Liquid-Liquid Extraction of Iron (III) Ions Using an (Azo) Derivative & it's Analytical Applications

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Abstract

The study of solvent extraction of Iron(III) ion by an azo derivative of 8-hydroxyquinolin (DPDQ) had been made. The effect of various parameters on the extraction and distribution ratio such as acidity of medium; time of extraction; polarity of solvents; some anion and cation effected; redox agent effected; metal concentration effect; salting out &effect of temperature. The thermodynamic functions (ΔH, ΔG, ΔS) were calculated. The extraction stoichiometry was studied using two methods Job's &Molar ratio. It was found to be (M: L) (1:3). The constant of stability of complex in method's mole ratio was calculated. The spectroscopy of UV-visible, F.T.I. R, HNMR, CNMR & mass were study for both the reagent & complex in organic phase. Other physical constants such as melting point & conductivity were studied.

Keywords: Azo, liquid extraction, Ligand, Complex, DPDQ1.Introduction

1. Introduction

The general purpose of solvent extraction is the selective isolation of the target compounds from the sample with minimal matrix contamination. Solvent extraction is often employed as an initial step in sample preparation and, if required, is followed by additional sample clean up procedures, including further solvent extraction steps (liquid-liquid partition) or complementary separation techniques[1]. Solvent extraction is a mature technique in that extensive experience has led to a good understanding of the fundamental chemical reactions. At the same time, compared to many other chemical separation processes like precipitation, distillation, or pyro metallurgical treatment, the large-scale application of solvent extraction. New reagents are continually being developed the efficiency and high selectivity of solvent extraction should make it an increasingly competitive separation process both in research and in industry[2].

Solvent extraction in an indirect separation method in general depend on thermodynamic laws, as well as from the other hand less depend on kinetic laws, and from this truth we must know all effective parameters on extraction efficiency according to this method[3]. Azo dyes represent the largest production volume of dye chemistry today, and their relative importance may even increase in the future They play a crucial role in the governance of the dye and printing market. These dyes are synthesized from a simple method of diazotization and coupling. Different routes and modifications are made to obtain the desired color properties, yield and particle size of the dye for improved dispensability[4],[5].

The transition metals complexes with azo dyes used to extracted the metals, such as azo dye ligand based on p-phenylenediamine with 5-nitro-8-hydroxyquinoline and its Cu(II), Mn(II), Co(II)and Ni(II) complexes were synthesized[6].Co(II),Cu(II),Zn(II)&Ni(II) there complexes with(4-chloro-N(2(dimethylamino)ethyl) 5-((2-hydroxy-4,6-dimethylphenol)diazenyl)-2-methoxybenzamide) prepared[7] Complexes of Ni(II)&Cu(II) with a ligand of azo functional group derived from 4-aminoantipyrine&2, 4-dimethylphenol were prepared[8]. Nd+3, Gd+3, Dy+3 & Er+3 complexes were prepared[9] Heterocyclic Azo Dye Complexes with Y(III) and La(III)Ions synthesized[10]Complex of Cobalt with azo dye Sudan Red G was prepared[11], Fe(III) complex of BNAHP was prepared[12]. Quinoline-ampyrone complex with Cobalt was prepared[13], Ce(III) complex with (DTPPA) was prepared[14], New complexes of Cu+2,Ni+2&Co+2 were prepared with azo heterocyclic[15].Some complexes of Azo-triazole were prepared with Ni(II),Co(II) &Cu(II)[16] Fe3+complex with 2-(4-Formyl-3-hydroxy-naphthalen -2-ylazo)-benzoic acid was prepared[17], vanillin azo base[18] . In this study Iron(III) ion was extracted by a new azo derivative of 8-hydroxyquinoline (DPDQ), and study the best condition of extraction process to find the rapid and efficient method to extracted and determination of Fe(III) ion .

