Liquid Ion Exchange for Extraction and Spectrophotometric Determination of Tungestate $WO4^{=}$ by Use Azo-derivative.

Shawket K. Jawad and Nadia M. Muslim

Chemistry department –Collegc of Educution for Girls – Kufa University&Directorate-General for Education Najaf

Email: SStuv947JA@gmail.com

الخلاصة

استخدم الكاشف العضوي [FPADPI] لتكوين معقد ترابط أيوني عند pH=8 معطيا امتصاصيه عالية عند λ_{max}= 460 nm بتحضير [H-FPADPI]$^{+}$; HWO_4^{-} او $WO_4^{=}$ من 50 µg W^{6+} في 5mL[FPADPI] وتركيز 1×10^{-4} M, وتمت دراسة تركيب معقد الترابط الايوني فكانت 1:1 [2H-FPADPI]$^{2+}$; $WO_4^{=}$ ودراسة الثرموداينميكيه وطريقة الاستخلاص فكانت القيم الثرموديناميكيه ΔH_{ex} = 0.0287 K J mol^{-1} , ΔG_{ex} = -50.83 K J mol^{-1} و ΔS_{ex} = 167.857 J mol^{-1}K^{-1} أضافة الى دراسات أخرى .

Abstract

2-[(4–formylphenayl)azo]-4,5-diphenyl imidazole [FPADPI] used as complexation agent to form ion association complex. pH=8, which is giving higher absorbance at λ_{max}= 460nm , in presence of 50 µgW^{6+} as $WO_4^{=}$in 5mL and 1×10^{-4} M of [FPADPI], this study show ion pair complex extracted have a structure 1:1 [H-FPADPI]$^{+}$;HWO_4^{-}or [2H-FPADPI]$^{2+}$;$WO_4^{=}$, and thermodynamic study show extraction method of $WO_4^{=}$ was endothermic with thermodynamic data ΔH_{ex}=0.0287 K J mol^{-1}, ΔG_{ex}=-50.83 K Jmol^{-1} and ΔS_{ex}= 167.857 J mol^{-1}K^{-1}as well as this research contain another studies.

Introduction

Liquid ion exchange method is one of chelation and ion association method with high used for extraction any metal sensitive method for general aspect as anion in aqueous or can be change to anion complex in specific research extracted Cd(II) and Hg(II) as chloroanion complex from aqueous solution by liquid ion exchange method with α-Naphthylamin , 4-aminobenzoic acid cryptand C222 and azoderivatuic 4-CMePADPI under optimum conditions [1]. solvent extraction Ge (IV) from HCl media by N-octylcyclohexyl amine (N-n-OCA) dissolved in xylene–DCM , at 0.05 M of , with study the structure of complex extracted $[(RR'NH_2^{+})_2(Ge(OH)n(16-n)]$as well as study thermodynamic[2]. By used of 2-[Benzothiazolylazo]-4–Benzene naphthol as complexing reagent to from complex with Pb (II) having maximum absorbance at λ= 393 nm and Molar absorbtivty Ɛ =212 L mol^{-1}cm^{-1}at pH=9 with structure $[Pb^{2+}(BTABP)^{-2}]$with detection limit 3.492 $\times10^{-6}$µg ml^{-1}[3]. Extracted

