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Study for Liquid-Liquid Extraction of Thulium (III) Ion Using new Azo derivative And It's Thermodynamic Functions

Suad Torki Abd-Al abbas[1], Alaa Frak Hussain[2]

[1]*Department of Chemistry, University of Kerbala, Iraq*
Email: suad.t@s.uokerbala.edu.iq
[2]*Department of Chemistry, University of Kerbala, Iraq*
Email: Alaa.frak@uokerbala.edu.iq

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Abstract

The research contains two parts , The first part contained the process of synthesis a new azo derivative called 3-(4-(dimethylamino)phenyl)diazenyl)-2-hydroxy-5-sulfobenzoic acid from diazonium salt pairs of (N^1,N^1-dimethylbenzene-1,4-diamine dihydrochloride) with 2-hydroxy-5-sulfobenzoic acid dihydrate , The reagent Chemical Formula ($C_{15}H_{15}N_3O_6S$) and the molecular weight was (365.36 g/mol) , The reagent powder has greenish color , The pure reagent melting point is (183-185 °C) , It is soluble in alcoholic solvent like ethanol absolute , the reagent characterizes by many spectroscopic methods (UV-Visible, FT-IR, mas spectrum ^{13}CNMR and ^{1}HNMR). The second part of the research is development an extraction process for Thulium (III) by liquid –liquid extraction and using the new azo reagent as ligand to form new complex, Many and different parameters on the extraction and distribution ratio were study like the acidity of medium, shaking time, the organic solvents polarity, the foreign ions effected, salting-out, redox agent , concentration effect of (metal and reagent) , and the temperature effect. The thermodynamic functions values were determine (ΔH, ΔG, ΔS), (Job's and Molar ratio) methods was using to explained the complex extracted stoichiometry and it was found that the complex was (M:L) (1:3) , Then the complex stability constant was calculated by using mole ratio method .

Keywords

New azo (DPDBA) , Thulium (III) ion , Extraction.

Many human love color , Azo dyes are a crucial pigments, Azo dyes consider an important material to synthetic color , azo compounds are used as industrial colorants for garments, beverages, and food., cosmetics , Azo plays a significant part in the pharmaceutical industry to protect drugs from unfavorable reactions, as well as being used in plastics and as acid-base indicators. ,Azo color changes due to the change of the electrons delocalization , low delocalization give shorter wavelength absorption while more delocalization the absorption shifts appeared in the longer wavelength so light absorbed red color[1-3] , Azo dyes compound contain a nitrogen to nitrogen double bond as a chromophore group , Azo classify according to number of (N=N) monoazo dyes have only one , while the two and three (N=N) components of diazo and triazo pigments respectively, Azo dyes history divide in to pre-aniline and post -aniline [4], Azo dyes synthesized by a simple reaction between a diazotization and coupling [5], [6] Azo compound used to form complex when react with metal ion, many ways and modifications were made to get the desired color[7-8], Lanthanides or lanthanones are the f-block (inner transition) elements with partly filled 4f-subshells. Actinides and lanthanides are both categorized as f block elements. With an oxidation state of (+3), lanthanides share the same chemical and physical characteristics as rare earth elements [9–10]. Major sources of lanthanides include monazite sand, which is made up of phosphates of thorium, cerium, neodymium, and lanthanum, Also the nuclear operation produces contain a lot of lanthanides as wastes [11-13] ,Lanthanide has many application like luminescent material manufacture ,catalytic process , electron component producing , industry, which must be recovered quickly in order to save energy and safeguard the environment[14] , For the removal and recovery of lanthanides metal a variety of methods are available, such as the chemical precipitation method, adsorption process , extraction , ion exchange and Valency change .[15-16].

