

Solvent Extraction Studies of Copper(II) with Tri-*n*-Octylamine-Chloride System

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Summary: Studies were carried out for the extraction and recovery of copper (II) with tri-*n*-Octylamine from different aqueous chloride media. Parameters, such as, the effect of concentrations of extractant, copper, various chlorides of alkalis & ammonium, and the effects of time of contact as well as diverse ions were optimised. Maximum percentage extraction and recovery of copper (II) ions were achieved with 5% solution of tri-*n*-octylamine(TOA) in benzene and 0.10 M NH₄Cl.

Introduction

Solvent extraction/liquid-liquid extraction using solvents have been employed for the separation of metal ions in aqueous solutions in the laboratory for many years. In recent years, solvent extraction as a tool in analytical and analytical chemistry has become very popular that is, primarily due to its ease, simplicity, speed and applicability to both trace and macro-level of metal ions and wide scope [1-5]. Liquid-liquid extraction is similar to liquid anion exchanger on one hand and with solid resins on the other. It has been found for example that, extraction curves using this technique have the same general form as observed with solid anion exchanger [6-7].

A number of research papers have been published in the field of inorganic-analytical chemistry of copper metal. Copper was extracted from concentrates with zinc and iron by dilaurylamine anion exchangers dissolved in benzene [8], and from sulphate solutions with 2-hydroxy-5-ter-butylbenzaldehyde oxime [9]. The equilibrium studies of copper extraction was examined with hydroxime from sulphate media [10], the kinetic studies with hydroxyoximes [11] and with *n*-hexane solution of versatic acid [12]. Selective extraction and separation of copper was achieved with poly(2-5-vinyl-1,3,4-thiadiazole-5-thiol) [13], di-(2-ethylhexyl) phonic acid dissolved in isopar-H [14], 2-mercaptobenzothiozole into chloroform [15], penta-azomacrocyclic Schiff base ligand [16], terdodecylthioglycolic acid [17] with a mixed extractant (2-ethyl-hexanoic acid and trioctylamine) in toluene [18], by cyclictetrathio ethers-12,13,15 and 16 membered cyclictetrathio sulphur ethers into dichloroethane [19], with di-*n*-pentylsulphoxide and

di-*n*-octylsulphoxide [20], with didodecyl-naphthalene sulphuric acid using the principles of equilibrium analysis [21] and with impregnated resins containing D2EHPA from nitrate solutions [22]. The present paper extends the previous studies to the extraction as well as recovery of copper(II) from different aqueous solutions of alkalis and ammonium chlorides with 5% solution of tri-*n*-octylamine(TOA) in benzene and dilute solution (0.10M) of HCl.

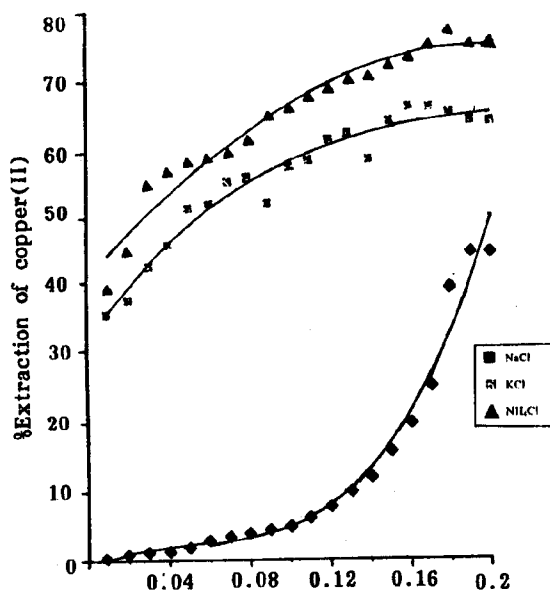
Results and Discussion

Single extraction with 5 ml of 5% TOA in benzene from different aqueous chloride media

The extraction of copper from various aqueous media i.e. NaCl, KCl and NH₄Cl solutions were made in the molar range 0.01 M to 0.20 M with 5 ml of 5% solutions of tri-*n*-octylamine in benzene. Maximum extraction (76.80%) was obtained from 0.18 M NH₄Cl solution with 5% solution of tri-*n*-octylamine in benzene. The comparative results are illustrated in Fig.1.

