Synthesis, Characterization of Schiff Base and its Complexes Derived from 4-Aminoantipyrine and using in Extraction of Nickel (II) Ion

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Abstract: New Schiff base was synthesized by two steps. In the first step a solution of 4-Aminoantipyrine in Ethanol react

under reflax with Salicyaldehyde to give a percursore compound which reacted in the second step with 3,4-Diaminotoluene to give the ligand .The complexes were prepared by direct reaction of the metal salt with the ligand (L): [2,2'-((1Z,1'E)-((3E,3'E)-3,3'((4-methyl-1,2-phenylene)bis(azanylylidene)) bis(1,5-dimethyl-2-phenyl-2,3-dihydro-1H-pyrazole-4-yl-3-ylidene))bis(azanylyidene))bis(methanylylidene)) diphenol]. The liqand and its complexes were characterized by elements analyses , FT-IR , Mass and ^{1}H NMR .Schiff base has been studied by liquid-liquid extraction twards the metal Ion Ni^{2+} from aqueos phase to organic phase . The study of condition of extraction shows that the optimam PH values for extraction was (PH=9) in addition to the optimam shaking time to reach equilibrium was (15 min.) .

Keywords: Schiff Base, Solvent extraction , 4-aminoantipyrine . 3,4diaminotoluene.

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Introduction

Solvent extraction is one of the most versatile procedures among the separation techniques used for the removal and separation of metals[1]. It is the process of separation between the mixture components of solids or liquid depends on the difference between the solubility of these components. It is also achieved by solvent extraction selectivity .This method is usually used in analytical chemistry, petroleum, food and pharmaceutical industries as it gained way solvent extraction in recent years a prime location as one method of high-efficiency technologies so as to ease .This mothed is so fast and simple process and It also demands only very simple equipments [2] .It became interest in schiff bases as a multiple chalet ligands continuously growing because their characteristics and unique use in the extraction operations where they are used on a large scale as to have the ability to interact with many of the metals because they contain atoms of donor for dual-mail.The presence of two donors atoms dual-mail where at least gives in the existence of associative sites between them and the metal ion[3]. Where is characterized by high nitrogen susceptibility on the link metals.Schiff bases are compounds which contain an azomethine group (-CH=N-).These bases are often formed by condensation of a carbonyl compound with a primary amine[4]. Schiff bases represent an important series of chelatingagents .Schiff-base compounds have been potentially used as fine chemicals and medical substrates[5]such as antibictrial, antifungal [6] and anticancer[7]. These ligands are widely use for analytical purposes such as their use as extraction techniques such as their use as extarction agents in liquid-liquid , solid face[8] and cloud-point .In the present paper , a new Schiff base derived from 4-Aminoantipyrin , Salicyadehyde and 3,4-DiaminoToluene. And this ligand is used for extracting the nickel(‖) ion.

Experimental

Materials and Methods

All chemicals were obtained from commercial sources and were used without further purifications. the chemicals materials are 4-aminoantipyrin , Salicyadehyde, Acetic acid glacial .We also used 3,4-DiaminoToluene, $NiSO_4.6H_2O$, $NiCl_2.2H_2O$, $CoCl_2.6H_2O$, $Cu(CH_3COO)$. H_2O , Ethanol absolute, from (BDH and G.C.C).UV-Visible Spectra were recorded in dimetheyl sulphoxide (DMSO) using Uv-1650PC Spectrophotometer. The FTIR spectra of the ligand and its complexes were recorded using IR affinity (Spectrometer Shimadzu) as KBr disc. Proton nuclear magnetic resonance (^{1}H-NMR; 500MHz) spectra were obtained at room temperature with Bruker DRX System using TMS as an internal standard in dimethyl sulfoxide (DMSO-d6). The element analyses of carbon, hydrogen and nitrogen contents were performed using a Perkin Elmer Thermofinigan flash(CHN2400). The molar conductivities of freshly prepared 10^{-3}M dimethyl sulfoxide (DMSO) solutions were measured for the dissolved complexes using Inolabcond720.The Mass spectral of the compounds were recorded by Work mass selective Detector 5973. At the end we used the pH of the solutions was controlled with Metrohm pH-meter (Romania) model: 713 and Shaking Water bath model: YCW-012S for extracting Nickel ion.

