



SELECTIVITY IN EXTRACTION OF COPPER AND INDIUM WITH CHELATE EXTRACTANTS

D. Živković¹, Z. Kamberović², S. Stefanović², A. Onjia³

¹Scientific Research Center, Nikole Pašića 26, Užice, Serbia

²Faculty of Technology and Metallurgy, Karnegijeva 4, University of Belgrade, Serbia

³The Vinca Institute of Nuclear Sciences, P.O.Box 522, Belgrade, Serbia

Abstract: Simultaneous extraction of copper and indium with chelate extractants (LIX84 and D2EHPA) was described. Stoichiometry of metal-organic complexes examined using the method of equimolar ratios resulted in CuR_2 and InR_3 forms of hydrophobic extracting species. A linear correlation was obtained between logarithm of distribution coefficients and chelate agents and pH, respectively. Selectivity is generally higher with higher concentrations of chelate agents in the organic phase, and is decreased with increase of concentration of hydrogen ions in feeding phase.

INTRODUCTION

Extraction of metal ions with selective extractants has a great significance in small hydrometallurgy plant due to potentially high efficiency and economics [1]. The solvent extraction may be used for copper and indium recovery from low grade ores, and also for the recovery from raw materials, secondary materials, and scraps [2].

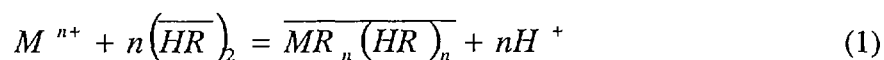
In aqueous phase metals most often exist in form of ions and as such are inconvenient for extraction with nonpolar organic extractant. Modification of ions with the aim of transferring into suitable hydrophobic forms is mostly accomplished by complexing metal cations with suitable chelate anion in order to get a neutral complex.

Due to presence of chemical reaction, the coefficient of distribution which can be used as a measure of extraction efficiency is very dependant on concentrations of reactants and products in the system.

The organic phase in the process of metal extraction by reactants complexing, mostly consists of three components: extractant (chelate agent), solvent and a modifier.

1. THEORETICAL BACKGROUND

Since indium and copper are present in small concentrations, it can be considered that polynuclear complexes of MR_n type are built. If LIX84 and D2EHP are expressed as HR, copper and indium as M, extraction of copper and indium with this extractants dissolved in kerosene can be expressed as follows:



Equilibrium constants of extraction are:

$$K_{ex} = \frac{[\overline{\text{MR}_n(\text{HR})_n}][H^+]^n}{[M^{n+}][\overline{(\text{HR})}_2]^n} \quad (2)$$

Hyphens above designate components in the organic phase.

Distribution coefficient of an m component, in water and organic phases is defined by ratio of concentration in the organic phase towards the concentration of the same component, in the aqueous phase in equilibrium.

The extent of extraction depends of initial concentrations of metals and acid (sulphuric acid) in aqueous phase. It was shown that indium extraction takes place in wide temperature range with temperature increase, which indicate that process has exothermal character [3].



Mathematically, distribution of metal ions, M^{n+} as extracted in the presence of chemical reaction (Eq. 1), can be expressed as follows:

$$m = \frac{\overline{MR}_n}{(HR)_n} [M^{n+}]^{-1} = K_{ex} [(HR)_2]^n [H^+]^{-n} \quad (3)$$

Using logarithms, this may be expressed as:

$$\log m = \log K_{ex} + n \log [(HR)_2] + n pH \quad (4)$$

By plotting:

$$\log m = f\{[(HR)_2]\} \quad (5)$$

a straight line is obtained for constant values of pH. K_{ex} can be determined from the value of intercept on ordinate.

2. EXPERIMENTAL

2.1. CHEMICALS, REAGENTS AND SOLUTIONS

Di-(2-ethyl hexyl) phosphoric acid, (D2EHPA, Fluka) and 2-hydroxy-5-nonylacetophenone oxim (LIX 84, Henkel Co.) in kerosene were used without previous treatment. Indium (metal), NH_{3conc} and CH_3COOH_{glac} were used for adjusting pH in the range from 4 to 10. Na_2SO_4 was used for maintaining constant ionic strength of feeding solution. H_2SO_4 was used for dearomatization of kerosene. NaOH was used for adjusting pH of feeding solution. HNO_3 was used for reextraction of metals from organic phases. H_2O was used as a diluent for all aqueous solutions. Kerosene was used like a solvent for preparing organic solutions. Prior to use, dearomatization of kerosene was done. The following solutions were used: $[Cu^{2+}]_I = 78.7 \cdot 10^{-3} \text{ mol/dm}^3$ for determination of capacity of organic phase, $[Cu^{2+}]_I = 1.0 \cdot 10^{-2} \text{ mol/dm}^3$ in the feed phase, $[In^{3+}]_I = 1 \cdot 10^{-2} \text{ mol/dm}^3$ in the feed phase, $[LIX 84]_{II} = 20\%$ in the organic phase, $[D2EHPA]_{II} = 10\%$ in the organic phase.

