of copper. However, these methods suffer from limitations, such as the use of salting-out agents,[1,4] long extraction periods,[3,5] preequilibration of the organic phase,[5] incomplete extraction[6] and the control of the critical temperature.[8]

* Corresponding author fax: 91 22 4145614.

Bis-2-ethylhexyl phosphoric acid (D2EHPA) and 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester, (PC-88A) have been used in liquid-liquid extraction for the hydrometallurgical processing of various metals. Most of the earlier work related to the extraction of Zn(II) and Cu(II) with D2EHPA and PC-88A were devoted towards studying the distribution equilibria of the metals in extractions from various media.[15,16]

Perchloric acid is a non-complexing media. Also its oxidizing effect, acidic strength and the high solubility of its salts makes perchloric acid a stable reaction media. Hence, it was preferred over other commonly used chloride and nitrate media.[17,18]

The present study considers the extraction of Zn(II) and Cu(II) from perchlorate media with both the extractants, D2EHPA and PC-88A. The proposed methods permit the separation of Zn(II) and Cu(II) from each other and have been successfully employed for the extraction and determination of Zn(II) and Cu(II in pharmaceutical samples.

EXPERIMENTAL

Apparatus

A GBC-911A UV-Visible spectrophotometer and an Elico pH meter with combined glass electrode were used for the absorbance and pH measurements, respectively.

Reagents and chemicals

Stock solutions of Zn(II) and Cu(II) were prepared by dissolving their oxides in perchloric acid. The solutions were standardized[19] and working solutions of lower concentrations were obtained by dilution. The extractants bis-2-ethylhexyl phosphoric acid, D2EHPA, and 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester, PC-88A, obtained from Daihachi Chemical Industries Ltd., Japan, were used for extractions without further purification. All other chemicals used were of analytical reagent grade.

Procedure

The extraction/stripping experiments were performed by shaking the appropriate organic and aqueous solution (10 ml) at an O/A phase ratio of 1 for 20 min. All the distribution equilibria studies were carried out at 25 ºC. The initial concentration of Zn(II) and Cu(II) were maintained at 5 μg/ml and 3 μg/ml, respectively, throughout the experiments (unless otherwise stated) and the metal content in the equilibrated aqueous phase was determined spectrophotometrically by Zincon and PAR methods, whereas the content of metal ions in the organic phase was calculated by mass balance. The distribution coefficient D was calculated as the ratio of the equilibrium concentration of Zn(II) and Cu(II) in the organic phase to that in the aqueous phase.

All experiments were repeated on average three times and the accuracy of the metal concentration in the loaded phase determined by mass balance was checked by complete stripping of the loaded organic phase and analysing the stripped solution.

RESULTS AND DISCUSSION

Effect of pH

The effect of pH on the percentage extraction of Zn(II) and Cu(II) was studied in the pH range of 1 to 14 with D2EHPA and PC-88A in toluene. The extraction of Zn(II) was found to be quantitative in the pH range 2.5 to 3.0 and 3.0 to 4.0 with 1.0×10^{-1} mol dm^{-3} D2EHPA and 1.0×10^{-2} mol dm^{-3} PC-88A in toluene, respectively, while Cu(II) was extracted quantitatively in the pH range 6.0 to 8.0 and 5.5 to 7.0 with 1.0×10^{-2} mol dm^{-3} and 1.0×10^{-3} mol dm^{-3} D2EHPA and PC-88A in toluene, respectively.

