



ISSN NO. 2320-5407

*Journal homepage: <http://www.journalijar.com>***INTERNATIONAL JOURNAL  
OF ADVANCED RESEARCH****RESEARCH ARTICLE****Effect of light on liquid-liquid extraction of some transition metal cations through liquid membrane containing Sudan Azo dyestuffs as Ionophore****\*Kirti Yadav and Vijay R. Chourey**

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**Manuscript Info****Manuscript History:**

Received: 10 November 2013

Final Accepted: 29 November 2013

Published Online: December 2013

**Key words:**

Liquid membrane extraction, Non-cyclic ionophore, Sudan dyestuffs, Transition metal cations, Photo responsive properties.

**Abstract**

Extraction of metal cation through liquid membrane is one of the important application of supramolecular chemistry. This work investigates the use of synthetic carrier (ionophore) for the extraction of transition metal cations. In this work effect of light on extraction of metal cations through chromophoric ionophore have been tested. For this purpose a series of non-cyclic ionophore, 1-phenylazonaphthalen-2-ol (Sudan-I), 1-((4-(phenyldiazenyl)phenyl)azonaphthalen-2-ol (Sudan-III) and 1-(2-methyl-4-(2-methylphenyldiazenyl)phenyl)azonaphthalen-2-ol (Sudan-IV) have been used to extract transition metal cations ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ). Chloroform is used as a solvent. The extracted amount of metal cations depends mainly upon the structure and the concentration of the ionophore and also on the concentration of metal ions. These studies were focused on the capacity of the ionophore to extract metal cation from an aqueous phase into an Organic phase by complexation. On comparing the results of extraction of metal cations ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ) with ionophores (S-I, S-III and S-IV) in the presence of artificial light source (100W bulb) and natural light it is observed that these ionophores exhibit the photo responsive properties. The results reveals that the effect of light radiation on extraction process are opposite from the results obtained by the extraction process in the natural light source. The presence of chromophoric mono azo ( $-\text{N}=\text{N}-$ ) and diazo moiety in the ionophores S-I, S-III and S-IV may be attributed for the same.

*Copy Right, IJAR, 2013., All rights reserved.***Introduction**

The field of supramolecular chemistry has brought in light of the new binding sites with improved selectivity. Logically, the idea of coupling these ionophores to chromophores or fluorophores emerged some years later, leading to the so-called chromoionophore and fluoroionophore<sup>1</sup>. The chromo- and fluoro-ionophores form a particularly interesting class of probes since they can combine recognition properties with optical transduction, i.e. changing colour or fluorescence<sup>2</sup>.

Dyes<sup>3</sup> have been extensively used in such as in ink-jet printing, imaging and in electronics. These required functional dyes which are able to form organized supramolecular assemblies<sup>4</sup>, the properties of which can be controlled as a function of self-assembly process. Supramolecular control dye arrangement is important for providing the improved performance of existing devices and to create new dye-based materials with tunable optical and electronic properties. Now a dyes considerable efforts are being made towards the modification of the structure of organic dyes in the direction of the self-organization. These studies have generated a wealth of knowledge in the designing of variety of materials and complexes with intriguing properties.



## Material and Methods

All chemicals, throughout the course of experimental work, used were of AnalaR or GR grade and were used as supplied.

In the liquid-liquid extraction<sup>5</sup> studies 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.

To study the special effect of artificial light radiation on the extraction processes, the experiments have been carried out in the following two conditions:

- (1) Extraction in presence of artificial visible light source (100W tungsten filament).
- (2) In total darkness.

These studies have been performed to assess the effect of light on the extraction of metal ions in the presence of visible light source.

In this method aqueous metal salt solution was vigorously stirred with ionophore solution in organic solvent (chloroform) in a small beaker. The solution was magnetically stirred using Teflon coated capsule. The beaker was covered by the paraffin to minimize the rate of evaporation. The photo irradiation was carried out using visible light source (100W bulb) and intensity of light were measured by ms6610 Lux meter. This process was continued up to 4 hours. After well stirring, the mixture was allowed to stand for 5 minutes for the separation of two phases. The depleted aqueous phase was removed and the metal content was analyzed by volumetric method. The amount of metal cation extracted by ionophore was measured by their difference in aqueous phase before and after extraction (tables- 1 to 6).

