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Extraction, Isolation and Transport studies of Transition Metal cations through bulk liquid membrane using 1-(phenylazo)-2-naphthol in Organic Layer

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Abstract

The Isolation, Extraction and Transportation studies of transition metal cations (Cu^{2+}, Co^{2+},Ni^{2+} and Zn^{2+}) with Ionophore 1-phenylazo-2-naphthol or (S-I)were examined. The Isolation studies were performed to study the interaction between Metal ions and Ionophore in Organic solvent. These studies were focused on the capacity of the ionophore to extract metal cation from an aqueous phase into an organic phase by complexation. In the Extraction and Transportation studies chloroform is used as an Organic Phase. On comparing the results of Extraction and Transportation studies it is observed that some cations have been found selective for extraction while others are more selective for transportation with ionophore. This selectivity can be applied for ion selective electrode and other redox devices. It is also helpful for environmental studies. The results of this study will be useful for various applications in Chemistry, Biochemistry, molecular sensors and switches, liquid crystals and for artificial systems.

Key words: Isolation, Extraction, Liquid Membrane Transport, Azo dyes.

Introduction

Azo dyes are a very important class of organic compounds receiving attention in the scientific literature[1]. Recently, azo metal chelates have drawn the attention of some research due to their excellence in sensitivity and stability as optical recording medium[2,3], ink-jet printing and other applications. Moreover, the complexes of some azo dyes with metal ions have been recently investigated.[4,5] Azo dyes containing hydroxy or carboxylic acid group substituents adjacent to the azo group react with transition metal ions to produce complexes[6]. These metal dyes are more stable to light then their unmetallized precursor.

In recent years much attention has been paid to chemical separation techniques and the design and synthesis of new extraction reagents for ions and molecules[7]. In this respect, the Supramolecular chemistry has provided a much better solution to the search for molecular structures[8].

Among the separation techniques, ion transport is a selective, efficient and simple method. In the recent years, the liquid membrane has widely been used to study ion transport with a concentration gradient[9-13]. Ion transport through the liquid membrane plays an important role in simulating biological membrane functions and separation technologies because of the high transport efficiency, excellent selectivity and economic advantages of the liquid membrane. Selective transport of transition metal ions through liquid membranes has become increasingly noteworthy. A number of carriers for heavy metal ions, particular Cu(II), which is both vital and toxic to many biological systems, have been reported[14-16].

Solvent extraction[17] process based on simple organic complexing extractants are often used commercially for the recovery and purification of metal ions. Metal ion extraction depends up on number of parameters. Some of these include ligand structure, pH of solutions, solvent, temperature and time of extraction[18].

This paper reports the results of the studies of the complexation behavior of mono azo dye *i.e*, 1-phenylazo-2-naphthol with transition metal cations (copper (II), Nickel(II), Cobalt(II) and Zinc(II)) through their extraction[19] and transport properties which were conducted to understand complexation process and optimization of various parameters in dye recovery[20,21].

Material and Methods

Reagents :

Ionophore Sudan-I was purchased from Sd fine-chem. limited Mumbai. Distilled ethanol and methanol were used as a solvent in isolation studies. Chloroform from CDH was used as a solvent in extraction and transport studies. All metal salts ($Co(NO_3)_2$, $NiSO_4$, $Cu(NO_3)_2$, $ZnSO_4$) were AR grade from BDH and the respective solutions were prepared in doubly distilled water. EBT, FSB and Murexide were used as indicators. EDTA was used as a titrant.

Experimental Studies :

The isolation studies were performed by mixing each metal salt with ionophore in different ratio (L: M). The mixture was warmed and then allowed to crystallize. Initially complexes were characterized by melting points and by thin layer chromatography. In the extraction study aqueous metal salt solution was vigorously stirred with ionophore solution. The amount of the cation extracted by the ionophore was determined by its difference in aqueous phase before and after extraction. Bulk liquid membrane transport (BLM) studies were carried out in "U" shaped glass cell.

Ionophore solution was placed at the bottom of tube to serve as liquid membrane. Aqueous solution of metal salt was placed in the one limb of the tube to serve as the source phase (S.P.) and doubly distilled water was placed in another limb of the tube to serve as the receiving phase (R.P.). The membrane phase was stirred well and the sample of both S.P. and R.P. were analyzed by volumetric method.

