

## LIQUID- LIQUID EXTRACTION METHOD FOR EXTRACTION ZN(II) FROM AQUEOUS SOLUTIONS BY ORGANIC REAGENT

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### ABSTRACT

Extraction experiments for  $Zn^{+2}$  ion from aqueous phase by new laboratory prepared Azo derivation as complexation agent 2- [(4-Benzyloxy phenyl)azo]- 5- nitro-4-phenyl imidazole (BANI) shows the optimum conditions for this extraction method was (pH= 9) (10 minutes) shaking time and  $100\mu g$  ( $1.5 \times 10^{-4} M$ ) concentration of  $Zn^{+2}$  ion in aqueous phase. Organic solvents effect study shows there is not any linear relation between distribution ratio (D) for extraction of  $Zn^{+2}$  ion and dielectric constant ( $\epsilon$ ) for organic solvents used but there is an effect for organic solvent structure on the extraction of  $Zn^{+2}$  ion and distribution ratio (D) values. Stoichiometric studies demonstrated the more probable structure ion pair complex extracted for  $Zn^{+2}$  was 1:1.

**KEYWORD:** Zn (II), Solvent extraction, azo ligand.

### INTRODUCTION

Extraction of Cd(II) and Zn (II) complexes by using 2-[(4-Hydroxy phenylazo)-4,5-diphenyl imidazol and 2-[2-pyridil azo]-4-benzen naphthol. The optimization of extraction parameters such as pH, metal concentration, shaking time and organic solvents was studied. The stoichiometry shows the extracted species which was  $[M^{+2}(HPADPI)]_2Cl^-$  and  $[M^{+2}(PABN^-(Cl^-))]$  when ( $M^{2+} = Cd^{2+}, Zn^{2+}$ ).<sup>[1]</sup> New imidazol ligands were synthesized and used for extraction and spectrophotometric determination of cobalt (II), nickel(II) and copper(II).<sup>[2]</sup> Chromium in steel was determined spectrophotometrically after its complexation with 4-[thiozoly] azo-resorcinol (TAR)<sup>[3]</sup>, extraction of Zn(II) and Ni(II) complexes with 1-octyl imidazol and 1-octyl-2-methyl imidazole.<sup>[4]</sup> Study by use 2-(2-benzimidazolyl azo)-4-

acetoamidophenol by use complex formation with Fe(III),Co(II),Ni(II),Cu(II),Zn(II) and Cd(II).<sup>[5]</sup> The extraction of Zn(II) and Cd(II) with mixtures of neutral organophosphorus extractants (branched cyclic trialkyl phosphine oxide, Cyanex 925 or aliphatic trialkyl phosphine oxide, Cyanex923) and amine extractants, (trialkyl amine, N235) or (N,N-di(1-methylheptyl) acetamide, N503. Synergistic effects were observed for Zn(II) with N503+Cyanex 923 also for Cd(II) with N235+ Cyanex 923 and N235+ Cyanex 925. However, the other mixing systems do not have synergistic effects on Zn(II) and Cd(II).<sup>[6]</sup> Extraction procedures for Ag<sup>+</sup> from aqueous solutions by 2-[(4-Chloro-2-Methoxy phenyl) azo]-4,5-diphenyl imidazole (4-CIMePADPI) shows aqueous solutions must be at (pH=10) and concentration of Ag<sup>+</sup> ions is (40µg)(7.36×10<sup>-5</sup> M), with shaking time (11minutes), organic solvents effect on extraction method demonstrate there is not any linear relation between dielectric constant (ε) for organic solvents used and distribution ratio values (D), but there is effect for structure of organic solvent. Stoichiometry studies shows more probable structure of ion pair complex extracted was (1:1) (Metal:Ligand) [Ag(4-CIMePADPI)]+NO<sub>3</sub><sup>-</sup>, temperature effect shows from thermodynamic viewpoint the reaction between Ag<sup>+</sup> ions and ligand (4-CIMePADPI) was endothermic reaction, synergism studies appear there is one molecules of TBP participate in ion pair complex extracted [Ag(4-CIMePADPI)(TBP)]+NO<sub>3</sub><sup>-</sup>.<sup>[7]</sup>

## EXPERIMENTAL

### Instruments

All spectrophotometric measurements and absorbance were registered by using a double beam (UV-Vis) spectrophotometer shimadzu UV 1700 (Japan) and a Single beam (UV-Vis) spectrophotometer TRIUP international corp. TRUV 74,S (Italy), IR-Spectra for the complexes were recorded by using FTIR S 8400 (England).

