Efficient Method Cloud Point Extraction for Separation Preconcentration and Trace amount Determination of Bismuth (III) from Different Samples by New Laboratory Prepared Azo Derivative

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Abstract

By cloud point extraction methodology extracted Bi (III) after produced ion association complex with new laboratory prepared azo derivative AMIBSHA,in presence non-ionic surfactant Tritonx-100, the experiments show complex formation performed at pH=9 and heating for 20 minute at 90°C, the research involved determination all optimum values effect on the extraction efficiency, in addition to thermodynamic study and stoichiometry as well as interferences studies and electrolyte effect. With spectrophotometric determination in different samples. With detection limit $=(7.764 \times 10^{-7} \mu g.mL^{-1})$ and Sandell's sensitivity $(9.749 \times 10^{-10} \mu g.cm^{-2})$ and $\varepsilon = 21480.8$ L.mol^{-1}.cm^{-1} and RSD% =0.00541.

Keywords: Bismuth(III) , Cloud point layer ,Tritonx-100.

Introduction:

Bismuth is the last element in group (Va) of periodic table with an important properties and usages .There is many procedures used for separation and determination It in different samples as well as in general these methods used for separation preconcentration elements other than bismuth. In very sensitive method used cloud point extraction to microamount separation and determination of lead (II) and cadmium (II) by used 2-[(Benzo thiazolyl) azo]4-benzyl phenol and 2-[(3-Bromo phenyl)azo]-4,5-diphenyl imidazole respectively and study all optimum condition and effective parameters on extraction Efficiency [1]. The study aboutseparation preconcentration. Coupled with suitable spectrophotometric determination of Nickel (II) from HCl acidic media as chlorocomplex anion by use crown ether DB18C6 according to cloud pointextraction method as well as in presence optimum concentration of NaCl , this study demonstrate the wave length for maximum absorbance was (λ_{max}=295nm), for the ion pair complex extracted to the cloud point layer CPL as well as this study involved limitation optimum conditions for favorable extraction and many parameters effective on the extraction efficiency in addition to thermodynamic study[2].From acidic HCl media separated , extracted and spectrophotometric determination of zinc(II) as chloroanionby use 3[(2-pyridyl azo)]-1-nitroso 2-naphthol by application cloud point extraction method. With DL=0.0292 ppm and Sandell's sensitivity = 63×10^{-9} µg/cm$^{2[3]}$,By CPE method extracted and separated platinum(II) from acidic HCl media as chlorocomplex anion to form ion association complex with Janus green, spectrophotometric study appear wave length for maximum absorbance to ion association complex extracted to cloud point layer was λ_{max}=690 nm , and extraction efficiency recorded detection limit= 6.8028×10^{-6} and Sandell's sensitivity was 0.003133 µg.cm^{-1} with R.S.D= 0.00888 [4] separation and preconcentration of trace amount of lead in food and water as determination. by FAAS , by use rapidly synergism cloud point extraction (CBS-CPE), this method accomplished in room temperature and by use nonionic surfactant Tritonx-114 , as synergic reagent used octanol , as well as this study involved determination the optimum condition and parameter effect on extraction efficiency such as pH , amount of octanol , amount of Tritonx-114, extraction time and interferencesWith D.L=1.6 µL$^{-1[5]}$.For preconcentration and determination of nickel and cloud point extraction method coupled with UV-VIS spectrophotometric determination, by formation complex with 1,5-bis(di-2-pyridylmethylene) thiocarbonohydrazide at pH= 5.4 in buffer acetate and used Tritonx-114 , the optimal condition of extraction were studied , this study show detection limit was 15 µg.mL^{-1} wave length for maximum absorbance of Nickel complex was (λ_{max}=458nm) [6] Trace gold (III) extracted by CPE methodology so that preconcentration and determination by (AAS) , complexing agent used was sulphathiazolyl azo resorsin and non-ionic surfactant Tritonx-100 , detection limit 0.75 µgL^{-1} the extraction at pH=4 and 1×10^{-5}M sulphathiazolyazoresorsin[7] . For simple spectrophotometric determination of selenium used complex formation with dithiazone bycloud point extraction using Tritonx-100 from 0.4 M HCl media[8]. Cloud point extraction method with molecular spectroscopy used for determination. Norfoxacin and iron(III) in biological pharmaceutical samples. The drug norfoxacin reacts with Fe(III) ions in dilute acidic medium and form complex Fe(III)(NOR) this complex extracted to cloud point layer Tritinx-114 [9]. By application CPE method and AAS determined lead , cadmium and palladium in some food and biological samples with complexing agent 3-(1-(1-H-Indol-3-yl)-3-phenylallyl)-1H –indole at pH=8 evaluated all variablessuch as pH , amount of ligand, Tritonx-114, temperature and heating time [10]. By used new synthesized reagent 3,5-

dimethoxy-4-hydroxy benzaldehyde isonicotinoyl hydrazone for separation ,preconcentration and determination. Gold(II) in presence non-ionic surfactant Tritonx-100 and acidic media at pH=4 .The molar absorptivity for complex $1.14×10^5$L.mol^{-1}.cm^{-1} and Sandell'ssensitivity is 0.004587 μg/cm^2[11]. Ultra trace levels of palladium preconcentrated and determined in real samples by 1-(2-pyridyl azo)-2-naphthol (PAN), from acidic HCl medium in presence non-ionic surfactant Tritonx-114 ,cloud point layer dissolved in concentrated HNO$_3$ after phase separation and the determination of element by electrothermal atomization . The optimum conditions of extraction was pH=4.5 and cloud pointtempreture 55˚c with $1.2×10^{-4}$M PAN[12]. For the extraction of Bi(III) from thiocyanate and sulphuric acid media used N-n-hexylalanine in xylene in 1.5% concentration , and thiocyanate 0.3-0.7 and HCl 0.1-3M as well as the complex extracted was [RR′ NH$_2$$^+$Bi(SCN)$_4$$^-$] [13]. By using sodium hexamethyleneimicarbodithioate NaHMICd$^+$.2H$_2$Oas chelating agent for spectrophotometric determination of Bi(III) , The complex formation at pH range 1-3 with $λ_{max}$=370nm , withstoichiometry 1:3 (M:L) and molar absorptivity $1.04233×10^4$L.mol^{-1}.cm^{-1}and Sandell's sensitivity0.0202 μgcm^{-2}[14] .By use of dithiazone as complexing agent separated and extracted microamount of Bi(III) at pH=9 and 0.042 mmol.L^{-1} concentration of dithiazone as well as study effect of extraction time, salt , Interferences[15].

