Solvent extraction of Cu(II) by purified cyanex 272

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The solvent extraction of Cu(II) from 0.10 mol/dm$^3$ sulphate medium by purified cyanex 272 (bis-2,4,4-trimethylpentylphosphinic acid, BTMPPA, H$_2$A$_2$) dissolved in distilled aliphatic kerosene has been investigated. The equilibration time is less than 15 min. The distribution ratio is found to decrease appreciably with equilibrium Cu(II) concentration in the aqueous phase, particularly, at its higher concentration region indicating some sort of association of Cu(II) species in either of the phases. The pH and the extractant concentration dependences on distribution ratio are 1 and 1.2, respectively. The distribution ratio is almost independent of sulphate ion concentration in the aqueous phase. The $\Delta H$ value is 27.3 ± 0.5 kJ/mol. The 60% extraction equilibrium reaction is suggested to be: CuHSO$_4$ + H$_2$A$_{2(o)}$ $\cap$ CuHSO$_4$A.0.5 H$_2$A$_{2(o)}$ + H$^+$ and some 40% extraction is likely to occur via the reaction, CuHSO$_4$ + 1.5 H$_2$A$_{2(o)}$ $\cap$ CuHSO$_4$A.H$_2$A$_{2(o)}$ + H$^+$ satisfying the extractant dependence of 1.20. The apparent extraction equilibrium constant ($K_{ex}$) is estimated to be 10$^{-3.15}$. The loading capacity of BTMPPA is 13.47 g Cu(II)/100 g BTMPPA. Among H$_2$SO$_4$, HCl and HNO$_3$ solutions as stripping agent, 1 mol/dm$^3$ H$_2$SO$_4$ solution is found to be the best; 99.6% Cu(II) in the organic phase can be stripped off in three stages (O/A = 1 in each stage). The Cu(II) distribution ratio measured at pH = 4 in different diluents does not show good correlation with the cross-sectional area of BTMPPA molecules at interfaces formed by different diluents at pH 0.80.

Keywords: Liquid-liquid extraction, Copper(II), Sulphate medium, Cyanex 272, BTMPPA, Kerosene
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Cyanex 272 (active component being bis-2,4,4-trimethylpentylphosphinic acid, abbreviated as BTMPPA, H$_2$A$_2$) is a proprietary technical grade extractant of Cytec Canada Inc. It has found wide commercial application in the separation of Co(II) from Ni(II)$^{1-3}$. Moreover, it has been proposed for the extraction of a number of other metal ions$^{6-14}$. Now-a-days, almost 90% of the world production of copper results from the hydrometallurgical routes, where, copper bearing primary sources [i.e. ores like chalcopyrite (FeCuS$_2$), chalcocite (Cu$_2$S), cuprite (Cu$_2$O), etc.] and secondary sources (such as copper dust, sphalerite or Co-Ni concentrates) are first leached to take copper dissolved in the aqueous leaching agent (usually H$_2$SO$_4$ or NH$_4$OH solution). The resulting leach solutions contain large number of other metal ions as impurity. It therefore appears that the success and the economics of a hydrometallurgical copper plant depend entirely on the development and use of a very good copper-extractant which could be able to extract copper selectively from the aqueous solution together with the easy and selective stripability.

Extractants used for the extraction of Cu(II) prior to 1976 have been referenced by Sekine and Hasegawa$^{15}$. After that the hydroxyoximes i.e. LIX-reagents have been proposed$^{16-29}$ extensively for the extraction of Cu(II) from leach solutions containing it. Beside these reports, the extractions of Cu(II) by di-2-methylnonylphosphoric acid$^{30}$, the commercial trialkylamine-ADOGEN 364$^{31}$, 2-butythiododecanoic acid$^{32}$ and Shell SME 529$^{33}$ have been reported. In addition to these, the extractions of Cu(II) from 0.10 mol/dm$^3$ nitrate medium by purified cyanex 272 (98% BTMPPA) in Isopar-H$^{34}$ and from 0.50 mol/dm$^3$ sulphate medium by as-received cyanex 272 dissolved in a mixture of o- and p-xylene$^{35,36}$ together with the separation of Cu(II) from Co(II)$^{37}$ and from Zn(II)$^{38}$ using cyanex 272 have been reported. In previous studies$^{34-36}$, the extractions have been studied in the Cu(II) concentration range of 0.10-1.0 mmol/dm$^3$. There appears no report on the mechanistic equilibrium study on the extraction of Cu(II) in its higher concentration level from sulphate medium by purified cyanex 272. In a previous paper$^{39}$, the extraction of Fe(III) from sulphate medium by purified cyanex 272 has been reported. This paper presents a thorough investigation on the equilibrium of Cu(II) extraction (for its higher concentration region) from 0.10 mol/dm$^3$ sulphate medium by purified cyanex 272 dissolved in kerosene.
Experimental Procedure

