

Solvent Extraction Method for the separation of Ni(II) By use New ligand

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ABSTRACT

Extraction experiments for Ni(II) ions from aqueous phase by new laboratory prepared Azo derivation as complex agent 2- [4-bromo-2,6-diethyl phenylazo] -4,5-diphenylimidazole(LIGAND) shows the optimum conditions for this extraction method was (pH= 10) (10 minutes) shaking time and 50µg concentration of Ni(II) ions in aqueous phase. Organic solvents effect study shows there is not any linear relation between distribution ratio (D) for extraction of Ni=+2 ions and dielectric constant (ε) for organic solvents used but there is in effect for organic solvent structure on the extraction of Ni=+2 ions and distribution ratio (D) values. Stoichiometric studies demonstrated the more probable structure ion pair complex extracted for Ni=+2 was 1:1.

Keywords: Ni(II), Solvent extraction.

I. INTRODUCTION

Previously used the azo compounds and its derivatives for the extraction methods and used to spectrophotometric determination of transition elements, Determination of Ni(II) 2-[2-pyridil azo]-4-benzen naphthol and 2-[(4-Hydroxy phenyl azo)-4,5-diphenyl imidazol were synthesized and used for the extraction of Ni(II) and Cd(II) from aqueous solutions. Study effective factors on the extraction method such as pH, metal concentration, shaking time organic solvents. Stoichiometry shows the complex extracted was $[M+2(L-(Cl-))]$ and $[M+2(HPADPI)]2Cl-$ when $(M2+=Ni2+,Cd2+)$ [121] [1]. The extraction of Ni(II) and Cd(II) with mixtures of neutral organophosphorus extractants (aliphatic trialkyl phosphine oxide, Cyanex 923, or branched cyclic trialkyl phosphine oxide, Cyanex 925) and amine extractants (N,N-di(1-methylheptyl) acetamide, N503, or trialkyl amine, N235) Synergistic effects were observed for Ni(II) with Cyanex 923+N503 and for Cd(II) with Cyanex 923+N235 and Cyanex 925+N235. However, the other mixing systems do not have synergistic effects on Ni(II) and Cd(II). The

stiochiometry of extracted species studied with slope analysis and constant moles in the three synergistic systems [2].] Extraction of micro amount Coper (II) and Nickel(II) by organic reagent 2-[(3-Acyl methyl phenyl)azo]-4,5-di phenyl imidazole(3-AMePADPI) and spectrophotometric determination of Copper (II) and Nickel(II) used for in different samples, studies conditions for complex formation was pH= 10 and 11 , shaking time 15 minutes for Cu+2 and Ni+2 respectively[3].

II. METHODS AND MATERIAL

Reagents - Materials and Solutions:

All chemical materials received from commercial sources with high purity and used as received [4] The stock solution of Ni(II) ions (1 mg/ml) prepared by dissolved 1 gm of Ni metal in (15 ml) of dilute hydrochloric acid (1 : 1) and then diluted this solution to 1 liter by distilled water in volumetric flask. A working standard solutions prepared by dilution with distilled water, needful prepared buffer solution (pH = 5) for determination of Ni(II) by dissolved (60 gm) of anhydrous sodium acetate

and (30 gm) of glacial acetic acid in 250 ml volumetric flask, as well as necessarily prepared sodium thiosulphate solution (10%) also for Ni(II) determination.

Synthetic of organic reagents:

The organic reagents was synthesized according to the procedure published elsewhere [5] by dissolving (2.28 g 0.01 mole) of 4-bromo-2, 6-diethyl aniline. In a solution of 4 mL concentration HCl and 25 distilled water. After cooling this solution 0 °C, added 1.4 g of sodium Nitrite dissolved in 10 mL distilled water with maintaining the temperature at 0 °C. The mixture was set aside for 15 min in order to complete diazotization reaction. Afterward, the diazonium solution was added drop by drop to solution contain (2.2 g , 0.01 mole) of 4,5-diphenyl imidazole and 1.2 g sodium hydroxide dissolved in 150 mL ethanol with keeping temperature at 0 °C. After complete addition, the left contains for two hours, then added 150 mL of cooled distilled water was added, the pH of the solution maintained at 6 by HCl, a brown molecules was precipitated and left for 24 h.

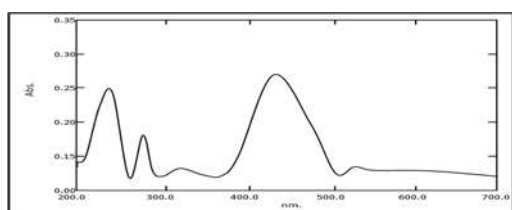


Fig 1: IR-spectrum of organic reagent (LIGAND).

TABLE I: DEMONSTRATE THE STRUCTURE OF AZO LIGAND PREPARED.