The most prevalent chemical method for separating and purifying many of the metals present in the periodic table is solvent extraction [17–18]. Liquid-liquid extraction is a method for extracting a solute from a solution in a certain solvent, by another solvent the two phases should be immiscible when extracting (metal cations) species from liquids, Such as the f-ions can be readily coordinated by made soluble compound in an organic phase so they allowed to transfer from the aqueous phase to the organic phase when being extracted, The lanthanides (M^{+3}) ions form complexes with (F^-) and(O^-) donor ligands such as EDTA , β-diketones , oxalic acid and citric acid ligands [19] So the objective of this study is include using of a new monoazo dye to extracted thulium (III) ion as complex with high coordination number by depend on the liquid -liquid extraction method.

Materials Compounds And Methods

2.1 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 used to prepare azo dye compound [20,21], At first the aromatic anime (N^1, N^1-dimethylbenzene-1,4-diamine dihydrochloride) (2.091 g , 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)^{0}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 figure (1-1) explains the reagent prepare .

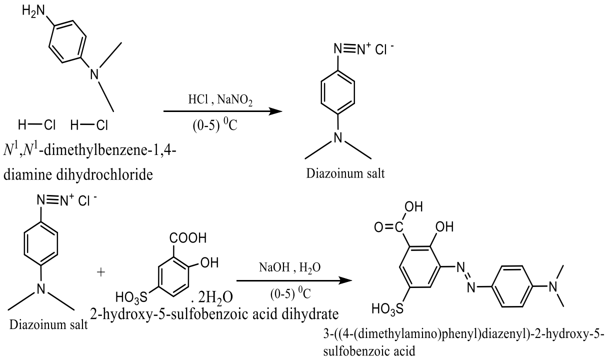

Figure 1.1 The new reagent (DPDBA) synthesis

2.2 Instrumentals requirement

- ✓ pH –meter Hanna.
- ✓ Double beam UV-Visible Spectrophotometer Cecil 7200.
- ✓ Gemmy Orbit Shaker VRN-480.
- ✓ Water bath Bs-11.
- ✓ FTIR –IR 8400, Shimadzu.

2.3 Preparation of stander solution

All analytical reagents and solutions prepare at high purity.

- ✓ [1mg/mL] from thulium (III) ion.
- ✓ [0.2% W/V] from (DPDBA) reagent.
- ✓ [0.05% W/V)] from Arsenazo (III)
- ✓ [1%] from ascorbic acid
- ✓ [60mL, formic acid & 28gm, NaOH, dilute to 1L distill water] from formate buffer (pH=3.5).

2.4 Extraction of thulium (III) ion

The aqueous phase was contained of 250 μg / (2.5 mL) (6.359 x 10^{-4}M) of Tm (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 (40) minutes. The solution was leaved after shaking to settle and separate. The residue Tm (III) ion in the aqueous layer was determined spectrophotometrically with arsenazo (III) by following the same working method as in the calibration curve.

3. Result and Discussion

3.1 Identification for a new reagent (DPDBA)

3.1.1 physical properties

Some physical properties of the new reagent was characterized, Table (1.1) show the result of this study , Also the reagent identify by spectroscopic (UV-Vis., FT-IR, ^{1}HNMR, Mass spectrum and ^{13}CNMR) .

Table 1.1 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) ^{0}C
Solubility	Alcohol solution (ethanol)
λ_{max}	(406) nm

3.1.2 (UV-Vis.) spectrum of a new reagent

The reagent (UV-Vis) spectrum at figure (1.3) explained that the highest absorption peak at (406) nm .

