

SOLVENT EXTRACTION OF COPPER (II) BY SYNERGISTIC MIXTURES OF TRIOCTYLPHOSPHINE OXIDE AND LAURIC ACID

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ABSTRACT: The liquid-liquid extraction of copper (II) by mixtures containing tri-n-octyl phosphine oxide (TOPO) and lauric acid (LA) was studied. The effects of the concentration of the extracting agent in the organic phase and KCl in the water phase were investigated. The comparison between the results of extraction tests obtained with each separate extracting agent and those obtained with their mixtures, showed a synergistic effect. Yield of 100% in a single stage was attained in the cases of mixture. The ratio TOPO/LA in the complex in cyclohexane solution was determined as 1: 1. The complex formed in the organic phase may be $(\text{CuCl})_2 \text{ TOPO (LA-H)}_2$.

The coordination bonds of the Cu-complex were determined by infrared spectroscopy.

KEYWORDS: Copper; Separation; Tri-n-octyl phosphine oxide; Lauric acid, Complexation,

INTRODUCTION

Metal complexation in wastewaters is an effective and convenient route to prevent environment from contamination. For example, fatty acids are used in the extraction of metal ions and in particular the naphthenic and versatic acids have found commercial applications in the hydrometallurgy process of metals [1]. These acids were employed for the separation of Ni (II) and Co (II), rare earths and in the recovery of Gallium and Indium [2, 3]. The extraction of copper (II) by the fatty acids has been the subject of much work research [4 -7]. Tri-n-octyl phosphine oxide (TOPO) is used as an extracting agent, but is often associated with a second extracting agent to produce synergic effect [8, 9]. Studies relating the use of a mixture of extracting agents in the liquid-liquid extraction of copper (II) with a synergic effect is well documented [10, 11].

In current work, we have carried out extraction tests of copper chloride using a mixture of lauric acid (LA) and tri-n-octylphosphine oxide (TOPO). The results obtained were compared to results obtained with only one pure extracting agent.

EXPERIMENTAL

Reagents

Lauric acid, tri-n-octyl phosphine oxide, cyclohexane, copper (II) dichloride and potassium chloride were the purest quality Fluka products.

Analysis methods

Aqueous phases were analyzed with a Shimadzu type AA-6200 atomic absorption spectrophotometer before and after extraction.

The stoichiometry of the complex $\text{TOPO}_x\text{-LA}_y\text{-Cu}_z$ was determined by Job's methodology [12], by UV spectroscopy at $\lambda_{\text{max}[\text{Cu}^{2+}]} = 230 \text{ nm}$, with $[\text{Cu}^{2+}] = 0.1 \text{ mmole.l}^{-1}$, $[\text{TOPO}] = 10 \text{ mmole.l}^{-1}$ and $[\text{LA}] = 0.1 \text{ mmole.l}^{-1}$. UV spectroscopy was carried out on Perkin Elmer Lambda 800.

The conductimetric study was employed to find out the number of complexes present in the organic phase after extraction. The extraction of the Cu (II) (1 mmole.l^{-1}) was carried out with TOPO and LA in equal proportions (1:1). The conductimeter used was a Consort C831 with a cell's constant of 1.0.

Infrared spectra were taken on Perkin Elmer Lambda-2 equipped with a thermostat in order to maintain the temperature of the cell, holding the sample, at 25°C .

All reagents used for experiments and analyses were of analytical grade. Solutions were prepared with freshly distilled water.

Extraction procedure

The extraction tests were run using lauric acid (LA) and tri-n-octyl phosphine oxide (TOPO) as extracting agents. The solvent was varied as was the volumetric ratio $V_{\text{aq}}/V_{\text{org}}$ for $[\text{Cu}^{2+}] = 1 \text{ mmole.l}^{-1}$, $[\text{TOPO}] = 5 \text{ mmole.l}^{-1}$ and $[\text{LA}] = 50 \text{ mmole.l}^{-1}$.

The organic solution of TOPO (10 ml, 5 mmole.l⁻¹ to 40 mmole.l⁻¹) and an aqueous copper (II) dichloride solution (20 ml, 1 mmole.l⁻¹) were vigorously shaken for 40 min at 20°C. Extraction tests of Cu²⁺ by LA in cyclohexane were carried out for concentrations of 5 mmole.l⁻¹ to 300 mmole.l⁻¹ LA, and for a 1 mmole.l⁻¹ copper solution. The extraction of Cu (II) by the mixture of TOPO and LA was achieved in two steps:

- the concentration of TOPO was fixed at 10 mmole.l⁻¹ and the concentration of LA varied,
- the concentration of LA was fixed at 5 mmole.l⁻¹ and the concentration of TOPO varied.

