

STUDY OF THE EXTRACTION OF COBALT(II) FROM SULPHATE MEDIUM BY USING CAPRIC ACID DISSOLVED IN CHLOROFORM

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ABSTRACT

In this work we have first investigated the extraction of cobalt(II) from sulphate medium using capric acid dissolved in chloroform and then the effect of other diluents on the extraction process at 25°C. This study aims to understand the behaviour followed by this metal or, in other words, find its stoichiometry at the end of the extraction. This department is strongly dependent on many parameters like pH of the aqueous solution, acid concentration and the nature of the solvent. Each one of these parameters will be discussed. Temperature is another parameter that will be studied in this work. At the end of this research, we have found that stoichiometry of Co(II) complex is of the type $\text{CoA}_2(\text{HR})_2$ (HR is an abridgment of capric acid). The equilibrium constant K_{ex} and the thermodynamic parameters H° , S° , and G° have been evaluated.

Keywords: Capric acid; Cobalt(II); Sulphate medium; Solvent polarity, Temperature effect.

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1. INTRODUCTION

Environnemental pollution is getting more and more complex. It is, however, still attracting but marginal attention. Solvent extraction is a technique widely used for separation of one or more component from aqueous solutions and it can be one of the most effective solutions for the pollution problem, because of its sensibility and high efficiency [1-7]. Carboxylic acids occupy an important place in solvent extraction [8]. Outstanding works about carboxylic acids



properties were established by Fletcher et al [9-12]. Capric acid was also used for the same purpose in many studies it had given a promising results. Tanaka et al [13] reported the formation of monomer $\text{CoR}_2(\text{HR})_4$ at lower loading of organic phase formed from capric acid dissolved in benzene and a dimer $(\text{CoR}_2)_2(\text{HR})_4$ at high loading of the organic phase. Given the importance of the solvent nature in the extraction process, its selection must be done with the utmost caution. For this consideration solvent effect has been the subject of many studies one of them is the effect of solvent in the extraction of gallium(III) with capric acid established by Yamada et al [14]. Where they found out that the degree of polymerization of extracted decanoates is even higher in the solvent with the lesser polarity than in its counterpart with higher polarity. Temperature is another important parameter that can positively or negatively influence the extraction process, sometimes temperature has no effect on this process. In this paper we investigate the solvent extraction of cobalt(II) from sulphate medium with capric acid where complex structure's formed in the organic phase was found, the effect of a number of solvents in extracting cobalt ions was studied and the effect of temperature was also discussed.

2. EXPERIMENTAL

2.1. Reagents and solutions

Capric acid (98%, Fluka) used without further purification, organic diluents chloroform, toluene and cyclohexane were pre-equilibrated with aqueous solution which did not contain any metal. Sodium Hydroxide prepared in (0.2M) for the pH adjustment, cobalt sulphate solutions were prepared by dissolution of the respective sulphates in demineralized water (reagent grade extra pure from (Merck).

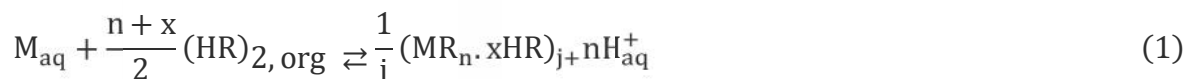
2.2. Extraction and analytical procedure

A mixture of equal volumes of cobalt sulphate (6.8×10^{-3} M, 400ppm) and capric acid (0.02M, 0.04M and 0.08M) dissolved in chloroform, 30ml of each one, is mechanically shaken up in a double-walled glass vessel at 25°C, for 30 minutes which is sufficient for reaching suitable equilibrium. The pH is adjusted by adding an NaOH solution (0.2M). The ionic strength of the aqueous phase was assumed to be unity $[\text{Na}_2\text{SO}_4] = 0.33\text{M}$. The solution was allowed to settle for half an hour in order to separate the phases (the two phases are completely separated). The cobalt concentration in the aqueous solution is photometrically calculated at 510 nm using a Philips UV-VIS SP6-36. The organic phase concentration is the difference between the initial concentration of cobalt(II) in the aqueous solution and after the extraction.