Materials
Cyanex 272 was gifted by Cytec Canada Inc. It was found to contain about 84% BTMPPA, 5% RPO(OH)₂ and 11% R₃PO. As-received Cyanex 272 was purified to contain about 99% BTMPPA by the microemulsion formation method. The purified cyanex 272 had a viscosity of 120 cp at 25°C, density at 25°C of 0.9152 g/mL and refractive index of 1.4566. Kerosene from the local market was distilled to collect fraction distilling over at 200-260°C. The collected fraction was mostly aliphatic in nature and colourless. Other diluents were of analar grade (except 1-hexanol and 1-heptanol were of GPR grade) and bought from E. Merck - BDH. These diluents were used after distillations. Other chemicals were of reagent grade (from E. Merck - BDH) and used without further purifications.

Methods
The copper(II) content of the aqueous phase was determined either by the conventional iodometric titration method or by the Atomic Absorbtion Spectrophotometer (Tokyo Photoelectric Co. Ltd., ANA 180). The pH values of the aqueous solutions were determined by a Mettler Toledo 320 pH-meter. For pH adjustment of the aqueous solutions either anhydrous Na₂CO₃ or dil. H₂SO₄ solution was used.

Procedure for extraction of Cu(II)
In the case of extraction, an aliquot of the aqueous phase (25 mL) containing specific concentrations of Cu(II) and SO₄²⁻ at a definite pH was agitated with an equal aliquot of the organic phase consisting of BTMPPA and kerosene (otherwise stated) in a 100 mL separating funnel for a predetermined time (15 min) at 298±1 K. The phase agitation was achieved by a Stuart Flask Shaker, controlled at 300 strokes/min and the temperature was controlled by putting the agitating flasks in a thermostatic water-bath. After equilibration, the phases were allowed to settle within the water-bath and disengaged. Separated aqueous solutions were subjected to equilibrium pH-measurements and Cu(II)-estimations. The concentration of Cu(II) in the organic phase at equilibrium was calculated by difference. The distribution ratio (D) was calculated on dividing the Cu(II) concentration in the organic phase by that in the aqueous phase at equilibrium.

In the cases of the loading of the organic phase by Cu(II) and stage-wise stripping, a definite amount of the organic phase was repeatedly contacted with equal volumes of fresh aqueous solutions. In the case of stripping, 25 mL portion of an organic phase containing Cu(II) and free BTMPPA in kerosene was equilibrated for 20 min at 298±1 K with an equal volume of a H₂SO₄, HNO₃ or HCl solution of definite concentration (0.01-1.00 mol/dm³) and the stripping ratio (s) was calculated as inverse of D.

Treatment of Cu(II)-extraction equilibrium data
BTMPPA being a dialkyl derivative of phosphinic acid, H₂PO(OH) acts as a mono-acidic chelating agent. If Cu(II) exists in the aqueous phase as CuLₐ(2−n)+ (L being the co-existing anion of unit charge) and BTMPPA is considered as dimeric (H₂A₂) in non-polar solvents like kerosene, then the extraction equilibrium reaction may be depicted as:

\[
\text{CuL}_a(2^{-n}) + x\text{H}_2\text{A}_2{}^{(o)} \cap \text{CuL}_{a-x}\text{A}_{(2-n+x)} + \frac{2x-2+n-z}{2}\text{H}_2\text{A}_2^{(o)} \cap z\text{L}^{-} + (2-n+z) \text{H}^{+} \quad \ldots (1)
\]

where, subscript (o) represents organic species.

