

Study of Liquid – Liquid Extraction of Neodymium (III) by derivative of amino acid N-Acetylcysteine(NAC).

دراسة في استخلاص سائل – سائل للنيوديميوم الثلاثي باستخدام مشتق الحامض الأميني N - اسيتايل- سستائين

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Abstract

The study of liquid - liquid extraction of neodymium (III) with N-Acetyl-cysteine that refers by (NAC) had been made. The effect of different parameters on the percent of extraction and distribution ratio such as type of medium , time of equilibration , type of solvent , effect of some cations and anions, effect of redox agents , enrichment extraction , concentration of metal ; reagent, effect of batch extraction, salting out , and effect of temperature . The function of thermodynamic parameter of (ΔH , ΔG , ΔS) were calculated .The stoichiometry of the extraction was determined using two methods mole ratio and job' s methods. It was found to be (M: L) (1:3). The stability constant of complex in mole ratio method was calculated. The study of UV-visible and FT-IR spectra were studied for both the reagent and complex in organic phase. Other physical constant namely such as temperture,melting point and specific conductivity.

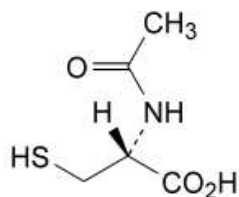
الخلاصة:-

أجريت دراسة استخلاص سائل – سائل لأيون النيوديميوم الثلاثي بواسطة مشتق الحامض الأميني N -اسيتايل- سستائين (NAC) المذاب في الايثانول , حيث تم دراسة تأثير مجموعة من العوامل التي تؤثر على قيمة نسبة التوزيع والنسبة المئوية للاستخلاص متمثلة بوسط الاستخلاص , زمن الاتزان , نوع المذيب العضوي , تأثير المتداخلات (ايونات موجبة – ايونات سالبة) , تأثير عوامل الأكسدة والاختزال , طريقة الاغناء , تركيز العنصر والكاشف , عملية التملح , تقنية الدفعات , درجة الحرارة , حساب الدوال الترموديناميكية الخاصة بالنظام (ΔH , ΔG , ΔS) كما تم دراسة تكافؤية المعقد المستخلص في الطور العضوي بطريقتين هما النسب المولية وطريقة جوب وقد أثبتت الطريقتين إن نسبة الليكاند إلى الفلز (M: L) هي نسبة (1:3) وبالاستعانة بطريقة النسب المولية تم حساب ثابت استقرارية المعقد المستخلص وتمت دراسة طيف الأشعة المرئية – فوق البنفسجية وطيف الأشعة تحت الحمراء لكل من الكاشف والمعقد المستخلص كما تم دراسة بعض الصفات الفيزيائية للمعقد مثل درجة الانصهار والتوصيلية النوعية للمعقد .

Introduction:-

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 pyrometallurgical 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⁽¹⁾.

N-Acetyl-Cysteine (NAC) (Acetylcysteinum) was a derivative of Cysteine , acetylated form of amino acid cysteine. It is one of the compound which on one side has a free Thiol group(SH), and on the other side its α -amino group is been protected with acetyl group. In fact acetyl group forms the simplest peptide bond in proteins. Many binary and ternary complexes of some metal ions with NAC and amino acid were prepared⁽²⁾.



Neodymium is a chemical element (a rare earth metal) with the symbol Nd and atomic number 60. didymium was discovered in 1885 by the Austrian chemist Carl Auer von Welsbach ⁽³⁾. Neodymium has a bright, silvery metallic luster, but as one of the more reactive lanthanide rare-earth metals, it quickly oxidizes in ordinary air. Neodymium reacts slowly with cold water and quickly with hot water. It quickly tarnishes in air and so is usually kept under paraffin or sealed in plastic. Neodymium exists in two allotropic forms, with a transformation from a double hexagonal to a body-centered cubic structure taking place at about 863 °C.⁽⁴⁾⁽⁵⁾.

Many studies to extract neodymium were obtained. In , 2006 Hsiang-Chien Kao et al. ⁽⁶⁾ reported equilibrium and kinetic studies on solvent extraction of single and binary La(III) and Nd(III) from nitrate solutions with (2- ethylhexylphosphonic acid mono-2-ethylhexyl ester) in kerosene at 298 K were studied. I. Dukov et al. ⁽⁷⁾ , 2006 , investigated the synergistic solvent extraction of the lanthanoid(III) ions(La, Ce, Pr, Nd, Sm, Eu and Gd) with a ternary mixture of (4-benzoyl-3-methylphenyl-2-pyrazolin-5-one) and (2-thenoyltrifluoroacetone, Hexafluoroacetylacetone), and the quaternary ammonium salt Methyltrialkyl(C8,-C10) ammonium chloride (Aliquat 336,QCI) in C₆H₆ has been investigated. In 2006 , Maria Atanassova ⁽⁸⁾ studied the solvent extraction of trivalent lanthanoids (La, Nd, Eu, Ho, and Lu) with mixtures of the chelating extractant (2-thenoyltrifluoro-acetone. HTTA) or (HP) and (4-(2-pyridylazo)-resorcin) in CHCl₃. In 2009, A. N. Turanova et al. ⁽⁹⁾ reported the extraction of lanthanides(III)(La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y)from aqueous nitrate solutions with several phosphoryl-containing podands in 1,2-dichloroethane has been studied. In 2009 , Shanshan Tong et al. ⁽¹⁰⁾ study the extraction of rare earths(La⁺³,Nd⁺³) with mixtures of (HPMBP,HA) 1- phenyl-3-methyl-4-benzoyl pyrazalone-5 and (CA12,H₂B₂) Sec-octylphenoxyacetic acid in benzene from chloride medium. The synergistic enhancement coefficient decreases with increasing atomic numbers of rare earths . the synergistic extraction of La⁺³ is endothermically driven. The extracted complexes are determined as LaH₂ClA₂B₂ and NdH₃ClA₃B₂. In later studies, V.VBelova et al. ⁽¹¹⁾ showed that the extraction of rare earth metals(La, Nd, Sm Eu,Gd ,Dy,Ho, Er,Yb) from chloride and nitrate solutions by various binary extractants based on dialkylphosphinic, dialkylmonothiophosphinic and dialkyldithiosphinic acids has been examined under different conditions. In 2010 , S.Radhika et al. ⁽¹²⁾ study the Extraction of mixture of heavy rare earths (Tb, Dy, Y, Ho, Er, Yb ,Lu) and mixture of (La , Ce, Pr and Nd) from phosphoric acid solutions(3-5)M extractant used are, Talcher organic phosphorus solvent(Di-2- ethylhexyl phosphoric acid), (2- ethylhexylphosphonic acid mono-2-ethylhexyl ester) and (Bis(2,4,4-trimethylpentyl)phosphinic acid) . In this study neodymium(III) was extracted by using derivative of amino acid (NAC) and study the best conditions for this extraction to find fast and efficient method to extracted and determination of Nd(III) ion.

Experimental

Chemical

All chemicals and solvent were obtained from commercial and used as received

Preparation of standard solutions.