3. DISCUSSION OF RESULTS

3.1. General treatment of the extraction equilibrium of cobalt(II) with capric acid [3]

In the most generalized way the overall extraction of a metal ion from an aqueous layer with an acidic extractant may be written as follows:



The extraction constant can be written as the following expression:

$$K' = \frac{[C]_{org}^{\frac{1}{j}} [H]_{aq}^n}{[M]_{aq} [(HR)_{2,org}]^{\frac{(n+x)}{2}}} \cdot \frac{\gamma_{C,org}^{\frac{1}{j}} \gamma_{nH,org}^n}{\gamma_{M,org} \gamma_{(HR)_{2,org}}^{\frac{(n+x)}{2}}} = KB \quad (2)$$

Where $[C] = (MR_n \cdot xHR)_j$

The equation for D then follows eqn. (3)

$$D = \frac{[M]_{tot,org}}{[M]_{tot,aq}} \quad (3)$$

$$[C]_{org}^{\frac{1}{j}} = \left[\frac{1}{j} M \right]^{\frac{1}{j}} = [M]_{org}^{\frac{1}{j}} \left(\frac{1}{j} \right)^{\frac{1}{j}} = [M]_{org}^{\frac{(1-j)}{j}} \left(\frac{1}{j} \right)^{\frac{1}{j}}$$

Further, it follows from eq.3 that $[M]_{org} = D[M]_{aq}$, and hence

$$[C]_{org}^{\frac{1}{j}} = D[M]_{aq} [M]_{org}^{\frac{(1-j)}{j}} \left(\frac{1}{j} \right)^{\frac{1}{j}} \quad (4)$$

Substitution of eq.4 into 2 gives for K'

$$K' = \frac{\left\{ D[M]_{org}^{\frac{(1-j)}{j}} \left(\frac{1}{j} \right)^{\frac{1}{j}} \right\} [H]_{aq}^n}{[(HR)_{2,org}]^{\frac{(n+x)}{2}}} B$$

If we take the logarithms,

$$\log D = \log K' - \log B + \left(\frac{j-1}{j} \right) \log [M]_{org} + \left(\frac{1}{j} \right) \log j + npH + \left(\frac{n+x}{2} \right) \log (HR)_2 \quad (5)$$

Nomenclature

M: metal ion.

HR: acidic extractant.

R: anion of extractant.

B: activity coefficient of product.

[HR]: initial extractant concentration.

$a_{a,b}$: activity coefficient for the species a in phase b.

n: number of extractant groups bound to M in a « salt like » manner.

x: number of extractant molecules bound as solvation molecules.

j: degree of polymerization of the extracted complex.

C: extracted complex.

K: equilibrium constant with respect to concentrations.

K': equilibrium constant with respect to activities.

3.2. Effect of equilibrium pH

Profile of extracted Co(II) as a function of equilibrium pH at three different concentrations of capric acid: 0.02M, 0.04M and 0.08M is presented in Figure 1. The experimental results show that the extraction percentage of cobalt increases when equilibrium pH values increase, it can reach 90% in the end of the extraction. For high loading of the extractant extraction takes place more quickly than low loading of the extractant $pH_{50} = 7.35$ for $[HR] = 0.08M$, $pH_{50} = 7.45$ for $[HR] = 0.04M$ and $pH_{50} = 7.51$ for $[HR] = 0.02M$.

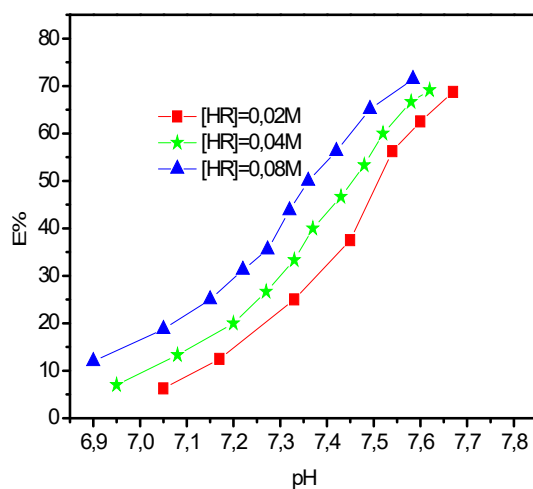


Fig.1. Percentage of extracted Co(II) with capric acid dissolved in chloroform against the pH.

