ORIGINAL ARTICLE

Selective transport of zinc and copper ions by synthetic ionophores using liquid membrane technology

Jyoti Tomar · Praval Singh Chauhan · Uma Sharma

Abstract This work highlights the role of synthetic carrier (ionophore) in the separation of heavy metal ions. A new series of ionophores; 4,4′-nitrophenyl-azo-O,O'-phenyl-3,6, 9-trioxaundecane-1,10-dioate (R_1), bis[4,4′nitro-phenylazo-naphthyl-(2,2-dioxydiethylether)] (R_2) 1,8-bis-(2-naphthyl-oxy)-3,6-dioxaoctane (R_3), 1,11-bis-(2-naphthyloxy)-3,6,9-trioxaunde-cane (R_4), 1,5-bis-(2-naphthyloxy)-3-oxa-pentane (R_5) have been synthesized and used as extractant as well as carrier for the transport of various metal ions (Na^+, K^+, Mg^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) through liquid membranes. Effect of various parameters such as metal ion concentration, ionophore concentration, liquid–liquid extraction, back extraction, comparison of transport efficiency of BLM and SLM and different membrane support (hen's egg shell and PTFE) have been studied. In BLM ionophores (R_2–R_5) transport Zn^+ at greater extent and the observed trend for the transport of Zn^{2+} is $R_2 > R_4 > R_3 > R_5$ respectively. Further transport efficiency is increased in SLM. In egg shell membrane ionophores (R_2–R_5) transport Zn^+ due to their non-cyclic structure and pseudo cavity formation while ionophore R_1 transports Cu^{2+} ions at greater extent due to its cyclic structure and cavity size. Among the membrane support used egg shell membrane is found best for the transport of zinc ions because of its hydrophobic nature and exhibits electrostatic interactions between positively charged zinc ions and –COOH group of egg shell membrane. Thus structure of ionophores, hydrophobicity and porosity of the membrane support plays important role in separation of metal ions.

Keywords Ionophores · Transition metal cations · Bulk liquid membrane · Supported liquid membrane

J. Tomar (✉)
Department of Engineering Chemistry, ITM University,
Opposite Sithouli Railway Station, NH-75 Sithouli, Jhansi Road,
Gwalior 474001, Madhya Pradesh, India
e-mail: jyt_tomar@yahoo.co.in

P. S. Chauhan
School of Studies in Zoology, Jiwaji University,
Gwalior 474001, Madhya Pradesh, India

U. Sharma
School of Studies in Chemistry and Biochemistry,
Vikram University, Ujjain 456010, Madhya Pradesh, India
e-mail: umasharma10@rediffmail.com

Introduction

The phenomena of ion transport across liquid membrane have received much attention in developing new separation science methodology [1, 2]. Supported liquid membrane has advantage of higher transport rates as compared to other conventional chemical techniques [3]. Liquid membranes (SLMs) are composed of an organic solution of ionophore, this solution being immobilized in porous material (in general, a polymer). SLM incorporated with crown ethers, di(2-ethylhexyl) phosphate, 8-hydroxyl quinoline as carriers have been successfully used to extract copper (II), lead (II), magnesium (II), cadmium (II) and chromium from natural water [4, 5]. SLM technique comprises of three simultaneously occurring processes molecular extraction from an aqueous source phase, diffusion through hydrophobic liquid membrane and release to aqueous receiving phase [6–9].

Non-cyclic ionophores complexes with metal ions through non covalent interactions such as electrostatic interaction between cation and anion centers, ion dipole, Vander Waal, hydrogen bonding and π stacking [10–12]. The selectivity of these ionophores can be increase by the addition of aromatic end groups [10].

Earlier we have reported synthesis of photoresponsive ionophores R_1 and R_2 [13] and non-cyclic ionophores R_3–R_5 [14]. In the present work, the extraction and carrier mediated transport (bulk liquid membrane and supported liquid membrane) of Li^+, Na^+, K^+, Mg^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions in by synthetic ionophores (R_1–R_5) has been investigated.