- 1- Standard solution of neodymium (III)(1mg/ml)prepared by dissolving (0.1160 gm) of Nd_2O_3 in (1 mL) of concentrated hydrochloric acid and the volume was completed to 100 ml with double distilled water in a volumetric flask. Dilute Nd (III) solutions are prepared by further diluting of the standard solution with the necessary volume of water.
- 2- Reagent (NAC) solution (0.2% w/v) prepared by dissolving (0.2gm) of (NAC) in absolute ethanol and the volume was completed to (100 mL) with ethanol in a volumetric flask.
- 3- Ascorbic acid solution (1% w/v) prepared by dissolving (1gm) of ($\text{C}_6\text{H}_8\text{O}_6$) in double distilled water and the volume was completed to (100 mL) with double distilled water in a volumetric flask..
- 4-Arsenazo (III) solution (0.05%(w/v)) prepared by dissolving (0.05gm) of arsenazo (III)in double distilled water and the volume was completed to (100 mL) with double distilled water in a volumetric flask.
- 5- Format buffer solution (pH=3.5) prepared by dissolving (28 gm) of NaOH and (60 mL) of formic acid in water, and dilute the solution with water to 1 liter.
- 6-Sodium hydroxide solution (1M) prepared series of NaOH solution from (0.1 to 1.0 M) by dissolving suitable weight of NaOH in double distilled water.
- 7- Cations solution of [Cd(II) , Hg(II) , Ni(II) , Mn(II) , Co(II) ,Fe(III) , Cr(III)] chloride salt prepared by dissolving salts of them depending on the molecular weight of salt used for these elements in (25mL) of distilled water.
- 8- Anions solution of (Cr_2O_7^- , Br^- , MnO_4^- , SO_4^- , PO_4^- , ClO_3^- , NO_3^- , CO_3^-) potassium salt prepared by dissolving salts of them depending on the molecular weight of salt used for these elements in (25mL) of distilled water.
- 9-Tin chloride solution (0.1M) prepared by dissolving (0.5640gm) of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in (1mL) of hydrochloric acid and the volume was completed to (25 mL) with double distilled water in a volumetric flask.
- 10-Ammonium chloride solution (1M) prepared by dissolving (1.3375 gm) of NH_4Cl in double distilled water and the volume was completed to (25 mL) with double distilled water in a volumetric flask.

Instruments:

- 1- Single beam UV-visible spectrophotometer Sp-300 (Japan).
- 2- pH-meter-WTW-720-ionlab (Germany).
- 3- Electrical shaker. (Scientific technical supplies W-Germany) .
- 4- Melting point apparatus, England.
- 5- Digital conductivity meter-WT-270-iolab (Germany).
- 6 - Temperature control circulator laboratory supply company.
- 7- FT-IR 8400, Shamadzu, (Japan).
- 8- UV-visible spectrophotometer -1800, Shamadzu, (Japan).
Equipped with quartz cells (1cm).

Procedures

Calibration curve was prepared for Nd(III). depending on the colorimetric method for solution of arsenazo(III)⁽¹³⁾. To measure the absorption of the concentrations of standard solutions of Nd(III) as follows: -

1- Construction of calibration curve of Nd(III)

(5mL) of solutions containing different concentrations of Nd(III) ranged from ($6.9328 \times 10^{-6}M - 1.0399 \times 10^{-4}M$) equivalent to (5 μg - 75 μg .) Nd(III) were taken. To each solution (1mL) of (1%) ascorbic acid solution were added. After a few minutes (1mL) of the formate buffer (pH= 3.5) and (2mL) of arsenazo(III) solution (0.05%) were added. Diluted with double distilled water to (~ 20ml). The colored solution adjusted to pH (2-2.6) with (0.3 M) hydrochloric acid or sodium hydroxide. Transfer the solution to a volumetric flask (25mL), made up to the mark with double distilled water. The absorbance measured at ($\lambda_{\text{max}} = 650\text{nm}$) against a reagent blank solution using cell absorption radiance (1cm). The relationship between the absorption and concentration prepared for the calibration curve was drawn.

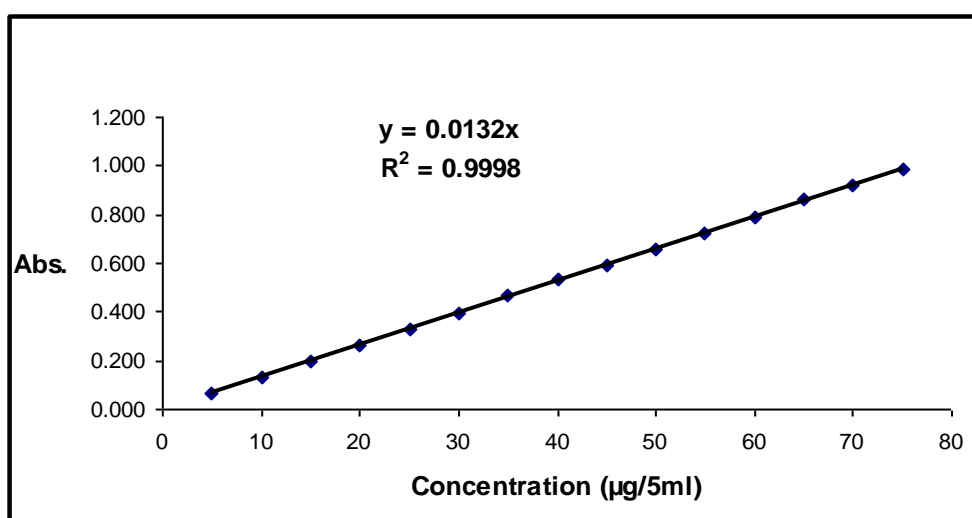


Fig. (1) Calibration curve for neodymium (III).

2-Extraction of Nd(III) ion by using reagent (NAC)

A solution containing (2.5mL) ($1.3865 \times 10^{-3} M$) of Nd (III) and (2.5mL) (0.2%) of Ligand (NAC) in ethanol was poured into a separatory funnel as aqueous phase. The pH of the solution was adjusted with diluted HCl /and NaOH solutions. The aqueous phase was equilibrated with (5ml) of chloroform for (60) minutes. The aqueous and the organic phase were allowed to be separate. An aliquot of the aqueous phase in the cells for absorbance measurements at ($\lambda_{\text{max}} = 650 \text{ nm}$).

Results and discussion

To reach the best conditions of extraction, the effects of the following factors in the value of distribution ratio (D) were studied, represented by: -

1-Effect of pH

In order to select the solvent extraction system for the extraction of Nd(III) the effect of pH on the extraction was studied for the pH range of (1-10)with (NAC) solution dissolved in ethanol with chloroform as organic phase .The result in table (1).

Table: (1) The influence of pH in the extraction of Nd(III) by using(NAC).

pH	D	E%
1.08	2.818	73.808
2.05	2.884	74.253
3.02	2.857	75.269
4.06	3.040	75.247
5.02	3.176	76.074
6.06	3.258	76.523
7.33	3.365	77.093
8.09	3.406	77.313
9.27	3.507	77.823
10.02	3.507	77.823

Aqueous phase: - (2.5 mL) solution of Nd (III) ion concentration (500 μ g) , (1.386x10⁻³ M) with (2.5 mL) solution of (0.2%) of reagent (NAC) dissolved in ethanol in different acidic functions, organic phase: - (5mL) solution of chloroform.

