

Solvent Effects on the Extraction of Copper(II) with Lauric Acid

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Abstract

The solvent extraction of copper(II) from nitrate medium with lauric acid (HL) at 25°C is studied as a function of various parameters: pH, concentration of lauric acid and the nature of solvent. The solvent effects on the extraction of copper(II) using polar and nonpolar solvents are treated. Extracted species differs from solvent to solvent: $\text{CuL}_2(\text{HL})_2$ for cyclohexane, dichloromethane, toluene or chloroform and CuL_2 for 1-octanol and methyl isobutyl ketone. The extraction constants, percentage extraction (%E) and free energy (ΔG°) are also calculated for different solvents.

Keywords: Solvent extraction; Copper(II); Lauric acid; Solvent effects; Free energy

Introduction

Solvent extraction system is one of the effective techniques used for separation of metal cations from aqueous solutions [1-8]. It is a suitable method for preventing and protecting environment from pollution. The extraction of copper(II) using carboxylic acids has been a subject of much work research [9-13]. Lauric acid was employed as an extractant for the separation of numerous cations, the composition of extracted species and their extraction constants were reported [14-16]. Ghanadzadeh et al. [17] established that lauric acid extracts capably copper(II) from aqueous solutions and it was shown that in the organic phase dimeric complexes of the $(\text{CuR}_2\cdot\text{HR})_2$ formula are formed. The solvents have a great importance on the extraction efficiency and distribution ratio due to their polarity [18]. As a consequence, studies of the effect of solvents on the extraction of metal ions have been reported by many researchers [19-23]. Yamada et al. [24] studied the extraction of gallium (III) with decanoic acid in different solvents. They established that the extracted decanoates were more extensively polymerized in the less polar solvent than the more polar solvent. However, Ghebhoub et al. [25] investigated the effect of diluents on the extraction of copper(II) with di(2-ethylhexyl)phosphoric acid. They found that in the extracted species were CuL_2 and $(\text{CuL}_2\cdot 2\text{HL})$ in polar and nonpolar diluents respectively. The present paper describes the results obtained from the solvent extraction of copper(II) from nitrate medium by lauric acid in several organic solvents. The scope of the work is to determine the stoichiometries coefficients of the extracted species and their equilibrium constants. In addition, the solvent effects on this extraction system are examined and the interaction with several solvents is interpreted.

Materials and Methods

Reagents and solutions

Lauric acid (Biochem), Copper nitrate (Biochem) and sodium nitrate (Biochem) were used without further purification. Chloroform, toluene, dichloromethane, cyclohexane, 1-octanol and methyl isobutyl ketone (MIBK), were employed as the organic solvents after washing several times with distilled water. The ionic strength of the aqueous medium was assumed to be unity ($[\text{NaNO}_3]=1\text{M}$). Aqueous phase: $[\text{Cu}^{2+}]=1.57 \times 10^{-3} \text{ M}$; $[\text{NaNO}_3]=1\text{M}$. Organic phase: $[\text{HL}]=0.01, 0.02$ and 0.04M .

Extraction and analytical procedures

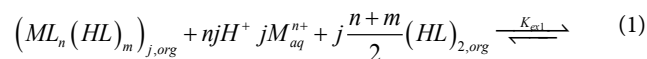
Experiments were carried out by shaking equal volumes (25 ml) of both phases in thermostatted vessels. The time required to reach

the equilibrium state was 30 min. The pH of the aqueous phase was adjusted by adding the necessary amount of 0.1M NaOH. Then, after the two phases were separated completely by gravity, concentrations of the metal remaining in the aqueous phase were determined photometrically at 820 nm using a Philips UV-VIS SP6-36. 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. All the experiments were carried out at constant temperature $T=25^\circ\text{C}$.

Results and Discussion

General treatment of extraction equilibrium of Copper (II) with lauric acid

It is well known that carboxylic acids are present as dimeric species in nonpolar solvents such as toluene, hexane or benzene [14,26] and as monomeric species in polar solvents such as: 1-octanol, and 4-methyl-2-pentanone. [26,27]. The extraction process may be described by the following equilibrium in nonpolar solvents:



Where, equilibrium constant K_{ex1} is defined as Equation (2) and it can be rewritten as (Equation 3) by using the distribution ratio, D of copper (II).

$$K_{\text{ex1}} = \frac{\left[\left(\text{ML}_n(\text{HL})_m\right)_j\right]_{\text{org}} \left[\text{H}^+\right]^{nj}}{\left[\text{M}^{n+}\right]_{\text{aq}}^j \left[\left(\text{HL}\right)_2\right]_{\text{org}}^{j(n+m)/2}} \quad (2)$$

$$\log D = (j-1)\log\left[\text{M}^{n+}\right]_{\text{aq}} + j\frac{n+m}{2}\log\left[\left(\text{HL}\right)_2\right]_{\text{org}} + (nj)\text{pH} - \log\alpha_{\text{Cu}} + \log j + \log K_{\text{ex1}}$$

Where the distribution coefficient, D, is defined as the ratio between the concentration of metal in organic and aqueous phase.

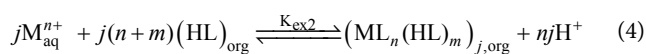
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However, in polar solvents equations (1), (2) and (3) have:



$$K_{ex2} = \frac{[(ML_n(HL)_m)_j]_{org} [H^+]^{nj}}{[M^{n+}]_{aq}^j [HL]_{org}^{j(n+m)}} \quad (5)$$

$$\log D = (j-1) \log[M^{n+}]_{aq} + j(n+m) \log[HL]_{org} + (nj) \text{pH} - \log \alpha_{Cu} + \log j + \log K_{ex2} \quad (6)$$

Where, the species in the aqueous and organic phases are designated by the subscripts aq and org respectively. Other parameters are defined as:

$M=Cu^{2+}$, n =cationic charge, m =number of monomeric acids contained in the complex, j =degree of polymerization, $(HL)_2$; (HL) =extractant in dimeric and monomeric form respectively, α_{Cu} =the side reaction coefficient allowing for metal complexation in the aqueous phase.

