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Preparation and Extraction study of Zinc (II) as complex with new organic reagent of 2,3 dimethyl-5-phenyl azo-8-hydroxy qunoline (DMPAHQ).

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ABSTRACT

This study includes the synthesis of organic reagent 2,3dimethyl-5-phenylazo-8-hydroxy qunoline (**DMPAHQ**) by reacting adiazonium salt (**2,3dimethyl aniline**) with (**8-hydroxy qunoline**) in alkaline ethanoic solution. And then study optimum conditions for preparation of zinc complex and extractit with the reagent mentioned. The **DMPAHQ** prepared reagent was identified by using (**Uv-vis**) , (**FT-IR**), (**H^1NMR**) techniques, it was $\lambda_{max} = 474nm$ for the complex. We have conducted a study of Zinc(II) ion extraction with the reagent included the Optimum condition such as $pH_{ex} = 8$ for wide range of pH(5-11) and concentration which obey to Beer-Lambert law.

The metal ion concentration=2.1*10^{-4}M, shaking time =20Min, the Ligand concentration=1*10^{-4}M.

Organic solvent effect study shows there is not any linear between dielectric constant and distribution ratio (**D**). the nature of the complex. We're investing a ted by using the continuous variation and molar ratio methods, and found to be (1:2) (metal - Ligand).

Temperature effect studies on extraction method for wide range of (5-50) C^o it was the thermodynamic data ($\Delta H_{ex}, \Delta G_{ex}, \Delta S_{ex}$) for extraction processes of Zinc(II) ion indicated that ΔH_{ex} is positive (**Endothermic**) value as well ΔS_{ex} are found to be positive value, while ΔG_{ex} value indicated that the extraction processes are spontaneous ($\Delta G_{ex} = -ve$).

The melting point of reagent (**DMPAHQ**) is found to be (**130**)C^o its complex with Zinc(II) ion are found to be (**320**)C^o.

The conductivity measurement for solutions at (1*10^{-3}M) in ethanol solution have shown non-ionic character with Zinc(II) ion.

The infrared spectrum of chelating complex also studied and it's compared with the reagent. They give notice change with free reagent spectrum, these showed new bands that were not found original in reagent spectra but other bands have been changed in shape, in trinity and location. This may indicate that a coordination between the metal ion and the reagent prepared.

The H^1NMR spectrum of chelating complex also studied and it's compared with the reagent. They give notice change with free reagent spectrum, where we noticed the disappearance of same peaks, this may indicate that a coordination between the metal ion and the reagent prepared.

Materials: All materials used in the search are from the company B. D. H , Fluka, Riedel-Dheang seelz-Hannover, and Merk.

Apparatus: FTIR spectrophotometer (FTIR-8400s) from shimadzu company, UV-vis-spectrophotometer single Beam UV-vis-(uv-1650pc) spectrophotometer from shimadzu company, UV-vis-spectrophotometer Biotech, uv-vis. Spectrophotometer (uv-9200), pH meter instrument, pH-meter HANN Instrument, Melting point instrument electro thermal malting point 9300-u-k, Electrical balance Bl210s, Water bath:- GFL 1083, Molar conductivity meter:- Cand- 720 (WTW), C.H.N analysis Euro vector instrument & software, Atomic absorphion spectrophotometer Atomic Abosorphtion 2600, H^1NMR spectro photometer (400MHZ) Fourier Trans formation Bruker.

Keywords: DMPAHQ, Zinc (II), extraction.

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INTRODUCTION

Azo dyes: Aso pigments from (60-70)% in all dyes(1), the reason for their desighation is the presence of the azo group (-N=N-) hybrization sp^2 and related to the aromatic system(2), inorder to prepare azo properties, we should choose amine first, which is the process of aldidze, then the reaction(3), the azo group may be associated with many different groups (R-N=N-R). These are dyes and their metal complexes are very low indispersion to nitrogen and hydrocarbons, such as aromatics, which are called aromatic dyes, which are characterized by their high stability dueto the high stability of these compounds. The color intensity is high dueto the resonance phenomenon found in these aromatic compounds (4), one example is the simplest compounds of azo benzene.

