

THERMODYNAMICS OF THE EXTRACTION OF Cu(II) WITH CAPRIC ACID IN CYCLOHEXANE

ETUDE THERMODYNAMIQUE DE L'EXTRACTION DU Cu(II) AVEC L'ACIDE CAPRIQUE DANS LE CYCLOHEXANE

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ABSTRACT

The liquid–liquid extraction of Cu(II) from sulfate medium $[\text{Na}_2\text{SO}_4] = 0.33 \text{ mol l}^{-1}$ of constant ionic strength ($I=1.0 \text{ mol kg}^{-1}$) with capric acid (HL) in cyclohexane at 283K, 293K, 303K, 313K, and 323 K has been investigated. By using the slope analysis method the stoichiometry of the organometallic complex extracted was determined. At the end of this research, we have found that stoichiometry of Cu(II) complex is of the type $\text{CuL}_2(\text{HL})_2$. The extraction of this metal increased with the increase of temperature. The values of the equilibrium constant have been calculated as well as the values of the thermodynamic parameters ΔH° , ΔS° and ΔG° .

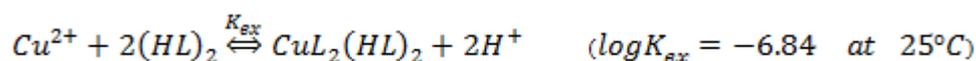
KEYWORDS: liquid–liquid extraction; Capric acid; Stoichiometry; Transition metal ions; Thermodynamic.

RESUME

L'extraction liquide-liquide du Cu(II) à partir de milieu sulfate $[\text{Na}_2\text{SO}_4] = 0.33 \text{ mol l}^{-1}$ de force ionique constante ($I=1.0 \text{ mol kg}^{-1}$) avec l'acide caprique (HL) dans le cyclohexane à 283K, 293K, 303K, 313K, et 323 K a été étudié. En utilisant la méthode d'analyse des pentes, la stœchiométrie du complexe organométallique extrait a été déterminée. A la fin de cette recherche, nous avons trouvé que la stœchiométrie du complexe Cu(II) est du type $\text{CuL}_2(\text{HL})_2$. L'extraction de ce métal a augmenté avec l'augmentation de la température. Les valeurs de la constante d'équilibre ont été calculées ainsi que les valeurs des paramètres thermodynamiques ΔH° , ΔS° et ΔG° .

MOTS CLES: liquid–liquid extraction; Capric acid; Stoichiometry; Transition metal ions, Thermodynamic.

GRAPHICAL ABSTRACT



* $\Delta H^\circ = 35,39 > 0$; $\Delta S^\circ = -11,308 < 0$; $\Delta G^\circ = 38,80 > 0$

1 INTRODUCTION

Solvent extraction system is one of the effective techniques used for the separation of metal ions from aqueous solutions [1-3]. The recovery of copper(II) from aqueous solutions is very important for environmental protection and the chemical equilibria involved in the extraction processes have been studied [4–6]. Carboxylic acids have been studied as extractants for numerous metals and have been shown to exhibit good extraction and separation efficiency. The extracted species involved in the extraction of copper(II), nickel(II), cobalt(II) and iron(III) with carboxylic acids has been investigated by many authors [7-10]. The formation of a dimerized extracted species was first reported for the extraction of copper(II) with propanoic acid [11]. Yamada et al.[12] studied the extraction of copper(II) with capric acid in several inert solvents at aqueous ionic strength of 0.1 M (NaClO₄). The extracted species were determined to be (CuR₂HR)₂ and the extraction constants were calculated in all solvents. The solvent extraction of Co(II) from sodium sulfate solution by capric acid dissolved in chloroform was performed at 25°C [13]. It has been found that the extracted complex as a mononuclear species CoL₂.2HL in the lower concentration region of capric acid and a binuclear one (CoL₂.2HL)₂ in the higher of capric acid concentration region.

