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Spectrophotometric determination of micro amount of mercury (II) using an (Azo) derivative in the presence of surfactant: Study of thermodynamic functions and their analytical application

Saif Ali Diwan

Department of Chemistry- College of Science-University of Kerbala, Kerbala, Iraq

Alaa Frak Hussain

Department of Chemistry- College of Science-University of Kerbala, Kerbala, Iraq

Abstract --- Imidazole azo ligand (DPIDA), one of the azo compounds, was prepared and tested in the sample. In addition to the regular azoth protocol. Because of their ability to form stable complexes with metal ions in some oxidation states, imidazole azo ligands are important heterocyclic azo ligands in coordination chemistry. The complexation of the imidazole azo ligand (DPIDA) was accomplished by adding 4,5-diphenyl imidazole and N1, N1-dimethylbenzene1,4diamine dihydrochloride. Measurements of 1HNMR, IR, UV-Vis, and molarity Their conductivity demonstrates their octahedral geometry with a bidentate ligand coordinated from an (N3) atom of the imidazole ring and one nitrogen atom of the azo group. The thesis also looked at using this reagent was used to do spectroscopy with the mercury (II) ion in binary water solution, and it was revealed that the reagent is difficult with the ion and has the highest sensitivity. The exact wavelength of absorption is (554) nm (pH = 6). Even though the pH was higher in the concentration range of (0.1 - 6.0 g / mL) with adherence to Beer's law, it was revealed to be a dynamic mercury pair reagent with the stability of more than (24 hours). The influence of reagent concentration, reaction duration, masking agent, Works investigated sophisticated stoichiometry with reagent-metal molar ratios, as well as various parameters such as the effect of cations and anions on absorption, as well as the effect of ionic strength and temperature (the constant changes) According to the mallard equation, the metal reincarnation the proportion is (1:2), the ability to absorb substances at a molar level (3.4x104 L. mol⁻¹. cm ⁻¹). Detection and evaluation limits are (0.019 g/mL) and (0.627 g/mL)

International Journal of Health Sciences ISSN 2550-6978 E-ISSN 2550-696X © 2022. **Corresponding author**: Hussain, A.F.; Email: alaa.frak@yuokerbala.edu.iq Manuscript submitted: 27 Feb 2022, Manuscript revised: 18 March 2022, Accepted for publication: 09 April 2022 4754 correspondingly. As a part of the complex the preparation of the solid, as well as some of its physical properties including solubility and molar conductivity, as well as the moment at which the complex melts away, were all investigated. Spectroscopic methods [FT.IR., UV-Vis] were used to classify both substances. As compared to the free reagent, the bathochromic transition is visible in (UV-Vis) absorption spectra, demonstrating the exactness and exactitude of the tool used to make educated guesses about the element mercury the standard deviation from the mean (RSD per cent), although the relative error (E per cent) differed from (4.011 per cent, 0.803 per cent). The thermodynamic functions (Δ H, Δ G, Δ S) were determined as well by investigating the influence of temperature. The approach was extended to both models of the environment and industry, producing results that were surprisingly precise and informative.

Keywords---Azo dye (DPIDA), Mercury (II), Spectrophotometry.

Introduction

Azo dyes are a rapidly expanding family of organic compounds within the known dye families due to their wide range of applications in textile dyeing, metallochromic markers, pharmaceuticals, cosmetics, inkjet printing, and food coloring [1,2]. Azo dyes having a heterocyclic moiety have also made strides in electronics, such as storage, optoelectronic, and photoswitchable devices [3]. Furthermore, as compared to simple aromatic chemicals [4], heterocyclic azo dyes have a significant batho effect.

Furthermore, azo dyes dependent on heterocyclic compounds were discovered to have potent antioxidant, anticancer [5,6], antituberculosis, antibacterial, insecticide, antidiabetics, antiviral, and other chemotherapeutic characteristics [7,8,9,10], the shape of a stable five-member ring with each ion passing through the (N3) atom of the imidazole ring and one of the nitrogen atoms of the azo group [8], In addition to the contribution of the imidazole molecule in the preparation of certain ligands that have a conjugated system that enhances their stability and follows the colour shift of them before and after coordination with metal ions [9], Since most azo dyes have acid-base properties and a fixed number of isosbestic points (which reflect the number of equilibriums in such an azo dye)[10,11], they are used as acid-base indicators.