Ga(III) from HCl media as $GaCl_3$. 2L, with studying effect of HCl concentration and all optimum condition [4]. Extracted mercury (II) from aqueous solution by use organic reagent [2-(4-Carboxymethy phenyl azo)-4,5-diphenyl imidazole] at pH=6 ,and structure of complex extracted was $[Hg(4\text{-}(MePADPI)_2]^{+2},(NO_3)^{-}{}_2$[5]. Spectrophotometric determination of mercury (II) (Isonitrosop-iso propyl Acetophenone phenyl Hydrazone) (HIPAPH), and the structure of complex was Hg $(HIPAPH)_2$ extracted with solvent MIBK . Give higher absorbance at λ= 395 with molar absorptivity equal to $\varepsilon = 2.678\times10^3$ L $mol^{-1}cm^{-1}$[6]. A simple and selective method was developed for the determination of platinum (IV) with n-octylaniline in toluene. In present study, the use of n-octylaniline in toluene for the extraction of platinum (IV) from ascorbate media was carried out[7]. Adopting ionic liquids in extraction, synthesis and processing of metals with an emphasis on the electrolysis of active/light, rare earth, and platinum group metals. Becausethe research and development of ionic liquids in this area are still emerging, various, more fundamental approaches are expected to popularize ionic liquids in the metal manufacturing industry[8]. A simple new micelle mediated preconcentration method was developed for analysis of sunset yellow(SY) prior to its spectrophotometric determination. The method was based upon cloud point extraction of the ion associate of SY and trioctylamine (TOA) in HCl–Triton X-100 [9]. The extraction equilibrium constant for the complex formation between Th(IV) and L was $\log K_{ex}$ = 6.95 ± 0.15 (25 C), and the Gibbs free energy, DGo (25 C), of the 1:2 Th–L complex in dichloromethane was -39.56 kJ/mol. The L ligand in dichloromethane only slightly extracted Th(IV) from HNO_3 solution at pH = 1–3[10]. In this work, nitrile-based ionic liquids (ILs) 1-propyronitrile-3-butylimidazolium chloride [C2CNBim]Cl, 1-propyronitrile-3-allylimidazolium chloride [C2CNAim]Cl, 1-propyronitrile-3-(2-hydroxyethyl) imidazolium chloride [C2CN HEim]Cl and 1-propyronitrile-3-benzyllimidazolium chloride [C2CN Bzim]Cl[11]. The operating conditions of a solvent extraction method as the most widely used procedure for determining WSOCs in particulate matter (PM) samples. A solvent mixture of methanol/dichloromethane (90:10) and a volume of 10 ml were the optimum conditions that permit the simultaneous analysis of 30 target WSOCs, including dicarboxylic acids and sugars [12]. The liquid extraction of molybdenum(VI) in presence of 2M hydrochloric acid has been studied in presence of lithium chloride as a salting agent with 0.233 M of 2-n-octylaminopyridine in xylene when equilibrium is maintained for 1 min. The back extraction of molybdenum(VI) has been

performed by using 1 M ammonia [13].The heteroligand complex of manganese with 2,2′-dipyridyle and 2,4-dinitrobenzolazosalicylic acid have been investigated by new spectrophotometric method. The condition of complexing and extraction, physical-chemical and analytical characteristics of this complex have been found. Complex formation is observed in the pH range 5.5-10.5 [14]. In the present work, bentonite (Bn) clay, from Egypt, has been modified using HCl to produce the acid-activated bentonite (A-ABn). Both Bn and A-ABn adsorbents have been characterized using Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and nitrogen adsorption measurements [15]. A simple rapid new spectrophotometric method has been developed for the determination of copper at trace level using 1-nitroso-2-naphthol (NNPh) as complexing reagent in presence of anionic aqueous micellar solution surfactant 1.0% sodium dodecyl sulphate (SDS). NNPh reacts with copper (II) to form bis(1-nitroso-2-naphtholato) copper complex [16].

Experimental

Instruments Used

For spectrophotometric measurement and absorbance determination used Double bean (UV-Vis) spectrophotometer, shimadza (UV-700) Japan and single beam (UV-Vis) spectrophotometer TRIUP International crop. TRUV 74,S-Italy . and used pH-meter , WTW , Listed ,Laboratory Equipment , E163694 ,CE , Germany , Electrical sharker HY-4 vibrator with AD Just about speed multipheusay , function , TripInternational crop . made in Italy .

Materials and Solutions

All chemical used as received from commercial sources without father purification and prepared tungston as $WO_4^{=}$ solution in concentration 1mg / ml by dissolved sodium tungstate $Na_2WO_4.2H_2O$ by weight in 100 mL distilled water by used volumetric flask and other working solution prepared by dilution with distilled water, organic reagent 2-[(4–formylphenayl)aza]- 4,5- diphenyl imidazole [17] as well as all solution for another material prepared as we are need .

Essential Method

Take 5ml solution of organic reagent [FPADPI] dissolved in 1,2-DCE at 1×10^{-4} M concentration shaking with 0.1 M HCl for 5min after that separate organic solution and adding to 5mL aqueous solution contain 50µg tungsten as $WO_4^{=}$ and shaking for 10 minutes , afterward separate organic phase from aqueous phase and measure absorbers of organic phase at λ_{max} of ion pair complex formed and extracted ,in addition to treated aqueous phase

according to spectrophotometric thiocyanate method and return calibration carve in Fig (2) to determine remainder quantity of tungsten in aqueous solution and transfared to organic phase and calculate distribution ratio D.