Experimental

Synthetic ionophores (R_1–R_5) [13, 14] were used as such (Fig. 1). Metal picrates were prepared by reported methods [15]. Copper nitrate, zinc sulphate and nickel sulphate were obtained from (Aldrich). Solvents such as $CHCl_3$, nitrobenzene (Qualigens) were used as such. In the extraction and transport (BLM and SLM) concentration of metal ion is varied from 1×10^{-1} to 1×10^{-5} M and for ionophores (R_1–R_5) is 1×10^{-1}–1×10^{-5} M. Metal ions (i.e., Li^+, Na^+ and K^+) were estimated by using flame photometer (Systronics 121). Estimation of Ni^{2+} and Mg^{2+} were done by visible spectrophotometer (Systronics 108) and estimation of Cu^{2+} and Zn^{2+} were done by complexometric titrations. All the experiments were performed using single metal ion, ionophore (membrane) and deionised water hence interference of alkali and alkaline earth metal ions were not observed in complexometric titration.
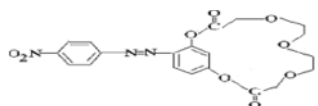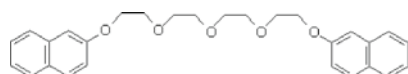

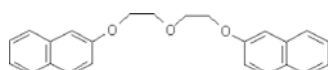4,4'-nitrophenyl -azo-O, O'-phenyl- 3, 6, 9-trioxaundecane-1,10-dioate (**R$_1$**)
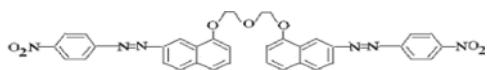
bis-[4,4'-nitrophenyl-azo-naphthyl-(2,2-dioxydiethylether)] (**R$_2$**)
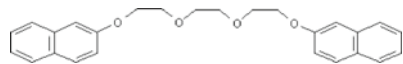
1, 8 – bis (2-naphthyloxy)-3, 6-dioxaoctane (**R$_3$**)

1, 11 – bis (2-naphthyloxy)-3, 6, 9-trioxaundecane (**R$_4$**)

1, 5 –bis (2-naphthyloxy)-3-oxapentane (**R$_5$**)

Fig. 1 Structure of ionophore

Method for liquid–liquid extraction studies

In the liquid–liquid extraction [16] studies, 10 mL of aqueous metal salt solution was vigorously stirred with 10 mL of ionophore solution (in organic solvent) in a 50 mL beaker using magnetic stirrer, the beaker was covered. The amount of cation in aqueous phase was initially determined by flame photometer. After 4 h of stirring the mixture was allowed to stand for 5 min for the separation of two phases. The depleted aqueous solution was removed and analyzed for metal content. The amount of metal ion extracted by ionophore was found by measuring its difference in aqueous phase before and after extraction. Triplicate measurements were taken for each set to check reproducibility.

For back extraction studies, aliquots from the loaded organic phase were withdrawn and subsequently back extracted for 4 h with the strippent which is deionized water.

Method for bulk liquid membrane transport (BLM) studies

Bulk liquid membrane transport studies were carried out in a U shape glass cell (diameter 2.5 cm), 25 mL of ionophore solution was placed at the bottom of U tube to serve as liquid membrane, 10 mL of aqueous solution of metal salt was placed in one limb of the U tube to serve as the source phase (S.P.) and 10 mL of double distilled water was placed in another limb of the U tube to serve the receiving phase (R.P.).The membrane phase was stirred by magnetic stirrer for 24 h. The sample of both S.P. and R.P. were analyzed after 24 h. Cation flux (J_M) values [17, 18] were calculated using the following relation:

$$J_M = \frac{C\,(\text{receiving}) \times V}{At}$$

where C (receiving) = the concentration of cation in R.P. mol/dm^3, V = volume of R.P., dm^3, A = effective area of the membrane, cm, t = time in second.

Method for supported liquid membrane transport (SLM) studies

In supported liquid membrane transport studies [19] we have used natural hen's egg shell membrane and polytetrafluoroethylene (PTFE) membrane as support.

Preparation of supported liquid membrane

Egg shell membrane was prepared by dissolving the egg shell in dilute HCl and the remaining thin sheet like membrane was used as a membrane support after repeated washing. Synthetic PTFE membrane (Sartorius AG,

Goettingen, Germany) is used as such. The egg shell membrane is thinner (thickness 29 μm, pore size 2.5 μm) [20] in comparison to PTFE membrane (thickness 65 μm, pore size 0.2 μm) [21]. The thickness and pore size of both membrane supports have been confirmed by scanning electron micrographs (Figs. 2, 3, 4, 5) of the egg shell, PTFE membrane before and after transport of zinc ions with ionophore (Figs. 3, 4).