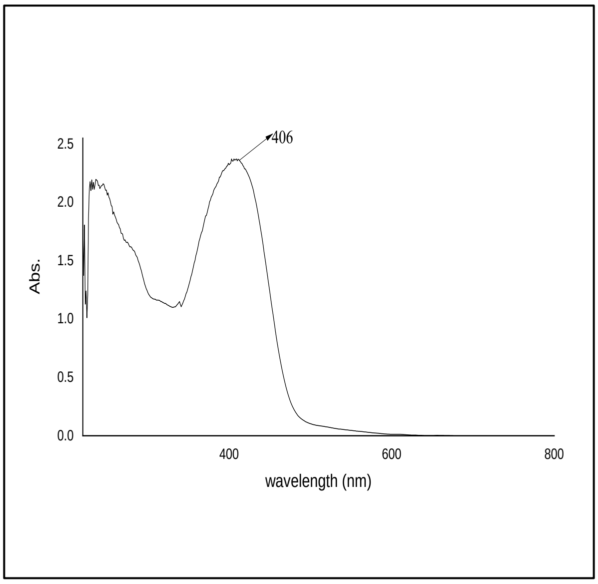

Figure 1.3 The Electronic spectrum of (DPDBA) reagent

3.1.3 FT.IR spectra for the 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 (1.4) results displays the results .

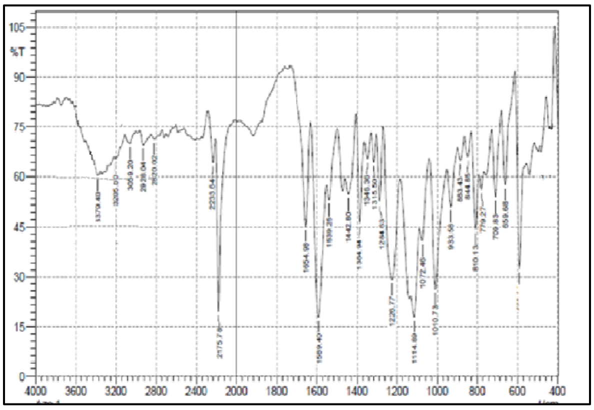

Figure 1.4 FT.IR spectra of (DPDBA)

3.1.4 1 HNMR spectrum for the ligand:

The reagent (DPDBA) ^{1}H NMR spectrum displayed in figure (1.5).

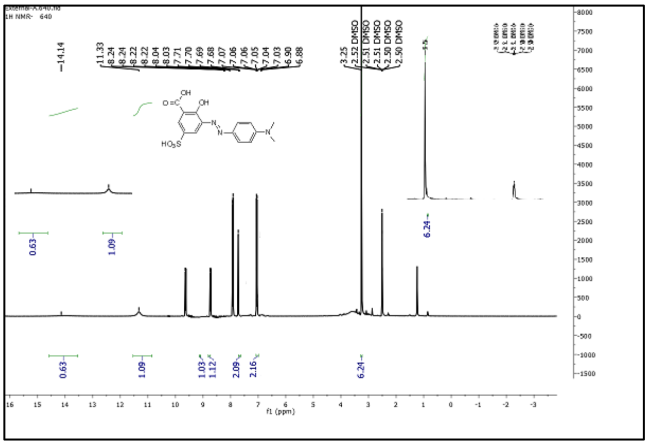

Figure 1.5 ^{1H} NMR spectrum for (DPDBA) reagent

3.1.513C-NMR of the ligand: -

The reagent (DPDBA) ^{13}CNMR spectrum displayed in figure (1.6).

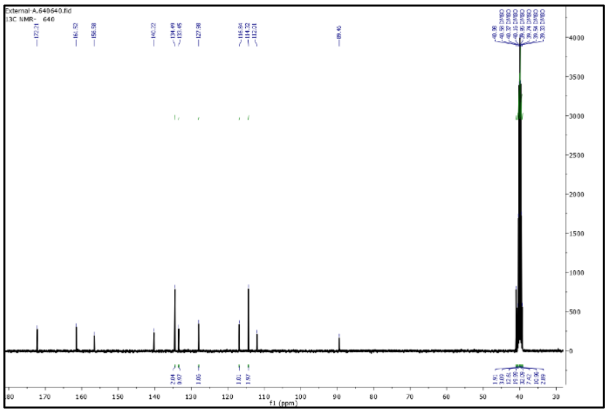

Figure 1.6 13C NMR spectrum for (DPDBA) reagent

3.1.6 Mass spectrum of the ligand

The reagent (DPDBA) mass spectrum was explained in figure (1.7) 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].