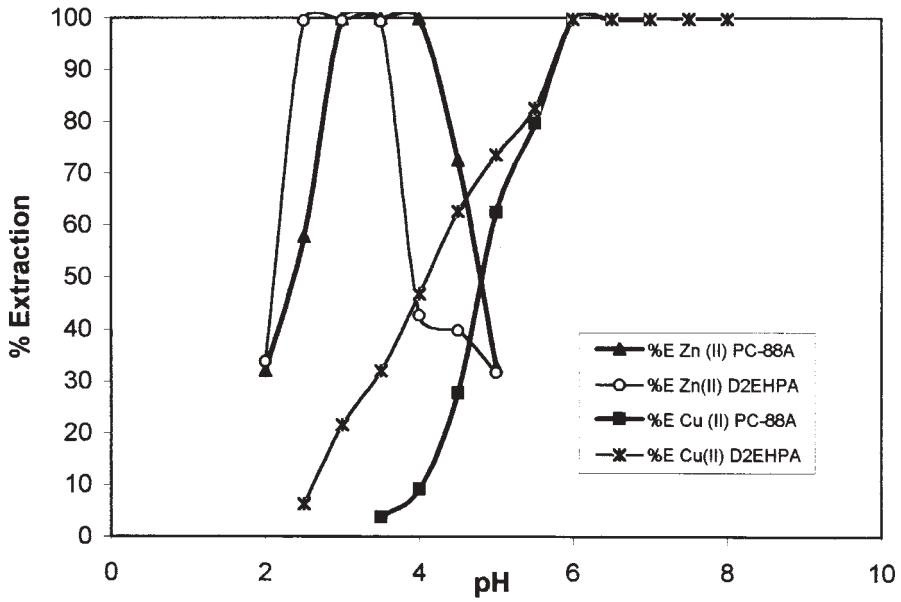

Fig. 1. Effect of pH on the extraction of Zn(II) and Cu(II) with D2EHPA and PC-88A from perchloric acid.

Hence all the extractions of Zn(II) and Cu(II) were carried out at pH 3.0 and pH 6.0 with D2EHPA and PC-88A in toluene, respectively.

Effect of reagent concentration

Extractions of Zn(II) and Cu(II) were also carried out with varying concentration of reagent in the range of 1×10^{-6} to 1×10^{-1} mol dm^{-3} D2EHPA or PC-88A in toluene to optimize the reagent concentration, while other parameters, like pH, period of equilibration, diluent and temperature, were kept constant. Extraction was found to increase with increasing reagent concentration. The extractions of Zn(II) and Cu(II) were quantitative with 1.0×10^{-1} mol dm^{-3} and 1.0×10^{-2} mol dm^{-3} D2EHPA in toluene, respectively, and with 1.0×10^{-2} mol dm^{-3} and 1.0×10^{-3} mol dm^{-3} PC-88A in toluene, respectively.

The reagent concentration required for extraction of Zn(II) and Cu(II) is less with PC-88A as compared to D2EHPA.

Nature of extracted species

The nature of the extracted species was investigated by the slope analysis method. Graphs of log D *vs*. log [D2EHPA/PC-88A] were plotted for Zn (II) and Cu (II) and the slopes were found to be ≈ 2.0 with both the reagens. Therefore, the metal to reagent stoichiometry of the Zn(II): D2EHPA / PC-88A and Cu(II): D2EHPA / PC-88A complexes were 1:2. These results suggest that Zn(II) and Cu(II) were extracted from the perchlorate media as $ZnR_2 \cdot 2HR$ and $CuR_2 \cdot 2HR$ with both the reagents, where HR is the extractant D2EHPA or PC-88A in dimeric form in the organic phase. These ex-