Results and Discussion

Results of isolation, extraction and transportation of MX (metal salt) ($Co(NO_3)_2$, $NiSO_4$, $Cu(NO_3)_2$, $ZnSO_4$) with ionophore S-I is discussed in the following Para. Reproducibility of all experiments was checked.

Isolation Studies:

The isolation studies were performed to study the interaction of metal ions with ionophore. Ethanol + methanol are found to be suitable solvents for complexation. The complexes were characterized by M.P. & IR spectral analysis. IR spectra of isolated complexes are shown in figure 1, 2 and 3. With the help of these spectra it is observed that ionophore S-I forms complexes with metal cations ($Co(NO_3)_2$, $Cu(NO_3)_2$, $ZnSO_4$).

Extraction Studies:

Extraction studies were conducted to ascertain the occurrence of complexation between MX salts and ligand in solution state[20]. The studies were focused on the capacity of the various ionophores to extract metal cation from an aqueous phase into an organic phase by complexation. In the present study extraction of transition metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) with ionophore S-I conducted at various concentration ranges. The results of extraction and transportation indicate that the concentration variation affects the complexation of S-I with metal cations.

Effect of metal ion and ionophore concentration variation:

The metal salts concentrations were varied from 1.0 x 10^{-1} M to 1.0 x 10^{-3} M and ionophore (S-I) concentration was varied from 1.0 x 10^{-2}M to 1.0x10^{-5}M. From figure 4 it is observed that optimum concentration of ionophore is found to be 1.0 x 10^{-4}M for extraction of Ni^{2+}, Co^{2+}, Cu^{2+} and Zn^{2+} ions. (Table 1). From the results the trend of extraction of metal ions with ionophore (S-I) is observed in order of $Co^{2+} > Ni^{2+} > Cu^{2+} > Zn^{2+}$.

Transportation Studies:

The liquid membrane system have much importance as model for cation transport across bio-membrane and are helpful in understanding the complex behavior in biochemical transport process across liquid membrane with ionophore[21].

BLM's transportation of metal cations (Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}) using ionophore S-I in organic solvent were carried out at various concentration range from 1.0 x 10^{-2}M to 1.0 x 10^{-5}M. The salt concentrations were varied from 1.0 x 10^{-1}M to 1.0 x 10^{-3}M. From figure 5, it is found that the optimum concentration of ionophore for transport of metal ions Ni^{2+}

and Co^{2+} is 1.0 x 10^{-3}M and for Zn^{2+} ion it is 1.0 x 10^{-4}M while Copper does not shows transportation with ionophore S-I.

Thus, from the results it is observed that the trend of transportation of metal ion with ionophore S-I is in order of $Ni^{2+} > Co^{2+} > Zn^{2+} > Cu^{2+}$.

Conclusion

The results of this study are as follows:-

1. In the isolation studies shifting in IR peak of complexes are observed towards the higher and lower frequency regions due to the metal ionophore interaction.
2. On comparing the results of Extraction and transport studies of metal ion (Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}) with S-I. This results shows that Co^{2+} is more selective for extraction while Ni^{2+} is more selective for transportation studies with ionophore S-I.
3. These results indicate that the extraction and transport studies depend upon the uptake and release of metal ion. The amount of metal ion extracted and transported depends upon the structure of ionophore, their concentration and also on the concentration of metal ion.
4. Furthermore, with the help of these studies industrial waste water can be treated and dyes can be reused in the form of metal complexs.

IR – Spectra of Metal Complexes of Azo Dyes.