Azo compounds are one important organic compounds in many fields such as pharmaceuticals and cosmeties(5,6). The use of dates back to the prehistoric are and all sources used in this peried are natural sources (7,8), at the beginning of the 20th century, hatural dyes were replaced with industrial dyes and the researcher was able (William Perkin) 1856 from the preparation of the purple aniline dye (9,10), it considered the first cast trade mission until the year 1970 was called a dye Brown the composition of the compound as an average of pigments in clouds Yellow, orange, Red, Purple , Blue, Each compound is different depending on the initial material and the breadth of the additives if the system containing the π a specific wavelength porticles (11), azo dyes are important in the field organic synthesis as reagents in measuring chromatography(12), and are used in medical fields(13), azo dyes are used in chemistry analysis corrective processes such as or gage and dreddish pigment as wea as used in the woll in dustry, wood and silk(14).

In the field of drugs, these compounds have been used as drugs because they have in hibitory rala of bacteria(15), and these germs germicidal colon and bacteria causing chronic brwel disease(16,17), and cancer(18), the article was used prontisal itison azo anti-cancer drug and ulcer(19) classification of azo compounds are classified according to the azo compounds founds in the knees, such as mono clonal, bifocal or train gulor(20), or can be classified into two main categories depending on the rings associated with the two groups of the two.

1) Hormo cyclic azo compounds.
2) Hetro cyclic azo compounds.

Solvent extraction (21,22)

The extraction technique with solvent is characterized by sensitiving, efficiency, accuracy and ease of application. It also has awide range of application as it interferes with many other branches of chemistry, such as ecology, medicine agriculture and biological studies, but it is a method of separation and estimation as it uses a separation component of the other components in addition to the estimate of the small concentrations of the component in the water solution and rely on this technology on the distribution of the distribution in subject to balancing process that accurs when the free energy (ΔG) of the dissolved substance is equal in both phase when the chemical potential of the component is equal in both phases and is subject to the Nirenst equation.

Some solvent extraction system are based on the creation of chemical balances(23,24). That organic salts and as ascientific are solubility in the organic solvent. Organic compounds, their solubility in organic solvents more than their solubility in water only if it contains water loving groups where the presence of these groups makes their distribution in favor aqueous ions can be extracted from the inorganic salts of the inorganic salts to the water after converting them in to non-water loving varieties. When using some organic reagents, which eanbe uncharged complexes where the metal ions. Is part of alarg complex so that the water becomes an unsuitable medium for its presence and is transferred to the organic phase in order to facilitate the extraction process.

Zinc element

Zinc is a shing white element (424C°) and boiling point (904C°), but loses its shine after ashort period because of the at exospheric conditions, which is one of the few elements spread in nature, but it's known sinceacient times for easy to get from the materials dissolves, Zinc can be solubility in the strong base because of its abitity to from Zn(II) as ($Zn^{-2}O_2$)$^{(25)}$.

Zinc has oxidation properties (I,II) as it is easily oxidized to Zn(II) and is more stable, the reacts when heated with the air to give oxidation as it intereats with halogens and some non-metals such as (S , P , Se , …….etc). Zinc (II) is colorless and hydrolyzed to give acidic solutions. Zinc complex are of great biological importance as we use compounds like Zinc carbonate $ZnCO_3$ and Zinc oxide ZnO it is amedicalde vice, as Zinc works to kill bacteria and accelerate wound healing$^{(26)}$.

EXPERIMENTAL

Preparation of organic reagents $^{(27)}$

It was melted (0.004mole) from 2,3-dimethyle aniline in (10ml) from ethanol and place the mixture under cooling (0-5C°), then add (1ml) from Hcl with stirring and then add (0.004mole) from $NaNO_2$ dissolved in (10ml) from water at (0-5C°), then leave the mixture for (5-10Min) period to complete the dialysis process, then add this solution (0.004mole) from 8-hydroxy qunoline dissolved in (20ml). form ethanol and the same degree warm (0-5C°), then add to mixture (5ml) from NaOH with concentration (0.1M), the leave the mixture under the cooling from th next day. Then wash the precipitate several times with disilled water and leave to dry. As in the chart(1).

