Journal of Engineering and Applied Sciences 13 (17): 7215-7222, 2018
ISSN: 1816-949X

Extraction and Determination of Ni (II) Using Cryptand C222 and 8-Hydroxy Quinoline from Basic Solutions via the Liquid Ion Exchange Method

Shawket Kadhim Jawad and Maha Abbas Hussain
Department of Chemistry, Faculty of Education for Girls, University of Kufa, Al-Najaf, Iraq

Abstract: Liquid ion exchange was used as a sensitive method for extraction of Ni (II) as an ion pair association complex using cryptand C222 and 8-hydroxy quinoline from aqueous basic solutions, the study looked at wave length for maximum absorbance of extracted complexes which was 400 nm. The extraction experiments showed optimum condition for extraction at higher efficiency 0.7 M KOH in presence of 100 μg Ni^{+2} after shaking the two layers for 15 min, therefore, 0.25 M of 8-hydroxy quinoline is necessary to produce an ion pair association complex, it is important to note that increasing the concentration of cryptand C222 creates a relatively straight line which matches previous research studies about effective parameters for extraction efficiency. Undoubtedly, this method can be used for determination of Ni (II) in different samples spectrophotometrically.

Key words: Liquid ion exchange, cryptand, 8-hydroxy quinoline, nickel (II), solvent extraction, determination

INTRODUCTION

From acidic solutions, researchers extracted Ni^{2+} and Zn^{2+} by using Di (2-ethylhexyl) phosphoric acid and bis (2, 4, 4-trimethyl pentyl) phosphoric acid (Cyanex 272) after using di-(2-ethylhexyl Phosphoric Acid (DFHPA) optimum pH = 2 For Ni^{2+} at 36 and Zn^{2+} 98%, the extraction efficiency increased along with the increase in pH but by using Cyanex 272 at pH 3.5, the extraction was more efficient, other applications used mixing of (DEHPA) and Cyanex 272 for extraction (Gharabaghi *et al*., 2013). By using CPE methodology extracted Zn (II) in the presence of new laboratory prepared organic reagent 2-(N-5-methyl isoxazol-3-yl)-Benzen Sulfonamideazo-1-Naphthal-Benzen (AIBSNB) as complexing agent at pH = 9 in existence TritonX-100 as nonionic surfactant with heating at 90°C for 15 min, the extracted ion pair have more probable structure (Zn(AIBSNB);Cl-) or (Zn(AIBSNB-) (Cl-)) (Jawad and Abed, 2015). 4-(N-5-methyl isoxazol-3-yl)-benzone sulfonamideazo)-1, 2-dihydroxy-9, 10-anthracenedione used as a complexing agent for spectrophotometric determination of Bi (III) in entity TritonX-100 as a non-ionic surfactant this extraction happen at pH = 9 as well as heating at 90°C for 20 min (DL = 7.764×10^{-7} μg/mL) $\varepsilon = 21480.8$ L $mol^{-1}cm^{-1}$ and Sandell's sensitivity = 9.749×10^{-10} μg cm^{-2} and RSD% = 0.00541 (Shawket and Salih, 2015). 2-((Benzo thiazolyl azo)-4-benzyl phenol was used as a complexing agent for spectrophotometric determination of Pb^{+2} as well as 2-[3-Bromophenyl azo]-4, 5-diphenyl imidazole for Cd^{+2}, the ion pair association complex for each ion was extracted into a non-ionic surfactant TritonX-I00, this study involved all optimum conditions necessary for higher efficiency of extraction as well as the effective parameters to determine what metal ions were under study in different samples (Shawket and Jihan 2012). Extraction and spectrophotometric determination of Cd (II) as chloro anion complex $CdCl_4^{=}$ after formation ion pair association complex with crystal violet in acidic HCl solution by liquid ion exchange after incorporation with cloud point extraction method with the existence of TritonX-100 (Khamas *et al*., 2016).

Experimental: A biochrom double beam UV-visible spectrophotometer model biochrom libra 560 Cambridge UK with 1 cm path length was used for all spectrophotometric studies as well as all absorbance measurements. Electrical balance CE, HR 200 (Japan) was used for all weight. Electrical shaker HY-4-vibrator with AD just about speed multiple Japan.

