



Study for Liquid-Liquid Extraction of Gadolinium (III) Ion using New Azo Derivative and Its Thermodynamic Functions

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ABSTRACT:

Colored azo compounds can be considered one of the most widely used chemicals, as they have many applications in colorful plastics and polymers, pharmaceutical, printing, food, cosmetic, and biomedical industries, as well as for advanced organic synthesis applications. This work aims to prepare and characterize a new azo compound and use it in the process of separating one of the rare earth elements, the element gadolinium. so that the study contains two processes, The first process includes the synthesis a new azo derivative called 3-(4-(dimethylamino)phenyl) diazenyl-2-hydroxy-5-sulfobenzoic acid (DPDBA) from diazonium salt pairs of (N1,N1-dimethylbenzene-1,4-diamine dihydrochloride) with 2-hydroxy-5-sulfobenzoic acid dihydrate, The reagent chemical formula (C15H15N3O6S) and the molecular weight was (365.36 g/mol), The reagent powder has greenish color, The pure reagent melting point is (183-185 °C), the reagent characterizes by many spectroscopic methods (UV-Vis., FT-IR, 1HNMR, Mass spectrum and 13CNMR). The second process was used the new azo as reagent to separate the gadolinium (III) ion by a solvent extraction process, Effect of the various parameters on the extraction process this is done by calculating (D & %E). The best pH was (2), The best period time for equilibrium was (20) minute, Chloroform was the best solvent for the extraction. The results also showed that (D) and (%E) values increase with the (DPDBA) reagent concentration increase as well as with the increase of Gd(III) concentration increase, Investigating the role temperature on the extraction, and calculating the thermodynamic function (ΔH_{ex} , ΔG_{ex} , ΔS_{ex}), The chelating ratio of metal to ligand also determined by Job's and mole ratio techniques, was found to be (1:3) M:L.

Introduction

A homogeneous set of 17 elements is known as the rare-earth elements (REEs). They are equivalent to the elements 21 (Sc), 39 (Y), and 57-71 (La-Lu) in terms of IUPAC nomenclature[1], [2], Although the latter grouping should be referred to as lanthanoids. lanthanides (Ce-Lu) is still the most common name for metallic elements 57–71 [3], There is a lot of ambiguity when it comes to splitting lanthanides. Chemists frequently rely on the Ln (III) trivalent ions' electrical structure, La-Gd are the unpaired 4f electrons in the light lanthanides (LREEs), while Dy-Lu are the unpaired 4f electrons in the heavy lanthanides (HREEs) [4], The main source of lanthanides is monazite sand, which is made up of phosphates of lanthanum, thorium, cerium, and neodymium. The phosphate portion of monazite also contains trace amounts of other lanthanide ions[5].

Promethium is the only lanthanide that is produced artificially through nuclear reaction, Bastnaesite is a mixed fluorocarbonate, or $M^{+3}CO_3F$, that is discovered in the United States and Madagascar. M is La or one of the lanthanide metals. It supplies 20% of the world's lanthanides [6], Gadolinium is a heavy metal with atomic number 64 that belongs to the lanthanide family, Gadolinium has a stable oxidation state of +3 and an ionic radius of 0.99. Gadolinium's ionic radius is almost identical to that of calcium, and Gd^{+3} can displace calcium and become poisonous in biological systems.[7], Gadolinium widely utilized in a variety of industrial and medical applications[8], Gadolinium employed in magnetic resonance (MR) imaging due to its high paramagnetic properties (a paramagnetic material is not naturally magnetic but can be made magnetic, for example, in MR imaging, by application of an external



magnetic field) and long relaxation time (relaxation time is a measure of the time taken for a substance to return to the resting or ground state following excitation). Gd-based MR contrast agents (GBMCA) were used for the first time on humans in 1988, So Gadolinium the main ingredient in most magnetic resonance imaging (MRI) contrast agents [9 -10].

Many method are available used to recovery and removal the lanthanides metal such as chemical precipitation process, adsorption process, extraction, ion exchange and Valency change , Liquid-Liquid Extraction mean dispersion of analyte between two solution liquid phase and organic phase . This method is commonly utilized in a variety of industries where organic or inorganic solutes may be present. The solutes are distributed across the two phases due to differences in their affinities to water and organic solvents. Chemical characteristics and composition also have an impact on the solutes' distribution[9].

Materials and Methods

Synthesis of a new azo reagent 3-(4-(dimethylamino) phenyl) diazenyl) -2-hydroxy-5-sulfobenzoic acid (DPDBA)

The new reagent was prepare by depending the traditional method[10][11] used to prepare azo dye compound ,At first the aromatic anime (N^1 , N^1 -dimethylbenzene-1,4-diamine dihydrochloride) (2.091g , 0.01mol) with presence of hydrochloric acid converted to diazonium salt pairs by reaction with sodium nitrite solution (0.689g , 0.01mol) at (0-5) $^{\circ}$ C , then the diazonium salt coupling with 2-hydroxy-5-sulfobenzoic acid dihydrate (2.542g , 0.01mol) , The green precipitate was filtrate ,washed by distilled water , and purification by recrystallization process from ethanol ,The pure reagent yield was 63%,the scheme (1) explains the reagent prepare.