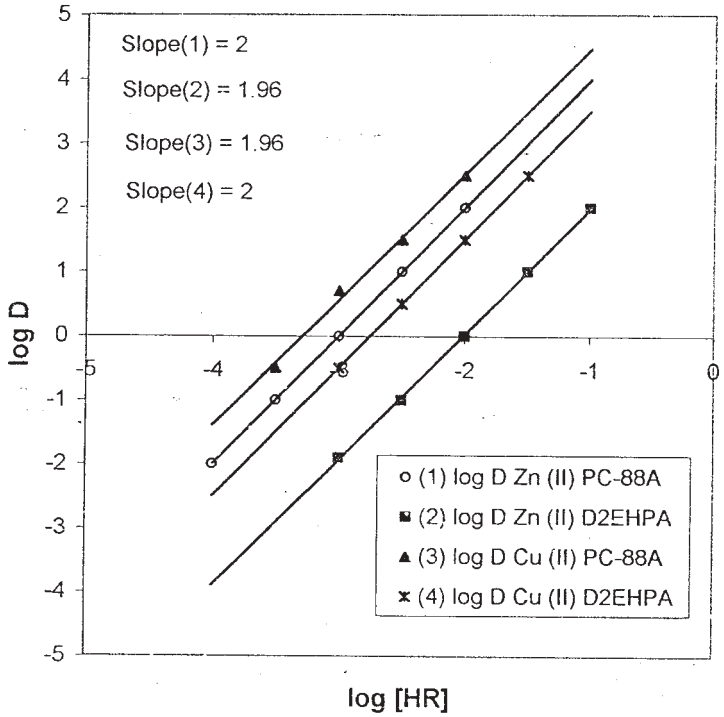

Fig. 2. Stoichiometric ratio of metal to reagent for Zn(II) and Cu(II) with D2EHPA and PC-88A from perchloric acid.

tracted species are in close agreement with those proposed for Zn(II) and Cu(II) from other media with the same reagents.[16]

As only trace amounts of the metal ions were initially present, metal ions initially present in the aqueous phase are at trace levels, it is accepted that there are no polynuclear organic complexes formed when metal ions are extracted with acidic organophosphorus compounds.

Assuming initially that no aqueous counter-ion ligands are involved in the extraction reaction, the probable extracted species for Zn(II) and Cu(II) extraction with D2EHPA and PC-88A can be given as $ZnR_2(HR)_2$and $CuR_2(HR)_2$.

The probable reaction mechanism may be given as:

$$Zn^{2+} + 2(HR)_2 \rightarrow Zn{\cdot}R_2{\cdot}2HR + 2H^+ \quad (1)$$

and

$$Cu^{2+} + 2(HR)_2 \rightarrow Cu{\cdot}R_2{\cdot}2HR + 2H^+ \quad (2)$$

Influence of various diluents

Various aromatic and aliphatic organic diluents, such as toluene, chloroform, carbon tetrachloride, benzene, cyclohexane, *n*-hexane and xylene, were employed for the extrac-

tion of both the metal ions, Zn(II) and Cu(II). It was found that in case of PC-88A the extraction of Zn(II) was quantitative with all the above mentioned diluents, while the extraction of Cu(II) was found to be quantitative only with toluene, benzene and cyclohexane.

TABLE I. Effect of diluents on the percentage extraction of Zn(II) and Cu(II). Aqueous phase: Zn(II) = 5 μg/ml, Cu(II) = 3 μg/ml. Phase ratio: 1 (*i.e.,* 10 ml of aqueous phase : 10 ml of organic phase)

Diluents	Percentage extraction with PC-88A		Percentage extraction with D2HEPA	
	Zn(II)	Cu(II)	Zn(II)	Cu(II)
Toluene	99.7	99.8	99.3	99.6
Xylene	99.7	70.0	86.9	98.5
Chloroform	98.9	67.3	77.9	67.3
Benzene	98.3	99.8	99.3	79.9
Hexane	98.8	70.1	89.9	88.6
Cyclohexane	99.7	99.8	69.9	99.6

Results are the mean of triplicate values

With D2EHPA, the extraction of Zn(II) was quantitative with toluene and benzene, while the extraction of Cu(II) was quantitative with toluene, xylene and cyclohexane. Toluene is preferred as the diluent for both the extractants because of the better phase separation.

Effect of various stripping agents

Zn(II) Cu(II) were stripped out from their loaded organic phases with different strength of acids, such as HCl, HNO_3, H_2SO_4, and bases, such as NaOH and KOH. Zn(II) was stripped with 4.0 mol cm^{-3} HCl while Cu(II) with 2.0 mol dm^{-3} H_2SO_4 and 3.0 mol dm^{-3} HNO_3 from organic phase containing D2EHPA and PC-88A, respectively. The use of other acid strengths did not result in complete stripping.