Distilled water was used for preparing all the solutions with suitable volumetric flasks stock solution of Ni^{2+} ion at concentration 1000 μg/mL prepared by dissolving 0.4053 g of $NiCl_2$. $6H_2O$ in 100 mL distilled water contain 1 mL of cons. HCl by used volumetric flask 100 mL in volume other working solution prepared by dilution with distilled water in volumetric flasks. 2M 8-hydroxy quinoline was prepared by dissolving a fixed quantity in chloroform in a volumetric flask. Cryptand C222 was prepared at 1×10^{-2} M by dissolving an

Corresponding Author: Shawket Kadhim Jawad, Department of Chemistry, Faculty of Education for Girls, University of Kufa, Al-Najaf, Iraq

adequate weight and suitable volume of chloroform in a volumetric flask. And other solution for extraction and determination was prepared as needed.

MATERIALS AND METHODS

Aqueous solution 5 mL in volume contained 100 μg of Ni^{2+} and suitable fixed concentration of KOH, added 5 mL of organic phase consisting of 1×10^{-4} M C222 and optimum concentration of 8-HQ dissolved in chloroform after shaking those two layers for the optimum shaking time then separating the organic phase from the aqueous phase and measuring the absorbance of the organic phase at λ_{max} against a blank preparation in the same manner in the absence of metal ions but the aqueous phase was treated according to Dimethylglyoxime DMG spectroscopic method (Marczenko and Balcerzak, 2000) and returned to the calibration curve Fig. 1 to determine the remaining quantity of Ni^{2+} in the aqueous solution after extraction, then this quantity was subtracted from the original quantity of Ni^{2+} in aqueous solution to determine transferred quantity to the organic phase to forms ion pair association complex extracted. Afterward the distribution ratio D was calculated:

$$D=\frac{\left[Ni^{2+}\right]_{org.}}{\left[Ni^{2+}\right]_{aq.}} \qquad (1)$$

It is possible to determine the transferred quantity of Ni^{2+} in the organic phase by stripping and shaking the organic phase with two portions of 5 mL in volume of 1 M HCl to destroy the ion pair complex and return Ni^{2+} into an acidic aqueous solution after determining this quantity by applying the DMG method. But in experimental procedures, the transferred quantity of Ni^{2+} determined with stripping was equal to that quantity determined by the subtraction method then to determine the transferred quantity in all experiments used subtraction method because it is faster and easier.

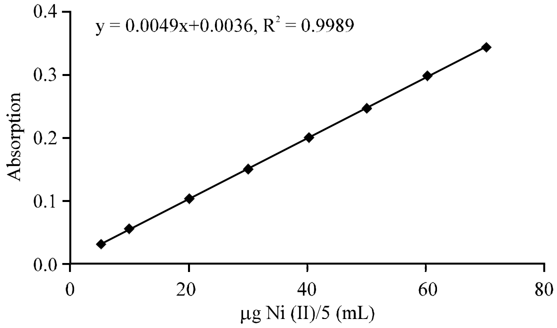

Fig. 1: Calibration curve for determined Ni^{2+} in aqueous solution according to DMG methody

RESULTS AND DISCUSSION

Spectrophotometric study for ion pair complex was extracted into the organic phase which involved preparing a 5 mL aqueous solution containing 100 μg of Ni^{2+} and 0.5 M KOH, then added to this solution 5 mL chloroform solution containing 1×10^{-4} M of cryptand C222 and 0.2 M 8-hydroxy quinoline then shaking this solution for 15 min in an electrostatic shaker and afterward separating the organic phase from the aqueous phase and taking the spectrum to the organic phase against a blank prepared in the same manner with the absence of Ni^{2+} ion, the results are displayed in Fig. 2.

The spectrum shows the wave length for maximum absorbance of the complex was λ_{max}= 400 nm, this wave length was used for the absorbance measurement of the organic phase in all experiments.

Variation KOH concentration effect: The 5 mL aqueous solutions contained 100 μg Ni^{2+} and rising concentrations of KOH were added to the solutions and then added 5 mL chloroform solution containing 1×10^{-4} M C222 and 0.2 M 8-hydroxy quinoline to each solution and shaken in an electrostatic shaker for 15 min and then separated the two organic phases. The process was completed with the comprehensive method and the results are shown in Fig. 3 and 4.

