Journal of Advanced Scientific Research

Available online through http://www.sciensage.info

ISSN 0976-9595

Research Article

LIQUID LIQUID EXTRACTION AND BULK LIQUID MEMBRANE TRANSPORT OF TRANSITION METAL IONS (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) USING HEXADENTATE SCHIFF BASE

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ABSTRACT

A hexadentate Schiff base N, N'-Bis[2-(salicylidene amino)]ethane-1,2-diamine (TTS) has been synthesized by condensation reaction of salicylaldehyde with triethylenetetramine (TETA) in ethanol and characterized by TLC, M.P., spectral analysis and mass spectrometry. This Schiff base has been used for liquid-liquid extraction and bulk liquid membrane transport studies of transition metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}). The effect of metal ion concentration variation on extraction and transport is studied. The observed trend for extraction and transport of transition metal ions using Schiff base (TTS) is $Cu^{2+} > Fe^{3+} > Co^{2+} > Zn^{2+} \rightleftarrows Ni^{2+}$ and $Zn^{2+} > Fe^{3+} > Ni^{2+} > Co^{2+} \rightleftarrows Cu^{2+}$ respectively. The result of extraction study shows that TTS has highest extraction efficiency for Cu^{2+} metal ions followed by Fe^{3+}, Co^{2+}, Zn^{2+} and Ni^{2+} metal ions. This can be explained on the basis of cavity fit concept, size and charge density of metal ions and Pearson's HSAB concept. The results of extraction and transport studies reveals that in general the TTS has high extraction efficiency as compared to that of transport, this may be due to TTS adopts a *cis* conformation with both arms at the same side, which leads to a better predisposed ionophore for metal complexation by bringing the nitrogen and oxygen donor sets closer proximity and form pseudo cavity.

Keywords: Hexadentate Schiff base, Transition metal ions, Extraction, Bulk liquid membrane transport.

1. INTRODUCTION

Schiff base is class of compounds which contains carbon nitrogen double bond. Schiff bases are easily prepared by the condensation reaction or microwave irradiation of primary amine with carbonyl compounds, these carbonyl compounds may be aldehydes, ketones and acids [1, 2]. The Schiff base and their transition metal complexes are of great interest due to their diverse reactivity and wide applications in catalysis, pharmaceuticals, functional materials [3-8] etc. However despite extensive scientific reports on the synthesis, characterization, crystalline structure and application of the transition metal complex, there are limited report on the use of Schiff base as ionophore in supramolecular chemistry [9-12]. L. Mishra *et al.* studied tetradentate thioiminato Schiff base as carriers for transport of nickel ions through chloroform liquid membrane [13] and S. Dubey *et al.* synthesized mixed donor ionophore using Schiff base and studied liquid membrane transport of transition metal ions and the effect of donor site of ionophore on separation of metal ions [14, 15], still very little attention paid in this field.

In the present work we synthesized a hexadentate Schiff base (TTS) and investigated its extraction and transport potential towards transition metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) at different concentrations of metal ions. This type of studies give various information about structural unit of ionophores and nature of donor groups which govern extraction and transport, this may help to design and select ionophores capable of mimicking natural ionophores and also to set conditions to ensure maximum transport of metal ions.

2. MATERIAL AND METHODS

2.1. Chemicals

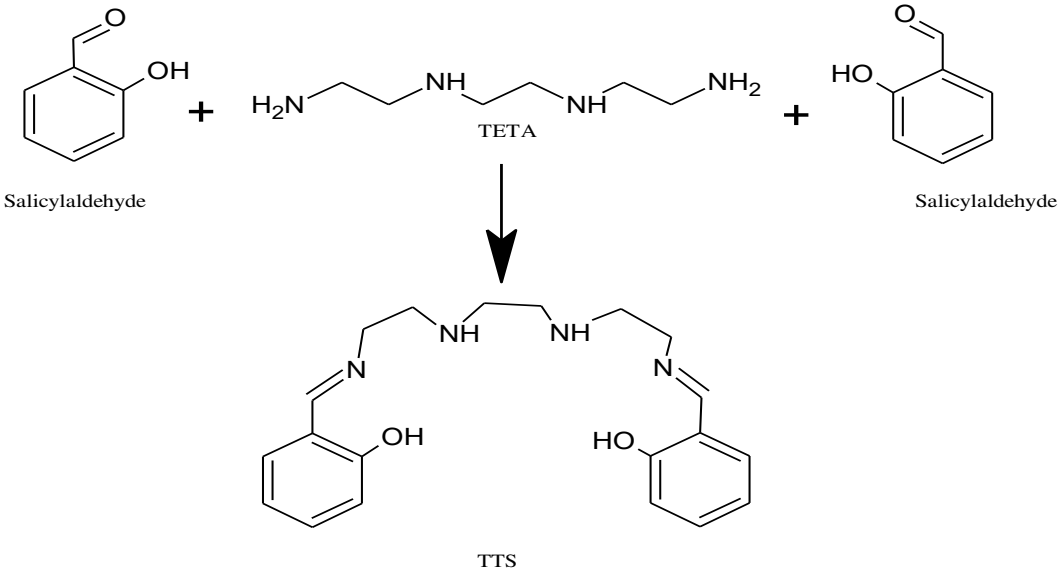
Salicylaldehyde and TETA used for synthesis of Schiff base were purchased from Merck and used without further purification. Metal salt $FeCl_3$, $Co(NO_3)_2.3H_2O$, $Ni(NO_3)_2.6H_2O$, $CuSO_4.5H_2O$, $ZnSO_4.7H_2O$ were obtained from CDH. Solvents chloroform and ethanol were obtained from Qualigens, India and used without further purification. Metal salt solutions were prepared in double distilled water.