Mercury may occur in a variety of ways [12], all of which are poisonous. Metallic mercury is the most common form of mercury found naturally in the atmosphere [13]. Microorganisms and natural processes may convert these mercury types from one to the other [14]. The most popular source of mercury released by these natural processes is methyl mercury. This compound is of special interest because it has the potential to bioaccumulate and bio amplify in the food chain [15].

Acute organic mercury intoxication causes blindness, deafness, tremors, sleeplessness, memory loss, neuromuscular abnormalities, headaches [16],

sluggish visual and slow motor nerve activity, and a decline in cognitive function [17]. When inorganic mercury compounds are eaten, they cause a metallic taste in the mouth, nausea, vomiting, and severe stomach discomfort [18].

Chronic mercury exposure can result in a number of disorders, including acrodynia (pink disease), neurological diseases, Hunter-Russell syndrome, crazy hatters' disease, leukemia, and Minamata sickness [19]. In comparison, some mercury compounds are typically non-toxic and have been used as medications, such as to treat syphilis. Human activity contributes a substantial quantity of mercury to the environment, mostly through chlor-alkali plants, plastics industries, electrical, paint, and pharmaceutical sectors.[20].

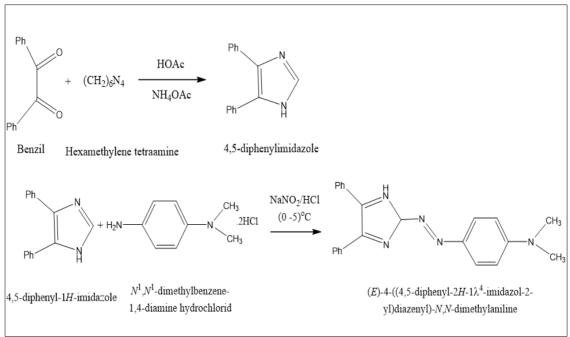
Experimental Preparation of (DPIDA) ligand

A/ preparation of starting materials (4,5 Diphenyl imidazole)

The alpha Di carbonyl condensation method was adopted with ammonia and aldehyde to form a derivative imidazole, and the precursor was prepared with benzyl with both hexamethyl tetra amine and amino acetate in the presence of ice acetic acid to obtain the product, it was added (50 ml of ice acetic acid to a mixture of (2.1 g,0.01 mole) of benzene, (0.015 moles, 21 hexamethyl tetraamine) and (0.07 mole 3.7 g) of ammonium acetate in a100 ml) glass flask and raised the mixture for a while. One hour with continues stirring, then transfer the solution after cooling it to a Baker s capacity (1 L) and dilute by adding (400 ml) of distilling water and after adding ammonium hydroxide precipitate the imidazole derivative the To clear the residue, it was filtered and rinsed with distilled water.excess base and dried in the air and was recrystallized from ethanol and obtain on a white precipitate it dried and its melting point was measured (229 - 230 C) and the yield ratio was (75 %).

B/Coupling reaction between 4,5 diphenyl imidazole and N 1, N 1 dimethyl benzene 1,4 diamine dihydrochloride Two and thirty-one gram of N1, N1dimethylbenzene1,4 diamine dihydrochloride was dissolved in twenty-five ml of distilled water then one ml of hydrochloric acid added gradually to this solution which cooled in an ice bath 0 5 o C the formation of diazonium salt occurred by addition the solution of sodium nitrate which prepared by dissolved0.70 gm of it in Drop by drop, 10 ml of distilled water with stirring, This solution left in the ice bath for 30 minute then coupled with alcoholic solution of 4,5diphenyl imidazole which prepared by dissolving 2.21 gm of imidazole derivative and 0.44gm of sodium hydroxide in 25 ml of ethanol, the orange precipitate was appeared after the completing of addition, f and dried then recrystallize d from ethanol yield percentage 71 % as shown in scheme 1.

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Scheme 1: Preparation of (DPIDA) ligand

Materials and Methods

This study contains the following materials and methods. All of the instruments and supplies for scientific investigationand the preparation's ingredients and solutionsare of the highest quality.

Standard Solution Preparation:

- 1-Mercury (II) solution (1000 g/mL): was made by dissolving (0.135g) of [HgCl₂] in 100 mL of purified water.
- 2-Solution of sodium hydroxide (NaOH) (0.1M): This solution was made by adding 100 mL of distilled water to 0.4 g of sodium hydroxide.
- 3-Hydrochloric acid solution (0.1M): This solution was made by diluting 0.40 mL of concentrated hydrochloric acid (38 percent, 1.19 g/mL) in 50 mL of purified water.
- 4-Solution for reagents (DPIDA) (0.001 M): -was made by dissolving the necessary weight (0.091g) in absolute ethanol and filling the remaining capacity (250mL) with ethanol.