Results and Discussion

Spectroscopic Study

Spectrumorganic reagent [FPADPI] With complex $WO_4^{=}$ as shown in Fig(1)

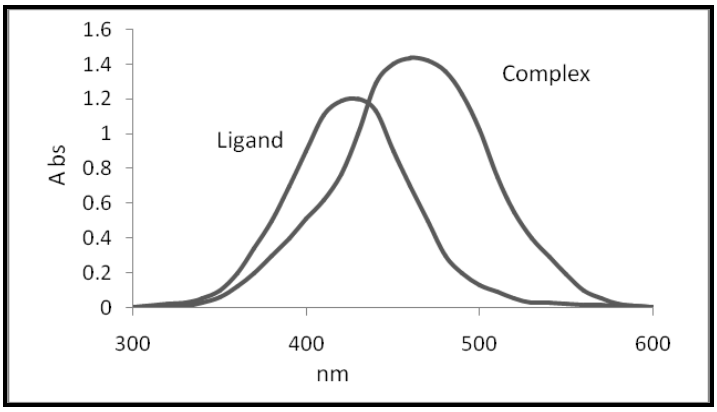


Fig (1): UV-VISSpectrum of organic reagent [FPADPI] and its complex with $WO4^{=}$ in 1,2-DCE The spectrum show λ_{max} for ion pair complex extracted was 460 nm.

Calibration Carve

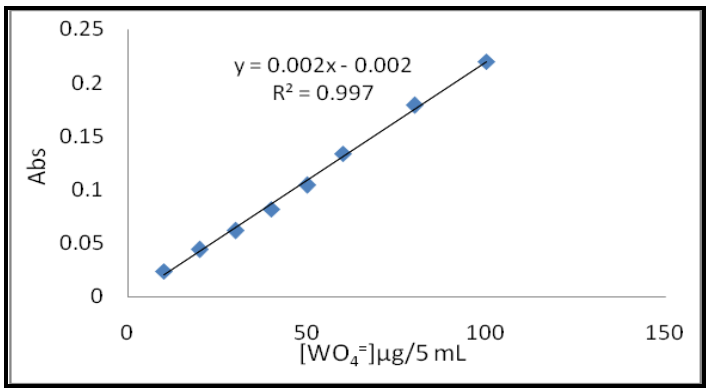
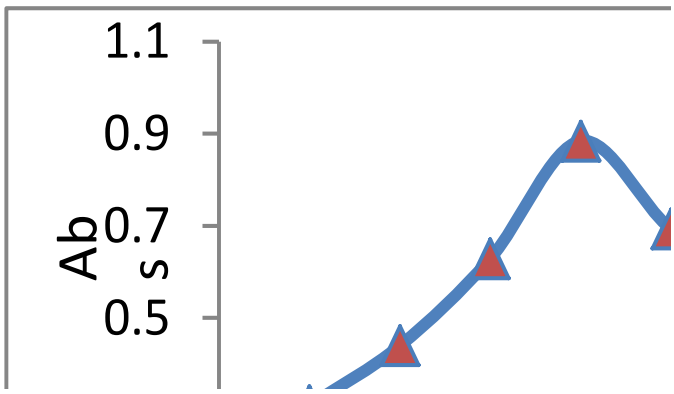


Fig (2): Calibration curve to estimate $WO_4^{=}$ in aqueous solution to calculate (D) value.

Effect of pH

Aqueous solution 5mL in volume contain 50µg tungsten as $WO_4^{=}$at different pH (2-12) as well as take 5mL of organic phase shaking with 5mL of 0.1M HCl for 5 minutes and separate, organic solution . then adding organic phase to the aqueous solution at different pH and shaking the two imiscible phase for 10minutes afterward separate organic phase from

aqueous phase and measure the absorbance of organic phase at λ_{max}=460 nm against FPADPI solution as blank and treated aqueous phase according to thiocyanate spectrophotometric method to calculate distribution ration (D) after return to calibration curve (2), the results as in Fig (3,4).



Fig(3): Effect of pH on ion pair complex formation

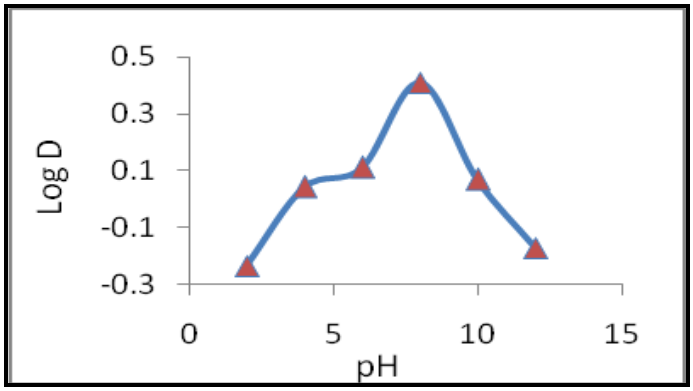


Fig (4): Effect of pH on D values

The results show pH=8 was favorable pH for extraction tungsten as $WO_4^{=}$ which is the optimum value giving best, thermodynamic equilibrium for extraction. According to liquid ion exchange method , pH – values more that optimum value effect to decline absorbance of ion pair complex extracted and D values by effect of participate OH^- ion to form ion pair association complex and pH less than optimum value not allow to reached thermodynamic equilibrium and decrease absorbance and D values .

