

SEPARATION OF COPPER AND ZINC CATIONS FROM EACH OTHER IN AQUEOUS ACID SULPHATE SOLUTION USING TRI-N-BUTYL PHOSPHATE (TBP)

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ABSTRACT

The separation of copper and zinc cations from each other in aqueous acid sulphate solution using tri-n-butyl phosphate was investigated. The effects of the aqueous Zn^{2+} and Cu^{2+} concentrations, organic phase concentration of tri-n-butyl phosphate (TBP), pH and temperature on the degree of extraction of copper and zinc cations were studied. The loading of Copper and Zinc cations from the aqueous phase into the organic phase were pH dependent, a pH of 5 for copper (11) and pH 7 for Zinc (11) appeared to be most favourable. The respective increased concentrations of Cu^{2+} , Zn^{2+} and TBP favored Cu^{2+} and Zn^{2+} extraction. Temperature had little effect. The experimental data suggested that, the separation of Cu^{2+} and Zn^{2+} from each other could be carried out by changing the pH at $32 \pm 2^\circ C$. The separation of Cu^{2+} from Zn^{2+} is most favourable at pH 5, while Zn^{2+} from Cu^{2+} is most favourable at pH 7. The experimental results also indicate that this method of extraction could be employed to obtain up to 90% of each metal ion from the aqueous mixture.

KEYWORDS: extraction, aqueous phase.

INTRODUCTION

Solvent extraction is the most common technique of metal extraction from a solution or aqueous mixture. The separation that can be performed are simple, clean, rapid and convenient. In many cases, separation may be effected by shaking in a separatory funnel for a few minutes (Morrison and Fraiser, 1957). This technique has been employed in the metallurgical industry for many years for broad range of separations. (Zygmunt, 1986) reported the removal of Cd, Cr, Co, Cu, Ni, Mo, V, and Zinc from waste water. Solvent extraction can also be employed in the separation of elements whose chemistry are extremely similar such as actinides, rare earths or members of same periodic table (McKay, 1967). For any separation process to be effective, there must be sufficient differences in the distribution coefficients of the metal ions to be separated (Zygmunt, 1986). Copper and Zinc are transition elements, they form alloys such as brass and bronze. (Hill and Holman, 1995). They are also found in minerals for examples, Rosasite $\{Cu,Zn\}_2 \{CO_3\}\{OH\}_2$ Cuprodescloizite $(Cu, Zn)Pb(VO_4(OH))$, Zincchalcantite $(Zn, Cu)SO_4 \cdot 5H_2O$ and descloizite $(Zn, Cu)Pb(VO_4(OH))$. They are also found as impurities in phlerite (ZnS) and pyrotite (FeS). Ashidi, (1985). In the refining of Zinc, roasted concentrates are dissolved with dilute sulphuric acid to produce a solution containing Zinc sulphates and copper as impurities, the tendency of copper is to be alloyed with Zinc which corrodes the aluminium cathode. (Ritcey and Ashbrook, 1984).

Many works have been carried out on the solvent extraction of copper(II) and Zinc (II) Cations from their aqueous solutions using TBP. (Ipinmoroti 1994), (Fletcher, 1955)

The present article describes the solvent extraction method for the separation of Cu^{2+} and Zn^{2+} from each other.

MATERIALS AND METHOD

All the reagents used were of analytical grade. Tri-n-butyl Phosphate (TBP) (East Angelic Chemicals), $ZnSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$ (BOH), benzene, HCL and NaOH (May and Baker). Copper (II) and Zinc(II) cations in the aqueous phase were determined using atomic absorption spectrometry.

photometer, (Buck scientific 200-A.) pH was measured with a KENT EIL 7020pH meter.