TABLE II. Effect of the stripping agent on the % recovery of Zn(II) and Cu(II). Aqueous phase: varying concentrations of stripping agents. Organic phase: Zn(II) = 5 μg/ml, Cu(II) = 3 μg/ml in D2EHPA / PC-88A. Phase ratio: 1 (*i.e.,* 10 ml of aqueous phase : 10 ml of organic phase)

Extractants	Acid/Alkali	Percentage recovery							
		Zn(II)/mol dm^{-3}				Cu(II)/mol dm^{-3}			
		1.0	2.0	3.0	4.0	1.0	2.0	3.0	4.0
D2EHPA	HCl	17.6	42.8	56.6	99.3	–	12.3	37.8	43.2
	H_2SO_4	–	11.4	27.6	43.0	46.8	99.6	99.6	99.3
	HNO_3	–	13.6	22.3	40.0	–	6.8	21.9	51.3
	NaOH	–	–	–	–	–	3.1	9.4	9.1
	KOH	–	–	–	–	–	12.8	13.3	13.9
PC-88A	HCl	21.3	51.6	77.1	99.7	–	9.1	21.7	29.3
	H_2SO_4	4.3	18.4	31.6	31.0	–	11.2	27.9	39.7
	HNO_3	–	23.4	42.6	61.8	31.6	61.8	99.4	99.1
	NaOH	–	–	3.2	13.2	–	–	–	–
	KOH	–	–	–	6.4	–	–	–	–

Bases were found to be poor stripping agents as both NaOH and KOH proved to be completely ineffective in stripping Zn(II) from the organic phase of D2EHPA and Cu(II) from PC-88A. A maximum Cu(II) stripping of 9.4 % and 13.9 % from the organic phase containing D2EHPA was observed with 3.0 mol dm^{-3} NaOH and 4.0 mol dm^{-3} KOH, respectively. A maximum of 13.2 % and 6.4 % of Zn(II) was stripped from the organic phase containing PC-88A using 4.0 mol dm^{-3} NaOH and KOH, respectively.

Effect of equilibration time

Zn(II) and Cu(II) were equilibrated with D2EHPA and PC-88A in toluene for periods between 1.0 to 20 min. With PC-88A quantitative extraction for Zn(II) and Cu(II) was found within 4.0 and 3.0 min, respectively, while with D2EHPA 10.0 and 8.0 min were required, respectively. Extraction remained constant up to 20 min.

Effect of temperature

The extractions of Zn(II) and Cu(II) were also studied at different temperatures (303 to 343 K) with D23EHPA and PC-88A in toluene. It was observed that increasing the temperature did not have any effect on the percentage extraction of these metal ions. This unusual behavior may probably be attributed to strong metal–extractant complexes which remain stable even at such elevated temperatures.

Hence all the extractions were carried out at room temperature.

TABLE III. Effect of temperature on the perecentage extraction of Zn(II) and Cu(II). Aqueous phase: Zn(II) = 5 μg/ml , Cu(II) = 3 μg/ml. Organic phase: D2EHPA and PC-88A. Phase ratio: 1 (*i.e.,* 10 ml of aqueous phase : 10 ml of organic phase)

Temperature K	Copper(II)		Zinc(II)	
	D2EHPA	PC-88A	D2EHPA	PC-88A
303	99.6	99.8	99.3	99.7
313	99.6	99.8	99.3	99.7
323	99.6	99.8	99.3	99.7
333	99.6	99.8	99.3	99.7
343	99.6	99.8	99.3	99.7

Effect of diverse ions

The effects of various diverse ions on the extraction of Zn(II) and Cu(II) were studied with both the reagents, D2EHPA and PC-88A in toluene. The tolerance limit of individual foreign ions was set so that the error in percentage recovery was not more than ±2 %. Co(II) and Mn(II) interfere seriously in the extraction of Zn(II) while Co(II), Pd(II) and Al(III) interfere in the extraction of Cu(II) by the proposed method.