Equilibrium time: - Sixty minutes, temperature: - (25 \pm 3) C^o.

From the results in the table (1) the distribution ratios and the (E%) increase with increasing pH till (9) and after that it became approximately constant .Thus could be due to the nature of the properties of organic reagents used in solvent extraction process and its impact on pH . Derivatives of amino acids behaves as di dentate ligand in acidic and basic media , therefore Nd(III) had high (E%) in basic media .This results are in agreement with the previously studies⁽¹⁴⁾ .

2-Effect of shaking time

For the contact of two phase of extraction method studied effect of shaking time on the extraction activity and distribution ratios values, the results of this study in table (2) demonstrate the optimum shaking time of two layers was (50 min) to reach the equilibria of extraction and at this time obtain the maximum distribution ratio value, down optimum shaking don't reached the equilibria of extraction, and over optimum shaking time favorite the dissociation equilibria and minimize the distribution ratio. This results in agreement with the previously studied⁽¹⁵⁾⁽¹⁶⁾ .

Table (2): The effect of time of equilibrium in the extraction of Nd(III) by using (NAC) .

Time	D	E%
10	3.316	76.829
15	3.385	77.192
20	3.420	77.374
30	3.602	78.272
40	3.802	79.174
50	4.436	81.936
60	3.507	77.823
70	3.217	76.284
80	3.162	75.974

Aqueous phase: - (2.5 mL) solution of Nd (III) ion concentration(500 μ g) , (1.3865x10⁻³ M) with (2.5 mL) solution of (0.2%) of reagent (NAC) dissolved in ethanol in (pH=9),Organic phase: - (5ml) of chloroform, Equilibrium time: - (X)minutes , Temperature: - (25 \pm 3) Co.

3-Effect of organic solvents:

According to solvent extraction method which was depend on the organic solvent used in extraction method the results in table (3) demonstrate there is no any linear relation between distribution ratio and dielectric constant of the organic solvent .This is in contrast with Born relationship of the following equation ⁽¹⁷⁾: -

$$\Delta Gt = \frac{Z^2}{Zr} \left(\frac{1}{\epsilon_w} - \frac{1}{\epsilon_o} \right) \dots\dots (1)$$

Where Z is the ion charge, r the radius of the ion, ϵ_w , ϵ_o dielectric constant of water and organic solvent, respectively, ΔGt free energy to move the ion. Figure (2) appear that toluene was the best solvent for extraction Nd(III) ion .

Table (3): The effect of polar organic solvent to extract Nd(III) by using (NAC).

Organic Solvent	ϵ	$1/\epsilon$	D	E%
Nitrobenzene	35.600	0.028	3.521	77.879
Benzaldehyde	17.800	0.056	3.261	76.530
1,2-dichloroethan	10.420	0.095	3.286	76.667
chloroform	4.810	0.207	4.536	81.936
Toluene	2.380	0.420	8.910	89.909
Benzene	2.280	0.438	4.100	80.394
Carbon tetra chloride	2.240	0.446	4.898	83.045

Aqueous phase: (2.5 mL) from Nd(III) ion with (2.5 mL) (0.2% NAC) at (pH = 9)

Organic phase: (5 mL) from different solvents, Contact time: Fifty min, Temperature: (25 ± 3) C°

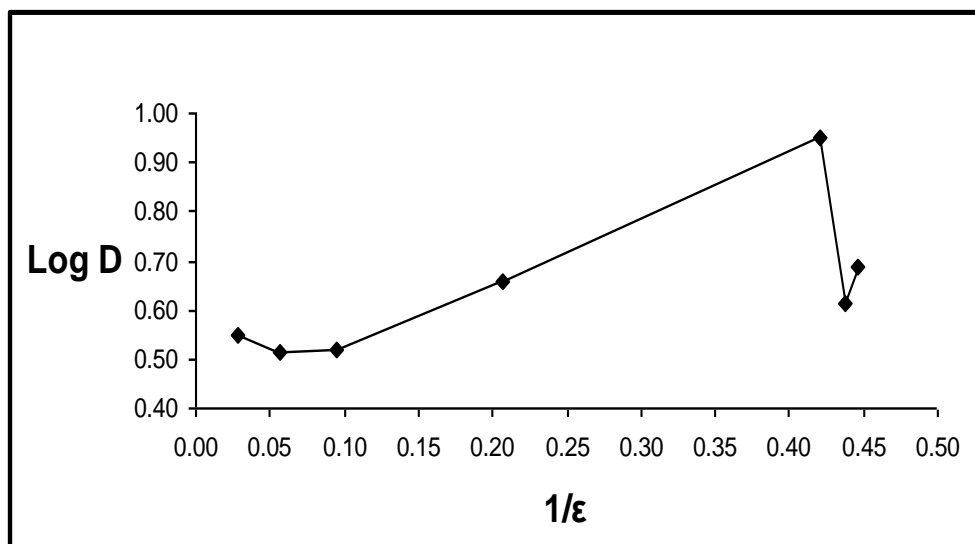


Fig. (2) The effect of polar organic solvent to extract Nd(III) by using (NAC).

This demonstrated that the system of extraction in this study can not be controlled by the dielectric constant of the solvent and the reason was attributed to the extracted complexes were no charge chelate. These types of complexes were affected by many factors including the solubility of the extracted complex or geometry of organic solvent. This is supported the role of organic solvent composition to achieve the best extraction away from the polar organic solvent that used as to have

a role in creating the best extraction, but its role was not a major, it's not exclude the possibility of participation of organic solvent in the process of extraction, the results of these study are in agreement with the previously studies ⁽¹⁴⁾.

4- Effect of anions on the extraction

The results in the table (4) shows that the presence of anions disparate influence in the process of extracting of Nd(III) ion depending on the nature of the anions added .Some anions had a great effect on decreasing the values of distribution ratio and therefore effect on the (% E) to extract Nd(III) ion , these ions were (SO_4^- , Br^- and CO_3^{2-}), where these ions added to the aqueous phase which contains the elements of lanthanides formed compounds do not dissolved in aqueous solution⁽¹⁸⁾.They behaves as masking agent working to reduce the combination of cations with reagents⁽¹⁹⁾. Anions had a great effect on increase the values of distribution ratio and (E%) to extract Nd(III) ions by using (NAC), these ions were ($\text{Cr}_2\text{O}_7^{2-}$ and MnO_4^-) .These ions decrease hydration energy for ions and facilitate formation of complex in organic phase . This result are in agreement with the previously studies ⁽²⁰⁾ .