The extraction experiments were also carried out in complete darkness (absence of light).

## Results and Discussion

To study the effect of light radiation on extraction process the experiments have been carried out at two different concentrations of ionophores ( $1.0 \times 10^{-3}\text{M}$  and  $1.0 \times 10^{-4}\text{M}$ ), in the following conditions.

- (1). Extraction in the presences of artificial visible light source (100 W tungsten filament)
- (2). In the natural light
- (3). In total darkness

The results of extraction of metal cations ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ) with ionophores (S-I, S-III and S-IV) are listed in the tables (1 to 6).

On comparing the results of extraction of metal cations ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ) with ionophores (S-I, S-III and S-IV) in the presence of artificial light source (100W bulb) and natural light it is observed that these ionophores exhibit the photo responsive properties.

The experiments were carried out at two different light intensities ( $126 \times 10$  Lux and  $73 \times 10$  Lux) as measured by Lux meter<sup>6</sup>. The results indicate that  $73 \times 10$  Lux is suitable intensity of light for extraction of metal cations with ionophore S-I. Ionophores S-III and S-IV shows higher extraction capacity at  $126 \times 10$  Lux.

The observed trend of extraction of selected metal cations ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ) by ionophores S-I, S-III and S-IV in the presence of artificial light source and in natural light is found different.

The observed trend of extraction of selected metal cations by ionophores S-I in the presence of artificial light source (100W bulb) is  $\text{Zn}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+}$  while  $\text{Co}^{2+}$  does not shows extraction in the presence of light source. The observed trend of extraction of selected metal cations by ionophores S-I in the natural light is  $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+}$  while  $\text{Zn}^{2+}$  does not shows extraction in the natural light with ionophore S-I (table- 2).

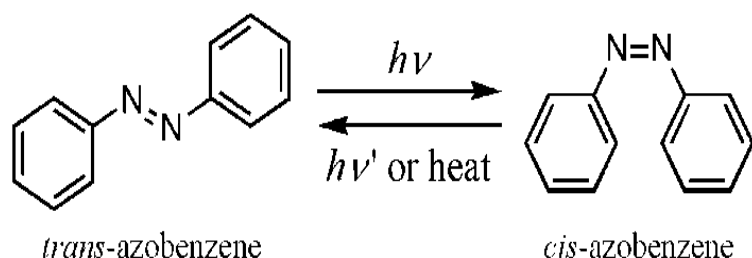


The observed trend of extraction of selected metal cations by ionophores S-III in the presence of artificial light source (100W bulb) is  $\text{Zn}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+}$ . The observed trend of extraction of selected metal cations by ionophores S-III in the natural light is  $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$  (table- 3).

The observed trend of extraction of selected metal cations by ionophores S-IV in the presence of artificial light source (100W bulb) is  $\text{Zn}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$  while  $\text{Co}^{2+}$  does not shows extraction in the presence of light source. The observed trend of extraction of selected metal cations by ionophores S-IV in the natural light is  $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+}$  while  $\text{Ni}^{2+}$  does not shows extraction in the natural light with ionophore S-IV (table- 5 and 6).

On the basis of results it can be concluded that the effect of light radiation on extraction process are opposite from the results obtained by the extraction process in the natural light source. The presence of chromophoric mono azo (-N=N-) and diazo moiety in the ionophores S-I, S-III and S-IV may be attributed for the same.

The *trans*- isomer of azobenzene can be photomerized to the *cis*-isomer, which can be converted thermally back to the *trans* form again<sup>7</sup>. The isomerization is completely reversible, free from side reactions<sup>8</sup>. It can be concluded that in the presence of artificial light source these ionophores (S-I, S-III and S-IV) form *cis* configuration and shows more selectivity towards the  $\text{Zn}^{2+}$  ions.



**Figure- 5.1: *Trans* (left) and *Cis* (right) geometric isomers of azobenzene**

The extraction experiments have also been carried out in the complete darkness. Furthermore, no any progress in extraction process is observed. These results also supports that all ionophores are photo-responsive in nature.