Separation of Zn(II) from Cu(II)

The separation of Zn(II) and Cu(II) can be achieved by taking advantage of the difference in the extraction and stripping conditions.

In order to separate Zn(II) and Cu(II), the aqueous solution containing these metal ions was extracted with 1.0×10^{-2} mol dm^{-3} PC-88A in toluene at pH 3.0. At this pH only Zn(II) is extracted into the organic phase, whereas Cu(II) remained unextracted

in the aqueous phase and was hence separated. The Zn(II) was stripped from organic phase using 4.0 mol dm^{-3} HCl and determined spectrophotometrically.

TABLE IV. Effect of various diverse ions on the extraction of Zn(II) [5 μg/ml]

Metal ions	D2EHPA Tolerance limit (ion ratio)	PC-88A Tolerance limit (ion ratio)
Mg(II), Al(II), citrate and chloride	1 : 35	1 : 40
Cr(VI), iodide, fluoride	1 : 18	1 : 25
Ag(I), Ba(II), Ca(II), Fe(III), Sb(III), Se(IV), oxalate and nitrate	1 : 15	1 : 20
Sn(IV), Bi(III), Mo(VI), W(VI), ascorbate	1 : 10	1 : 15
Te(IV), Ti(IV), Zr(IV), Hf(IV), Nb(V)	1 : 6	1 : 10
Pb(II), Cu(II), V(V)	1 : 2	1 : 5
Co(II) and Mn(II)	1 : 0	1 : 0

TABLE V. Effect of various diverse ions on the extraction of Cu(II) [3 μg/ml]

Metal ions	Tolerance limit [D2EHPA] (ion ratio)	Tolerance limit [PC-88A](ion ratio)
Mg(II), Ag(I), Sb(III), Pt(IV), tartarate, thiourea, phosphate bromides, sulphate, iodide, nitrate and chloride	1 : 45	1 : 50
Pb(II), Ni(II), Zn(II), Sn(IV), Mo(VI) and thiocynate	1 : 28	1 : 33
Hg(II), Cd(II), As(III), Au(III) and Cr(VI)	1 : 11	1 : 16
U(VI) and Mn(II)	1 : 6	1 : 8
Fe(III) and Ce(IV)	1 : 3	1 : 3
Bi(III), V(V)	1 : 1	1 : 1
Co(II), Pd(II) and Al(III)	1 : 0	1 : 0

The separation efficiency of D2EHPA in toluene for separating Zn(II) from Cu(II) was also compared with this method. An aqueous solution containing these metal ions was equilibrated with 1.0×10^{-1} M D2EHPA at pH 3.0. It was observed that Cu(II) (6.30 %) is coextracted along with Zn(II) into the organic phase. The organic phase was first stripped with 4.0 mol dm^{-3} HCl to obtain Zn(II) and then with 2.0 mol dm^{-3} H_2SO_4 to obtain Cu(II).

Separation of Zn(II) and Cu(II) from associated metals

Zn(II) and Cu(II) were separated from commonly associated metal ions by taking advantage of the difference in the extraction and stripping conditions.

TABLE VI. Separation of Zn(II) and Cu(II) from multi component mixtures. Organic phase: PC-88A in toluene. Aqueous phase: appropriate concentration of metal ion in 10 ml of aqueous phase. Phase ratio: 1

No.	Mixture	Amount μg/10 ml	pH	Extractant mol dm^{-3}	Stripping agent mol dm^{-3}	% Recovery
1	Fe(III)	25.0	1.0	0.005	1.0 H_2SO_4	98.1
	Zn(II)	50.0	3.0	0.001	4.0 HCl	99.7
2	Zn(II)	50.0	3.0	0.01	4.0 HCl	99.7

TABLE VI Contd.