The results show that 0.7 M KOH was the optimum concentration of KOH which increased extraction efficiency because the concentration reached its optimum equilibrium to form ion pair association complexes that could be extracted with higher stability as described:

$$C222+K^{+}OH^{-}\rightarrow\left[K-C222\right]^{+};OH^{-}$$

$$Ni^{2+}+8\text{-}HQ\xrightarrow{KOH}Ni(OX)_3$$

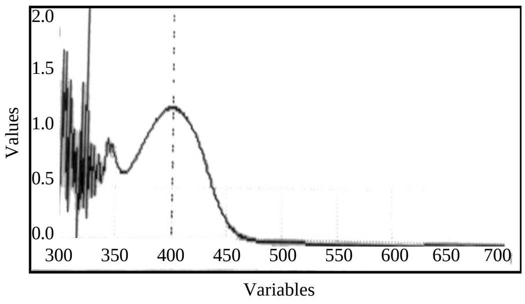

Fig. 2: Absorption UV-Vis spectrum for ion pair association complex for Ni^{2+} extracted

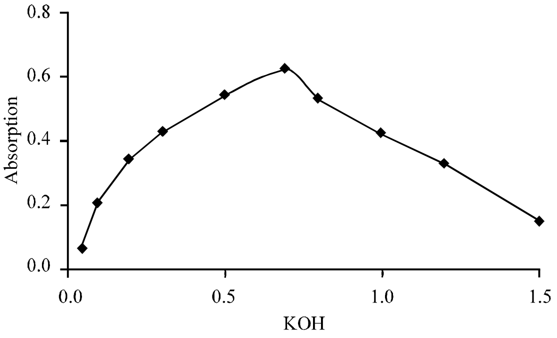

Fig. 3: Effect of KOH concentration on ion pair and association formation stability

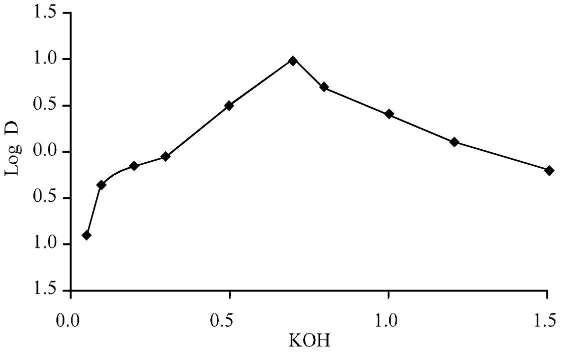

Fig. 4: D = f [KOH]

$$[\text{K-C222}]^{+};\text{OH}^{-}+\text{Ni}(\text{OX})_{3}^{-} \rightleftharpoons [\text{K-C222}]^{+};\text{Ni}(\text{OX})_{3}^{-}+\text{OH}^{-}$$

This concentration of KOH is very suitable to the formation and exchange with a less than optimum KOH concentration which prevents it from reaching equilibrium and causes a decrease in extraction efficiency but any concentration with a more than optimum value appears to decline in extraction efficiency also because the formation of a stable structure was dissolved but not extracted and therefore caused a decrease in formation of ion pair association complex.

Variation Ni (II) concentration: Extraction was performed of a 5 mL aqueous solution according to the comprehensive method with an increasing quantity of metal ions Ni^{+2}, the results are shown in Fig. 5 and 6.

The results show there is an increase in extraction efficiency by increasing metal ion concentrations in an aqueous solution which means increasing the rate of forward direction of the equilibrium of forming the ion pair association complex extracted into the organic phase whereas increasing the metal ion concentration suggests an increase of anion complex $Ni(OX)_3^-$ then increasing in liquid ion exchange to form ion pair complexes as well as increasing metal concentration more than 100 µg effect to decrease extraction efficiency because this increase caused an increase in the rate of backward direction for equilibrium of anion complex formation $Ni(OX)_3^-$. That means an increase in equilibrium and a decrease of the concentration of $Ni(OX)_3^-$ and this caused a decrease in the concentration of the ion pair complex formed and transferred according to mass action law.

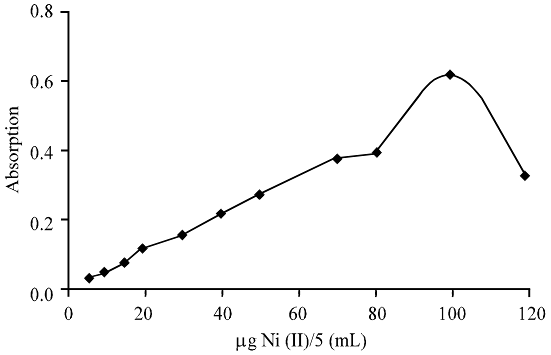

Fig. 5: Effect of metal ion concentration on ion pair complex formation and absorbance