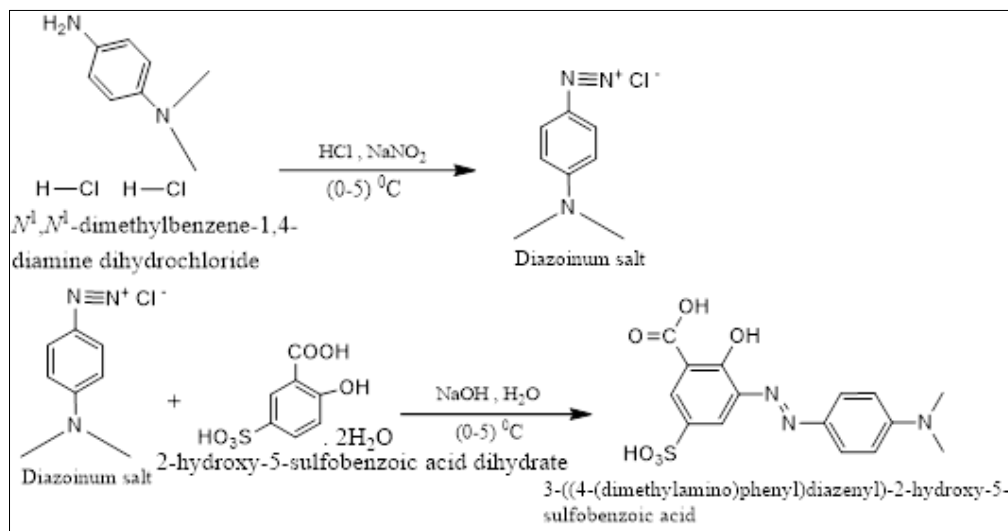


Figure 1: The new reagent DPDBA synthesis

Gadolinium (III) ion Extraction by new reagent (DPDBA)

The aqueous phase was contained of 250 μ g / (2.5 mL) (6.359×10^{-4} M) of Gd (III) and [2.5ml, 0.2%] of reagent (DPDBA) soluble in ethanol putted in a conical flask. The solution pH was adjusted to (2) by add diluted solution [HCl, NaOH] solutions. [5mL, CHCl_3] was used as organic phase, Shaker the solution for (20) minutes. The solution was leaved after shaking to settle and separate. The residue Gd (III) ion in the aqueous layer

was determined spectrophotometrically with arsenazo (III) by following the same working method as in the calibration curve.

Results and Discussion

Identification for a new reagent (DPDBA) :

Physical properties

Some physical properties of the new reagent were characterized, Table (1) show the result of this study, Also the reagent identify by spectroscopic (UV-Vis., FT-IR, ^1H NMR, ^{13}C NMR and Mass).

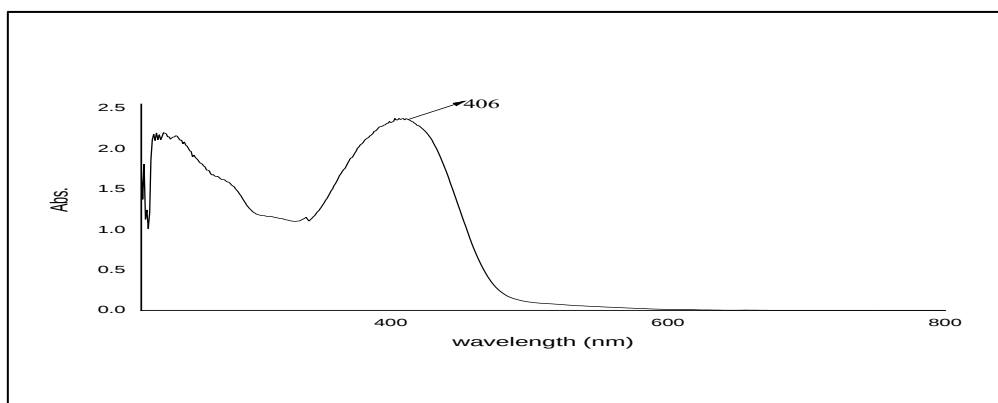
**Table 1** Physical properties of (DPDBA)

Compound	DPDBA
Structure formula of compound	$C_{15}H_{15}N_3O_6S$
M.WT	365.36 g/mol
Color	Green
Melting point	(183-185) °C
Solubility	Alcohol solution (ethanol)
λ_{max}	(406) nm

UV-Vis spectrum of a new reagent

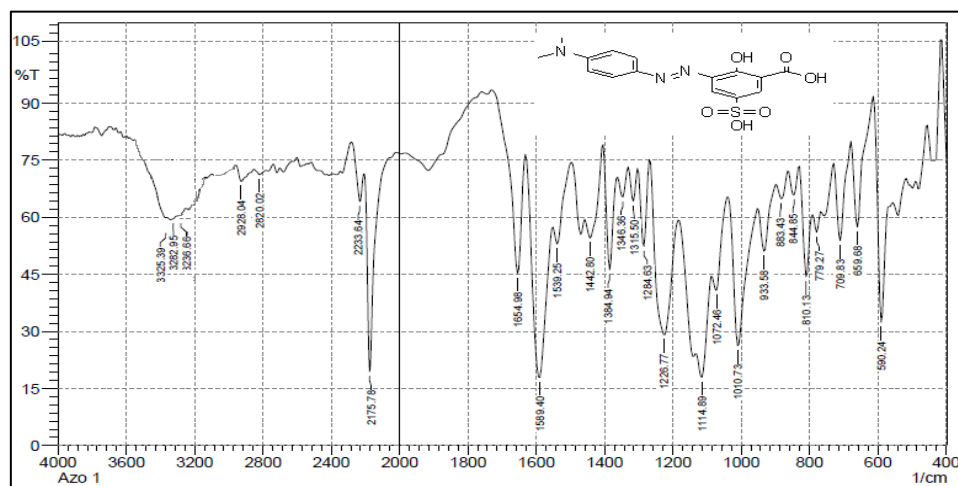
The reagent (UV-Vis) spectrum at figure 2 explained that the highest absorption peak at (406) nm , note that this

absorption peak is due to transitions($n-\pi^*$) in the(DPDBA) azo reagent

**Figure 2:** The Electronic spectrum of DPDBA reagent**FTIR spectra of new reagent**

FT.IR spectroscopy is a famous methods used to diagnose and study the new ligands and their new complexes compounds in terms of their composition.