No.	Mixture	Amount μg/10 ml	pH	Extractant mol dm^{-3}	Stripping agent mol dm^{-3}	% Recovery
	Pb(II)	25.0	3.0	0.01	1.0 HNO_3	99.4
	Cd(II)	25.0	3.0	Unextracted	Aq. phase	98.6
3	Fe(III)	30.0	1.0	0.005	1.0 H_2SO_4	99.3
	Cu(II)	30.0	3.0	0.001	3.0 HNO_3	99.8
	Cd(II)	25.0	3.0	Unextracted	Aq. phase	98.6
4	Fe(III)	25.0	1.0	0.005	1.0 H_2SO_4	99.4
	Zn(II)	50.0	3.0	0.01	4.0 HCl	99.7
	Cr(VI)	30.0	3.0	Unextracted	Aq. phase	99.3
5	Fe(III)	25.0	1.0	0.005	1.0 H_2SO_4	99.7
	Cu(II)	30.0	6.0	0.001	3.0 HNO_3	99.8
	Ni(II)	25.0	6.0	0.001	2.0 NaOH	99.2

TABLE VII. Separation of Zn(II) Cu(II) from multi component mixtures. Organic phase: D2EHPA in toluene. Aqueous phase: appropriate concentration of metal ion in 10 ml of aqueous phase. Phase ratio: 1

No.	Mixture	Amount μg/10 ml	pH	Extractant mol dm^{-3}	Stripping agent mol dm^{-3}	% Recovery
1	Fe(III)	25.0	1.0	0.05	1.0 H_2SO_4	98.7
	Zn(II)	50.0	3.0	0.1	4.0 HCl	99.3
2	Zn(II)	50.0	3.0	0.1	4.0 HCl	99.3
	Pb(II)	25.0	3.0	0.1	1.0 H_2SO_4	99.4
	Cd(II)	25.0	3.0	Unextracted	Aq. phase	98.6
3	Fe(III)	30.0	1.0	0.05	1.0 HNO_3	99.3
	Cu(II)	30.0	3.0	0.01	2.0 H_2SO_4	99.6
	Cd(II)	25.0	3.0	Unextracted	Aq. phase	98.6
4	Fe(III)	25.0	1.0	0. 05	1.0 HNO_3	99.4
	Zn(II)	50.0	3.0	0.1	4.0 HCl	99.3
	Cr(VI)	30.0	3.0	Unextracted	Aq. phase	99.2
5	Fe(III)	25.0	1.0	0.05	1.0 HNO_3	99.4
	Cu(II)	30.0	6.0	0.01	2.0 H_2SO_4	99.6
	Ni(II)	25.0	6.0	0.01	1.0 HCl	99.2

With PC-88A

A ternary mixture of Fe(III), Zn(II) and Cr(III) was extracted from an aqueous solution at pH 1.0 with 5.0×10^{-3} mol dm^{-3} PC-88A in toluene, whereby Fe(III) is extracted, while Zn(II) and Cr(III) remained unextracted in the aqueous phase. The extracted Fe(II) was stripped with 1.0 mol dm^{-3} H_2SO_4.

The remaining aqueous phase containing Zn(II) and Cr(III) was equilibrated again with 1.0×10^{-2} mol dm^{-3} PC-88A at pH 3.0, whereby Zn(II) is extracted, while

Cr(III) remains unextracted in the aqueous phase. Zn(II) was then stripped with 4.0 mol dm^{-3} HCl and determined spectrophotometrically in the aqueous phase.

With D2EHPA:

A ternary mixture of Fe(III), Ni(II) and Cu(II) was extracted from an aqueous solution at pH 1.0 with 5.0×10^{-3} mol dm^{-3} D2EHPA in toluene, whereby Fe(III) is extracted while NI(II) and Cu(II) remain unextracted in the aqueous phase. The extracted Fe(II) was stripped with 1.0 mol dm^{-3} HNO_3.