2.2. PROCEDURE

2.2.1. EXTRACTANT CAPACITY.

Extractant capacity was determined by successive mixing of 10 cm^3 fresh solution of Cu^{2+} in 0.5 mol/dm^3 $NaHSO_4$ solution with 5% D2EHPA solution in kerosene (for D2EHPA) or with 10% solution LIX 84 in kerosene (for LIX 84), with volume ratio aqueous phase-organic phase 2:1, at constant pH value and constant temperature ($t \approx 25 \text{ }^\circ\text{C}$). Ten solutions of copper (one after another) were balanced with one solution of organic phase in a separating funnel for 10 minutes and with periodical mixing. pH value of Aqueous solutions was adjusted by adding H_2SO_4 , NaOH, or Na_2SO_4 , and is controlled by using pH-meter (Iskra MA 5725). For adjusting pH value from 4 to 10, CH_3COOH and NH_3 were used. After phases separation from 3 cm^3 of organic phase, copper was reextracted with 30 cm^3 of 3.0 mol/dm^3 HNO_3 and copper concentration is directly measured by atomic absorption spectrometry (AAS) (PYE Unicam SP9).

2.2.2. SPECTROPHOTOMETRIC EXAMINATION OF METAL COMPLEXES.

Characterization of the metal complex, formed in the extraction process is done by the method of continual variation of equimolar solutions [3, 4], as well as the method of molar relations [5]. The intensities of AAS absorbance were measured in the function of molar part of chelate agent (HR) in the organic phase and metal (X_m) in the aqueous phase at constant total concentration $[M+HR] = 5.0 \cdot 10^{-3} \text{ mol/dm}^3$. With the method of molar relations, metal concentration was $1 \cdot 10^{-3} \text{ mol/dm}^3$. The aqueous phase (10 cm^3) which contains Cu^{2+} or In^{3+} ions of concentration from 0.5 to $4.5 \cdot 10^{-3} \text{ mol/dm}^3$ in 0.5 mol/dm^3 solution of $NaHSO_4$ in distilled water and organic phase (10 cm^3) which contains LIX 84 or D2EHPA solution in kerosene with concentration from 0.5 to $4.5 \cdot 10^{-3} \text{ mol/dm}^3$ are extensively mixed



in the separation funnel for 10 minutes. After phase separation the aqueous phase is filled up to 50 cm³ with distilled water and metal concentration in the aqueous phase was determined by the AAS method. Concentration of metal in the complex form in the organic phase was determined by disintegration of complex and stripping the metal ions into the aqueous reextraction phase. Then, 10 cm³ of this solution was diluted with distilled water up to 25 cm³ for spectrophotometric measurements. With the method of molar relations, concentration of ion metal in the aqueous phase was maintained constant (1·10⁻³ mol/dm³) and HR concentration in the organic phase was changed in the range from 1,9 to 12·10⁻³ mol/dm³. Complexation and AAS measurements were performed in the same way.

2.2.3. PROCEDURE FOR MONITORING THE EXTRACTION EQUILIBRIUM.

Aqueous solutions of metal ions were prepared by dissolving of metal indium and CuSO₄·5H₂O in 0,5·10⁻³ mol/dm³ solution NaHSO₄ in distilled water. The PH value of these solutions was adjusted by adding H₂SO₄, NaHSO₄ and Na₂SO₄. Organic solutions contain LIX84 or D2EHPA diluted in dearomatic kerosene. Equal volumes (10 cm³) of organic and aqueous phases were taken into the funnel for separating and intensive mixing with periodical interruptions 20 minutes, at room temperature (25 °C). Upon phases separation, metal ion concentration was determined as described above. Some of the samples are additionally diluted in order to get absorbancy in the linear calibration range. Equilibrium pH of aqueous phase were controlled with pH-meter.