Interferences

Cation solutions of $(Cd^{2+}, Ni^{2+}, Fe^{3+}, Ba^{2+}, pb^{2+}, Cr^{3+}, Co^{2+})$ ions (0.1mg/mL) were made by means of dissolution (0.163g) of $CdCl_2$, (0.221g) of $NiCl_2$, (0.226g) of FeCl₃.6H₂O, (0.190g) of BaCl₂, (0.159g) of pbCl₂, (0.403g).

Preliminary study

A prepared Mercury (II) solution containing 100 g/ml of mercury was placed in a test tube, and 1ml of a ligand (DPIDA) solution (0.001M) was added dropwise with shaking to the test tube, noting the color formation of a precipitate. Drops of hydrochloric acid (0.1 M) were added to one part of this mixture, and drops of NaOH (0.1 M) were added to the other part.

Results and Discussion

Figures 2 and 3 show the absorption spectra of the reagent and mercury (II) complex. A considerable rise in absorbance and bathochromic shift are both associated with complex formation in the reagent solution spectrum (max=476 nm), whereas the mercury (II) complex produced at pH=6 has an absorption maximum (max=554 nm).

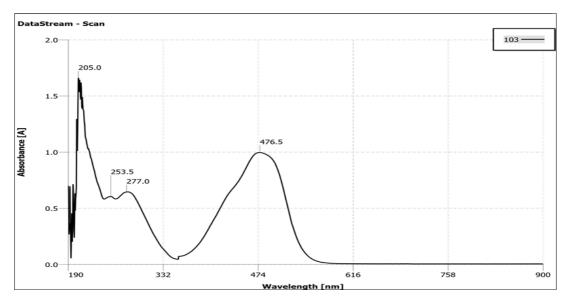


Figure 1. The reagent's molecular spectrum (DPIDA)

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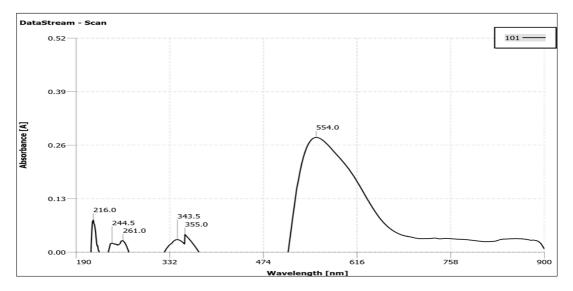


Figure 2. The Hg (II) complex (DPIDA) spectral profile

The effect of adding surfactants (micelle medium)

Among the surfactants had a great impact on spectrophotometry and chromatography, especially in the development of new methods for estimating ions. Numerous studies have given the issue of the formation of(metal-ligand) complexes in the systems

containing the (Micellar) system, the great importance for reasons including the formation of the complex may be more stable in these systems, so the effect of adding (Triton X-114) was studies. and (Triton X-100) and (Tween-80) with different concentrations in the absorbance of mercury (II), as shown in table (1).

Absorpti	on values of mercury	complex in different m	iediums
ntrotion of	Absorption volues	Absorption volues	Absorption w

Table 1		
Absorption values of mercury complex in different med	iums	

Concentration of	Absorption values	Absorption values	Absorption values of
surfactant (v/v %)	of Hg complex in	of Hg complex in	Hg complex in
	(TWEEN-80)	(TRITON-114)	(TRITON-100)
1%	0.549	0.490	0.412
2%	0.601	0.514	0.450
3%	0.615	0.430	0.477

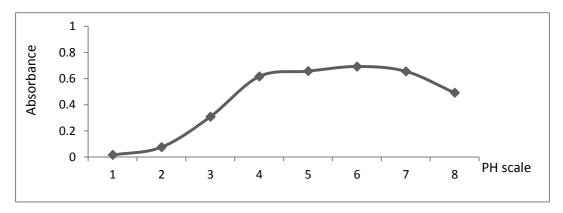


Figure 3: - Effect of pH value

Optimization of Reaction Conditions Effect of PH value

How pH affects things The final pH of each solution was calculated using a pHmeter and the absorbance at (560 nm) at 20 Co was measured using a standard amount of Mercury (II) and reagent (DPIDA). The buffered solution included a standard amount of Mercury (II) and reagent (DPIDA).