It was found that cobalt(II) extraction increases with the increase of pH of the aqueous solution (figure1). The extraction of cobalt from the sulphate solution containing about $6.78 \times 10^{-3} \text{M}$ of the metal was studied by varying capric acid concentrations (0.02M, 0.04M and 0.08M), within the pH range 6.5–8. As shown in Figure 2 the plot of $\log D$ against pH is a linear relationship with a slope of 2 which indicates that two deprotonated capric acid have bonded with one cation of cobalt(II) forming a complex during the extraction process ($n=2$). The logarithmic equilibrium constant of cobalt(II) extracted with capric acid in chloroform at 25°C was calculated ($\log K_{\text{ex}} = -12.8$).

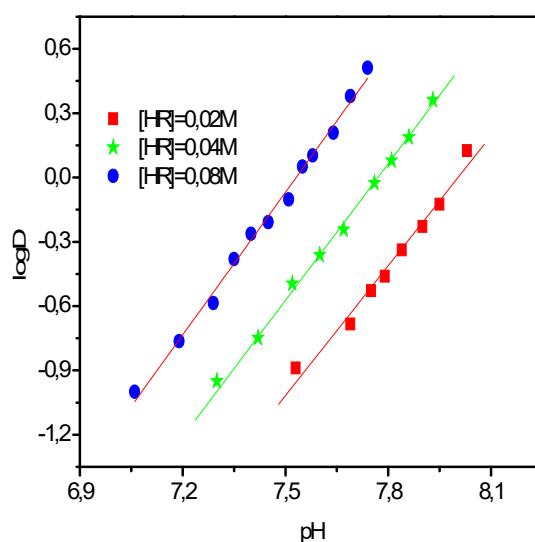
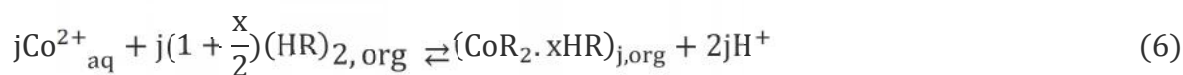


Fig.2. Effect of pH on the extraction of cobalt(II) from sulphate medium with capric acid dissolved in chloroform.

3.3. Degree of polymerization

When Co(II) is extracted into the organic phase in a form of j -mer $(\text{CoR}_n \cdot x\text{HR})_j$, the corresponding equilibrium can be expressed as follows



$$K_{jx} = \frac{[(\text{CoR}_2 \cdot x\text{HR})_j]_{\text{org}} [\text{H}]_{\text{aq}}^{2j}}{[\text{Co}^{2+}]_{\text{aq}}^j [(\text{HR})_2]_{\text{org}}^{\frac{j(2+x)}{2}}} \quad (7)$$

We will use the method applied by Tanaka in his works[15-18]

$$C_{Co,org} = \sum_j^J \sum_{x=0}^X J[(CoR_2 \cdot xHR)_j]_{org} = \sum_{j=1}^J \sum_{x=0}^X j K_{jx} (C_{Co,aq})^j [(HR)_2]_{org}^{\frac{j(2+x)}{2}} [H]_{aq}^{-2j} (\alpha_{(Co)})^{-j} \quad (8)$$

Where

$$D = \sum_{j=1}^J \sum_{x=0}^X j K_{jx} (C_{Co,aq})^{j-1} [(HR)_2]_{org}^{\frac{j(2+x)}{2}} [H]_{aq}^{-2j} (\alpha_{(Co)})^{-j} \quad (9)$$

When only $(CoR_2 \cdot xHR)_j$ is responsible for the extraction, summation in equation (8) can be dropped and $\log C_{M,org}$ is equated as follows:

$$\log C_{Co,org} = j(\log C_{Co,aq} + 2pH - \log \alpha_{(Co)}) + \log j + \log K_{jx} + j \left(1 + \frac{x}{2}\right) \log [(HR)_2]_{org} \quad (10)$$