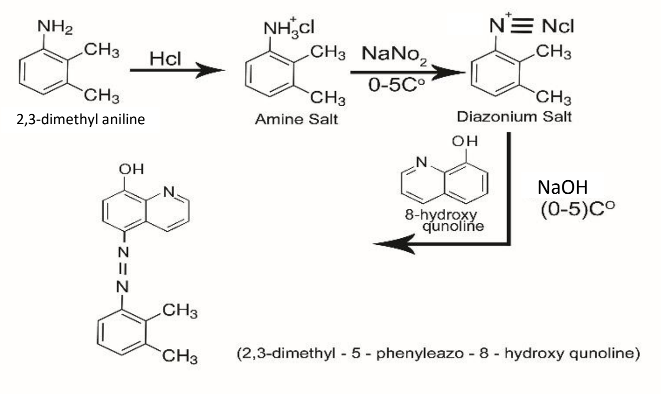


Chart (1): steps to prepare organic reagent (DMPAHQ)

Determination of ion spectroscopy $^{(28)}$.

Zinc is estimated by spectroscopy using the dye method, the daithiazone method, which include the following. Water solutions are placed in the size (5ml) of Zinc ion with concentration ($5 \times 10^{-4} M$) equivalent ($16 \mu g$) and make the acidic function (pH=2-3) in the suppression of separation of capacity (50ml) and the addition of batches of daithiazone solution with concentration ($1 \times 10^{-4} M$) dissolved in the (ccl_4), then shake for two minutes, after finishing separate the organic layer from the water layer.

Then combine the organic layers so that the last batch does not change gree when shaking, then add (5ml) dilute ammonia solution to dispose of daithiazone, then put the organic layer extracted with the ion zinc in the botte volume of (250ml) capacity and complete the size of the mark with (ccl_4), and then measured the absorptivity of the organic layer (the color is pink) at wavelength ($\lambda_{max} = 538 nm$) versus (ccl_4) as ablanck solution using cells of quartz (1cm).

Calibration curve of Zinc ion

The calibration curre of Zinc ion is followed by the chromatic process, wher concentration of water solutions are achieved with increasing concentration of Zinc ion under size (5ml) ranged from ($0.3 \times 10^{-5} - 7.5 \times 10^{-5} M$).

These solution were treated by chromatography method (dia thiazon methode) for determination of Zinc in advance, and then the absorption value of the organic layer extracted at the wavelength ($\lambda_{max} = 538nm$) versus chloroform as a blank solution. He then drew alink between the absorption (A) of the organic layer rersus the molary conceutration and we obtained a straight line as in fig (1).

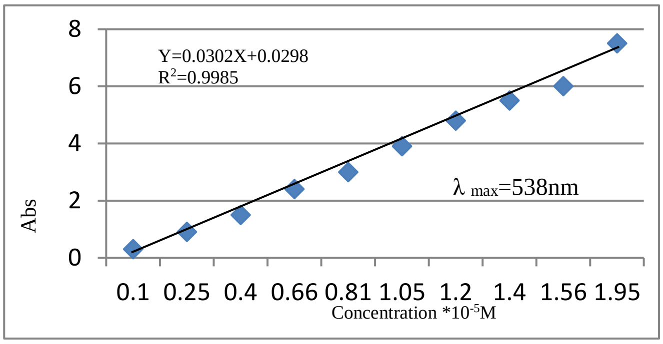


Fig (1) calibration curve of Zinc ion

RESULTS AND DISCUSSION:

The effect of pH

Extraction were carried out with awide rany of acidic functions pH (4-12) to extract Zinc ion of its water solution under volum (5ml). after the concentration of metal ions has been established. ($5 \times 10^{-5}M$) equivalent ($16\mu g$) and using (5ml) from organic reagent dissolved in (ccl₄) and with concentration ($1 \times 10^{-4}M$). After shaking the soles of time (10min) and temperature (25C°), the organic class was separated from the water the ionic metal value was calculated using the dai thiozone method and the distribution value was calculation as in fig (2).