The equilibrium slope method has been used to analyze the experimental data for each extraction system. The stoichiometries of the extracted species were determined on the basis of some equations derived from Equations. (3) and (6). With a predetermined lauric acid concentration in the organic phase, the relationship $\log D + \log[M^{n+}]_{aq} = f(\log[M^{n+}]_{aq} + npH)$ should yield a straight line of slope j . On the other hand, if only $(ML_n(HL)_m)_j$ is the extractable species in the extraction system and when j and α are equal to unity, the plot of $\log D$ versus pH at constant concentration of the extractant should yield a straight line with a slope of n . In addition, the plot of $\log D$ versus $\log[(HL)_2]$ and $\log[HL]$ at constant pH should give a straight line of slope $j(n+m)/2$ and $j(n+m)$ respectively, from which the value of m may be calculated. Therefore, the extraction constants can be also determined by intercept with the axis. The percentage extractions (%E) of Copper (II) can be calculated by:

$$\%E = \frac{D}{D+1} \times 100 \quad (7)$$

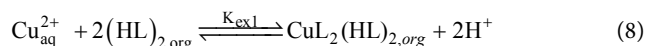
Analysis of the extraction equilibrium in nonpolar solvents

In order to investigate stoichiometries of the extracted species in organic phase and to find out which chemical equation applies to the extraction process, a series of Copper(II) extractions were carried out with lauric acid.

First, the degree of polymerization of the extracted copper laurates is given by the slope of the plot ($\log D + \log[Cu^{2+}]_{aq}$) versus ($\log[Cu^{2+}]_{aq} + 2pH$) at a constant $[(HR)_2]$. The results obtained for chloroform, toluene, dichloromethane and cyclohexane are illustrated in Figure 1. It is evident from Figure 1, linear relations are observed with the slope of one ($j=1$) which indicates that in organic phase monomeric species with lauric acid occur. Second, according to equation (3) the relationships $\log D$ versus pH are determined at a constant $[(HR)_2]$ in chloroform, toluene, dichloromethane and cyclohexane. The results are shown in Figures 2a-d linear relations are observed with the slope of two ($n=2$), confirming that the monomeric extracted species in organic phase is $CuL_2(HL)_m$ ($j = \alpha_{Cu} = 1$).

Finally, a study on the effect of lauric acid concentration on Copper(II) extraction enables us to determine the number of lauric acid molecules involved in the extracted species. This effect was investigated by making a series of copper(II) extractions at various $[(HR)_2]$ dissolved in chloroform, toluene, dichloromethane and cyclohexane. Concentration of dimer was calculated as $[(HL)_2] = [HL]/2$.

According to equation (3) Plots of $\log D$ versus $\log[(HL)_2]_{org}$ at constant pH were linear with the slope about of 2, as shown in Figure 3, that is, $(2+m)/2=2$ or $m=2$. Consequently, the composition of the extracted species is $CuL_2(HL)_2$. A same complex was obtained by Baba et al. [10] in the solvent extraction of copper(II) with 2-butylthiododecanoic acid and 2-bromododecanoic acid in hexane. Therefore, equations (1) and (3) could be rewritten as:



$$\log D = 2 \log [(HL)_2]_{org} + 2 \text{pH} + \log K_{ex1} \quad (9)$$

Percentage extraction (%E) and the distribution coefficient (D) were calculated to determine the extracting capability of lauric acid diluted in cyclohexane, dichloromethane, toluene and chloroform (Tables 1- 4). The distribution coefficient (D) and extraction percentage (%E) increased with increasing pH. The visible spectra of the loaded organic phase were performed in dichloromethane, toluene chloroform, and cyclohexane (Figure 4). Copper laurates shows an absorbance in the 660-678 nm region which indicated to octahedral geometry coordination of the extracted species [12]. In this study, it was found that two molecules of dimeric lauric acid coordinating with the central copper ion, water molecules would complete the coordination sphere so that the Copper ion could obtain a stable structure. On the basis of this interpretation, the plausible structure of the monomeric copper laurates $CuL_2(HL)_2$ in nonpolar solvents may be written as shown in Figure 5. This structure is similar with that obtained by Adjel [28] on the extraction of copper (II) by capric acid in chloroform.

Analysis of the extraction equilibrium in polar solvents

The degree of polymerization of the extracted copper laurates is given by the slope of the plot ($\log D + \log[Cu^{2+}]_{aq}$) versus ($\log[Cu^{2+}]_{aq} + 2pH$) at a constant $[HR]$. The results obtained for 1-octanol and MIBK are illustrated in Figure 6. It is evident from Figure 6, linear relations are observed with the slope of one ($j = 1$) which indicates that in organic phase monomeric species with lauric acid occur.