The extraction equilibrium constant \(K_{ex}\) of the above reaction can be expressed as follows [D represents distribution ratio of Cu(II)]:

\[
\log D = \log K_{ex} + (2-n+z) p\text{H} + x\log[H_2A_2^{(o)}] - z \log[L^{-}] \quad \ldots (2)
\]

Results and Discussion
The rate of Cu(II) extraction by purified cyanex 272 is illustrated in Fig. 1, as [Cu²⁺] versus time plot. It is found that equilibrium is
reached within 12 min of shaking. In subsequent experiments, shaking time of 15 min has been used.

Figure 2 shows the variation of D of Cu(II) with the variation of the initial concentration of Cu(II) in the aqueous phase. It is found that the log D values are decreased with increasing logarithm of initial concentration of Cu(II) in the aqueous phase particularly in the higher concentration region, where the asymptotic slope approaches to -1.2. It is expected from Eq. (2) that the distribution ratio (D) should be independent on initial Cu(II) concentration at fixed equilibrium pH and concentrations of BTMPPA and co-existing anion. But in the above case, the equilibrium pH and the concentrations of BTMPPA and SO$_4^{2-}$ are not constant for varying extents of extraction. Figure 2 also represents the log D$_C$ versus log[Cu$^{2+}$]$_{\text{ini}}$ and logD$_C$ versus log[Cu$^{2+}$]$_{\text{eq}}$ plots, where, D$_C$ is the corrected distribution ratio at $pH_{\text{eq}}^{\text{const}} = 3.86$, [BTMPPA]$_{\text{o,eq}}^{\text{const}} = 0.10$ mol/dm$^3$ and [SO$_4^{2-}$]$_{\text{eq}}^{\text{const}} = 0.10$ mol/dm$^3$; and it has been calculated using the following relationship after getting the pH, extractant and sulphate ion dependences:

$$\log D_C = \log D + y \left( pH_{\text{eq}}^{\text{const}} - pH_{\text{eq}} \right)$$
$$+ x \log \left[ \text{BTMPPA}_{\text{o,eq}}^{\text{const}} - \log \left[ \text{BTMPPA}_{\text{o,eq}} \right] \right)$$
$$+ z \log \left[ \text{SO}_4^{2-} \text{eq}^{\text{const}} - \log \left[ \text{SO}_4^{2-} \text{eq} \right] \right)$$

... (3)

where, $y = \text{pH dependence} = 1$, $x = \text{extractant dependence} = 1.2$ and $z = \text{sulphate ion dependence} = -0.08$ (considered as zero). The values of [BTMPPA]$_{\text{o,eq}}$ have been calculated from the relation:

$$[\text{BTMPPA}]_{\text{o,eq}} = [\text{BTMPPA}]_{\text{o,ini}} - x[Cu^{2+}]_{\text{o,eq}}$$

... (4)

The logD$_C$ versus log[Cu$^{2+}$]$_{\text{ini}}$ and the logD$_C$ versus log[Cu$^{2+}$]$_{\text{eq}}$ plots are also curves having relatively lower asymptotic slopes (-0.60) in the higher concentration regions of Cu$^{2+}$ in the aqueous phase. Upto about 30 mmol/dm$^3$ Cu$^{2+}$, the D value remains almost unaltered as expected. At concentration above 30 mmol/dm$^3$ of Cu$^{2+}$, some sort of speciation change in one or either of phases might occur.

The variations of D$_C$ of Cu(II) on equilibrium pH in the aqueous phase are displayed in Fig. 3 at [BTMPPA]$_{\text{o,ini}}$ = 0.05 and 0.10 mol/dm$^3$. In both cases, D$_C$ is found to increase with increasing equilibrium pH of the aqueous phase. The logD$_C$ versus pH$_{\text{eq}}$ plots have a slope of unity. The values of D$_C$ have been calculated using Eq. (3) after neglecting...
the second term of the right hand side. It is, therefore, concluded that one gram ion of H⁺ is liberated during the reaction of one gram ion of Cu²⁺ with the extractant, BTMPPA. The value of \((2-n+z)\) in Eq. (2) is 1, so that the value of \((n-z)\) equals to 1.