Table (4): The effect of adding anions to extract Nd(III) by using (NAC)

Anions	0.2% (gm/mL)		0.4% (gm/mL)	
	D	E%	D	E%
-----	4.436	81.604	4.436	81.604
$\text{Cr}_2\text{O}_7^{2-}$	7.178	87.773	5.483	84.576
PO_4^{3-}	3.441	77.485	2.896	74.333
SO_4^-	3.502	77.788	2.441	70.939
ClO_3^-	4.054	80.212	2.402	70.606
NO_3^-	7.494	88.227	3.125	75.758
CO_3^{2-}	3.161	75.970	2.034	67.042
Br^-	3.701	78.727	2.695	72.939
MnO_4^-	4.482	81.757	18.702	94.924

Aqueous phase: - (2.5 mL) solution of La(III) ion concentration of(500 μg), ($1.3865 \times 10^{-3}\text{M}$) +(2.5 mL) ,(0.2% NAC) dissolve in ethanol +(1mL) (0.2% and 0.4%) from some of the anions at (pH = 9),Organic phase: - (5 mL) of chloroform.

Equilibrium time: - fifty minutes, Temperature: - (20 ± 3) C°.

5- Effect of some cations on the extraction

A number of cations surrounding Nd(III) ion in periodic table were selected to study the influence of the extraction of Nd(III) ion by using (NAC). Table (5) shows the data of this study

Table(5): The effect of some cations in the extraction of Nd (III) with(NAC)

Cations	500 µgm/2.5mL		1000 µgm/2.5mL	
	D	E%	D	E%
-----	4.436	81.604	4.436	81.604
Cd⁺²	5.587	84.818	20.782	95.409
Hg⁺²	7.168	87.758	24.450	96.071
Ni⁺²	7.656	88.500	32.674	97.030
Mn⁺²	4.898	83.045	33.737	97.121
Co⁺²	6.783	87.151	39.000	97.500
Fe⁺³	5.215	83.909	39.500	97.530
Cr⁺³	6.701	87.015	40.000	97.560

Aqueous phase: - (2.5mL) solution of Nd(III) ion concentration of (500 µg), ($1.3865 \times 10^{-3}M$)+(2.5 mL)(0.2%NAC) dissolve in ethanol +(0.5 mL) of some cations (500 µg) and(1000µg)at (pH = 9),Organic phase: - (5mL) of chloroform.

Equilibrium time: - fifty minutes, Temperature: - (20 ± 3) C⁰.

The results in table (5) show that the extraction of Nd(III) ion by (NAC) in presence of a number of cations such as (Cd⁺², Hg⁺², Ni⁺², Mn⁺², Co⁺², Fe⁺²and Cr⁺²) is working on increasing the value of distribution ratio (D) and (E%). The reason was attributed to these cations probably absorbed at the same λ_{max} for the complex .

6- Effect of oxidation and reduction on the extraction .

The effects of oxidation was studied by adding (1mL) solution of hydrogen peroxide with concentration (35%) as an oxidant agent in extraction of Nd(III) ion with (NAC) under the experimental conditions . Distribution values of Nd(III) ion with (NAC) was calculated after separating aqueous phase from organic phase . The amount of remained ion was calculated in aqueous phase by using colorimetric method ⁽¹³⁾. To study the influence of reducing agent on (D) value to extract Nd(III) ion with (NAC) , (1mL) of SnCl₂.2H₂O solution (1M) had been added to the aqueous phase and by following the same method used with the studying the influence of oxidizing agent . Results had been obtained in the table (6).

Table (6): The effect of oxidation - reduction factors in the extraction of Nd(III) with (NAC)

Extraction	D	E%
Nd (III) with (NAC) In absence of oxidation- reduction factors	4.436	81.604
Nd(III) with (NAC) In presence of oxidation factors	3.955	79.818
Nd(III) with (NAC) In presence reduction factors	20.359	95.318

Temperature:-(20 ± 3)C⁰.

The results of this study show that the extraction processes is inefficient in presence of oxidizing agents because of its effect on the reagent. It probably works on the oxidation and changing nature of chelating reagent. As well as the oxidation of Nd(III) ion is also expected . This oxidation distorts the system of complex formation extracted. The results of reducing agent show that

distribution ratio was increased because of increasing in stability of trivalent oxidation state Nd(III) , so Nd(III) ion do not reduced by using $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$.

7-Effect of enrichment extraction on the extraction

The values of distribution ratios for extraction of Nd(III) ion was calculated from volumes ranged from (7.5- 152.5 mL) of aqueous phase by using (5 mL) of organic phase . Table (7) shows the results.

Table (7): The effect of enrichment method to extract Nd (III) by using (NAC).

Volume of Aqueous phase (mL)	Volume of Organic phase (mL)	D	E%
5	5	4.436	81.604
7.5	5	6.399	81.010
12.2	5	5.627	69.236
17.5	5	5.180	59.676
22.5	5	5.548	55.213
27.5	5	4.573	45.398
52.5	5	2.143	16.949
102.5	5	1.112	5.144
152.5	5	1.136	3.591

Aqueous phase: - (XmL) of a solution of Nd(III) ion concentration of(500 μg), ($1.3865 \times 10^{-3}\text{M}$) with (2.5mL) of (0.2 % NAC) at (pH=9),Organic phase: - (5 mL) of chloroform, Equilibrium time: - fifty minutes, Temperature:-(20 ± 3) $^{\circ}\text{C}$.

The results of table (7) show the possibility to extract Nd(III) ion by the reagent (NAC) under study from large volumes of aqueous phase , but in low distribution ratio and (E%) was an efficient . The results of this study approved with other recent studies ⁽²¹⁾.

8-Effect of metal ion concentration

Nd(III) ion was extracted from aqueous solution which containing increasing concentrations of the ion ranged from (12.5 $\mu\text{g}/2.5\text{mL}$ to 1250 $\mu\text{g}/ 2.5\text{mL}$) , ($3.4664 \times 10^{-5}\text{ M}$ to $3.4664 \times 10^{-3}\text{ M}$) with the reagent(2.5 ml),(0.2% NAC) and within the best conditions reached from the previous experiences of this study. Results of this study was described in figures (3).