Effect of Metal Ion Concentration

5mLof 1×10^{-4} M[FPADPI] shaking with 5mL of 0.1 M HCl for 5 minutes after separate organic reagent solution adding to 5mL of aqueous solution contain different concentration of $WO_4^{=}$ at pH =8 and shaking for 10 minutes and separate the organic phase from the aqueous

phase . After that measure absorbance, of organic phase at λ_{max}= 460nm against organic reagent solution as blank and plot absorbance values against µg of W^{6+} as $WO_4^{=}$, the results giving Fig (5).

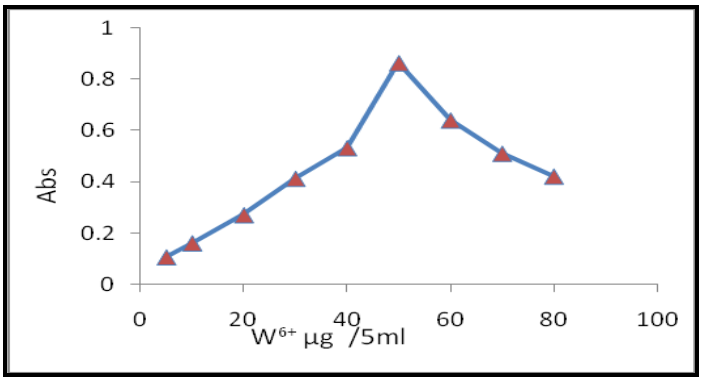


Fig (5): Effect of metal ion concentration on ion pair complex formation

But aqueous solution treated according to spectrophotometric method [18] (thiocyanate method). And determine remainder quantity of W^{6+} in aqueous solution after extraction and transferred quantity and calculate distribution ratio D then plot log D against µg W^{6+} /5mL giving Fig (6).

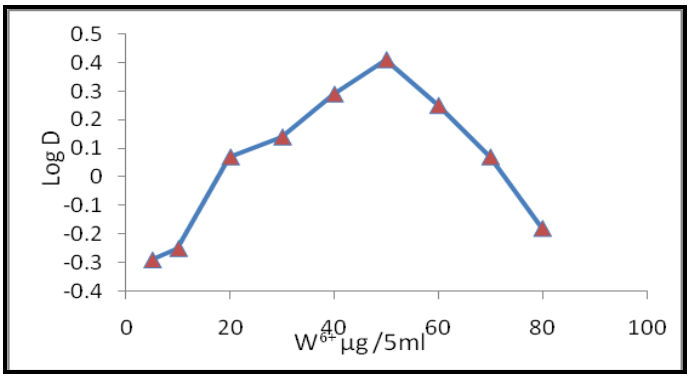


Fig (6): Effect of metal concentration on efficiency of extraction.

The results show 50 µg/5mL aqueous solution is the suitable concentration of W^{6+} as $WO_4^{=}$to reach thermodynamic equilibrium for extraction according to:

$$FPADPI + H^+ + Cl^- \rightleftharpoons [H - FPADPI]^+ ; Cl^-$$

$$FPADPI + 2H^+ + 2Cl^- \rightleftharpoons [2H - FPADPI]^{2+} ; 2Cl^-$$

$$[H - FPADPI]^+ ; Cl^- + HWO_4^- \rightleftharpoons [H - FPADPI]^+ ; HWO_4^- + Cl^-$$

$$[2H - FPADPI]^{2+} ; 2Cl^- + WO_4^{=} \rightleftharpoons [2H - FPADPI]^{2+} ; WO_4^{=} + 2Cl^-$$

Any concentration of tungsten less than 50µg/5ml not allow to reach thermodynamic equilibrium and giving decrease in absorbance of ion pain complex extracted and distribution ratio as well as concentration more than optimum value lead to decline extraction activity by effect of mass action law and the chatlier principle

Effect of Organic Reagent Concentration

After extraction tungsten W^{6+} as $WO_4^{=}$ from aqueous solution at pH = 8 and 50µg $WO_4^{=}$ /5mL by different concentration of [FPADPI] (10^{-6} – 10^{-3}) M according to liquid ion exchange method at later plot absorbance values against [FPADPI] giving Fig (7) as well after treated aqueous solution according to thiocyante method and Calculate D values and plot Log D against [FPADPI] giving Fig (8) .