3. RESULTS AND DISSCUSION

3.1. ACTIVE COMPONENT IN THE ORGANIC PHASE

For studying mechanisms according to which the extraction process is going on, it is necessary to have right knowledge about nature and properties of all chemical species present in the system. Since the extraction of a vast number of metals with participation of complexing reactivities of (HR) type, where LIX 84 and D2EHPA belong, takes place with presence of chemical reaction, it is very important to know concentration of all participants in the reaction. D2EHPA and LIX 84 represent commercial extractant, where D2EHPA is one of the most often used extractant for extraction of great number of metals and LIX 84 is a new one and very selective towards copper, is within the group of so-called β-dikeones (or hydroxyoximes). For the both of above mentioned extractant when obtained from commercial sources, with no previous treatment, exact concentration of active chelate component in extractant has to be determined. There are more methods for determination of active component in multi-component extractants. Here, a simple method using the copper extraction from fresh aqueous solutions were employed. The obtained results are shown in Fig. 1 as a relation of copper quantity transfered into the organic phase and volume of the organic phase, depending on pH of a fresh aqueous copper solution. Maximum at the curve which shows dependence of copper concentration in the organic phase from initial pH value of aqueous phase represents the capacity of the organic phase at the given temperature.

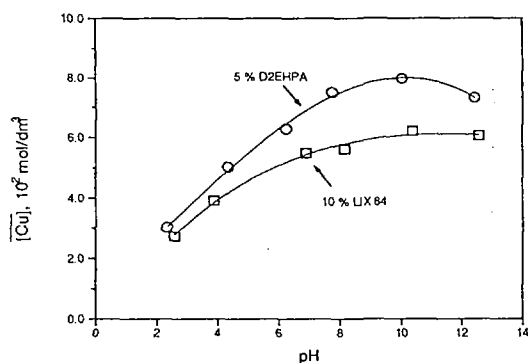


Fig. 1. Maximum capacity of extractants for systems: Cu²⁺, 0,5 mol/dm³ NaHSO₄/HR (in kerosene), t = 25°C

From Fig. 1 it can be seen that curves reach maximum at pH=10,7 for LIX 84 and pH=10,1 for D2EHPA, whereas the maximum capacity of the organic phase is: 61,7·10⁻³ mol/dm³ for LIX 84 and 78,2·10⁻³ mol/dm³ for D2EHPA. From these values, concentration of active components in extractant can be determine assuming the sthechiometry MR_n (n=2 for copper, n=3 for indium): (a) 1.23 mol active component/1 dm³ LIX 84, (b) 1.59 mol active component /1 dm³ D2EHPA.



The active component represents the chelate agent HR, the concentration of which is relevant for transportation of solute from water to organic phase. For solutions with D2EHPA it is the concentration of di-(2-ethyl hexyl) phosphoric acid, and 2-hidroxy-5 nonialacetophenon oxym concentration for commercial LIX 84 solutions.

3.2. SPECTROPHOTOMETER ANALYSIS OF METALS COMPLEXES

Having done active component determination, stochiometry MR_n was assumed, where $n=2$ for copper and $n=3$ for indium was taken. Metal÷chelate agent ratio in the metal complex, has to be confirmed, however, prior to further consideration of the two-phase multi-component system, since a wrong assumption leads to impossibility for process analysis. Stochiometry was considered with conventional spectrophotometer analysis using either method of continual variation of equimolar solutions or method of equimolar ratios. Only exceptionally high concentrations of D2EHPA and LIX 84 in kerosene as well as of their complexes with copper and indium give colored solutions, which can be analyzed to a certain extent spectrophotometrically in the visible part of spectrum. In a wide range of concentrations of these components, the molecular absorbance spectrum in a range of wavelengths $\lambda=400-750$ nm, do not have, or have just negligible intensity. However, for determination of stochiometry coefficients it is enough and also suitable to observe change of concentration of metal ions only. The method of continual variation of equimolar solutions of metals in water and HR in the organic phase, for 4 individual cases is shown in Fig.2. From Fig. 2 it can be seen that maximums of absorbance appear at $x_{In}=0.25$ for indium and $x_{Cu}=0.33$ for copper in both cases which show molar relations in complexes In/HR and Cu/HR, 1/3 and 1/2, thus confirming InR_3 and CuR_2 stochiometry, respectively. Confirmation of this stochiometry was done by the method of equimolar relation (Fig. 3). Fig. 3 shows that all four dependencies rise linearly in the beginning, reaching the plateau at the value 3 for indium with both extractant and 2 for copper with the same extractants. The crossings are clearly defined, since the process of atomic absorbance is in question. Only in the case of indium extraction with LIX84, crossing is not sharp and absorbance values are very low, which in a certain way, can be used as an indicator of process efficiency, i.e. a ability of LIX 84 to chelating indium, respectively.