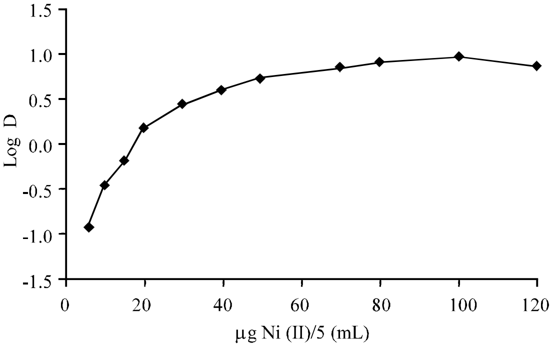

Fig. 6: Effect of metal ion concentration on extraction efficiency and D-value

Effects of shaking time: The 5 mL aqueous solutions were prepared and each one contained 100 µg of Ni^{2+} and 0.7 M KOH they were shaken with a 5 mL chloroform solution containing 1×10^{-4} M C222 and 0.2 M 8-HQ for different times in electrostatic shaker and then the experiment was completed with the comprehensive method and the results are shown in Fig. 7 and 8.

The results show that optimum shaking time was 15 min because it led to the best extraction efficiency when the extraction was done according to liquid ion exchange. This indirect method depends on thermodynamic and kinetic law, the shaking time is the kinetic side of extraction and this optimum time of shaking

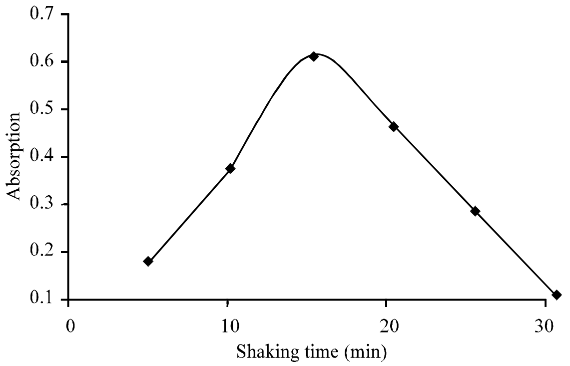

Fig. 7: Effect of shaking time on ion pair complex formation and stability

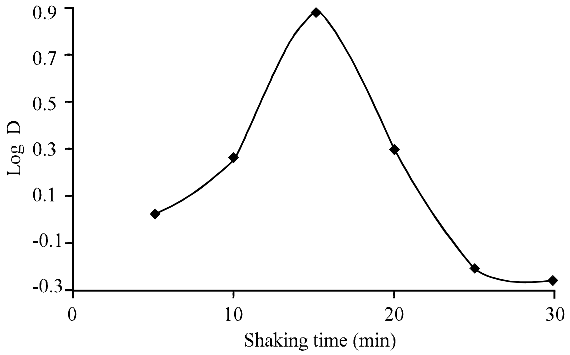

Fig. 8: Effect of shaking time on extraction efficiency and D-value

reaches the best equilibrium for formation Ni $(OX)_3^-$ and ion pair association complex $[K\text{-}C222]^+$; $Ni(OX)_3^-$ with higher concentration and stability. Any shaking time less than optimum value prevents optimum equilibrium and causes a decrease in extraction efficiency, so, shaking time longer than optimum leads to a decline in extraction efficiency also because the increase in kinetic energy causes an increase in diffusion and the dissociation of complexes in large quantities of energy content in solutions.

Variation 8-HQ concentration: Extraction was performed of 100 μg of Ni^{2+} from 5 mL aqueous solution in presence of 0.7 M KOH after 5 mL of chloroform was added to a solution containing 1×10^{-4} M C222 and different concentrations of 8-HQ, all the solutions were shaken for 15 min and the experiment was completed according to comprehensive method. The results are displayed in Fig. 9 and 10.

The results show that 0.25 M of 8-HQ was the optimum concentration for higher extraction efficiency because this concentration reached equilibrium to form the anion complex with high stability.