Synthesis of Schiff base (L)

An ethanolic solution (20 ml) of (2.03 g, 0.01 mol) (4-aminoantipyrine) was added to an ethanolic solution(15ml) of salicylaldehyde (1.22 g, 0.01 mol). On stirring the yellow coloured solid (X) was formed.It was filtered and re-crystallized from ethanol. The solid (X) (3. 07g, 0.01 mol) was added to an ethanolic solution (25 ml) of 3,4- Diamino toluene (0.6 g, 0.005 mol). The mixture was refluxed for ca 32 hr. The brown solid (L) product was separated. It was filtered and re-crystallized from ethanol Fig. 1. Yield: 74 %; m.p: 203-204 °C; Anal. calcd . for C_{43} H_{40} N_8 O_2: C, 73.69; H, 5.75; N, 15.99; Found: C, 73.85; H, 5.88; N 16.18.
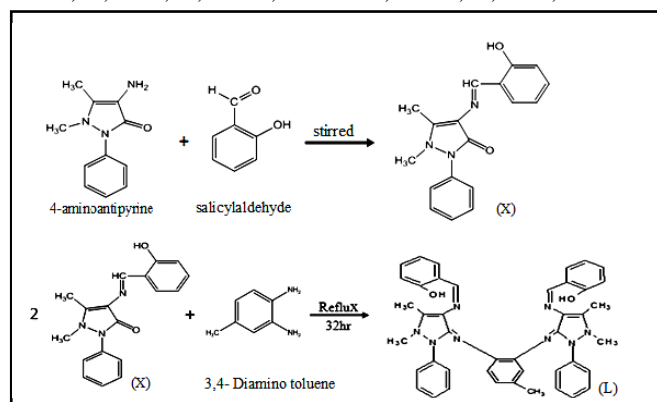

Figure 1. Formation of Schiff Base Ligand L

Nickel complex synthesis

The Schiff base (L) (0.35 g, 0.0005 mol) dissolved in hot ethanol (20ml) was added to a hot ethanolic solution (10ml) of the $NiCl_2.2H_2O$ (0.82 g, 0.0005 mol) and refluxed for 4 hr. The solid product separated was filtered and washed with hot ethanol. Yield: 62 %; m.p: 255-253°C .

Cobalt complex synthesis

The Schiff base (L) (0.35 g, 0.0005 mol) dissolved in hot ethanol (20ml) was added to a hot ethanolic solution (10 ml) of the $CoCl_2.6H_2O$ (0. 11g, 0.0005 mol) and refluxed for ca 4 hr. The solid product separated was filtered and washed with hot ethanol. Yield: 56%; m.p: 269-268°C.

Copper complex synthesis

The Schiff base (L) (0.35 g, 0.0005 mol) dissolved in hot ethanol (20ml) was added to a hot ethanolic solution (10ml) of the $Cu(CH_3COO)_2$ $.H_2O$ (0.099 g, 0.0005mol) and refluxed for ca 4 hr. The solid product separated was filtered and washed with hot ethanol. Yield: 59%; m.p: 287- 285°C.
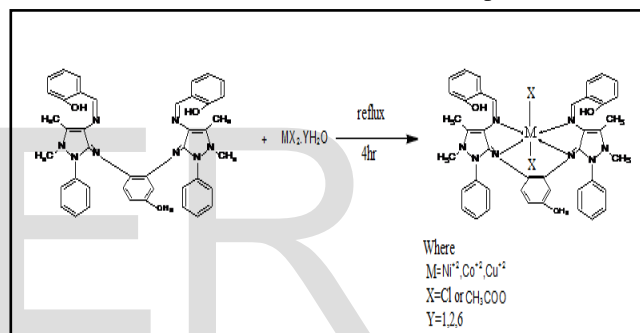

Figure 2. metal complexes from the prepared ligand L

Recommended procedure

For extraction experiments have to take (5ml) of a aqueous solution contain quantity of Ni^{+2}ions at fixed pH , adding (5ml) of organic solution for ligand (L) at concentration of (1×10^{-4}M) , shaking these two layers for suitable time afterward separate organic from aqueous phase ,after that determine remainder quantity of Ni^{+2} ions in aqueous phase by followed spectrophotometric method (dimethyl glyoxime)[9] for (5ml) aqueous phase add (1ml)of 1% di methyl glyoxime) solution and (5ml) of concentration ammonia solution NH_3 ,after that diluted with water to (50ml) by using volumetric flask, after(15minutes) determine the absorption of the solution at(λ=445nm) by use water as blank , from absorbance and calibration curve Fig.3 can be determine the quantity of Ni^{+2}ions in organic phase as complex with the ligand (L) by stripping method which include shaking organic phase with three portions nearly concentrated hydrochloric acid