Temperature is a parameter that can positively or negatively effect on the extraction process. The solvent extraction of copper(II), cobalt(II) and nickel(II) from sulfate medium with salicylideneaniline(SAN) have been studied with the following parameters: pH, the concentration of the extractant, nature of diluent, and temperature. The stoichiometry coefficients of the extracted complexes were determined by the slope analysis method. The temperature effect in the solvent extraction of each metal with (SAN) has been discussed [14]. Huff et al.[15] studied the extraction of Pb(II), Cu(II), Cd(II), Co(II), and Ni(II) from an aqueous nitric acid medium by mono-2-ethylhexyl phosphoric acid (H₂MEHP) dissolved in o-xylene at the temperature range 25–60°C. They found that the extractant aggregation and extraction stoichiometries for the metal ions did not change with temperature. The thermodynamics of the extraction process was studied by measuring extraction coefficients in this temperature range.

The solvent extraction of cobalt, nickel, and copper ions by the ligand o-diphenylamino benzoic acid in chloroform at 273, 293, and 318 K has been investigated [16]. The temperature effect on the extraction of octahedral and tetrahedral cobalt(II) was investigated by 8-hydroxyquinoline (HOX) and dibenzo-18-crown-6 (Db 18C6) or dibenzylamine (DBA)[17].

The objective of this work is to study the influence of temperature on the solvent extraction of Cu(II) ions, which is a highly toxic metal ion that is readily encountered in the environment.

The present paper describes the results obtained in the extraction of Cu(II) from sulfate medium with a solution of the capric acid such as the determine the stoichiometry of extracted species and their extraction constants and the

thermodynamic parameters (ΔH° , ΔS° et ΔG°).

2 EXPERIMENTAL

2.1 Reagents and solutions

Capric acid (98%, Fluka). The metal solutions were prepared from the copper sulfate (Fluka) (CuSO₄.6 H₂O) (Fluka) and sodium sulfate (Na₂SO₄) (Fluka). Organic diluent cyclohexane was pre-equilibrated with an aqueous solution which did not contain Cu(II). The initial compositions of the phases were as follows:

Aqueous phase: [Cu²⁺] = 1.5 10⁻³ M = 100ppm ;

[Na₂SO₄] = 0.33 M.

Organic phase: [HL]_i = 0.01, 0.02 and 0.04 M.

2.2 Extraction and analytical procedure

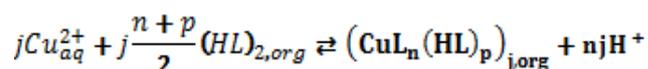
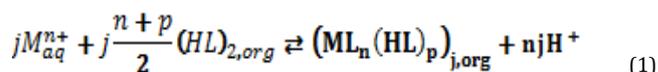
An aqueous solution of Cu(II) (40 mL), was placed in thermostated vessels at 25°C with an equal volume of cyclohexane solutions, containing 0.01, 0.02 and 0.04M of capric acid. The mixture was shaken for 20min, this time was sufficient since the equilibrium was reached rapidly and then both phases were separated by gravity. The pH was adjusted to the desired level by the addition of sodium hydroxide (0.2M). The pH of the aqueous phases was measured by pH-meter with an accuracy of 0.02 pH unit. The ionic strength was maintained at 1 with Na₂SO₄. The temperature was measured with an accuracy of 0.2°C. After phase separation by gravity, the solutions were then allowed to settle a little while in the bath. After this, The metal ion concentrations were determined in aqueous phase photometrically at 820nm using a shimadzu UV-VIS 1240. The metal ion concentrations in the organic phase were calculated from the difference between the metal ion concentrations in the aqueous phase before and after extraction.

3 RESULTS AND DISCUSSION

3.1 General expressions for extraction equilibrium of Cu(II) with capric acid

The carboxylic acid is considered as the dimeric species (HL)₂ in the solvents of low polarity [12, 18, 19]. However, in the polar solvent exist in the form monomeric due to the destroyed owing to their preferential hydrogen bonding with the molecules of polar solvent.