2.ExperimentA. Synthesis of ligand 7-((4-(dimethylamino) phenyl) diazenyl) quinolin-8-ol

Preparation of ligand (7-((4-(dimethylamino) phenyl) diazenyl) quinolin-8-ol) was prepared from diazonium salt pairs of the (4-Amino-N, N-dimethylanilindihydrochloride) with (8-hydroxyquinolin) in an alcoholic medium by dissolving (2.0912 gm, 0.01 mol) of 4-Amino-N, N-dimethylanilindihydrochloride in a solution obtained by mixing (2 mL) of concentrated hydrochloric acid with (25 mL) distilled water. (0.69 gm, 0.01 mol) of sodium nitrite dissolved in (10 mL) of distilled water drop by drop, stirring keep the temperature blow 5C°, and tack the solution stile for (30 minutes) to complete the azoniated process and obtain a solution of diazonium chloride This salt solution was

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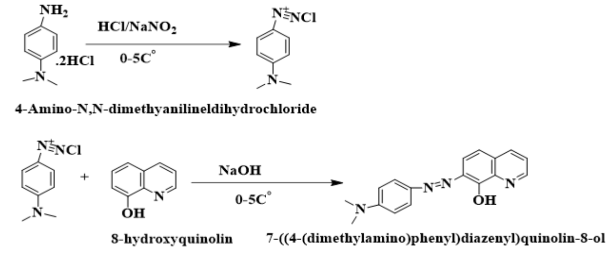
added slowly with continuous stirring to a solution (1.4516 gm,0.01mol) from 8-hydroxyquinolin that dissolved in a mixture of (25 mL) of ethanol and (15mL) of sodium hydroxide (2.5M), was observed to discolour the solution in a reddish orange colour .The solution was left over night,and modified the acidic function to (pH=5-6) to obtain reddish orange precipitate .The precipitate was filtrated and washed with distilled water to remove the sodium chloride that produced from the pairs and neutralization process,and it dried and recrystallization from ethyl alcohol, the yield was 75% .The equation blow explain how to obtain the ligand .

Scheme1: Synthesis of ligand (DPDQ)

B. Used instrumentals



a/Double beam UV-Visible Spectrophotometer Cecil 7200 (England)
b/ pH –meter Hanna
c/ FTIR –IR 8400, Shimadzu (Japan)
d/ Water bath type Bs-11 (Korea)
e/ Gemmy Orbit Shaker VRN-480 (England)

C.Material and methods: In this research all analytical reagents and solutions used in preparation are in high purity. Preparation of standard solution.Iron (III) solution (1000µg/mL) was prepared by dissolving (0.7236gm) from Fe(NO3)3.9H2O in deionized water and complete the volume to the mark in volumetric flask 100 mL.

Ammonium thiocyanate (20% w/v) was prepared by weight (20gm) and dissolved in deionized water in 100 mL volumetric flask.

1. Reagent solution (DPDQ) (1000µg/ml): was prepared by dissolving appropriate weight (0.1gm) in chloroform and complete the volume to (100 ml).

Interferences cations solution of (Pb^{2+}, Ag^{1+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Cr^{3+}) ions (0.1g/100mL) were prepared by dissolving (0.1598gm) of Pb $(NO_3)_2$, (0.1575gm) of $AgNO_3$, (0.3660gm) of Cu $(NO_3)_2$. xH_2O, (0.4954gm) of Ni $(NO_3)_2.6H_2O$, (0.2744gm) of $Cd(NO_3)_2.4H_2O$, (0.2598gm) of $Cr(NO_3)_3.9H_2O$, (0.2416gm) of $Sr(NO_3)_2$ and (0.1708 gm) of $Hg(NO_3)_2.H_2O$ respectively in 100 mL distilled water for eac

D.Extraction procedure: A solution containing (200µg, 7.1626×10-4M) of Iron (III) ion and (0.1%) ligand (DPDQ) in chloroform is poured into a separatory funnel. The aqueous phase in completed to (5mL) with deionized water. The pH of solution adjusted with diluted nitric acid and/or sodium hydroxide solution, after shaking the aqueous and the organic phase are allowed to separate. An reduced ion was determined by thiocyanate procedure [19].

2. Results and Discussion

The solubility of the ligand in different solvent is shown in table (1), the ligand was characterized by spectroscopic methods (FT.IR, UV-Vis, NMR^{H}, $NMR^{C,}$ Mass). Table (2) shows physical properties of the prepared ligand.