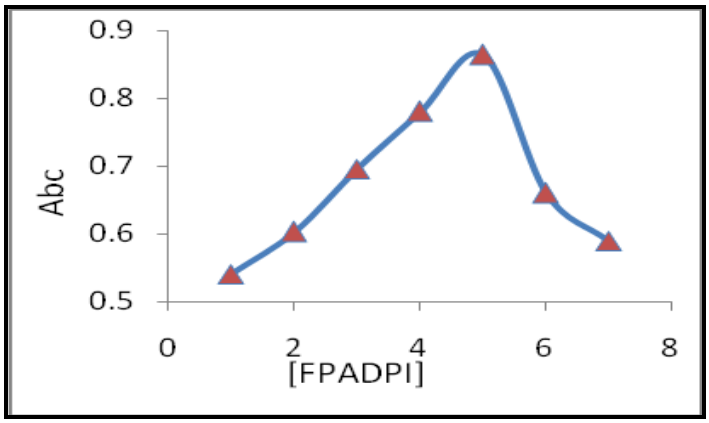


Fig (7): Effect of organic reagent concentration on ion pair complex formation

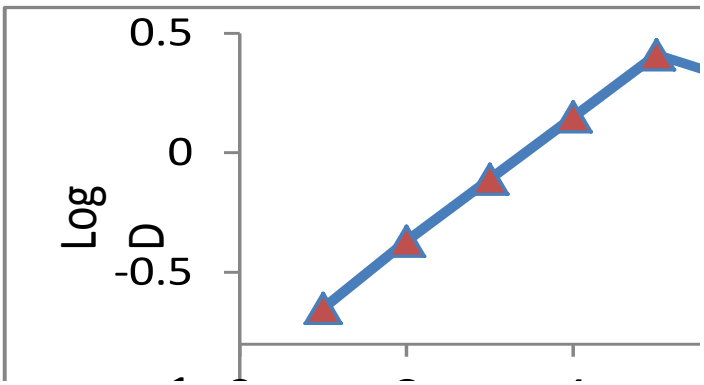


Fig (8): Effect of organic reagent concentration on efficiency of extraction

The results show absorbance and distribution ratio increase as a function for organic reagent increase and proof organic reagent concentration is a thermodynamic value control the thermodynamic equilibrium.

Effect of Shaking Time

Extraction tungsten as $WO_4^{=}$ from aqueous solution at optimum conditions with different shaking times (5-25) min., according to liquid ion exchange method and plot absorbance measured and logarithm distribution ratio against shaking time the results appear as in Fig (9,10).

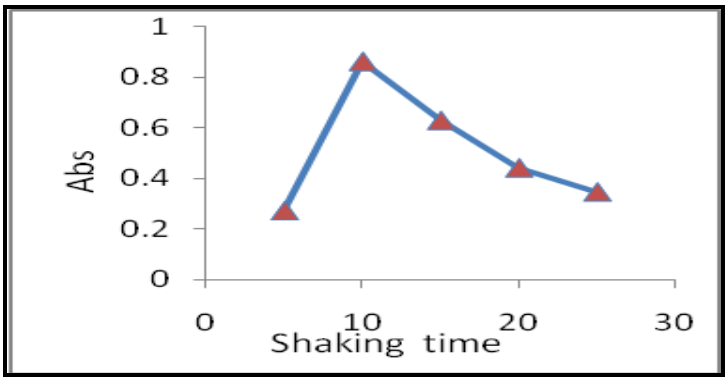
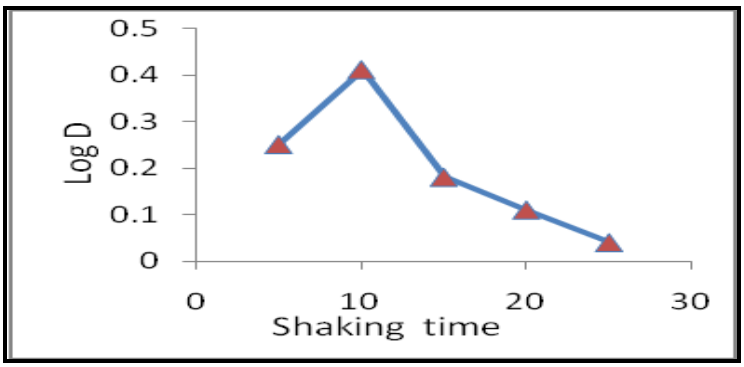


Fig (9): Effect of shaking time on ion pair complex formation



Fig(10): Effect of shaking time on efficiency of extraction

The results show 10 minutes was the suitable shaking time which is help to reach to the thermodynamic equilibrium ,but shaking less than 10min .are not allow to reach thermodynamic equilibrium but shaking time more the optimum effect to increase dissociation equilibrium and in the two state shaking time less or more effect to decline extraction activity