Thus the degree of polymerization of the caprate can be found from the slope of the plot of $\log C_{Co,org}$ against $\log C_{Co,aq} + 2pH - \log \alpha_{(Co)}$ at constant $[(HR)_2]$. Under our experimental condition the hydrolysis of cobalt(II) in the aqueous phase is neglected, i.e. $\alpha_{(Co)}=1$. j being the degree of polymerization of the cobalt-Capric acid compound; were calculated from the $\log C_{Co,org}$ graph versus $\log C_{Co,w} - 2 \log [H^+]$ as shown in figure 3, We got a straight lines with a slope of the unity for each one this means $j=1$. Therefore, the extracted species are monomers of the $(CoR_2 \cdot xHR)$ type. We have to say that extraction with fatty acids like capric acid proceeds by cation exchangers where proton of the acid is exchanged by metal ion.

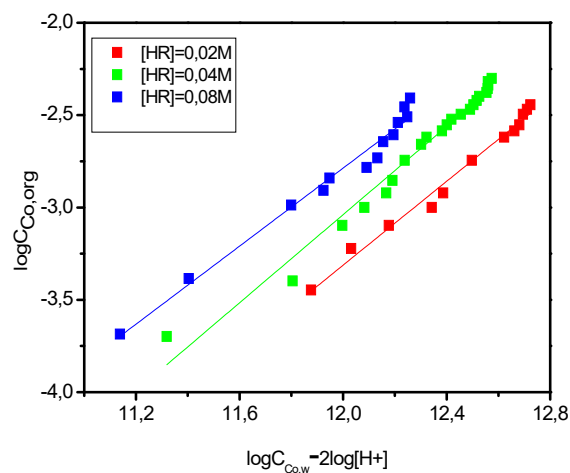


Fig.3. Determination of the degree of polymerisation of cobalt(II) caprylates.

3.4. Effect of extractant concentration

The x number of capric acid involved in the monomeric species was determined from the logD slope versus $\log[(HR)_2]$ (according to equation 5). Drawing of logD versus $\log(HR)_2$ produces straight lines with slopes of 2 (figure 4) which lead to conclude that x takes 2 as a value. Three unknown are determined ($n=2$, $j=1$ and $x=2$) which allow us to know the extracted complex stoichiometry which is $CoR_2(HR)_2$. The stoichiometry of the extracted species is in agreement with that found in earlier works [19-21] and is the same found in the extraction of cobalt(II) with hexanoic, octanoic and capric acid in heptanes determined by Kopach et coll [22]. However Tanaka et coll [13] found that the two forms existed when working with high concentrations of the extractant suggesting that formed species depend on experimental conditions.

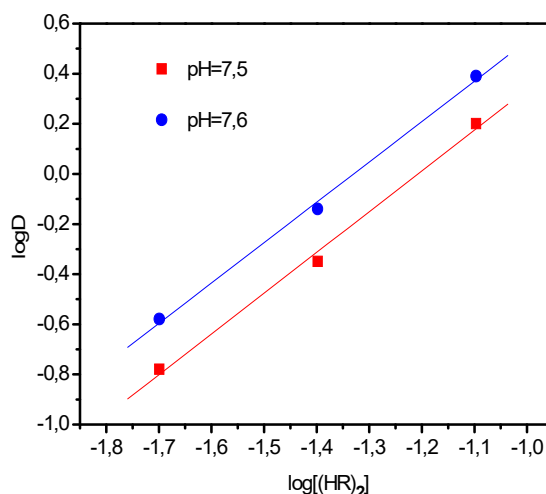


Fig.4. Effect of the extractant concentration on the extraction of cobalt(II) with capric acid at 25°C

We can then re-formulate equilibrium 1 as follows



The UV-visible spectrum of deep pink complex Co(II) that appears in figure 5 is characterized by a single broad shoulder with a maximum at approximately 500 nm. This is related to the absorptions expected for an octahedral geometry of cobalt(II) complex [23]. As figure 6 shows the coordination sphere of Co(II) is occupied by two molecules of capric acid that are coordinated to the central metal while the remaining two sites have a high probability of being occupied by two water or solvent molecules.