Table (1): The solubility of the prepared ligand in different solvents.														
Comp.	H2O	CCl4	Methanol	Ethanol	1-Propanol	2-Propanol	1-Butanol	Chloroform	DMF	DMSO	Acetone	Dichloromethane	Acetonitrile	n-Hexane
DPDQ	-	+	+	+	+	†	+	+	+	+	+	+	†	-
(+) soluble, (-) insoluble, (†) partial solubility														

Table (2): the physical properties of the prepared ligand	
Compound	DPDQ
Compound formula	$C_{17}H_{16}N_4O$
Molecular weight	292.1324
Yield	75%
Melting pointe	164-166C°
Colour	Reddish orang

Identification of DPDQ prepared ligand: The ligand was characterized by spectroscopic methods (UV-Vis,FT.IR, NMR^{H},

NMRC and Mass spectroscopy) (UV-Vis.) spectrum for the ligand: The (UV-Vis) spectrum for the ligand (DPDQ), figure (1) exhibits a high intense absorption peak at(244nm), (260.5nm), (324.5nm) and (442.5nm) which assigned to (π→π*), (π→π*),(π→π*)and (n→π*) transition respectively .

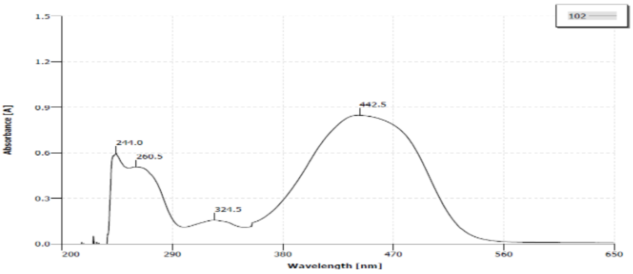


Figure (1) electronic spectral data of the ligand

FTIR spectrum for the ligand

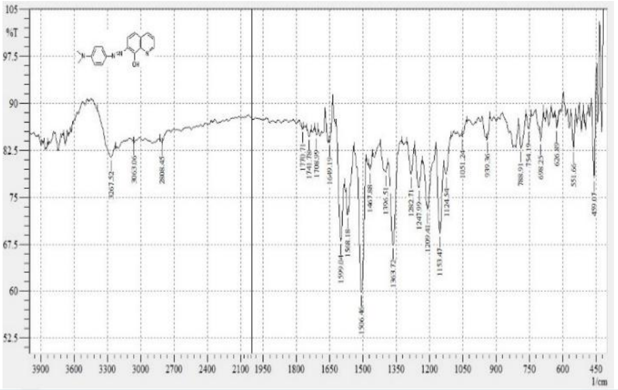


Figure (2) F.T.I.R spectrum of (DPDQ)

Figure (2) show the FTIR spectrum for the ligand, the band at (3267.52) cm^{-1} refer to the v (OH), the band at (1649.19) cm-1 refer to (C=N), the bands at (1599.04) cm-1, (1568.18) cm-1 and (1467.88) cm-1 refer to the starching vibration of aromatic (C=C), the band at (1506.46) cm-1 refer to (N=N), the band at (3063.06) cm-1 refer to aromatic (C-H).

1H NMR spectrum for the ligand

The 1H NMR spectrum of ligand (DPDQ) shown in figure (3).

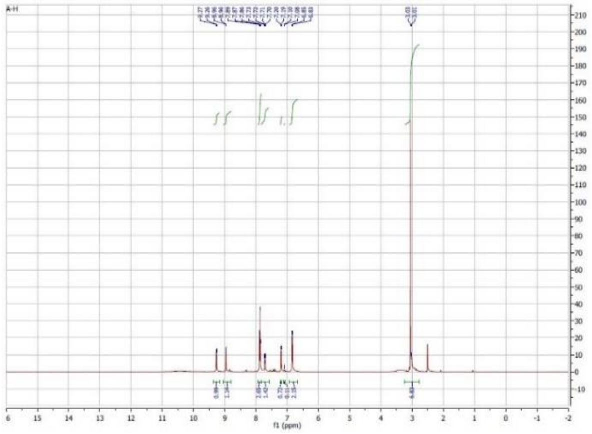


Figure (3) 1H NMR spectrum of (DPDQ)

^{13C}-NMR of the ligand the 13C NMR spectrum of ligand (DPDQ) shown in figure (4).

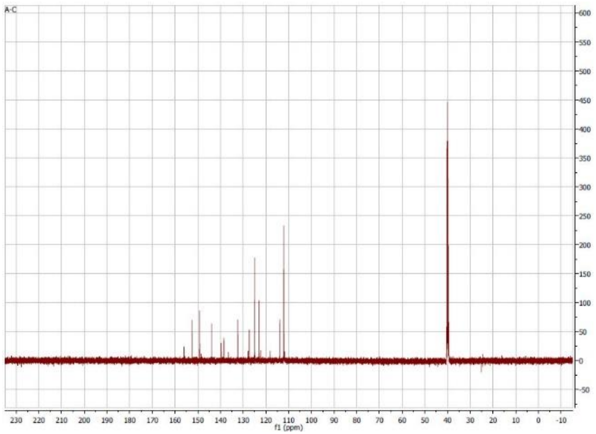


Figure (4) 13C-NMR spectrum of the ligand.