### Materials

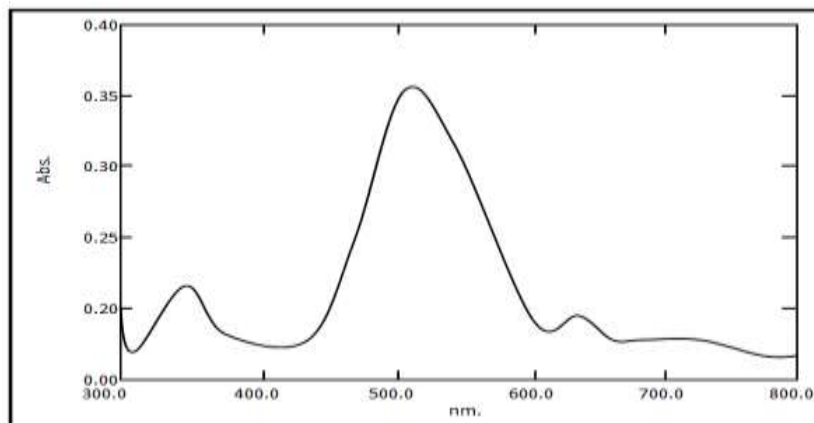
All chemicals used provided from Fluka and Merck.

### General procedure

Aqueous solution 5ml in volume contain limited concentration of metal cation Zn(II) at optimum pH shaking with 5ml of chloroform solution (BANI), after complete shaking separate aqueous solution from organic phase and determine remainder quantity of metal cation in aqueous solution by spectrophotometric method (dithizone method)<sup>[8]</sup>, at later calculate distribution ratio(D) for each ion.

## RESULTS AND DISCUSSION

The UV-Vis. spectrum and IR spectrum as well as the results obtained by in Figures 1,2 demonstrate the structure of azo ligand prepared.<sup>[9]</sup>



Figures 1:-absorption UV-Vis spectrum for ion pair complex.