Experimental

All absorbance measurements and absorption spectra were carried out by using Biochrom double-beam: M(80-7000-11) Libra s60 cambridge CB4 0FJ England.
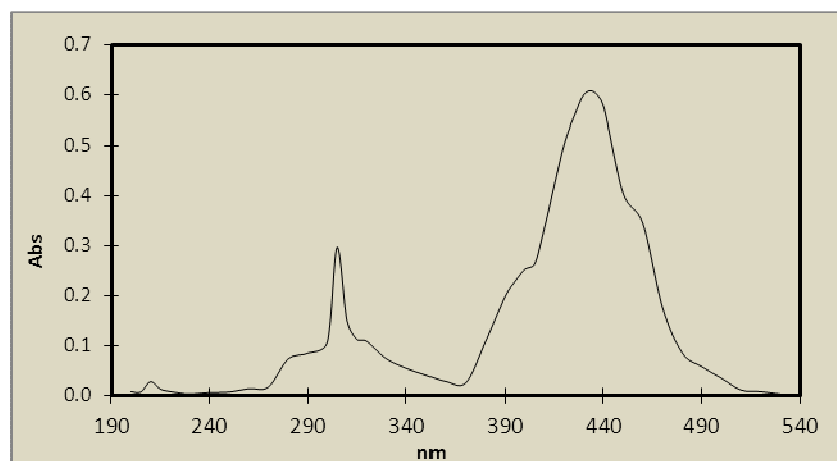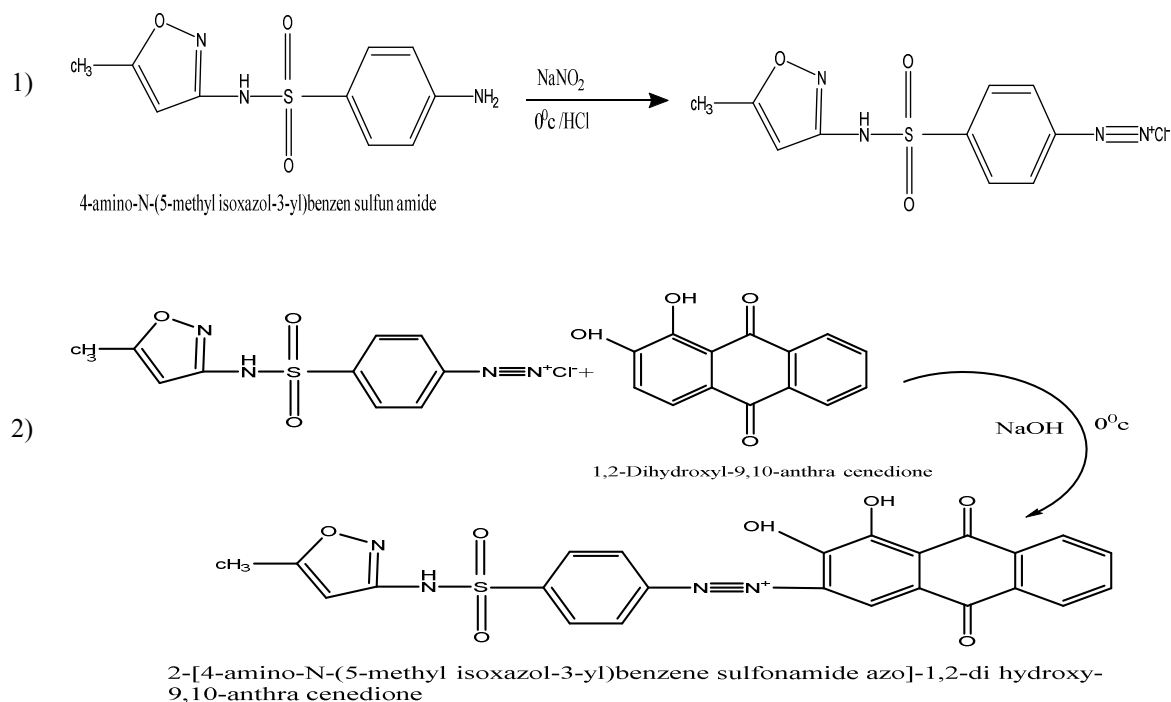
For the checking pH of the solution used pH meter (HANNA Germany) and for CPE experiments used Thermostatic water bath (WNB7-45) (England) .FTIR-spectrophotometer was FTIR 8400S, Shimadzu corporation, serial No.A21274501282LP , Kyoto Japan.

Chemicals and solutions

All materials and reagent used as received from companies without more purifications, stock solution of Bi^{3+}at concentration of 1mg/mL prepared from Bi(NO$_3$)$_3$.5H$_2$O (Merck 99.9%) by dissolved 0.232 gm in 100 mL of (1:3) Nitric acid solution in volumetric flask , but other working solution prepared by dilution with 0.01 M HNO$_3$ by used suitable volumetric flask . Tritonx-100 which is non-ionic surfactant was purchased from (Sigma ultra->99.6%) (UK) and ammonium chloride (98.5%) , Hydrochloric acid (37%) ,potassium cyanide (99%) were purchased from BDH(UK),Dithiazone Fluka purchased (99.4%), solution of $1×10^{-2}$M from dithiazone prepared by dissolved 0.02565gm in 10mL CCl$_4$ by used volumetric flask ,other working solutions prepared by dilution with CCl$_4$ in suitable volumetric flask. All other chemical obtained from different company with high purity.

## Synthesis and characterization of new reagent

New reagent 2-[4-amino-N-(5-methyl isoxazol-3-yl)benzene sulfonamide azo]-1,2-dihydroxy-9,10-anthracenedione (AMIBSHA) synthesized according to procedure detailed[16].by dissolving (7.53gm 0.03mole) of 4-amino-N-(5-methyl isoxazol-3-yl)benzene sulfonamide in mixture of 4mL of concentrated HCl and 25mL of distilled water, keep the solution at 0°C, then added 2.0gm of sodium nitrite dissolved in minimum quantity of distilled water without change the temperature from 0°C, and to complete the reaction of diazotization the mixture was set aside for 15 min. afterward diazonium solution added drop by drop into beaker containing (7.59gm 0.03mol) of 1,2-dihydroxy-9,10-anthra cenedione with 1.2gm sodium hydroxide dissolved in 150 mL ethyl alcohol and keeping temperature at 0°C,at the end of addition left The solution for two hours, then added 150mL of cooled distilled water and maintained pH of the solution at(6), then left the solution 24 hours, the solid product filtered off, washed with cold water, recrystallized from hot absolute ethanol and dried over CaCl$_2$,as well as the UV-VIS spectra for synthesized organic reagent as in Figure(1).