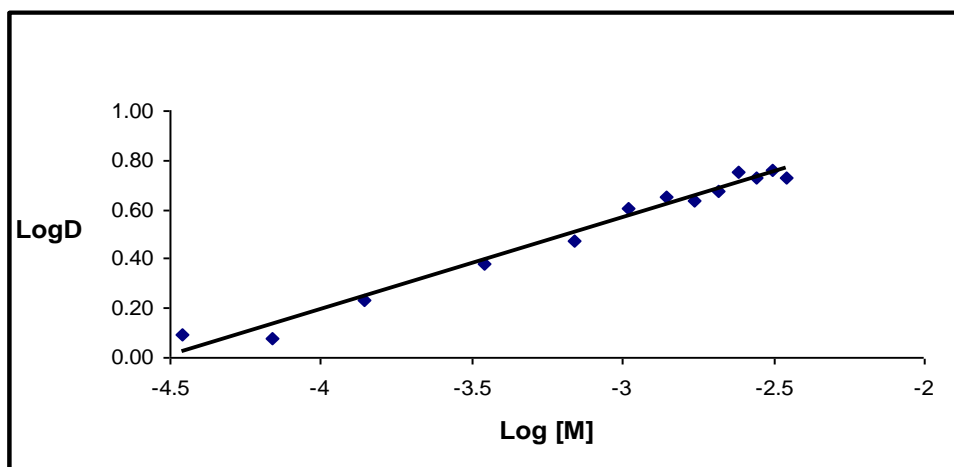
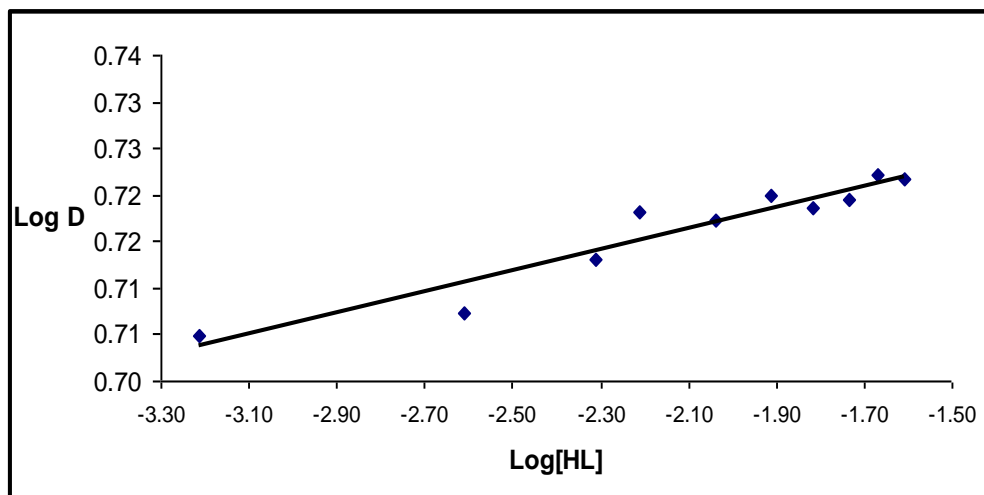


Figure (3) The effect of different concentration of Nd(III) by using (NAC) in the extraction.

Figure(2) show that the value of (D) increased with increasing concentration of Nd(III) in aqueous phase when extracted by (NAC) , It should be noted that this expected behavior due to continued interaction between the ion and NAC .Thus enhancing fully interaction in constant mole ratio without any adduct that leads to deviation from the linearity. This results are in agreement with the previously studied ⁽²²⁾.

9-Effect of reagent (NAC) concentration on the extraction.

Values of distribution ratios was calculated to extract a fixed amount of Nd(III) (3.4568×10^{-3} M), (1250 $\mu\text{g}/2.5$ ml) ion by different concentrations of reagent (NAC) under the experimental conditions. The results of this study illustrated in figure (4).



Plots of Log D vs. Log NAC gave straight line . An expected result to increase the extraction of Nd(III) ion with (NAC) according to the following equation: -

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

The results of this study approval with the results of a recent study ⁽²³⁾.

10-Effect of salting out on the extraction

Table (8) shows that the value of distribution ratio (D) to extract Nd(III) ion with (NAC) increased in the presence of salting factor. The reason for this could be attributed to that salting process decreased hydration energy for Nd(III) extracted and lead to facilitate replacement of water molecules with reagent molecules ⁽²⁴⁾ . This result are in agreement with the previously studies ⁽²⁵⁾.

Table (8): The effect of salting to extract Nd (III) with (NAC).

Extraction conditions	D	E%
Nd(III) with (NAC) In absence of salting factor	5.248	83.994
Nd(III) with (NAC) In presence of salting factor	12.377	92.524

Aqueous phase: - (2.5mL) of a solution of Nd(III) ion concentration of(1250 μg), (3.4664×10^{-3} M) with (2.5mL) of (0.2 % NAC) at (pH=9),Organic phase: - (5 mL) of chloroform, Equilibrium time: - fifty minutes, Temperature:- (20 \pm 3) $^{\circ}$.

11- Effect of batch method on the extraction

The effect of using batch extraction to extract (1250µg),(3.4664x10⁻³ M) Nd(III)ion with (NAC) was studied. Extraction held in three stages after partition of organic phase into three volumes. Equal volume for each extraction stage has been part of this phase . Values of distribution ratio had been calculated after the end of part three of extraction process , table (9) show the results of this study.

Table (9): The influence of batch method in the extraction of Nd (III) with (NAC).

Extraction Technique	D	E%
Nd(III) with (NAC) Continuous extraction	5.248	83.994
Nd(III) with (NAC) Batch extraction	6.392	86.473

Temperature:-(20±3)C°.

The results of table (9) show increasing in the values of distribution ratio (D) and (% E) for Nd(III) ion extraction with (NAC), so using a single batch extraction save effort and time.

12-Effect of temperature

Extraction of Nd(III) ion from aqueous solution at optimum by temperature from (15-45 C°) as illustrated in table (10) .

Table: (10) The values of distribution ratios for the extraction of Nd(II) ion by using the reagent (NAC) at different temperatures.

T(K)	1/T*10 ⁻³	D
15	3.470	4.920
20	3.410	5.248
25	3.350	5.405
30	3.300	5.944
35	3.240	6.827
45	3.400	9.120

Aqueous phase : - (2.5mL) solution of Nd(III) ion concentration (1250 µg) , (3.4664x10⁻³ M) with (2.5 ml) of (0.2 %NAC) dissolve in ethanol at (pH = 9).

Organic phase: - (5mL) of chloroform, Equilibrium time: - fifty minutes, Temperature: - (x) C°.

By using Vant-Hoff Equation: ⁻⁽²⁶⁾

$$2.303 \text{ Log } K_{\text{ex}} = \frac{-\Delta H}{RT} + C \dots\dots(3)$$

By drawing the relationship between Log D versus 1 / T the figures (5) had been obtained and the value of enthalpy (ΔH_{ex}) had been calculated.

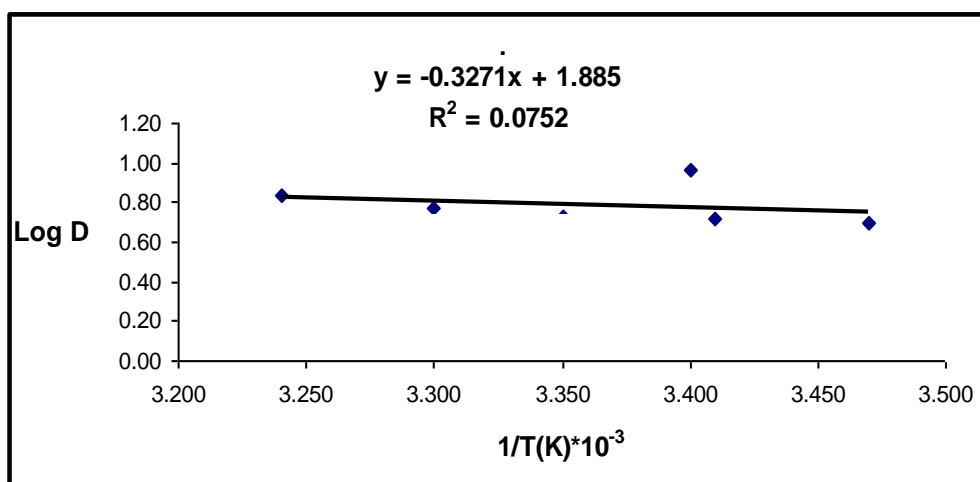


Fig.(5) The effect of temperature to extract Nd(III) by using(NAC).