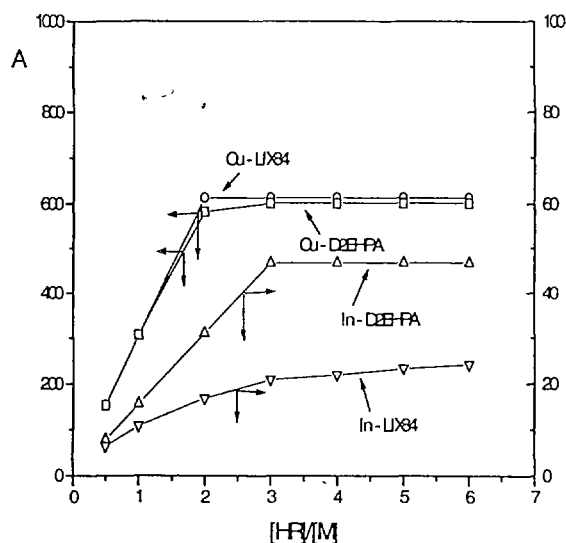


Fig. 2. Continual variations of equimolar solutions of metals in the aqueous phase and chelate agents in the organic phase

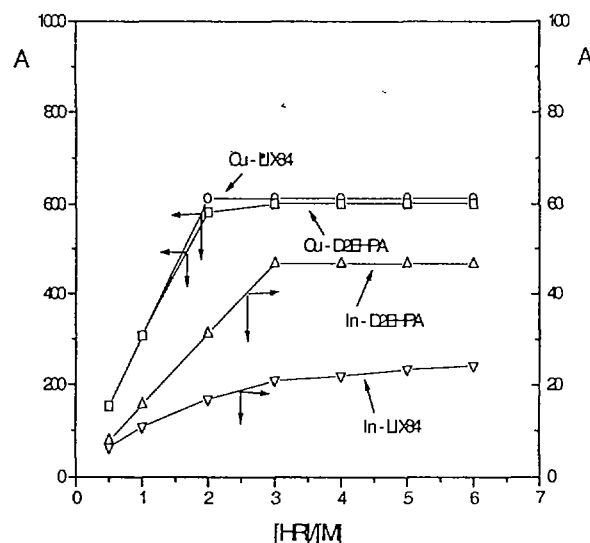


Fig. 3. Determination of stochiometry of complexes by the method of molar ratio



Fig. 4. represents log distribution coefficient in extraction equilibrium as a linear function of the concentration of chelate agent in the organic phase. The following K_{ex} values were obtained: $K_{ex,In-D2EHPA} = 2,5 \cdot 10^{-3} \text{ mol/dm}^3$, $K_{ex,Cu-D2EHPA} = 1,4 \cdot 10^{-3} \text{ mol/dm}^3$, $K_{ex,In-LIX84} = 1,9 \cdot 10^{-3} \text{ mol/dm}^3$, $K_{ex,Cu-LIX84} = 1,1$.

From Fig. 5 it can be seen that degree of separation varies with pH change. Separation factor can be calculated from the relation of distribution coefficients in equilibrium, as follows

$$\log \beta_{In/Cu} = \log m_{In} - \log m_{Cu} \quad (6)$$

Separation factors at different pH values are shown in the Table I.

Table I. Separation factors in the extraction process for different pH.

pH	$\log \beta_{In/Cu}$	
	LIX 84	D2EHPA
2,0	- 4,1	3,2
2,5	- 3,9	3,7
3,0	- 3,7	4,2

The values in Table I show a high selectivity of copper and indium in extraction with LIX 84 and D2EHPA. This selectivity can be ascribed to differences in K_{ex} . Generally, it can be concluded that for the mentioned systems, due to the presence of chemical reaction, the reactants concentrations have a huge influence on the process. Accordingly, these parameters should be kept under controlled.

4 CONCLUSION

Several general conclusions can be brought about the process of simultaneous extraction of copper and indium. From the point of view of process efficiency, the equilibrium constants and concentrations of present chemical species have a great influence. Selectivity of process can change towards increase or decrease with changing values of single parameters, which are included in mathematical expressions for elementary process in the system. Examination of copper extraction from acid sulphate solutions with D2EHPA and LIX 84 shows that used chelate extractant have a great importance for selectivity, which points out that a great attention should be paid to selection of chelate agents, during the optimization process. Selectivity is higher in higher concentrations of metal ions in feeding chelate agents in the organic phase, and is decreased with increase of concentration of hydrogen ions in feeding phase. All the changes of selectivity caused by change of the mentioned parameters are limited up to certain levels. During simultaneous copper and indium extraction with D2EHPA