1)

4-amino-N-(5-methyl isoxazol-3-yl)benzen sulfun amide

$NaNO_2$
0^0c /HCl

2)

1,2-Dihydroxyl-9,10-anthra cenedione

NaOH 0^0c

2-[4-amino-N-(5-methyl isoxazol-3-yl)benzene sulfonamide azo]-1,2-di hydroxy-9,10-anthra cenedione

Figure(1) :UV-VIS spectrum for organic reagent

The UV-Vis spectra for the synthesized organic reagent 2-[4-amino-N-(5-methyl isoxazol-3-yl)benzene sulfonamide azo]-1,2-dihydroxy-9,10-anthracenedione (AMIBSHA) show three distinct absorption peak, the first at wave length 213 nm due to π-π* in benzene ring [17] and the second peak at 305nm due to π-π* transition in aromatic rings [18]as well as the third peak at 433nm due to interior intra molecular charge transfer n-π*which is belong to the –N=N- bridge azo, this finding in spectra was in harmony with elsewhere foundation [19].

But IR spectrum in Figure(2):
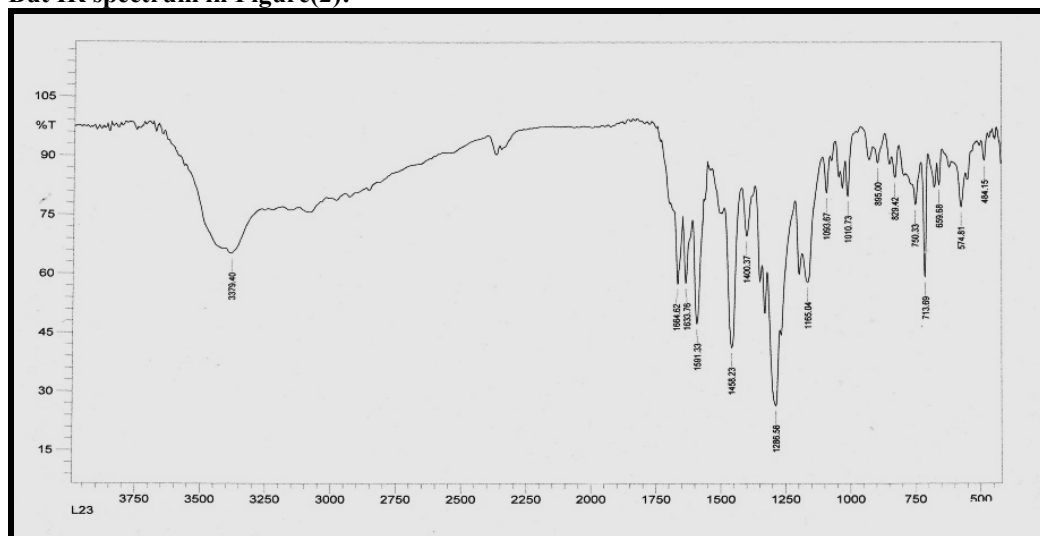
Figure(2) :FTIR spectrum for organic regent.

The spectra show absorption band in 3379 cm^{-1} belong to O-H as well as a weak band showed at 659 belong to O-H out of plane bending vibrations, this band at 3379 may be interfere with absorption bond for N-H. The absorption bandat 1664 cm^{-1}belong to stretching vibration of C=O in the ring as well the strong band at 1591cm^{-1} due to N-O stretching vibration but strong absorption band at 1458 cm^{-1}due to –N=N- , the C=N appear stretching and bending vibration at 1633cm^{-1}and 1400cm^{-1}. Absorption band at 1156 cm^{-1}belong to stretching vibration of O=S=O isolated stretching vibration of O-H appear at absorption band 1286cm^{-1}, absorption band at 1093cm^{-1} due to ring structure of oxazol.

So that elemental analysis show the results in Table(1).

Table (1): elemental analysis.

Element	Theoretical	Experimental
%C	57.14	57.08
%H	3.17	3.15
%N	11.11	11.04
%O	22.22	22.17
%S	6.35	6.31

From all this studies the suggested structure of organic reagent is in mechanism equation was true.

Comprehensiveprocedure

10mLaqueous solution contain fixed quantity of Bi^{3+}and controlled the pH at optimum value, as well as presence 1×10^{-4}M (AMIBSHA) ,and 0.5mL of 1% Tritonx-100 afterward heating the solution in electrostatic water bath at optimum temperature and time, until produce cloud point layer (CPL) with smallest volume and highest density , then separate the CPL from aqueous solution, and dissolved cloud point layer in 5 mL ethanol to measure its absorbance at wave length of maximum absorbance of complex extracted to cloud point layer against blank prepared at the same manner without Bi^{3+}ion, But aqueous solution treated according to spectrophotometric dithiazone method[20] to determine the remainder quantity of Bi^{3+}in aqueous solution after extraction by return to calibration curve Figure(3), thereafter the remain quantity of Bi^{3+}subtraction from the original quantity to determine the transferred quantity to the cloud point layer and then divide transferred quantity on the remain quantity to calculate the distribution ratio (D). as well as by application the stripping method to determination the transferred quantity. Shaking cloud point layer with three 5 mL portion of middle concentration hydrochloric acid, after transferred Bi^{3+}ion from the cloud point into aqueous HCl medium then determined by spectrophotometric dithiazone method[20], the experiments show quantity of Bi^{3+}ion determined by stripping is equal to the same quantity determined by subtraction remainder quantity from the origin quantity then for all experiments used subtraction to determine the transferred quantity because easier and faster.

Results and Discussion

Spectrophotometric study on the complex extracted to the Cloud point layer involved taken 10mL aqueous solution contain 50μgBi^{3+}ion at pH=8-9 and 1×10^{-4}M(AMIBSHA) with 0.5mL 0f Tritonx-100, heated the solution in electrostatic water bath between 80-90°C for 15 minute until form the cloud point layer, then separated cloud point layer (CPL) and dissolved in 5mL ethanol and taking the spectrum for the ethanolic

solution against blank prepared at the same manner without Bi^{3+}ion, the spectrum in Figure (4) demonstrate wave length of maximum absorption for complex was (λ_{max}=550nm).
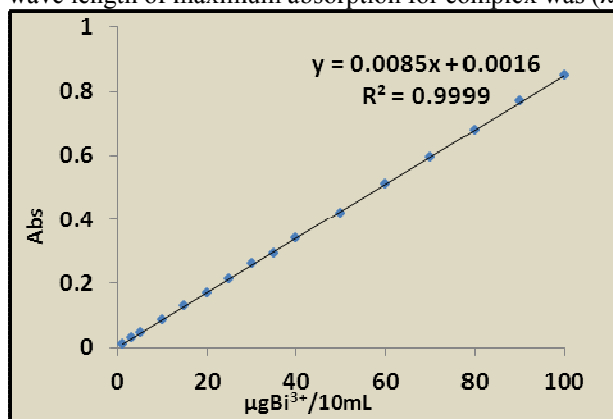