Absorbance increased smoothly from (1.0 - 8.0) to (10.0), but then rapidly decreased (see Figure 3). (above pH 6.0), In these conditions, an increase in the reagent's sensitivity at this pH value might explain the rise in mercury complex solution absorbance.

The Time Effect: The Impact of the Passage of Time on the Stability of Complex Systems When the circumstances are ideal, as shown in table (1), the reagent reacts with the ion to form a complex, and these results show the composition of the mercury (II) ion, they remain stable for 90 minutes after the experiment starts.

Time/Min.	Abs.
1	0.661
10	0.685
20	0.698
30	0.712
40	0.707
50	0.705
70	0.702
100	0.698
24h	0.653
48 h	0.653

Table 1
The effect of time

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Table 2 shows the effect of reagent concentration on mercury complex absorbance at (pH=6) as shown in the experiment. The results showed that when the reagent concentration was raised, the absorbance increased.

Volume Conc. of L. _× 10-3	0.25	0.5	0.75	1.0	1.25	1.5
Absorbance	0.222	0.309	0.350	0.430	0.115	0.101

Table2 How reagent amount affects reaction rates

Effect of Sequence

To study the sequence of the reaction content in a complex absorbance, the three arrangements of addition was depending, and the result given in table (3)

Table 3 The effect of sequence

Sequence of Number	Sequence of Addition	Abs. of Cu Complex	
1	M+L+PH	0.677	
2	L+M+PH	0.621	
3	M+PH+L	0.562	

M = mercury ion, L = ligand, pH = hydrogen ion functions the results in table (3) show that the first arrangement is the best one, while the other sequence results in a decrease in complex absorbance, which may be attributed to the effect of acid, base inions with metal, so the addition of the first sequence was relied on to determine the mercury ion complex in this method.

Temperature Affects

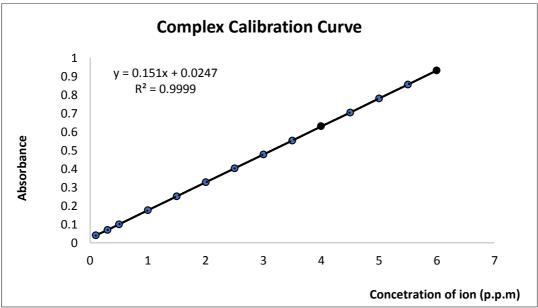
The influence of temperature variation a comprehensive investigation was conducted on complicated structure. The findings of this investigation are shown in Table (4), which demonstrate that the complex's absorption values on the creation of a complex maximum and give the optimum hue and saturation at 30 CO, after which the absorption values decline, presumably due to a diminution of complex's stability. The complex should be prepared at a temperature no greater than 30 degrees Celsius.

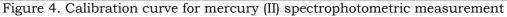
Temperature /c	Abs. of Hg ²⁺ complex
10	0.673
20	0.679
30	0.684
40	0.621
50	0.591
60	0.537

Table 4 Temperature Fluctuation

Calibration Curve

Beverages with low concentrations obeyed in the concentration range (0.1 - 6.0%) with an absorbance of (3.4x104Lmol cm 1), Figure (3) showed the calibration curve of mercury ion and the table (4) provided analytical data to quantify mercury ion by reagent (DPIDA).





Analytical Data	Value
linear equation	Y=0.151x
Linear range [M]	0.1-6.0
Detection limit(µg/mL) ^a	0.019

Table 5 Data collected for mercury (II) analysis

Limit of quantification (µg/mL) ^b	0.627
Molar Absorptivity (Lmol ⁻¹ cm ⁻¹)	3.4×10 ⁴
Correlation coefficient	0.9989
λ_{max}	554nm
Temp.	30°C
Time	90 min
Colour of product	purple

LOD detection = (SD/S) *3.3 (Limit of quantification) LOQ = (SD/S) *10, where SD is the standard deviation and S is the calibration curve's slope.