2.2. Instruments

Melting point of Schiff base (TTS) was obtained on capillary melting point apparatus. FTIR spectrum was recorded using a Shimadzu 8400 FTIR spectrometer in the range of 4000-600 cm^{-1} at Central Analytical Laboratories, Indore. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance II 400 NMR spectrometer (in $CDCl_3$) at Sophisticated Analytical Instrumentation Facility (SAIF), Punjab University, Chandigarh. Elemental analysis (CHN) was carried out using Eurovector EA 3000 Elemental Analyzer and mass spectral analysis on positive ESI mode was recorded using Waters UPLC-TQD Mass Spectrometer at SAIF, Lucknow UP.

2.3. Preparation of Schiff base (TTS)

The Schiff base (TTS) was synthesized by the reaction of salicylaldehyde with TETA in 2:1 molar ratio [16]. A 0.10 mol solution of salicylaldehyde in ethanol (10.48 mL of salicylaldehyde in 25 mL ethanol) was refluxed with 0.05 mol solution of TETA in ethanol (7.5 mL of TETA in 25 mL ethanol) in the presence of 1 mL acetic acid at 80°C for 4 h in a round bottom flask. After cooling the solution in the ice bath, yellow crystals obtained, which were filtered, washed with hexane followed with water and recrystallized with ethanol (Scheme 1) and characterized as - Yield: 78%. Melting Point: 110C. Solubility: Soluble in hot ethanol, methanol, chloroform, DMF and DMSO. Elemental analysis calculated (%) for $C_{20}H_{26}N_4O_2$: C 67.8, H 7.4, N 15.8; Found (%): C 72.9, H 10.1, N 18.0. IR (cm^{-1}): 3550 (N-H), 3380 (O-H), 2923, 2850 (C-H), 1631 (C=N). ^{1}H NMR ($CDCl_3$, ppm): 8.34 (s, 2H, CH=N), 6.80-7.33 (m, 8H, Ar-H), 2.59-3.73 (m, 12H, CH_2-N), 1.23 (m, 2H, -NH-). ESI + MS (m/z): 355 ($C_{20}H_{26}N_4O_2$). ^{13}C NMR ($CDCl_3$, ppm): 51-56 (CH_2-NH-CH_2-), 58 (CH_2-N=CH), 117-132 (Ar-C), 161 (C=N), 165 (Ar-O).



Scheme 1: Synthesis of Schiff base (TTS)

2.4. Extraction studies

For extraction studies, equal volume (10 mL) each of the aqueous solution of metal salts ($FeCl_3$, $Co(NO_3)_2.3H_2O$, $Ni(NO_3)_2.6H_2O$, $CuSO_4.5H_2O$, $ZnSO_4.7H_2O$) and Schiff base (TTS) in chloroform was vigorously stirred in a 50 mL beaker for 4 hours on a magnetic stirrer [17-21]. The amount of metal ions extracted by Schiff base (TTS) was determined by the difference in amount of metal ions before and after the extraction. The extraction experiments were carried out twice to check reproducibility.

2.5. Transport studies

Bulk Liquid Membrane transport experiments carried out in a "U" shaped glass cell, also known as "Pressman Cell". 15 mL solution of Schiff base (TTS) in chloroform was placed at the bottom of U tube, to serve as an organic layer with teflon coated magnetic capsule, 10 mL of the aqueous solution of metal salt was placed in one limb of the U tube which serve as source phase/feed phase and 10 mL of double distilled water was placed in another limb of the U tube to serve as receiving/striping phase. The organic phase was stirred

for 24 hours using a magnetic stirrer. The source and receiving phase were sampled and analyzed for metal ion concentration after 24 hours [17-21]. The bulk liquid membrane transport experiments were carried out twice to check reproducibility.

The concentration of Schiff base (TTS) was varied from $1x10^{-3}$ to $1x10^{-5}$ M and the concentration of metal salts was also varied from $1x10^{-3}$ to $1x10^{-5}$ M for Fe^{3+} and Ni^{2+} metal ions and from $1x10^{-2}$ to $1x10^{-4}$ M for Co^{2+}, Cu^{2+} and Zn^{2+} metal ions.

2.6. Estimation of metal ions

The amount of Co^{2+}, Cu^{2+} and Zn^{2+} metal ions was estimated by complexometric method using di-sodium salt of ethylenediaminetetraacetic acid (EDTA) as complexing agent and Murexide, Fast Sulphon Black F and EBT as indicator respectively. Standardization of EDTA is carried out using $CaCO_3$ solution as primary standard. The amount of Fe^{+3} and Ni^{2+} is estimated by spectrophotometric method using 1, 10 Phenanthrolein and dimethylglyoxime (DMG) respectively [22, 23].

3. RESULTS AND DISCUSSION

3.1. Synthesis

The hexadentate Schiff base (TTS) has been synthesized by the reaction of salicylaldehyde with triethylene-tetramine (TETA) in 2:1 molar ratio using ethanol as solvent (Scheme 1). The Schiff base was characterized by elemental analysis, IR (Fig. 1), ^{1}H and ^{13}C NMR (Figs. 2and 3) and Mass spectra (Scheme 2 and Fig. 4).