The infrared spectroscopy was studied within range 400-4000 cm^{-1} for a new ligand and complex and the figure 3, Results displays the results.

**Figure 3:** FTIR spectra of (DPDBA)

**¹H NMR spectrum of the reagent**

The reagent (DPDBA) ¹H NMR spectrum displayed in figure 4.

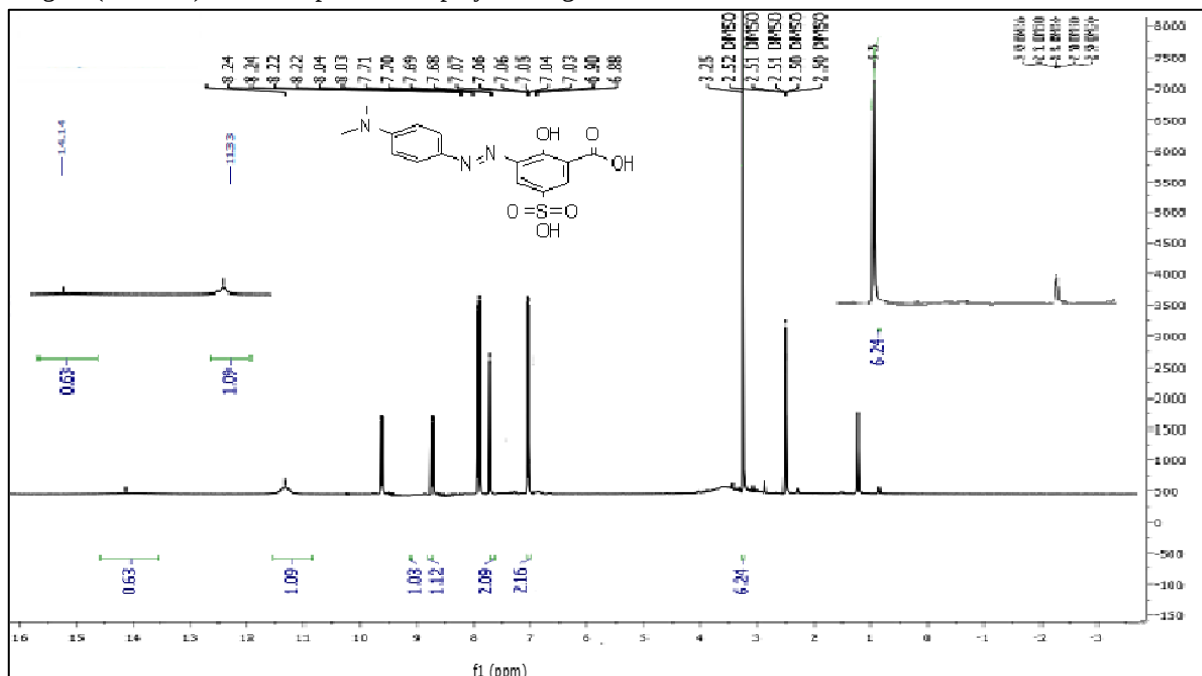


Figure 4: ¹H NMR spectrum for (DPDBA) reagent

The measurement spectra of ¹H-NMR for (DPDBA) azo reagent are given in Figure 4, from figure 4 showed that ¹H-NMR chemical shift spectra of compound show board peak at 14.14 ppm (OH) for carboxylic acid and peak at 11.20 ppm (OH) for hydroxyl group of benzoic

acid, The other chemical shift δ (7.12–9.60) ppm return to the (H of two aromatic ring of reagent), the last peak 3.20 ppm return to the (H of the two CH₃ group).

¹³C-NMR of the ligand: - The reagent (DPDBA) ¹³C NMR spectrum displayed in figure (5).

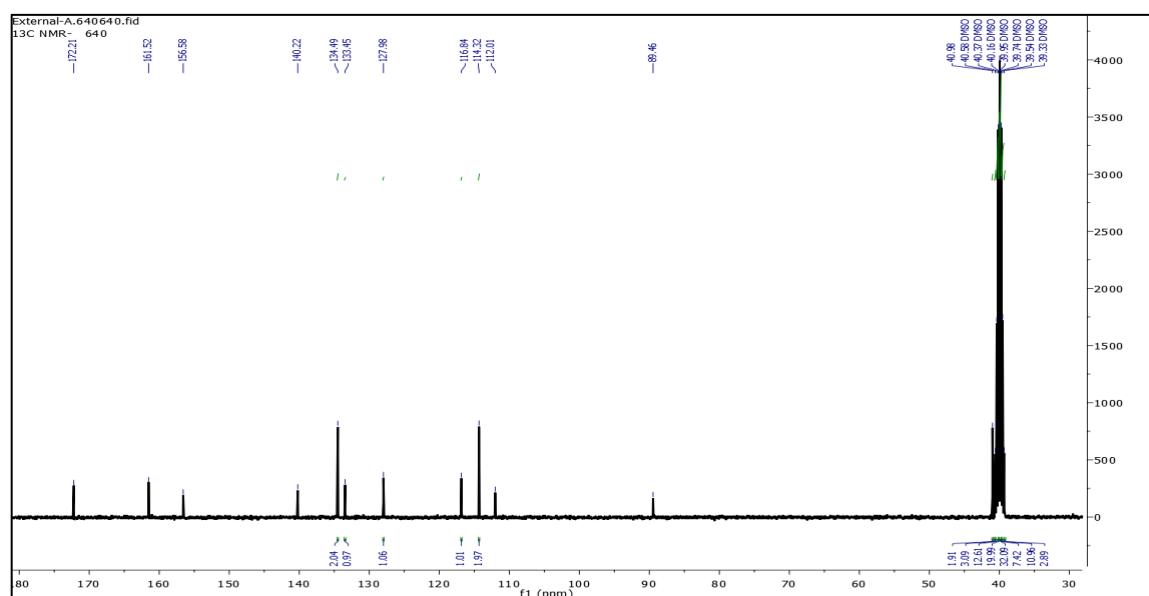


Figure 5: ¹³C NMR spectrum for (DPDBA) reagent

**Mass spectrum of reagent (DPDBA)**

The reagent (DPDBA) mass spectrum was explained in figure 6 that the theoretically calculated molecular

weight (365.07g/mol) was agreement with that value obtained experimentally by using the mass spectrometry technique [365 g/mol].