PROCEDURE

Aqueous copper solution (25ml) was pipetted into a clean 250ml separatory funnel, 25ml of TBP in benzene was carefully added. The mixture was manually shaken for two minutes while opening the stop cock intermittently to vent any pressurized air. The mixture was then shaken vigorously for five minutes on a mechanical shaker (criffins) and allowed to stand for 1-2 minutes for the two phases to separate. About 10ml of the aqueous layer was then carefully run into a clean 250ml conical flask and taken for analysis on atomic absorption spectrophotometer. Similar procedure was used for the extraction of Zn^{2+} .

SEPARATION OF Cu^{2+} and Zn^{2+} from each other.

$CuSO_4 \cdot 5H_2O$ (0.04M) was prepared by taking 100ml of 0.1M stock solution in a 250ml using distilled water. $ZnSO_4$ (0.04M) was also prepared by taking 100ml of 0.1M stock solution into 250ml with distilled water. 25cm³ of each of the solutions were taken and transferred into a clean conical flask. The extractions were carried out at pH 5 and pH 7 respectively while 30% v/v TBP in benzene and room temperature of $32 \pm 2^\circ C$ were kept constant.

After adjusting the parameters to the desired levels, the aqueous mixture was transferred into a clean separatory funnel and the extraction carried out as described above.

RESULTS AND DISCUSSION

Effect of pH on extraction

Tables 1a and 1b shows the effect of pH on the extraction of Cu^{2+} and Zn^{2+} respectively. It is observed that the percentage metal extraction increased with increase in pH and appeared to reach a maximum at pH 5 and pH 7 for Cu^{2+} and Zn^{2+} respectively (figures 1A and 1B). The tendency for the degree of metal extraction to fall at high pH has been noticed by several workers (Baird and Hanson 1983), (Ipinmoroti, 1994) (Ipinmoroti, 1993) and this observation has invariably been attributed to the possibility of the metal cation getting hydrolysed at high pH. When the pH is high there is the possibility of the metals forming non-extractable negative ions.

Table 1a: Effects of pH on Cu^{2+} Extraction

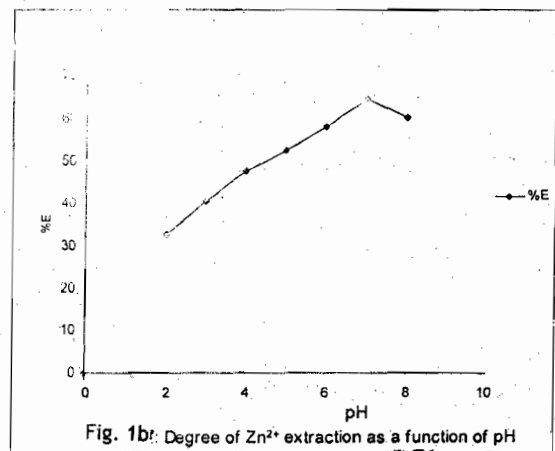
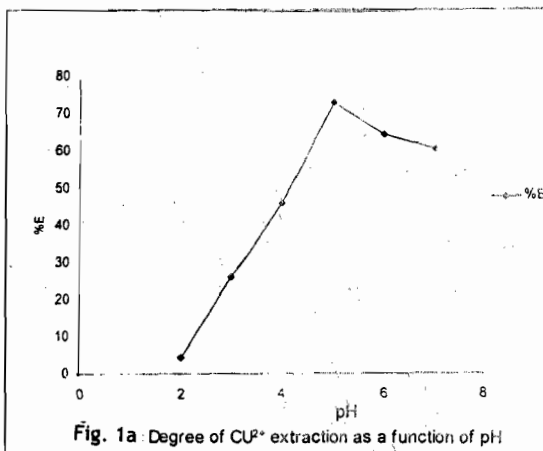
pH	Cu^{2+} (aq) mg/l	Cu^{2+} (TBP) mg/l	% Extraction	D
2.0	2431.90	108.10	4.26	0.04
3.0	1877.30	662.70	26.09	0.35
4.0	1378.90	1161.10	45.71	0.84
5.0	692.80	1847.20	72.72	1.05
6.0	910.10	1629.0	64.17	1.79
7.0	1009.4	1530	60.26	1.52