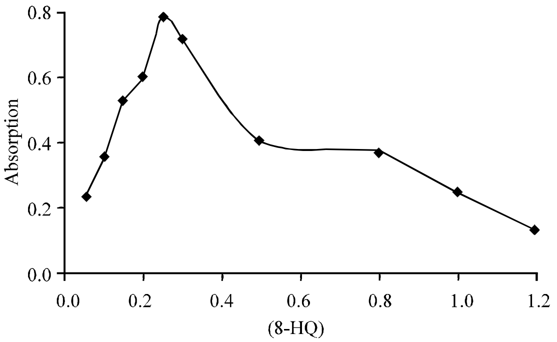

Fig. 9: Effect of 8-HQ concentration on ion pair complex formation and stability

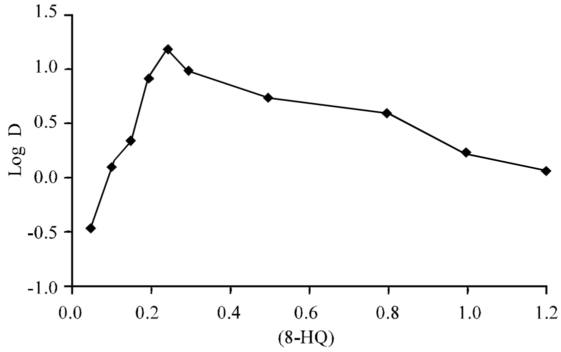

Fig. 10: Effect of 8-HQ concentration on extraction efficiency and D-value

$$Ni^{2+}+3OX^- \rightleftharpoons Ni(OX)_3^-$$

Leading to the best equilibrium for formation, stability and partition into the organic phase leading to higher extraction efficiency:

$$[K\text{-}C222]^+;OH^-+Ni(OX)_3^- \rightleftharpoons [K\text{-}C222]^+;$$
$$Ni(ox)_3^-+OH^-$$

Any concentration of less than the optimum value prevented it from reaching the ideal equilibrium levels and decreased extraction efficiency, so that, the 8-HQ concentration higher than optimum value caused a decline in extraction efficiency also because it increased the rate of dissociation due to the effects of mass action law.

Effect of methanol: Extraction was performed of 100 μg Ni (II) from 5 mL aqueous solutions containing different percentages of methanol according to the comprehensive method and the results are displayed in Fig. 11 and 12.

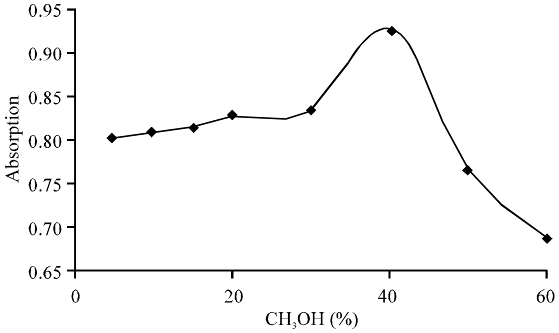

Fig. 11: Effect of CH_3OH% on ion pair complex formation and stability

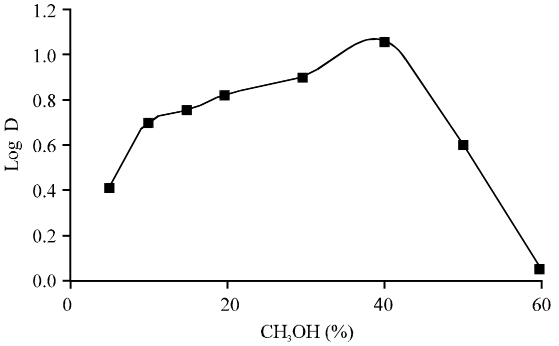

Fig. 12: Effect of CH_3OH% on extraction efficiency and D value

The results show the presence of methanol in the aqueous phase, increasing the extraction efficiency but this increases the percentage of CH_3OH until it reaches 40% CH_3OH which is the optimum percentage value giving the highest extraction efficiency because CH_3OH decreases the polarity of the aqueous phase and destroyed the hydration shell of metal ions Ni^{2+} to increase formation of anion complex Ni $(OX)_3^-$ and increase anion complex formation at 40% CH_3OH increasing in ion pair complex extraction but any concentration of CH_3OH % less than optimum causes a decrease in anion complex formed and a decline in extraction efficiency, so that, CH_3OH % more than optimum value leads to a decline in extraction efficiency also because it causes a decrease in dielectric constant and polarity of aqueous solution which causes transfer of some cryptand into the aqueous phase and decreases the ion pair complex extracted into the organic phase.

Interference effect: Extraction was performed of 100 μg Ni^{2+} from 5 mL aqueous solutions in presence of some foreign ions according to the comprehensive method at other optimum conditions, the results are shown in Table 1.