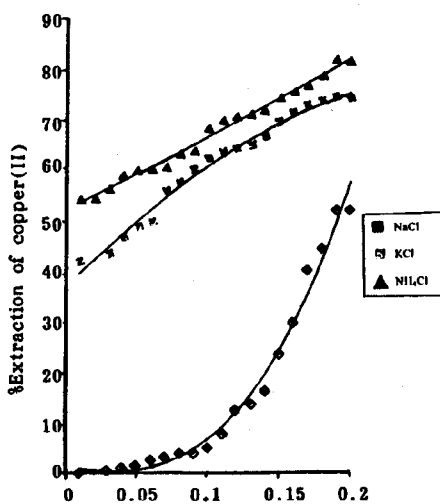
*Single extraction with 10 ml of 5% tri-*n*-octyl amine from various aqueous chloride media*

The above studies were also carried out with 10 ml of the tri-*n*-octyl amine in benzene from various aqueous media (NaCl, KCl, and NH₄Cl solutions) with the same molar concentrations (0.01-0.20 M). The extraction made from 0.19M NH₄Cl aqueous solution was however found to be the maximum(81.85%). The comparative results are summarised in Fig.2.



Concentration of alkalis and ammonium chlorides (M)

Fig. 1: Comparative studies with alkalis and ammonium chloride - Single extraction with 5 ml of 5% TOA/Benzene



concentration of alkalis and ammonium chlorides (M)

Fig. 2: Comparative studied with alkalis and ammonium chlorides for the extraction of copper (II) -Single extraction with 10 ml of 5% of TAO/Benzene

Double extraction/extraction in portions with 10 ml of 5% tri-n-octylamine(TOA) in benzene from different aqueous chloride media

Further more extraction studies were performed in portions (10 ml divided in 5 ml portions) with 5% solutions of tri-n-octylamine(TOA) in benzene from various aqueous media (NaCl, KCl, and NH_4Cl solutions). The extraction of copper(II) undertaken in portions with NH_4Cl solutions was found to be maximum i.e. it increased from 81.85% to 85%. The rest of the studies were undertaken with 0.19M NH_4Cl aqueous solution The data obtained are depicted in Fig.3.

Effect of Shaking time

The effect of shaking time on the % extraction of copper(II) in the range 0.50-5.00 minutes, was carried out. 2 to 3 minutes was optimum shaking time for maximum % extraction of copper(II). The results are presented in Fig.4.

Effect of phase-volume ratios

The phase-volume ratio ($V_{\text{org}}/V_{\text{aq}}$) was varied by keeping the volume of organic phase as constant [10 ml (in 5 ml + 5 ml portions)], and changing the volume of the aqueous phase from 5 ml up to 30 ml. The ratio 1:2 was found to be the most suitable ratio for efficient extraction of Cu (II).

Effect of extractant concentration

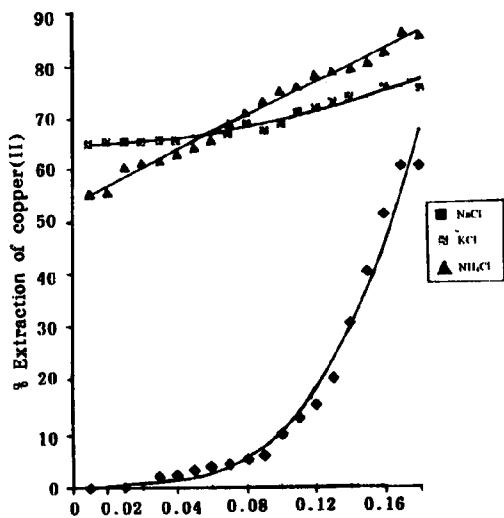
Having studied the effect of shaking time and phase-volume ratio, the effect of extractant (TOA in benzene) concentration was also optimised in molar range (0.01M-0.23M). 0.2M extractant concentration was however, found to be optimum concentration. These observations are presented in Fig.5.