Stoichiometry and Formation Constant Estimation

1- Method of the Mole Ratio

The mole ratio approach and the addition of Job's methodof using a known and constant concentration from continuous variations were chosen to study the mercury (II) ion (1.994 x 10-5 M) with the increasing composition of the complex formed, with results shown in concentration from reagent (DPIDA) (1.994x10-5 - Figs 7 and 8). Both methods revealed that the ratio of 13.958x10-5M), The method demonstrates that mercury ion metal ion to reagent molecules (M:L) was (1:2) at pH=6, forming a (1:2) (metal -L) complex with reagent...

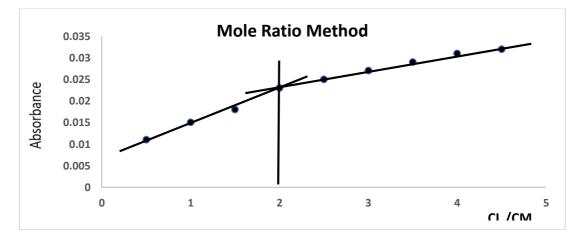


Figure 5. Mole ratio method

The equilibrium reaction of the colored complex was utilized to derive the stability constant using the mole ratio technique. In the following table, the calculated results are shown (6).

$$\begin{array}{l} M^{+n} + nL \leftrightarrow MLn \dots \dots \dots \dots \dots \dots \dots (4-3) \\ \alpha + nc\alpha \leftrightarrow (1-\alpha)c \end{array}$$

$$K = \frac{[MLn]}{[M^{+n}][L]} \dots \dots \dots \dots \dots \dots (5-3)$$

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Where (Am) denotes to the greatest extent possibleand (As) denotes absorption at the stoichiometric concentration.

Table 6 The complex's equilibrium stability constant

Complex	Am Value	As Value	degree of dissociation a	Stability Constant K
[Hg (DPIDA) ₂]	0.023	0.032	0.281	$1.3 x 10^{8}$

The results in Table (6) demonstrate that the complex has great stability, allowing the ligand (DPIDA) to be used in the spectrum estimate of mercury ions.

Job's approach

In this procedure, a combination of various same concentrations in different amounts of solution $(1 \times 10^{-3} \text{ M})$ from both the ion (Hg^{+2}) and the ligand was prepared.

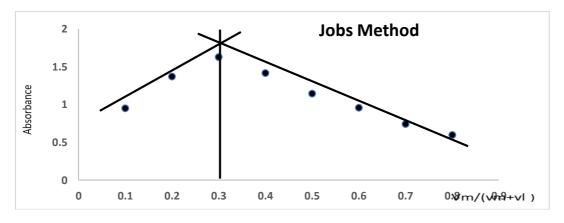


Figure 6. Job's method of continuous variations

Addition of buffer solutions and their results

To investigate how a buffer solution affects things type on the absorbance of the mercury (II) complex, They experimented with four different kinds of buffer solutions, and the difference in the absorption values of the mercury (II)ion

complex with the reagent (DPIDA) making use of the ideal circumstances is shown in Table (7).

Type of emulsifying agent	Amount of mercury absorbed by complex	
Phosphate	0.629	
Citric acid	0.420	
Acetate	0.617	
Ascorbate	0.579	
Absorbance value without addition buffer solution of Hg complex = 0.677		

Table 7 A study on the impact of buffer solutions

As a consequence of these findings, the mercury (II) complex absorbs less light than hydrochloric acid and dilute sodium hydroxide, therefore the acidic function was modified to provide excellent sensitivity and accuracy for mercury (II) ion measurement by utilizing simply an acid or a base.

Strong ions have a different effect. To find out how much of an impact adding different amounts of Na2SO4 and NaNO3 to the complex solution has, the results are provided in Table (8).

Added salt	The molar concentration of added salt	Absorption after adding salt	Added salt	The molar concentration of added salt	Absorption after adding salt	
NaNo3	0.0005 0.005 0.05 0.5	0.602 0.621 0.647 0.673	Na2SO4	0.0005 0.005 0.05 0.5	0.622 0.668 0.674 0.683	
Absorption before adding salt to the Hg complex at 560 nm=0.677						

Table 8 Ionic strength solutions and their effects

Foreign Ion Effect

To investigate the interference effect, a specific concentration of several cation and anion solutions employed as though there were alien ions mixed with an iron solution:

The cation effect A- The ion effect B- The ion effect

Interfering ion	Ion salt formula	4 µg/ml		10µg/ml	
		The	Mistake	The	Mistake
		absorption	percentage	absorption	percentage
		values after	E%	values after	E%
		adding the		adding the	
		ions		ions	
_	_	0.677	_	0.677	_
Fe ³⁺	FeCl3.6H2O	0.406	- 40.029	0.486	- 28.212
Cu ²⁺	CuCl2.6H2O	0.061	- 90.098	0.084	- 87.592
Cr ³⁺	CrCl3.6H2O	0.738	9.010	0.593	- 12.407
Co ²⁺	CoCl2.6H2O	0.169	- 75.036	0.075	- 88.921
Ba ²⁺	BaCl2.2H2O	0.649	- 4.135	0.652	- 3.692
Ni ²⁺	NiCl2.6H2O	0.043	- 93.648	0.192	- 71.639
Cd ²⁺	CdCl2	0.379	- 44.017	0.131	- 80.649

Table 9 Cation's Effect

Table10 Inion's impact

Interfering	Ion Formulary	4 μg / ml		40µg/ml	
ions	Structure	The absorption	Mistake	The absorption	Mistake
		values after	percentage	values after	percentage
		adding the ions	E%	adding the ions	Е%
_	_	0.677	_	0.677	_
Cr207 ²	K2Cr2O7	0.885	30.723	0.716	5.760
SCN1 ⁻	KSCN	0.555	- 18.020	0.541	- 20.088
CO3 ²	K2CO3	0.712	5.169	0.309	- 54.357
SO4 ²	K2SO4	0.434	- 35.893	0.557	- 17.725
IO3 ²	KIO3	0.565	- 16.543	0.636	- 6.056
CrO4 ²	K2CrO4	0.464	- 31.462	0.445	- 34.268
Br ¹	KBr	0.552	- 18.463	0.493	- 27.178

Some ions were chosen to explore the influence of Hg (II) ion interferences (Table 9). Some ions enhanced absorbance while others lowered absorbance, which was owing to rivalry between these in order to form a compound with Hg (II), which reduced competition and increased the sensitivity of this technique to the Hg (II) ion. Hg-specific but yet being delicate response (II).

The ability to be discerning in the response is possible validated by applying appropriate agents of omission and substitution.

Precision and Accuracy of the Methods Explained

The implemented method's accuracy and precision were measured in terms of recovery and relative standard deviation (RSD percent). The table shows the recovery and RSD percent results (11).

1						
Conc.of	Hg^{+2}	Conc. of	Hg^{+2}	RSD%	Recovery%	Error%
present[M]		found[M]				
9.971×10-6		9.752×10-6		1.651	100.609	-0.609
19.941×10 ⁻⁶		19.473×10-		1.004	100.596	-0.596
		6				
29.911×10-6		29.693×10-		0.803	100.105	-1.057
		6				

Table 11 Studies on precision and accuracy

Table (11) shows that the devised approach was exact, with a relative standard deviation of 0.4 percent.

The influence of temperature on the stability constant of the [Hg(DPIDA)2] complex:

Table 12 The levels of stability remain constant as temperature rises

T (C)	T (k)	α	$k \times 10^8$
10	283.15	0.299	1.0146
15	288.15	0.289	1.1282
20	293.15	0.282	1.1937
25	298.15	0.277	1.2163
30	303.15	0.271	1.2739

12 demonstrated that temperatures had a minimal influence on the complex's stability.

Thermodynamic Function of the Complex:

Thermodynamic functions H, G, and S were computed, and the results are shown in Figure (6) and Table (12).

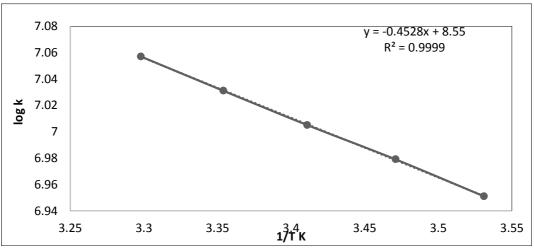


Figure 7 depicts the relationship between Log K and 1/T values for the mercury (II) complex.

The influence of temperature on the thermodynamic function of the mercury (II) complex is shown
in Table 13.

T(K)	(1/T)	Log K	∆H Kj. Mol ⁻¹	∆G Kj. Mol⁻¹	∆S Kj. Mol ⁻¹ .k ⁻¹
283.15	3.531	6.951		- 43.397	0.1838
288.15	3.470	6.979	_	- 44.416	0.1842
293.15	3.411	7.005	_	- 45.324	0.1841
298.15	3.354	7.031	8.669	- 46.145	0.1838
303.15	3.298	7.057	_	- 47.033	0.1837

A positive value of enthalpy stated that the reaction was endothermic, which may be observed by increasing the temperature. The complex formation will be reduced, and the reaction was spontaneous based on the negative sign of free energy.