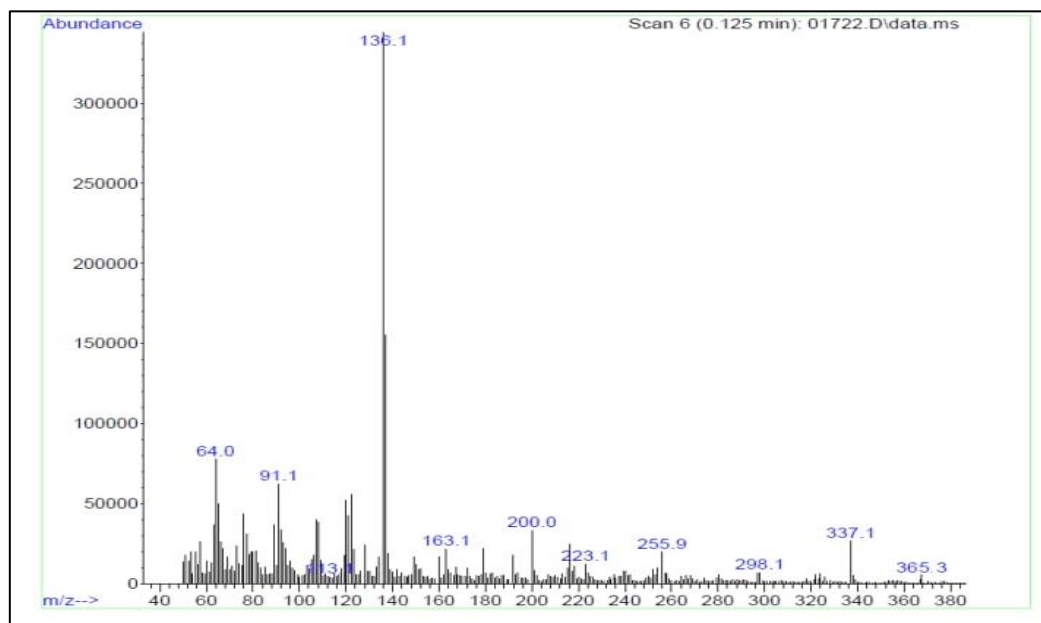


Figure 6: The (DPDBA) reagent mass spectrum

The gadolinium (III) Calibration curve [12]

At first, a number of solution containing different amount (5-75) $\mu\text{g}/5\text{mL}$ were prepared from the storage solution. After that, ascorbic acid [1 mL, 1%] was added to each 5 mL, then after 1-2 minute [1 mL] formate buffer was added, and finally [2 mL, 0.05 w/v] of Arsenazo solution was added, then each solution was diluted to 20 mL with

double distilled water. The pH solution was adjusted to [2-2.6] by added dilute solution (HCl, NaOH) solution, and complete the volume to 25 mL with double distilled water. The absorbances of all solutions were measured at λ_{max} 650 nm, finally, to obtain calibration curve the relation between absorbance and concentration was drawn as in figure 7.

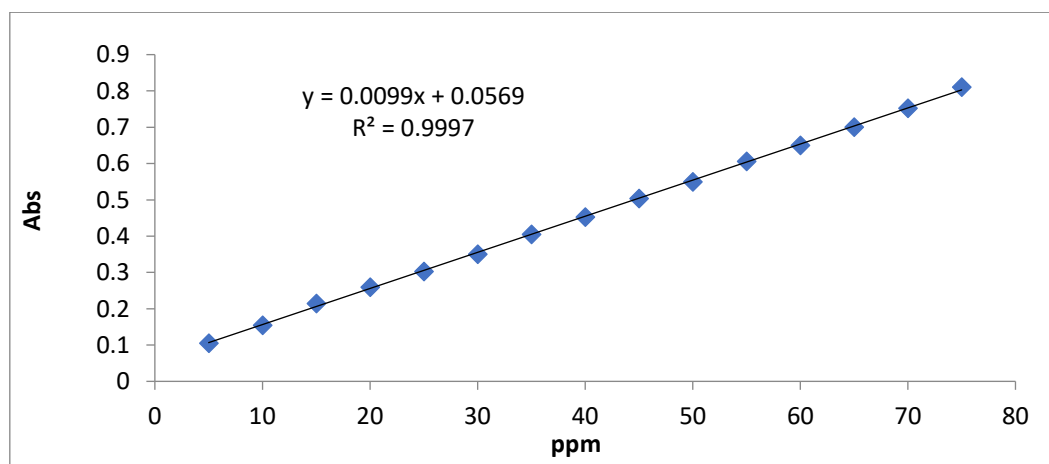


Figure 7: The gadolinium (III) ion Calibration curve

**Different factors effect on extraction processes****Effect of pH**

The impact of pH was investigated at range (1-9). The complex had the greatest distribution ratio (D) and

extraction percentage (E%) at pH (2). Despite having a higher pH value, the complex formed in acidic media The final result, as shown in table 2,.

Table 2 The pH effect on extraction

pH	D	E%
1	9.549	90.520
2	16.361	94.239
3	4.507	81.841
4	5.297	84.119
5	4.952	83.199
6	3.673	78.600
7	4.399	81.478
8	3.202	76.202
9	2.715	73.082

The reason for this may be attributed to the nature of the new organic reagents used, which act as bi dentate organic reagents or it might be caused by the properties of the organic reagents employed in the solvent extraction process and how those affect pH, this was consistent with the research [13][14].