According to equation (6), the plots of $\log D$ versus pH were determined at a constant $[HR]$ in 1-octanol and MIBK, The results are shown in Figure 7a and Figure 7b, linear relations are observed with the slope of 2 ($n=2$), confirming that the monomeric extracted species in organic phase is $CuL_2(HL)_m$ ($j = \alpha_{Cu} = 1$). In the other hand, the

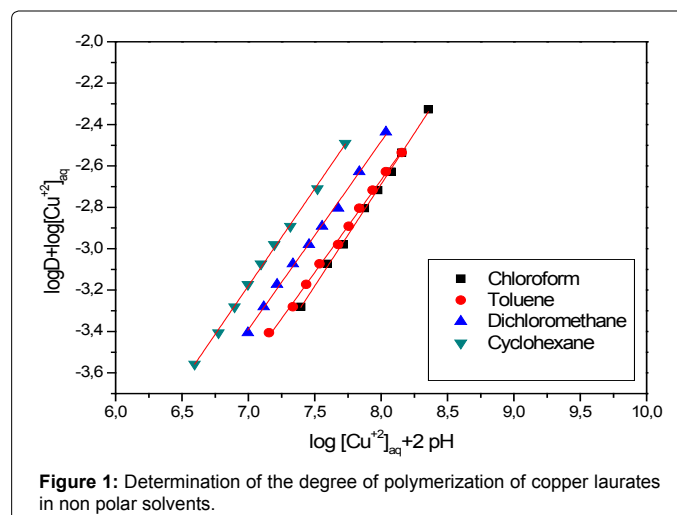
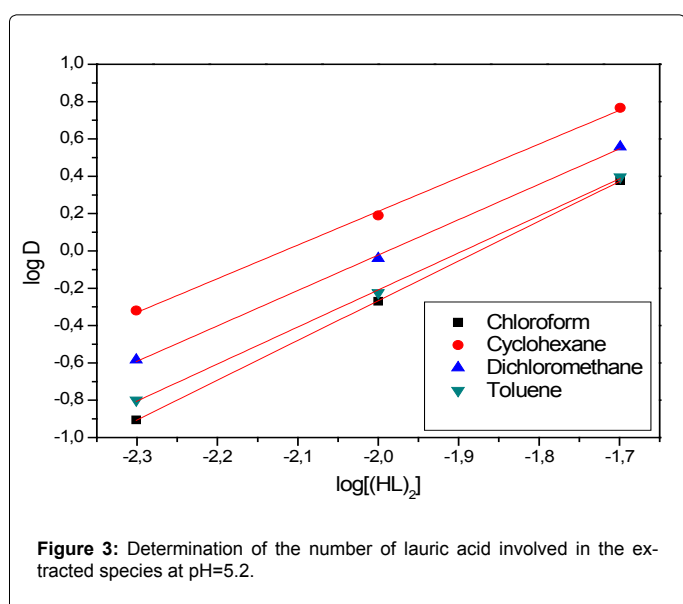
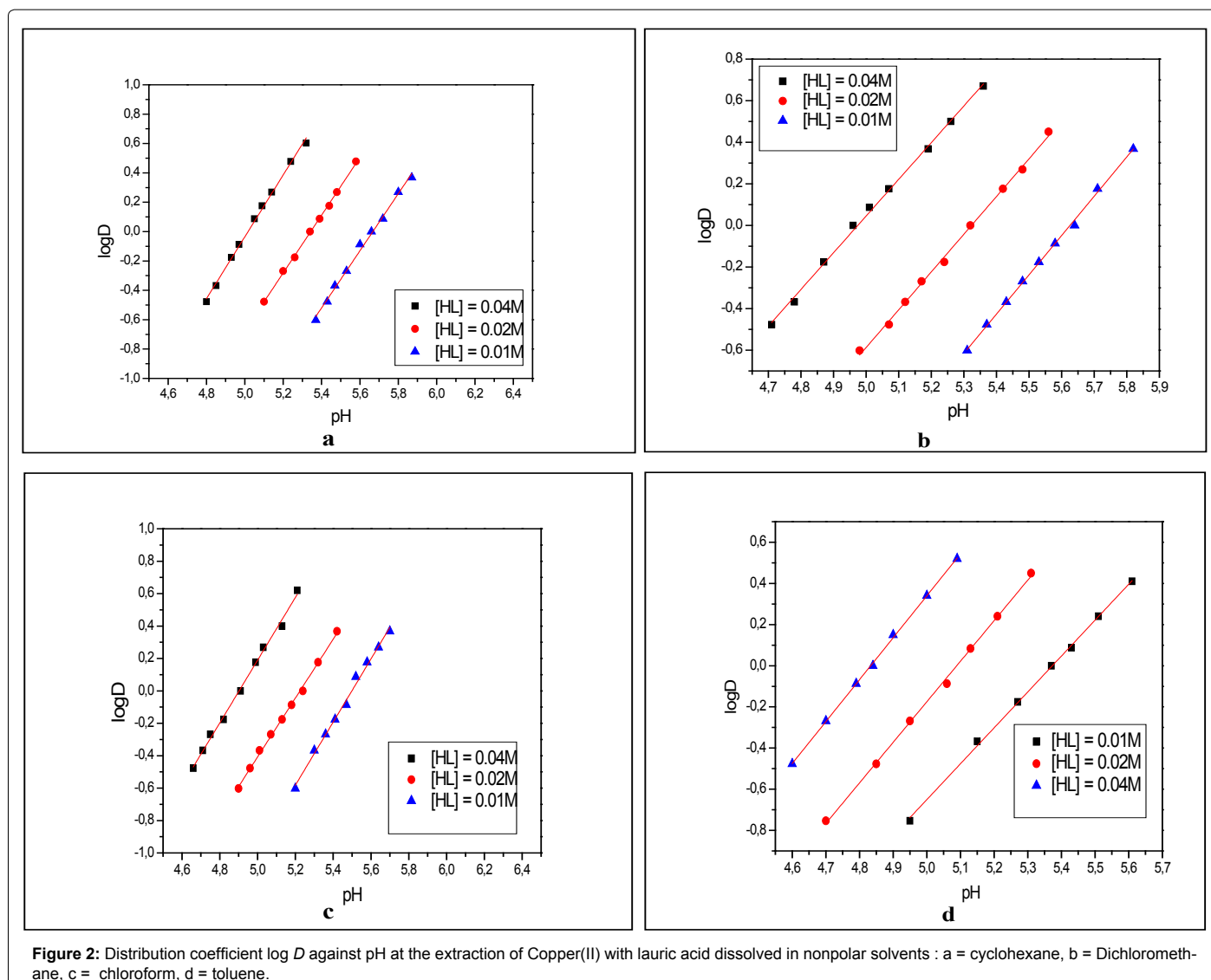
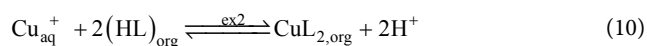


Figure 1: Determination of the degree of polymerization of copper laurates in non polar solvents.



effect of lauric acid concentration on Copper (II) extraction enables us to determine the number of lauric acid molecules involved in the extracted species. This effect was investigated by making a series of Copper (II) extractions at various $[\text{HL}]$ dissolved in 1-octanol and MIBK.