Figure(3) :Calibration curve for Dithiazone method.
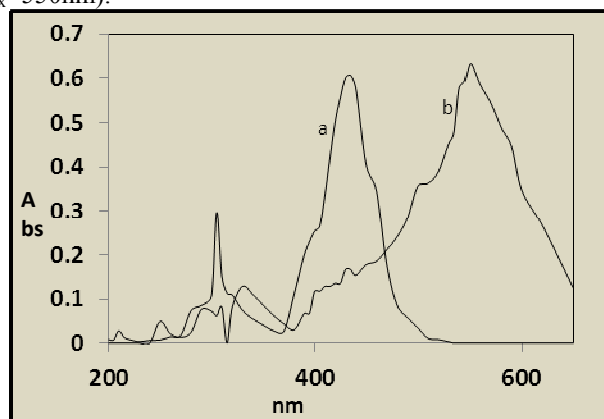
Figure(4): UV-Vis spectrum a)organic reagent (AMIBSHA) . b)Bi^{3+} complex.

Effect of pH

According to comprehensive procedure extracted 40μgBi^{3+}in 10mL aqueous solutions in presence 1×10^{-4} M (AMIBSHA) and 0.5mL of 1% Tritonx-100 at range (pH=5-12),heated all solutions in electrostatic water bath at suitable temperature and time until form (CPL) , at latter dissolved CPL in 5mL ethanol after separated and measure the absorbance against blank prepared at the same manner without Bi^{3+}. But aqueous solutions treated according to spectrophotometric determination (dithiazone method)the results was as in the Figures(5,6).
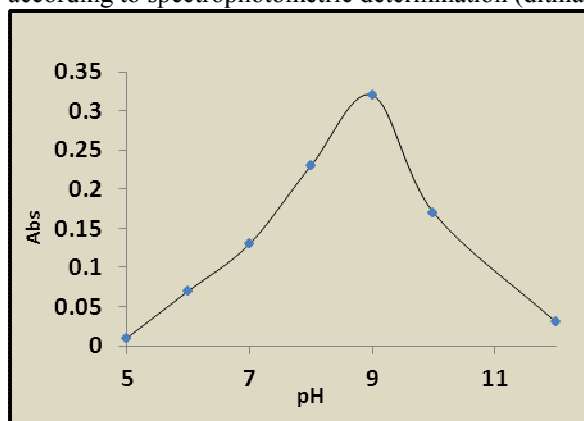
Figure(5): complex extracted formation depend on pH of aqueous solution.
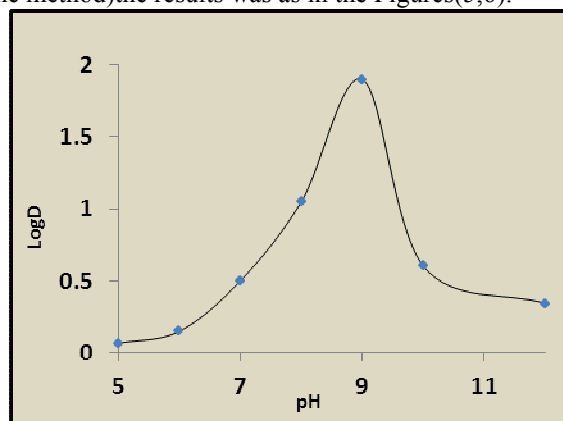

Figure(6): D = F(pH)

The results demonstrate the optimum pH of extraction was pH=9,at this pH complete equilibrium for complex formation happen and giving higher quantity of complex extracted into (CPL), any pH less than optimum value not allow to reach equilibrium of formation and effect to decline extraction efficiency, but pH more than optimum value effect to increase extraction ability also because Bi(III) produce stable Bismuth hydroxide and change into $Bi_2O_3.nH_2O$ appear as precipitate in solution.

Effect of metal ion concentration

10mL aqueous solution contains different quantity of Bi^{3+} ion (5-60)μg at pH=9 and in presence 1×10^{-4} M(AMIBSHA) and 0.5mL 1% Tritonx-100, heated this solutions in electrostatic water bath for suitable temperature and time until produce (CPL) then according to the comprehensive procedure measure the absorbance of ethanolic CPL as well as calculate D-value . The results was as in Figures(7,8).
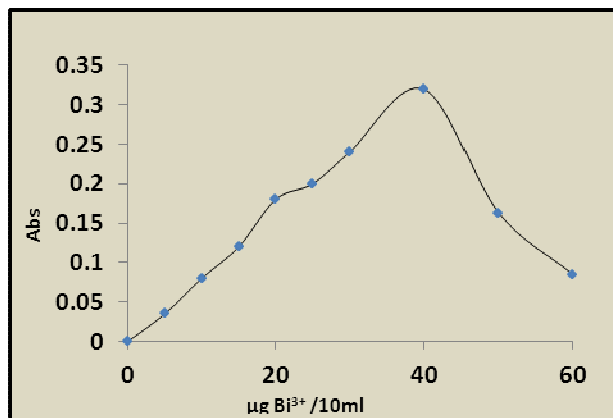
Figure(7): Complex formation change with Bi^{3+} concentration change.
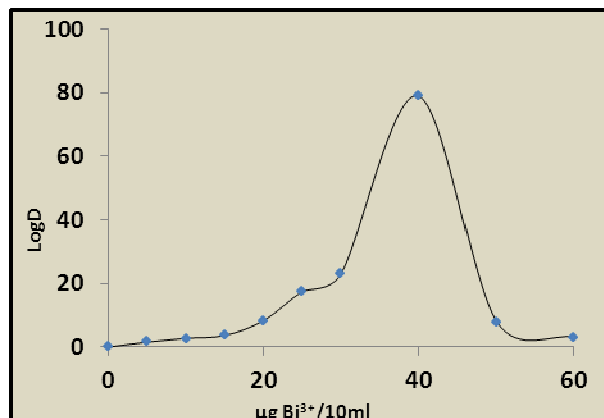
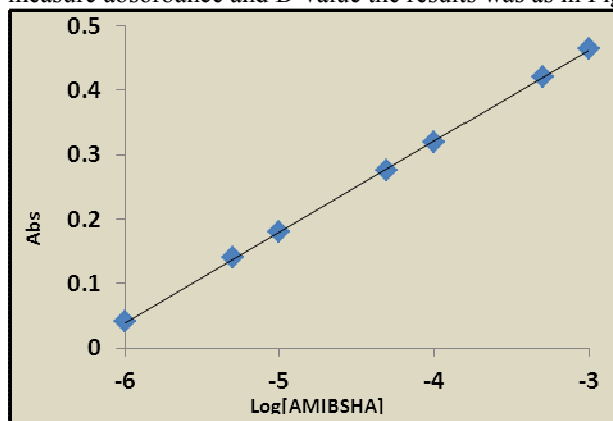**Figure(8): extraction efficiency effect with Bi^{3+} concentration.**