Effect of shaking time (time equilibrium)

To study the kinetic side of extraction the effect of shaking time on the extraction was down period (5- 40) min., (D & E%) was calculated, Table 3 of the study's findings displays the highest distribution ratio value and period extraction equilibrium was (20 min).

Table 3 Time effect on extraction

Time	D	E%
5	3.579	78.161
10	5.234	83.959
15	9.504	90.479
20	16.361	94.239
30	10.061	90.959
40	11.136	91.760

The longer shaking times result in more interaction between the organic and aqueous phases, this refers to

expanding the surface area between the phases, whose initially free energy varies based on the various phase



components and shaking process, accelerating the access to phase equilibrium, While a decrease in (D) value after the maximum value when the shaking time has passed may be caused by a variety of factors such as destroying the complex that was created, deviating from equilibrium to generate the third phase, or both. These findings are consistent with the earlier investigation.[15]

Effect of organic solvents

The results in figure 8 and table 4, explain the effect of the organic solvent, The results Chloroform has a constant dielectric value of (4.810) the (D) value were (16.361) is the highest so it's the more suitable solvent to extraction of Gadolinium (III) ion by (DPDBA), also the result show that there is no linear relationship between the distribution ratio and the organic solvent's dielectric constant, so that in contrast, the following equation's born relationship

$$\Delta G = -\frac{Z^2}{2r} \left[\frac{1}{\epsilon_w} - \frac{1}{\epsilon_o} \right] \quad \dots\dots (1-1)$$

where ΔG is free energy of ion, Z is the charge of ion, r : is the ion radius, ϵ_w , ϵ_o : water and an organic solvent dielectric constant, respectively.

This showed that the extraction method used in this work cannot be regulated by the solvent's dielectric constant, and the cause may be attribute to complex was no charge, complex of this type influenced by a variety of variables, such as the extracted complex's solubility, the organic solvent's shape, and whether or not the solvent contained oxygen atoms, This provided evidence that the composition of organic solvents, as opposed to the polar organic solvents utilized, played a factor in achieving the optimal extraction, These results agreement with some study like extraction of cobalt ion by Using New Azo Derivative [16] and Extraction of Lanthanum (III) and Neodymium (III) by using amino acid [17].

Table 4 The organic solvent effect on extraction

Organic Solvent	ϵ	$1/\epsilon$	D	E%
Carbon tetra chloride	2.240	0.446	6.402	86.490
Benzene	2.280	0.438	7.591	88.359
Toluene	2.380	0.420	6.962	87.440
Chloroform	4.810	0.207	16.361	94.239
1,2-dichloroethan	10.420	0.095	3.546	78.003
Benzaldehyde	17.800	0.056	4.495	81.802
Nitrobenzene	35.600	0.028	7.278	87.919

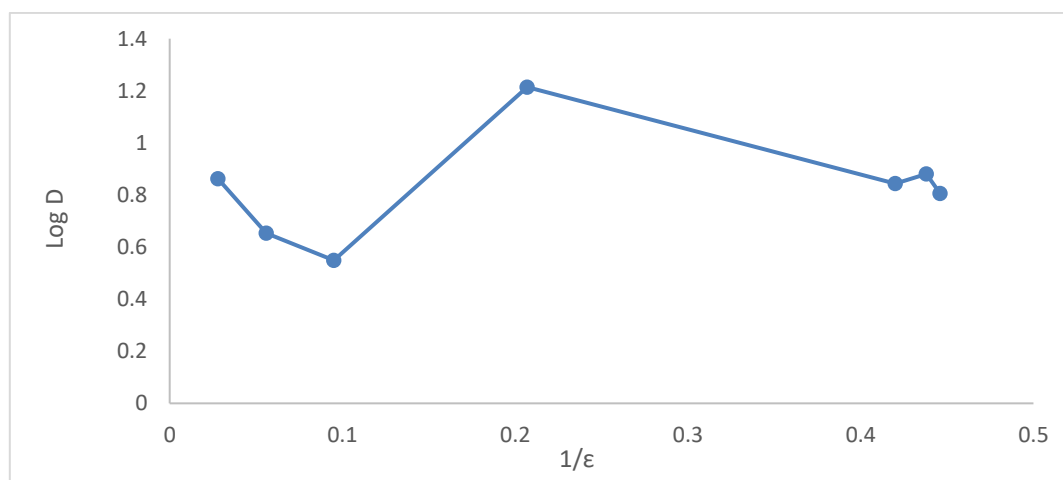


Figure 8: The organic solvent effect



The metal ion concentration Effect

In order to extract the Gd (III) ion from these aqueous solutions under the best conditions possible, different concentrations of Gd (III) solutions ranging from (50 µg - 400 µg)/2.5 mL, (1.272×10^{-4} to 10.175×10^{-4}), were produced. Table 5 displays the findings of this

investigation. These behaviors were expected due to the continued reaction between the Gadolinium (III) ion and (DPDBA) azo reagent. Then stabilizes somewhat and finally the extraction decreases; this may be due to the saturation of the reagent with metal ion when complex formed [18].

Table 5 The gadolinium ion concentration effect

{M}x10⁻⁴	D	E %
1.272	1.083	51.992
2.544	2.289	69.596
3.816	5.667	85.000
5.087	12.889	92.800
6.359	16.361	94.239
7.631	17.750	94.667
8.903	18.663	94.914
10.175	16.094	94.149

The reagent (DPDBA) concentration Effect

Under optimal conditions, a known quantity of Gd (III) solution (250 µg /2.5 mL) was made and extracted using

a variable concentration of (DPDBA). The table 6 in below explains the results.