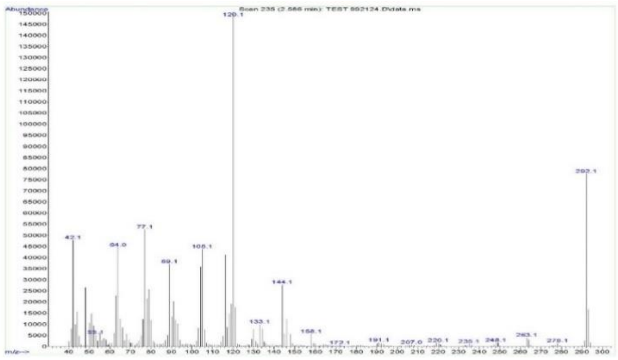


Figure (5) Mass spectrum of the ligand.

Mass spectrum of the ligand: The mass spectrum of ligand (DPDQ) shown in figure (5).

Calibration carve: - Calibration carve was prepared for Iron (III) ion depending on the color method for solution of thiocyanate [19]. Figure (6) shown the calibration carve of Fe (III) ion.

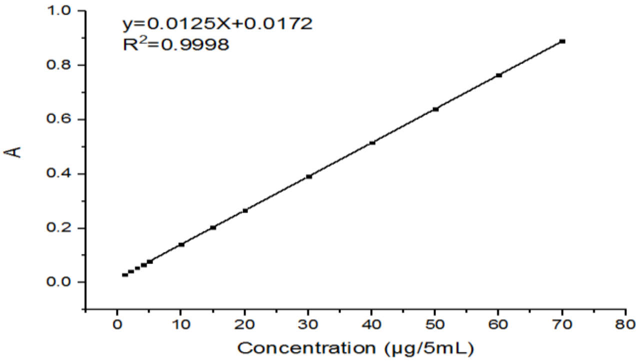


Figure (6) Calibration carve of Iron (III) ion.

Study the effect of different parameters on the extraction

Effect of pH

In order to settle the solvent extraction system for the separation of Fe3+ ion the effect of pH was studied for pH rang (2-12) .it is found that the complex given highest distribution ratio (D) and an extraction percentage (E%) at pH (7). the complex formed at neutral media although lower high pH value gives lower extraction yield, table (4).

Table (4) pH effect on the extraction

pH	2	3	4	5	6	7	8	9	10	11	12
D	0.270	0.118	3.580	2.245	5.365	20.222	7.538	9.625	9.832	0.543	5.101
E%	21.288	10.528	78.168	69.188	84.288	95.288	88.288	90.588	90.768	75.208	83.608

Effect of shaking time

For the kinetic side of extraction of extraction method studied effect of shaking time on the extraction activity and distribution ratio values, the result of this study shown in table (5), the maximum distribution ratio value and reach the equilibria of extraction was found at time (15 min).

Table (5) shown the effect of shaking time on the extraction.

Time (min)	2	5	10	15	20	25	30
D	5.816	7.84	19.358	30.133	11.481	10.531	7.256
E%	85.33	88.69	95.088	96.788	91.988	91.328	87.888

Effect of metal ion concentration

The result in figure (6) show the metal ion concentration effected on extraction method and distribution ratio. The metal ion concentration 200μg (7.1626×10-4 M) was the optimum concentration.

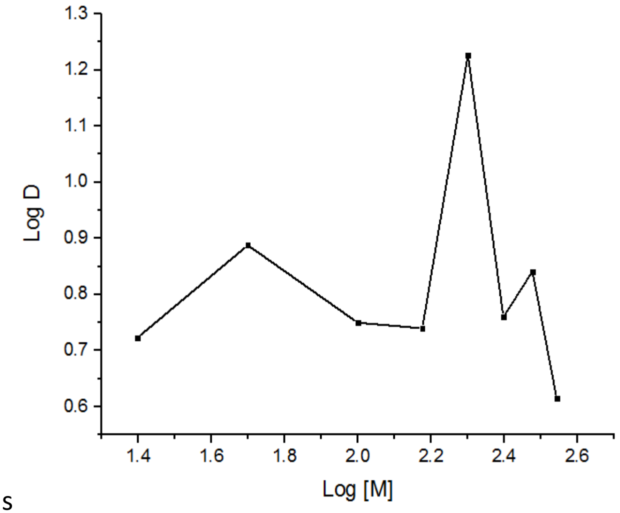


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Figure (7) effect of metal ion concentration on extraction of Fe (III) ion using (DPDQ) reagent.

