J. Appl. Eng. Sci. Technol. (2017) 3(1): 43-48

Extraction, synthesis and characterization of nickel (II) and cobalt (II) caprate complexes

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Received 27 November 2015
Revised 26 March 2016
Accepted 18 September 2016
Published online: 29 May 2017

Keywords
capric acid
metal (II) complexes
UV-VIS spectroscopy
IR spectra
Cobalt Decanoate

Abstract: Liquid-liquid extraction is one of the most useful technique for selective and recovery of metal ions aqueous solutions, applied in purification processes in numerous chemical industries. In this work the liquid-liquid extraction of nickel (II) and Cobalt (II) from aqueous solution by capric acid(HL) in chloroform at 25±0.05°C has been studied. The nickel and cobalt in capric acid monomeric complexes, having formula of the type $[M(HL)_2L_2]$ (M :Co(II) and Ni(II). The complexes have been characterized with the help of elemental analysis, the apparatus used is a laser granulometer Malvern Mastersizer Type 2000/3000, this device can measure the particle sizes, conductance measurements, electronic UV-Visible suggest that the octahedral . Fourier transform infrared confirm the presence of bidentate carboxylate in the complexes. The thermal behavior of complexes was studied by thermogravimetry (DTG), differential thermal analysis (DTA).The final decomposition products namely NiO and Co_3O_4.

1. Introduction

The separation of cobalt and nickel in an industrial environment mainly uses the technique of liquid-liquid extraction with complexion agents. This method is used in many chemical processes for the production of inorganic salts such as chlorides of nickel or cobalt. There are a wide variety of complexion agents and separation conditions to effect liquid-liquid extraction of cobalt and nickel. These extractants are mostly organic phosphoric acids which have the ability to complex with nickel or cobalt. The separation is performed using two phases; an organic that has a high affinity for complexion agent and an aqueous phase. The organic phase is the most commonly used jet fuel. It is necessary to adjust with high accuracy the parameters such as pH, the concentration of complexion agents and the addition of salts to optimize the separation.

Carboxylic acids are organic compounds contain in their molecule the characteristic group (COOH) called carboxyl. They are characterized by their ability to from salts with number of metals, including alkali and alkaline earth (Barkat and Kameche 2007; Aidi and Barkat 2010). Carboxylic acids have been studied as extractons for numerous metals and have shown to exhibit good extraction and separation efficiency (Adjel and Barkat 2011). The carboxylate of the higher fatty acids with the metal ions have many applications in different industrial spheres such as driers in paints, the components of lubricating greases, stabilizers of plastics, catalysts, the additives at fuel, as well as the corrosion preventive materials, promoters of rubber–steel cord adhesion, etc (Barkat et al. 2001). Therefore metal carboxylate have promising applications depending upon the metal used to make the complex. The objective of this work is calculated the stoichiometric coefficient of cobalt (II) and nickel (II) with capric acid and also studied the synthesis and characterization of these complexes.

2. Experimental

2.1. Reagents and solutions

Capric acid (98%, Fluka) used as purchased. Chloroform was pre-equilibrated with aqueous solution which did not contain nickel and cobalt (II). The ionic strength of the aqueous medium was assumed to be unity ($[Na_2SO_4]$ = 0.33 mol dm^{-3}). The initial concentrations of nickel (II) and cobalt (II) are 400ppm.

2.2. Materials and instruments

Conductivity measurements were performed at 25±1°C on a conductivity meter (DDSJ-308A) an electrode. The cell constant was determined by use of KCl standard aqueous solution. The molar conductivity (ΛM) of the complexes was measured using $1.0{\cdot}10^{-3}$mol.dm^{-3} solution in dimetylformamide (DMF).

An electron microscopy (MEB) coupled energy dispersive spectrometer microanalysis (EDX) is used in chemical composition.

Electronic UV-Visible spectrophotometer (SHIMADZU UV VIS1240) of complexes dissolved in chloroform ($CHCl_3$) covering the range of 1200-300 nm.