Synthesis of complexes

HCl for dissociation the complex and transfer the Ni^{+2}ions to aqueous phase then determine Ni^{+2}ions transferred by dithizone method, as well as can be determine the quantity of Ni^{+2}ions in organic phase by subtraction remainder quantity of Ni^{+2}ions in aqueous phase from the initial quantity before extraction method, at later divided the quantity of Ni^{+2}ions in organic phase on the quantity of Ni^{+2}ions in aqueous phase to determine distribution ratio(D).
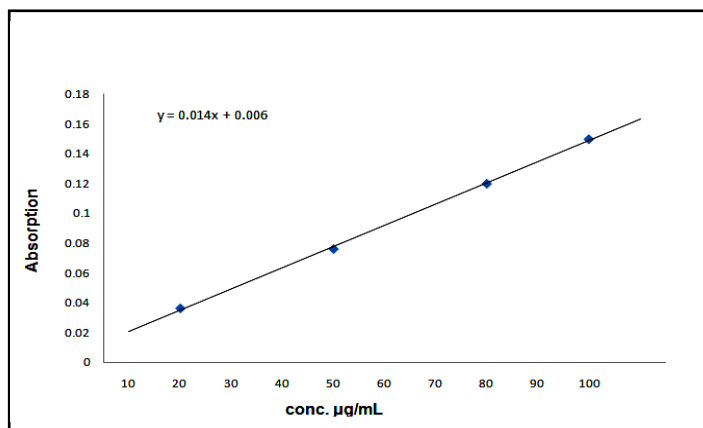

Fig3 :Calibration curve of Ni^{+2}ions with DMG

Results and Discussion

FT- IR spectra

The IR spectrum of the ligand shows a broad band in the region $3452 cm^{-1}$, assignable to intra molecular hydrogen bonded –OH groups. The appearance of this peak in all the spectra of the complexes indicate that the –OH group is free from the complexation. The spectrum of the ligand shows two different –C=N bands in the region $1624-1665$ cm^{-1}, which are shifted to lower frequencies in the spectra of all the complexes ($1658 -1604 cm^{-1}$) indicating the involvement of –C=N nitrogen in coordination to the metal ion[10,11]. Accordingly, the ligand acts as a tetra dentate chelating agent, bonded to the metal ion via the four nitrogen (–C=N) atoms of the Schiff base. Assignment of the proposed coordination sites is further supported by the appearance of medium bands at 450-400 cm-1 which could be attributed to $vM-N$[12,13] The figures4 ,5,6 and 7 show the FTIR (L), nickel, Cobalt and copper complexes respectively.
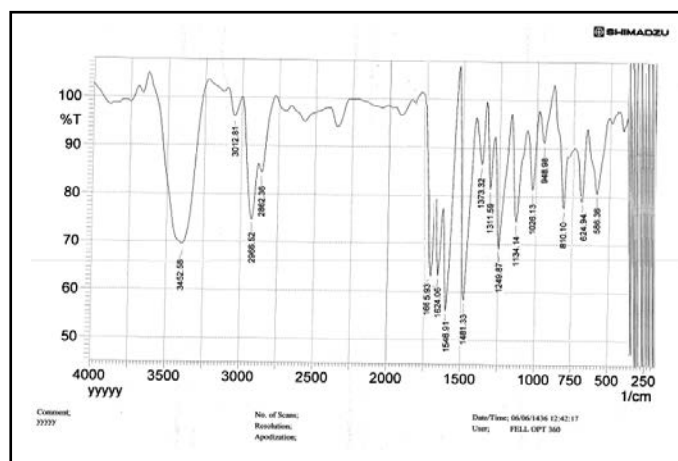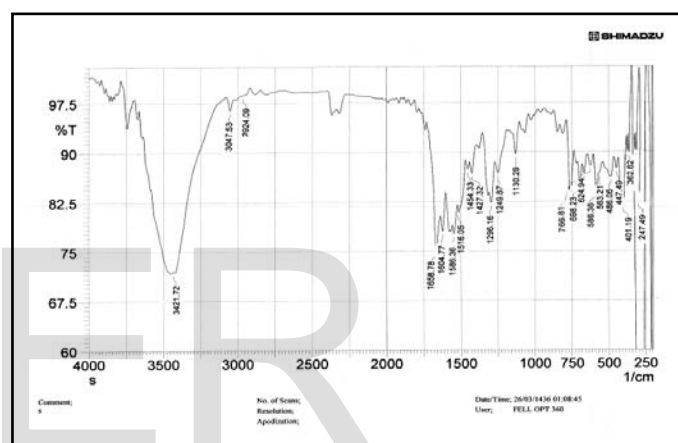