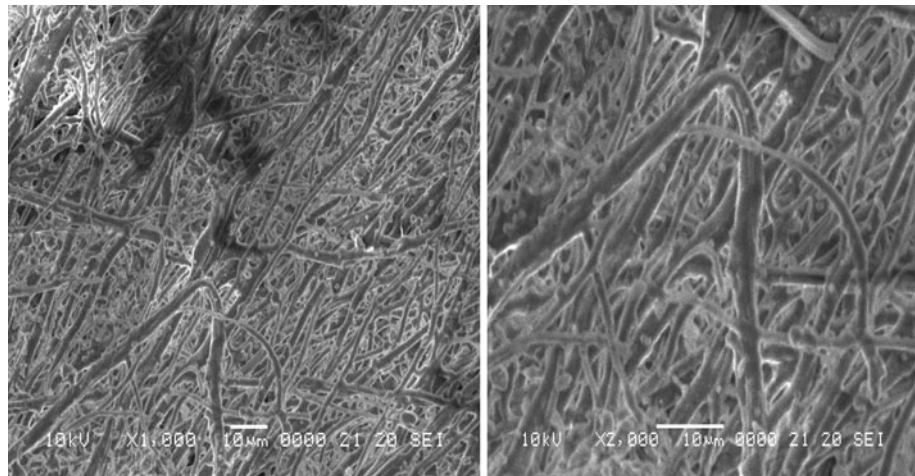Fig. 2 SEM of impregnated egg shell membrane before transport

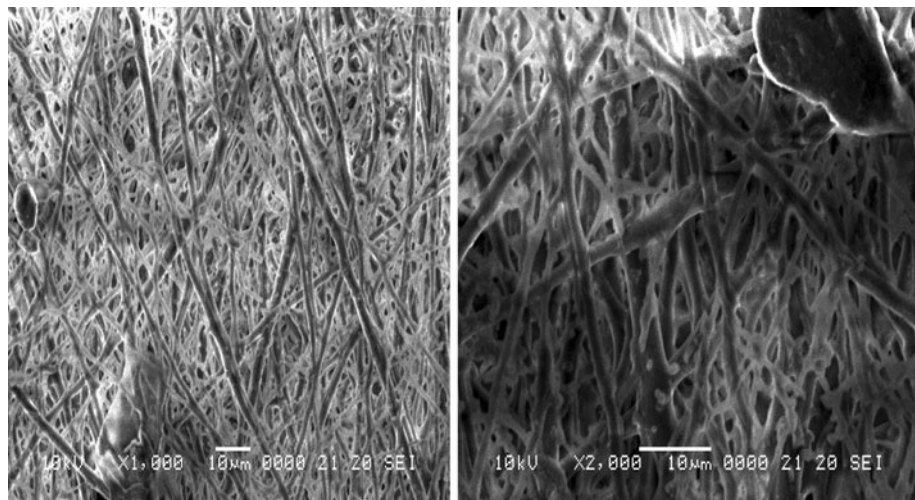Fig. 3 SEM of impregnated egg shell membrane after transport

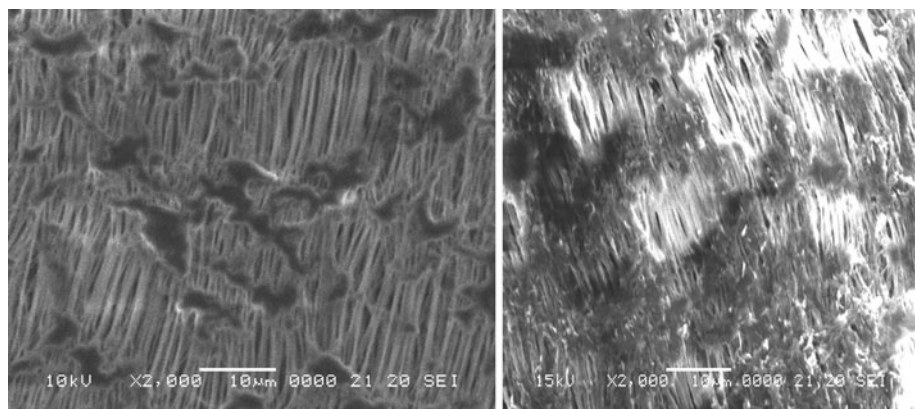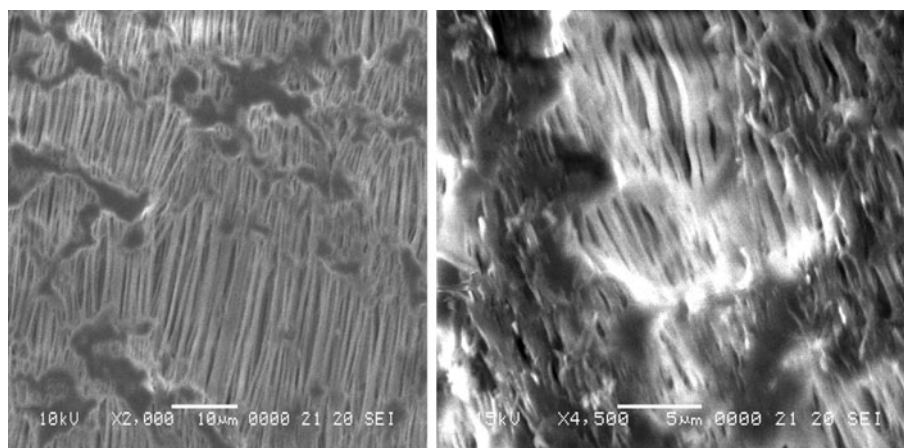Fig. 4 SEM of impregnated PTFE membrane before transport