Figure 4 shows the logD versus log\([BTMPPA]_{(o,ini)}\) plots for two constant equilibrium pH values of 5.0 and 4.6. In both cases, straight lines are obtained with slope equaling to about 1.50 (1.47 and 1.58 for \(pH_{eq}\) values of 4.6 and 5.0, respectively). The logD versus log\([BTMPPA]_{(o,eq)}\) plots at the same constant \(pH_{eq}\) values given above are shown in Fig. 5. In this case, straight lines of lower slope values are obtained. The slopes are 1.16 and 1.25 at \(pH_{eq}\) values of 4.6 and 5.0, respectively. It is therefore concluded that 60% of the extraction reactions occur via the Cu²⁺ to BTMPPA stoichiometric ratio of 1 and the rest 40% of the extraction reaction occurs via the Cu²⁺ to BTMPPA stoichiometric ratio of 2:3. The value of \(x\) in Eq. (2) is 1.20.

The effect of sulphate ion concentration on \(D\) is displayed in Fig. 6 for \([BTMPPA]_{(o,eq)}\) and \(pH_{eq}\) values of 0.10 mol/dm³ and 3.4, respectively. It is found that \(D\) is almost independent of sulphate ion concentration (the log-log plot has a slope of only -0.08). It is, therefore, concluded that sulphate or bisulphate ion is neither associated to or dissociated from the copper(II) species existing in the aqueous phase during extraction. The value of \(z\) in Eq. (2) is considered to be zero. It appears, therefore, that the value of \(n\) equals to 1. This means that CuSO₄ or CuHSO₄⁺ species take part in the extraction reaction.

Since the stability constants \(^{13}\) of Cu(OH)⁺ (= \([\text{CuOH}^+]\) \([\text{Cu}^{2+}]\) \([\text{OH}^-]\)), HSO₄⁻ (= \([\text{HSO}_4^-]\) \([\text{SO}_4^{2-}]\) \([\text{H}^+]\)) and CuHSO₄⁺ (= \([\text{CuHSO}_4^+]\) \([\text{Cu}^{2+}]\) \([\text{HSO}_4^-]\)) are \(10^{6.3}, 10^{2.36}\) and \(10^{6.3}\), respectively, it can be assumed that at around pH 5, the monohydroxylated Cu(II) concentration is

Fig. 5 — Effect of equilibrium extractant concentration on extraction of Cu(II) by purified cyanex 272 (BTMPPA) dissolved in kerosene. \([\text{Cu}^{2+}]_{(ini)} = 0.8811 \text{ g/dm}^3 = 13.88 \text{ mmol/dm}^3, \text{ Equilibration time} = 15 \text{ min, Temp} = 298 \text{ K, } [\text{SO}_4^{2-}] = 0.10 \text{ mol/dm}^3\).

Fig. 6 — Effect of sulphate ion concentration in the aqueous phase on extraction of Cu²⁺ by purified cyannex 272 (BTMPPA) dissolved in kerosene. \([\text{Cu}^{2+}]_{(ini)} = 0.9234 \text{ g/dm}^3 = 14.14 \text{ mmol/dm}^3, \text{ BTMPPA}_{(o,ini)} = 0.10 \text{ mol/dm}^3, \text{ [BTMPPA]_{eq}} = 0.10 \text{ mol/dm}^3, \text{ pH}_{(ini)} = 4.70, \text{ pH}_{eq} = 3.40, \text{ Equilibration time} = 15 \text{ min, Temp} = 298 \text{ K}\).
almost zero and the CuHSO$_4^+$ species take part in the extraction reaction. As found earlier, $n = 1$, which suggest the reaction of CuHSO$_4^+$ with BTMPPA [cf. Eq.(1)]. On putting the values of $n$, $x$ and $z$, Eq. (1) takes the form:

$$\text{CuHSO}_4^+ + 1.2 \text{H}_2\text{A}_2(\text{aq}) \Leftrightarrow \text{CuHSO}_4\text{A}.0.7 \text{H}_2\text{A}_2(\text{aq}) + \text{H}^+$$