Fig.4 FT-IR spectrum of ligand L
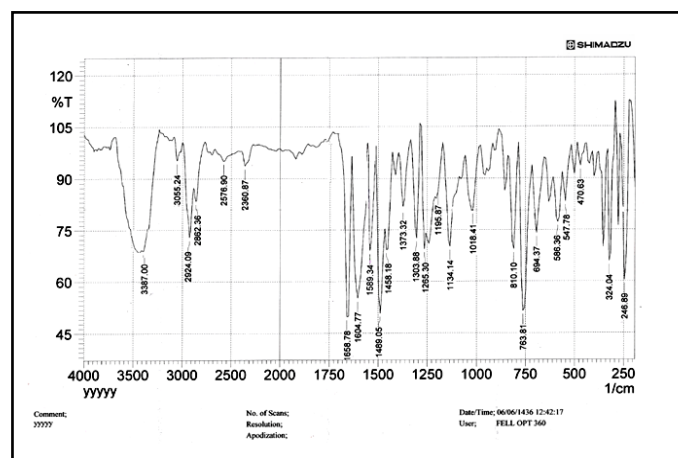

Fig.5 FT-IR spectrum of Ni complex

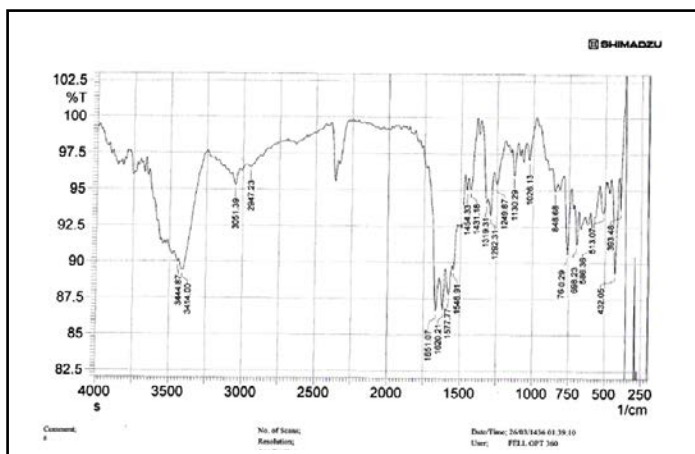**Fig.6 FT-IR spectrum of Co complex**

Fig.7 FT-IR spectrum of Cu complex

^{1}H NMR

The ^{1}H NMR spectrum of ligand (L) in $CDCl_3$ gives the following signals: phenyl a multiple at 7.5-8 ppm, $=C–CH_3$ at 2.3ppm, $–N–CH_3$ at 3.4ppmand $–CH=N–$ protons at 8.9ppm. The peak at 9.9ppm is attributable to thephenolic –OH group present in the salicylaldehyde. (Fig.8)
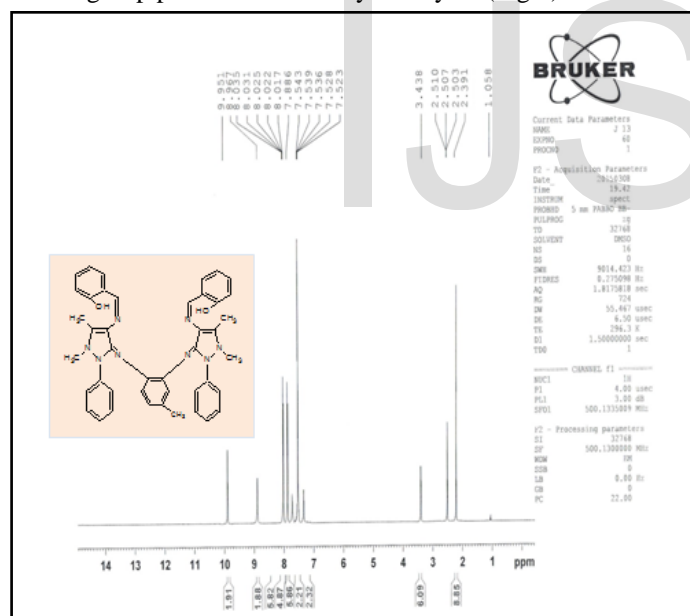

Fig.8 ^{1}H NMR spectrum of ligand L

Mass spectra

The mass spectra of the ligand molecular ion peak for the ligand is observed at 700 m/z ratio which is also supported by the "Nitrogen Rule", since the compound possesses the even number of nitrogen atoms. The molecular ion peak for