The FTIR spectrum of Schiff base (TTS) shows the imine (C=N) band at 1631 cm^{-1} with disappearance of carbonyl (C=O) band at around 1700 cm^{-1} indicate the condensation between ketone moiety of salicylaldehyde and amino group of TETA, confirms the formation of Schiff base which also confirmed by the presence of imine (-CH=N-) peak at 8.34 ppm (s, 2H) in ^{1}H NMR and at 161ppm in ^{13}CNMR spectrum of Schiff base [16].

The mass spectrum is used to confirm the molecular structure along with molecular mass of the compound. The base peak is the most abundant peak which indicates the most stable fragment of the compound while the molecular ion peak shows the molecular mass of the compound. The peaks obtained from the cleavage indicated the position of the side chain and cyclic ring structure of the compound. The mass spectrum of Schiff base (TTS) illustrated the base peak at m/z 230 while the molecular ion peak at m/z 355 suggested its molecular formula be $C_{20}H_{26}N_4O_2$. Abundant peaks are found at m/z 178 and 269.

3.2. Extraction and transport studies

The extraction and transport efficiency of the Schiff base (TTS) for transition metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) through liquid-liquid extraction and bulk liquid membrane transport was investigated. The blank experiments were performed in which the organic phase was devoid of Schiff base (TTS), no amount of metal ions was extracted and transported in blank experiments which indicate that there was no leakage of metal ions. All the experiments were performed twice to check reproducibility. The results of extraction and transport studies are reported in Table 1-4 and represented in Figs. 5-8.