According to equation (6), Plots of $\log D$ versus $\log[\text{HL}]_{\text{org}}$ at constant pH were linear with a slope of 2, as shown in Figure 8, that is, $2 + m = 2$ or $m = 0$. Consequently, the composition of the extracted species is CuL_2 . This result is in accordance with that reported by Yamada et al. [27]. Therefore, equations (4) and (6) could be rewritten as:



$$\log D = 2\log[\text{HL}]_{\text{org}} + 2\text{pH} + \log K_{\text{ex2}} \quad (11)$$

Percentage extraction (%E) and the distribution coefficient (D) were calculated to determine the extracting capability of lauric acid diluted in 1-octanol and MIBK (Tables 5 and 6). The distribution coefficient (D) and extraction percentage (%E) increased with increasing pH .

The visible spectra of copper laurates in MIBK and 1-octanol showed an absorbance at 668 and 700 nm respectively (Figure 9). This

pH	[Cu] _{aq} × 10 ⁻³ (mol/l)	[Cu] _{org} × 10 ⁻³ (mol/l)	D	%E
4.53	1.25	0.31	0.24	19.75
4.60	1.18	0.38	0.32	24.77
4.70	1.02	0.54	0.53	34.80
4.79	0.86	0.70	0.81	44.83
4.84	0.78	0.78	0.99	49.84
4.93	0.62	0.94	1.49	59.87
5.04	0.47	1.09	2.32	69.90
5.15	0.31	1.25	3.98	79.93
5.27	0.15	1.41	8.96	89.96

Table 1: The distribution coefficient (D) and extraction percentage (%E) for extraction of copper (II) with lauric acid (0.04M) diluted in cyclohexane. [Cu]_{aq,initial} = 1.57 × 10⁻³ M.

pH	[Cu] _{aq} × 10 ⁻³ (mol/l)	[Cu] _{org} × 10 ⁻³ (mol/l)	D	%E
4.66	1.18	0.38	0.32	24.77
4.71	1.10	0.46	0.42	29.78
4.75	1.02	0.54	0.53	34.80
4.82	0.94	0.62	0.66	39.81
4.86	0.86	0.70	0.81	44.83
4.91	0.78	0.78	0.99	49.84
4.94	0.70	0.86	1.21	54.86
4.99	0.62	0.94	1.49	59.87
5.03	0.55	1.01	1.84	64.89
5.13	0.39	1.17	2.98	74.92
5.24	0.23	1.33	5.64	84.95

Table 2: The distribution coefficient (D) and extraction percentage (%E) for extraction of copper (II) with lauric acid (0.04M) diluted in dichloromethane. [Cu]_{aq,initial} = 1.57 × 10⁻³ M.

pH	[Cu] _{aq} × 10 ⁻³ (mol/l)	[Cu] _{org} × 10 ⁻³ (mol/l)	D	%E
4.71	1.18	0.38	0.32	24.77
4.78	1.10	0.46	0.42	29.78
4.87	0.94	0.62	0.66	39.81
4.92	0.86	0.70	0.81	44.83
4.96	0.78	0.78	0.99	49.84
5.01	0.70	0.86	1.21	54.86
5.07	0.62	0.94	1.49	59.87
5.14	0.55	1.01	1.84	64.89
5.19	0.47	1.09	2.32	69.90
5.29	0.31	1.25	3.98	79.93
5.44	0.15	1.41	8.96	89.96

Table 3: The distribution coefficient (D) and extraction percentage (%E) for extraction of copper (II) with lauric acid (0.04M) diluted in toluene. [Cu]_{aq,initial} = 1.57 × 10⁻³ M.

result indicated to octahedral geometry coordination of the extracted species [27]. In this study, it was found that two molecules of monomeric lauric acid coordinating with the central Copper ion, water and/or solvent molecules coordinate to copper atoms in place of lauric acid molecules. On the basis of this interpretation, the plausible structure of the monomeric copper laurates CuL₂ in polar solvents may be written as shown in Figure 10. A similar structure was obtained by Yamada et al. [27] on the extraction of Copper (II) with decanoic acid into 1-octanol.

Analysis of the extraction equilibrium in nonpolar and polar solvents

In order to compare the extraction properties of several solvents, a

series of Copper (II) extractions were performed using lauric acid 0.02 M dissolved in toluene, dichloromethane, chloroform, cyclohexane, MIBK and 1-octanol. The results obtained are presented in Figure 11 as plots of log D against pH. The relationships have a linear nature of

pH	[Cu] _{aq} × 10 ⁻³ (mol/l)	[Cu] _{org} × 10 ⁻³ (mol/l)	D	%E
4.8	1.18	0.38	0.32	24.77
4.85	1.10	0.46	0.42	29.78
4.93	0.94	0.62	0.66	39.81
4.97	0.86	0.70	0.81	44.83
5.05	0.70	0.86	1.21	54.86
5.09	0.62	0.94	1.49	59.87
5.14	0.55	1.01	1.84	64.89
5.24	0.39	1.17	2.98	74.92
5.32	0.31	1.25	3.98	79.93

Table 4: The distribution coefficient (D) and extraction percentage (%E) for extraction of copper (II) with lauric acid (0.04M) diluted in chloroform. [Cu]_{aq,initial} = 1.57 × 10⁻³ M.