Fig. 5 SEM of impregnated PTFE membrane after transport

Impregnation of supported liquid membrane in ionophore solution

The membrane support was dipped in ionophore solution (10 mL) overnight and used as supported liquid membrane. The impregnated membrane is used as support for carrier mediated transport of metal cations.

Carrier mediated transport across supported liquid membrane

The supported liquid membrane was positioned between two cylindrical half cells (Fig. 6). One cell compartment (S.P.) contained an aqueous solution of the metal salt (50 mL) and the other cell contained the R.P. (50 mL) double distilled water separated by membrane having an effective diameter of 1 cm. Both phases were stirred with magnetic stirrer at 120 rpm at room temperature, The sample was withdrawn from the R.P. after 24 h and metal content was analyzed. The amount of cation transported is reported in ppm. Cation flux (J_M) values are reported.

Detection of metal ions

Spectrophotometric method [22] for the estimation of Mg^{2+} by Solochrome Black T

Reagents: Buffer solution (pH = 10.1); 0.75% w/v solution of A.R. NH_4Cl in dilute ammonia solution, prepared by mixing 5 volumes of concentrated ammonia solution (sp. gr 0.088) and 95 volumes of water. Solochrome Black T solution; 0.1% in methanol warm and filter.

Procedure: 1.0 mL of sample solution was taken in 10 mL standard volumetric flask, 2.5 mL buffer solution was added and solution was diluted with water up to 9.0 mL and in last 1.0 mL of solochrome indicator was added. Absorbance was measured at 520 nm against that of a blank solution, similarly prepared but containing no

Fig. 6 Apparatus of SLM
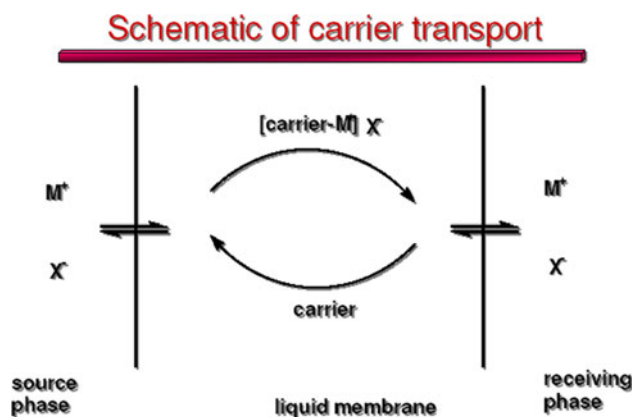
Fig. 7 Mechanism of liquid membrane transport

magnesium. Calibration has been carried out by known concentrations of Mg^{2+} by the same procedure.

Spectrophotometric method [22] for the determination of Ni^{2+} by dimethylglyoxime

Reagents: 0.1% Nickel sulphate solution, 50% liquor ammonia, bromine solution, 1% DMG in ethanol.

Procedure: 1.0 mL of sample solution was taken in 10 mL standard volumetric flask, 2.5 mL ammonia solution, 2.0 mL bromine solution was added and solution was

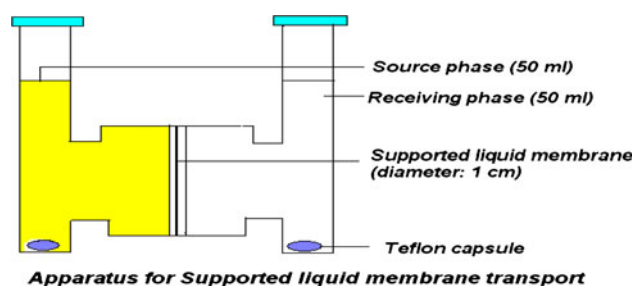diluted with water and in last 1.0 mL of nickel sulphate was added. Absorbance was measured at 460 nm against that of a blank solution, similarly prepared but containing no Ni^{2+}. Calibration graph has been plotted by known concentrations of Ni^{2+} by the same procedure.