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Nomenclature

aq	Aqueous phase
$C_{M,aq}$	Concentration of metal in aqueous phase
$C_{M,org}$	Concentration of metal in organic phase
D	distribution coefficient of the metal between organic and aqueous phases
j	degree of polymerization of the complex

Greek symbols

α_M	separation factor of metal
Λ_m	molar conductivity

Subscripts

Kex	Extraction constant
M^{2+}	Co^{2+} or Ni^{+2}
n	Cationic charge
org	Organic phase
p	Number of monomeric acid contained in the complex

Infrared spectroscopy is a method of identifying based on absorption or reflection by the sample, the electromagnetic radiation. This technique can provide information about the particularities of structures since the vibration frequency of cation-oxygen depends on the mass of the cation, the shape of the cation-oxygen bond and the lattice parameter.

All samples were analyzed by infrared spectrophotometers Transform fourrier (FTIR- SHIMADZU 8400s), the extent of which is between 400 and 4000 cm^{-1}. All samples were packed indispersion in KBr pellet (approximately 1 mg of sample and 200mg of KBr were used for preparing the granule).

Differential thermal analysis (DTA) is a method used to determine the temperature corresponding to changes in the material depending on the heat treatment. It consists in measuring the temperature difference between a sample (Te) and a reference (Tr) (thermally inert material) in function of time or temperature, when subjected to a variation programmed temperature in a controlled atmosphere. In general, the phase transitions and solvent evaporation are reflected by peaks endothermic. By cons, crystallization, oxidation reactions and certain decomposition are characterized by exothermic peaks. The differential thermal analysis (ATD) is usually associated with a thermal gravimetric analysis (TGA) to measure the variation of weight of a sample as a function of the heat treatment temperature. This mass variation can be lost weight such that the emission of fumes or weight gains when setting a gas for example. The apparatus used is of type (Device Linseis STA PT1600M).

The particle size allows quantitatively assess repair size of the powders. The measurement technique is based on different kind'sinteraction between the particles and the laser radiation.

For the measurement, the powders are previously dispersed in a solution and subject, ultrasonically then takes a sufficient amount of the solution very diluted is introduced into the vessel during the measurement, the powders are dispersed in a sampling module equipped with an ultrasonic probe, a circulation driven following the suspended powder in the optical cell through which the laser, knowledge of the optical properties of the powders and those solvents is necessary.

The apparatus used is a laser granulometer Malvern Mastersizer Type 2000/3000, this device can measure the particle sizes in the range 0.3 microns to 300 microns which gives it the ability to cover a wide range of size particles and we have utilized to determine the size distribution particle powders. It provides access to information such as the shape of the distribution characteristics diameters whose average diameter, the median diameter.

2.3. Extraction and analytical procedures

Experiments were carried out by shaking equal volumes (30 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 0.2M hydroxide of sodium solution (NaOH). Then, after the two phases were separated completely by gravity, concentrations of the metal cobalt and nickel remaining in the aqueous phase were determined photo metrically at 511 and 720 nm using a (SHIMADZU UV VIS1240). 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±0.05°C.

2.4. Preparation of the complexes

Capricacid (0.86 g, 0.005 mol) were dissolved in chloroform (50 cm^3) as added respective metal sulphate hydrates $Ni(SO_4).6H_2O$ (e. g 0.9g, 0.015 mol)and (e.g. 0.97 g, 0.016 mol of $Co(SO_4).7H_2O$ in 50 cm^3 of distilled water and (0.4g, 0.01mol)of NaOH gradually added with continuous stirring. The mixture was left at ambient temperature. After several days, the complexes were washed with ethanol and water.

The contents of C, O, Ni (II) and Co (II) were determined by elemental analysis in table 1 (Kumar et al. 2011).

3. Results and discussion

3.1. Extraction equilibrium of nickel(II) and cobalt(II)with capric acid

Capric acid is known to exist as dimer in solvent of low polarity such as chloroform, hexane, benzene and dichloromethane (Adjel and Barkat 2011).

The extraction of the metal, by a dimerizedcapric acid, $(HL)_2$, in chloroform can be represented by the general equation:

Table 1. Elemental analysis of complexes at 25°C.