Stoichiometry

Slop Ratio Method

Extracted tungsten as $WO_4^{=}$ from 5mL aqueous solution contain 50 µg in 5mL organic reagent dissolved in 1,2-DCE at different concentration (1×10^{-6}-1×10^{-3})M at optimum condition and after measured the absorbance of ion pair complex extracted plot absorbance

values against concentration of organic reagent obtained straight line relation with slope equal to (490.5) as shown in Fig(7) , after that extraction tungsten as $WO_4^{=}$ from aqueous solution contain different concentration of tungsten (1×10^{-6}-1×10^{-3})M by 1×10^{-4}M organic reagent dissolved in 1,2-DCE of optimum condition , after that measure the absorbance of ion pair complex and plot absorbance values against concentration of tungsten obtain straight line relation with slope equal to (510.5)as in Fig(8) ,after divided the slope values over each other giving the value (1.04) ,that is mean ion pair complex extracted having the structure 1;1 [H-FPADPI]$^{+}$;HWO_4^{-} or [2H-FPADPI]$^{2+}$;$WO_4^{=}$.

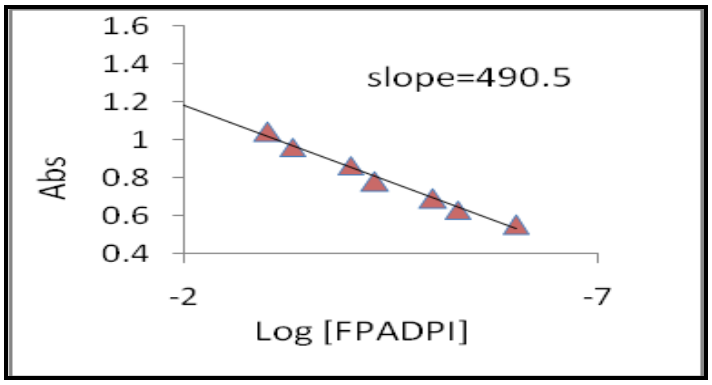


Fig (11): Absorbance as function of [FPADPI] concentration

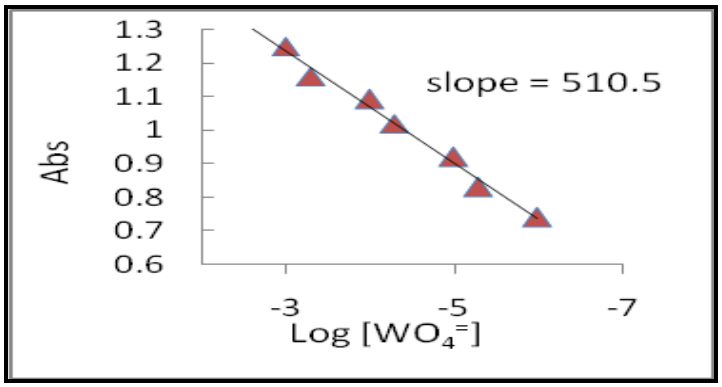


Fig (12): Absorbance as function of [$WO_4^{=}$] concentration

Slope Analysis Method

Extraction tungsten as $WO_4^{=}$ from aqueous solution contain 50 µg $WO_4^{=}$ in 5mL with 5mL of [FPADPI] dissolved in 1,2-DCE at different concentration (1×10^{-6}-1×10^{-3})M at optimum conditions , after separate organic phase from aqueous phase treat aqueous phase according to thiocyanet method to determine remainder quantity and transferred quantity of $WO_4^{=}$ and calculate distribution ratio D after that plot Log D against different concentration

of [FPADPI] giving straight relation Fig (13) with slope (0.61) demonstrate the ion pair complex extraction having a structure of 1:1 [H-FPADPI]$^{+}$;HWO_4^{-} or [2H-FPADPI]$^{2+}$;$WO_4^{=}$

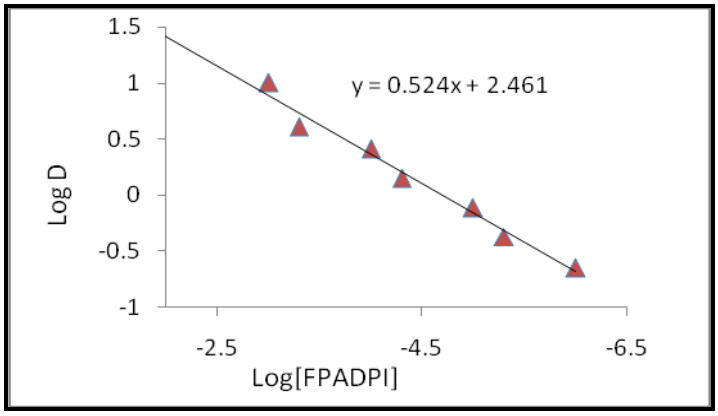


Fig (13): Effect of [FPADPI] concentration on distribution ratio (D) of extraction