Complexometric titration [22] for the determination of Cu^{2+} using fast sulphone black F

Reagents: 0.1 M EDTA solution (standardized with 0.72 g of zinc sulphate using ammonia buffer (pH = 10) and EBT)

Fast sulphone black F (0.5% aqueous solution of indicator), liquor ammonia solution.

Procedure: 5.0 mL of sample solution was pipette out into a conical flask and diluted with equal volume of water. In this solution 0.5 mL of liquor ammonia and 2–3 drops of indicator was added and the solution was titrated with 0.1 M EDTA until the color changes from dark blue to green. The calibration graph has been plotted by using known concentrations of solution of copper nitrate (1×10^{-2}–1×10^{-4} M) by the same procedure.

Complexometric titration [22] for the determination of Zn^{2+} using EDTA

Reagents: 0.1 M EDTA solution (standardized with 0.72 g of zinc sulphate using ammonia buffer (pH = 10) and EBT).

Procedure: 5.0 mL of sample solution was pipette out into a conical flask and diluted with 20 mL of water. In this solution 0.5 mL of ammonia buffer (pH = 10) and 2–3 drops of indicator was added and the solution was titrated with 0.1 M EDTA until the color changes from wine red to blue. The calibration graph has been plotted by using known concentrations of zinc sulphate (1×10^{-2}–1×10^{-4} M) by the same procedure.

Results and discussion

Blank experiments were carried out for extraction, BLM and SLM transport for each cation in which the membrane was devoid of carrier. No detectable amount of metal ions could be observed across membrane in R.P. All measurements were performed in triplicate to check reproducibility. The results of liquid–liquid extraction, bulk liquid membrane transport (BLM) and supported liquid membrane transport (SLM) (egg shell and PTFE) of metal ions are shown in Tables 1, 2, 3, 4, 5.

In liquid–liquid extraction and transport (BLM and SLM) the optimum concentration of metal ion is found to be 1×10^{-2} M, for ionophores (R_1 and R_2) is 1×10^{-4} M

and for ionophores (R_3, R_4 and R_5) is 1×10^{-3} M. The best time for maximum extraction is observed in 4 h while for maximum transport is 24 h [11, 13, 18].

In extraction, ionophore R_1 extracts Na^+ at greater extent (Table 1). It has cyclic crown like structure and 4, 4′-nitrophenyl azo phenyl side chain hence the selectivity of R_1 for Na^+ can be explained by cavity fit concept, the ionic radius of Na^+ (0.97 Å) matches with the cavity size of the R_1 and it forms stable complex with Na^+ as compared to other metal ions [23, 24].

R_2 has bis-(4,4′-nitrophenyl azo-naphthyl) end group and rigid diethylene chain (Fig. 1) complexes with small size and high charge density lithium ion. The extent of interaction is further confirmed by back extraction, in back extraction R_1 and R_2 do not release Na^+ and Li^+ which

Table 1 Amount of metal ions extracted and back extracted from ionophores (R_1 and R_2)

S. no.	Metal salts	Amount of metal ion extracted in ppm		Back extraction	
		R_1	R_2	R_1	R_2
01	Li^+	0.4	19.0	–	–
02	Na^+	15.6	–	–	–
03	K^+	2.0	–	1.5	1.0
04	Mg^{2+}	–	–	–	–
05	Ni^{2+}	4.5	5.7	2.0	–
06	Cu^{2+}	3.7	3.5	–	–
07	Zn^{2+}	–	9.8	–	–

Experimental conditions: source phase, 10 mL of 1×10^{-2} M metal ion . 10 mL of 1×10^{-3} M membrane phase, (ionophore in nitrobenzene); 10 mL of deionised water for back extraction = 10 mL; stirring speed = 200 rpm; stirring time; 4 h; temperature = 30 °C

Table 2 Amount of metal ions extracted and back extracted from ionophores (R_3–R_5)

S. no.	Metal ion	Amount of cation extracted (ppm)			Back extraction		
		R_3	R_4	R_5	R_3	R_4	R_5
01	Li^+	3.5	5.0	3.5	–	1.0	–
02	Na^+	10.0	15.0	6.0	–	1.5	–
03	K^+	76.9	82.9	18.0	5.0	4.5	–
04	Mg^{2+}	–	–	–	–	–	–
05	Ni^{2+}	–	2.4	–	–	–	–
06	Cu^{2+}	3.0	2.5	–	–	–	–
07	Zn^{2+}	–	6.5	–	–	–	–