ComplexL=$C_{10}H_{19}O_2$	colour	%C%	Ni	%Co	%O
$[Ni(HL)_2I_2]$	green	80.15	07.53	-	11.19
$[Co(HL)_2I_2]$	pink	70.48	-	09 .48	17.18

$$jM^{n+}{}_{aq} + j\left(\frac{n+p}{2}\right)(HL)_{2org} \Leftrightarrow ML_n(HL)_p org + 2H^+ \tag{1}$$

The extraction constant Kex can be represented by the following formula:

$$k_{ex} = \frac{\left[ML_n p(HL))_{iorg}\right]\left[H^+\right]^{jn}}{\left[M^{n+}\right]^J \left[(HL)_{2org}\right]^{j(\frac{n+p)}{2}}} \tag{2}$$

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

$$D = \frac{C_{M,0rg}}{C_{M,aq}} = \sum_j \sum_a \frac{j\left[\mathrm{M}Ln\mathrm{H}L\ p\right]org}{\left[M^{2+}\right]\cdot \alpha_M} \tag{3}$$

$$= \sum_j \sum_p \left(jK_{ex(jah)}[M^{n+}]_{aq}^{(j-1)} \alpha_M^{-1} [(HL)_2]_{org}^{\frac{n+p}{2}} [H^+]^{-nj} \right) \tag{4}$$

Where $c_{M,org}$,$c_{M,aq}$ are the total concentrations of the metal in the organic and aqueous phases, and the side reaction coefficient allowing for metal complications in the aqueous phase, respectively. If only $(ML_n(HL)_p)j$ is responsible for the extraction system, equation (5) is derived from equation (4).

$$\log D = (j-1)\log[M^{n+}]\,aq + \frac{n+p}{2}\log[(HL)_2]org$$
$$+ njpH - \log \alpha_M + \log j + \log Kex \tag{5}$$

3.2. Extraction of nickel and cobalt (II) with capric acid

The stoichiometry of the extracted species was determined by analyzing the experimental data. The conventional slope analysis method was used. The experimental results are arranged according to equation (5). Figure 1 and figure 2 shows the results obtained for the extraction of nickel and cobalt (II) with solutions of various capric acid concentrations.

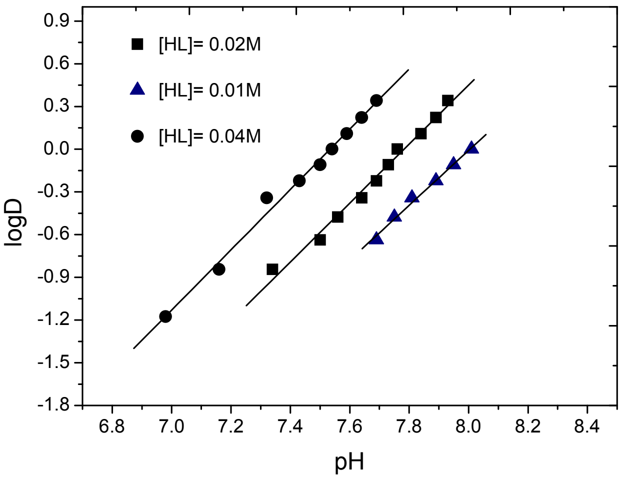

Fig. 1. Extraction of nickel (II) with capric acid dissolved in chloroform.

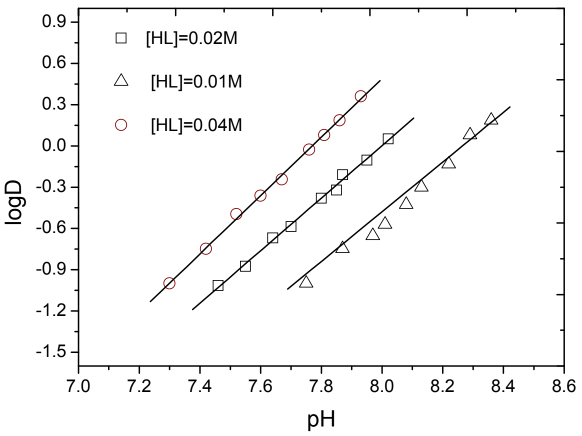

Fig. 2. Extraction of cobalt(II) with capric acid dissolved in chloroform.