Bands (cm ⁻¹)	Assignments
344.4	N-H stretching
3329.03	Aromatic CH stretching
1616.4,1392.65	C=N stretching and bending
1500	for -N=N-
1549.19	C=C
3048	CH aliphatic

Comprehensive method for extraction:

For extraction experiments have to take (5 ml) of aqueous phase contain exact quantity of Ni(II)ions at optimum pH, and then adding (5 ml) of organic phase contain exact concentration of ligand in organic solvent, afterward shaken the two phases at optimum time, after complete the shaken time separate the two layers and determine the Ni(II)ions remainder in aqueous phase by

spectrophotometric method [4], for (5 ml) aqueous phase add (2 ml) of buffer solution and (2 ml) of thiosulphate solution and shaken with five portions of (1×10^{-4} M) dithizone solution, every portion equal to (1 ml), until the last portion do not change their green color. Afterward collect the portions in (5 ml) volumetric flask and then shaken with 5 ml of dilute ammoNia solution to separated unreacted dithizone, after that determine the absorption of solution at $\lambda_{\text{max}} = 570$ nm by use CCl₄ as blank, from absorbance and calibration curve Figure (2) can be determine the quantity of Ni(II)remainder in aqueous phase. But for determination the quantity of Ni(II)ions in organic phase as a complex with the ligand, by stripping method which is include shaken the organic phase three times with nearly concentrated hydrochloric acid HCl for dissociation the Zn – complex and transfer the Ni(II)ions to the aqueous phase and then determine the quantity of Ni(II)ions by spectrophotometric method, previous method, afterward divide the quantity of Ni(II)ions in organic phase on the quantity of Ni(II)ions in aqueous phase to determined distribution ratio (D).

III. RESULTS AND DISCUSSION

Absorption UV–Vis spectrum:

Absorption UV–Vis spectrum in Figure 2 shows maximum absorption for ion pair complex extracted at $\lambda_{\text{max}} = 580$ nm.

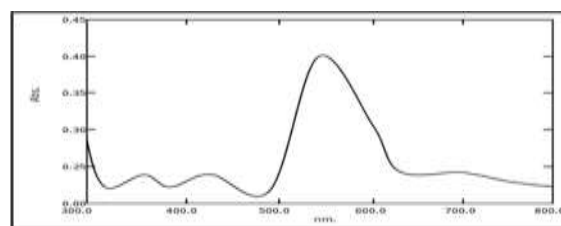


Fig 2: Absorption UV–Vis spectrum for ion pair complex

Effect of acidic function:

Extracted 60µg Ni(II) in 5mL aqueous phase with 5ml of (1×10^{-4} M) organic reagent solution (LIGAND) dissolved in chloroform at different pH of aqueous phase (6-12) and shaking the two phases for (10 minutes) after that separate the two phases and determination of distribution ratio (D) as in the general method, as well as determine absorbance of organic phase against organic reagent as blank. The result as in figures 3 and 4.

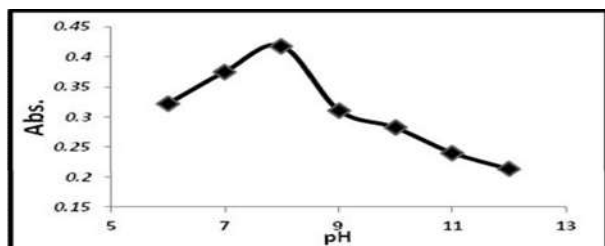
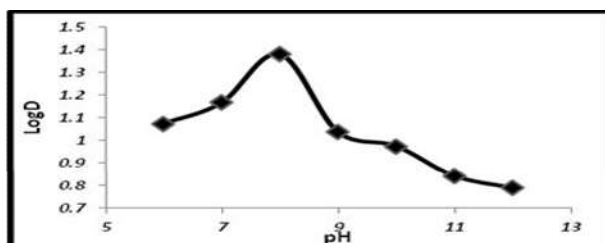


Fig 3: Effect of pH on complex formation as extraction.

Fig 4: Effect of pH on $D=f(pH)$.

The results shows optimum pH for extraction was pH=8 at the pH obtained higher Absorbance and D- value that is measure reached higher extraction .Efficiency at this pH and at pH less than pH=8 our suitable to reach favorable thermodynamic equilibrium for extraction and by decrease pH value increase hydration shell of Ni(II) as well as increase protonated of complex agent and decrease complexation ,but at pH value more than optimum value also lead to decrease extraction efficiency.

Effect of Metal ion concentration:

Extraction of different concentrations of Ni(II) ions (1-70) μg in (5ml) aqueous solution at (pH=8) by (5ml) of (1×10^{-4} M of (LIGAND)) dissolved in chloroform, shaking the two layers for suitable time, and separate the two layers and determine the remainder quantity of Ni(II) ion in aqueous phase by followed spectrophotometric method [5], and calculation distribution ratio (D) as well as determine absorbance of organic phase at $\lambda_{\text{max}}=548\text{nm}$ against organic reagent as blank. The result was as in figures 5 and 6.