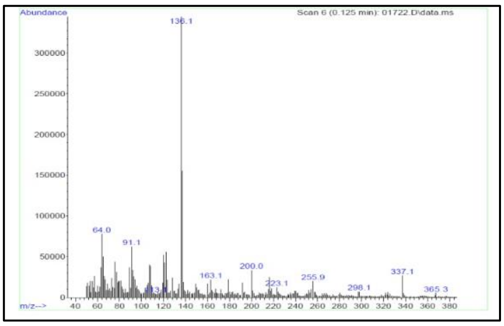

Figure 1.7 mass spectrum of (DPDBA)

3.1.7 Calibration curve for Tm (III) [22]

At first , a number of solution containing different amount of Tm (III) range (5-75) µg/5mLwere prepare from the storage solution. After That, ascorbic acid [1 mL, 1%] was added to each 5 mL, Then after 1-2 minute [1mL] 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 1.8 .

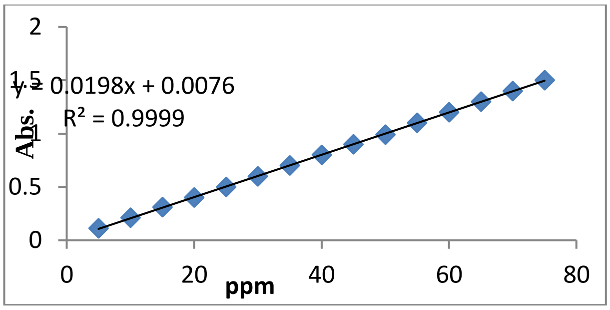

Figure 1.8 Calibration curve of Tm (III)

3.2 Different factors effect on extraction processes

3.2.1 pH factor

The hydrogen ion effect was studied from range (1-8) by adjusted the pH with (acid or base) dilute solution, Then the (D &E%) calculated ,Table (1.2) show the result .

Table 1.2 The effect of pH

pH	D	E%
1	**10.189**	**91.063**
2	8.618	89.603
3	6.833	87.236
4	6.019	85.578
5	5.803	85.363
6	5.836	85.371
7	5.337	84.226
8	5.181	83.822
9	4.881	82.991

The result in table (1.2) explain that the suitable pH to separate Tm (III) ion equal to 1 due to the largest (D & %E) and extraction of Tm (III) decrease with increasing pH from (2 - 9), The result may be because of used of the new reagent as a component of solvent extraction, The result was consistent with many studies [23,25] .

3.2.2 Shaking time factor

The shaking time was studied as a function of equilibrium time between two phases ranged (5-60) min, The result showed in (1.3) table.

Table 1.3 The shaking time effect

Time	D	E%
5	4.332	81.264
10	6.086	85.881
15	6.476	86.619

20	8.242	89.178
30	10.189	91.063
40	**10.219**	**91.084**
50	9.774	90.723
60	9.773	90.718

The table (1-3) explain increasing the value of (D&%E) with time till (40) min. this due to fact that increasing the shaking time results in more contact between the two phases, increasing their surface areas, whose different free energies rely on various compounds. in the two phases and the shaking, So that access equilibrium between organic and aqueous phase ,The result was agreement with other old and new studies[26,27].

3.2.3 Organic solvent effect

Some organic solvent different in dielectric constant using to studied the effect of it on the Tm (III) ion extracted under experimental condition , After each extraction and separation (D&%E) calculated then explained in table (1.4) .