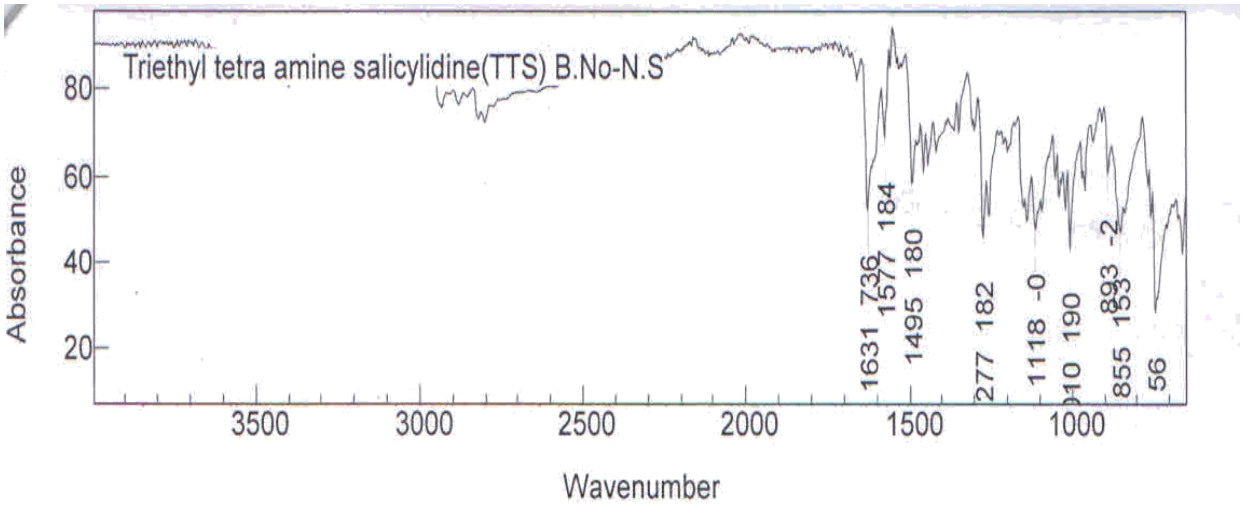


Fig. 1: FTIR spectrum of TTS

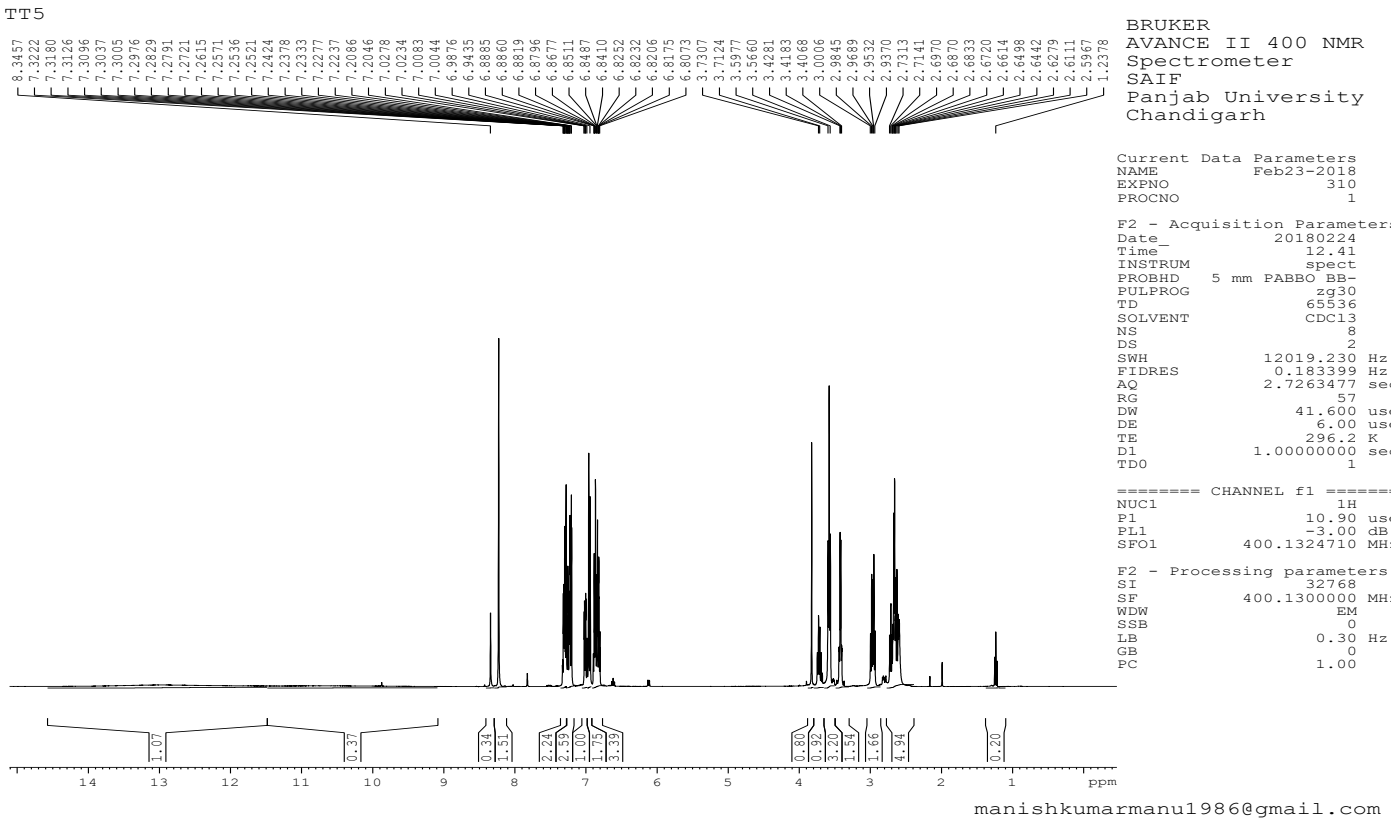


Fig. 2: ^{1}H NMR spectrum of TTS

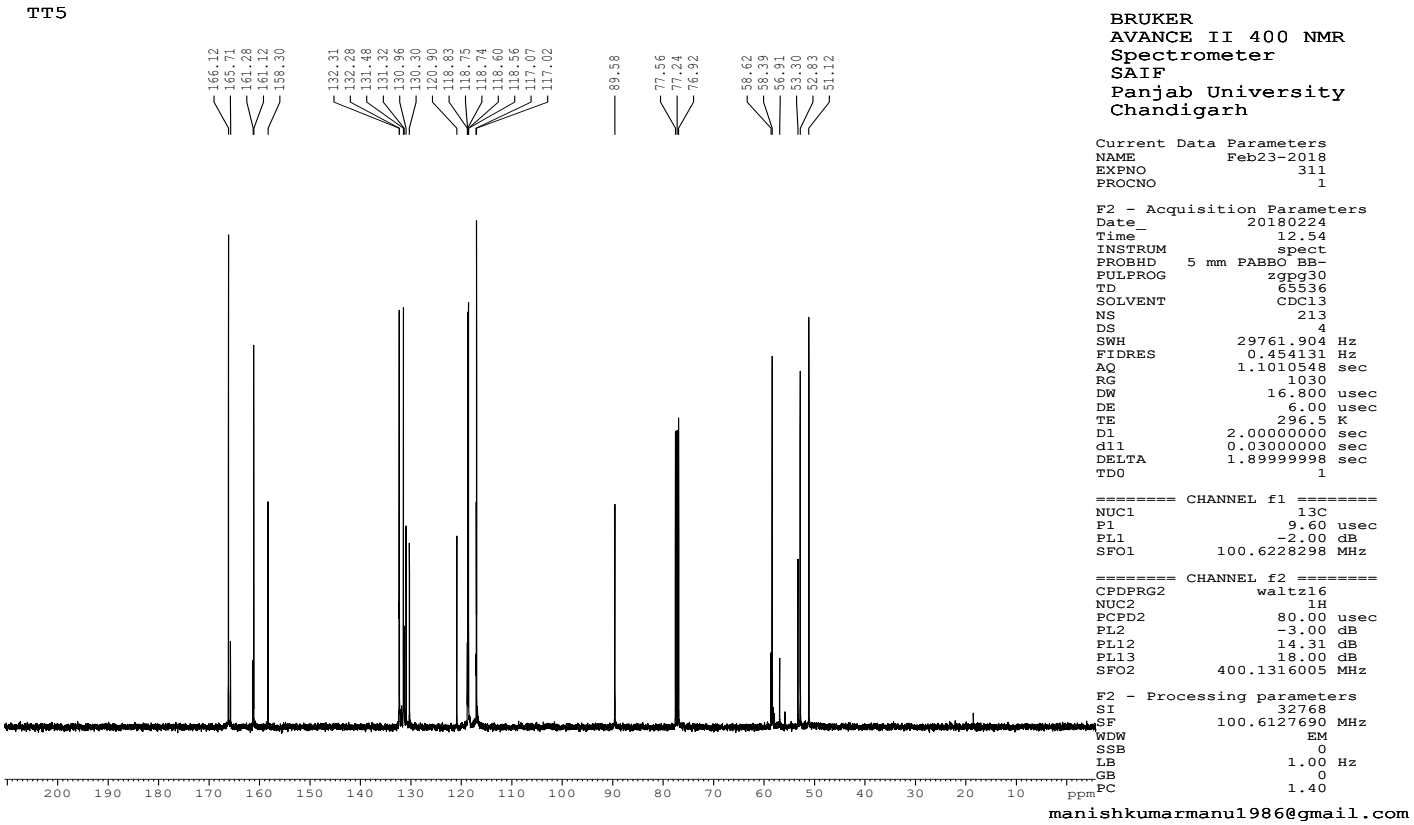


Fig. 3: ^{13}C NMR spectrum of Schiff base (TTS)