Experimental conditions: source phase, 10 mL of 1×10^{-2} M metal ion. 10 mL of 1×10^{-3} M membrane phase, (ionophore in chloroform); 10 mL of deionised water for back extraction; stirring speed = 200 rpm; stirring time; 4 h; temperature = 30 °C

Table 3 Amount of metal cation transported in 24 h by ionophores (R_1–R_5) through BLM

IP	Amount of metal cation transported in ppm													
	Li^+	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})	Na^+	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})	K^+	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})	Mg^{2+}	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})	Ni^{2+}	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})	Cu^{2+}	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})	Zn^{2+}	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})
R_1	1.0	5.7	3.8	21.0	6.0	34.0	2.0	11.0	–	–	–	–	–	–
R_2	8.0	23.0	3.2	18.0	1.2	6.0	1.5	2.0	–	–	–	–	**22.7**	131
R_3	5.5	31.0	8.5	49.0	4.5	26.0	–	–	–	–	–	–	8.5	49.0
R_4	3.4	19.0	9.0	52.0	11.0	63.0	3.0	17	–	–	–	–	**13.2**	105
R_5	6.0	34.0	7.2	41.0	1.2	6.0	–	–	–	–	–	–	8.0	23

Experimental conditions: source phase, 10 mL of 1×10^{-2} M metal ion. 25 mL of membrane phase, ionophore (R_1 and R_2) 1×10^{-4} M metal ion. 25 mL of membrane phase, ionophore (R_3, R_4 and R_5) 1×10^{-3} M in chloroform; receiving phase, 10 mL of deionised water

IP ionophore; J_M cation flux

The results in bold highlights greater transport of Zn^{2+} by ionophore R_2 & R_4 respectively

Table 4 Amount of metal cation transported in 24 h by ionophores (R_1–R_5) through SLM by using egg membrane support

IP	Amount of metal cation transported in ppm													
	Li^+	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})	Na^+	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})	K^+	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})	Mg^{2+}	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})	Ni^{2+}	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})	Cu^{2+}	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})	Zn^{2+}	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})
R_1	–	–	6.5	75	2.3	29	–	–	–	–	**18.0**	208	13.9	160
R_2	–	–	1.5	15	1.2	13	–	–	–	–	8.5	100	**45.0**	520
R_3	3.0	35	9.0	104	12.0	135	–	–	–	–	8.0	95	17.0	196
R_4	6.5	75	10.5	125	20.1	235	–	–	–	–	6.9	79	22.0	270
R_5	–	–	2.5	28	1.5	20	–	–	–	–	3.0	39	4.0	46

Experimental conditions: source phase, 25 mL of 1×10^{-2} M metal ion. Egg shell membrane support impregnated with ionophore; receiving phase, 25 mL of deionised water; ionophore R_1 and R_2 1×10^{-4} M in nitrobenzene; ionophore (R_3, R_4 and R_5) 1×10^{-3} M in chloroform

IP ionophore; J_M cation flux

The results in bold highlights greater transport of Cu^{2+} & Zn^{2+} by ionophore R_1 & R_2 respectively

Table 5 Amount of metal cation transported in 24 h by ionophores (R$_1$–R$_5$) through SLM by using PTFE membrane as support

IP	Amount of metal cation transported in ppm													
	Li$^+$	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})	Na$^+$	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})	K$^+$	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})	Mg^{2+}	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})	Ni^{2+}	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})	Cu^{2+}	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})	Zn^{2+}	$J_M = 10^{-5}$ (mol cm^{-2} s^{-1})
R$_1$	–	–	1.2	13.0	0.5	5.7	–	–	–	–	1.0	11.0	1.2	13.0
R$_2$	–	–	1.5	17.0	0.8	9.0	–	–	–	–	1.0	11.0	2.0	23.0
R$_3$	–	–	–	–	1.0	11.0	–	–	–	–	0.5	5.7	1.1	12.7
R$_4$	–	–	–	–	–	–	–	–	–	–	–	–	–	–
R$_5$	–	–	–	–	–	–	–	–	–	–	–	–	–	–

Experimental conditions: source phase, 25 mL of 1 × 10^{-2} M metal ion. PTFE membrane support impregnated with ionophore; receiving phase, 25 mL of deionised water; ionophore R$_1$ and R$_2$ 1 × 10^{-4} M in nitrobenzene; ionophore (R$_3$, R$_4$ and R$_5$) 1 × 10^{-3} M in chloroform

IP ionophore; J_M cation flux

indicates the stronger interaction with respective metal ions.