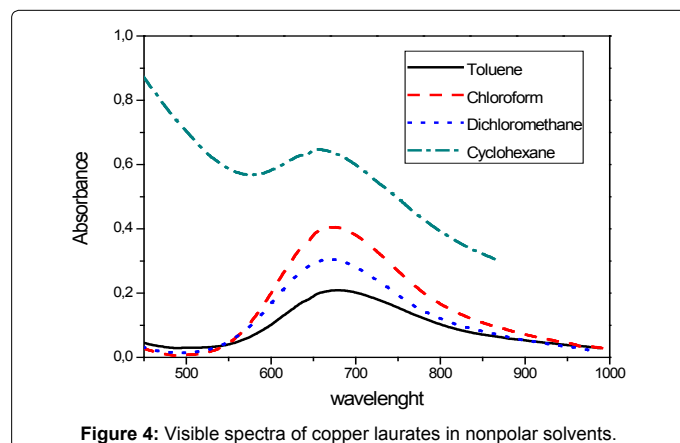


Figure 4: Visible spectra of copper laurates in nonpolar solvents.

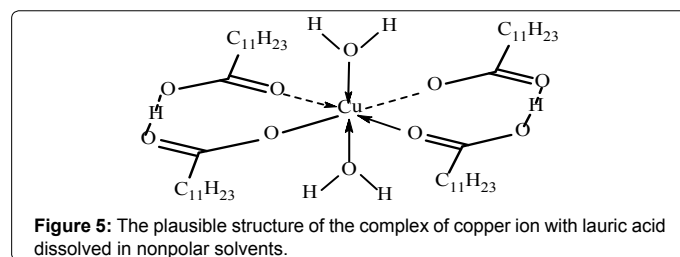


Figure 5: The plausible structure of the complex of copper ion with lauric acid dissolved in nonpolar solvents.

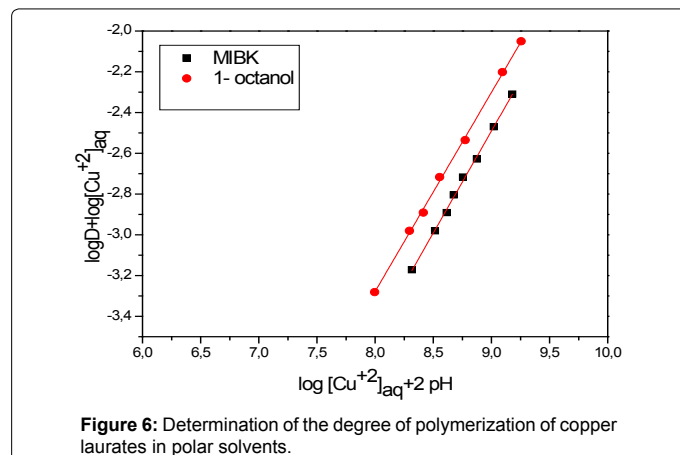


Figure 6: Determination of the degree of polymerization of copper laurates in polar solvents.

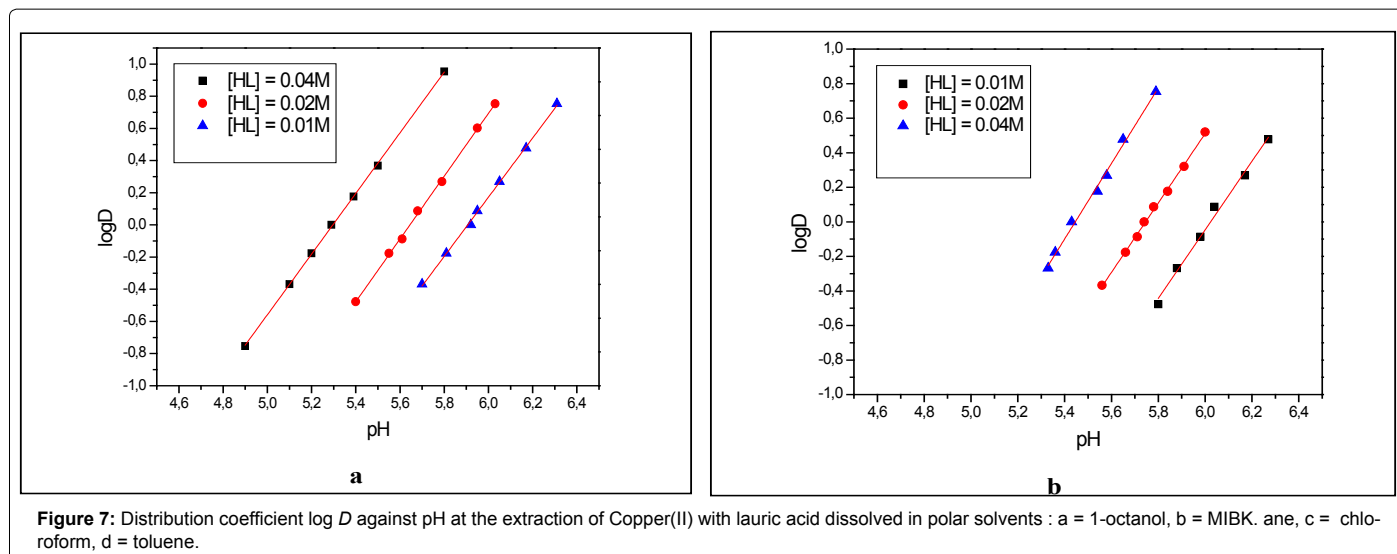


Figure 7: Distribution coefficient $\log D$ against pH at the extraction of Copper(II) with lauric acid dissolved in polar solvents : a = 1-octanol, b = MIBK. ane, c = chloroform, d = toluene.