Table 1: Effect of presence some Foreign ion on extraction efficiency of Ni^{2+} ion

Foreign ion	Abs. at λ_{max} = 400 nm	D
Al^{3+}	0.132	2.85
Ca^{+2}	0.222	1.22
Mg^{+2}	0.184	1.67
Hg^{+2}	0.132	2.85
Cu^{+2}	0.280	1.15

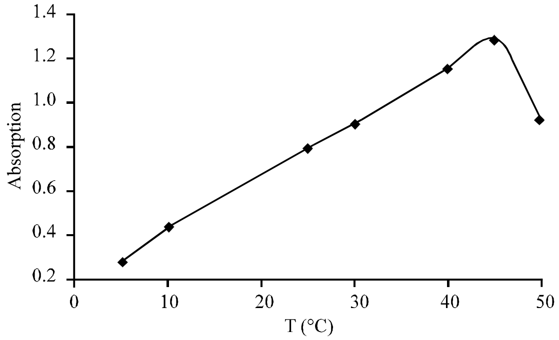

Fig. 13: Effect of temperature on ion pair complex formation and stability

The results show there is an interference for all foreign metal cations present in the aqueous solution which means these ions participate in the formation of anion complexes or stable compounds with $(OX)^-$ in basic solution and this behavior causes the consumption of part of 8-HQ and the remaining quantity of 8-HQ less than optimum value necessary to achieve equilibrium, so that, giving a part of cryptand C222 to form an ion pair complex will have the effect of decreasing the extraction efficiency of Nickel (II).

Thermodynamic study: Extraction was performed of 100 μg Ni^{2+} from 5 mL aqueous solutions in existence 0.7M KOH by 5 mL chloroform solution containing 1×10^{-4} M C222 and 0.25 M 8-HQ and shaking each solution for 15 min at different temperatures. This was done in a shaker water bath with a regulator and the experiment was completed according to the comprehensive method, the results are shown in Fig. 13 and 14.

The results demonstrate the extraction method was endothermic and 45°C was the optimum temperature after calculating the extraction constant k_{ex}, at each temperature according to the relationship:

$$K_{ex} = \frac{D}{\left[Ni^{2+}\right]\left[C222\right]} \quad (2)$$

The results illustrated in Fig. 15. From the slope of the straight line in Fig. 15 and the points below, thermodynamic data was calculated for the extraction of ions and the results are displayed in Table 2.

Table 2: Thermodynamic data for extraction

Variables	Values
ΔS_{ex} (J mol^{-1} K-^{1})	0.0602
ΔG_{ex} (KJ mol^{-1})	-56.72
ΔH_{ex} (KJ mol^{-1})	178.55

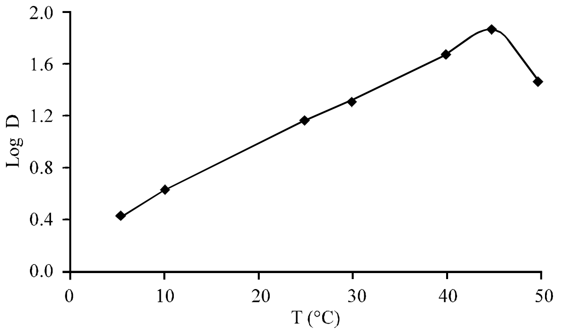

Fig. 14: Effect of temperature on extraction efficiency and D value

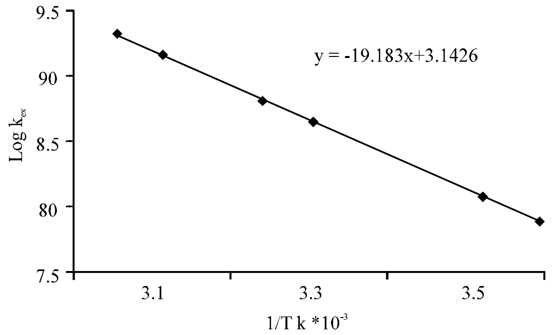

Fig. 15: Effect of temperature on extraction constant of Ni^{2+}

$$\text{Slope} = \frac{-\Delta H_{ex}}{2.303\,R}$$

$$\Delta G_{ex} = -RT \text{ Ln } K_{ex}$$

$$\Delta G_{ex} = \Delta H_{ex} - T\,\Delta S_{ex}$$

The small value of enthalpy reflects the increased attraction of the ions in ion pair association complex, so that, large positive value of entropy ΔS_{ex} demonstrated the major effective parameters for formation of ion pair association complex as well as extracted into the organic phase, so that, the extraction method is entropic in region.