Temp. $32 \pm 2^\circ\text{C}$. 30% v/v TBP Cu^{2+} 0.04 M, D = distribution ratioTable 1b: Effects of pH on Zn^{2+} Extraction

pH	Zn^{2+} (aq) mg/l	Zn^{2+} (TBP) mg/l	% Extraction	D
2	1296.4	653.6	32.52	0.50
3	1157.9	792.1	40.62	0.68
4	1021.6	928.4	47.61	0.91
5	921.1	1025.6	52.60	1.11
6	817.4	1132.6	58.08	1.39
7	694.8	1255.2	64.37	1.81
8	777.0	1173.0	60.15	1.51

 Zn^{2+} 0.03 MTemp. $32 \pm 2^\circ\text{C}$. 30% v/v TBP in benzene. D = distribution ratio.

FIGURES



At low pH, the organic extractant TBP can also solvate giving rise to the extraction of acids (Ritcey and Ashbrook, 1984). It has been observed that metals appeared to be best extractable at a pH just below that at which they hydrolysed.

Effect of metal ion Concentration on extraction.

When the concentration of the metal ions (Cu^{2+} and Zn^{2+}) in the aqueous phase were varied between 0.01-0.06 mol dm^{-3} (Tables 2A and 2B) the degree of metal extraction increased gradually with increase in aqueous metal concentration. Degree of metal extraction was at maximum at 0.04 mol dm^{-3} and 0.04 mol dm^{-3} for Cu^{2+} and Zn^{2+} respectively and subsequently went down very gradually. (figures 1A and 1B). In a solvent extraction process, an increase in the concentration of metal ion in the aqueous phase will bring about an increase in the degree of metal extracted to compensate and maintain the equilibrium constant, according to Le-Chatelier's principle, provided there is sufficient free extractant available in the solvent to extract more metals (Hanson, 1971). Generally the extraction of metals have been noticed to be most favourable at low metal concentration. (Ipinmoroti, 1994).

Effect of concentration of TBP on extraction.

Tables 3A and 3B shows that the extraction coefficient of Cu^{2+} and Zn^{2+} increased with increased in the extractant concentration in the organic phase. This trend has also been observed for some other metal solvent extraction systems. (Baird and Hanson, 1983), (Ritcey and Ashbrook, 1984). Apart from the extractant being more available for metal, complexing at high concentration, a relatively large concentration of the extractant could also lead to further solvation of the metal-extractant complex by the extractant molecules and this would enhance the solubility of the complex in the organic phase and thus prevent third phase formation. The non-linear increase in the degree of metal extraction with increase in TBP concentration figures. (3A and 3B) might also be due to dimerization or polymerization of the extractant in the inert solvent, benzene, at high concentration as previously observed by many workers (Sekine and Hasegawa, 1977), (Matsuo, et al, 1966) (Jack werth, 1964). (Ipinmoroti 1993).

Table 2a. Effect of Aqueous Concentration of copper on Cu^{2+} Extraction.

Cu^{2+} (M)	Cu^{2+} (aq) mg/l	Cu^{2+} (TBP) mg/l	% Extraction	D
0.01	459.1	175.9	22.70	0.38
0.02	778.1	491.9	38.73	0.63
0.03	965.4	939.6	49.32	0.97
0.04	794.7	1745.3	68.71	2.20
0.05	1621.9	1553.1	48.92	0.96
0.06	2139.2	1678.8	43.97	0.78

Temp. $32 \pm 2^\circ\text{C}$. 30% v/v TBP in benzene

pH 5. D = distribution ratio

Table 2b. Effects of Aqueous Concentration of Zinc on Zn^{2+} Extraction.