Table 1.4 Organic solvent effect

Organic Solvent	E	1/ε	D	E%
Carbon tetra chloride	2.240	0.446	7.961	88.842
Benzene	2.280	0.438	10.219	91.087
Toluene	2.380	0.420	3.520	77.876
Chloroform	**4.810**	**0.207**	**10.219**	**91.084**
1,2-dichloroethan	10.420	0.095	5.940	85.591
Benzaldehyde	17.800	0.056	5.063	83.507
Nitrobenzene	35.600	0.028	4.807	82.779

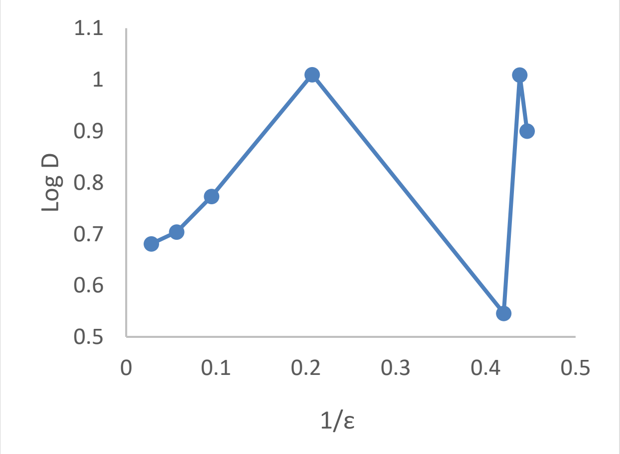

Figure 1.9 The organic solvent effect

From the result in the table (1.4) and the figure (1.9) demonstrate that the effect of the organic solvent on extraction was different from one solvent to another, so there is no liner relation between (D) and (ε) of organic solvent and found the best one to extract Tm (III) ion was a chloroform due to the highest (D&%E) , The result agreement with other study [26] .

3.2.4 The foreign ion effect

A number of metal ions (cation & anion) add with Tm(III) ion aqueous phase to studied the effect of foreign ion on the separated of thulium ion , After the extraction process finish the ion solution determine by colorimetric method and calculate the Tm concentration ,then calculated the value of (D&E%) , The tables (1.5) , (1.6) show the result of this factor .

Table 1.5 The anions effect

Anion ion	2%		4%	
	D	E%	D	E%
-----	10.219	91.084	9.846	90.780
$[Fe(CN)_5NO].2H_2O^{=}$	9.261	90.254	10.664	91.427
$Cr_2O_7^{-2}$	10.189	91.063	10.240	91.110
CrO_4^{-2}	7.817	88.658	7.770	88.597
$S_2O_3^{-2}$	12.889	92.800	13.628	93.164
CO_3^{-2}	9.568	90.537	9.545	90.516
SCN^{-}	8.979	89.979	9.705	90.659

Table 1.6 The effect of cation

Ions	250µg		500µg	
	D	E%	D	E%
Tm^{+3}	**10.219**	**91.084**	**14.782**	**93.664**
Mn^{+2}	6.658	86.942	6.928	87.386
Cu^{+2}	5.169	83.790	6.318	86.331
Zn^{+2}	6.587	86.820	5.459	84.518
Hg^{+2}	6.658	86.942	6.658	86.942
Ni^{+2}	7.1360	85.810	6.815	87.204
Co^{+2}	8.280	89.224	7.678	88.477
Fe^{+2}	8.952	89.952	9.568	90.537

From the results in table (1,5) showed that ($S_2O_3^{-2}$) increasing the extraction process of Tm (III) this due to that anion has low the hydrogen energy so it facilitate form complex compound in organic layer . While the result in table (1,6) showed that (D&E%) was reduce when cations ions presence in aqueous phase this due to the competition between Tm (III) ion and the cations with the reagent to form complexes [29].