The degree of extraction of nickel and cobalt (II) increases with increase in pH and capric acid concentration. The plots of logD versus pH for various concentration of capric acid are straight lines with slope equal to two (n=2), This suggests full neutralization of nickel and cobalt (II) valency leading to release of two protons as given by equation (6). The data in figure 1 also reveal no dependence of nickel and cobalt distribution upon the aqueous Ni(II)and Co(II) concentrations, thereby confirming the monomeric nature of the extracted complex (j=1, α_{Co}=1 and α_{Ni}=1).

$$M_{aq}^{2+} + \frac{2+p}{2}(HL)_{2org} \Leftrightarrow ML_2(HL)_p org + 2H^+ \tag{6}$$

Under the present experimental conditions the concentration of metal in organic phase is negligible compared to the concentration of extractant therefore concentration of dimer was calculated as $[(HL)_2]=[HL]/2$. According to equation (5), the number of capric acid molecules involved in the monomeric species can be determined from the slope of the plots of (log D) against $\log[(HL)_2]_{org}$ at constant pH. The Plots of log D versus log $[(HL)_2]$org at constant pH values were also linear with a slope of (2+p)/2=2, i.e., p = 2, as shown in figure 3 and figure 4. This suggest that two molecule of dimericcapric acid take part on the extraction of one ion of metal. This means that only the complex Ni $L_2(HL)_2$ and Co $L_2(HL)_2$ are extracted into chloroform (Adjel and Barkat 2011).

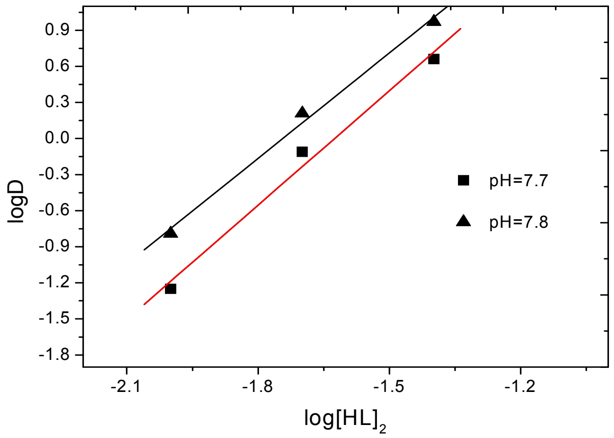

Fig. 3. Effect of concentration on the extraction of nickel (II) with capric acid in chloroform.

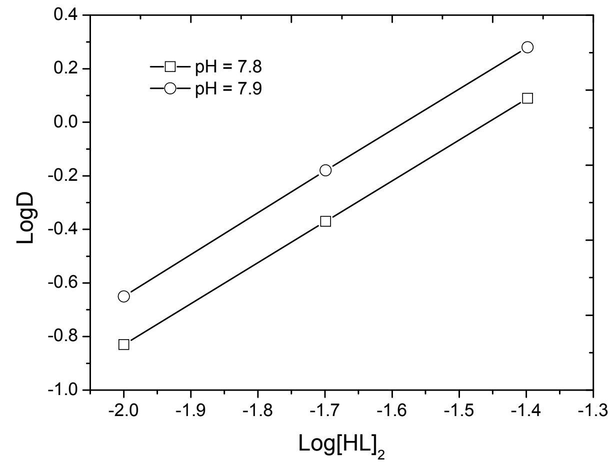

Fig. 4. Effect of concentration on the extraction of cobalt (II) with capric acid in chloroform.

The same type of extracted species was reported for the extraction of nickel and cobalt (II) with cyclopentyl acetic acid and α-bromostearic acid in benzene (Barkat et al. 2001). The complex formed has a structure of an addict, in which particular places in the coordination sphere of metal ion is occupied in total by four molecules of the extractant. At the same time, two of them, as acid anions, form polarized covalence bonds, and the other two, as non dissociated molecules Coordinate bonds via the carbonyl oxygen atom shown in figure 5.

The logarithmic value of K_{ex} of nickel and cobalt (II) can, therefore, be calculated for each experimental point (logK_{ex} Ni=-9.22 and logK_{ex}Co=-10.05).