Effect of copper concentration

Further investigations were also carried out to see the effect of copper concentration ranging 10 μg to 100 μg , on the overall extraction with TOA in benzene. However, minor difference was noted in the extraction efficiency above 50 μg . This effect is illustrated in Fig.6.

Effect of organic diluents

Various organic solvents were used as diluent for tri-n-octylamine(TOA). Benzene was however, found to be the most suitable diluent. The effect is summarised in the form of Table-1.



Concentration of alkalis and ammonium chlorides (M)

Fig. 3: Comparative studies with alkalis and ammonium chlorides for the extraction of copper(II) - Double extraction with 10 ml (5ml + 4ml) of 5% TOA/Benzene.

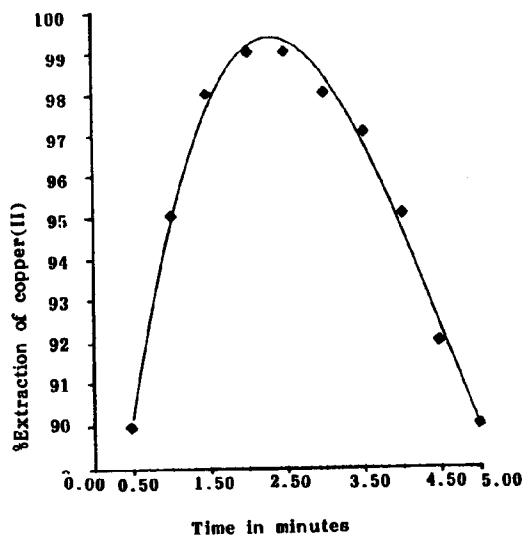


Fig. 4: Effect of time on % extraction of copper(II)- Double extraction with 10 ml (5ml+5ml) of 5% TOA/Benzene.

Effect of diverse ions

The copper concentration (20 μ g) was kept constant and the effect of diverse ions, in the range 100-1000 μ g/ml (25-50 fold excess), that may

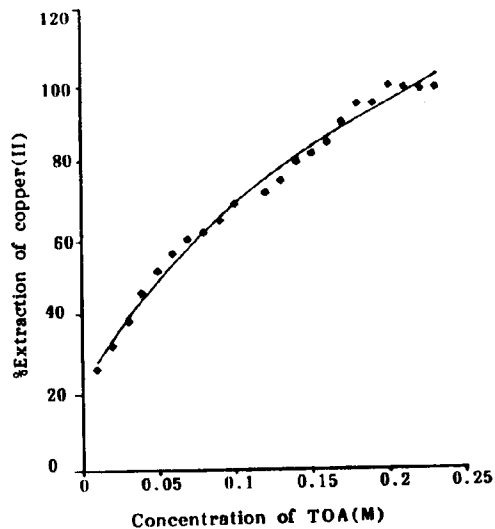


Fig. 5: Effect of TOA concentration on %extraction of copper(II)-Double extraction with 10 ml(5ml+5ml) of 5% TOA/Benzene.

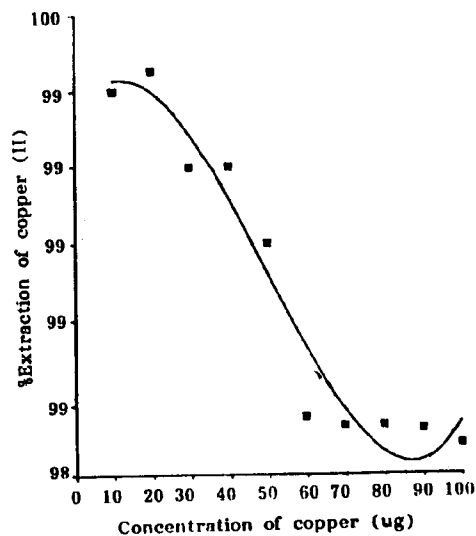


Fig. 6: Effect of copper concentration on % extraction of copper(II)-Double extraction with 10ml(5ml+5ml) of 5% TAO/Benzene.

probably cause interference during the extraction and recovery of the metal with 5% TOA in benzene was studied. It was noted that Fe(II) and Fe(III) do not interfere even if present in the 50 fold excess. Similar results were achieved with Al(III) when present in 5-20 fold excess.