The results in figure (5) demonstrate that the reaction between Nd(III) and ligand(NAC) was endothermic .

Values of (ΔG_{ex}), (ΔS_{ex}) were calculated by using Gibbs equations described below ⁽²⁶⁾: -

$$\Delta G_{ex} = \Delta H - T\Delta S \dots\dots(4)$$

$$\Delta G_{ex} = -RT \ln K_{ex} \dots\dots(5) \quad , \text{ where } \text{Log } D = \text{Log } K_{ex}$$

Table (11) The values of thermodynamic functions to extract Nd(III) by using (NAC).

T (K)	$\Delta H(\text{Kj.Mol}^{-1})$	$\Delta G(\text{Kj.Mol}^{-1})$	$\Delta S(\text{Kj.Mol}^{-1}\text{K}^{-1})$
15	15.301	-3.809	0.0663
20	15.301	-4.032	0.0659
25	15.301	-4.173	0.0653
30	15.301	-4.483	0.0653
35	15.301	-4.910	0.0656
45	15.301	-5.834	0.0665

From the results in table (11) the positive sign of the values of enthalpy show that the reaction between Nd(III) ion with (NAC) was Endothermic and thus means increase in the possibility of formation extract complex with increasing temperature ,while the negative sign of free energy for extraction demonstrate that reaction is and this is favorite thermodynamically in high temperature this study agree with a lot of studies⁽²⁷⁾.

13-Stoichiometry determination

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

a. Job's method :

The results in figure (6) demonstrate that the more probable structure of Chelate complex extraction was (1:3)(M: L) identify with the results of mole ratio for structure which is [Nd (NAC)₃].

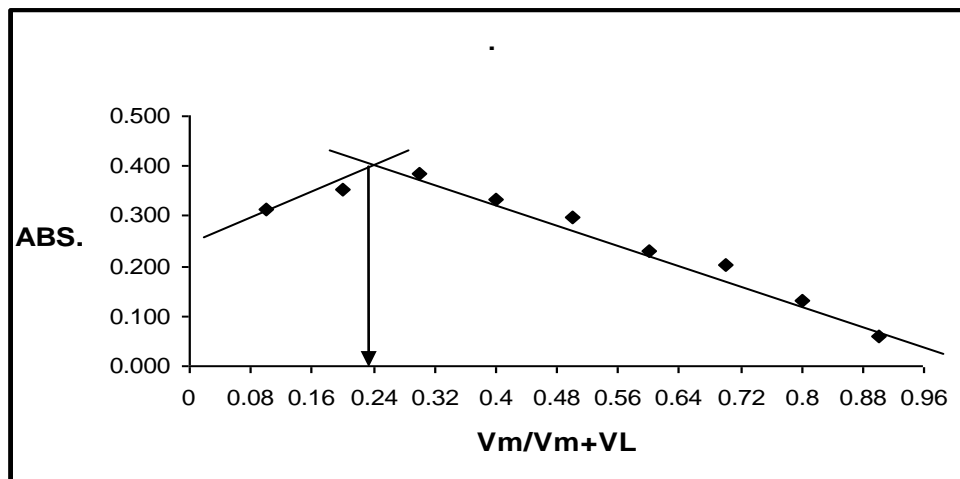


Fig.(6) Job's method (continuous variables) for the Nd(III) ion with (NAC) dissolved in ethanol .

b. Mole ration method

The results in figure (7) for mole ratio method study demonstrate that the more probable structure of chelate complex extraction was (1:3) (M: L) [Nd(NAC)₃] which is identify with the results in Job's analysis.

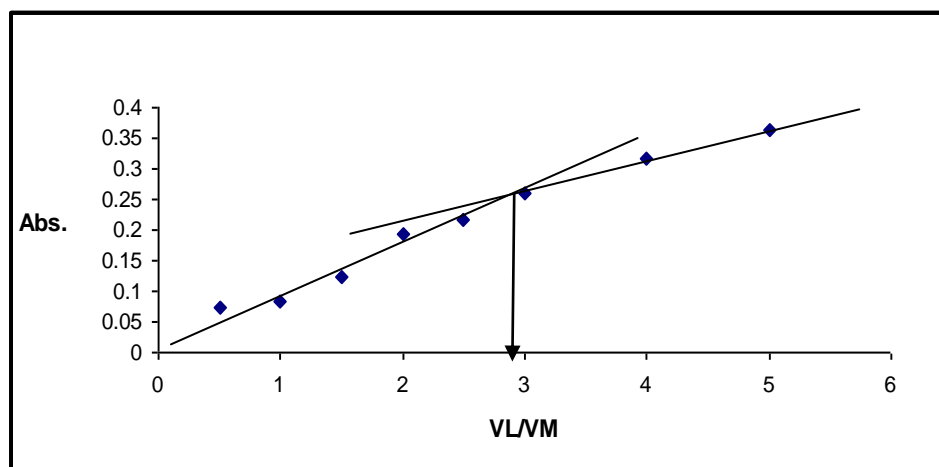
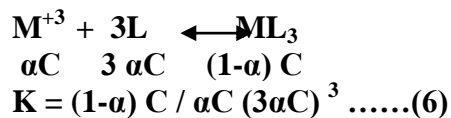


Fig.(7) The molar ratios method to extract Nd(III) by using(NAC)

Study the stability for the extracted complex in organic Phase.

Stability constant of the extracted complex in the organic phase was calculated (ML_3) by drawing the equilibrium reaction for extracted complex



$$\alpha = \frac{A_m - A_s}{A_m} \dots\dots(7)^{(28)}$$

- where α : the degree of dissociation.
- C : Concentration of metal.
- K : Stability constant.
- A_m : The greatest absorption.
- A_s : Absorption at the end point.

Table (12) Data of dissociation constant and stability constant for extracted complex.

Complex	A_m	A_s	α	$K_{sta.}$
Nd(NAC) ₃	0.364	0.261	0.2829	4.8857×10^{16}

(UV –Vis.) spectrum

1- The (UV –vis.) spectrum for the ligand (NAC) (at pH=9) dissolve in ethanol, figure (8) exhibits a high intense absorption peak at (241nm).