3.3. Molar conductivity

The very low molar conductance of the complexes (Λm=11.27 and 7.09 S.cm^2.mol-^{1} for the nickel(II) and cobalt(II) complexes, respectively) are measured in temperature 25±1°C indicate that these complexes nom electrolyte in dimethyl formamide(DMF) (Olmez et al. 2004; Kumar et al. 2011)

3.4. X-Ray Diffraction (XRD)

The measurement of lattice parameters of the powders was carried out using a Bruker D8 model type diffract meter with copper anticathode λcuαk = 1,54A°. The recording condition and 0.04°/ 5 s to 2θ taken between 10° and 90° as shown in figure6.

The crystallographic data for the complexes cobalt and nickel are listed in table 2.

Table 2. The crystallographic data for the complexes.

Complex	[Ni I_2 (HL)$_2$]	[Co I_2 (HL)$_2$]
Crystalsystem	monoclinic	monoclinic
Space groups	P21/c	P21/c
a (A°)	11	10.8
b (A°)	5.3	5.4
c (A°)	11.2	11.1
α(°)	90	106
β(°)	104	90
γ (°)	90	90
(h, k, l)	-2≤h≤ 2; 0≤K≤ 2; 0≤l≤3	-4≤h≤ 4; 0≤K≤2; 0≤l≤4

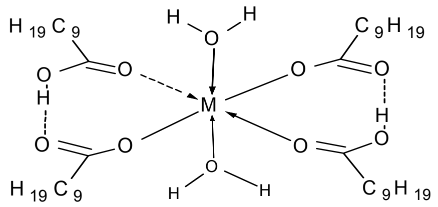

Fig.5. Structures of the complexes.

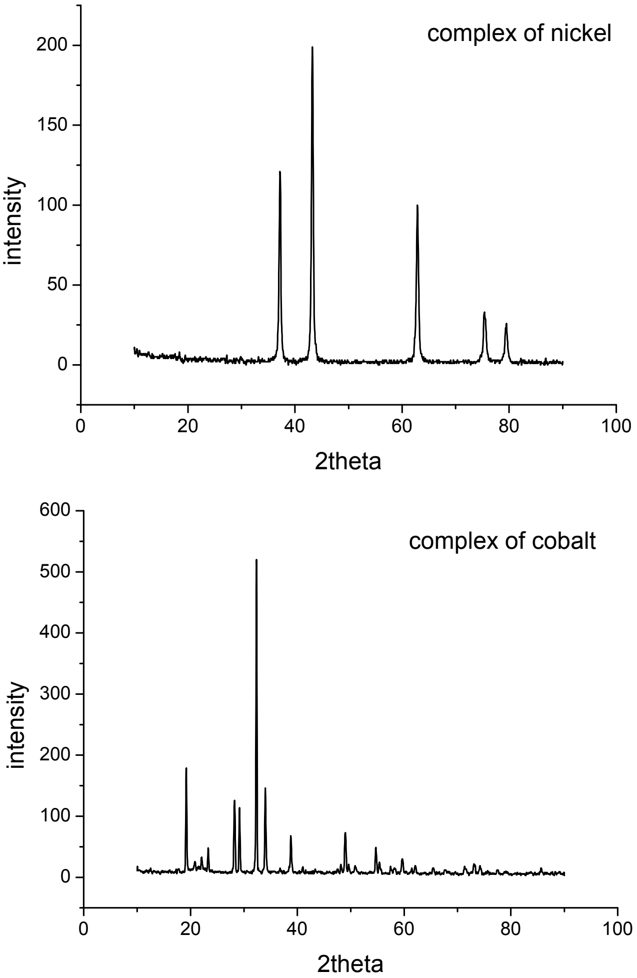

Fig. 6. X-ray diffraction of complex cobalt and nickel caprate.

3.5. Infraredspectra

The main bands from the IR spectra of the ligand and its metal complexes are presented in table 3. The infrared spectrum of the ligand shows a band at 3411 cm^{-1} which can be attributed to the OH group.

This band is absent in all the complexes(Ferenc et al. 2006) The strong band of C=O at 1711 cm^{-1}, the bands assigned to asymmetric and symmetric vibrations of the OCH_3 groups occurring at 2920 and 2849 cm^{-1} respectively. Some of the results of IR spectra analysis are presented in table 3.

Table 3. IR data for complexes at 25°C.