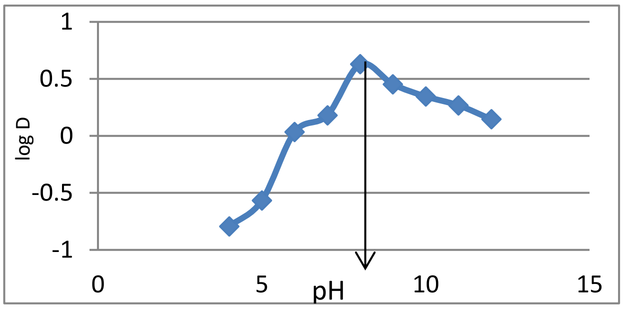


Fig (2) effect of pH

Effect of concentration

To illustrate the effect of concentration in the extraction process and to clarify the bonding between metal ions and organic reagents, whe have taken (5ml) of the water solutions of the metal and contain different can centrations in the range between ($0.75 \times 10^{-5} - 2.7 \times 10^{-4}M$) when the acidic (pH=8) and using (5ml) from the organic reagent withe concentration ($1 \times 10^{-4}M$), and after shaking of water and organic solvents for (10min) and (25C°), after the separation process, the amount of metal was calculated using the dai thiazone method and then the distribution ratios were calculated as in fig (3).

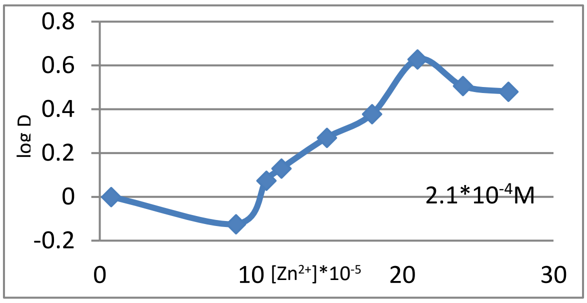


Fig (3) Effect of concentration

Effect of shaking time

For the purpose of explaining the effect of saking time and its effect on the stability of the resulting complex place (5ml) from the best concentration of metal ions $(2.1 \times 10^{-4}M)$ and using (5ml) from organic reagent with concentration $(1 \times 10^{-4}M)$, dissolved in (ccl_4) and the (pH=8), and shaking the two solution and different tiems range from (5mon-25min) and temperature (25C°), after separating the water and organic layer, the amount of metal ions was calculated in water phase using the dai thizone method, then the distribution ratio was calculated as in fig (4).

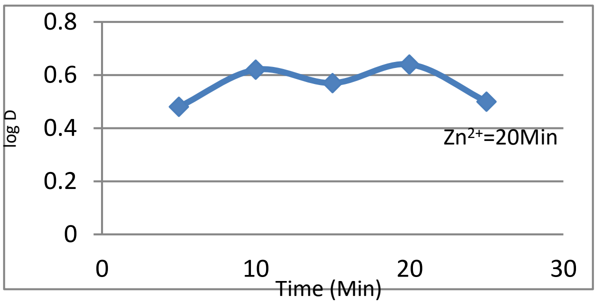


Fig (4) Effect of shaking time

Determination possible composition

Mole ration method

The process was performed using (5ml) of metallic ions and with a concentration of $(2.1 \times 10^{-4}M)$ and after addition (5ml) of organic reagent and the range between $(10^{-3} - 10^{-6}M)$ with all optimum conditions and room temperature, we get apercentage (L-M) as (2:1) as in fig (5).