the copper complex was observed at m/z =882, which confirms the stoichiometry of metal chalets as $MLCl_2$ type. It is also supported by the mass spectra of other complexes. Micro analytical data are also in close agreement with the values calculated from molecular formula assigned to these complexes, which is further supported by the mass studies of representative complexes. (Fig. 9,10,11,12)
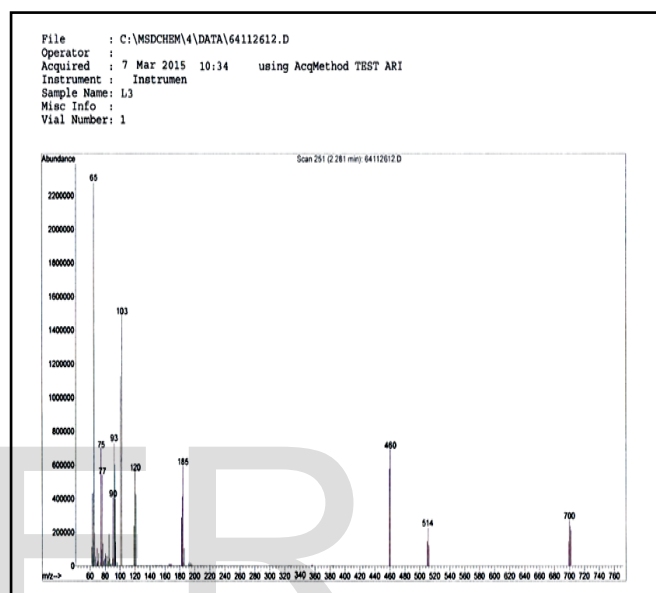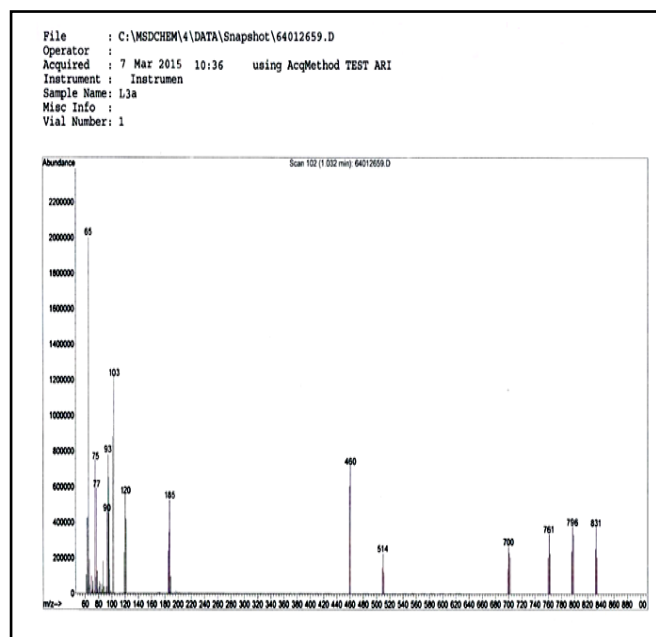

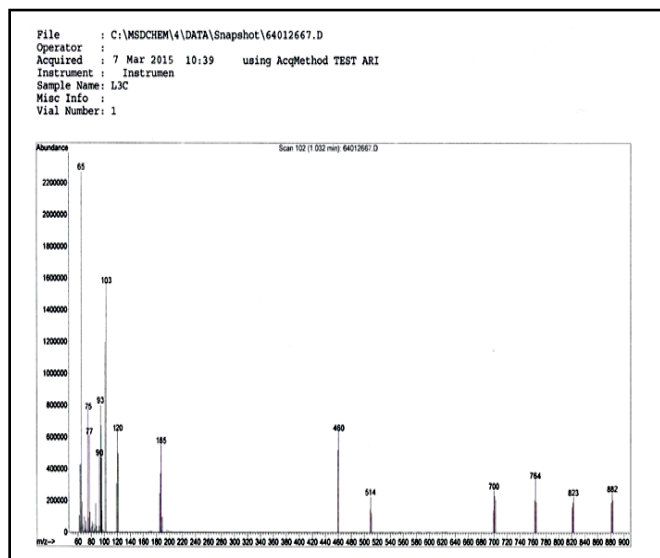**Fig.9 Mass spectrum of ligand L**

Fig.10 Mass spectrum of the Ni complex
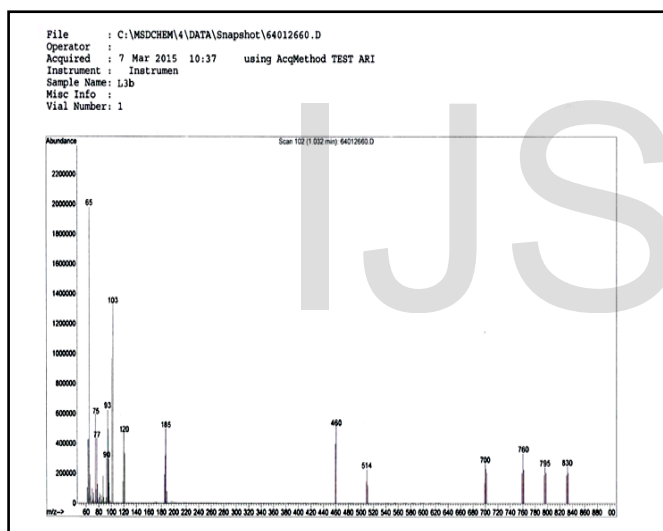
Fig.11 Mass spectrum of Co complex

Fig.12 Mass spectrum of Cu complex

Molar conductance

The analytical data for the ligand and complexes together with some physical properties are summarized in (Table 1). The analytical data of the complexes correspond well with the general formula $MLCl_2$, where M =Co(II), Ni(II) and Cu(II); L = $C_{43}H_{40}N_8O_2$. The Molar Electrical Conductivity of the complexes at room temperature are consistent with octahedral geometry around the central metal ion. The Lowland conductance values of the chalets support their electrolytic nature of the metal complexes.