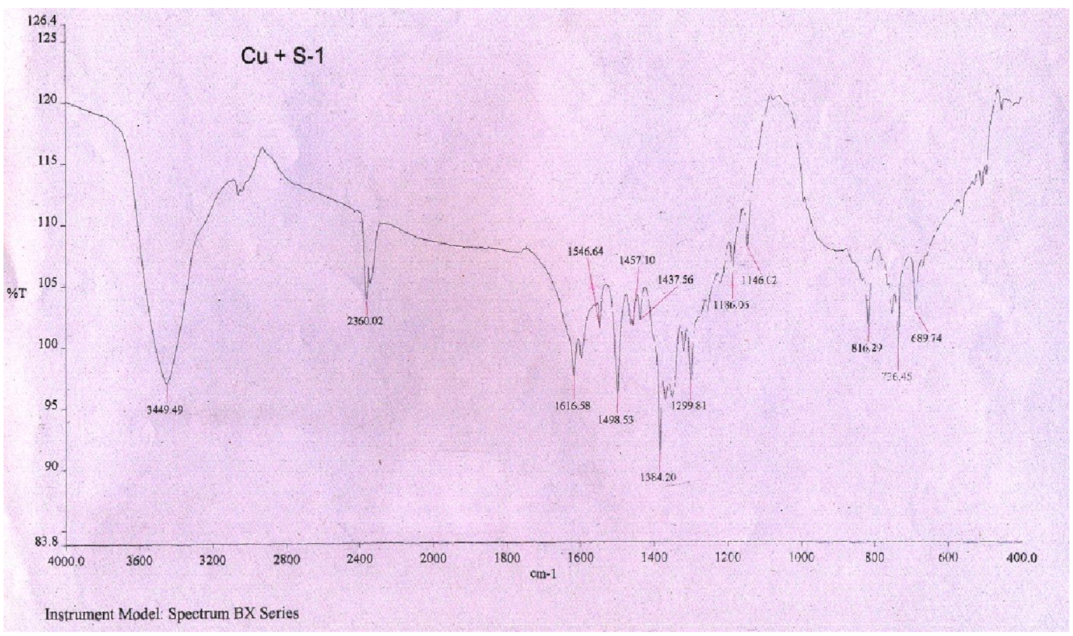

Figure-1

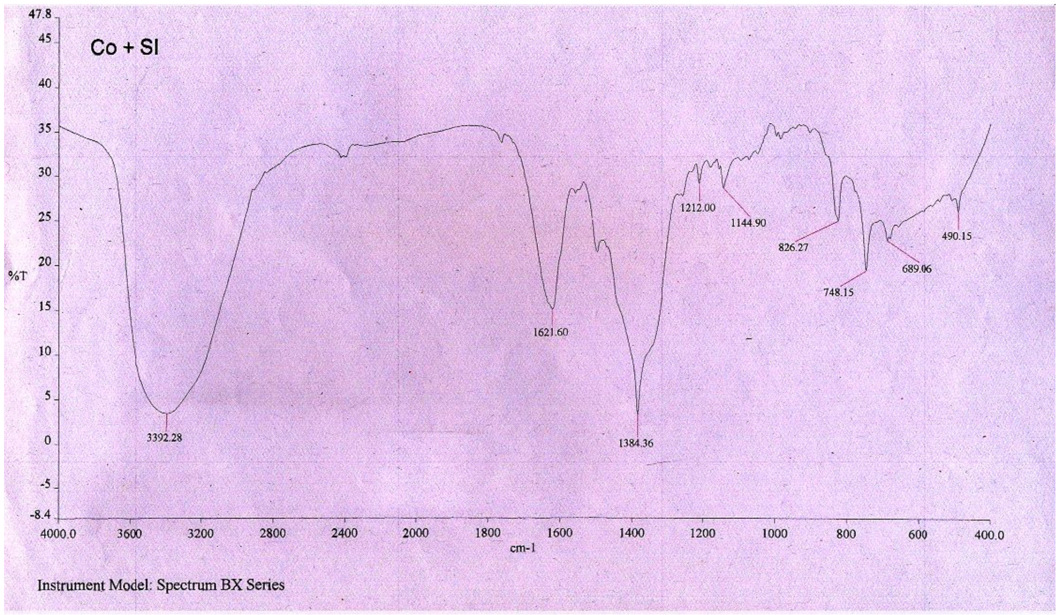

Figure-2

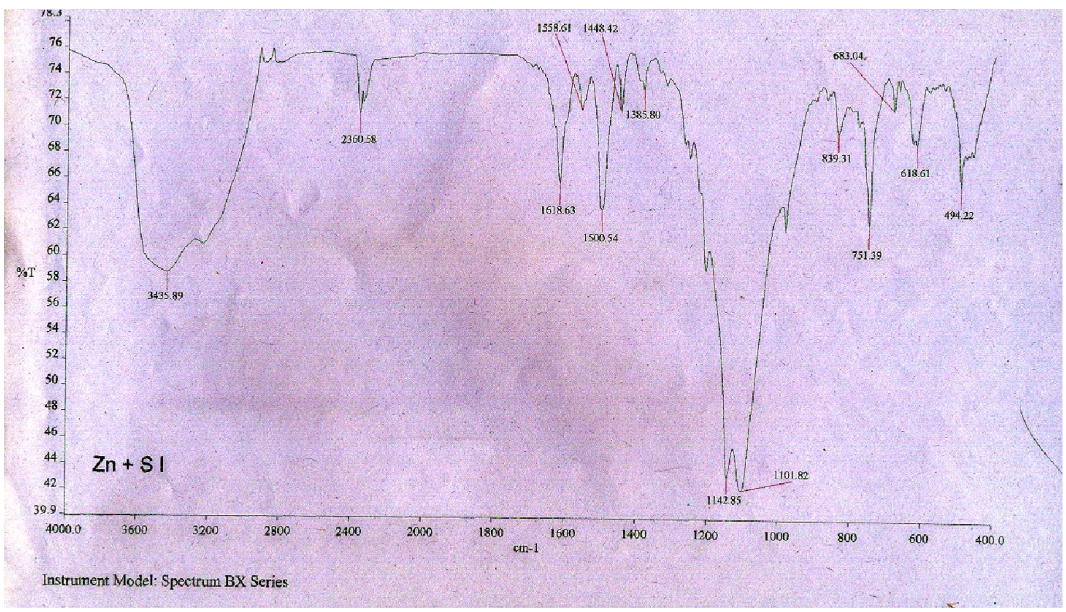

Figure-3