Complex	vas(COO) [cm^{-1}]	vs(COO$^-$) [cm^{-1}]	Δv(COO$^-$) [cm^{-1}]	v(MO) [cm^{-1}]
[Ni(HL)$_2$I$_2$]	1678	1412	266	452
[Co(HL)$_2$I$_2$]	1680	1417	263	425

In the IR spectra of caprate of Nickel and Cobalt the band at 1711 cm^{-1} disappears, which indicates that C=O group is not present in the analyzed complexes (Geary 1971). Strong aliphatic C-H stretches are observed at 2930 and 2865 cm^{-1} (Konstantinović et al. 2007). These are to be expected due to the long length of the carbon chain in the carboxylate ligand. The absorptions in the range of 1688–1678 cm^{-1} and 1394–1352 cm^{-1} correspond to the asymmetric and symmetric νCOO^- frequencies of the metal bound carboxylates. The large difference in $\Delta\nu COO^-$ frequencies is indicative of bidentate coordination of both the carboxylate groups (Olmez et al. 2004). The weak band of complexes Co (II), Ni (II) and at 425and 453 cm^{-1} results from VM–O stretching vibration (Ferenc et al. 2006; Geary 1971).

3.6. UV- Visible Spectra

The electronic absorption spectra of complexes were recorded in the 1100-400 nm range, at room temperature. Electronic spectrum of nickel complex exhibits the characteristic features of $Ni^{2+}(d^8)$ ion octahedral environment (Geary 1971; Rao 2010).

The band located in the ranges 690-680 nm are assigned to the $^3A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ transition (Nakamoto 1986**;** Rao 2010). The spectrum of nickel complex also exhibits a charge transfer band in the range 380-400nm tailing into the visible region(Konstantinović et al. 2007).

The electronic spectra of cobalt decanoate complex show a broad band in region 530 -520nm. This has been attributed to $^4T_{1g}(F) \rightarrow {}^4T_{1g}$ (P) transition, suggesting in a octahedral geometry around Cobalt (II) ion (Rao 2010; Mohamed and Abd El-Wahab 2003; Turek et al. 2004).

3.7. Particle size analysis

The distributions of average diameters of grains presentment only population of complex nickel and cobalt decanoate , the mode of population nickel decanoate is the central peak is 178µm of the distribution volume 5.8% (Fig. 7).

The mode only 5.52% of the distribution whose particle of complex cobalt caprate diameter(d) is 317µm (Fig. 8).

The main characteristics that can be extracted analysisparticle size complexes are summarized in Table 4.

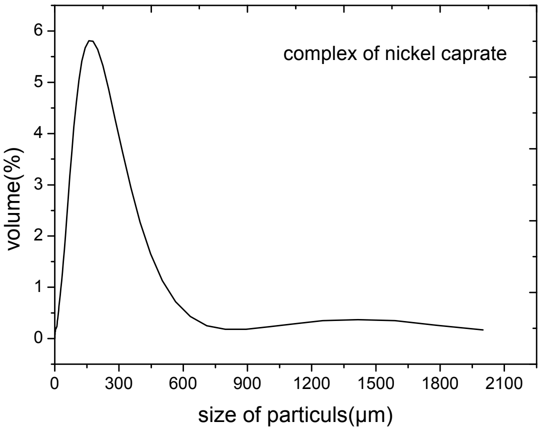

Fig. 7. Distribution of particle nickel caprate

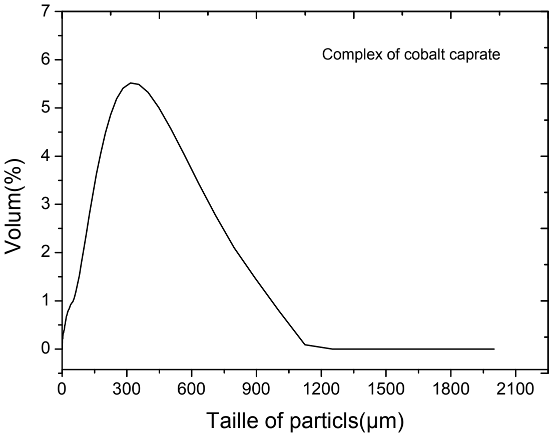

Fig. 8. Distribution of particle cobalt caprate

Table. 4. Analysis particle size of complexes.