Table1: Molar conductance data of the ligand and its complexes

Compound	Molecular formula	Colour	Molar Conductance Λ m (mho cm^2 mol^{-1})
L	$C_{43}H_{40}N_8O_2$	Pale Brown	- - -
$[Ni(L)Cl_2]$	$[Ni(C_{43}H_{40}N_8O_2)Cl_2]$	Green	21
$[Co(L)Cl_2]$	$[Co(C_{43}H_{40}N_8O_2)Cl_2]$	Red	12
$[Cu(L)(CH_3COO)_2]$	$[Cu(C_{43}H_{40}N_8O_2)(CH_3COO)_2]$	Black	10

Effect of shaking time

From the side of kinetic effect on the complexation reaction between Ni^{+2} ions and regent (L) ,extracted $(120\mu g)(4.5 \times 10^{-4}M)$ of Ni^{+2} ions in (5ml) aqueous solution at(pH=9) by (5ml) organic solution of (L) dissolved in chloroform ,after that shaking the two layers at different shaking time(5-30min.)the remainder quantity Ni^{+2} ions in aqueous phase and transferred quantity Ni^{+2} ions to organic phase to produce ion pair complex with the regent (L),and calculate the distribution ratio (D) and percentage of extraction (%E) by followed the method detailed in general procedure . Note through the table (2) and Fig. 13 that best shake to extract ion nickel duo time with (L) is 15 minutes due because of the increased surface area between the different phases in their components and thus the process of shaking speed up access to the equilibrium between the phases. Later we noted with increasing agitation time less than the value of the distribution ratio and thus less the percentage to extract nickel ion duo that could be due to the complex formed crash or be the third phase and these results are consistent with the results of other studies [14,15].

Table 2 Effect of shaking time on extraction of Ni^{+2} ions.

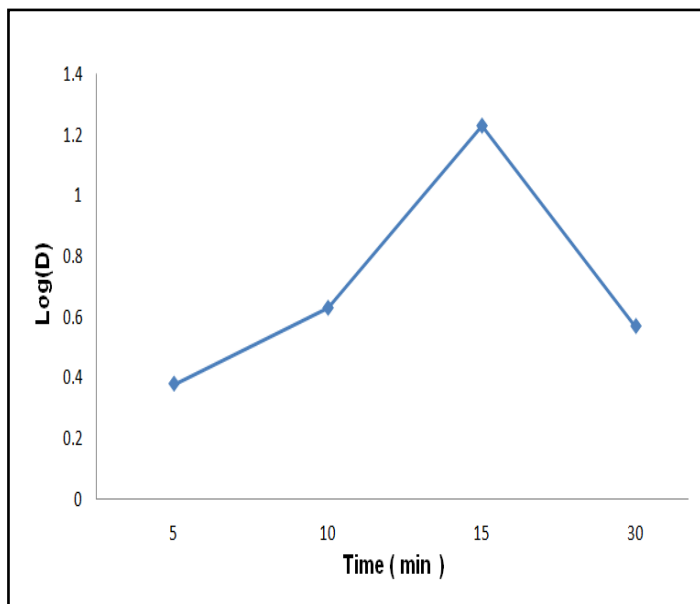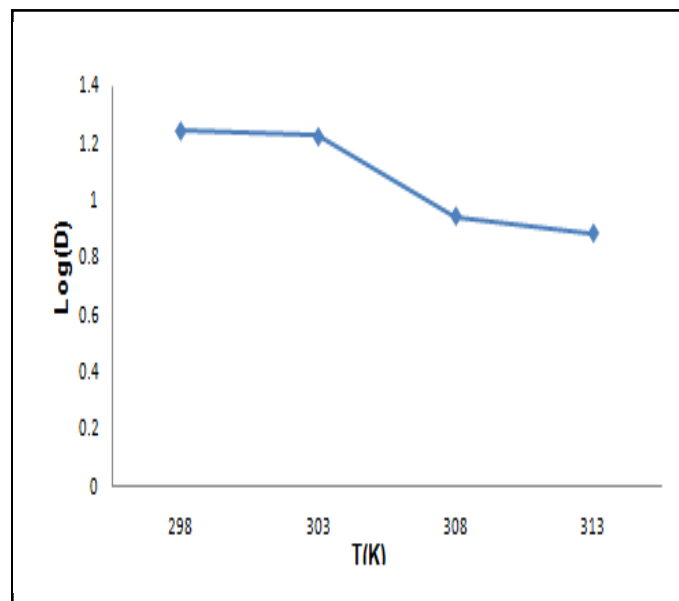| Time(min)	5	10	15	30
D	4.2	4.35	17.2	3.76
%E	71	81	94	79

Fig.13 Effect of shaking time on extraction Ni^{+2} ions.