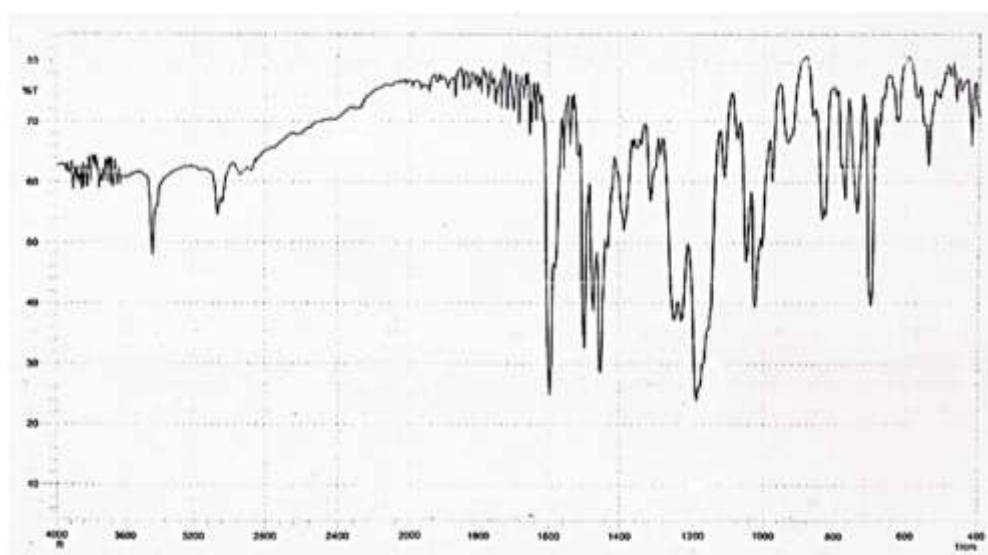


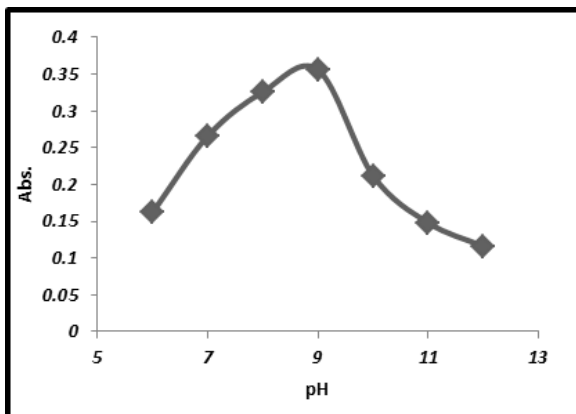
Figure (2): FTIR-spectrum of organic reagent 2- [(4- Benzyloxy phenyl)azo]- 5- nitro-4-phenyl imidazole (BANI).<sup>[9]</sup>

Table(1):- FTIR-spectrum of organic reagent 2- [(4- Benzyloxy phenyl)azo]- 5- nitro-4-phenyl imidazole (BANI).<sup>[9]</sup>

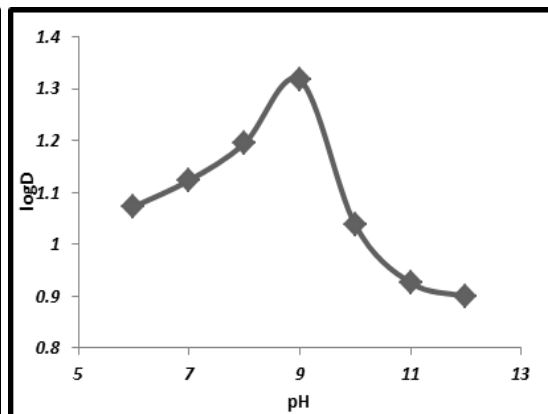
Bands (cm <sup>-1</sup> )	Assignments
3414.12	N-H stretching
3339.03	aromatic CH stretching
1616.4,1392.65	C=N stretching and bending
1494.88	for -N=N-
1556.16	C=C
3045.7	CH aliphatic

**Effect of pH**

Extraction of 50  $\mu\text{g Zn}^{2+}/5\text{ml}$  by ligands at different pH(1-12) as in general procedure and calculate D value at each pH, Figures(3,4) shows optimum  $\text{pH}_{\text{ex}}$  for  $\text{Zn}^{2+}$  was  $\text{pH}_{\text{ex}}=9$  with (BDPI).



**Figure (3): Effect of pH on complex formation and extraction efficiency**

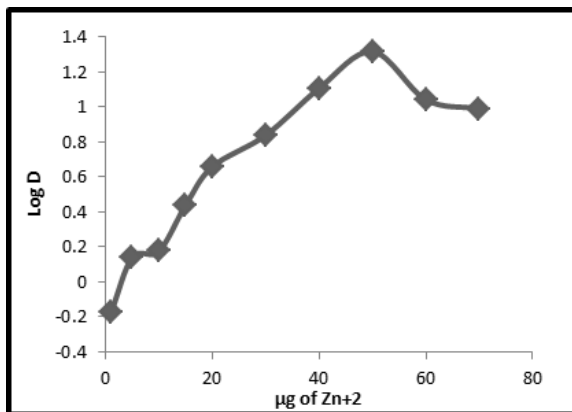


**Figure(4):D=f(pH)**

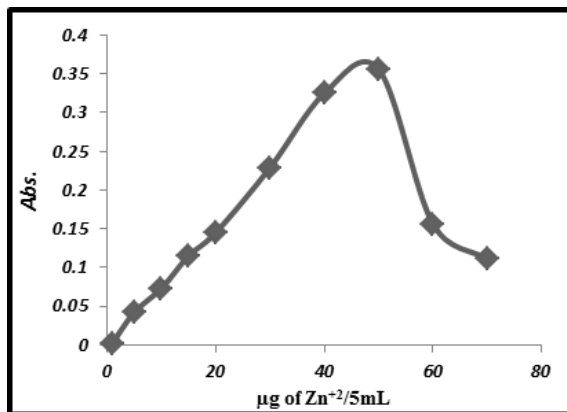
Acidic media not suitable for extraction because effect to protonated ligand molecule and decline extraction and distribution ratio (D), also pH more than optimum value not as well suitable for extraction because dissociation of complex and formation stable species' of metal cation.