The observed trend for the extraction of metal cations by non cyclic ionophores R$_3$, R$_4$ and R$_5$ is K$^+$ $\gg$ Na$^+$ > Li$^+$ $\sim$ Ni^{2+}, K$^+$ $\gg$ Na$^+$ > Zn^{2+} > Li$^+$ > Cu^{2+} $\sim$ Ni^{2+}, K$^+$ > Na$^+$ > Li$^+$ respectively. The results reveal that ionophores R$_3$–R$_5$ are better extractant for K$^+$ ions. Among them R$_4$ shows maximum selectivity for K$^+$. Ionophores R$_3$, R$_4$ and R$_5$ have naphthyl end groups and tri, tetra and diethylene glycol chain length (Fig. 1), adopt pseudocavity conformation [10, 25] and as the oxygen donor sites (CH$_2$–O–CH$_2$) increases from di, tri to tetra ethylene glycol chain the selectivity increase towards bigger size Potassium ions. The back extraction values for K$^+$ ions are negligible (Table 2).

In BLM transport, the observed trend for the transport of metal ions by R$_1$ is K$^+$ > Na$^+$ > Mg^{2+}. It does not show transport of transition metal ions (Ni^{2+}, Cu^{2+} and Zn^{2+}). The observed trend for the transport of metal ions by ionophores R$_2$, R$_3$ and R$_5$ is Zn^{2+} $\gg$ Na$^+$ > Li$^+$ > K$^+$ and by R$_4$ is Zn^{2+} $\gg$ K$^+$ > Na$^+$ > Li$^+$ > Mg^{2+} (Table 3; Fig. 8). Due to bis-(4,4′-nitrophenyl azo-naph-thyl) end group and rigid diethylene chain R$_2$ shows higher transport of Zn^{2+}. Ionophores (R$_2$–R$_5$) adopt pseudocavity conformation and size of cation matches with the cavity formed [10]. Non cyclic ionophores form weaker complex with Zn^{2+} which is released at membrane receiving interface (Fig. 7). Thus ionophores (R$_2$–R$_5$) are better carrier of Zn^{2+}, No detectable amount of Ni^{2+} and Cu^{2+} was transported by these ionophores.

In supported liquid membrane transport (egg shell membrane), the observed trend for the transport of metal ions by ionophores R$_1$ and R$_2$ is Cu^{2+} $\gg$ Zn^{2+} $\gg$ K$^+$ > Na$^+$, Zn^{2+} $\ggg$ Cu^{2+} $\gg$ Na$^+$ > K$^+$ ions (Table 4; Fig. 9). No detectable amount of Ni^{2+} is transported by these ionophores. It is found R$_1$ transport Cu^{2+} while it was not transported in BLM. Ionophore R$_2$ transports Zn^{2+} at greater extent at membrane/(R.P.) interface. The observed trend for the transport of metal ions by ionophores R$_3$ and R$_4$ is Zn^{2+} $\gg$ K$^+$ > Na$^+$ > Cu^{2+} > Li$^+$ > Mg^{2+} and by R$_5$ is Zn^{2+} > Na$^+$ > Cu^{2+} > K$^+$. In BLM as well as in SLM ionophores (R$_2$–R$_5$) transport Zn^{2+} at greater extent. On comparing BLM and SLM, better selectivity and efficiency transport of Zn^{2+} has been observed in egg shell membrane.

No selectivity is observed in PTFE membrane (Table 5; Fig. 10). Our objective is to investigate the best membrane support among egg shell and PTFE. It is found that, all the ionophores show higher transport flux with egg shell membrane which has big pore size (2.5 μm and thickness 29 μm) and As compared to PTFE membrane support (pore size 0.2 μm and thickness 65 μm). The egg shell membrane is found best for the transport of zinc ions because of its hydrophobic nature and exhibits electrostatic