Fig. 14: Temperature effect on the extraction of Ni^{+2} ions.

Effect of temperature

Extraction of 120μg (4.5×10^{-4}M) of Ni^{+2} ions in (5ml) aqueous solution at (pH=9) by (5ml) organic solution of (L) dissolved in chloroform at (1×10^{-4}M) and different temperature (25-40C°) after shaking for (15min) of fixed temperature separate organic phase from aqueous phase , afterward determine the remainder Ni^{+2} ions in aqueous phase and transferred Ni^{+2} ions to organic phase by dimethyl gluoxime method which is detailed in general procedure . Results shown in the table (3) and Fig.14 shows that the distribution values (D) and the percentage of extraction (% E) nickel ion duo with regent L_3 decreases with increasing temperature .Therefore abstract composition of the complex low because of reducing stability of the complex with high temperatures and this is consistent with the results of other studies [14,15].

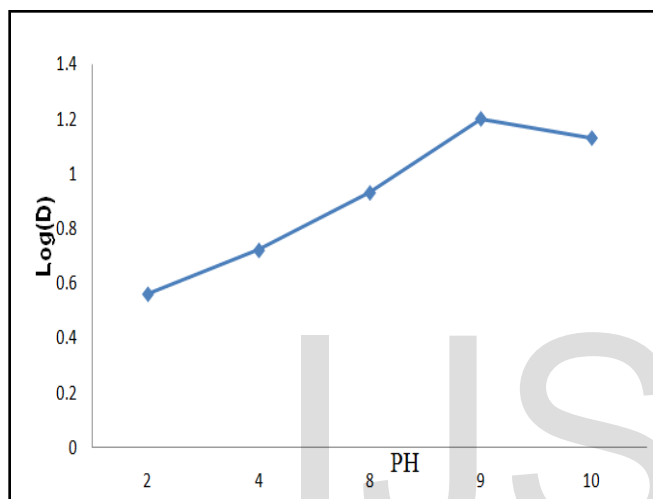**table 3:Temperature effect on the extraction of Ni^{+2} ions.**

T°K	298	303	308	313
D	17.89	17.07	8.98	7.88
%E	94.7	94.4	89	88

Effect of pH

Extracted of (120μg) (4.5×10^{-4}M) Ni^{+2} ions in (5ml) aqueous solution of different pH (2-10) ,adding (5ml) organic solution of reagent (L) dissolved in chloroform at (1×10^{-4}M) concentration ,afterward shaking these two layers for(15minutes),at later separate the organic phase from aqueous phase ,afterward determine the remainder quantity in aqueous phase and transferred quantity to the organic phase and calculate the distribution ratio(D) and percentage of extraction (E) by followed the spectrophotometric method[7] detailed in general procedure . Seen from the table (4) and Fig.15 that the best extraction of ion nickel duo using reagent (L) in basic medium (PH$_X$ = 9) where we note a better percentage extraction (% E) Nickel ion duo, that the function of acid and a clear effect on the process solvent extraction as the low distribution ratio (D) of the nickel ion duo with reagent (L) in the acidic medium move may be due to the busy dual-mail free of nitrogen atom in schiff bases that prepared from proton acid, while at the basic medium increase distribution ratio (D) and thus increasing the percentage of extraction (% E) because the dual-mail is freed from the influence of the proton acid extraction becoming more and more an opportunity where these results are consistent with results of previous studies [16,17].

Table (4):Effect of pH on the extraction of Ni^{+2}ions

PH	2	4	8	9	10
D	3.66	5.29	8.54	17.7	13.74
%E	78	84	89	94	93

Table 5: Effect of Ni^{+2}ions concentration on the extraction

μg Ni^{+2}	50	80	100	120	150
D	3.5	4.81	6.92	9	7.57
%E	79	82	87	90	88

Fig.15 pH effect on the extraction of Ni^{+2}ions .