Table 3: Effects of organic solvent on the extraction efficiency

Organic solvent	ε_r	Wave length (nm)	Abs.	D
Amyl alcohol	15.800	418	0.655	7.330
1,2-DCM	10.650	426	0.880	6.140
DCM	9.080	411	0.182	11.50
Bromo benzene	5.400	410	0.763	4.490
$CHCl_3$	4.806	400	0.795	15.13
Benzene	2.804	349	0.964	3.260
Toluene	2.438	369	0.215	11.05

Table 4: Thermodynamic data of extraction with different organic solvents

Organic solvent	$-\Delta Gt$	K_A*10^4	K_{ex}*10^8	$-\Delta Gex$
Amyl alcohol	0.147	2.440	15.76	52.47
1,2-DCM	0.236	2.095	11.06	51.59
DCM	0.283	3.670	38.78	54.70
Bromo benzene	0.500	1.610	5.91	50.04
$CHCl_3$	0.567	4.730	67.13	56.05
Benzene	0.998	1.250	3.12	48.45
Toluene	1.153	3.540	35.81	54.50

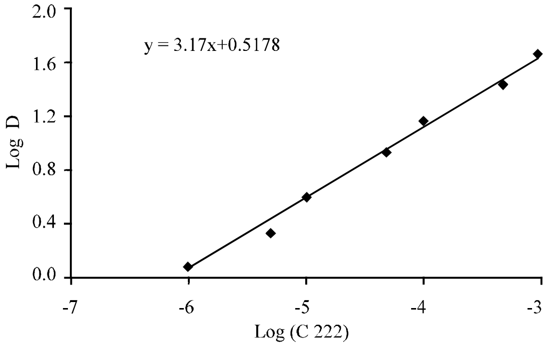

Fig. 16: Slope analysis method, Effect of (C222) concentration on D value

Effect of organic solvent: Extraction was performed of 100 μg Ni^{2+} from a 5 mL aqueous solution in presence 0.7M KOH by 5 mL organic solution prepared from and 0.25M 8-HQ dissolved in different organic solvents and different dielectric constants then these slutions were shaken for 15 min in an electrostatic shaker and separated then the spectrum for the organic phase was taken and compared against a blank prepared in the same manner in the absence of the metal ion but the aqueous phase was treated according to the procedure detailed in the comprehensive method, the results were what is displayed in Table 3. After thermodynamic data was determined for extraction of different organic solvents, the results are shown in Table 4.

The results show there is not any linear relation between the dielectric constant of organic solvents used and the distribution ratio for extraction with each organic solvent but it appears there is an effect for organic solvent structure on extraction efficiency through participation of the organic solvents on the formation of ion pair association complex extracted which is contact ion pair or loose ion pair.

Stoichiometry: To determine the more probable structure of the ion pair association complex of Ni (II), two spectrophotometric methods were used; Slope analysis and slope ratio methods. As the results are displayed in the Fig. 16 and 17:

$$\text{Slope ratio} = \frac{795.224}{704.499} = 1.127$$

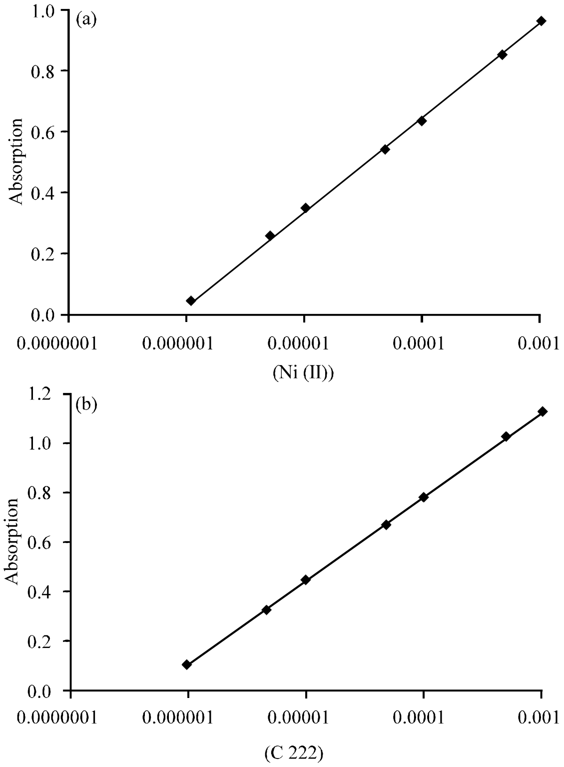

Fig. 17: Slope ratio; a) Effect of Ni^{+2} concentrations on ion pair complex formation and stability and b) Effect of C222 concentration on ion pair complex formation and stability