Zn^{2+} (M)	Zn^{2+} (aq) mg/l	Zn^{2+} (TBP) mg/l	% Extraction	D
0.01	527.7	122.3	18.82	0.23
0.02	778.6	521.9	40.15	0.67
0.03	693.6	1256.4	64.43	1.81
0.04	1278.0	1322.0	50.85	1.03
0.05	2137.4	1112.6	34.23	0.52
0.06	2643.3	1256.7	32.22	0.48

Temp. $32 \pm 2^\circ\text{C}$ 30% v/v TBP pH 7. D = distribution ratio**Table 3a.** Effect of Concentration of TBP in benzene on Cu^{2+} Extraction.

% v/v TBP in benzene	Cu^{2+} (aq) mg/l	Cu^{2+} (org) mg/l	% Extraction	D
10	1687.2	852.8	33.57	0.51
20	1163.8	1376.2	54.18	1.18
30	690.9	1849.1	72.80	2.68
40	953.6	1587.4	62.46	1.70
50	1150.7	1389.3	54.69	1.21
60	1513.2	1026.8	40.43	0.68

 Cu^{2+} 0.04 MRoom temp. $32 \pm 2^\circ\text{C}$. pH 5

D = distribution Coefficient

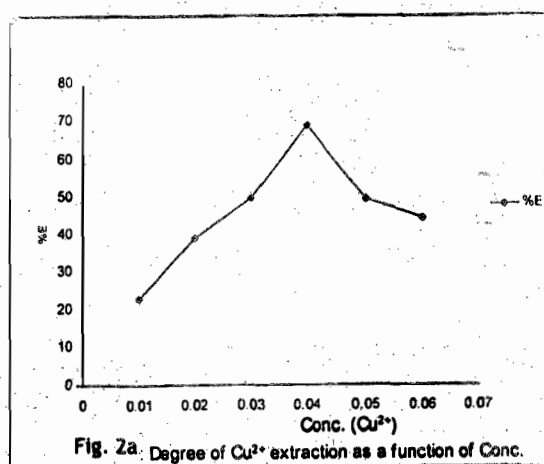
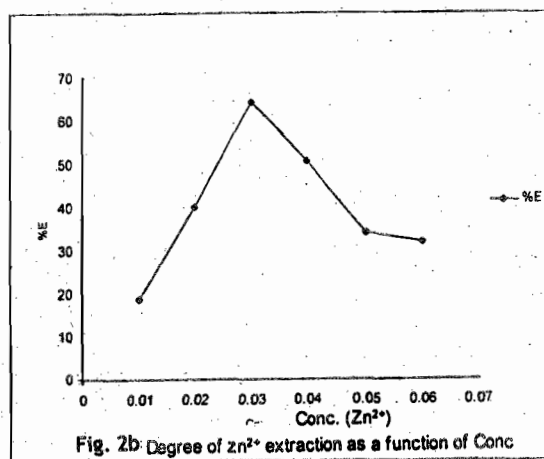
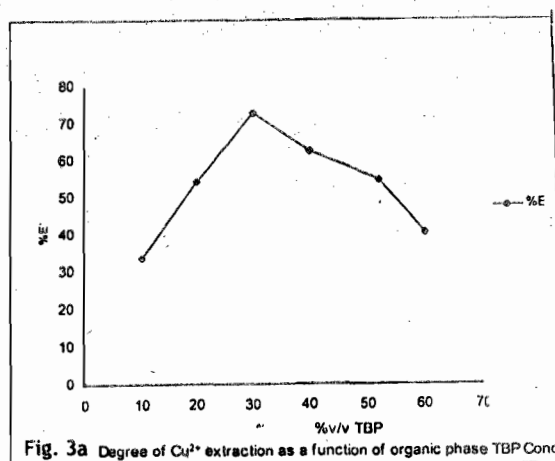
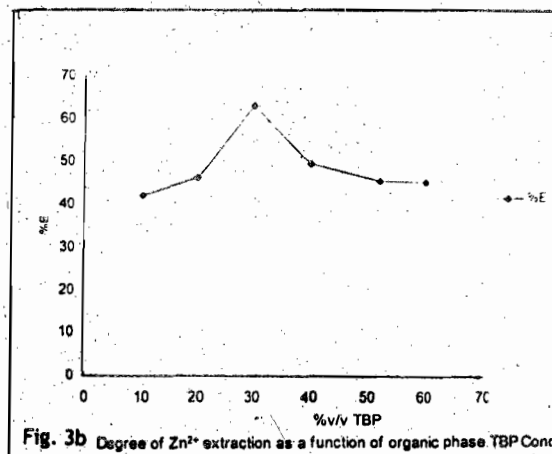
**Fig. 2a.** Degree of Cu^{2+} extraction as a function of Conc.**Fig. 2b.** Degree of Zn^{2+} extraction as a function of Conc.**Fig. 3a.** Degree of Cu^{2+} extraction as a function of organic phase TBP Conc.