The extraction of Cu (II), by a dimerized capric acid, (HL)₂, in cyclohexane can be represented by the general equation:



Where the subscripts aq and org correspond to the aqueous and organic phases, respectively and j, the degree of polymerization of the complex; $(HL)_2$, extractant in dimeric form; n, cationic charge; p, number of monomeric acids contained in the complex.

The extraction constant can be written as the following expression.

$$K_{ex} = \frac{[(CuL_n(HL)_p)_j]_{org} [H^+]^{nj}}{[Cu^{2+}]_{aq}^j [(HL)_2]_{org}^{j(n+p)/2}} \quad (2)$$

The distribution coefficient D of the metal between the organic and aqueous phases may be expressed as follows:

$$D_{Cu} = \frac{[Cu]_{org}}{[Cu]_{aq}} = \frac{[CuL_n(HL)_p]_{j,org}}{[Cu^{2+}]_{aq}} \\ = K_{ex} [Cu^{2+}]_{aq}^{(j-1)} [(HL)_2]_{org}^{j(n+p)/2} [H^+]^{-nj} \quad (3)$$

Where $[Cu]_{org}$ and $[Cu]_{aq}$ are the total concentrations of the metal in the organic and aqueous phases respectively.

The extraction constant, K_{ex} , is defined as equation (2) can be rewritten as equation (4) by using the distribution ratio of Cu(II).

$$\log D = (j-1) \log [Cu^{2+}]_{aq} + j \frac{n+p}{2} \log [(HL)_2]_{org} + (nj)pH + \log K_{ex} \quad (4)$$

Equation (4) shows that the function $\log D = f(pH)$ at a constant $[(HL)_2]_{org}$ should yield a straight line with a slope of nj only when j is equal to unity.

3.2 Extraction of copper (II) with capric acid

3.2.1 Effect of equilibrium pH

In order to investigate stoichiometries of the extracted species in organic phase and to find out which chemical Equation applies to the extraction process, at fixed Cu (II) concentration, capric acid concentration and ionic strength, the effects of pH on the extraction of Cu (II) with capric acid have been investigated, where the distribution equilibrium studies were carried out at the room temperature 25 °C.

The extraction of Cu(II) by capric acid was accompanied

by a slow development of blue color in the organic phase. The intensities of the colors were qualitatively observed to peak at five hours over a wide pH range 4.5 – 6, or that's the range of extraction of Cu(II) by capric acid.

According to equation (4), Plots of the $\log D_{Cu}$ versus pH for various concentrations of capric acid, are linear with a slope equal to 2 ($n=2$), as shown in figure 01. This suggests full neutralization of Cu(II) valence leading to the release of two protons as given by Eq. (5).

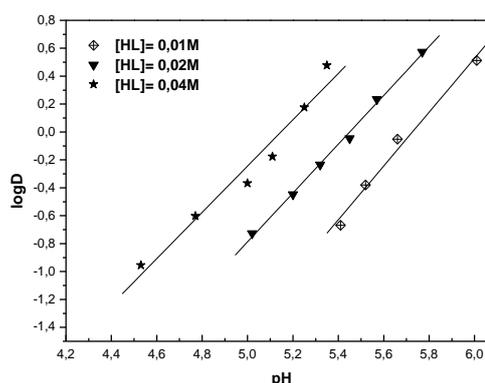
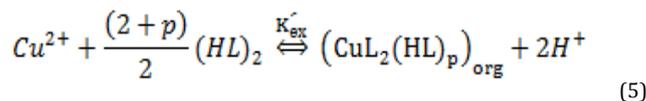


Figure 01: Effect of pH on the extraction of Cu(II) with capric acid in cyclohexane at 25°C.

The data in figure 1 also reveal no dependence of Cu(II) distribution upon the aqueous copper concentration, thereby confirming the monomeric nature of the extracted complex $CuL_2(HL)_p$ where $j=1$. The curves obtained show that the degree of extraction of Cu(II) increases with increase in pH of the aqueous phase and capric acid concentration. These results are similar to those which are obtained by Adjel et al [7] on the extraction of copper(II) using capric acid (HL) in the absence and presence of TOPO in chloroform.