Table- 1. Effect of various organic diluents on % extraction of copper (II)

S. No.	Solvents/Diluents*	Conc. of copper (μg)			% Extraction
		Added	Found	Extracted	
1.	Toluene	20.00	4.52	15.48	77.40
2.	Carbon tetrachloride	20.00	5.65	14.35	71.75
3.	1-Butanol	20.00	16.78	3.22	16.10
4.	Methyl Isobutyl Alcohol	20.00	13.95	6.05	30.25
5.	n-Pentane	20.00	3.01	16.99	84.95
6.	1-propanol	20.00	9.80	10.20	51.00
7.	Butyl Alcohol	20.00	10.93	9.07	45.35
8.	Methyl Benzol	20.00	6.31	13.69	68.45
9.	2-Methyl-propanol (I)	20.00	15.65	4.35	21.75
10.	Chloroform	20.00	5.84	14.16	70.80
11.	Ethylene Dichloride	20.00	3.20	16.80	84.00
12.	Cyclohexane	20.00	4.14	15.86	79.30
13.	o-xylene	20.00	3.96	16.04	80.20
14.	p-xylene	20.00	3.95	16.05	80.25
15.	Methyl Isobutyl-ketone	20.00	6.41	13.59	67.95
16.	Dioxane	20.00	10.93	9.07	45.35
17.	Trichloroacetic Acid	20.00	3.58	16.42	82.10
18.	Benzene	20.00	0.10	19.10	99.50

* Added in the ratio TOA:Diluent (1:19)

Table- 2 Effect of Diverse Ions on % extraction of copper (II)

S.No.	Diverse ions	Conc. of diverse ions (μg)	Concentration of copper (μg)			% Extraction
			Added	Found	Extracted	
1.	Zn ²⁺	100	20.00	1.90	19.10	90.50
		500	20.00	2.90	17.10	85.50
		1000	20.00	2.97	17.03	85.15
2.	Co ²⁺	100	20.00	1.25	18.75	93.75
		500	20.00	2.57	17.43	87.15
		1000	20.00	3.21	16.79	93.95
3.	Cr ³⁺	100	20.00	0.83	19.17	95.85
		500	20.00	3.36	16.64	83.20
		1000	20.00	3.77	16.23	81.15
4.	Mn ²⁺	100	20.00	0.35	19.65	98.25
		500	20.00	1.58	18.42	92.10
		1000	20.00	3.77	16.23	81.15
5.	Fe ²⁺	100	20.00	0.20	19.80	99.00
		500	20.00	0.20	19.80	99.00
		1000	20.00	0.20	19.80	99.00
6.	Fe ³⁺	100	20.00	0.20	19.80	99.00
		500	20.00	0.20	19.80	99.00
		1000	20.00	0.30	19.70	98.50
7.	Ca ²⁺	100	20.00	0.25	19.75	98.75
		500	20.00	2.77	17.23	86.15
		1000	20.00	2.37	17.63	88.15
8.	Mg ²⁺	100	20.00	0.23	19.77	98.85
		500	20.00	0.77	19.23	96.15
		1000	20.00	1.98	18.02	90.10
9.	Cd ²⁺	100	20.00	1.55	18.45	92.25
		500	20.00	1.56	18.44	92.20
		1000	20.00	1.49	18.51	92.55
10.	Al ³⁺	100	20.00	0.20	19.80	99.00
		500	20.00	0.40	19.60	98.00
		1000	20.00	0.70	19.30	96.50
11.	Pb ²⁺	100	20.00	0.55	19.45	97.25
		500	20.00	2.77	17.23	86.15
		1000	20.00	2.78	17.22	86.10
12.	Si ⁴⁺	100	20.00	0.76	19.24	96.20
		500	20.00	2.97	17.03	85.15
		1000	20.00	2.78	17.22	86.10

Table- 2 (continued)