3.2.5 The temperature effect

The extraction processes of Tm (III) from aqueous layer at the optimum conditions by temperature range (20-45) ^{0}C as illustrated in table (1,7)

Table 1, 7 The temperature effect

T(K)	1/Tx10-3	D	E%
293	3.413	**10.219**	**91.084**
298	3.356	9.478	90.456
303	3.300	7.470	88.194
308	3.247	6.966	87.447
313	3.195	6.139	85.992
318	3.145	5.641	84.942

The enthalpy energy was calculated by using Vant – Hoff Equation and drawing the relationship between log D versus 1/T as figure (1.10) was showed

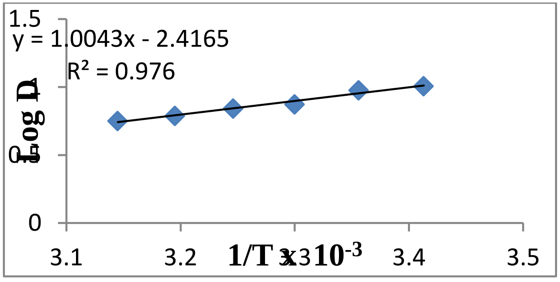

Figure 1.10 The temperature effect

The result in figure (1.9) explain that the reaction between Tm (III) and reagent was exothermal and the (ΔG_{ex} , ΔS_{ex}) values calculated by depend on Gibbs equations

$\Delta G_{ex} = \Delta H - T\Delta S$ ……… (1)

$\Delta G_{ex} = - RTln\ K_{ex}$ ……… (2)

Table 1,8 Thermodynamic function

T(K)	ΔH(KJ.Mol-1)	ΔG(KJ.Mol-1)	ΔS(KJ.Mol-1.K-1)
293	-19.224	-5.655	-0.0463
298		-5.572	-0.0458
303		-5.066	-0.0467
308		-4.970	-0.0462
313		-4.722	-0.0463
318		-4.574	-0.0461

The result in table 1,8 showed the negative values of enthalpy reaction between Tm and reagent and this means decreeing the extraction process with increasing the temperature also the negative value of free energy extraction was demonstrated and this is favorite thermodynamically at high temperature this study was agreed with many studies[28].

3.2.6 The Tm (III) ion concentration effect

Tm (III) ion was then extracted from these aqueous solutions by using 2.5 mL of 0.2% DPDBA as reagent at the best conditions found. Different concentrations of Tm (III) solutions ranging from (50 - 400) g/2.5mL, ($1.184x10^{-4}$ - $9.471x10^{-4}$) were produced. The findings of this research are shown in Table 1.9.

Table 1.9 Tm (III) concentration effect

{M}x10-4	D	E%
1.184	1.279	56.121
2.368	2.637	72.505
3.552	5.019	83.386
4.736	7.330	87.995
5.920	**10.219**	**91.084**
7.103	13.063	92.889
8.287	14.594	93.587
9.471	14.796	93.669

According to the findings, using DPDBA as a reagent under perfect conditions led to improved extraction and, as a result, higher levels of D. Increased contact between the ion and reagent can be used to explain this. In other tests, these outcomes were better. [29].

3.2.7 The DPDBA reagent concentration effect

A known amount of Tm (III) aqueous solution (250µg/2.5 mL, 5.920 $x10^{-4}$ M) was prepared and extracted by using different concentration of (DPDBA) under optimum conditions, Results in table (1.10) showed increasing in extraction of Tm (III) ion by using different concentration of (DPDBA) ligand and this are in agreements with recent study [30,31].

Table 1.10 The reagent concentration effect

[L]x10-3	D	E%
1.474	6.902	87.344
2.474	7.231	87.851
3.474	7.770	88.597
4.474	8.403	89.365
5.474	**10.219**	**91.084**
8.211	10.474	91.285
10.948	10.447	91.265

3.2.8 The oxidation –reduction factors effect

The hydrogen peroxide solution (35%,w/v) and $SnCl_2.2H_2O$ solution (1M) used to study the influence of oxidation –reduction process on the solvent extraction of Tm (III) with (DPDBA) reagent by adding 1mL from each solution to the thulium extracted solution , under the optimum conditions , (D&E%) determined after aqueous and organic phases were separated. Colorimetric calculations were used to determine how many ions were still present in the water phase. The table 1.11 presents the results. [33] .