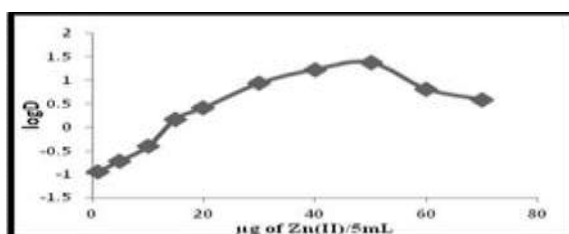


Fig 5: Effect of Ni(II) concentration on activity of extraction and D value.

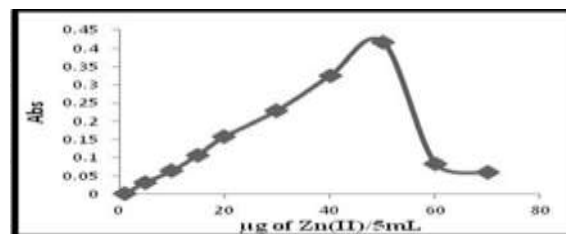


Fig 6: Effect of Ni(II) concentration on thermodynamic equilibrium for complex formation and extraction.

According to thermodynamic equilibrium for complexation reaction. $\text{Ni}^{2+} + \text{aq} + (\text{LIGAND})_{\text{org}} + 2\text{Cl}^{-}\text{aq} \leftrightarrow [\text{Ni}(\text{LIGAND})]^{2+} + 2\text{Cl}^{-}\text{org}$. [6,7]

The results show 50 μg $\text{Ni}^{2+}/5\text{mL}$ was the optimum concentration giving higher efficiency of extraction because effect to increase rate of forward direction of thermodynamic equilibrium that is mean increase formation and extraction of ion pair complex concentration of Ni(II) less than optimum value not enough to reach favorable thermodynamic equilibrium that is mean decrease in ion association complex formation and extraction so that Absorbance and D-value from other hand any concentration of Ni(II) more than optimum value effect to decline extraction efficiency and decrease absorbance and D-value became effect to increase rate of back ward direction of thermodynamic equilibrium according to the chatelier principle and mass action law.[8]

Effect of shaking time:

For the kinetic side of the extraction methods are carried out by studying the effect of shaking time on the extraction activity and distribution ratio values.[9] After extracted 60 μg Ni(II) ions in 5ml aqueous phase at (pH=10) by 5ml of (1×10^{-4} M) organic reagent (LIGAND) dissolved in chloroform by different shaking time, the results of this study in figure 7 and 8 demonstrate the optimum shaking time of two layers was (10min.) to reach the equilibria of extraction and at this time obtain the maximum distribution ratio value (D), and Absorbance at 570nm shaking time but less than optimum no allow to reached the equilibria of extraction, so that shaking time more than optimum favorite the dissociation equilibria and minimize the distribution ratio (D) and absorbance.[10]

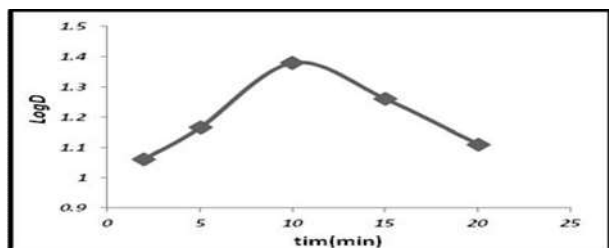


Fig 7: D=f (shaking times)

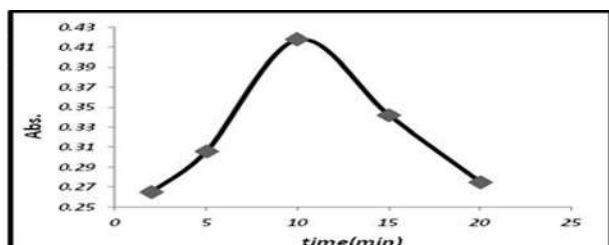


Fig 8: shaking time effect on complex formation and extraction

IV. CONCLUSION

By using spectrophotometric methods to know the more probable structure of complex extraction which are slope analysis, mole ratio, continuous variation method, slope ratio. Organic solvents effect study shows there is not any linear relation between distribution ratio (D) for extraction of Ni^{+2} ions and dielectric constant (ϵ) for organic solvents used but there is in effect for organic solvent structure on the extraction of Ni^{+2} ions and distribution ratio (D) values. Stoichiometric studies demonstrated the more probable structure ion pair complex extracted.

V. REFERENCES

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