The remaining aqueous phase containing Ni(II) and Cu(II) was equilibrated again with 1.0×10^{-2} mol dm^{-3} D2EHPA at pH 6.0, whereby both Ni(II) and Cu(II) are extracted. Cu(II) was stripped from the loaded organic phase with 2.0 mol dm^{-3} H_2SO_4 while NI(II) was stripped from the the organic phase with 1.0 mol dm^{-3} HCl and determined spectrophotometrically.

Determination of Zn(II) and Cu(II) in pharmaceutical sample

The proposed methods using D2EHPA and PC-88A were used for the separation and determination of Zn(II) and Cu(II) in pharmaceutical samples. Nycil powder, (Glaxo India Ltd) and Multivitamin Iron tablets (Meyer Organics India) were used as the pharmaceutical samples.

TABLE VIII. Determination of Zn(II) and Cu(II) in pharmaceutical samples

Sample	PC-88A				D2EHPA			
	Actual	Obs.	% R	R.S.D.	Actual	Obs.	% R	R.S.D.
Nycil powder (Glaxo) [India] Ltd. For Zn(II)	12.7 %	12.67 %	99.8	0.56	12.7 %	12.67 %	99.8	0.44
Multivitamin iron minerals (Meyer organics India). For Cu(II)	0.237[b] (mg)[a]	0.235[b] (mg)[a]	99.1	0.38	0.237[b] (mg)[a]	0.233[b] (mg)[a]	98.3	0.75

[a] Mean of triplicate analysis. [b] Per capsule

CONCLUSION

1. The obtained results indicate that both commercially available phosphorous based extractants bis-2-ethylhexyl phosphoric acid (D2EHPA) and 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (PC-88A) can be successfully used for the quantitative extraction of Zn(II) and Cu(II) from perchloric acid media.

2. The concentration of extractants required for the extraction of 5 μg/ml Zn(II) and 3 μg/ml Cu(II) is very small (1×10^{-2} mol dm^{-3}) as compared to extractants such as TBP (1.0 mol dm^{-3}), benzoylacetone (1 mol dm^{-3}) and cupferron (40 %).

3. The extractions of Zn(II) and Cu(II) from the perchlorate mediuim were observed at lower pH values with low reagent concentration as compared to the commonly used chloride and nitrate media, thereby facilitating the ease of separation of the metal ions from the associated metals.

4. The quantitative extractions of Zn(II) and Cu(II) with both the reagents do not require pre-equilibration of the phases as required with tri-*n*-butoxyethylphosphate.

5. At a constant organic to aqueous phase ratio of one, both the reagents, D2EHPA and PC-88A, extract Zn(II) and Cu(II) quantitatively without the use of salting-out agents as are required when using tributylphosphate or trioctylphosphine oxide.

6. At a constant organic to aqueous phase ratio of one, the extraction of Zn(II) is complete with both the reagents unlike (carboxy-2-ethyl)diphenyl phosphine oxide which extracts only 90 % of the Zn(II).

7. The extractions of Zn(II) and Cu(II) with both the reagents are independent of variations in temperature unlike extractions with tributylphosphate when the extraction efficiency decreases with increasing temperature.

8. Under comparable conditions, the two extractants, PC-88A and D2EHPA, showed similar behaviour in terms of the extraction condition necessary for Zn(II) and Cu(II), as well as for the extraction of various associated metal ions. This may be due to their similar chemical structures. However, among the two, PC-88A has a higher efficiency for the separation of Zn(II) from Cu(II).

Acknowledgements: The authors are thankful to Dai-hachi Chemical Industries, Japan, for supplying working samples of D2EHPA and PC-88A.