Amount of metal ions extracted after 4 hour with ionophore (S-I) .

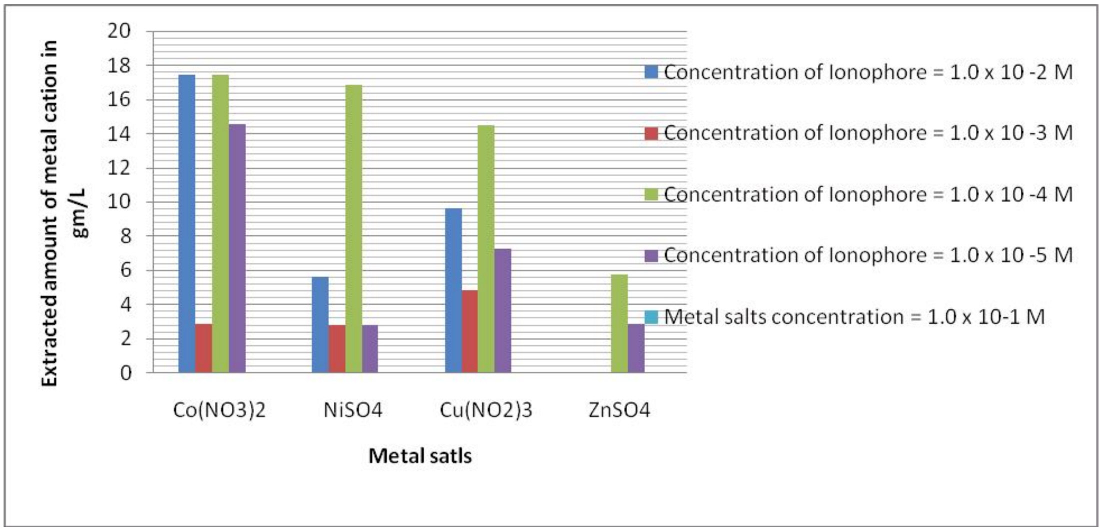

Figure-4

Amount of metal ions transported after 24 hour with ionophore (S-I).