Effect of Methanol

Extraction tungsten as $WO_4^{=}$ from aqueous solution 5mL in volume contain 50 µg at pH=8 and different percentage of CH_3OH (1-50)% by 1×10^{-4} M [FPADPI] at optimum condition , after separate the two layers measure the absorbance of organic phase at λ_{max}=460nm against organic reagent solution as blank ,as well as treat the aqueous layers according to thiocyanate method [18] . and calculate D values, at latter plot absorbance values of organic phases against methanol percentage giving Fig (14), and plot Log D against methanol percentage giving **Figure 15** these Figures show absorbance of ion pair complex extracted increase with increasing the percentage of methanol as well as distribution ratio D to 30% CH_3OH as optimum value and decrease extraction activity at more values methanol percentage.

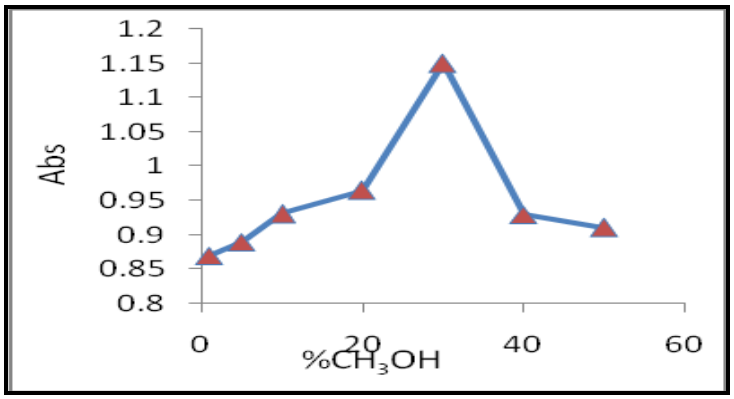


Fig (14): Effect of methanol on ion pair complex formation and stability efficiency of extraction

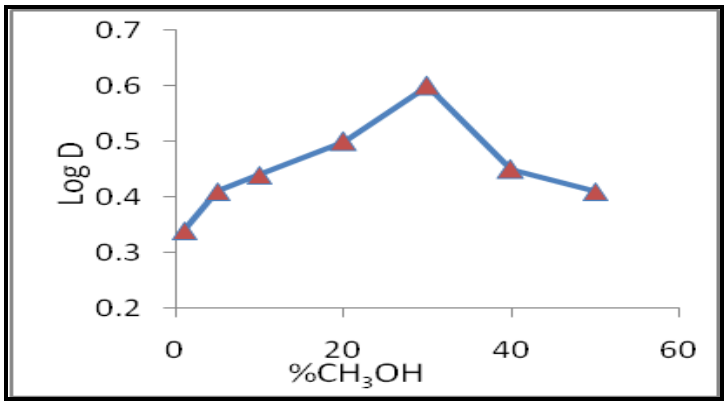


Fig (15): Effect of methanol on efficiency of extraction

Effect of Temperature

Extraction tungsten as $WO_4^{=}$ from aqueous solution contain 50 µg $WO_4^{=}$ in 5mL at pH=8 by 5mL of 1×10^{-4} M [FPADPI] solution at different temperature at latter calculate distribution ratio D and extraction constant K_{ex} in each temperature afterward plot , Log K_{ex} against 1/T K obtain straight line relation Fig (16) show thermodynamic data was ΔH_{ex}=0.0287 K J mol^{-1}, ΔG_{ex} = -50.390 K $Jmol^{-1}$ and ΔS_{ex}= 167.85 J $mol^{-1}K^{-1}$ the results show extraction was endothermic reaction and high vales of entropy reflect the reaction was entropic in region demonstrate degree of approach between two part of ion pain association complex .

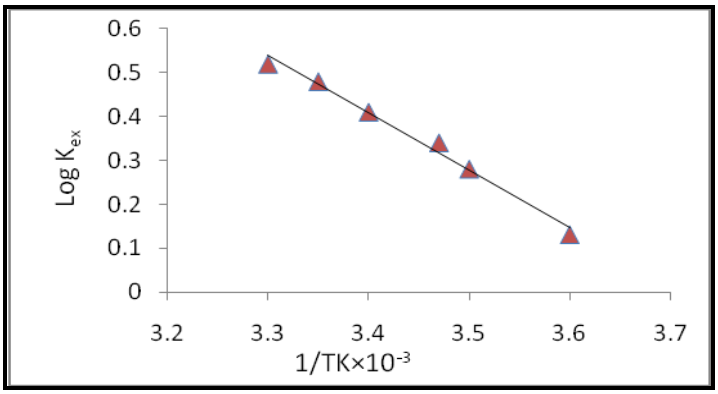


Fig (16): Effect of temperature on extraction constant.