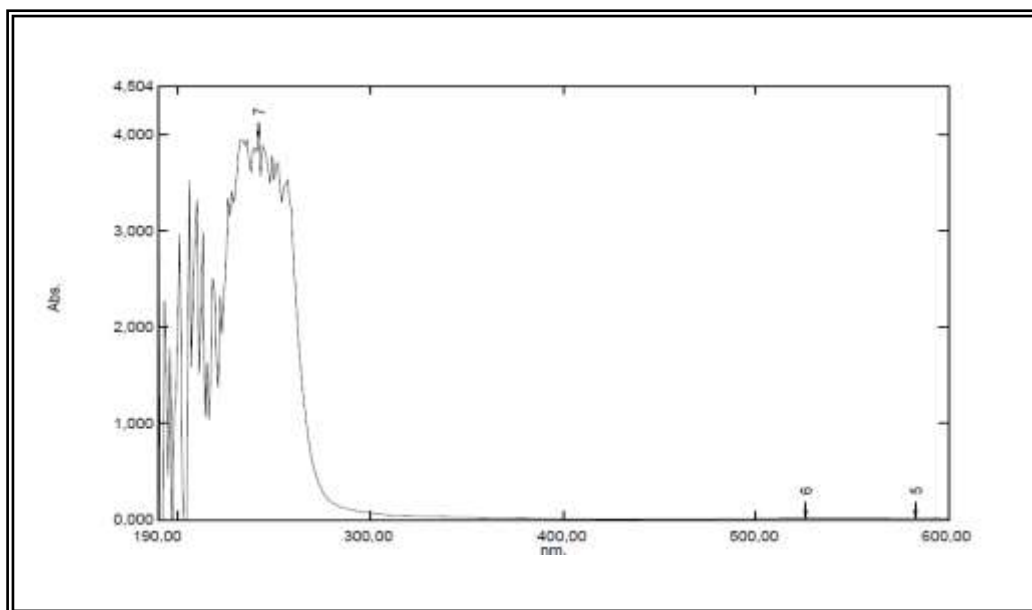


Figure (8) Electronic spectral data of the ligand (NAC)

2- The (UV –vis.) spectrum for the complex $[\text{Nd}(\text{NAC})_3]$, figure (9) exhibits a high intense absorption peak at (252 nm) which used to measured absorption of the complex .By comparing absorption spectrum of ligand there was red shift for complex.

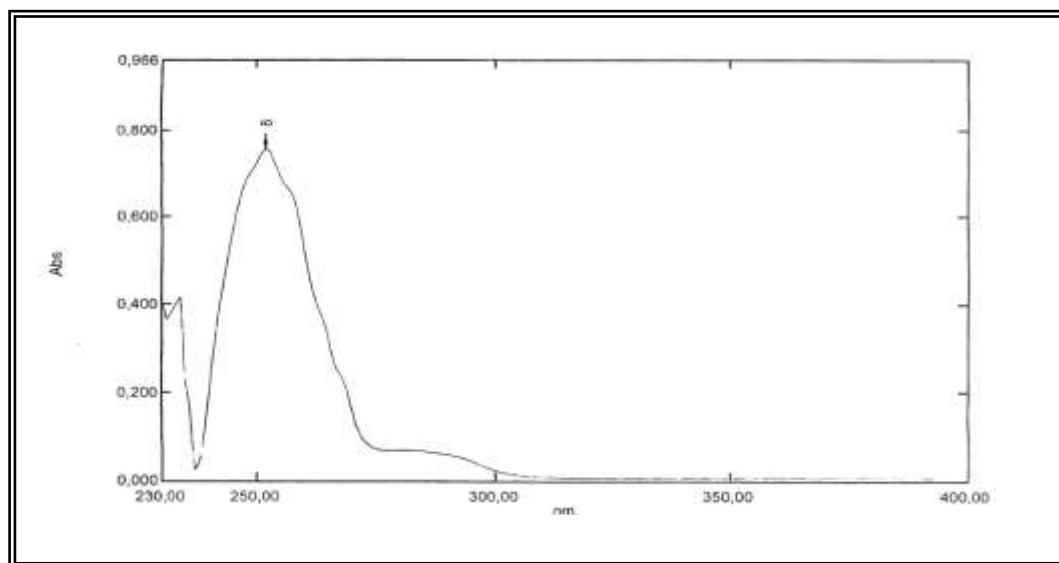
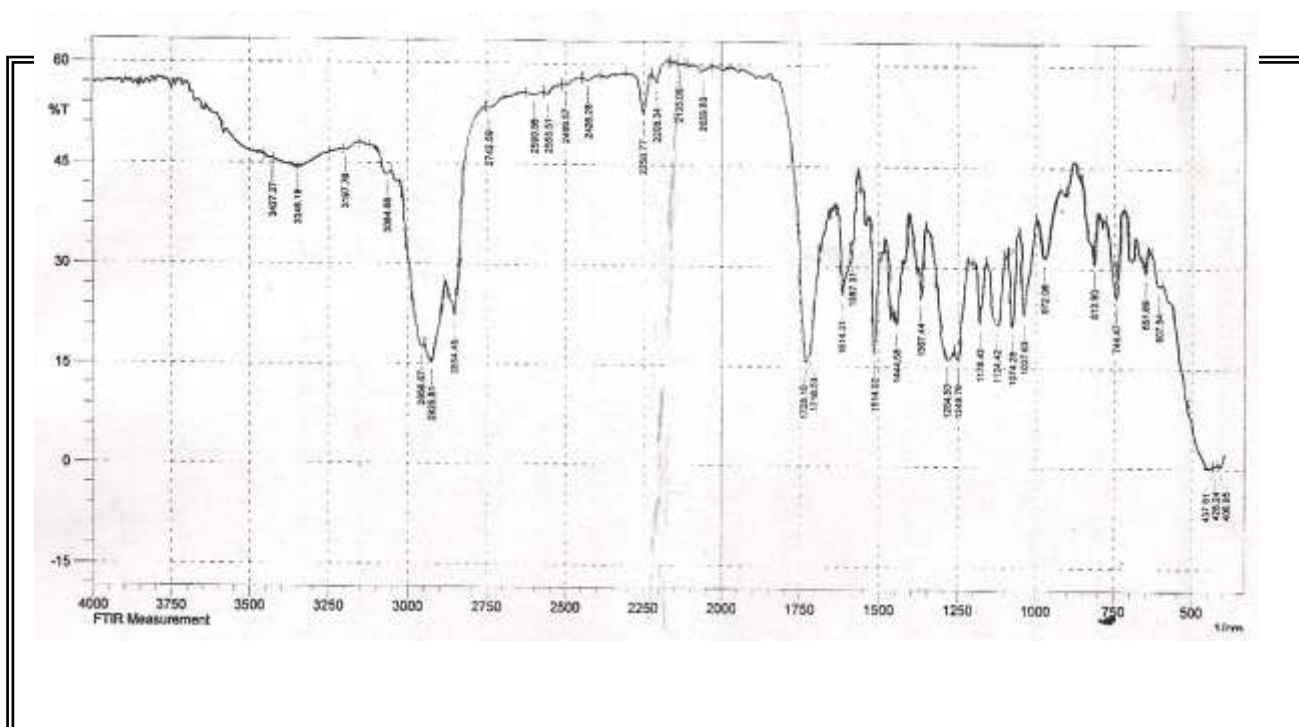


Figure (9) Electronic spectral data of the complex $[\text{Nd}(\text{NAC})_3]$

I.R spectrum

Figures (10) and (11) display the I.R spectrum for the (NAC) and the complex which exhibit bands in table (12).(NAC) coordinate link to metal through the oxygen of O-H group and electron pairs in N-H group .