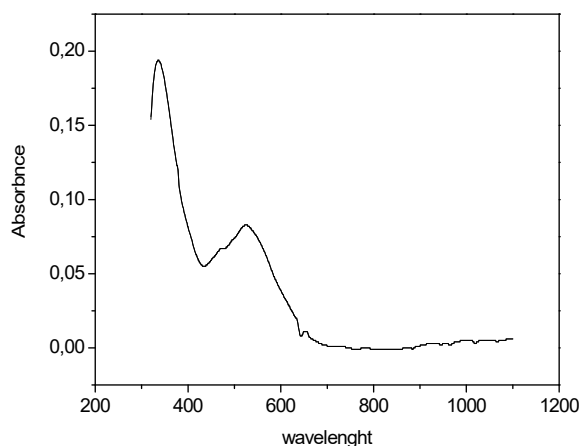


Fig.5. Visible spectrum of the organic phase during the extraction of Co(II) with 0.04M of capric acid dissolved in chloroform

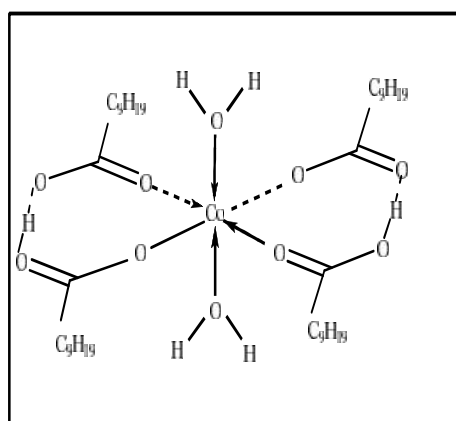


Fig.6. Possible structure of the cobalt(II) complex extracted with capric acid dissolved in chloroform.

3.5. Effect of organic solvent

Three different diluents were tested for the extraction of Co(II) from sulphate solutions using constant capric concentration (0.04M). We know that efficiency of extraction is affected by chosen solvents [24-25] extraction of cobalt(II) with capric acid was elaborated by using chloroform, cyclohexane and toluene. To clarify the effect of diluent the D_{Co} values were measured for selected diluents under the same conditions. The data obtained is plotted against pH (figure7) where we got the higher D_{Co} when using chloroform and the lower D_{Co} when using toluene, the best extraction order was: cyclohexane > chloroforme > toluene. Adjel studied the effect of diluents on the extraction of cobalt, she revealed that the extraction of cobalt(II) by capric acid decreased in the order: chloroform > dichloromethane > MIBK [26].

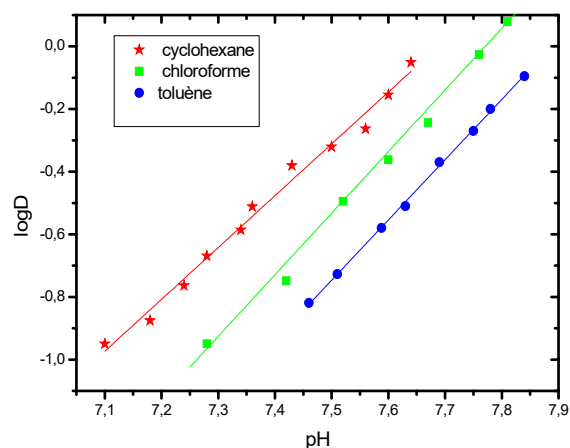


Fig.7. Effect of solvents on the extraction of cobalt(II) from sulphate medium with 0.04M of capric acid dissolved in chloroform.

3.6. Effect of temperature

Temperature impact on the extraction of of Co(II), using 0.04M of capric acid dissolved into chloroform was examined within a 10°C-50°C range at fixed aqueous and fixed extractant concentrations. LogD_{Co} profile as oppose to pH is displayed in figure 8. It is obvious that the rise in temperature entails a significant increase in the distribution coefficient and therefore extracted metal ratio. At higher temperatures viscosity of the organic phase is lower which guaranty better contact between organic and aqueous phase during mixing. Vander Zeeuw [27] had also found the positive effect of the temperature in the extraction of iron Fe(III) with versatic acid where increase of temperature from 20°C o 80°C causes an appreciable increase of distribution coefficient.