The result show optimum quantity of Bi^{3+} was 40μg/10mL giving higher absorbance and D value because this quantity giving the best equilibrium for complex formation. And produced higher concentration of complex extracted. As in equilibrium below:

$$Bi^{3+}+AMIBSHA+2NO_3 \rightleftharpoons [Bi(AMIBSHA)]^{2+};2NO_3^-$$
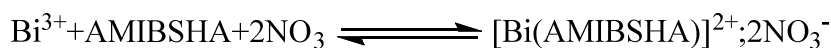
From the equilibrium show Bi^{3+} concentration help to increase the rate of forward reaction and formation, complete that is in optimum quantity of Bi^{3+}(40μg), But any quantity of Bi^{3+} less than 40μg being not enough to complete the equilibrium of complex formation and decrease extraction efficiency as well as at Bi^{3+} more than optimum also decrease absorbance and D value according to mass action law and Le chatelier principle.

Effect of AMIBSHA concentration

Aqueous solutions 10mL in volume contain 40μg Bi^{3+} ion at pH=9 and in presence AMIBSHA at different concentrations 1×10^{-6}-1×10^{-3}M and 0.5mL 1% Tritonx-100,heated these solutions in electrostatic water bath at suitable temperature and time until produce CPL. Complete according to comprehensive procedure detailed and measure absorbance and D-value the results was as in Figures (9,10).

Figure(9): extraction efficiency change as afunction of AMIBSHA concentration.
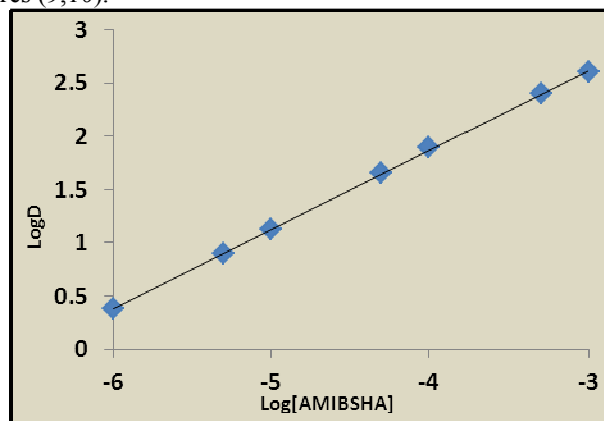
Figure(10): D= F[AMIBSHA].

The results illustrated extraction efficiency increase with complexing agent increase. Because effect to increase rate of forward reaction and increase complex formation extracted to CPL.

Effect of Tritonx-100

Extracted Bi^{3+} in 10 mL aqueous solution by application comprehensive procedure at optimum conditions and in presence different volume of 1% Tritonx-100 (0.1-1)mL after measurement of absorbance for ethanolic solution of cloud point layer. And calculate distribution ratio D. the results was as in Figures (11,12).
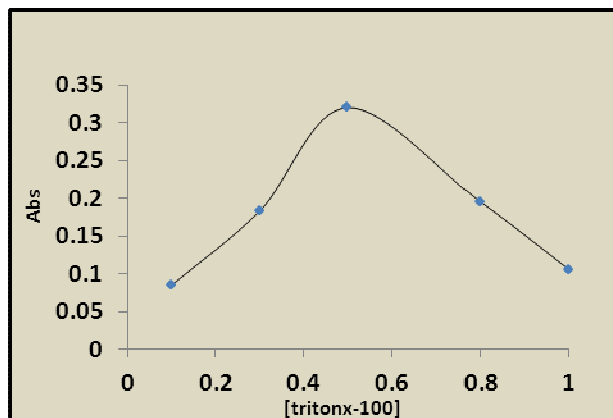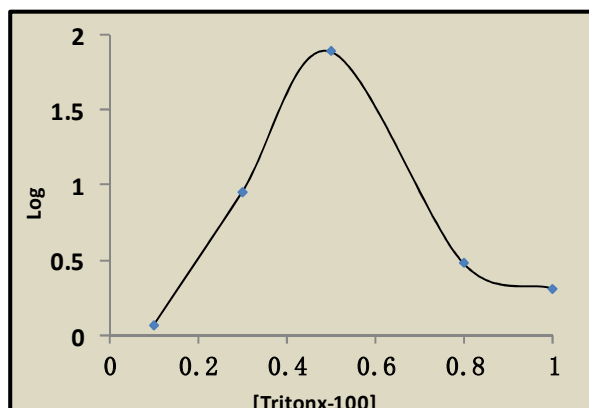
Figure (11): relation between ion pair complex extracted and volume of surfactant.
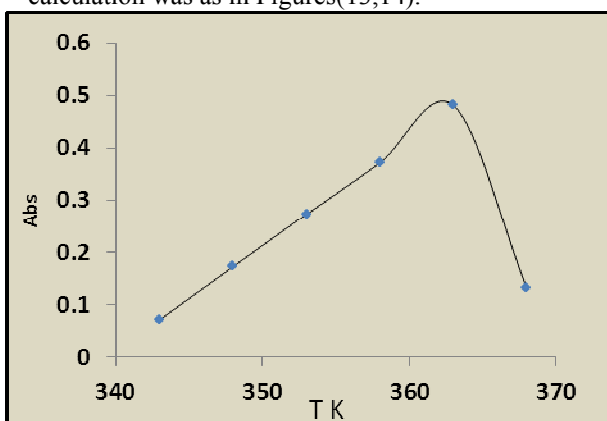

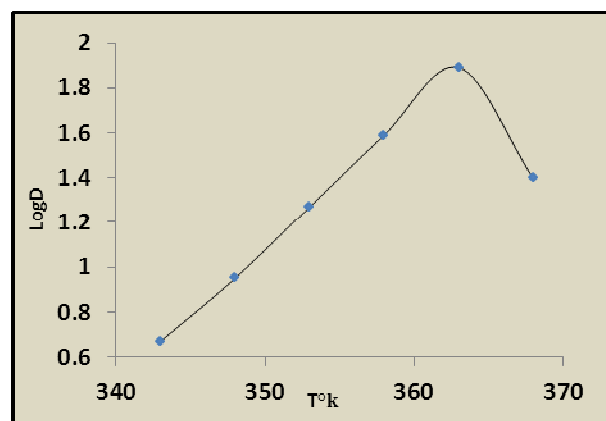**Figure(12): Relation between extraction efficiency and volume of surfactant.**

The results demonstrate 0.5mL was the optimum volume of surfactant 1% Tritonx-100 at other optimum conditions any volume less optimum 0.5mL not enough to extracted ion pair complex formed and effect to decrease extraction efficiency,as well as any volume more than optimum effect to decline extraction efficiency also by the effect of increase diffusion of surfactant.