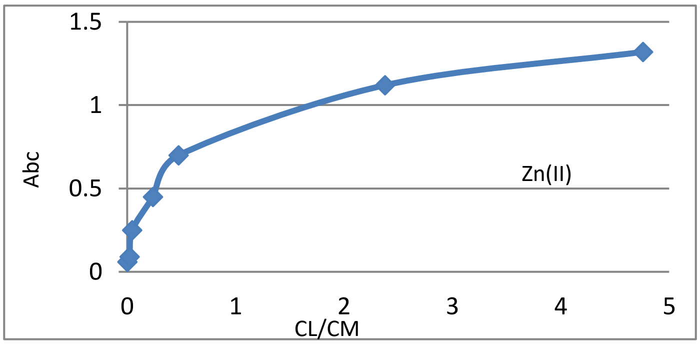


Fig (5) curved mole ration methodes

Continuous Variation Method

The process was performed using equal concentration of bothe organic reagent and metal ion were $(1 \times 10^{-4} M)$, increasing volumes of metal ions were mixed (1ml-9ml) and decreasing volumes of organic reagent (9ml-1ml) with all optimum conditions and room temperature, the result was (L-M) as (2:1) As in fig (6).

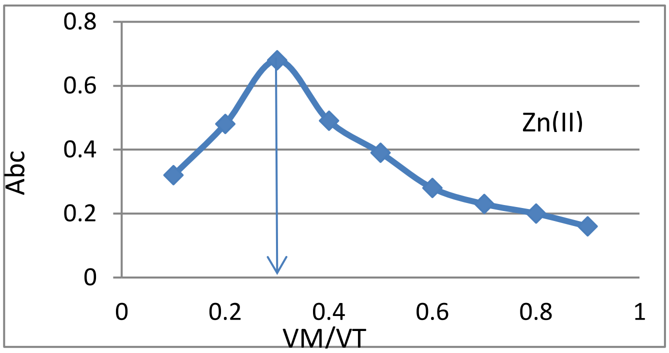


Fig (6) curved continuons variation methodes

Effect of temperature

Were carried out at different temperatures using (5ml) of metal ions with concentration $(2.1 \times 10^{-4} M)$, and (5ml) from organic reagent with concentration $(1 \times 10^{-4} M)$, after all the optimum conditions have been fixed. At different temperatures (5C°-50C°), after completion of the extraction process, the distribution ratios were calculated and the distribution constant, as well as thermodynamic values for extraction.as in fig (7) and (8) and table (1).

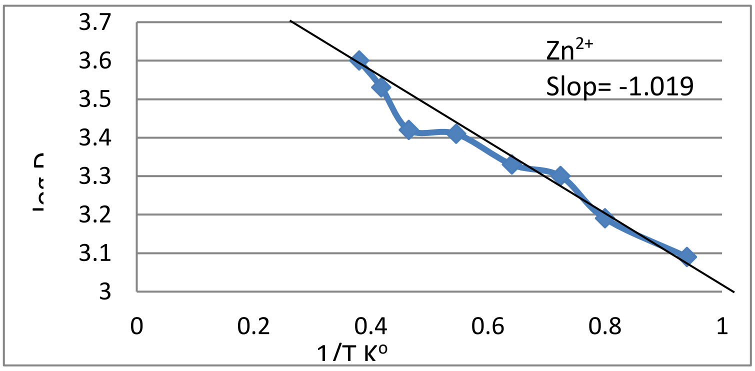


Fig (7) effect of tem perature on the distribution rations (D)

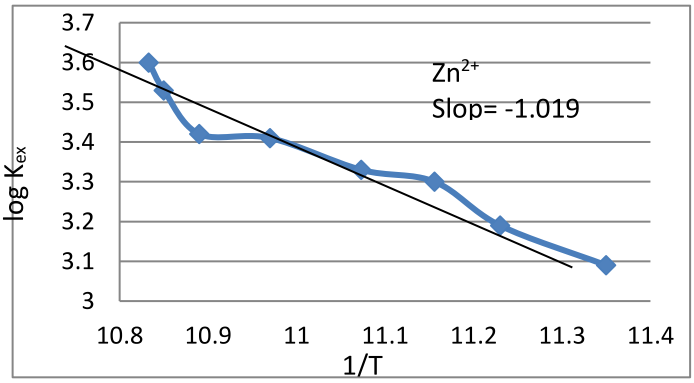


Fig (8) effect of Temperture on the K_{ex}

M^{2+}	ΔH_{ex} KJ/mole	ΔG_{ex} KJ/mole	ΔS_{ex} J/K.mole
Zn^{2+}	0.0195	-70.099	217.000