NOMENCLATURE

[ ] – concentration

D – Distribution ratio

% E – Percentage extraction

% R – Percentage recovery

aq. – Aqueous phase

org. – Organic phase

И З В О Д

ПРОУЧАВАЊЕ ЕКСТРАКЦИЈЕ И СЕПАРАЦИЈЕ ЦИНКА(II) И БАКРА(II) ПОМОЋУ D2EHPA И PC-88A ИЗ ПЕРХЛОРАТНЕ СРЕДИНЕ

RAJEEV K. SINGH and PURSHOTTAM M. DHADKE*

**Department of Chemical Technology, University of Mumbai, Mumbai – 400 019, India*

Испитивано је понашање Zn(II) и Cu(II) при екстракцији из перхлоратне средине помоћу бис-2-етилхексил фосфорне киселине (D2EHPA) и моно-2-етилхексил естра 2- етилхексил фосфорне киселине (PC-88A) у толуену. Нађено је да је екстракција Zn(II) квантитативна у pH области 2,5 до 3,0 и 3,0 до 4,0 коришћењем $1{,}0\times10^{-1}$ mol dm^{-3} D2EHPA, одн. $1{,}0\times10^{-2}$ mol dm^{-3} PC-88A, респективно. Cu(II) је екстрахован квантитативно у области pH 6,0 до 8,0, одн. 5,5 до 7,0 са $1{,}0\times10^{-1}$ mol dm^{-3} D2EHPA, одн. $1{,}0\times10^{-2}$ mol dm^{-3} PC-88A у толуену, респективно. Из органске фазе која је садржавала D2EHPA и PC-88A Zn(II) је уклањан помоћу 4,0 mol dm^{-3} HCl, а Cu(II) помоћу 2,0 mol dm^{-3} H_2SO_4 и 3,0 mol dm^{-3} HNO_3. На основу log D *vs.* log [HR] дијаграма закључено је да је вероватно да су екстраховане врсте биле $ZnR_2{\cdot}2HR$, одн. $CuR_2{\cdot}2HR$ у оба реагенса. Ове методе су коришћене за одређивање Zn(II) и Cu(II) у реалним узорцима. Изведена је и сепарација Zn(II) од Cu(II), као и од пратећих металних јона.

(Примљено 4. априла, ревидирано 17. јула 2001)

REFERENCES

1. V. M. R. Forrest, D. Scargill, D. R. Spikernell, *J. Inorg. Nucl. Chem.* **31** (1969) 187
2. D. Singh, O. V. Singh, S. N. Tandon, *Anal. Chim. Acta.* **115** (1980) 369
3. M. Matsui, T. Hirade, T. Shigematsu, *Anal. Lett.* **12** (1979) 1385
4. T. Sato, H. Yamatake, *Z. Anorg. Allg. Chem.* **174** (1972) 391
5. M. Halpern, T. Kim, N. C. Li, *J. Inorg. Nucl. Chem.* **24** (1962) 1251
6. J. L. Rocca, M. Porthault, *Anal. Chim. Acta* **55** (1971) 341
7. B. Raman, V. M. Shinde, *Talanta* **36** (1989) 467
8. M. Melnick, H. Frieser, *Anal. Chem.* **27** (1955) 462
9. C. L. Luke, *Anal. Chim. Acta* **39** (1967) 447
10. A. Hioki, N. Fudagawa, M. Kubota, A. Kawase, *Anal. Chim. Acta* **209** (1988) 281
11. M. Aihara, M. Kiboku, *Bunseki Kagaku.* **24** (1975) 447
12. V. M. Shinde, *Indian J. Chem.* **27** (1988) 921
13. G. S. Desai, V. M. Shinde, *Fresenius'Z. Anal. Chem.* **336** (1990) 575
14. I. Janousek, *Hutn. Listy* **37** (1982) 737
15. M. Morters, H. J. Bart, *J. Chem. Eng. Data.* **45** (2000) 82
16. F. Nakashio, K. Kondo, Y. Akiyoshi, *J. Chem. Eng. Japan.* **15** (1982) 4
17. C. F. Baes, R. Zingaro, C. F. Coleman, *J. Phys. Chem.* **62** (1958) 2
18. M. Kunzmann, Z. Kolarik, *Solv. Ext. Ion. Exchange* **10** (1992) 1
19. A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis,* Longmans, London, p. 1961.