Thermodynamic study

Study the extraction of Bi^{3+} according to comprehensive procedure at optimum conditions except heating in electrostatic water bath at different temperature (70-95)°c the results of absorbance measurements and D-value calculation was as in Figures(13,14).

Figure(13): The relation between temperature and extraction into CLP.

Figure(14): Effect of temperature on extraction efficiency.

The results show 90°C was the optimum temperature giving higher absorbance for complex extracted to CPL as well as D-value and the relation was thermodynamically endothermic after calculate extraction constant K_{ex} at each temperature to optimum according to relation below:
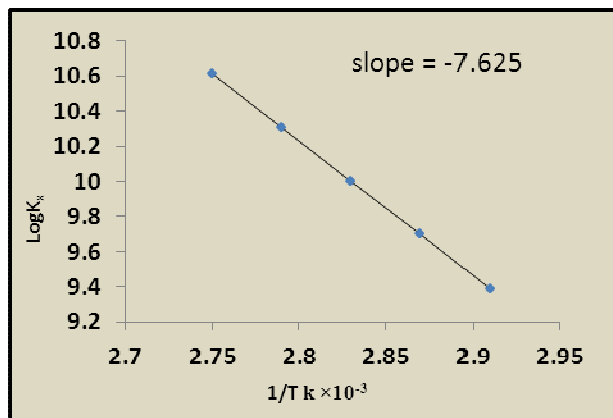
$$K_{ex} = \frac{D}{[Bi3+][AMIBSHA]}$$

The results giving straight line relation as in Figure(15) so from the slope of this straight line calculate thermodynamic data of extraction by relations below:

$$slope = \frac{-\Delta H}{2.303R}$$

$$\Delta Gex = -RT\, Lnkex$$

$$\Delta Gex = Hex - T\Delta Sex$$

Figure(15) : The relation between temperature and extraction constant.

| $\Delta H_{ex} = 0.1459$ KJ.mol^{-1}	$\Delta G_{ex} = -73.786$ KJ.mol^{-1}	$\Delta S_{ex} = 203.669$ J.mol^{-1}.k^{-1}

The small value of enthalpy reflect the very nearly of ion pair each ion together,as well as the high value of entropy demonstrate the method of extraction is entropic in region.

Effect of heating time

Extracted Bi^{3+}for 10mL aqueous solutions at optimum values for all parameters except time of heating in electrostatic water bath 2-25 minutes ,the results was as in figures(16,17):
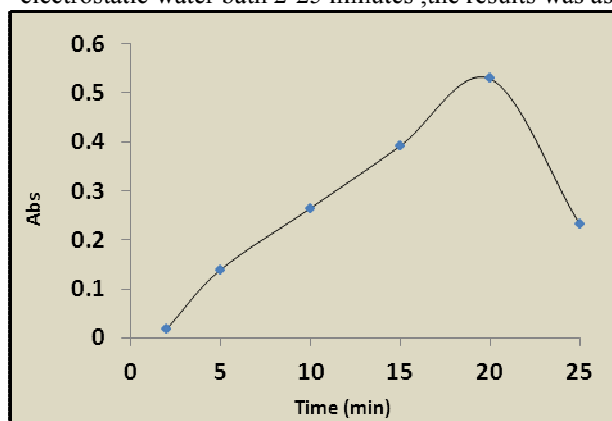
**Figure(16): relation between complex formation extracted and time for heating.**
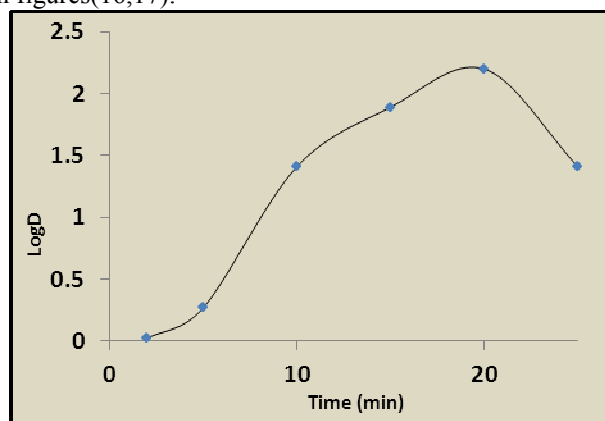
**Figure(17) : D = F(time of heating).**

The results show optimum time of heating was 20 min giving higher absorbance and D-value , because the time of heating indicate to quantity of heating in the solution which is help to produce cloud point layer and partition the ion pair complex in to CPL . Optimum heating time giving the best quantity of heating and produce favourable cloud point.But any heating time less than optimum giving quantity of heating not enough to formation cloud point and complete equilibrium of extraction. But heating time more than optimum value effect to increase quantity of heating in the solution as well as this increasing effect to increase diffusion of micelles and decrease cloud point layer formation and equilibrium of extraction then decrease absorbance and D-Value.
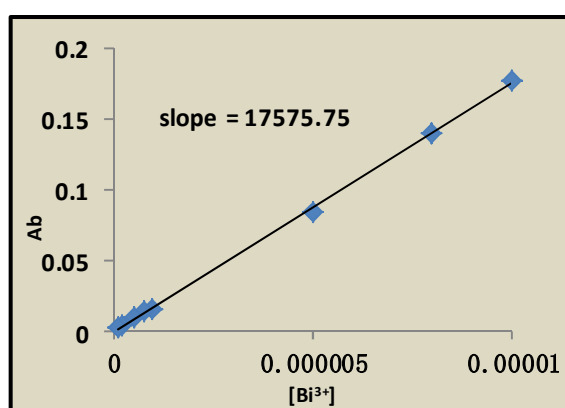