Table (1) the thermodynamic values for extraction

Stabitity of the resulting complex

Effect of time:

The absorptive index of the complex was measured at different times raning from (2-240) Min, as in fig (9).

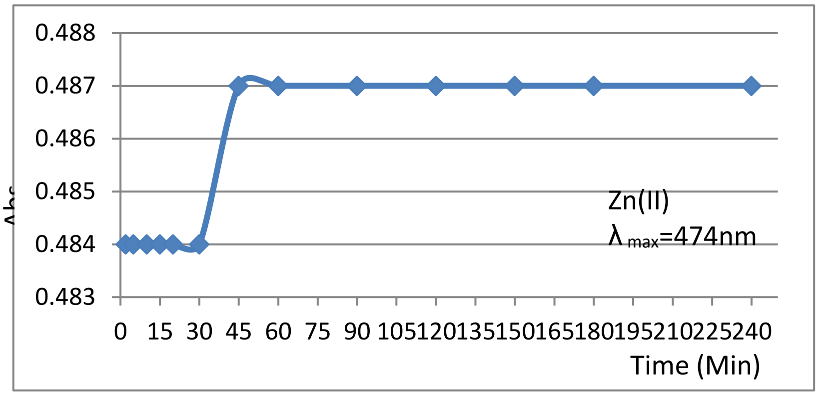


Fig (9) effect of time on the stability

Calculate the stability constant [(29)]:

The absorption values obtaind from the molar rations, we can calculate constant stability (β) as in the table (2).

Metal ion complex	A_S	A_m	α	β
$[Zn(R)_2]$	0.425	0.456	0.068	29.68×10^{10}

Table (2) the stabliting constant (β) for complex

Electrical conductivity measurement[(30)]:

The electrical conductivity (Λ_m) of the solution of the complex was measured by concentration ($1 \times 10^{-3} M$), using ethanol as solvent and at laboratory temperature, as in the table (3).

Complex with Reagent (DMPAHQ)	$\Lambda_m(S.mol^{-1}.cm^2)$ In Ethanol
$[Zn(R)_2]$	9.63

Table (3) condnctivity values of organic reagend

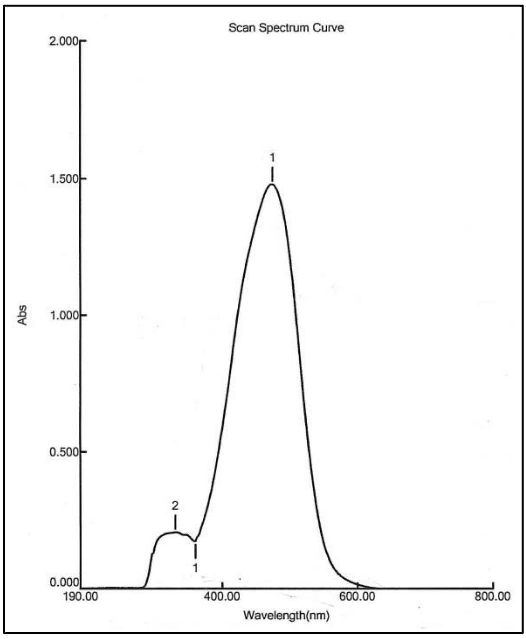
Melting point

The melting point of the reagent and its complex were recorded, as in the table (4).