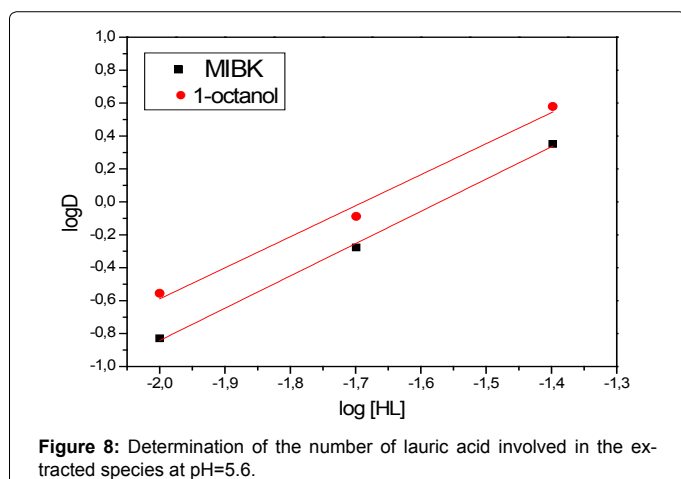


Figure 8: Determination of the number of lauric acid involved in the extracted species at $\text{pH}=5.6$.

pH	$[\text{Cu}]_{\text{aq}} \times 10^{-3}$ (mol/l)	$[\text{Cu}]_{\text{org}} \times 10^{-3}$ (mol/l)	D	%E
4.9	1.33	0.23	0.17	14.73
5.1	1.10	0.46	0.42	29.78
5.2	0.94	0.62	0.66	39.81
5.29	0.78	0.78	0.99	49.84
5.39	0.62	0.94	1.49	59.87
5.5	0.47	1.09	2.32	69.90
5.6	0.31	1.25	3.98	79.93
5.7	0.23	1.33	5.64	84.95

Table 5: The distribution coefficient (D) and extraction percentage (%E) for extraction of copper (II) with lauric acid (0.04M) diluted in 1-octanol. $[\text{Cu}]_{\text{aq,initial}} = 1.57 \times 10^{-3} \text{M}$.

slopes about to 2. From these results, it was observed that nonpolar solvents showed better performance in Copper (II) extraction than polar solvents. This result is in accordance with that obtained in literature [24]. Also, it is clear that the cyclohexane was as the preferred solvent for copper (II) extraction, may be explained by the total absence of interactions between lauric acid and the solvent. Oukebdane et al. [29] tested the extraction of copper (II) by a mixture of lauric acid and TOPO in different solvents (chloroform, nitromethane and cyclohexane). They observed that cyclohexane as the favored solvent.

On the other hand, the extraction of Copper (II) in dichloromethane is better than in chloroform and toluene, these results can depend on dielectric constants of the solvents. Dichloromethane having high dielectric constants is favored for the extraction of all the metal ions. In addition, the better solvation of the complexes by dichloromethane may be a valuable reason for better extraction [30,31]. The Copper (II) extraction in chloroform is weakest from the stronger interactions between extractant and chloroform in the organic phase, these interactions decreased the activity of lauric acid. However, in polar solvents, 1-octanol and MIBK, it was observed that the distribution coefficient decreased as the polarity of solvents increased. It can be explained that the polar solvents are capable to forming hydrogen bonds with electron donor atoms of lauric acid lead to a reduction in the active concentration of the lauric acid, consequently, poorer extraction of Copper results.

In MIBK, which is a more polar solvent, the extraction proceed rapidly and a lower amount of Copper (II) was extracted than that in 1-octanol, would probably explained by the stronger chemical interaction between MIBK and lauric acid in addition to the solubility of MIBK in aqueous phase. This result is in accordance with that observed by Ghebghoub et al. [25]. While a poor extraction was achieved when using MIBK as solvent on the extraction of Copper (II) by di(2-ethylhexyl)phosphoric acid. Table 7 gives the stoichiometries of the extracted copper species with lauric acid in different solvents and their extraction constants. The $\log K_{\text{ex}}$ values are higher in nonpolar solvents than in polar solvents. This result can be explained by the extensive solvation of lauric acid in polar solvents [32].

Thermodynamic studies of copper (II) extraction with lauric acid in different solvent

In order to investigate the solvent effects on the thermodynamic parameter of Copper (II) extraction, the free energy (ΔG°) was calculated for different solvents: chloroform, dichloromethane, cyclohexane, toluene, 1-octanol and methyl isobutyl ketone (MIBK) at constant temperature $T = 298.2 \text{ K}$. The ΔG° is expressed by the following equation [17,33].

$$\Delta G^\circ = -2.303 RT \log K_{\text{ex}} \quad (12)$$

Where R is the universal gas constant (8.314 J/mol K), T is the thermodynamic temperature and K_{ex} is the extraction constant. The

pH	[Cu] _{aq} × 10 ⁻³ (mol/l)	[Cu] _{org} × 10 ⁻³ (mol/l)	D	%E
5.33	1.023	0.54	0.53	34.80
5.36	0.94	0.62	0.66	39.81
5.43	0.78	0.78	0.99	49.84
5.54	0.62	0.94	1.49	59.87
5.58	0.55	1.01	1.84	64.89
5.65	0.39	1.17	2.98	74.92
5.79	0.23	1.33	5.64	84.95

Table 6: The distribution coefficient (D) and extraction percentage (%E) for extraction of copper (II) with lauric acid (0.04M) diluted in MIBK. [Cu]_{aq,initial} = 1.57 × 10⁻³ M.