Stoichiometry

For study the more probable structure of ion pair complex extracted into CPL. To apply four spectrophotometric method. Which are: slope analysis method, slope ratio method, mole ratio method, Job method. The results were as in Figures(18-22).
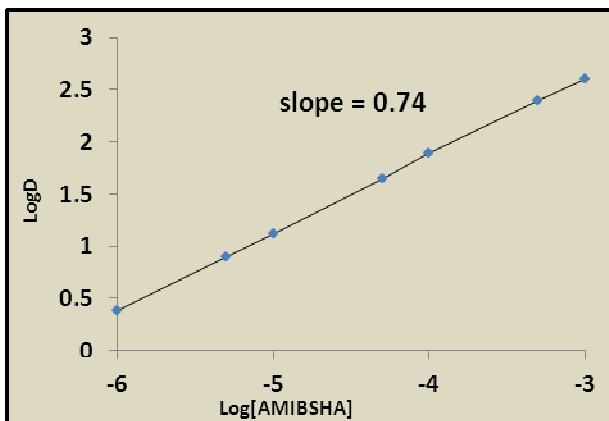
Figure(18): slope analysis method.
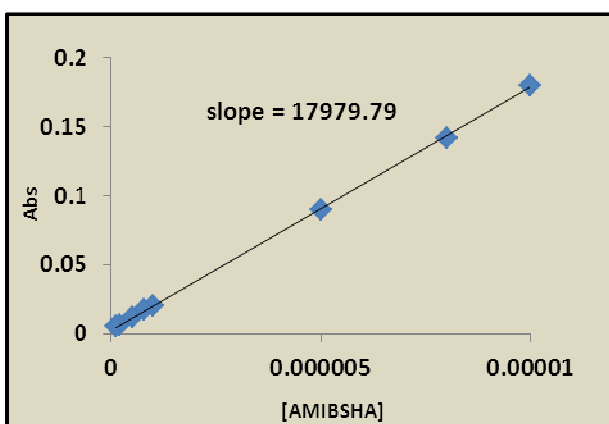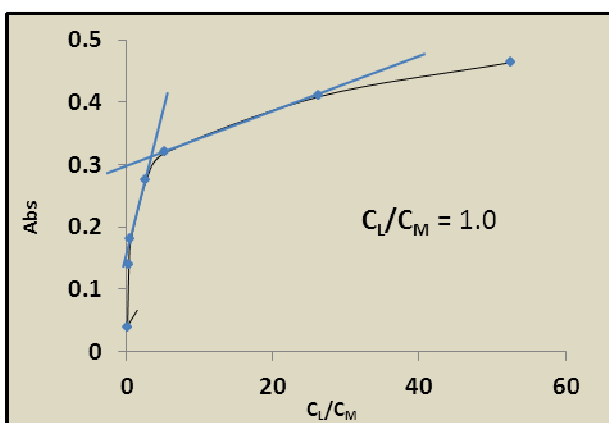

Figure(19) : slope ratio method between absorbance and [AMIBSHA].
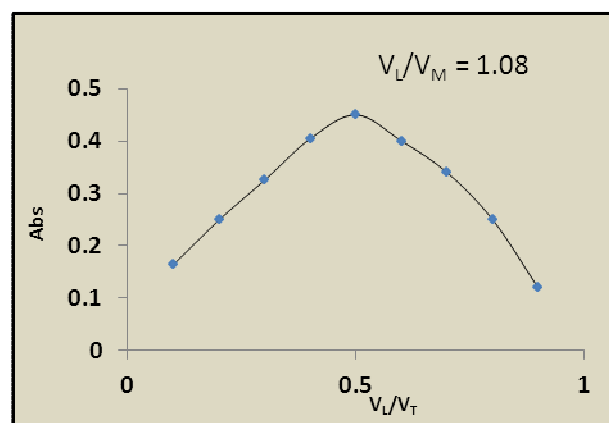

Figure(20) : slope ratio method between absorbance and Bi³⁺.

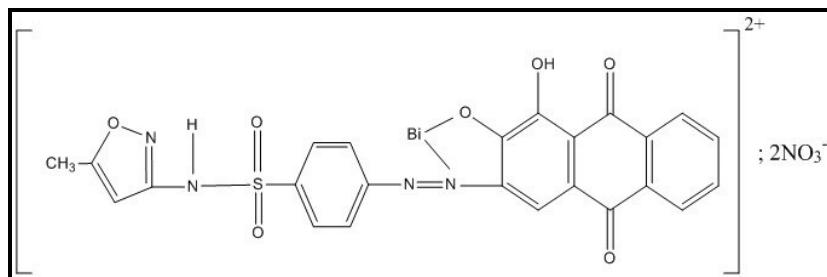$$\text{Slope ratio} = \frac{17979.79}{17575.75} = 1.02$$


Figure(21) : Mole ratio method.

Figure(22) : Job method.

The results show more probable structure of ion pair complex extracted was (1:1) $[Bi^{3+}:AMIBSHA]^{2+}, 2NO_3^-$

Synergism

Extracted Bi^{3+} from 10mL aqueous solutions at optimum conditions according to comprehensive procedure and in presence different concentrations of methyl isobutyl ketone (MIBK)or tributyl phosphate (TBP) each on alone, the result was as in Figures (23-26):

y = 0.112x + 1.2057

slope = 0.113
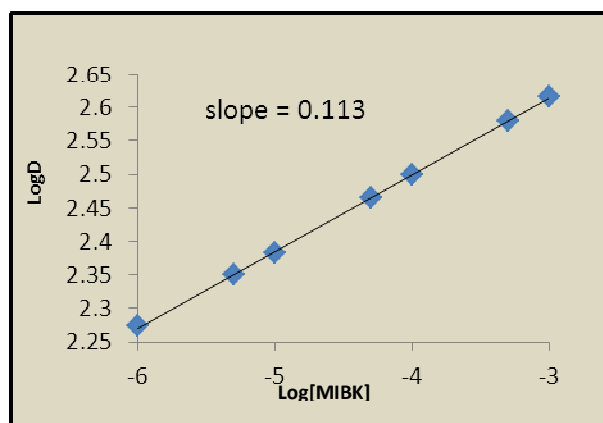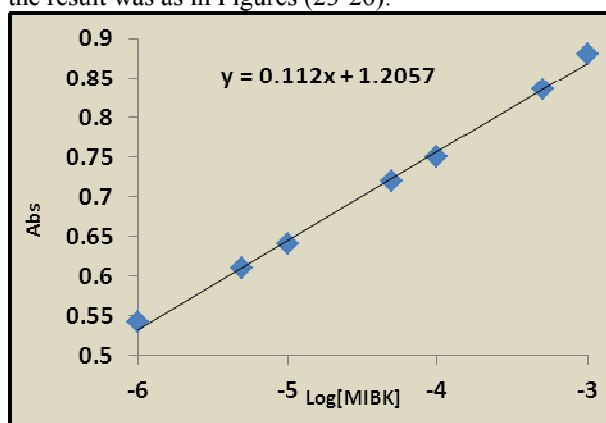
Figure(23) : Complex extracted change as a function with [MIBK]increase.