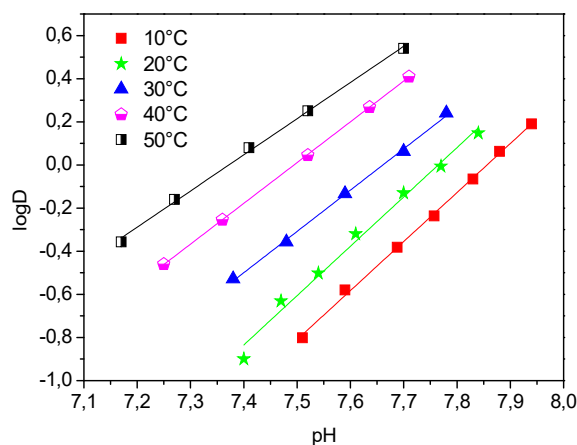


Fig.8. Effect of temperature on extracted cobalt(II) from sulphate medium with capric acid

The obtained values of $\log K_{\text{ex}}$ at different temperatures are summarized in table 1, the relation between $\log K_{\text{ex}}$ and the thermodynamic parameters can be expressed as

$$\log K_{\text{ex}} = \frac{-\Delta H^\circ}{2.303RT} + \frac{-\Delta S^\circ}{2.303R} \quad (12)$$

plotting $\log K_{\text{ex}}$ against $1/T$ gives a straight line of slope of $\frac{-\Delta H^\circ}{2.303R}$ and a y-intercept of

$\frac{-\Delta S^\circ}{2.303R}$ (figure 9), free energy can be then calculated from one of the followed equations

$$G = -RT \ln K_{\text{ex}} \quad (13); \quad G = H - T S \quad (14)$$

Table 1. Values of the extraction constants of cobalt(II) at different temperatures

T(°K)	283	293	303	313	323
Log K_{ex}	-13.01	-12.90	-12.74	-12.40	-12.01

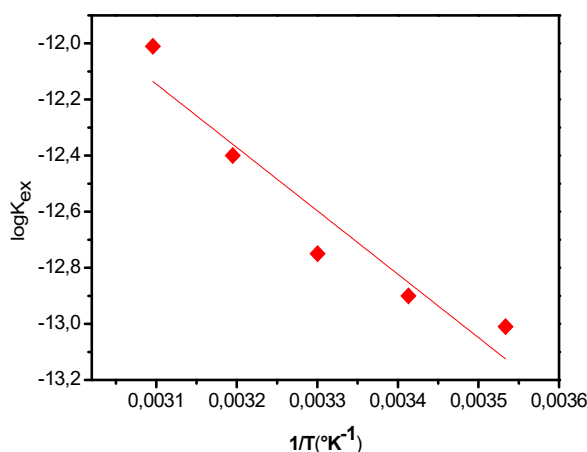


Fig.9. Relationship between distribution constant of extracted cobalt(II) and temperature

Table 2. Thermodynamic parameters for cobalt(II) extraction

H°(kJ mol ⁻¹)	G°(kJmol ⁻¹)	S°(J mol ⁻¹ K ⁻¹)
43.25	13.45	98.33

Where, H, G and S are the enthalpy change, the free energy change, and entropy change, respectively, R is the universal gas constant (8.314Jmole⁻¹K⁻¹), T is the absolute temperature and K_{ex} is the extraction constant. These thermodynamic parameters of the extraction of Co(II) were calculated and given in Table 2. The data obtained shows that the enthalpy variation, H, have a positive value indicating the endothermic character of the extraction process which explain the improve of extraction when increasing

temperature. The positive value of the free energy change (ΔG) means that the extraction of cobalt(II) in the investigated system is not a spontaneous reaction. The positive sign of ΔS value reveals the disordering nature of the extracted metal species in the investigated system.

4. CONCLUSION

Stoichiometry of cobalt(II) complex extracted with capric acid dissolved in chloroform is from the type $\text{CoR}_2(\text{HR})_2$. This result was found by the method of slopes, the formed complex has an octahedral structure where the coordination sphere of Co (II) is occupied by two molecules of capric acid that are coordinated to the central metal. According to the nature of the solvent, the extraction of Co(II) by capric acid decreased in the order: Cyclohexane>chloroform>toluene. Rising temperature in the range from 10°C to 50°C had a good impact on the extraction rate of Co(II) ions.

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