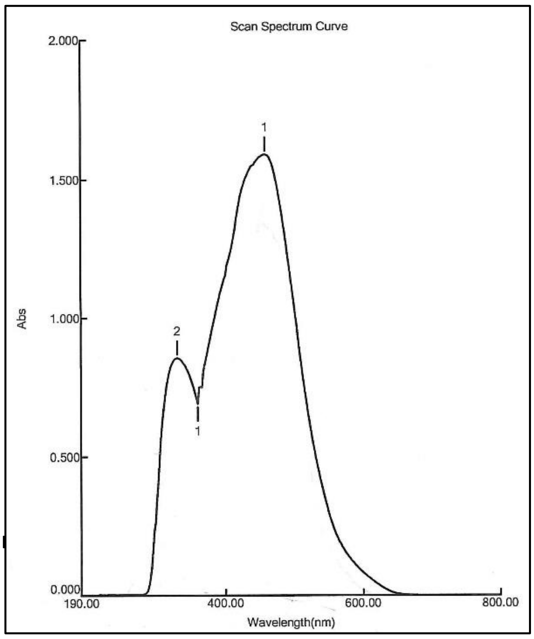
Compound	Melting Point C°	Color
Reagent (DMPAHQ)	130-132	Areddish orange
$[Zn(R)_2]$	320-322	umber

Table (4) melting point for reagent and complex

Spectrum of UV-vis



spect



Infrared spectrum

Infrared spectrum (FT-IR) for the free reagent (DMPAHQ) showed a wide absorption peak at the wave number (3441cm^{-1}) Due to the vibratory vibration of the (OH) group(31), as well as the appeared of low absorption peaks when (2920-3026cm^{-1}) Due to the vibratory vibration aromatic (C-H)(32).

As well as the medium of two absorption peak at (1477cm^{-1},1438cm^{-1}) due to (N=N) group. Also strong peak at (1238cm^{-1}) due to vibratory bending outside the level for (OH) group. Also week peak at (750cm^{-1}) due to for aromatic rings(31).

Either the infrared spectra (FT-IR) of the coordinate with the reagent appeard of wide absorption peak at (3275cm^{-1}) due to for water molecules with complex moistnre. Also appeard the two peaks at (2916-3061cm^{-1}) due to the vibratory vibration for group (C-H) the aromatic after at was (2920-3062cm^{-1}) in free reagent, OR (N=N) it has not changed(33), as in fig (11) , (12) .

We note disappeared for the peak (3441cm^{-1}) for (OH) group. And appeard a new peak at (422-445cm^{-1}) due to for interconnection between (M-N). OR appeard the medium peak at (501cm^{-1}) due to for interconnection between (M-O)(34,35).