...(5)

It is thought that 60% Cu(II) reacts to form the species CuHSO$_4$A. 0.5 H$_2$A$_2$, whereas the rest Cu(II) reacts to form species CuHSO$_4$A.H$_2$A$_2$. Mentioned two extracted species differ only in solvation number. Eq. (2) can be rewritten for Eq. (5) as:

$$\log D_C = \log K_{ex} + \rho H(\text{eq}) + 1.2 \log [\text{H}_2\text{A}_2]_{(\text{aq,eq})}$$

...(6)

Eq. (6) states that log$D_C$ versus $(\rho H(\text{eq}) + 1.2 \log [\text{H}_2\text{A}_2]_{(\text{aq,eq})})$ plot will be a straight line of unity slope and its intercept will be equal to log$K_{ex}$. Such a plot is shown in Fig. 7. The Least Squares slope and intercept of the line are 1.11 and –3.15, respectively with correlation coefficient of 0.992. Therefore, the apparent extraction equilibrium constant at 298 K is equal to $10^{-3.15}$ compared to $10^{-2.30}$ for Fe(III) extraction from 0.10 mol/dm$^3$ sulphate medium by BTMPPA$^{39}$ at 298 K.

The variation of distribution ratio of Cu(II) on temperature is displayed in Fig. 8 at two different experimental parameters. In both cases under investigation, log$D$ versus $(1/T) \times 10^3$ plots are straight lines. With the help of Vant’ Hoff equation$^{44}$, the apparent enthalpy change for the extraction reaction ($\Delta H$) values have been calculated from the slopes of the lines. Average $\Delta H$ value is 27.3 kJ/mol with a variation of ± 0.5. The positive $\Delta H$ value suggests that the extraction of Cu(II) from sulphate medium is endothermic in nature as in the case of Fe(III) extraction by BTMPPA$^{39}$.

The loading of Cu(II) in 0.10 mol/dm$^3$ BTMPPA solution has been examined. The cumulative concentration of copper(II) in the organic phase have been plotted in Fig. 9 against the number of stages. It is seen that 0.10 mol/dm$^3$ BTMPPA is saturated with

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Fig. 7 — Evaluation of equilibrium constant of copper(II) extraction reaction by BTMPPA graphically using Eq. (6) at 298 K.

Fig. 8 — Effect of temperature on extraction of copper(II) by purified cyanex 272 (BTMPPA) dissolved in kerosene. $[\text{Cu}^{2+}]_{(\text{aq})} = 0.9234$ g/dm$^3 = 14.54$ mmol/dm$^3$, $[\text{SO}_4^{2-}] = 0.10$ mol/dm$^3$, $[\text{BTMPPA}]_{(\text{aq,ini})} = 0.10$ mol/dm$^3$, Equilibration time = 15 min.

Fig. 9 — Loading of the organic phase containing BTMPPA in kerosene by Cu(II). $[\text{Cu}^{2+}]_{(\text{ini})} = 5.715$ g/dm$^3 = 0.09$ mol/dm$^3$, Volume of each phase = 100 cm$^3$, $[\text{BTMPPA}]_{(\text{ini})} = 0.10$ mol/dm$^3$, $\rho H_{(\text{eq})} = 5.5$, Temp = 298 K, Shaking time in each stage = 30 min. At every stage, aqueous phase is renewed.
7.812 g/dm³ (0.123 mol/dm³) Cu(II). Therefore, the molar ratio of Cu(II) to BTMPPA in the saturated complex is 1:0.81 and this value is lower than that obtained from the extractant dependence study (1:1.2). Thus the extraction mechanism near saturation is altered. It has been early reported that if 0.0001-0.001 mol/dm³ Cu(II) is extracted by about 0.10 mol/dm³ BTMPPA, then the extracted species is CuA₂H₂A₂. In this study around 0.015 mol/dm³ Cu(II) has been used in the extraction and in such a condition the extracted species is CuHSO₄A.0.7H₂A₂ which is changed to a composition of CuHSO₄A.0.31H₂A₂ at saturation with Cu(II). It is therefore concluded that the solvation number in the extracted complex depends largely on Cu(II) loadings in the organic phase and is decreased with increasing Cu(II) loading in the organic phase. The loading capacity of BTMPPA towards Cu(II) is 13.47 g Cu(II)/100 g BTMPPA.