Table 3b. Effect of concentration of TBP in benzene on Zn²⁺ Extraction

% v/v TBP	Zn ²⁺ (aq) (mg/l)	Zn ²⁺ (TBP) (mg/l)	% Extraction	D
10	1125.7	824.3	42.27	0.73
20	1047.3	902.7	46.29	0.86
30	719.8	1230.1	63.08	1.71
40	984.1	965.9	49.53	0.98
50	1060.1	889.9	45.63	0.84
60	1066.3	883.7	45.32	0.83

Zn²⁺ 0.03 M Temp. 32 ± 2°C pH7. D = distribution ratio

Fig. 3b Degree of Zn²⁺ extraction as a function of organic phase TBP ConcTable 4a: Effect of temperature on the extraction of Cu²⁺

Temp °C	Cu ²⁺ (aq) (mg/l)	Cu ²⁺ (TBP) (mg/l)	% Extraction	D
10	2060.2	479.8	18.89	0.23
20	1833.9	706.1	27.8	0.39
30	1364.0	1176.0	46.30	0.86
40	703.3	1836.7	72.31	2.61
50	735.5	1804.5	71.04	2.5
60	725.8	1814.2	71.40	2.5

Cu²⁺ 0.04 M

pH 5, 30% v/v TBP in benzene, D = distribution coefficient

Table 4b: Effect of temperature on Zn²⁺ Extraction

Temp °C	Zn ²⁺ (aq) (mg/l)	Zn ²⁺ (TBP) (Mg/l)	% Extraction	D
20	798.6	1151.4	59.05	1.44
30	715.1	1234.9	63.33	1.73
40	835.4	1254.3	64.32	1.80
50	835.4	1114.6	57.16	1.33
60	835.4	1114.6	57.16	1.33
70	835.4	1114.6	57.16	1.33

Zn²⁺ 0.03 M

pH 7, 30% v/v TBP benzene, D = distribution ratio

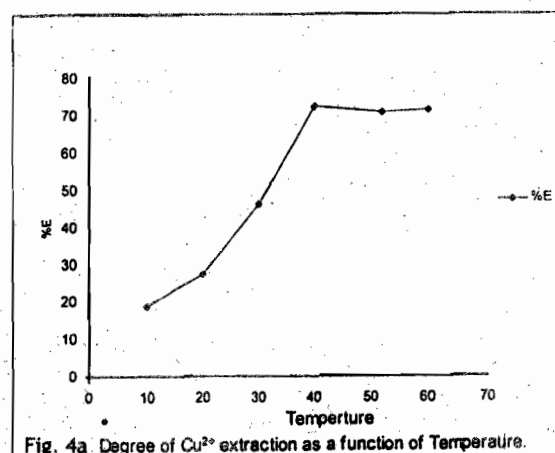
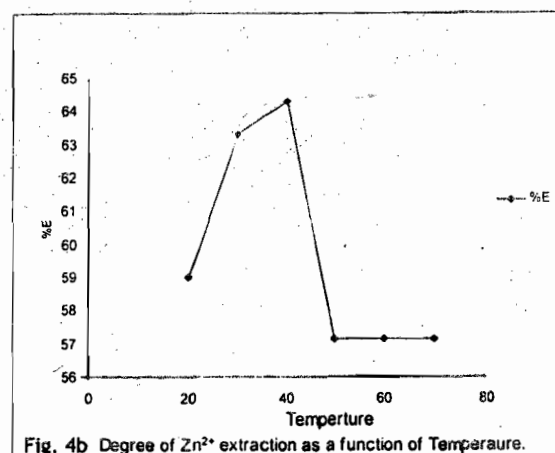
Fig. 4a Degree of Cu²⁺ extraction as a function of Temperature.Fig. 4b Degree of Zn²⁺ extraction as a function of Temperature.