S.No.	Diverse ions	Conc. of diverse ions(μg)	Added	Found	Extracted	% Extraction
13.	Bi^{2+}	100	20.00	0.93	19.17	95.85
		500	20.00	1.17	18.83	94.15
		1000	20.00	1.06	18.94	94.70
14.	Sn^{2+}	100	20.00	0.23	19.77	98.85
		500	20.00	2.77	17.25	86.15
		1000	20.00	3.75	16.25	81.25
15.	Ti^{4+}	100	20.00	0.39	19.61	98.05
		500	20.00	1.97	18.03	90.15
		1000	20.00	2.06	17.94	89.70
16.	W^{6+}	100	20.00	1.76	18.24	91.20
		500	20.00	4.96	17.04	85.20
		1000	20.00	3.19	16.81	84.05
17.	V^{5+}	100	20.00	2.51	18.49	94.45
		500	20.00	2.17	17.83	90.15
		1000	20.00	2.96	17.04	85.20
18.	U^{6+}	100	20.00	0.83	19.17	95.85
		500	20.00	2.36	17.64	88.20
		1000	20.00	2.37	17.63	88.15
19.	Eu^{3+}	100	20.00	0.67	19.33	96.65
		500	20.00	2.96	17.04	85.20
		1000	20.00	2.97	17.03	85.15
20.	Sm^{3+}	100	20.00	0.39	19.69	98.05
		500	20.00	1.57	18.43	92.15
		1000	20.00	1.27	18.73	93.65
21.	Ni^{2+}	100	20.00	0.53	19.47	97.35
		500	20.00	0.83	19.17	95.85
		1000	20.00	0.85	19.15	95.75
22.	Au^{+}	100	20.00	0.29	19.71	98.55
		500	20.00	0.80	19.20	96.00
		1000	20.00	0.85	19.15	95.75
23.	Ba^{2+}	100	20.00	0.60	19.40	97.00
		500	20.00	0.85	19.15	95.75
		1000	20.00	1.48	18.52	92.60
24.	Ag^{+}	100	20.00	0.84	19.16	95.80
		500	20.00	1.17	18.83	94.15
		1000	20.00	1.48	18.52	92.60
25	Nitrate	500	20.00	1.00	19.00	95.00
	Chlorate	500	20.00	2.00	18.00	90.00
	Sulphate	500	20.00	0.84	19.16	95.80

Mn (II), Ca (II), Mg (II), Sn (II), Au (II), Ti (IV), Pb(II), Ba(II), and Sm (III) also do not interfere if present in the 5 fold excess.

However, this trend decreases by 10 to 15% if the diverse ions concentration is increased from 25 to 50 fold excess. Moreover, the % extraction of copper decreases from 4-15% due to the presence of Si (IV), W (VI), U(VI), Eu(III), Cr (III), Zn (II), Co(II), and Cd(II) but this diversity is not so pronounced in case of Bi(II), V(V), Ni (II) and Pb (II) and show minor diverse effect. These observations are tabulated in Table-2.

Analysis of synthetic mixtures

As a final check on the method, various synthetic mixtures were prepared and analysed

following the foregoing procedure. The data are given in Table 3

Experimental

Instrumentation

Hitachi Polarized Zeeman atomic absorption spectrophotometer (Model Z-8000) in the flame-mode was used throughout these studies by setting the instrumental conditions as lamp current 7.5mA, wave length 324.8nm, spectral slit 1.3nm, oxidant pressure 1.6(kg/cm²), fuel pressure 0.3 (kg/cm²) and burner height 7.5nm.