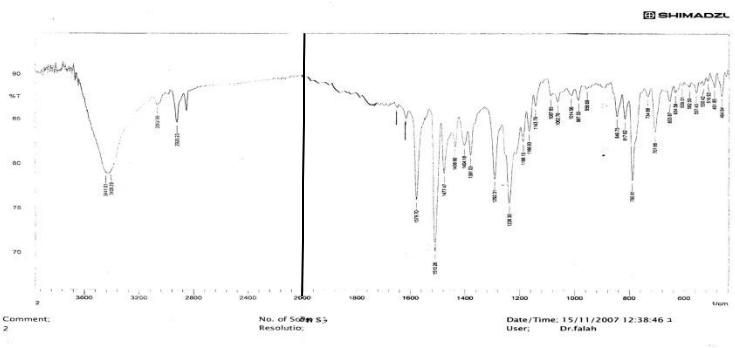


Fig (12) Infrared spectrum for free organic reagent

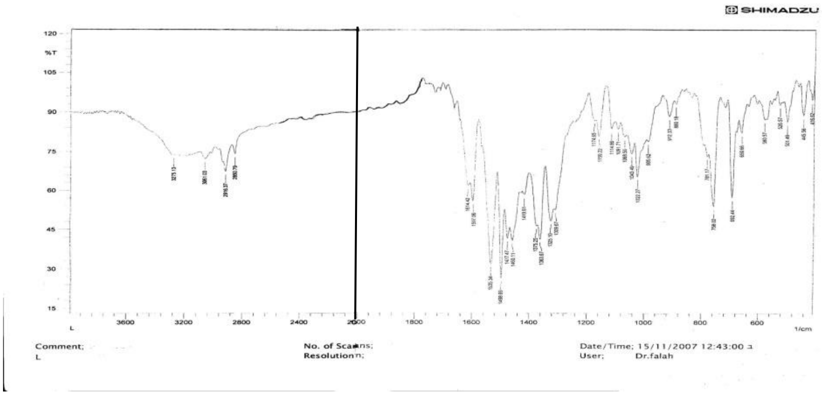


Fig (13) Infrared spectrum for free complex

H^{1}NMR Spectrum

The free spectrum of the reagent showed a peak absortion at (2.52ppm) and (2.27ppm) which is due to (C-CH$_3$) in the aromatic ring and another absorption peak at (2.52ppm) is due to group (OH) in 8-hydroxy qunoline, as well as multiple absorption of (6.94 – 7.2ppm) due to (H-phenyl)(36,37).

As for the complex spectrum the absorplion of (C-CH$_3$) and the disappearance of the peak (OH) were abserved because of their participation in interconnection(36,37), as in fig (13) and (14).

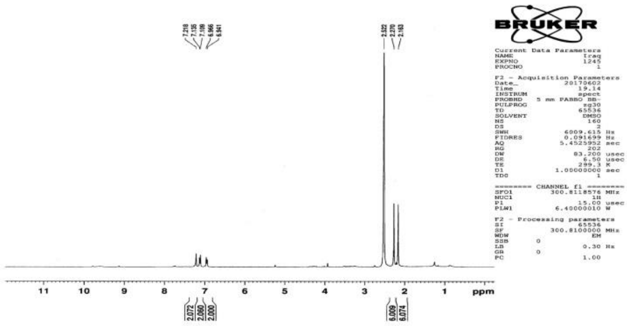


Fig (14) H^{1}NMR spectrum for free organic reagent

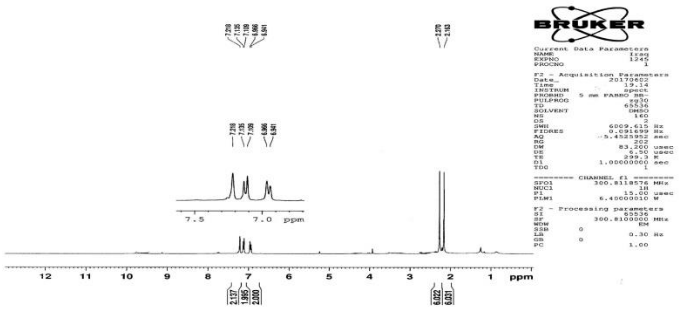


Fig (15) H^1NMR spectrum for for complex

Recommendations

1- Preparation of new derinatives for the organic reagent for the parpose of impoved selection with aview to their use in other elements.
2- Due to the high stability of these compounds, various complexes of these compounds can be prepared with other elements of the periodic table.
3- Study the biological officacy of the recorded reagent (DMPAHQ) due to the offective enjoyment of the dyes and other medical applications.
4- Study the effect of this complex on bacteria in living tissue.
5- The possibility of using the reagent recorded in the fields of the application of other multi-valued elements, for example in steel and soil.

CONCLUSIONS

1- Easy to prepare the organic reagent by obtaining diazione salt for aromatic salts in normal conditions.
2- Easy to prepare of the chelating complex ofter the installation of optimum conditions of concentration and its proportion.
3- Organic reagent (DMPAHQ) exhibits the behavior of abinary reagent.
4- The results of the calculations for the Mo dynamic values showed that the reactions of the preparation of the complex with the reagent and the extraction processes are heat-absobent reactions as well as high values of the entropy as well as the reactions.
5- The reagent has the ability to extract the metal ions under study after installing the best conditions.
6- Results of percentages and constant changes showed that the ratio between (ion:reagent) she (1:2).

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