Fig.16 Effect of Ni^{+2}ions concentration on the extraction

Effect of metal ion concentration

Extracted Ni^{+2}ions from(5ml) aqueous solution contain different quantity of Ni^{+2}ions at (pH=9) by 10^{-4}M ligand solution (L) dissolved in chloroform ,after shaking these two layers for(15 min) separate organic phase from aqueous phase and determine the remainder Ni^{+2}ions in aqueous phase and transferred Ni^{+2}ions to organic phase by followed spectrophotometric method detailed in general procedure, afterward calculate distribution ratio (D) and percentage of extraction(%E).The results in table (5) and Fig .16 shows the optimum quantity of Ni^{+2}ions in (5ml) aqueous solution giving highest (D) value, (E)value was (120μg) (4.5×10^{-4}M) according to equilibrium relation below. Note from the table (5) and Fig.16, the value of the distribution ratio (D) and the percentage to derive (% E) nickel ion duo increases with increasing nickel ion concentration where interaction continues between the ion and the regent (L) that up to better concentration then distribution values starts (D) downward because the increase nickel ion duo concentration in the aqueous phase leads to the formation of other varieties of the complex is not able for extraction , which lead to lack percentage extraction (% E) and the results of this study are compatible with other studies[17,18] .

Organic solvent effect

Extracted(120μg) (4.5×10^{-4}M) Ni^{+2}ions in (5ml) aqueous solution at (pH=9) by (5ml) reagent solution (L) dissolved in different organic solvents differ in dielectric constant (ε) at concentration of (1×10^{-4}M).After shaking these two layers for (15min) ,separate the organic phase from the aqueous phase and determine the remainder quantity of Ni^{+2}ions in aqueous phase and transferred quantity of Ni^{+2} ions to the organic phase to form ion pair association complex , afterward calculate distribution ratio (D) and percentage of extraction (E) .The results at table (6) shows there is not any linear relation between distribution ratio (D) and dielectric constant (ε) for organic solvents used. Seen through the results shown in the table (6) and Fig.17that the best distribution value (D) and best extraction ratio (% E) Ni^{+2}ions with reagent (L)when using chloroform as a solvent organic for reagent where the extracted complex is chalet balanced complex and this type of complexes are affected by factors such as solubility of the extracted complex or spatial structure of organic solvent or contains oxygen or not, and this supports the installation of the role of the organic solvent to reach the best extraction . These results are consistent with other studies [16,19].

Table 6: Organic solvents effect on the extraction

Organic solvents	ε	D	% E
Nitrobenzene	35.70	7.19	87
Chloroform	4.81	17.26	94
CCl$_4$	2.28	12.55	92
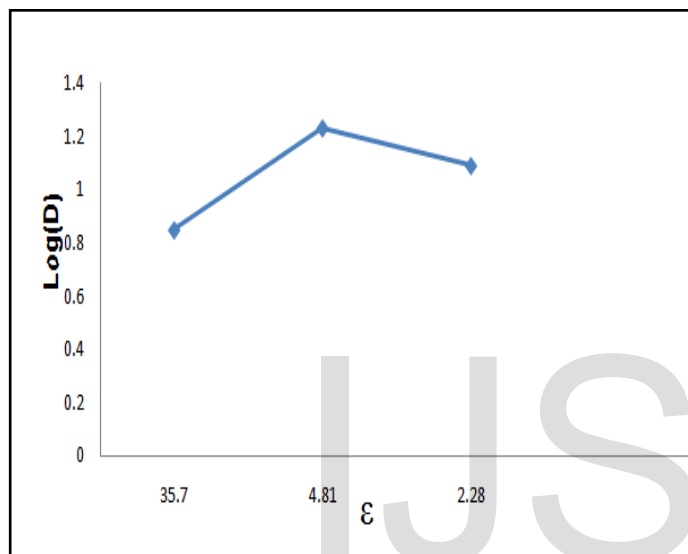
Fig.17 effect Organic solvents on the extraction of Ni^{+2}ions.

Application of the proposed method

Applied study included the appointment of nickel ion in the water of the Euphrates River City of Nasiriyah in using the method of color where the nickel ion concentration by extraction (5.35×10^{-3} µg / ml) and after doing the extraction process using nickel ion reagent (L) in the water of the river sample was a nickel ion concentration equals (0.92×10^{-3} µg /ml) and by the difference between the value of concentrations distribution ratio calculation (D) and the percentage of extraction (%E) nickel ion in the sample and the results obtained are shown in Table (7) Through the results it is clear that the reagent (L) features with high efficiency to extract nickel ion of the sample used.

Table 7: appointment of nickel ion in the river water

Samples	D	%E
River water	4.81	82

CONCLUSIONS

In this study for the first time it was shown that the Schiff bases could be used as a ligand for liquid-liquid extraction and spectrometric determination of traces of metal ions. The important features of the method are simplicity, freedom from interferences, high selectivity, it is judged that the procedure have considerable potential for determination of nickel in river water samples.

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