**Table: 1 Comparative amount of metal ion extracted after 4 hours with ionophore S-I (concentration  $1.0 \times 10^{-3}$  M) in the absence and presence of artificial light source (100 W bulb) at two different intensities in chloroform.**

Concentration of metal salt =  $1.0 \times 10^{-1}$  M  
 Concentration of ionophore (S-I) =  $1.0 \times 10^{-3}$  M  
 Intensity of light =  $126 \times 10$  Lux  
 Intensity of light =  $73 \times 10$  Lux

Metal Salts	Amount of cation extracted (in gm/ L) by ionophore	Amount of cation extracted (in gm/ L) by ionophore at 126×10 Lux	Amount of cation extracted (in gm/L) by ionophores at 73×10 Lux
	(absence of light source)	(Presence of light source) 100 W bulb	
$\text{Co}(\text{NO}_3)_2$	2.9103	-	-
$\text{NiSO}_4$	2.8085	-	8.4255
$\text{Cu}(\text{NO}_3)_2$	4.8320	4.8320	4.8320
$\text{ZnSO}_4$	-	14.3770	20.1278



**Table: 2**

**Comparative amount of metal ion extracted after 4 hours with ionophore S-I (concentration  $1.0 \times 10^{-4}$  M) in the absence and presence of artificial light source (100 W bulb) at two different intensities in chloroform.**

Concentration of metal salt =  $1.0 \times 10^{-1}$  M

Concentration of ionophore (S-I) =  $1.0 \times 10^{-4}$  M

Intensity of light =  $126 \times 10$  Lux

Intensity of light =  $73 \times 10$  Lux

Metal Salts	Amount of cation extracted (in gm/ L) by ionophore	Amount of cation extracted (in gm/ L) by ionophore at $126 \times 10$ Lux	Amount of cation extracted (in gm/L) by ionophores at $73 \times 10$ Lux
	(absence of light source)	(Presence of light source) 100 W bulb	
$\text{Co}(\text{NO}_3)_2$	17.4618	-	-
$\text{NiSO}_4$	16.8510	-	5.6170
$\text{Cu}(\text{NO}_3)_2$	14.4960	4.8320	2.4160
$\text{ZnSO}_4$	-	14.3770	17.2524

**Table: 3**

**Comparative amount of metal ion extracted after 4 hours with ionophore S-III (concentration  $1.0 \times 10^{-3}$  M) in the absence and presence of artificial light source (100 W bulb) at two different intensities in chloroform.**

Concentration of metal salt =  $1.0 \times 10^{-2}$  M

Concentration of ionophore (S-III) =  $1.0 \times 10^{-3}$  M

Intensity of light =  $126 \times 10$  Lux

Intensity of light =  $73 \times 10$  Lux

Metal Salts	Amount of cation extracted (in gm/ L) by ionophore	Amount of cation extracted (in gm/ L) by ionophore at $126 \times 10$ Lux	Amount of cation extracted (in gm/L) by ionophore at $73 \times 10$ Lux
	(absence of light source)	(Presence of light source) 100 W bulb	
$\text{Co}(\text{NO}_3)_2$	1.1641	-	0.2913
$\text{NiSO}_4$	-	3.3702	1.1234
$\text{Cu}(\text{NO}_3)_2$	4.8320	2.4160	0.7248
$\text{ZnSO}_4$	1.7252	3.4504	1.1501

**Table: 4**

**Comparative amount of metal ion extracted after 4 hours with ionophore S-III (concentration  $1.0 \times 10^{-4}$  M) in the absence and presence of artificial light source (100 W bulb) at two different intensities in chloroform.**

Concentration of metal salt =  $1.0 \times 10^{-2}$  M

Concentration of ionophore (S-III) =  $1.0 \times 10^{-4}$  M

Intensity of light =  $126 \times 10$  Lux

Intensity of light =  $73 \times 10$  Lux



Metal Salts	Amount of cation extracted (in gm/ L) by ionophore	Amount of cation extracted (in gm/ L) by ionophore at $126 \times 10$ Lux	Amount of cation extracted (in gm/L) by ionophores at $73 \times 10$ Lux
	(absence of light source)	(Presence of light source) 100 W bulb	
$\text{Co}(\text{NO}_3)_2$	2.9103	0.2910	-
$\text{NiSO}_4$	-	4.2127	2.8085
$\text{Cu}(\text{NO}_3)_2$	-	2.4160	2.1744
$\text{ZnSO}_4$	-	4.3131	2.5878