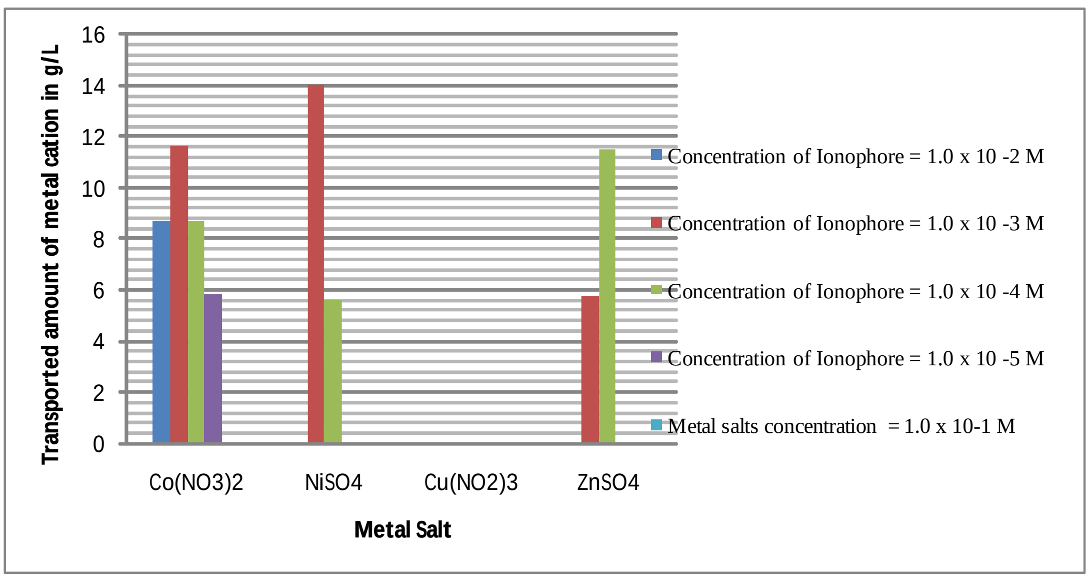

Figure-5

Table 1. Amount of metal ions extracted after 4 hour with ionophore (S-I) . Metal salts concentration – 1 X 10^{-1} M

Metal Salts	Concentration variation of Ionophore (M)	Amount of cation extracted (in gm/ L) by ionophore in chloroform
$Co(NO_3)_2$	1 X 10^{-2}	17.4618
$Co(NO_3)_2$	1 X 10^{-3}	2.9103
$Co(NO_3)_2$	1 X 10^{-4}	17.4618
$Co(NO_3)_2$	1 X 10^{-5}	14.5514
$NiSO_4$	1 X 10^{-2}	5.6170
$NiSO_4$	1 X 10^{-3}	2.8085
$NiSO_4$	1 X 10^{-4}	16.8510
$NiSO_4$	1 X 10^{-5}	2.8085
$Cu(NO_3)_2$	1 X 10^{-2}	9.6640
$Cu(NO_3)_2$	1 X 10^{-3}	4.8320
$Cu(NO_3)_2$	1 X 10^{-4}	14.4960
$Cu(NO_3)_2$	1 X 10^{-5}	7.2480
$ZnSO_4$	1 X 10^{-2}	-
$ZnSO_4$	1 X 10^{-3}	-
$ZnSO_4$	1 X 10^{-4}	5.7508
$ZnSO_4$	1 X 10^{-5}	2.8754

Table 2. Amount of metal ions transported after 24 hour with ionophore (S-I) Metal salts (MX) concentration=1.0X10^{-1} M

Metal Salts	Concentration variation of Ionophore (M)	Amount of cation transported (in gm/L) by ionophore
$Co(NO_3)_2$	1 X 10^{-2}	8.7308
$Co(NO_3)_2$	1 X 10^{-3}	11.6416
$Co(NO_3)_2$	1 X 10^{-4}	8.7308
$Co(NO_3)_2$	1 X 10^{-5}	5.8206
$NiSO_4$	1 X 10^{-2}	-
$NiSO_4$	1 X 10^{-3}	14.0424
$NiSO_4$	1 X 10^{-4}	5.6170
$NiSO_4$	1 X 10^{-5}	-
$Cu(NO_3)_2$	1 X 10^{-2}	-
$Cu(NO_3)_2$	1 X 10^{-3}	-
$Cu(NO_3)_2$	1 X 10^{-4}	-
$Cu(NO_3)_2$	1 X 10^{-5}	-
$ZnSO_4$	1 X 10^{-2}	5.7508
$ZnSO_4$	1 X 10^{-3}	11.5016
$ZnSO_4$	1 X 10^{-4}	-
$ZnSO_4$	1 X 10^{-5}	-

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