Effect of Organic Solvent

Extraction at optimum conditions and different organic solvents differ in dielectric constant for dissolve organic reagent, this method giving the results at **Table 1**.

Table 1: Effect of organic solvents on distribution ratio (D) K_{ex} and thermodynamic ΔG_{ex}

Organic Solvents	*Abs*	*D*	$K_A \times 10^6$	$K_{ex} \times 10^{10}$	$-\Delta G_{ex}$ *KJ/mol*
Amyl alcohol	0.095	1.78	0.01	0.11	50.63
DCM	0.24	3.17	0.26	0.63	54.87
Chloroform	0.92	4	0.40	1.28	56.60
Bromo benzene	0.28	2.85	0.22	0.46	54.11
1,2-DCE	0.86	2.57	0.18	0.33	53.30
Toluene	0.19	2.33	0.16	0.25	56.63

The results show there is not any liner, relation between dielectric constants of organic solvents and distribution ratio which is reflect there is not any effect of polarity of organic solvents on ion pair complex formation and extraction activity but there is an effect for structure of organic solvent on extraction ability

Applications about determination of $WO_4^=$ in different samples

Determined spectrophotometrically tungsten $WO_4^=$, After digested the sample according to moist method [19]. After that dealing the sample as evident in adoption method, the results demonstrated at **Table 2**.

Table 2: Concentration (ppm) of $WO_4^=$ in samples environment

Sample	$WO_4^=$ *ppm*
Agricultural soil	0.620
Agricultural soil(Mchkab)	0.760
Non Agricultural soil (sulam)	0.170
Non Agricultural soil(Mchkab)	0.260
Chiken meat	0.080
Chikenliver	0.090
Strawberry	0.012
date	0.002
Spinach	0.006
Radishes	0.004
Water Orr	0.030
Water tap	0.050

References

1) Shawket K . Jawad & Hameed S. M. [2011] **.J.** Ibn-AL-haiytham for pure and Applied Sciences 3 (2), p158-16.

2) Jagatap S, Kolekar S, Han S. & Anuse M. [2012]. J. International for analytical and bio analytical chemistry 2(4), 253-240.

3) Shawket K Jawad & Goson J Abas. [2011]. J. for Al –Qadisisya Scienes.17(1).

4) Ahmed. I. M, El-Nadi .Y.A. and El-Hefny .N.E.[2013]. 131-132 ,24-28.

5) Shawket K Jawad. [2007].J. of Kerbala University .5 (2), 49-60.

6) RaoBS , DubeySS & Kiran B.V. [2011].International **.J.** of Life Sciences and pharma Research.1, 75-79.

7) AshwiniP Gaikwad1, Ganesh S Kamble, Sanjay S Kolekar1 &MansingA Anuse1.[2013].**J**.Chromat Separation Techniq , Vol.4,2-4 .

8) JesikP, YeojinJ, Priyandi K, Jinyoung L, KyungjungK &Churl KLee.[2014].J.International of Molecular Sciences.15, 15320-15343.

9) El-ShahawiM.S, HamzaA, Al-SibaaiA.A,BashammakhA.S&Al-Saidi H.M,.[2013].J. of Industrial and Engineering Chemistry 19 , 529–535.

10) Qiao D, Yongdong.J ,Qinggui.W , Rongxin.Z ,Ning P ,Fuwan.Z ,Meiming. L & Chuanqin.X.[2013].J.RadioanalNucl Chem,295:125–133.

11) NawshadM, Zakaria M, Azmi B, Abdul M.M.I & Sikander R .[2013] .J. of Industrial and Engineering Chemistry ,19 ,207–214.

12) Maria CPietrogrande, Dimitri B & Sara C.[2013]. J. Anal Bioanal Chem, 405:1095–1104.

13) Leena E. Noronhaa, b, Ganesh S. Kamblea, Sanjay S. Kolekara,&Mansing A. Anuse1.[2013]. J.International of Chemical Science and Technology; 3(1) , 15-24.

14) Nushiravan K Rustamov & Gulu G Abbasova.[2014].J. Chem. Eng. Chem. Res, 1(2), pp. 110-113.

15) Youssef A, Al-Awadhi M&Akl.[2014].J. Anal .Bioanal Tech, 5(1) .

16) SharA & Soomro G Afshan1.[2014] .J. Res. Chem. Environ.4 (3) P 169-176.

17) Faten K A . [2009].Chemistry Department, College of education for Girls ,Kufa of University M.Sc. Thesis.

18) MarczenkoZ. [1986] :Separation and Spectrophotometric Determination of Elements', All is Horwoord limited .

19) Camp bell M . [1998]. preparation and Spectral Analysis for liquid ansamples , An Introductoryprogramed Text 2nd edition .