Table **1.11** Oxidation and reduction effect

Extraction	D	E%
Extraction in absence of oxidation – reduction factors	**10.219**	**91.084**
Extraction in presence of oxidation factor	9.434	90.042
Extraction in presence of reduction factor	9.705	90.659

From the result in table 1.11 showed that the solvent extraction of Tm with DPDBA do not change in the presence of (H_2O_2 & $SnCl_2.2H_2O$) this due to the thulium ion trivalent oxidation state is more stability [31,32].

3.2.9 The Salting out effect

To study the effect of the salting, Ammonium chloride was chosen for this purpose The values of (D) Was calculated to extract (250µg/2.5mL), ($5.920\ x10^{-4}$M) of Tm(III) ion, with the reagent (DPDBA) in the presence of (1M,1 mL) of NH4Cl solution under the optimum conditions, the result shown in table (1.12).

Table **1.12** The salting effect on extraction of Tm (III)

Extraction	D	E%
Extraction in absence of salting factors	**10.219**	**91.084**
Extraction in presence of NH_4Cl salting factor	9.990	90.901

Stoichiometry determination

Metal ion and new reagent stoichiometry determines with two method:

1. Job's approach (continuous variables)

Under ideal circumstances A known steady concentration of the ligand (DPDBA) was mixed with an increasing concentration of the Tm (III) ion. After extracting each solution with chloroform and measuring the organic layer's absorption at its highest wavelength (as shown in figure 1.11), It can be deduced that the chelating ratio between Tm (III) and the reagent M:L was (1:3).

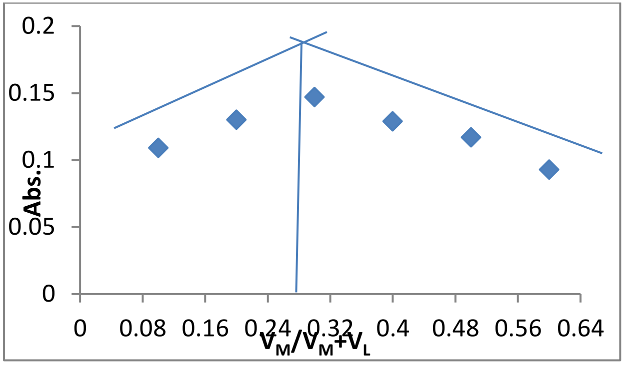

Figure **1.11** Job's method

2. Mole ratio approach

This procedure involved mixing a steady and well-known amount of Tm (I) with (DPDBA) reagent as the concentration increased from [(2.960-20.720)]x10^{-4}M. Results showed that the complex chelating between M:L was(1:3) explained by plotting in figure (1.12) , The results of Job's technique agreed with those of the mole ratio method.

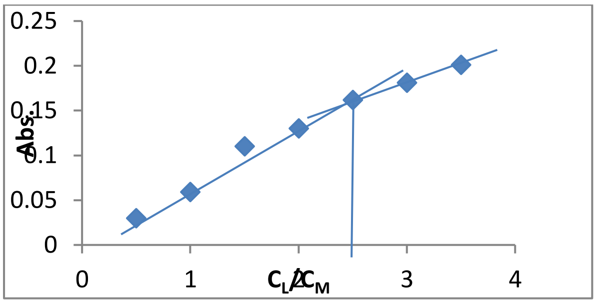

Figure **1.12** Mole ratio

Study of the Stability of complex

The equilibrium reaction of the extracted complex was used to determine the stability constant of the extracted complex in the organic phase

$M^{+3} + 3L \longrightarrow ML3$

αC 3αC (1-α) C

K = (1-α) C / αC $(3\alpha C)^3$

Table **1.13** The complex stability

Ion	Am	AS	A	Kstable
Tm	0.201	0.162	0.194	$10.158x10^{10}$

From results in table(1.13) showed that the complex has high stability , So that it is possible to use the reagent (DPDBA) to separation the thulium ion by liquid- liquid extraction ,

Study the complex Spectroscopic

UV-Vis. spectrum for the complex [Tm (DPDBA)3]

The extracted complex's electronic spectrum in figure (1.13) reveals that it displays a strong intense absorption peak at (502) nm, which is when it comparing with the reagent absorption spectrum can showed a red shift absorption for complex.