Table 5a: SEPARATION Cu²⁺ from Zn²⁺ At pH 5

	Cu ²⁺	Zn ²⁺
Metal Conc. In aq phase. (mg/l)	1035.3	1754.2
Metal conc. in organic phase (mg/l)	1504.7	845.8
% Extraction	59.24	32.53
D	1.45	0.48

Effect of Temperature on extraction

The effect of temperature on the equilibrium extraction of Cu²⁺ and Zn²⁺ was minimal. Tables 4A and figure 4B shows that a process plant for Zn²⁺ extraction based on TBP might be run at room temperature. This would save energy and consequently lower the production cost. As for Cu²⁺, the degree of extraction increases with increasing temperature from 10°C to 40°C and remaining constant as the temperature was further increased. (Table 4A and 4B). This suggests that high temperature favours the extraction of Cu²⁺ from the aqueous phase to the organic phase. Since solubility increases with increasing temperature. Hence, a process plant for Cu²⁺ extraction based on TBP might be run at a temperature slightly above room temperature

SEPARATION OF Cu²⁺ and Zn²⁺ FROM EACH OTHER.

The separation of Cu²⁺ and Zn²⁺ from each other in aqueous acid sulphate solution using TBP in benzene was carried out at two different conditions based on pH change. Table 1A shows that at pH 5, 59.24% of Cu²⁺ and 32.53% Zn²⁺ were extracted respectively. At pH 7, 24.58% (Cu²⁺) and 55.68% (Zn²⁺) were extracted from the aqueous mixture. The results obtained show that the position of equilibrium in the two metals depends upon the pH of the system. Thus, the distribution coefficient (D) varies as the pH changes.

Metal separation by solvent extraction has been reported by many workers (Zygmunt 1986) reported the extraction and separation of uranyl nitrate from fission product using TBP. Metal separations may be achieved by the control of pH and oxidation state. The pH of the aqueous phase plays a very important role in metal extraction. While increase in pH favours the extraction of metal species, a pH is reached at which hydrolysis and olation occur resulting in a decrease in the metal extraction, (Ipinmoroti, 1993). Hence, the well used statement that metals extract best at a pH just below that at which they hydrolyse (Ritcey and Ashbrook, 1984).

CONCLUSION

The results obtained showed that the separation of Cu²⁺ and Zn²⁺ from each other could be carried out by changing the pH of the aqueous phase at 32 ± 2°C. The separation of Cu²⁺ from Zn²⁺ is most favourable at pH 5, and 30% TBP in benzene. While Zn²⁺ would be separated from Cu²⁺ at pH 7 and 30% TBP in benzene.

The experimental result also indicate that subsequent extraction could be employed to obtain up to 90% of each metal ion from the mixture.

Tables 5b: SEPARATION of Zn²⁺ from Cu²⁺ At pH 7.

	Cu ²⁺	Zn ²⁺
Metal Conc. In aq phase. (Mg/l).	1915.7	1152.3
Metal Conc. In organic phase (mg/l)	624.3	1447.7
% Extraction	24.58	55.68
D	0.33	1.26

Temp. = (32 ± 2) °C

30% v/v TBP

Zn²⁺ = 0.04M. Cu²⁺ = 0.04M

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