Effect of organic solvents on extraction

According to solvent extraction method which was depend on the organic solvent used in extraction method the result in table (6) demonstrate there is not any linear relation between distribution ratio and dielectric constant of organic solvent and appear chloroform was the best solvent for extraction Iron(III) ion and suggest the different of organic solvent structure on the extraction method. These result is in contrast with born relationship of the equation blow [20]

$\Delta Gt = \frac{Ze2}{Zr}\left[\frac{1}{\varepsilon w} - \frac{1}{\varepsilon 0}\right]$ ----------- Born equation

Table (6) effect of organic solvents on the extraction.

Organic solvent	ε	D	E%
Toluene	2.24	3.4185	77.368
Benzene	2.28	6.0462	85.808
Chloroform	4.9	29.5623	96.728
ethyl acetate	6.02	1.8775	65.248
Dichloromethane	9.1	2.2245	68.988
Amyl alcohol	15.8	1.7478	63.608

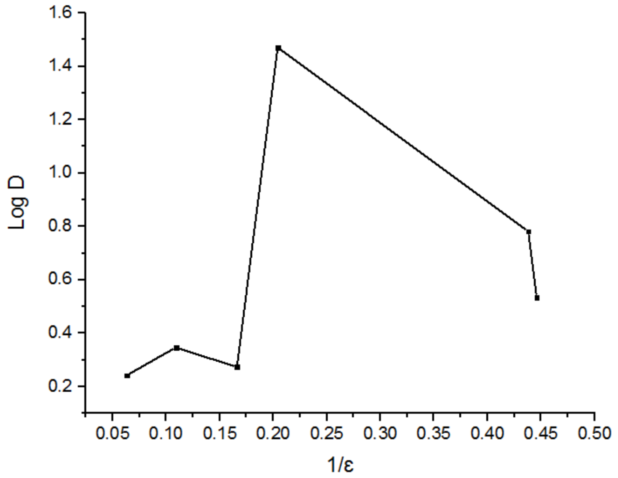


Figure (8) effect of polar organic solvent on extraction of Iron (III) ion using (DPDQ) reagent.

Effect of anions on the extraction

The results in the table (7) show the values of distribution ratio to extract (200µg) (7.1626×10-4 M) of Fe (III), from aqueous solutions were calculated under the optimum conditions by addition of different concentrations of some anions of potassium salts using the reagent (DPDQ) dissolved in chloroform.

Table (7) effect of anions on the extraction

Anions	500µg/mL		1000µg/mL	
	D	E%	D	E%
---------	29.5623	96.728	29.5623	96.728
Br-	22.1910	95.688	10.7481	91.488
SCN -	7.5382	88.288	9.2965	90.288
SO4 =	8.4232	89.388	7.8401	88.688
Cr2O7 =	13.6799	93.188	4.9129	83.088
CrO4 =	8.5129	89.488	7.5382	88.288
CO3 =	9.6247	90.588	10.8877	91.588
IO3 -	3.4818	77.688	0.5080	33.688

The aqueous phase contains (2mL) of Fe(III) ion solution (200µg) (1.7906×10-3 M) and (1mL) (500µg/mL, 1000µg/mL) from some of the negative ions at (pH=7) &distal water.
Organic phase: - (5mL) of (DPDQ) (0.1%) in chloroform.

j. Effect of cations on extraction

The results in the table (8) show the values of distribution ratio to extract (200 µg) (7.1626x10-4M) of Fe (III), from aqueous solutions were calculated under the optimum conditions by addition some cations of nitrate salts using the reagent (DPDQ) dissolved in chloroform