Complex	d[0.1µm]	d[0.5µm]	d[0.9µm]	Average vol. [µm]
$[Ni(HL)_2I_2]$	22.431	183.331	457.342	216.847
$[Co(HL)_2I_2]$	32.97	133.656	338.575	182.283

3.8. Melting Point

One type of device Melting Point Apparatus Stuart SMP3 Scientific (Tmax = 270°C) is used. A small amount of product (about 1 mg) is inserted in a capillary. The capillary then undergoes mentee in temperature of $1°C.min^{-1}$. The melting temperature is determined by visual observation. Some of these compounds have the feature to go through plastic or gels called phases. Others have temperature melting and very close degradation. These changes make it difficult to visual observation of the melting point of metal carboxylate. The melting point of complex nickel at 198°C and cobalt complex at 186°C.

3.9. Thermal analysis

The thermal data of the complexes are listed in table3. Thermal degradation study of only $[Ni\ L_2\ (HL)_2]$ complex has been made infigure .9. In the temperature range230 -400°C observed as four exotherm and one endotherm at (400,350,310°C and 230°C), (370°C) respectively. Final observed mass loss value of 82.2% is corroborated to the formation of end product oxide of nickel (Nakamoto 1986; Premkumar and Govindarajan 2005). $[Co\ L_2\ (HL)_2]$ complex gives an exothermal (DTA) peak at 210°C as shown in figure 10.

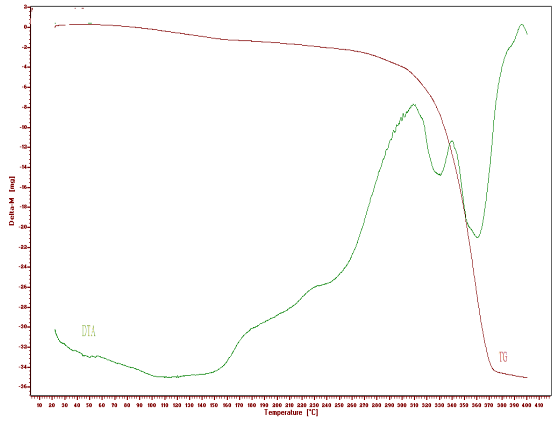

Fig. 9. TG-DTA of nickel caprate complex

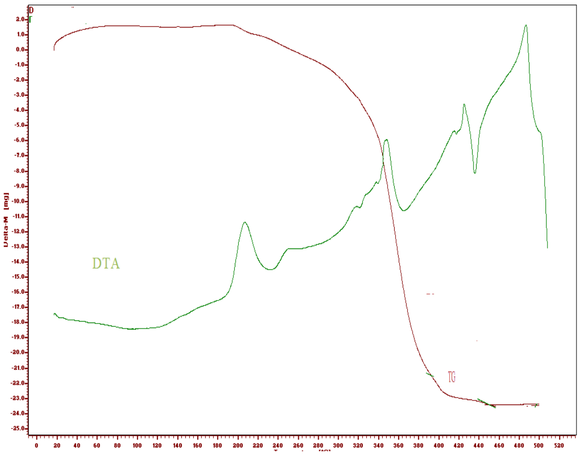

Fig. 10. TG-DTA ofcobalt caprate complex

Inthe temperature range 220-500°Cobserved as three exotherm and two endotherm(430 and 360°C), (240,440) respectively.

The final product formed at about 500°C, consists of oxide Co_3O_4 (Ferenc et al. 2006; Kurdekar et al .2012; Mohamed and Abd El-Wahab 2003).

4. Conclusion

The results obtained in this work have established the feasibility of using capric acid to remove the heavy metal ions like nickel and cobalt (II) from aqueous solutions. Capri cacid extracts nickel and cobalt (II) as a monomeric nickel and cobalt caprates from sulphate medium according to the following stoichiometric relations: $M^{2+}_{aq} + 2(HL)_{2org} \Leftrightarrow ML_2(HL)_2org + 2H^+$

All the complexes are found to be non-electrolytic. The results of electronic spectra studies of the complexes suggest that the nickel and cobalt complexes are of octahedral geometry.

Decanoate of Cobalt (II) and Nickel (II) were synthesized as anhydrous complexes. The final products of their following oxides: NiO and Co_3O_4.

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