**Table: 5**

**Comparative amount of metal ion extracted after 4 hours with ionophore S-IV (concentration  $1.0 \times 10^{-3}$  M) in the absence and presence of artificial light source (100 W bulb) at two different intensities in chloroform.**

Concentration of metal salt =  $1.0 \times 10^{-1}$  M

Concentration of ionophore (S-IV) =  $1.0 \times 10^{-3}$  M

Intensity of light =  $126 \times 10$  Lux

Intensity of light =  $73 \times 10$  Lux

Metal Salts	Amount of cation extracted (in gm/ L) by ionophore	Amount of cation extracted (in gm/ L) by ionophore at $126 \times 10$ Lux	Amount of cation extracted (in gm/L) by ionophores at $73 \times 10$ Lux
	(absence of light source)	(Presence of light source) 100 W bulb	
$\text{Co}(\text{NO}_3)_2$	-	-	-
$\text{NiSO}_4$	-	5.6170	2.8085
$\text{Cu}(\text{NO}_3)_2$	14.4960	7.2480	4.8320
$\text{ZnSO}_4$	14.3770	17.2524	8.6262

**Table: 6**

**Comparative amount of metal ion extracted after 4 hours<sup>1</sup> with ionophore S-IV (concentration  $1.0 \times 10^{-4}$  M) in the absence and presence of artificial light source (100 W bulb) at two different intensities in chloroform.**

Concentration of metal salt =  $1.0 \times 10^{-1}$  M

Concentration of ionophore (S-IV) =  $1.0 \times 10^{-4}$  M

Intensity of light =  $126 \times 10$  Lux

Intensity of light =  $73 \times 10$  Lux

Metal Salts	Amount of cation extracted (in gm/ L) by ionophore	Amount of cation extracted (in gm/ L) by ionophore at $126 \times 10$ Lux	Amount of cation extracted (in gm/L) by ionophores at $73 \times 10$ Lux
	(absence of light source)	(Presence of light source) 100 W bulb	



Co(NO <sub>3</sub> ) <sub>2</sub>	5.8206	-	-
NiSO <sub>4</sub>	-	8.4255	5.6170
Cu(NO <sub>3</sub> ) <sub>2</sub>	9.6640	14.4960	12.0800
ZnSO <sub>4</sub>	-	23.0030	20.1278

### Conclusion

On the basis of experimental findings it has been observed that ionophore S-I is better extractant for Co<sup>2+</sup> ions while ionophores S-III and S-IV are better extractant for Cu<sup>2+</sup> ions in the natural light.

All selected ionophores shows better extraction selectivity for Zn<sup>2+</sup> in the presence of artificial light source only.

On comparing the results of extraction of metal cations (Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup>) with ionophores (S-I, S-III and S-IV) in the presence of artificial light source (100W bulb) and natural light it is observed that these ionophores have photo responsive properties.

The extraction experiments have also been carried out in the complete darkness, but no progress in the extraction is observed.

### Acknowledgements

The authors are thankful to Dr. Ruplekha Vyas, Professor and Head, Department of Chemistry, Govt. Auto. Holkar Science College, Indore (M.P.), for providing laboratory facilities.

### References

1. Turback, A. F. (1967). J. Textile Research, 37: 350.
2. Okamoto, K., Chithra, P., Richards, G. J., Hill, J. P. and Ariga, K. (2009). Int. J. Mol. Sci., 10: 1950.
3. Zolinger, H. and Iqbal, A. (2003). Color Chemistry: synthesis, properties and applications of organic dyes and pigments: 3<sup>rd</sup> rev. ed.,.
4. Lehn, J. M. (1995). Supramolecular Chemistry, VCH, Weinheim, Germany.
5. Bhatnagar, M. and Sharma, U. (2002). J. Sci. I. R. Iran, 13: 2.
6. Thimijan and Heins, (1985). Hort Science, 18: 818.
7. Halabieh, R. H. El, Mermut, O. and Barrett, C. J. (2004). Pure Appl. Chem., 76 (7–8): 1445.
8. Rau, H. (1990). Photochemistry and Photophysics, Vol. 9, J. F. Rabek (Ed.): Chap. 4, CRC Press, Boca Ratan.