3.2.2 Effect of capric acid concentration

A study on the effect of capric acid concentration on Cu(II) extraction enables us to determine the number of capric acid molecules involved in the extraction species. This effect was investigated by making a series of Cu(II) extractions at various $[HL]_i$, = 0.01, 0.02 and 0.04 M dissolved in cyclohexane at 25°C

According to Eq(4), the variation of $\log D_{Cu}$ versus $\log [(HL)_2]_{org}$ to pH constants for this metal cation in cyclohexane, as shown in figure 02. The values of $[(HL)_2]_{org}$ were calculated by assuming: $[(HL)_2]_{org} = [HL] / 2$ with $[HL]$ the total acid concentration. The curves are straight lines with slope of $(2+p) / 2 = 2$ or $p=2$. Which indicate that two molecules of dimeric capric acid take part in the extraction of one ion of Cu(II). This means that one type of complex $CuL_2(HL)_2$ is extracted in

cyclohexane. The same type of extracted species was reported for the extraction of copper(II) with cyclopentyl acetic acid [20] and capric acid in chloroform [7].

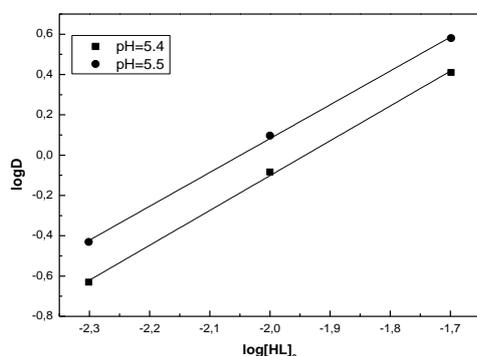
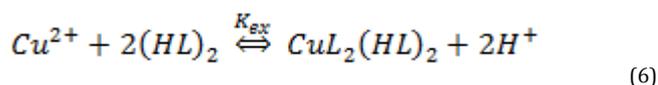


Figure 02: Effect of the extractant concentration on the extraction of in cyclohexane at 25°C

Therefore, Eqs. (1) and (4) could be rewritten as:



$$\log D_{\text{Cu}} = \log K_{\text{ex}} + 2 \log [(\text{HL})_2]_{\text{org}} + 2\text{pH} \quad (7)$$

The logarithmic value of K_{ex} of Cu(II) can, therefore, be calculated for each experimental point from Eq (8):

$$\log K_{\text{ex}} = \log D_{\text{Cu}} - 2 \log [(\text{HL})_2]_{\text{org}} - 2\text{pH} \quad (8)$$

$$\log K_{\text{ex}} = -6.84$$

3.2.3 Temperature dependency

The experimental data for the extraction of Cu(II), using 0.01M of capric acid dissolved into cyclohexane at different temperatures are given in figure 03. As it is shown in this figure, the extraction of the metal increases with increasing the temperature. At higher temperatures viscosity of the organic phase is lower which guaranty better contact between organic and aqueous phase during mixing. Vander Zeeuw [21] has also found the positive effect of the temperature in the extraction of iron Fe(III) with versatic acid where an increase of temperature from 20 °C to 80°C causes an appreciable increase of distribution coefficient.

The plots of $\log D = f(\text{pH})$ are linear of slopes. It should be mentioned that the obtained results reflect that, the temperature has no effect on the equilibria and the stoichiometry of the extracted complex.