Reagents

All the reagents and solvents used were of analytical grade. All aqueous solutions were prepared

Table- 3 Analysis of synthetic mixtures for copper (II)
Concentration of copper (μg)

S.No.	Present	Recovered	% Recovery	*Other elements present (μg)
1.	20.00	19.80	99.00	Ca: 100, Mg:100, SiO ₂ : 100,Al:100, Fe:100, Na:100, K:100, Ni:100, Co:100, Mn:100, Pb:100, Cr:100, Ag:100, Au:100, Ti:100, Zn:100, Ca:100
2.	20.00	19.91	99.55	Ca:100, Mg:100
3.	20.00	19.94	99.70	Ca:100, Mg:100, SiO ₂ :100
4.	20.00	19.73	99.65	Ca:100, Mg:100, SiO ₂ :100, Al:100
5.	20.00	19.93	99.75	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100
6.	20.00	19.96	99.80	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100
7.	20.00	19.88	99.40	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100
8.	20.00	19.87	99.35	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100, Ni:100
9.	20.00	19.88	99.40	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100, Ni:100, Co:100
10.	20.00	19.92	99.60	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100, Ni:100, Co:100, Mn:100
11.	20.00	19.95	99.75	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100, Ni:100, Co:100, Mn:100, Pb:100
12.	20.00	19.94	99.70	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100, Ni:100, Co:100, Mn:100, Pb:100, Cr:100
13.	20.00	19.85	99.25	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100, Ni:100, Co:100, Mn:100, Pb:100, Cr:100, Ag:100
14.	20.00	19.83	99.15	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100, Ni:100, Co:100, Mn:100, Pb:100, Cr:100, Ag:100, Au:100
15.	20.00	19.73	98.65	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100, Ni:100, Co:100, Mn:100, Pb:100, Cr:100, Ag:100, Au:100, Ti:100
16.	20.00	19.79	98.95	Ca:100, Mg:100, SiO ₂ :100, Al:100, Fe:100, Na:100, K:100, Ni:100, Co:100, Mn:100, Pb:100, Cr:100, Ag:100, Au:100, Ti:100

* Original values added to the mixture.

in distilled demineralised water. The working solutions were prepared by dilution as required. TOA (BDH) was used, without purification, diluted with benzene, but not pre-equilibrated with hydrochloric acid solution. Other chemicals were of analytical grade. The copper (II) solution was prepared by dissolving the requisite amount of the copper metal in 5.5M HCl solution of selected concentration. The working standards and the blanks were acidified to the same extent as the samples.

Procedure

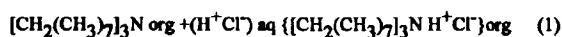
3.8 ml of 1.0 M aqueous NH₄Cl solution were added to known amount (20 μg) of Cu (II) solution in a 100 ml separating funnel. The solution was diluted to 20 ml with distilled water, so that the final NH₄Cl aqueous solution concentration is 0.19 M. 5 ml of 5% TOA in benzene solution were added to the resulting aqueous solution. The two phases were shaken manually or on a mechanical shaker for 2 minutes and left over for an hour, so that the two phases may get complete separation and attain equilibrium. The loaded organic amine phase was separated from the aqueous phase into a dried beaker

after passing through a Schwarzband 5.5 cm filter paper to remove the suspended water droplets. Fresh 5 ml of 5% TOA in benzene were added to the aqueous phase left in the separating funnel and the extraction was made again as earlier. The two batches of the loaded organic amine phases were combined and stripped with 0.10M. NH₄Cl aqueous solution. The stripped aqueous solution as well as the aqueous phase left in the separating funnel, were analysed for Cu (II), using atomic absorption spectrophotometry. The percentage extraction of Cu (II) was calculated from the difference of the known amount (20 μg) of Cu (II) added and left if any in the barren raffinate. Similarly the percentage recovery of Cu (II) was calculated from the known amount of Cu (II) added and the amount recovered back into the aqueous phase

Conclusion

It can be concluded from the preceding investigations that copper ion makes colourless chloro-complex with NH₄Cl at a specific molar concentration (0.19 M). The chloro-complex formed being anionic in nature is quantitatively extracted into the liquid ion exchanger (tri-n-octylamine). It is

obvious that 85% copper is quantitatively extracted into the organic amine phase from the synthetic mixtures even in the presence of 25 fold excess of most of the interfering metal ions. The same percentage of copper content is also recovered with a dilute solution of NH_4Cl (0.10 M) as its chloride salt. The hydrometallurgical method is being successfully applied for the extraction and recovery of copper from synthetic mixtures. The overall reaction between copper ion and trioctylamine may be represented by the following equations.



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