**Effect of metal ion concentration**

Aqueous solutions 5ml in volume contain (1  $\mu\text{g}$ -70  $\mu\text{g}$ ) Zn(II) extracted by (BDPI),. after calculate distribution ratio (D). The results in Figure(5,6) shows optimum concentration of Zn(II) was 50  $\mu\text{g}$  with (BDPI).



**Figure(5): Effect of Zn(II) concentration on activity of extraction and D value**

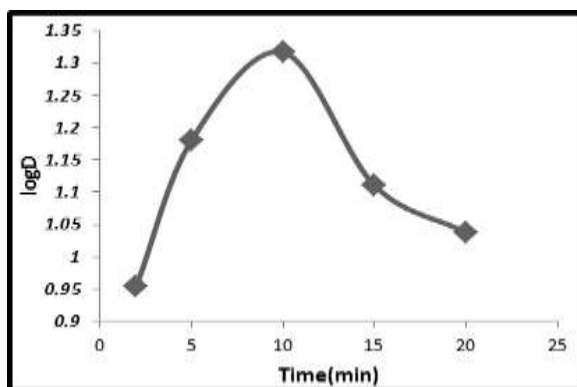


**Figure(6): Effect of Zn(II) concentration on thermodynamic equilibrium for complex formation and extraction**

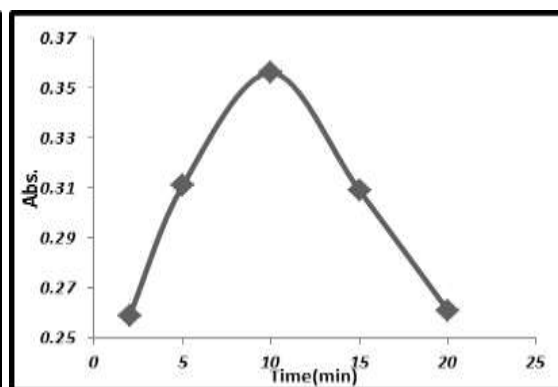
According to thermodynamic equilibrium for complexation reaction, concentration of metal cation play major rule for formation and stability of complex extracted.

### 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. After extracted 50 $\mu$ g Zn(II) ions in 5ml aqueous phase at (pH=9) by 5ml of ( $1 \times 10^{-4}$  M) organic reagent (BANI). dissolved in chloroform by different shaking time, the results of this study in Figure 7,8.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 438nm shaking time but less than optimum no allow to reached the equilibria of extraction, so that she shaking time more than optimum favorite the dissociation equilibria and minimize the distribution ratio(D)and absorbance.



Figure(7):D=f(shaking times).

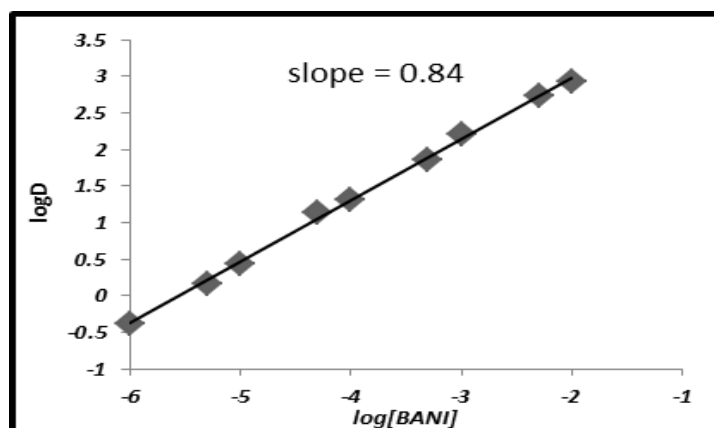


Figure(8): Shaking time effect on complex formation and extraction.

## STEREOCHEMISTRY

### Slope analysis method

Extraction metal cations from 5ml aqueous phase according to general procedure by 5ml ligands solution dissolved in chloroform at different concentration ( $1 \times 10^{-6}$ - $5 \times 10^{-4}$ M), sequentially separate the two layers after separate organic phase from aqueous phase, determine remain Zn(II) in aqueous phase and transferred quantity to organic phase and calculate distribution ratio (D) at each concentration of ligand, afterward plot log D against log[ligand] get the graph in Fig (9).



The slope of straight lines in Figure(9) demonstrate the complex extracted was 1:1 metal: ligand.