Table 6 The reagent concentration effect

[L]x10⁻³	D	E %
1.474	3.386	77.200
2.474	3.826	79.279
3.474	4.285	81.079
4.474	7.591	88.359
5.474	16.361	94.239
8.211	18.841	94.959
10.948	18.084	94.760

The findings in the tables 6 show that there was an expected result to increase the extraction of Gd⁺³ ion with increase the concentration of the azo reagent (DPDBA) according to the following equation:

$$\log D = \log K_{ex} + n \log [HL]_{org} + n \text{ pH} \dots\dots\dots (1-2)$$

Also the findings of this study are in agreement with those of a recent research. [19] [20].

The foreign-ion effect

To study the impact of foreign ions on the separation of gadolinium ion, a variety of metal ions (cation & anion) are added with Gd (III) ion in the aqueous phase. After the extraction procedure is complete, the ion solution is determined using a colorimetric method to determine the Gd (III) concentration, and the value of (D&%E) is then calculated. The results of this factor are displayed in tables (7) and (8).

Table 7 The anions effect

Anion ion	0.2%		0.4%	
	D	E %	D	E %
----	16.361	94.239	15.911	94.086
[Fe(CN) ₅ NO].2H ₂ O ⁼	6.267	86.239	5.631	84.919



$\text{Cr}_2\text{O}_7^{-2}$	8.843	89.840	6.645	86.920
CrO_4^{-2}	6.289	86.281	5.684	85.039
$\text{S}_2\text{O}_3^{-2}$	19.240	95.059	20.736	95.399
CO_3^{-2}	5.775	85.239	4.580	82.079
SCN^-	4.435	81.601	4.144	80.559

Table 8 The cation ion effect

Ion	250µg	E%	500µg	E%
	D		D	
Gd^{+3}	16.361	94.239	15.726	94.021
Mn^{+2}	4.376	81.398	3.864	79.441
Cu^{+2}	9.204	90.121	6.485	86.636
Zn^{+2}	4.319	81.199	3.789	79.119
Hg^{+2}	5.158	83.761	4.507	81.184
Ni^{+2}	5.596	84.839	4.924	83.119
Co^{+2}	4.365	81.361	3.596	78.242
Fe^{+2}	9.684	90.640	6.837	87.240

The results in table 7 indicated that no anions able to boosting the extraction process of Gd (III). This may return for that anions form unstable compound with gadolinium ion prevent it to form complex with (DPDBA) reagent. But the affect the cations on Gd (III) ion extraction it is attributed to the competition between cations ions and Gd (III) ion with the (DPDBA) reagent to form complexes, as evidenced by the finding in table 8 that (D&%E) was reduced when cations ions were present in the aqueous phase [21].

The oxidation and reduction Effect on extraction

A solution of hydrogen peroxide with a concentration of (35%) was added to study the effects of oxidation When

extracting the Gd (III) ion with (DPDBA) under experimental conditions, after that calculating the distribution values of the Gd (III) ion after separating the organic phase from the aqueous phase and utilizing the colorimetric approach, So the amount of the remaining ions in the aqueous phase were determined. The same procedure used for analyzing the influence of oxidizing agent was utilized to add 1mL of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ solution to the aqueous phase in order to analyze the impact of a reducing substance on the (D) value needed to extract a Gd (III) ion (DPDBA). Results showed in table (9).

Table 9 The oxidation and reduction on extraction

Extraction	D	E%
Extraction in absence of oxidation –reduction factors	16.361	94.239
Extraction in presence of oxidation factor	14.151	93.339
Extraction in presence of reduction factor	15.757	94.032

From the result in tables 9 showed that the solvent extraction of Gd^{+3} ion, with (DPDBA) as reagent do not change in the presence of (H_2O_2 & $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) this due to the Gd^{+3} ion trivalent oxidation state is more stability.

The Salting out effect

Ammonium chloride was selected to study the effects of the salting on extraction, (1M ,1 mL) of NH_4Cl solution



was add to aqueous layer composed under the optimum condition obtained, (D & %E) calculated and the results presented in table (10).

Table10 The salting effect

Extraction	D	E %
Extraction in absence of salting factors	16.361	94.239
Extraction in presence of NH ₄ Cl salting factor	9.162	90.159

The result in table 10 show that (D&E%) decreased when salting factor was present , The cause for this may be the negative ion which behavior as masking factor , which reduce the coordinate coupling between Gd⁺³ ion and (DPDBA), This could be explained by the idea that the salting process lowers the amount of extracted Gd⁺³ ions'

hydration energy, which makes it easier to substitute water molecules with reagent molecules.

The temperature effect

The extraction of the Gd (III) ion from aqueous solutions was studied at temperatures between 20°C and 45°C and the findings are shown in the table 11.

Table 11 The temperatures effect on extraction

T(K)	1/Tx10 ⁻³	D
293.0	3.413	19.010
298.0	3.356	16.361
303.0	3.300	8.259
308.0	3.247	7.772
313.0	3.195	4.376
318.0	3.145	3.854

According to the results in figure 8, the reaction between the Gd (III) ion and the (DPDBA) was exothermic, which means that the highest temperature was accompanied by the lowest (D&E%) values. This resulted in a reduction in the complex formed, causing more Gd⁺³ ions to remain

in the aqueous phase. The computations shown in table 12 and the equations of Vant Hoff and Gibbs were used to study the thermodynamic functions (ΔH , ΔG , and ΔS).