The resulting extraction experiments are discussed in term of extraction yield (Y) and distribution coefficient (D) defined as follows:

$$Y (\%) = (m_i - m_f) / m_i \cdot 100$$

$$D = (V_{aq} / V_{org}) \cdot (m_i - m_f) / m_f$$

Where: m_i = initial mass of Cu²⁺ in aqueous phase; m_f = mass of Cu²⁺ after extraction; V_{aq} = volume of the aqueous phase; V_{org} = volume of the organic phase.

The extraction results for the Cu²⁺ ion are reported in Figures 2 and 3.

Measurement of the ionic force was carried out by the addition of solid KCl to the copper solution with concentrations of KCl between 0.1 M and 5 M.

RESULTS AND DISCUSSION

Synergism effect

The principal factors which can influence the synergism of the extraction by organic solvents are the dipole moment of the solvent, the permittivity of the solvent and the capacity of the solvent to drive water molecules into the organic phase [13].

We have tested the extraction of Cu (II) by a mixture of extracting agents TOPO and LA in different solvents (chloroform, nitromethane and cyclohexane) and with different volumetric ratios ($V_{aq}/V_{org} = 1, 2, 4$). The results are reported in Fig. 1. From these results, we have selected cyclohexane as the preferred solvent with an optimum volumetric ratio of 2.

From the results of Dyrssen's method [14, 15], lauric acid (LA) is known to exist as a dimer a in cyclohexane with a dimerisation constant, K_d , equal to $1.31 \times 10^8 \text{ M}^{-1}$ and a distribution constant equal to 6.45×10^5 . LA is thus insoluble in water.

The infrared stretching band of the carbonyl group (C=O) is observed at 1720 cm^{-1} , this fact confirms that lauric acid is present as a dimer in alkane [16, 17].

A synergic effect was observed by the addition of lauric acid to a fixed concentration of TOPO (10 mmol.l⁻¹). The same phenomenon of synergism was observed by addition of TOPO to a fixed concentration of LA (5 mmol.l⁻¹).

For example, in the case where the concentration of TOPO was 10 mmole.l⁻¹, the distribution coefficient obtained was $D_1 = 0.05$. When the concentration of lauric acid was 5 mmol.l⁻¹ the distribution coefficient obtained was $D_2 = 0.11$, but for the mixture TOPO (10 mmol.l⁻¹) and LA (5 mmole.l⁻¹), distribution coefficient $D = 0.37$ was obtained. The effect of synergism (C_s) was 2.31 ($\text{Log } C_s = 0.838$).

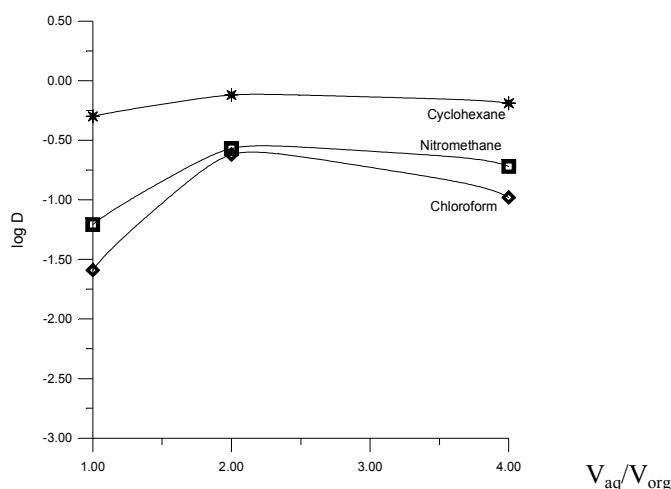


Fig. 1. Effects of changing the solvent and the volumetric ratio on Cu (II) extraction by a mixture of TOPO and LA

The current study of the ionic force effect on the extraction of Cu (II) with the LA and TOPO mixture showed that the increase in the extraction yield of Cu (II) was very significant when KCl was added to the LA/TOPO mixture thus augmenting the ionic force, (see Fig. 4).