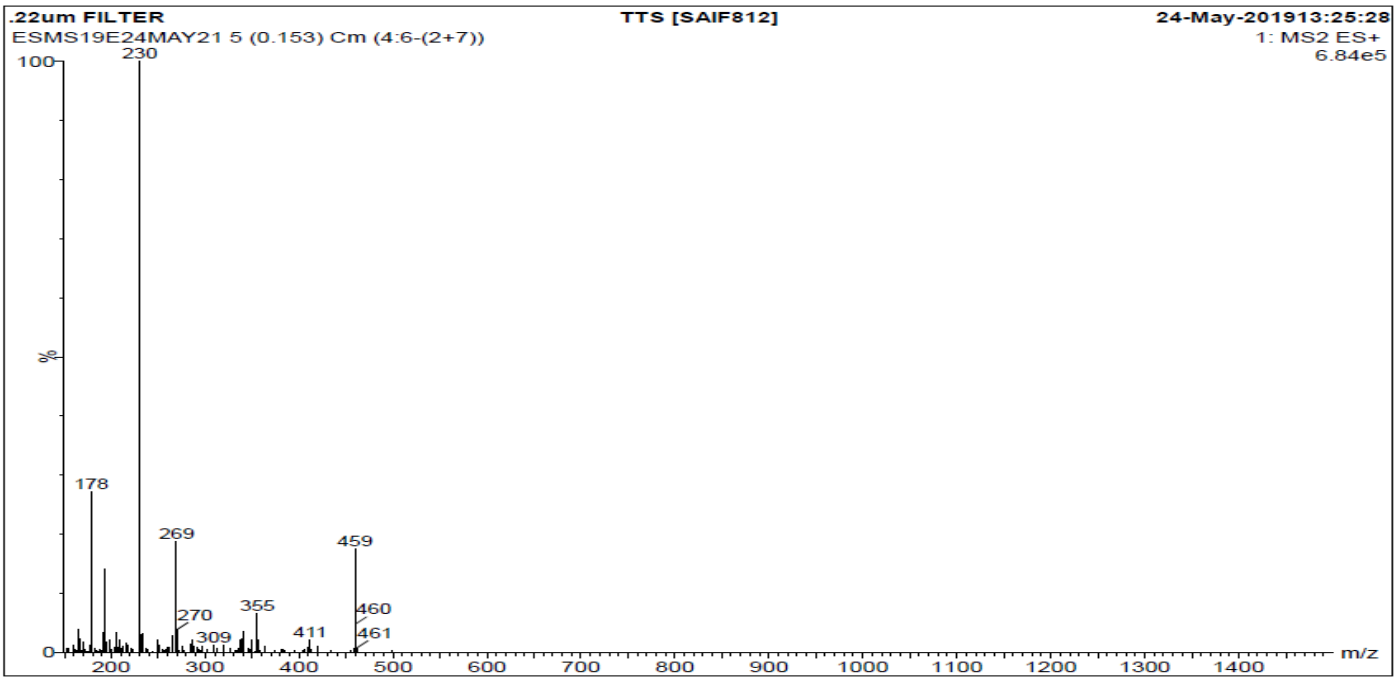
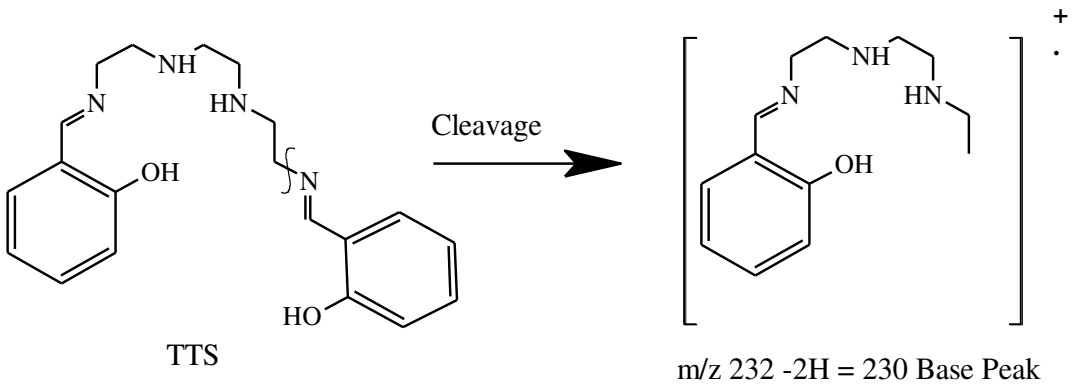


Fig. 4: Mass spectrum of TTS



Scheme 2: Mass spectrum analysis of Schiff base (TTS)