$$\Delta G_{\text{ex}} = \Delta H - T\Delta S \dots\dots\dots (1-3)$$

$$\Delta G_{\text{ex}} = - RT \ln K_{\text{ex}} \dots\dots\dots (1-4)$$

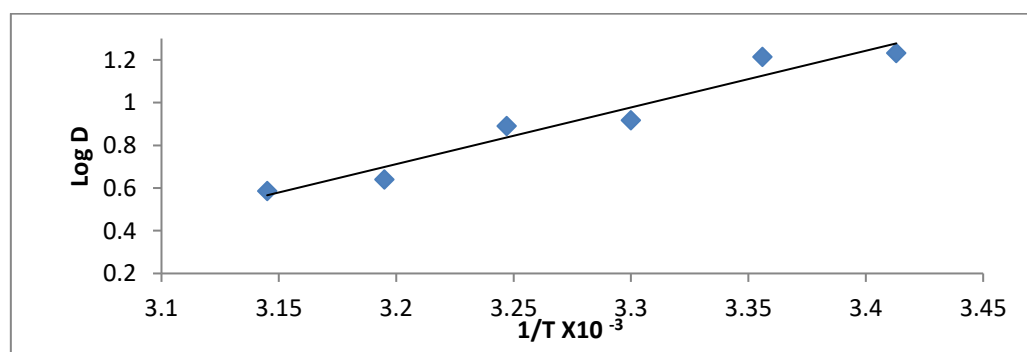


Figure 9: The temperature effect



Table 12 The thermodynamic function

T(K)	ΔH (KJ.Mol ⁻¹)	ΔG (KJ.Mol ⁻¹)	ΔS (KJ.Mol ⁻¹ .K ⁻¹)
293	-51.226	- 7.173	- 0.1504
298		- 6.925	- 0.1487
303		- 5.319	- 0. 1515
308		- 5.251	- 0.1493
313		-3.841	- 0.1514
318		-3.567	- 0.1499

From result in table 12 show the free energy of extraction reaction of complex formed was negative sign and this explain that reaction are spontaneously. These mean ion transfer spontaneously from the aqueous phase to the organic phase, which is preferred thermodynamically at low temperatures and causes the distribution ratio to increase as the temperature drops. Entropy values that are getting closer to zero and each other showed that the extracted compound was stable and reacted

spontaneously (less randomly), These studies agree with earlier research [22].

Stoichiometry determination

Different techniques are used to calculate the stoichiometry of the separation species (M: L).

continuous variables (Job's method)

The findings shown in Fig.10 demonstrated that the extraction of the chelate complex between the Gd (III) ion and the reagent (DPDBA) had a likely structure that was (1:3).

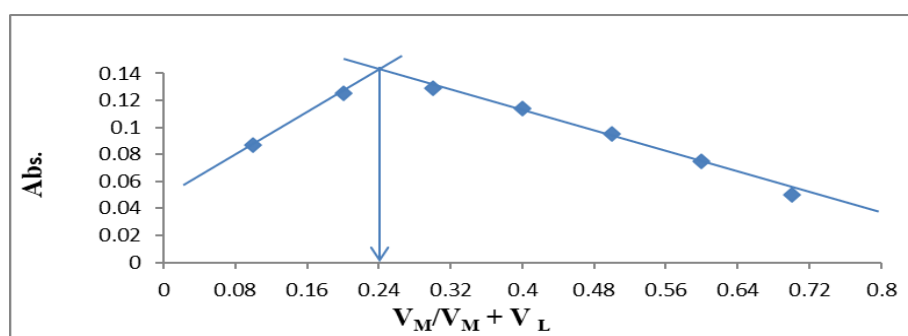


Figure 10: Job's method

Mole ratio method

The absorption of extracted complex was determined, after extract a fixed concentration ($1 \times 10^{-4} M$) of Gd^{+3} ion

with reagents (DPDBA) in a proportionate and increasing amounts, The outcomes of this methodology are shown in figure 11.

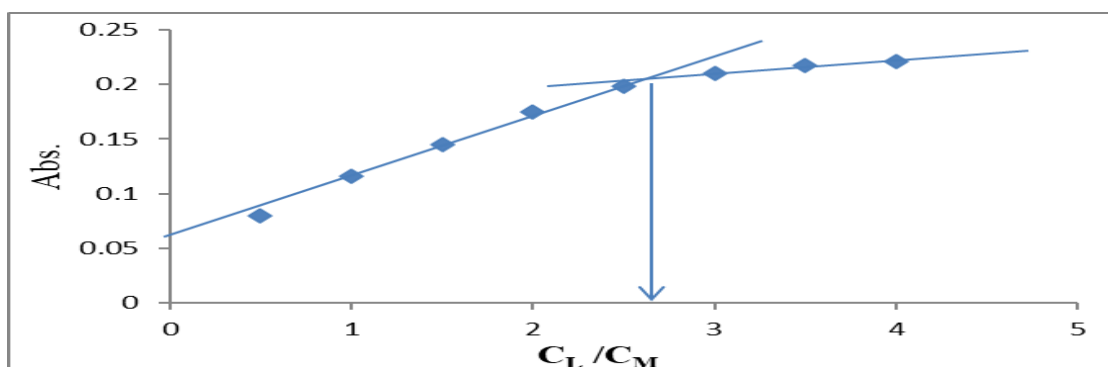


Figure 11: Mole ratio method



Results of the mole ratio method are shown in figures 11, It came in the same with job's method (continuous variables) which demonstrated the committed in the extracted complex have been (1:3) (M:L), that means one mole of metal with three mole of reagent and this means that the empirical formula was (ML_3) .

Study of the complex Stability

According to the findings of mole ratio approach and the result in figure (12) obtained, Using the mole ratio method to calculate the stability of gadolinium ion complex with (DPDBA) was.

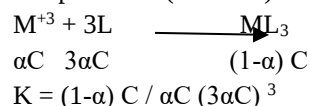


Table 13 The complex stability

Ion	A_m	A_s	A	K_{stable}
Gd	0.227	0.201	0.115	7.305×10^{11}

From results in table (13) showed the possibility to use the reagent (DPDBA) to make separation for gadolinium ion by liquid- liquid extraction and this return to the complex stability which is highest.