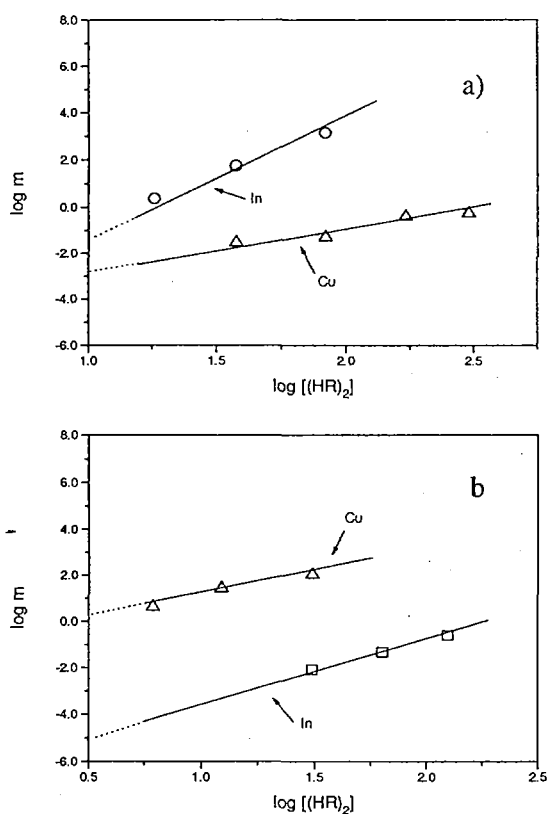


Fig. 4. Distribution coefficient vs. concentration of chelate agent in the organic phase, pH=2,5; $[M^{n+}] = 1,0 \cdot 10^{-3} \text{ mol/dm}^3$, a) HR=D2EHPA, b) HR=LIX 84

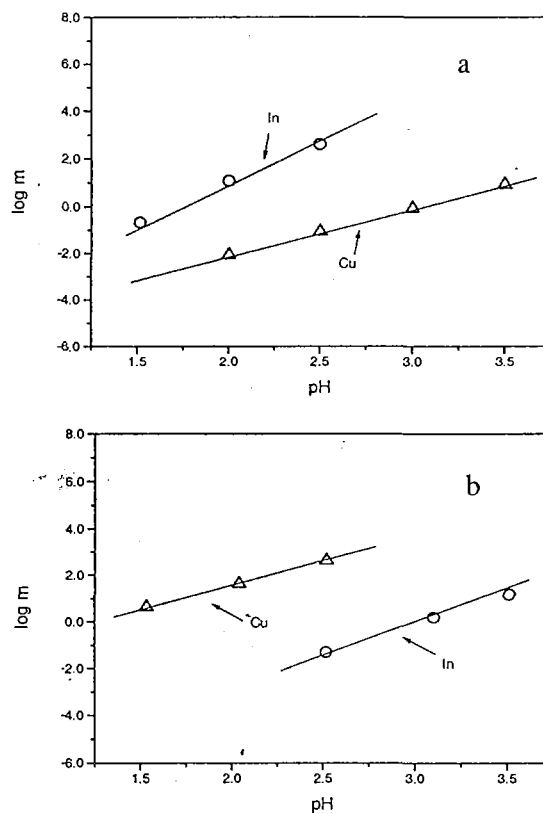


Fig. 5. Distribution coefficient vs. pH of the aqueous phase. $[M^{n+}] = 1,0 \cdot 10^{-3} \text{ mol/dm}^3$, a) [HR=D2EHPA], b) [HR=LIX84]

the same trends with changes of concentration and rate of streaming phases are observed. It is needed to know that all the mentioned considerations are derived for the given systems and experimental conditions as well, and the situation can be significantly different under other conditions. However, many derived conclusions can be used for designing and optimization extraction of other metal ions with other acid chelate extractant.

Apart from new chelate agents and introducing of additional components in the organic phase (modifiers, synergistic agents), in future research, a particular attention should be paid to examination of influences the other parameters (which are not included in this study), as well as to numerical solving of theoretical models.

References

- [1] Y. Jiaoyong; Proc. of ISEC '96, Melbourne, Vol. 1, (1996), 807.
- [2] T. Velea, T. Segarceanu, C. Vasiliu, Proc. of ISEC '96, Melbourne, Vol. 1, (1996), 807.
- [3] B. Nikov, Avtorezime na doktorskata disertacija, Skopje, 1995, 33.
- [4] P. Job, Ann. Chim. Phys. (Paris), 9 (1928) 113.
- [5] H. Irving, T. Pierce, J. Chem. Soc. (1959) 2565.
- [6] J. Yoe, A. Jones, Ind. Eng. Chem., Anal. Ed., 16 (1944) 111.