### CONTINUOUS VARIATION METHOD

In this spectrophotometric method for determining the probable structure of ion pair complex extract. prepared aqueous phase of Zn(II) and organic solution of ( BANI) dissolved in chloroform at same molar concentration( $1 \times 10^{-4}M$ ) and then mix different volumes of these solutions to maximum volume (10mL) at (pH=9) and shake each solution for (10minutes) afterward separate aqueous phase from organic phase and measure the absorbance of organic phase at wave length  $\lambda_{max} = (511 \text{ or } 501)nm$  respectively against organic reagent solution of (BANI). After plotting the absorption value against  $V_L/V_T$  the results were as in Figures (10).

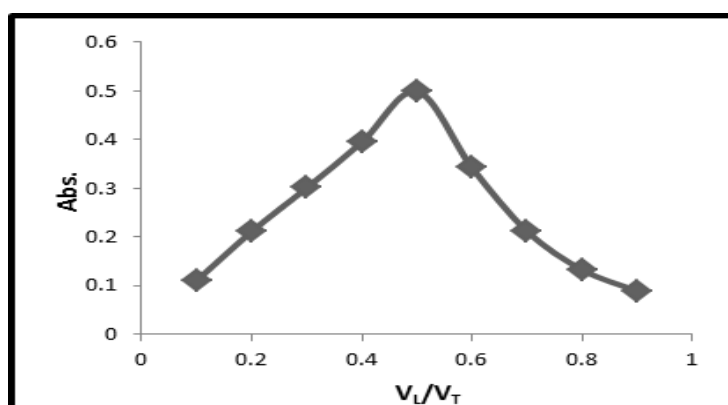
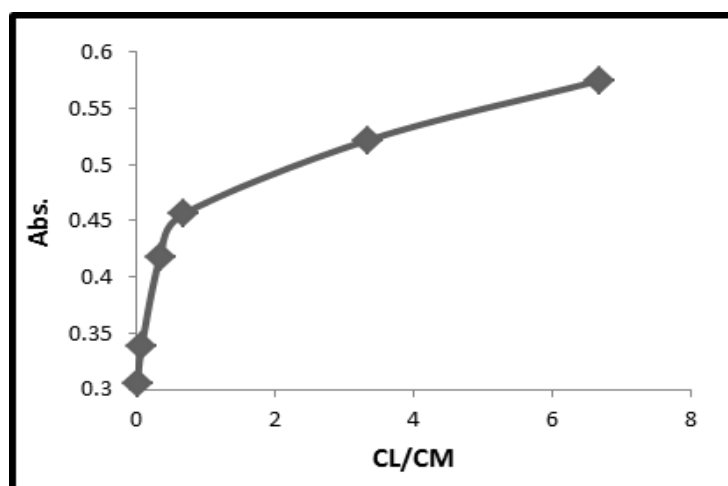


Figure (10): Job method by using organic reagent (BANI).

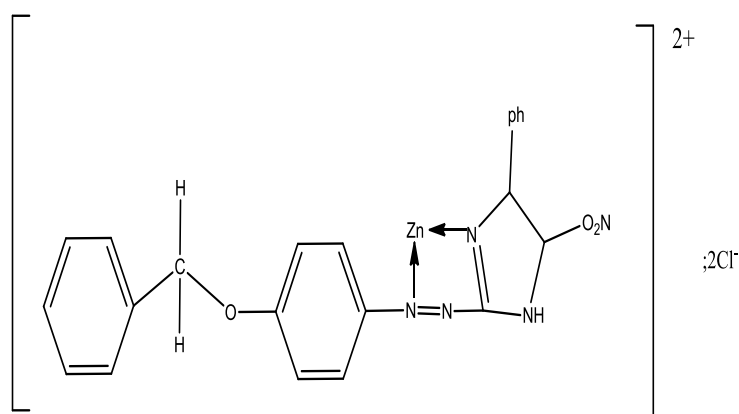
### Mole ratio method

Extraction metal cations from 5ml aqueous phase according to general procedure by 5ml ligands solution dissolved in chloroform at different concentration ( $1 \times 10^{-6}$ - $5 \times 10^{-4}M$ ),

sequentially separate the two layers, afterward plot absorbance vis CL/CM get the graph fig (11).



The graph in Fig (11) shows the complex extracted was 1:1 metal: ligand, so we can suggest the following structures of the complexes as shown below:



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