For fixed concentrations of TOPO, KCl and Cu (II) ($[TOPO] = 10 \text{ mmol.l}^{-1}$, $[Cu^{2+}] = 1 \text{ mmol.l}^{-1}$, $[KCl] = 3.5 \text{ M}$), the extraction yield of copper does not change whatever the quantity of LA added. Beyond a certain concentration of LA, its excess does not participate in the equilibrium, this point is similar to an isobestic point (Fig. 4).

Spectroscopy and determination of the complex stoichiometry

For Cu(II) extraction with $(LA)_2$, the $\log D$ variation versus pH gives a line whose slope is equal to two. The minimum optical density from UV for $\lambda_{max} = 230 \text{ nm}$ corresponds to the formation of a complex $(CuCl)_2 TOPO (LA-H)_2$.

We have studied by infrared spectroscopy the possible formation of a new complex. The stretching band ($P=O$) of pure TOPO was at 1180 cm^{-1} , while the stretching band of the carbonyl group ($C=O$) of pure lauric acid lies at 1720 cm^{-1} . In the mixture of TOPO and LA, a new band appeared at 1449 cm^{-1} , this band was attributed to the vibration of the carboxylate ion [16, 17]. The infrared of the copper complex with TOPO and LA presented a stretching carbonyl band $C=O$ at 1700 cm^{-1} due to the lauric acid ligand. A shift of 20 cm^{-1} was noticed in comparison to the free LA dimer. New bands appeared at 685 cm^{-1} and 544 cm^{-1} ; these bands were attributed to the vibrations of deformation of C-O-Cu and P-O-Cu respectively.

From the conductimetric study of Cu (II) with a mixture of TOPO and LA, the formation of only one main copper complex in organic solution was observed (fig. 5).

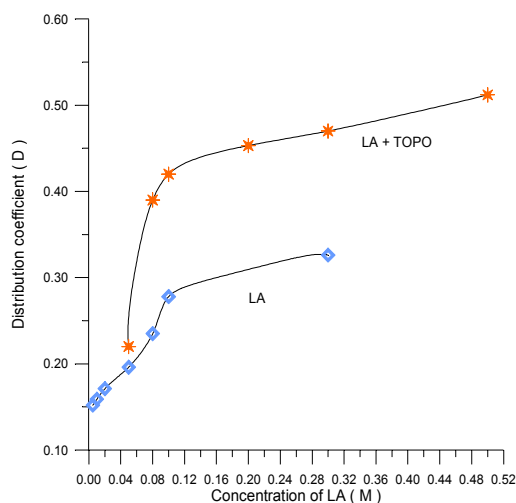


Fig. 2. Evolution of distribution coefficient of Cu (II), versus LA concentration ($V_{aq}/V_{org} = 2$, $T=20^{\circ}\text{C}$)

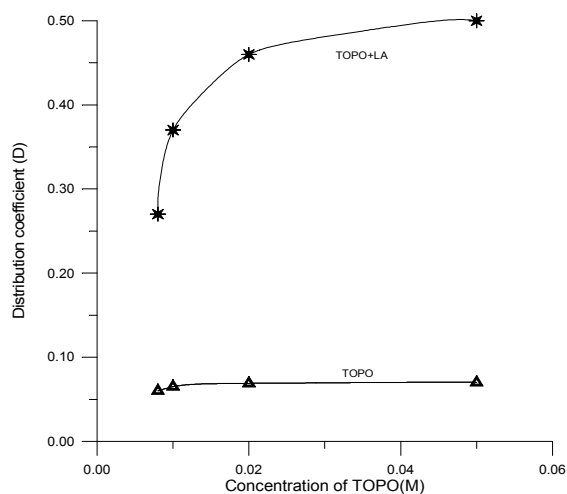


Fig.3. Evolution of distribution coefficient of Cu (II), versus TOPO concentration ($V_{aq}/V_{org}=2, T=20^{\circ}\text{C}$)