FT-IR Spectroscopy of Ligands and Complexes Research

To better understand the results of the FT-IR analysis and absorption frequencies of the complex and reagent, have a look at the figures and tables (DPIDA).

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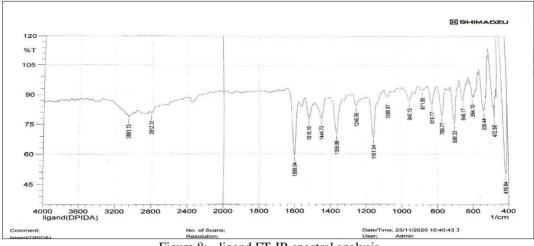


Figure 8: - ligand FT-IR spectral analysis

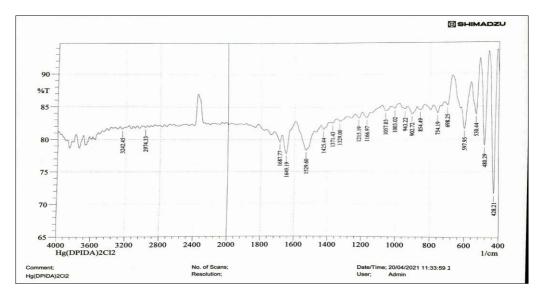


Figure 9: - ligand FT-IR spectroscopy

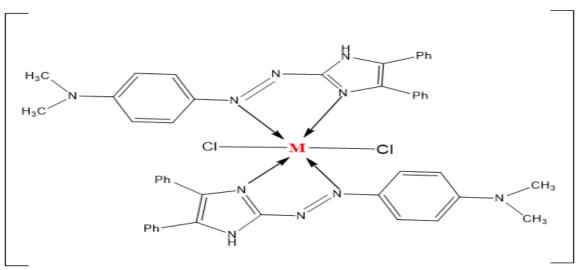
Table 14
Absorptivity and fluorescence measurements using Fourier transform
infrared imaging (DPIDA)

Compound	DPIDA	[Hg(DPIDA)2C12]
Compound	DPIDA	[Hg(DPIDA)2C12]
(N-H)	3061 m	3242 w
(C-H) Ar	2812 m	2974 w
(N=N)	1444 m	1425m
(C=N)	1599 m	1529 m
(C=C)	1516 m	1529 m
(C-O)	1200 m	1215 s
(M-O)		480 s
(M-N)		597 s

Compound Suggestion Chart

The complicated construction as seen in the accompanying diagram (10) is owing to analysis of the FT-IR spectra and stoichiometry of the Job and Mole ratio approaches.

S=strong, M=medium, W=weak



$$\begin{split} M &= Mn(II), \ Co(II), \ Ni(II) \ , \ Cu(II), \ Zn(II), \ Cd(II) \ , \ Hg(II) \\ Figure \ 7: \ Suggested \ structure \ of \ [M(DPIDA)_2 \ Cl_2] \end{split}$$

Application

Samples of tap water and well water were produced and then put to Ligand (DPIDA) to detect mercury concentrations here are some examples of, the findings are reported in Table (15).

Table 15 The outcome of the application of mercury (II) in samples

Sample	Spectrophotometric meth	od Flam atomic absorption
	µg/mL	µg/mL
Well water (west of		
the city of karbala)	4.52×10^{-5}	6.22×10^{-5}
Well water (east of		
the city of karbala)	1.85×10^{-6}	2.62×10^{-6}
Well water (north of		
city of karbala)	2.39×10^{-6}	3.02×10^{-6}
Well water (south of		
city of karbala)	3.38×10^{-6}	$1.99 \mathrm{x} 10^{-6}$
Tap water	9.02×10^{-6}	8.22×10^{-6}

Conclusion

a technique for assessing small changes with extreme sensitivity mercury in several samples, as well as a low-cost approach for measuring Hg, have been devised (II). Verification and application investigations revealed that the proposed approach is capable of quantifying Hg (II). The results showed that the reagent can detect mercury (II) in a variety of materials. Analytical criteria as an example: identification; detection limit; precision; and recovery show that this technique is capable of determining Hg (II).

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