Figure (10) Infrared spectrum of ligand



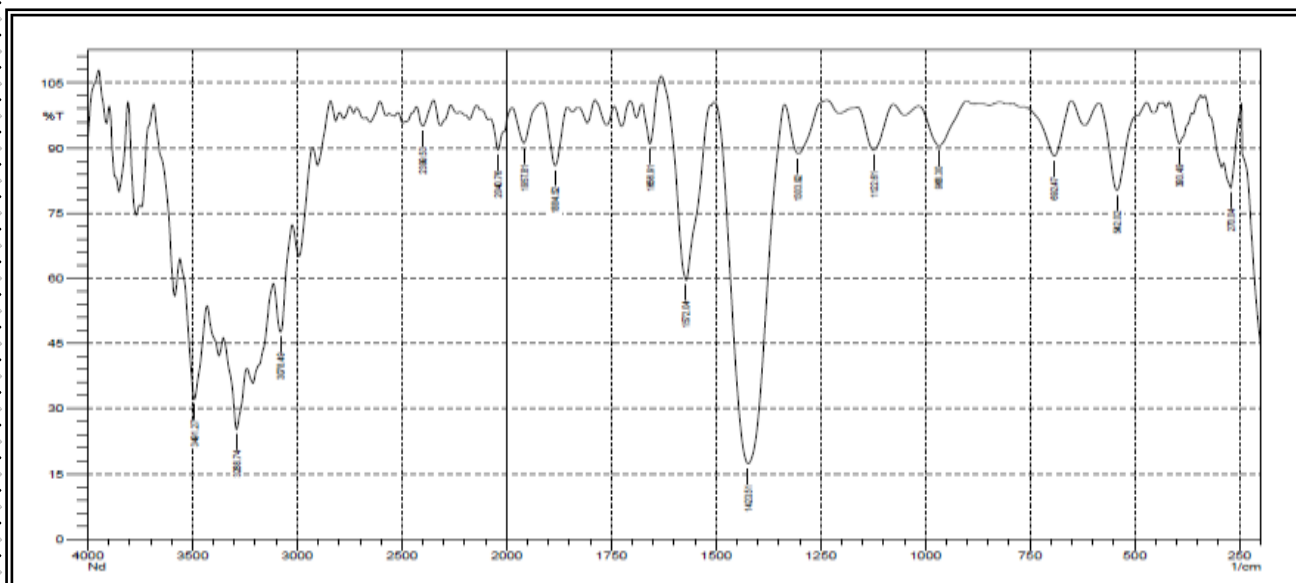


Figure (11) Infrared spectrum of complex

Table (13) Result of I.R spectrum for ligand and complex

Compound	Stretching vibration ν N-H	Amide group ν C=O	Acidity ν C=O	Bending Vibration ν O-H	δ N-H	δ O-H	ν S-H	ν M-O	ν M-N
Ligand	3380-3275	1623-1610	1742	3093-2891	1569-1521	1348-1272	2563-2522	-----	-----
complex	3288.74-3078	1658.84	1421.58	-----	1572.04-1124.54	-----	2560	395	450-500

Some physical properties of the extracted complex :-

1- Melting point

Melting point of extracted complex was measured. It was found (240 -242C^o) while melting point for Ligand (NAC) was (160-163C^o), so this complex was thermal stable.

2- Electrical conductivity

Table (14) show that the value of electrical conductivity of extracted complex at room temperature approaches to the conductivity of solvent so the conductivity for complex can be neglected

Table (14) Electrical conductivity

Material	Electrical conductivity μ S.cm ⁻¹
Chloroform	0
Complex	0.4

Statistical treatment of data

Relative standard deviation dependent as a measure for precision of data in all experiments . For this purpose extraction done in (0.347x10⁻³M)and (0.693x10⁻³M) of Nd(III)by using (2.5 mL) of reagent (NAC) dissolved in ethanol with (5mL)chloroform as organic phase .The results obtained in table(15) shows that (RSD)in permitted rang in the experimental .

Table (15) Statistical treatment of data

Exp.NO.	Abs. $0.347 \times 10^{-3} M$	Abs. $0.693 \times 10^{-3} M$
1	0.484	0.830
2	0.475	0.835
3	0.500	0.827
4	0.487	0.844
RSD%	2.1262	0.8919

The suggested figure for complexes

From the results in this study , The stiochiometry of complex (M:L) was found to be (1:3)
 .The suggested figure of complex explained in figure (12)

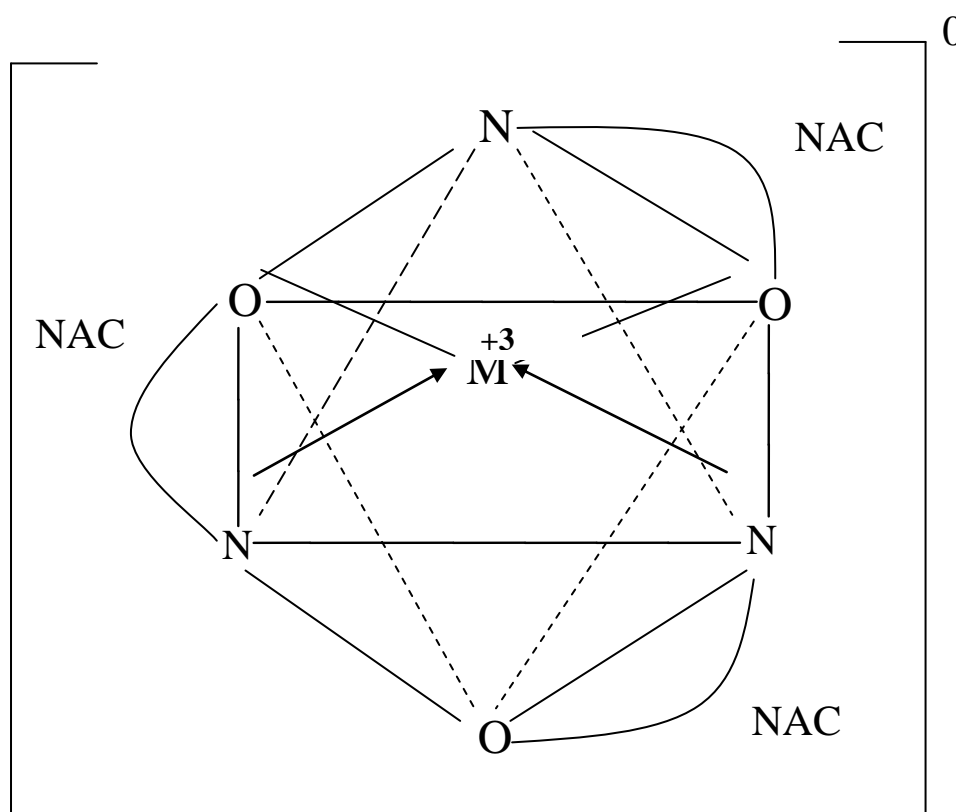


Fig. (12) the suggested figure for the complex

Where $M^{+3} = Nd^{+3}$

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