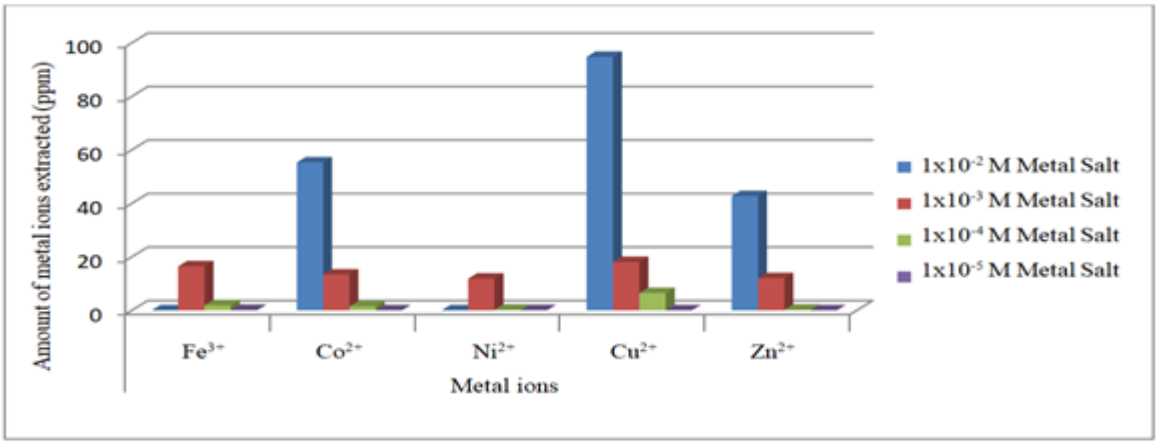


Fig. 5: Amount of metal ions extracted using Schiff base (TTS) ($1x10^{-3}$ M) in 4 hrs

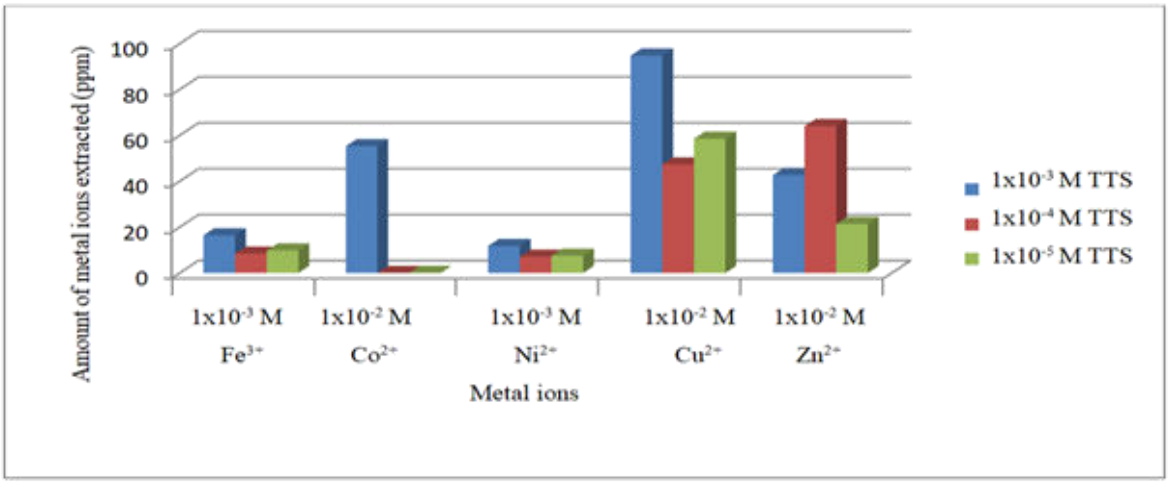


Fig. 6: Amount of metal ions extracted using Schiff base (TTS) in 4 hrs

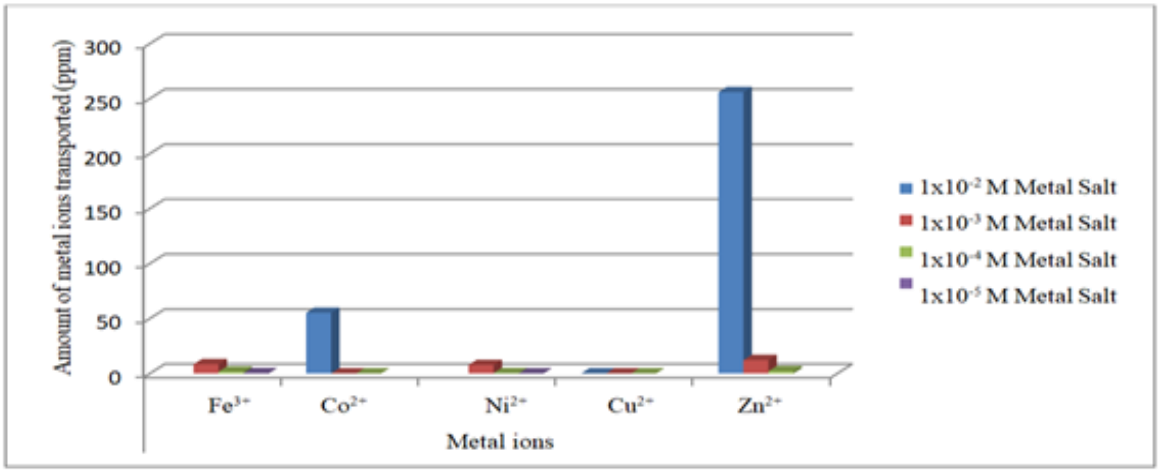


Fig. 7: Amount of metal ions transported using Schiff base (TTS) ($1x10^{-3}$ M) in 24 hrs.