Spectrophotometric studies

1- UV-Visible spectra for extracted complex

Figures 12 show the (UV-Visible spectra) for the combination of Gd (III) ion with (DPDBA) azo reagent.

from the figure 12 shows that the highest absorption peak is ($\lambda_{max} = 495nm$), and when compared with the highest absorption peak of the azo reagent (DPDBA) which is ($\lambda_{max} = 406nm$), Can notice a shift towards the higher wavelength (redshift), and this proves the formation of a new class, which is the extracted complex $[Gd(DPDBA)_3]$.

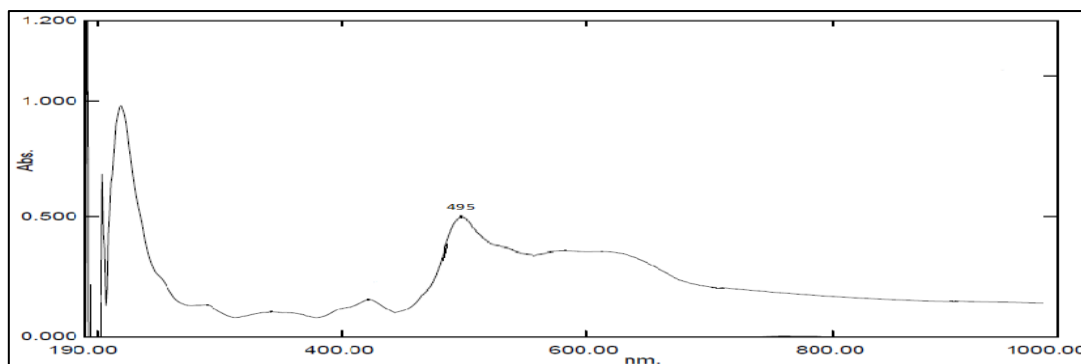


Figure 12: UV-Visible of complex

2- FT-IR Spectrum of extracted complex

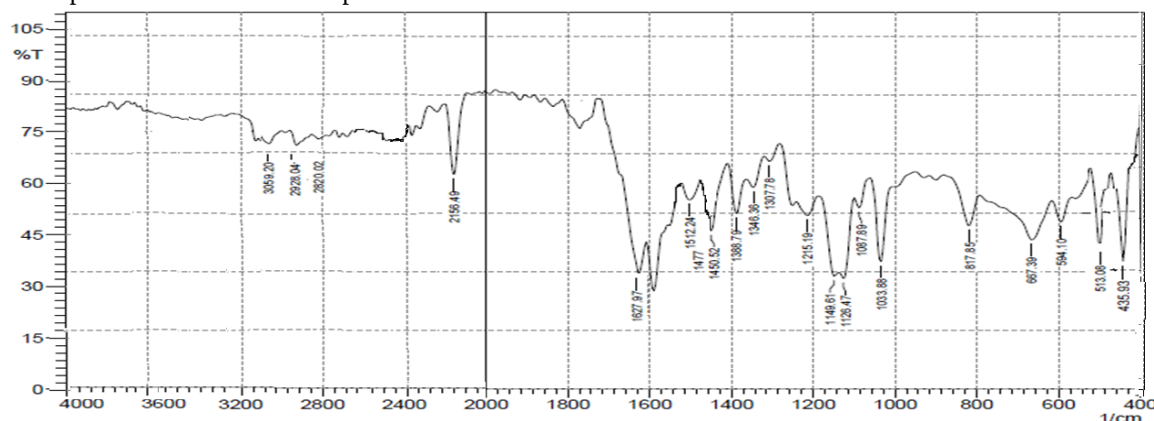


Figure 13: FT-IR spectrum of complex

**Table 14** some bonds for ligand & complex in FT-IR spectrum

Compound	St.(O-H)	St.(C-H) Aromatic	St. (SO ₃)	St.(C=C) Aromatic	St.(N=N)	St.(C-N)	St. (Gd-O)	St. (Gd-N)
Reagent	3325.39 3236.66	2928.04	2175.78	1654.98	1589.54	1226.77	-----	-----
Complex	-----	2924.18	2156.49	1627.97	1560.24	1215.19	513.08	435.93

The table 14 shows the locations of the reagent and complex absorption bands. The absorption bands of the free reagent (DPDBA) were identified and the change occurring in these bands in shape, intensity, and location was observed when the azo reagent (DPDBA) bonded with Gd⁺³ ion. the table also shows the disappearance of

a stretching band St.(O-H) from the spectrum of the complex and the formation of new stretching bands (St. (Gd-O), St. (Gd-N) in the spectrum of the complex explained the consistency between the azo reagent and the Gd⁺³ ion [23-25] [26].

Physical properties of extracted complex [Gd (DPDBA)₃]

Table 15 Some physical properties of complex

Compound	[Gd (DPDBA) ₃]
Color	Reddish purple
Melting point	(221-223) °C
Solubility	Alcohol solution (ethanol)
$\lambda_{\max}$	(495) nm

The Statistical treatment of data

The relative standard deviation was calculated in each test as a measure of data accuracy. because of this, the

separation took 3.816×10^{-4} . The results are shown in table 16.

Table 16 Statistical treatment of data

No. Read	Abs.(Xi)	Mean ($\bar{X}$)	(Xi - $\bar{X}$)	$\Sigma (Xi - \bar{X})^2$	$S = \sqrt{\Sigma (xi - \bar{x})^2 / N - 1}$	RSD = ($S/\bar{x}$) ×100
1	0.280		0.0037			
2	0.270	0.2763	-0.0063	7.132 x10 ⁻⁵	0.00479	1.7336
3	0.275		-0.0013			
4	0.280		0.0037			



Conclusion

In this study we synthesis a new ligand azo dye, this a new azo characteries by many spectroscopic techniques, the new reagent used to isolate the gadolinium (III) ion by liquid -liquid extraction process. Additionally, some factors, such as temperature, acidity, shaking time, and organic solvent, had an impact on the extraction process. etc.

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