Table (8) effect of anions on the extraction

Cations	D	E%
Non	30.3283	96.808
Pb2+	9.855406	90.788
Ag+	27.80184	96.528
Cu2+	24.56237	96.088
Ni2+	17.47746	94.588
Cd2+	14.59576	93.588
Cr3+	42.2526	97.688
Hg2+	12.90434	92.808
Sr2+	13.46759	93.088

k. The effect of oxidation agent and reduction agent on the extraction

The effects of oxidation were studied by adding (1mL) from 35 % (W/V) of hydrogen peroxide solution as an oxidant agent in extraction of Co (II) ion with (DPDQ), under the optimum conditions. Distribution ratios of Fe (III) ion with (DPDQ) were calculated after separating aqueous phase from organic phase. The amount of remained ions in aqueous phase were, calculated by colorimetric method.
The influence of reducing agent on (D) value to extract Fe (III) ion, with (DPDQ) were studied by adding (1mL) from (1M) of SnCl2.2H2O solution to the aqueous phase and by following the same method used with the studying of the influence of oxidizing agent. Results were illustrated in the tables (9).

Table (9) The effect of oxidation - reduction factors in the extraction of Fe(III) with (DPDQ)		
Extraction	D	E%
Fe (III) with (DPDQ) In absence of oxidation-reduction factors	30.3283	96.808
Fe (III) with (DPDQ) In presence of oxidation factors	3.365	77.088
Fe (III) with (DPDQ) In presence of reduction factors	1.956	66.168

l. The effect of salting out on the extraction

To study the effect of the salting, Ammonium chloride, Sodium chloride, Sodium sulphate &Sodium nitrate were chosen for this purpose, because these salts were not extracted from organic phase. it can be stripped and destroyed if we need to do that, so it is favorite as salting agent[21]

The values of distribution ratios were calculated to extract (200µg), (7.1626x10-4M) of Fe(III) ion, with the reagent (DPDQ) dissolved in chloroform in the presence of (1 mL) of above salts solution under the optimum conditions, the results shown in table (10).

Table (10) The effect of salting out in the extraction of Fe(III) with (DPDQ)		
Salt	D	E%
----	30.328	96.808
NH4Cl	2.464	71.128
NaCl	3.701	78.728
Na2SO4	3.547	78.008
NaNO3	4.941	83.168

m. Effect of temperature and calculate the thermodynamics functions

The extraction of Iron (III) ion from aqueous solution was studied by temperature from (20-45 C°) and the results in table (11). By using Vant-Hoff equation[22]

2.303Log Kex= $\frac{-\Delta H}{RT} + C$ ------------(Vant-Hoff equation)

Table (11) the values of distribution ratios for the extraction of Fe(III) ion by (DPDQ) reagent at different temperatures.		
T(K)	(1/T)×10-3	D
293	3.4130	21.1631
298	3.3557	13.0607
303	3.3003	9.1296
308	3.2468	4.2213
313	3.1949	3.8003
318	3.1447	3.5061

The aqueous phase: - (200µg/5mL) (7.1626×10-4 M) of Fe(III) ion solution at (pH=7).

Organic phase: - (5mL) of (DPDQ) (0.1%) in chloroform. Equilibrium time = 15 minutes.

the reaction between Iron(III) ion and the ligand was exothermic reaction and this mean the increase in temperature may be effect to increase the D&E% values. The thermodynamic functions (ΔH, ΔG and ΔS) were calculated by Gibbs equations

$\Delta G=\Delta H-T\Delta S$

$\Delta G_{ex}=RT\ln K_{ex}$ ……… where Log D=Log Kex

and the results in the table (12). the lower value of ΔHex demonstrate the dissociation of the complex as well as the large value of ΔSex appear the reaction in intropic region and these results appear the effect of Fe3+ in aqueous phase give easily for extraction by ligand and high stability of Fe3+-complex in chloroform solvent which used for extraction. The thermodynamic data of extraction Fe (III) ion in table (11).

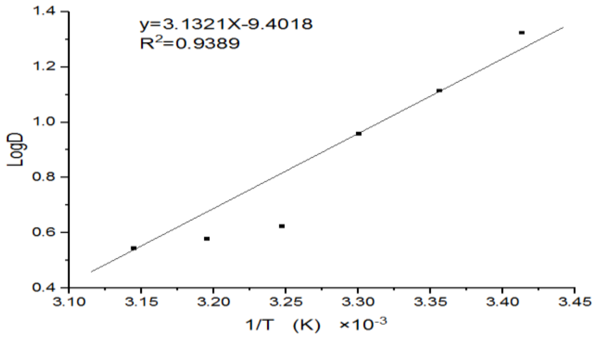


Figure (9) effect of temperature on extraction of Iron (III) ion using (DPDQ) reagent.