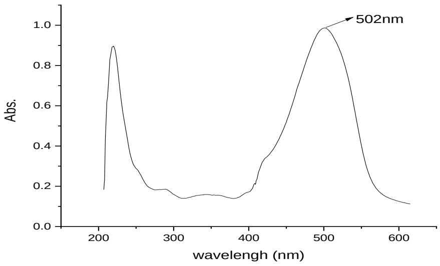

Figure 1.13 Electronic spectral data of the complex

F.T.I.R spectrum

The characteristic bands in table (1.14) (DPDBA) were apparent in the FTIR spectrum of the complex [Tm (DPDBA)3], which is illustrated in figure (1.14). Oxygen from the O-H group and electron pairs from the azo group (N=N) coordinate to the metal.

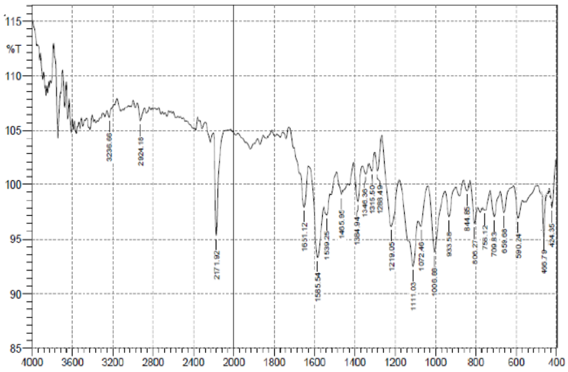

Figure 1.14 F.T.I.R spectrum of complex

Table 1.14 The data results of FTIR spectrum for reagent & complex

Compound	St. (O-H)	St. (C-H) Aromatic	St.(so3H)	St.(C=C) Aromatic	St. (N=N)	St. (C-N)	St. (Tm-O)	St. (Tm-N)
Reagent	3325.39 - 3236.66	2928.04	2175.78	1654.98	1589.54	1226.77	-----	-----
Complex	-------	2924.18	2171.92	1651.12	1585.54	1219.05	590.24	466.79

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

Table 1.15 Some physical properties of complex

Compound	[Tm (DPDBA)3]
Color	Reddish purple
Melting pointe	(227-230) ^{0}C
Solubility	Alcohol solution (ethanol)
λ_{max}	(502) nm

The Statistical treatment of data

In all experiments, the relative standard deviation was computed as a gauge of data precision. for this reason, the extraction was done in 3.552 x10^{-4}M The results obtained in table 1.16 .

Table 1.16 Statistical treatment of data

No. Read	Abs.(Xi)	Mean ($\bar{X}$)	(Xi-$\bar{X}$)	Σ(Xi-X)2	$S=\sqrt{\Sigma(xi-\bar{x})2 / N-1}$	$RSD = (S/\bar{\bar{x}})$ ×100
1	0.501	0.5003	0.0007	1.4760 x10^{-5}	2.220 x10^{-3}	0.4437 %
2	0.502		0.0017			
3	0.497		-0.0033			
4	0.501		0.0007			

Conclusion

As this paper demonstrate possibility of synthesis a new ligand azo dye and characteries a new azo by many spectroscopic technique, Azo dyes currently account for the majority of dye chemistry output, and their relative significance may even rise going forward. Azo dyes are frequently used in a variety of sectors, including those that produce food, medicines, paper, cosmetics, textiles, leather, and others. In addition of all that ,In mine study, we were concluded that azo dyes could be used in the process of isolating and purifying the rare earth element thulium ion (III) from aqueous solution .Also there are some variables that affect this extraction process, including temperature, acidity, shaking duration, and organic solvent.

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