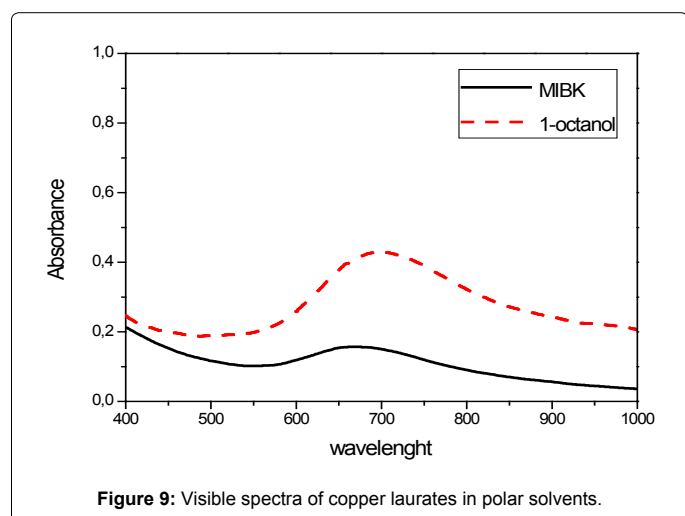


Figure 9: Visible spectra of copper laurates in polar solvents.

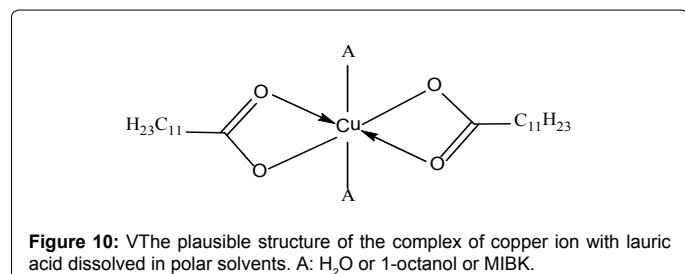


Figure 10: The plausible structure of the complex of copper ion with lauric acid dissolved in polar solvents. A: H₂O or 1-octanol or MIBK.

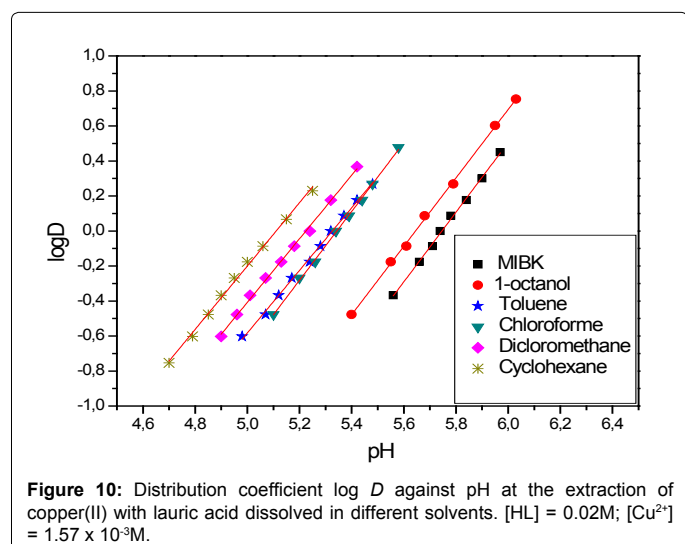


Figure 10: Distribution coefficient log *D* against pH at the extraction of copper(II) with lauric acid dissolved in different solvents. [HL] = 0.02M; [Cu²⁺] = 1.57 × 10⁻³ M.

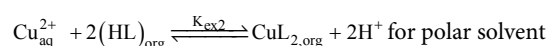
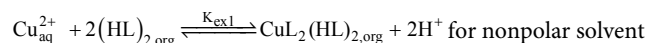
Solvent	logK _{ex}	ΔG° (kJ/mol)	Extracted species
Cyclohexane	-10.71	61.15	CuL ₂ (HL) ₂
Dichloromethane	-11.08	63.26	CuL ₂ (HL) ₂
Toluene	-11.31	64.57	CuL ₂ (HL) ₂
Chloroform	-11.39	65.03	CuL ₂ (HL) ₂
1-octanol	-11.89	67.88	CuL ₂
MIBK	-12.14	69.31	CuL ₂

Table 7: The extraction constant and free energy (ΔG°) for extraction of copper (II) with lauric acid diluted in several solvents at T = 298.2 K.

results obtained are shown in Table 7. It is evident from Table 7, the free energy (ΔG°) increases with the polarity of solvents. In addition, the (ΔG°) value is positive. The positive value of (ΔG°) indicated that the Copper (II) extraction with lauric acid didn't occurred spontaneously in all solvents examined.

Conclusion

The results obtained in this work have established the feasibility of using lauric acid to remove the heavy metal ions like Copper (II) from aqueous solutions. Lauric acid extracts Copper (II) as a monomeric Copper laurates from nitrate medium according to the following stoichiometric relations.



The choice of solvent, polar or nonpolar, has a greater effect on the extraction efficiency. The nonpolar solvents showed better performance than the polar solvents on the Copper extraction by lauric acid. The extraction capacity of lauric acid in different solvents decreases in the order: cyclohexane > dichloromethane > toluene ≥ chloroform > 1-octanol > MIBK. The positive value of the free energy (ΔG°) indicated that the copper(II) extraction with lauric acid didn't occurred spontaneously.