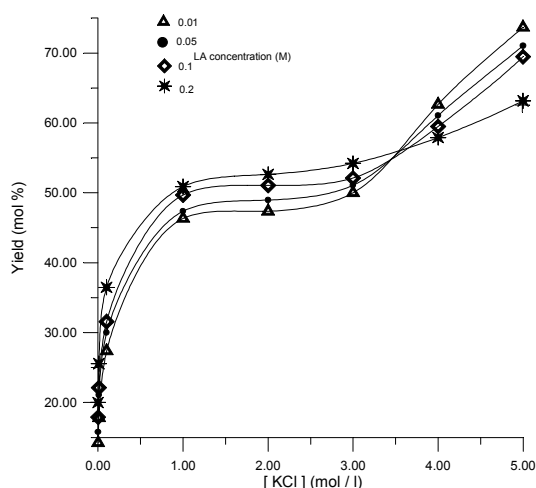


Fig. 4. Extraction yield of copper (II), versus the concentration of the KCl ($V_{aq}/V_{org} = 2$, $T=20^{\circ}\text{C}$)

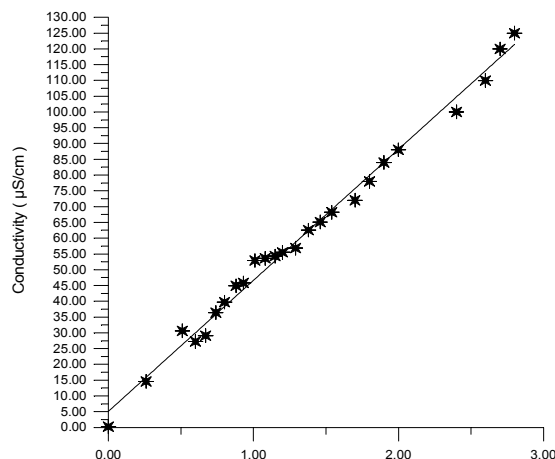


Fig. 5. Conductimetric study of Cu (II) in a mixture of TOPO and LA (1:1)

CONCLUSION

The results obtained herein allow concluding that in the copper complexation, TOPO exerts a synergic effect in the presence of lauric acid. It was also found that addition of KCl improved the yield of copper extraction. A 100% yield was attained in a single stage extraction procedure, using an optimal [LA + Cu] mixture. Equilibrium calculations gave a $(\text{CuCl})_2 \text{ TOPO (LA-H)}_2$ formula for the complex formed in the organic phase.

REFERENCES

1. Nishihama S., Hirai T., Komazawa I., *Industrial & Engineering Chemistry Research*, **40** (14), **2001**, 3085-3091.
2. Preston J.S., Di Preez A.C., *Hydrometallurgy*, **58** (3), **2000**, 239-250.
3. Shen Y., Gronberg L., Jonsson J.A., *Anal. Chim. Acta*, **292**, **1994**, 31-39.
4. Guyon F., Parthasarathy N., Buffle J., *Anal. Chem.*, **72** (6), **2000**, 1328-1333.
5. Hiromichi Y., Yoshihiro T., Hiroko W., *Talanta*, **41**, (4), **1994**, 573-579.
6. Kress N., Harel G., Schmucker G., *Solvent Extraction and Ion Exchange*, **7** (1), **1989**, 47-56.
7. Coetzee C. J., *Polyhedron*, **8** (9), **1989**, 1239-1242.
8. Ohashi K., Matsuta N., Imura H.; *Bunseki-kagaku*, **50** (7), **2001**, 493-499; *Chem. Abst*, 135, 282291.
9. Hanot T., Matsumoto M, Ohtake T., Sasaki K., Kawano Y., *Journal of Chemical Engineering of Japan*, **23** (6), **1990**, 734-738.
10. Zapatero M.J., Elizalde M.P., Castresana J.M., *Solvent Extraction and Ion Exchange*, **10** (2) **1992**, 281-295.
11. Olazabal M.A., Zapatero M.J., Elizalde M.P., *Solvent Extraction and Ion Exchange*, **10** (1), **1992**, 19-34.
12. Hill, Z.D., Mac Carthy P., Novel Approach to Job's Method, *Journal of Chemical Education*, **63**, **1986**, 162-167.
13. Flett D.S., Spink D.R., *Hydrometallurgy*, **1**, **1974**, 207-215.
14. Dyrssen D., *Acta chem. Scand.*, **11**, **1957**, 1771-1786.
15. Mrochek J. E., O'Laughlin J.W., Banks C.V., *J. Inorg. Nucl. Chem.*, **27**, **1965**, 603 – 623.
16. St Flett M., *J. Chem. Soc.*, **1951**, 962-967.
17. St Flett M., Characteristic frequencies of chemical groups in the infra-red, Elsevier, Amsterdam, **1963**.