The stripping abilities of H₂SO₄, HNO₃ and HCl solutions for the extracted complex have been examined. The results are given in Table 1. It is seen that 0.01 mol/dm³ acid solutions are not so effective. Solutions of 0.10 mol/dm³ H₂SO₄, HCl and HNO₃ are almost equally effective; 77.9, 81.8 and 81.8% Cu(II) are stripped, respectively, in single stages. However, the effectiveness of stage-stripping is better for the sulphuric acid solution. 97.7, 95 and 93.7% copper(II) are stripped by 1.0 mol/dm³ H₂SO₄, HCl and HNO₃ solutions, respectively, in three stages. Even better results are obtained with 1.0 mol/dm³ acid solutions. 99.6, 96.9 and 97% Cu(II) are stripped by 1.0 mol/dm³ H₂SO₄, HCl and HNO₃ solutions, respectively, in three stages. From these results, it is concluded that almost quantitative amount of Cu(II) extracted into the organic phase can be stripped off by 1.0 mol/dm³ H₂SO₄ in three stages.

When Cu²⁺ (0.9 g/dm³) is extracted from 0.50 mol/dm³ sulphate medium of pH(ini) = 4.0 by 0.30 mol/dm³ BTMPPA dissolved in different diluents, then the value of distribution ratio (D) is found to decrease in the following order: 1,2-dichloroethane (D = 0.92) > carbon tetrachloride (D = 0.64) > n-hexane (D = 0.53) > chloroform (D = 0.48) > toluene (D = 0.44) > cyclohexane (D = 0.39) > 1-heptanol (D = 0.35) > benzene (D = 0.31) > kerosene (D = 0.28) > 1-hexanol (D = 0.24). These values of D in the logarithmic form have been plotted against the logarithm of the cross-sectional area (Å²) of BTMPPA molecules adsorbed at the interface of a diluent / 0.50 mol/dm³ H₂SO₄ (pH = 0.8) in Fig. 10. Out of ten points, a very poor six point fit correlation is obtained. This failure to correlate D with A is

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<th>% Stripped</th>
<th>Cumulative % Cu²⁺ stripped</th>
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Fig. 10 — Correlation between distribution ratios of copper(II) in different diluents and the cross-sectional area of BTMPPA molecule at the interfaces. Extraction conditions: [Cu²⁺]_(ini) = 0.953 g/dm³, pH_(ini) = 4, [BTMPPA]_(o) = 0.025 mol/dm³, equilibration time = 15 min, Temp = 298 K, O/A = 1/1 (O = 25 mL).
attributed to the difference in the interfaces used in A measurements (pH = 0.8) and in D measurements (pH = 4). When interfacial conditions are kept constant, then it has been found that a very good correlation is obtained between D and A. The correlated line has a slope of about 0.6. In the case of D2EHPA, a sharp correlation was obtained between the D of TiO$_2$ and the cross-sectional area of D2EHPA as reported earlier. The extraction characteristics of BTMPPA is not so much dependent on the diluent used to constitute the organic phase.

Conclusion

The extraction of Cu(II) can be made effective by purified cyanex 272 in the pH$_{eq}$ region of around 5.4. The increase in [Cu$^{2+}$] in the aqueous phase and the lowering of pH, [BTMPPA] and temperature decrease the D value. The extracted species is solvated chelate complex of CuHSO$_4$$^3$. The apparent $K_m$ and $\Delta H$ values are $10^{-3.5}$ and 27.3 kJ/mol, respectively. The solvation number is decreased with increasing loading. The loading capacity is 13.47 g Cu(II)/100 g BTMPPA. A three-stage stripping by 1 mol/dm$^3$ H$_2$SO$_4$ (O/A = 1 in each stage) can bring 99.6% Cu(II) in the aqueous phase. D-value is found to be dependent on the diluent used; but its value in different diluent is poorly correlated with the cross-sectional area of BTMPPA molecule (A) at interfaces.

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References