Figure(24): D = F(Log[MIBK]).

slope = 0.114
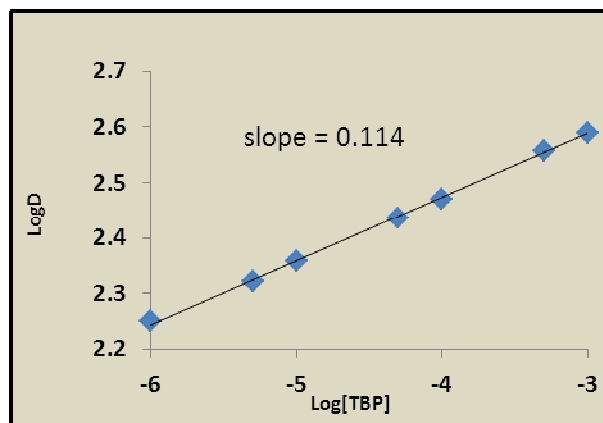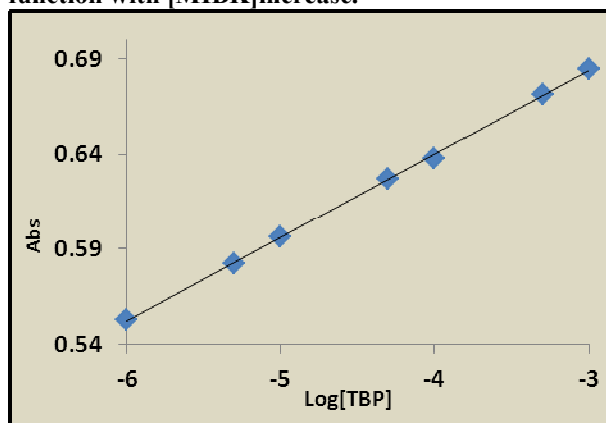
Figure(25) : complex extracted change as a function with [TBP] change.

Figure(26) : D = F[TBP]

The results show presence MIBK or TBP effect to enhancement extraction efficiency because the organic reagent AMIBSHA cannot saturated the coordination shell of Bi^{3+} when produce ion pair complex then all coordination shell position not occupied with organic reagent (complexing agent) occupied with water molecules and then the complex partitioning to the aqueous solution but when presence MIBK or TBP play to replace water molecule in coordination shell and increase whenhydrophobility of complex and partitioning into cloudpointlayer so that increase absorbance and D-value. As well as the results show from the slope there in one molecule of MIBK or TBP replaced water molecule in complex structure:

$[Bi(AMIBSHA)(MIBK)]^{2+};2NO_3^-$
$[Bi(AMIBSHA)(TBP)]^{2+};2NO_3^-$

Interferences effect

Extracted Bi^{3+} ion from 10mL aqueous solution contain 40µg at pH=9 and in presence 1×10^{-4} M (AMIBSHA)

and 0.5mL of 1% Tritonx-100 as well as 0.1M of different interferences cations, after heating the solutions at 90°C for 20 min and determine absorbance of ethanolic solution of CPL after separated and calculate D value according to comprehensive method. The result was as in Table (2).

Table(2) : Interferences effect.

Interfere	CPL Absorbance	D
$Cd(NO_3).4H_2O$	0.344	25.66
$Hg(NO_3)_2$	0.123	2.47
$AgNO_3$	0.189	3.44
$Ni(NO_3)_2$	0.268	5.66
$Pb(NO_3)_2$	0.296	12.33
$Mg(NO_3)_2$	0.776	236

The results show all the metal cations interfere with Bi^{3+}ion in extraction method by formation ion pair complex with organic reagent (AMIBSHA) except magnesium ion not giving any interferences that is mean not any tendency for $Mg^{2+}$to form complex with (AMIBSHA), as well as $Mg(NO_3)_2$ behave in solution as electrolyte effect to increase extraction efficiency of Bi^{3+}ion.

Electrolytes effect
Extracted 40μg Bi^{3+}ion in10mL aqueous solution at pH=9 and 1×10^{-4}M (AMIBSHA), 0.5mL of 1% Tritonx-100 and in presence 0.1M from electrolyte salts, after heating there solutions at 90°C for 20 min., and separated CPL from aqueous solution and measure the absorbance of ethanolic CPL as well as calculate D value according to procedure detailed in comprehensive method. The results was as in Table(3):

Table (3) : electrolyte effect.

Electrolytes	CPL Absorbance	D
$LiNO_3$	0.828	285
$Na\ NO_3$	0.800	228
$K\ NO_3$	0.785	207
$NH_4\ NO_3$	0.644	177
$Mg(NO_3)_2$	0.776	236
$Ca(NO_3)_2$	0.723	198
$Al(NO_3)_2$	0.762	203

The results show presence electrolyte slat effect to increase extraction efficiency by the effect of increase dehydration of Bi^{3+} ion and cloud point layer which is effect to increase complexation and extraction from the other hand effect of dehydration related to the kind of electrolyte salts , and the result show electrolytes of the first group elements giving highest effect, and the ion has smallest ionic diameter giving higher effect at the series $Li^+>Na^+>K^+>NH_4^+$ because smallest ion has larger hydration shell giving higher dehydration as well for group two cations.

Calibration curve for spectrophotometric determination:
Extracted Bi^{3+} from 10mL aqueous solution , contain different quantity of $Bi^{3+}1\rightarrow10$ ppm at optimum conditions and after complete the extraction according to comprehensive procedure and separate CPL from aqueous solution then dissolved CPL in 5mL ethanol and measure the absorbance at λ_{max}=550nm against blank prepared at the same manner without Bi^{3+}ion. The results giving straight line relationpass through the origin point as in Figure(27).
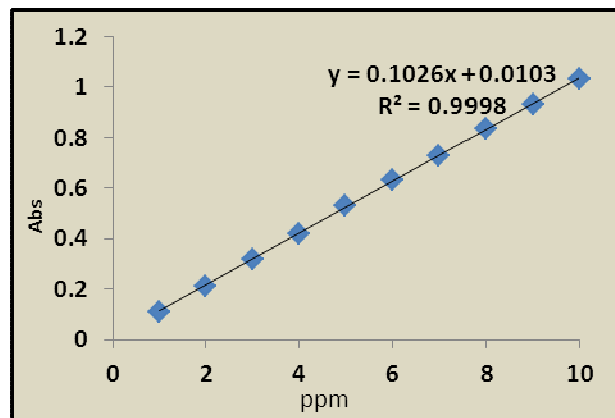
Figure(27) : Calibration curve for spectrophotometric Determination of Bi^{3+} in different samples.

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