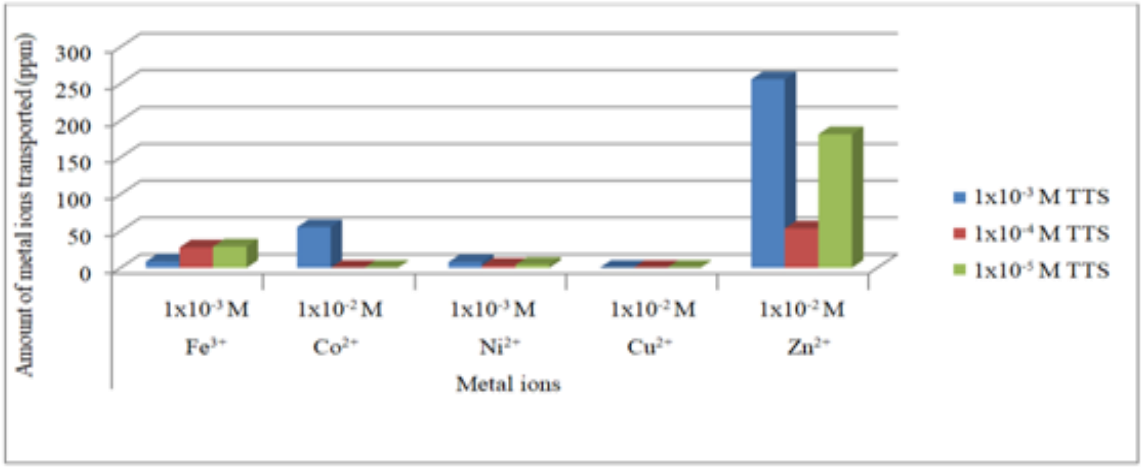


Fig. 8: Amount of metal ions transported using Schiff base (TTS) in 24 hrs

Table 1: Amount of metal ions extracted using Schiff base (TTS) ($1x10^{-3}$ M) in 4 hrs

Metal Salt Concentration	Amount of metal ions extracted (ppm)				
	Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
$1x10^{-2}$ M	-	55.25	-	94.74	42.69
$1x10^{-3}$ M	16.41	13.33	11.78	18.05	11.95
$1x10^{-4}$ M	01.84	01.37	00.20	06.42	00.22
$1x10^{-5}$ M	00.11	-	00.02	-	-

Table 2: Amount of metal ions extracted using Schiff base (TTS) in 4 hrs

TTS Concentration	Amount of metal ions extracted (ppm)				
	Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
	$1x10^{-3}$ M	**$1x10^{-2}$ M**	**$1x10^{-3}$ M**	**$1x10^{-2}$ M**	**$1x10^{-2}$ M**
$1x10^{-3}$ M	16.41	55.25	11.78	94.74	42.69
$1x10^{-4}$ M	08.40	00.00	07.10	47.34	64.03
$1x10^{-5}$ M	09.80	00.00	07.52	58.48	21.33
Optimum Concentration					
For Metal ions	$1x10^{-3}$ M	$1x10^{-2}$ M	$1x10^{-3}$ M	$1x10^{-2}$ M	$1x10^{-2}$ M
For TTS	$1x10^{-3}$ M	$1x10^{-3}$ M	$1x10^{-3}$ M	$1x10^{-3}$ M	$1x10^{-4}$ M

Table 3: Amount of metal ions transported using Schiff base (TTS) ($1x10^{-3}$ M) in 24 hrs

Metal Salt Concentration	Amount of metal ions transported (ppm)				
	Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
$1x10^{-2}$ M	-	55.25	-	00.00	255.94
$1x10^{-3}$ M	08.40	00.00	07.75	00.00	12.17
$1x10^{-4}$ M	01.65	00.00	00.34	00.00	02.14
$1x10^{-5}$ M	00.24	-	00.00	-	-

Table 4: Amount of metal ions transported using Schiff base (TTS) in 24 hrs.

TTS Concentration	Amount of metal ions transported (ppm)				
	Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
	$1x10^{-3}$ M	**$1x10^{-2}$ M**	**$1x10^{-3}$ M**	**$1x10^{-2}$ M**	**$1x10^{-2}$ M**
$1x10^{-3}$ M	08.40	55.25	07.75	00.00	255.94
$1x10^{-4}$ M	27.55	00.00	03.08	00.00	53.31
$1x10^{-5}$ M	28.79	00.00	04.17	00.00	181.31
Optimum Concentration					
For Metal ions	$1x10^{-3}$ M	$1x10^{-2}$ M	$1x10^{-3}$ M	-	$1x10^{-2}$ M
For TTS	$1x10^{-5}$ M	$1x10^{-3}$ M	$1x10^{-3}$ M	-	$1x10^{-3}$ M

In order to find out the optimum concentration of metal salts for extraction studies, the concentration of metal salts $FeCl_3$ and $Ni(NO_3)_2.6H_2O$ for Fe^{3+} and Ni^{2+} metal ions respectively was varied from $1x10^{-3}$ to $1x10^{-5}$ M and the concentration of metal salt $Co(NO_3)_2.3H_2O$, $CuSO_4.5H_2O$ and $ZnSO_4.7H_2O$ for Co^{2+}, Cu^{2+} and Zn^{2+} metal ions respectively was varied from $1x10^{-2}$ to $1x10^{-4}$ M while the concentration of Schiff base (TTS) was kept constant $1x10^{-3}$ M. It was found that $1x10^{-3}$ M was the optimum concentration for Fe^{3+} and Ni^{2+} metal ions whereas $1x10^{-2}$ M was the optimum concentration of Co^{2+}, Cu^{2+} and Zn^{2+} metal ions. In order to find out the optimum concentration of Schiff base (TTS) for extraction studies its concentration was varied from $1x10^{-3}$ to $1x10^{-5}$ M while the concentration for metal ions was kept constant, for Fe^{3+} and Ni^{2+} metal ions it was $1x10^{-3}$ M whereas for Co^{2+}, Cu^{2+} and Zn^{2+} metal ions it was $1x10^{-2}$ M. The optimum concentration of Schiff base (TTS) is found to be $1x10^{-3}$ M for Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} metal ions while $1x10^{-4}$ M for Zn^{2+} metal ions. The evaluation of extraction efficiency of Schiff base show that Cu^{2+} metal ions are more extracted this may be due to its size and high charge density [14, 15].