Table (12): Thermodynamic data of Iron (III) ion extraction by (DPDQ) reagent.			
T (K°)	ΔH (KJ.mol-1)	ΔG (KJ.mol-1)	ΔS (KJ.mol-1.K-1)
293	-57.2585	-7.4366	-0.1700
298	-57.2585	-6.3675	-0.17077
303	-57.2585	-5.5721	-0.17058
308	-57.2585	-3.6885	-0.1739
313	-57.2585	-3.4748	-0.17183
318	-57.2585	-3.3173	-0.1696

From the above results in table (12) the minus sign of the enthalpy values show that the reaction between Fe (III) ion with (DPDQ) was exothermic, thus mean the decrease in negativity of formation extract complex with decreasing temperature, while the negative values of free energy demonstrate that reaction is favorite thermodynamically in low temperatures this study agree with a lot of studies[23].

n. Stoichiometry determination

The extraction species (M: L) stoichiometry is determined by different methods.

1- Job's method: The result in Fig (10) demonstrate the more probable structure of chelate complex extraction was (1:3) (M: L) [Fe(L)3]. From the figure the result of mol ratio for structure which is [Fe $(DPDQ)_3$].

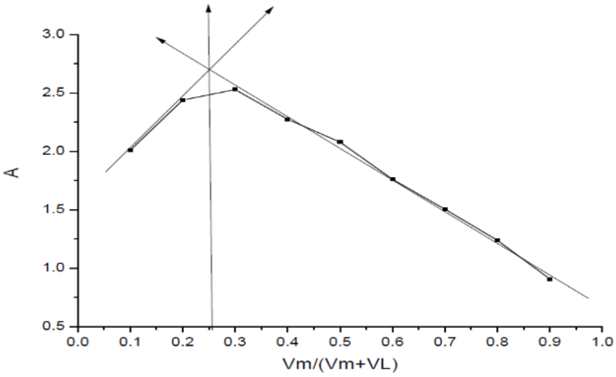


Fig (10) Job's method for Fe (III) ion with (DPDQ).

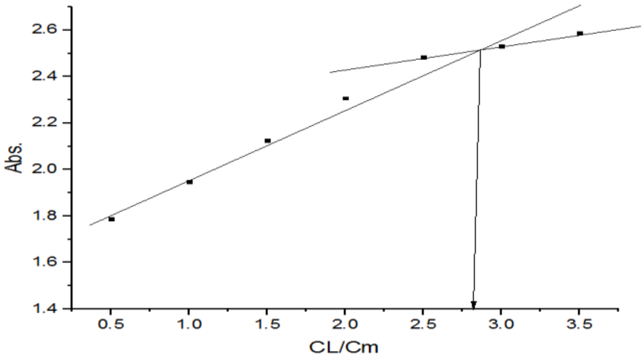
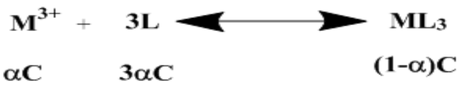


Fig (11) Molar ratios method to extract Fe (III) by (DPDQ)

2- mole ratio method: The result in fig (11) for mole ratio method study demonstrate the more probable structure of chelate complex extraction was (1:3) (metal: ligand) [Fe (DPDQ)3].

Study the stability for the extracted complex in organic phase.



$$\underset{\alpha C}{M^{3+}} + \underset{3\alpha C}{3L} \longleftrightarrow \underset{(1-\alpha)C}{ML_3}$$

The stability constant of extracted complex in organic phase was calculated (ML3) by drawing the equilibrium reaction for extracted complex

K =(1-α) C)/αC(3αC)3

$\alpha = \frac{Am-As}{Am}$ ---------------

Where α: dissociation degree

C: Metal concentration

K: Stability constant

Am: The greatest absorption

As: The absorption at end point

Table (13) dissociation constant & stability constant data for extracted complex				
Complex	Am	As	α	Ksta
Fe(DPDQ)3	2.587	2.482	0.0405	3.56675×1013

Spectroscopic study of complex

UV-Vis. spectrum for the complex [Fe(DPDQ)3]

figure (12) show the electronic spectrum of the complex, this spectrum exhibits a high intense absorption peak at (505.5nm) which used to measure the absorption of complex. The comparing absorption spectrum of ligand there was a red shift for complex.