References

- Aidi A, Barkat D (2010) Solvent extraction of copper (II) from sulfate medium with N-(2-hydroxybenzylidene) aniline. J Coord Chem 63: 4136-4144.
- Barkat D, Derriche Z (2001) Synergistic solvent extraction of zinc (II) and cadmium (II) from sulfate medium by a mixture of 1-phenyl-3-methyl-4-benzoylpyrazol-5-one and methyl-isobutyl ketone. Turk J Chem 25: 381-389.
- Barkat D, Kameche M (2007) Liquid-liquid extraction of copper (II) with Schiff's bases derived from salicylaldehyde. Phys Chem Liq 45: 289 - 293.
- Barkat D, Kameche M, Tayeb A, Benabdellah T, Derriche Z, et al. (2004) Ionic strength effect on the liquid-liquid extraction of zinc(II) and cadmium(II) from sulphate medium by 1-phenyl-3-methyl-4-benzoylpyrazol-5-one in chloroform. Phys Chem Liq 42: 53-61.
- Barkat D, Omari M (2005) Extraction of copper (II) with salicylideneaniline from sulphate and perchlorate media. Asian J Chem 17: 202-208.
- Zhang X, Li X, Cao H, Zhang Y (2010) Separation of copper, iron (III), zinc and nickel from nitrate solution by solvent extraction using LK-C2. Separation and Purification Technology 70: 306-313.
- Nakasuka N, Mitsuoka Y, Tanaka M (1974) Extraction of zinc and cadmium with capric acid. J Inorg Nucl Chem 36: 431-438.
- Parhi PK, Padhan E, Palai AK, Sarangi K, Nathsarma KC, et al. (2011) Separation of Co (II) and Ni (II) from the mixed sulphate/chloride solution using NaPC-88A. Desalination 267: 201-208.
- Adjel F, Barkat D (2011) Synergistic extraction of copper (II) from sulfate medium with capric acid and tri-n-octylphosphine oxide in chloroform. J Coord Chem 64: 574-582.
- Baba Y, Inoue K (1988) Solvent extraction equilibria of copper (II) by carboxylic acids with high acid dissociation constants. Hydrometallurgy 21: 203-212.

11. Preston JS (1985) Solvent extraction of metals by carboxylic acids. *Hydrometallurgy* 14: 171-188.
12. Bartecki A, Apostoluk W (1978) Extraction of copper(II) from ammonium chloride solutions with capric acid. *J Inorg Nucl Chem* 40: 109-116.
13. Tanaka M, Niinomi T (1965) Extraction of copper (II) with capric acid dissolved in benzene. *J Inorg Nucl Chem* 27: 431-437.
14. Elizalde MP, Castresana JM, Alonso MC (1985) Extraction of Ni(II) by n-dodecanoic acid dissolved in toluene. *Polyhedron* 4: 2097-2101.
15. Apostoluk W, Bartecki A (1985) Extraction of Chromium(III) from sodium chloride solutions by means of carboxylic acids. *Hydrometallurgy* 15: 191-202.
16. Elizalde MP, Castresana JM, Elorriaga AI (1987) Extraction of Fe(III) by n-dodecanoic acid dissolved in toluene. *Polyhedron* 6: 2155-2160.
17. Ghanadzadeh H, Abbasnejad S (2011) Separation of copper (II) with solvent extraction using lauric acid diluted in benzene. *J Thermodyn Catal* 2
18. Cui Y, Yang J, Yang G, Xia G, Nie Y, et al. (2012) Effect of diluents on extraction behaviour of rare earth elements with N,N,N',N'-tetrabutyl-3-oxy-glutaramide from hydrochloric acid. *Hydrometallurgy* 121-124: 16-21.
19. Rezaei K, Nedjate H (2003) Diluent effect on the distribution ratio and separation factor of Ni(II) in the liquid-liquid extraction from aqueous acidic solutions using dibutylidithiophosphoric acid. *Hydrometallurgy* 68: 11-21.
20. Van de Voorde I, Pinoy L, Courtijn E, Verpoort F (2005) Influence of acetate ions and the role of the diluents on the extraction of copper (II), nickel (II), cobalt (II), magnesium (II) and iron (II, III) with different types of extractants. *Hydrometallurgy* 78
21. Yamada H, Tanaka M (1976) Solvent effects on extraction of copper with capric acid. *J Inorg Nucl Chem* 38: 1501-1504.
22. Chowdhury M, Sanyal S K (1994) Diluent effect on extraction of tellurium (IV) and b selenium (IV) by tri-n butyl phosphate. *Hydrometallurgy* 34: 319-330.
23. El-Nadi Y A (2010) Effect of diluents on the extraction of praseodymium and samarium by Cyanex 923 from acidic nitrate medium. *J Rare Earths* 28: 215-220.
24. Yamada H, Imai S, Takeuchi E (1983) Solvent effects on the extraction of Gallium (III) with decanoic acid. *Bull Chem Soc Jpn* 56: 1401-1406.
25. Ghebghoub F, Barkat D (2009) The effect of diluents on extraction of copper(II) with di(2-ethylhexyl) phosphoric acid. *J Coord Chem* 62: 1449-1456.
26. Schweitzer G K, Morris D K (1969) The partition and dimerization of octanoic acid in several organic-aqueous systems. *Anal Chim Acta* 45: 65-70.
27. Yamada H, Suzuki S, Tanaka M (1981) Extraction of Cu(II) with decanoic acid into 1-octanol. *J Inorg Nucl Chem*. 43: 1873-1879.
28. Adjel F (2014) Mixtures of various synergists to capric acid in the extraction of transition metals.
29. Oukebdane K, Didi MA, Azzouz A, Villemin D (2004) Solvent extraction of copper (II) by synergistic mixtures of trioctylphosphine oxide and lauric acid. *Scientific Study and Research* (1-2): 59-64.
30. Al Zoubi W, Kandil F, Chebani M K (2012) Synthesis of macrocyclic schiff bases based on Pyridine-2,6-Dicarbohydrazide and their use in Metal Cations Extraction. *Organic Chem Current Res* 1
31. Strasser BO, Popov AI (1985) Influence of solvent properties on the kinetics of complexation of the sodium ion with 18-crown-6. *J Am Chem Soc* 107: 7921-7924.
32. Yamada H, Kato C (1993) Solvent and steric effects on the extraction of copper (II) with pivalic acid. *Talanta* 40: 1049-1057.
33. Choppin GR (2004) Complexation of metal ions, in: Rydberg J, Cox M, Musikas, Choppin GR (Eds.) *Solvent Extraction Principles and Practice*, Marcel Dekker Inc., USA.