In order to find out the optimum concentration of metal salts for transport studies, the concentration of metal salts $FeCl_3$ and $Ni(NO_3)_2.6H_2O$ for Fe^{3+} and Ni^{2+} metal

ions respectively was varied from $1x10^{-3}$ to $1x10^{-5}$ M and the concentration of metal salt $Co(NO_3)_2.3H_2O$, $CuSO_4.5H_2O$ and $ZnSO_4.7H_2O$ for Co^{2+}, Cu^{2+} and Zn^{2+} metal ions respectively was varied from $1x10^{-2}$ to $1x10^{-4}$ M while the concentration of Schiff base (TTS) was kept constant $1x10^{-3}$ M. It was found that $1x10^{-3}$ M was the optimum concentration for Fe^{3+} and Ni^{2+} metal ions whereas $1x10^{-2}$ M was the optimum concentration for Zn^{2+} metal ions. Co^{2+} metal ions were only transported at $1x10^{-2}$ M concentration with $1x10^{-3}$ M of Schiff base (TTS) while Cu^{2+} metal ions were not transported by Schiff base (TTS). In order to find out the optimum concentration of Schiff base (TTS) for transport studies, its concentration was varied from $1x10^{-3}$ to $1x10^{-5}$ M while the concentration of metal ions was kept constant, for Fe^{3+} and Ni^{2+} metal ions it was $1x10^{-3}$ M whereas for Co^{2+}, Cu^{2+} and Zn^{2+} metal ions it was $1x10^{-2}$ M. The optimum concentration of TTS is found to be $1x10^{-3}$ M for Co^{2+}, Ni^{2+} and Zn^{2+} metal ions while $1x10^{-5}$ M for Fe^{3+} metal ions and unable to transport Cu^{2+} metal ions are not transported at any concentration. The evaluation of carrier ability of TTS has shown that Zn^{2+} is the most and selectively transported metal ion by the Schiff base (TTS) [21-24].

The observed trend for extraction and transport of transition metal ions is $Cu^{2+} > Fe^{3+} > Co^{2+} > Zn^{2+} \rightleftharpoons Ni^{2+}$ and $Zn^{2+} > Fe^{3+} > Ni^{2+} > Co^{2+} \rightleftharpoons Cu^{2+}$ respectively. The result of extraction studies reveals that Schiff base (TTS) extract Cu^{+2} more efficiently, this may be due to size of Cu^{2+} metal ions and its charge density. It is also observed that Schiff base (TTS) extract Fe^{3+} more efficiently than Co^{+2} and Zn^{+2}. The extraction efficiency of Schiff base for Fe^{+3} ions can be explained using Pearson's HSAB concept. Schiff base contains oxygen and nitrogen atoms which act as hard base, Fe^{+3} is hard acid, Co^{+2} and Zn^{+2} is borderline acids due to this Schiff base show high extraction efficiency for Fe^{+3} [24, 25].

It was observed that Zn^{2+} metal ions are most transported and Cu^{2+} metal ions are not transported by Schiff base (TTS). This follows the common trend that the most extracted metal ions are least transported due to the formation of stable complex [26, 27].

The results of extraction and transport studies reveals that in general the TTS has high extraction efficiency as compared to that of transport this may be due to TTS adopts a *cis* conformation with both arms at the same side, which leads to a better predisposed ionophore for metal complexation by bringing the nitrogen and oxygen donor sets closer proximity and form pseudo cavity [15].

4. CONCLUSION

The objective of the present research work is to prepare Hexadentate Schiff base (TTS) and find its applicability as ionophore for the extraction and transport of transition metal ions. The TTS has highest extraction efficiency for Cu^{2+} as compared to Fe^{3+}, Co^{2+}, Zn^{2+}, Ni^{2+} metal ions. It is concluded from studies that suitable structure feature of ionophore, donor groups, nature of metal ions as well as concentration of metal ions and ionophore direct recognition of ionophores towards ions. The TTS was successfully incorporated into liquid membrane to function as ionophore for extraction and transport of transition metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and in future derivatives of TTS can be synthesized and used for the liquid membrane studies of other transition metal ions.

5. ACKNOWLEDGEMENT

The authors are thankful to Dr (Mrs.) Shubha Jain (Professor & HOD), School of Studies in Chemistry & Biochemistry, Vikram University, Ujjain (M.P.), for their valuable guidance. Help of Mr. Adarsh Katiyar, Quality Manager, Central Analytical Laboratoris, Indore and Mr .S. K. Mehta, Honorary Director, Sophisticated Analytical Instrumentation Facility, CIL and UCIM Panjab University Chandigarh for NMR and elemental analysis is also acknowledged.

Conflict of interest

There are no conflicts of interest.

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