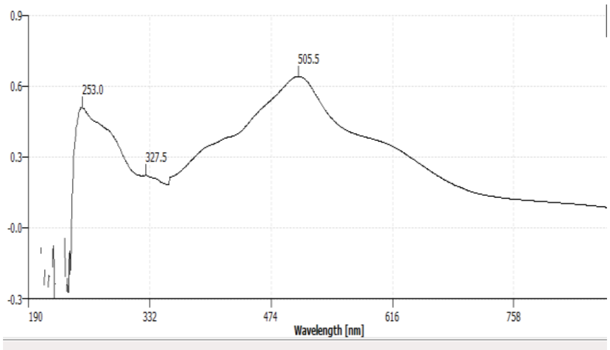


Fig (12) electronic spectral data of the complex [Fe (DPDQ)3]

F.T.I.R spectrum

Fig (13) show the FTIR spectrum of the complex which exhibit bands in table (14) (DPDQ) coordinate to the metal by oxygen of O-H group and electron pairs in azo group (N=N).

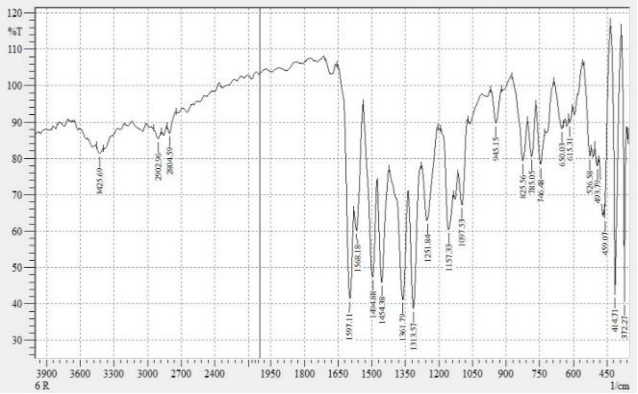


Fig (13) FTIR spectrum of the complex [Fe (DPDQ)₃]

Table (14) results data of FTIR spectrum for ligand & complex									
Compound	St.(C=N)	St.(C-N)	St.(C=C) Aromatic	St.(C-H) Aromatic	St.(N=N)	St.(O-H)	St.(C-H) Aliphatic	St.(Co-N)	St.(Co-O)
Ligand	1599.04	1363.72	1568.18	3063.06	1506.46	3267.52	2808.45	--	--
Complex	1597.11	1361.79	1568.18	3063	1494.88	---	2804.59	493.19	615.31

Some physical properties of the complex: Table (15) show some physical properties data of the complex [Fe (DPDQ)3]

Table (15) physical properties data for the complex		
Material	Melting point	Electrical conductivity µS.cm-1
[Fe (DPDQ)2]	304C°	16

Statistical treatment of data

For treatment of data, the Relative standard deviation was calculated as a measure for precision of data in all experiments. for this purpose, the extraction was done in (200,300 µg/5mL) (7.1626 x10-4M) & (10.744×10-4M) for Fe(III) ion. The results obtained in table (16).

Table (16) Statistical treatment of data		
Exp. No.	Abs. 7.1626 x10-4M	Abs. 10.744×10-4M
1	0.097	0.195
2	0.097	0.195
3	0.096	0.195
4	0.097	0.194
RSD%	0.5167	0.2567

Application

A sample of two drugs tablet containing Iron were used to extracted iron from its. Referum tablet (dextriferron (100mgFe3+/tablet), Ferrous Sulfate tablets (65mgFe2+/tablet) one tablet of each drug was taken were weighed and transferred in to250cm3 volumetric flask, distilled water was added up to the mark to dissolve into solution[24].

After samples prepared, Iron (III) ion (0.5 mL) was extracted by (DPDQ) reagent that dissolved in chloroform, the results in table (17).

Table (17) results of the application of Iron extraction from samples

Sample	Extracted amount
Referum tablet	175µg
Ferrous Sulfate tablets	109 µg

3. Conclusion

In this study we prepared a new ligand azo dye was used to extract Iron (III) ion from aqueous solution at neutral medium (pH=7). There is some parameter effected on this extraction process such as acidity, time extraction, temperature …., from this research we found the new ligand can use to extracted the iron ion from biological and drug samples with a good result.

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