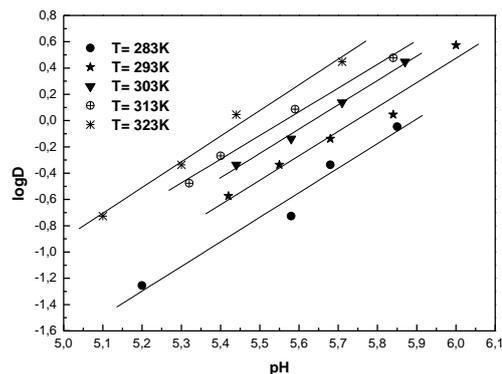


Figure 03: Effect of temperature on the extraction of Cu(II) with capric acid 0.01M in cyclohexane

The thermodynamic parameters for the organic phase were calculated from the Gibbs–Helmholtz equation written in the form:

$$\log K_{\text{ex}} = -\frac{\Delta G^\circ}{2.303RT} = -\frac{\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303RT} \quad (9)$$

Where: ΔH° extraction enthalpy of copper(II); ΔS° extraction entropy of copper(II); T temperature;

R(8.314 J mol⁻¹ K) gas constant

A plot of $\log K_{\text{ex}}$ against $1/T$ gives a straight line of slope $-\Delta H^\circ/2.303R$ and a y-intercept of $\Delta S^\circ/2.303R$ (figure 04).

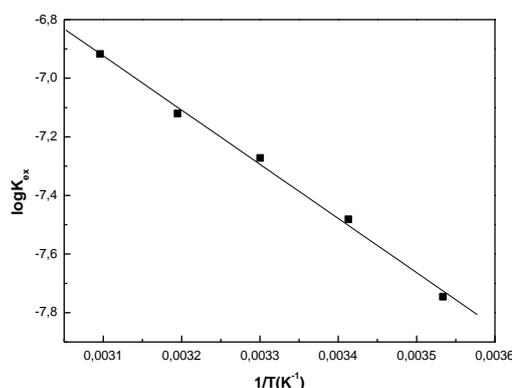


Figure 04: Variation of equilibrium constant with temperature on the extraction of Cu(II) with capric acid.

The values of $\log K_{\text{ex}}$ at different temperatures calculated from Eq. (8) are listed in table 01.

Table 01: Values of the extraction constants of Cu(II) at different temperatures

T, K	283	293	303	313	323
$\log K_{\text{ex}}$	-7,14	-6, 87	-6,67	-6,51	-6,31

The values of ΔH° and ΔS° of the extraction processes and free energy calculated from $\Delta G = -2.303RT \log K_{ex}$ are tabulated in table 02.

Table 02: Thermodynamic parameters of Cu(II) extraction

ΔH° (kJmol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)	ΔG° (kJmol ⁻¹)
35,39	-11,308	38,80

The results show that the extraction of Cu(II) from sulfate medium with capric acid in cyclohexane is an endothermic process which explains the improve extraction when increasing temperature. The negative entropy change ($\Delta S^\circ < 0$) due to the increase of order caused by the new bonds. On the other hand, it suggests strong bonding (metal-ligand) and the formation of a stable complex in the organic phase. The positive values of ΔG° imply that the reaction is not spontaneous. Comparing the values of the thermodynamic parameters of the extracted for copper(II) found in this work with those obtained by Fatibello-Filho et al [22] and Aidi et al [23], the same signs and similar values are found for copper(II) in similar experimental conditions.

4 CONCLUSION

The experimental data obtained in this work shows that the capric acid can be successfully used to remove the heavy metals ions such as Cu(II) from aqueous solutions. It was found that the degree of extraction of Cu(II) increases with increase in the pH of the aqueous phase and capric acid concentration. The stoichiometry of Cu(II) complex extracted with capric acid dissolved in cyclohexane is from the type $CuL_2(HL)_2$, this result was determined by the use of the slope analysis method. Rising temperature in the range from 283K to 323 K had a good impact on the extraction rate of Cu(II) ions, that is to say, the extraction increases with increasing temperature. Enthalpy (ΔH°) for the equilibrium is positive and reflected the endothermic character of the complexation reaction, and the negative entropy change ($\Delta S^\circ < 0$) due to the increase of the order of complexity in the organic phase. The positive values of ΔG° imply that the reaction is not spontaneous.

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