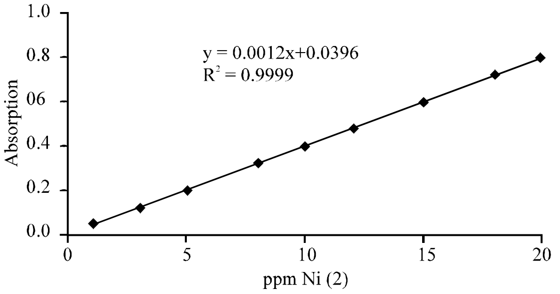

Fig. 18: Calibration curve for spectrophotometric Determination of Ni^{+2} by using C222 according to liquid ion exchange

From the slope value of the straight line in the slope analysis and slope ratio demonstrate the more probable structure of an ion pair association complex extracted were 1:1:1 $[K\text{-}C222]^+$; $Ni(OX)_3^-$.

Spectrophotometer determination: For spectrophotometric determination of Ni^{2+} in different samples, calibration curve was performed as in Fig. 18.

CONCLUSION

There are several applications for solvent extraction method to separate and spectrophotometric determination of different metal ions by using a suitable extractant as in research (Mahamuni *et al*., 2010; Waghmode *et al*., 2012; Bahram *et al*., 2013; Shawket and Faris, 2015, Noronha *et al*., 2013).

REFERENCES

Bahram, M., S. Shahmoradi, S. Mozaffari, A. Niko and K.A. Dilmaghani, 2013. Cloud-point extraction and selective spectrophotometric determination of PB (II) and Cu (II) using synthesized N1, N2-diphenylhydrazine-1, 2-dicarbothioamide and an anionic surfactant. Jordan J. Chem., 8: 45-55.

Gharabaghi, M., M. Irannajad and A.R. Azadmehr, 2013. Separation of nickel and Zinc ions in a synthetic acidic solution by solvent extraction using D2EHPA and Cyanex 272. Physicochem. Prob. Mineral Process., 49: 233-242.

Jawad, S.K. and A.S. Abed, 2015. Efficient method cloud point extraction for separation preconcentration and trace amount determination of bismuth (III) from different samples by new laboratory prepared Azo derivative. J. Nat. Sci. Res., 5: 39-51.

Jawad, S.K. and M.N.M. Salih, 2015. Cloud point extraction methodology for separation and extraction Platinum (II) as Chloro complex anion coupled with spectrophotometric method for determination in different samples. J. Nat. Sci. Res., 5: 195-201.

Khammas, Z.A.A., I.R. Ali and S.K. Jawad, 2016. Cloud point extraction and micro amount determination of cadmium as chloro anion complex in real samples by using molecular spectrophotometry. Kufa J. Chem., 6: 60-69.

Mahamuni, S.V., P.P. Wadgaonkar and M.A. Anuse, 2010. Liquid-liquid extraction and recovery of gallium (III) from acid media with 2-octylaminopyridine in chloroform: Analysis of bauxite ore. J. Serb. Chem. Soc., 75: 1099-1113.

Marczenko, Z. and M. Balcerzak, 2000. Separation, Preconcentration and Spectrophotometry in Inorganic Analysis. 1st Edn., Elsevier, Amsterdam, Netherlands,.

Noronha, L.E., G.S. Kamble, S.S. Kolekar and M.A. Anuse, 2013. Recovery of molybdenum (VI) from hydrochloric acid medium by solvent extraction with 2-n-octylaminopyridine. Intl. J. Chem. Sci. Tech., 3: 15-24.

Shawket, K.J. and H.H. Faris, 2015. Optimization cloud point extraction methodology for separation, extraction and spectrophotometric determination of Zn (II). J. Chem. Mater. Res., 7: 63-72.

Shawket, K.J. and R.M. Jihan, 2012. Cloud point extraction methodology for separation and microamounts determination of Lead (II) and Cadmium (II) ions. Iraqi Nat. J. Chem., 47: 401-412.

Waghmode, D.P., M.D. Jamdar, S.S. Kolekar and M.A. Anuse, 2012. Separation of antimony (III) with p-anisaldehyde thiocarbohydrazone by solvent extraction from hydrochloric acid medium for its spectrophotometric determination in real samples. Arch. Appl. Sci. Res., 4: 2400-2410.