Fig. 8 Transport flux for BLM

Cation flux of ionophores(R1-R5) in 24 hrs using BLM
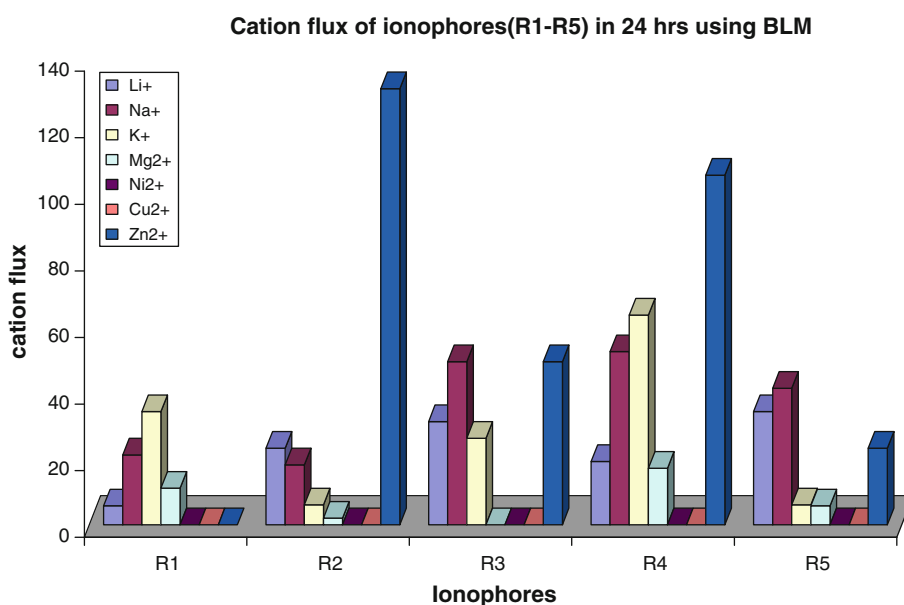
Cation flux (Jm) of ionophores (R1-R5) in 24 h in Eggshell membrane (SLM)
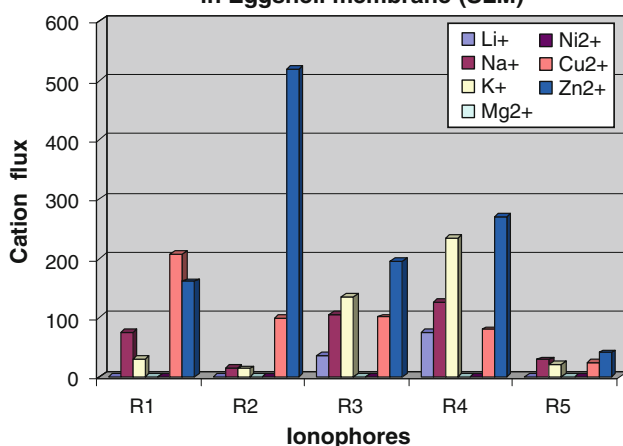

Fig. 9 Transport flux for egg shell SLM

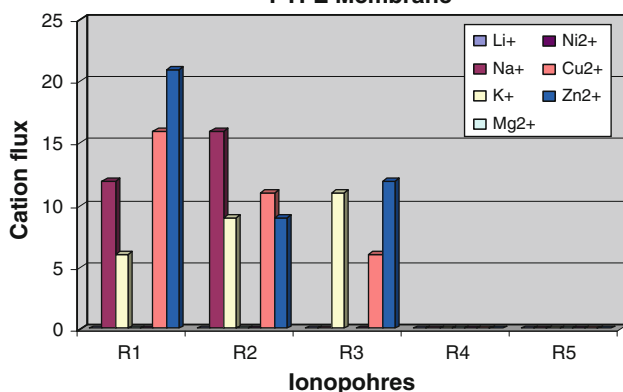### Cation flux(Jm) of ionopohores (R1-R5) in 24 h in PTFE Membrane

Fig. 10 Transport flux for PTFE SLM

interactions between positively charged zinc ions and –COOH group of egg shell membrane [20]. The efficiency transport increases due to donar nitrogen atoms as compared to oxygen atoms of ionophores.

Conclusion

The results here led to conclude that on insertion of azo-naphthyl and naphthyl moiety in simple glycols, the transport efficiency increases towards transition metal ions (Cu^{2+}, Zn^{2+}) as compared to alkali, alkaline earth metal ions (Li^+, Na^+, K^+, Mg^{2+}) [4] while ionophores (R_1–R_5) are better extractant for alkali metal ions (Li^+, Na^+, K^+). Ionophores R_1 and R_2 were shown to be best candidates for liquid membrane transport owing to their high selectivity for Cu^{2+} and Zn^{2+} respectively. Thus under optimum condition both BLM and SLM are quite effective and selective for the removal of trace as well as milligram amount of Zn^{2+}. Thus the structure of ionophore as well as hydrophobicity and porosity of the membrane also plays key role in metal ion separation. This selectivity helps in making of ion selective electrodes, chemical sensors and separation of metal ions.

References

1. Luccio, M., Smith, B.D., Kida, T., Alves, T.L.M., Borges, C.P.: Evolution of flat sheet on hollow fiber supported liquid membrane

transport for sucrose pertraction from a mixture of sugars. Desalination. **148**, 213–220 (2002)

2. Danesi, P.: A simplified model for the coupled transport of metal ions through hollow fiber supported liquid membranes. J. Memb. Sci. **20**, 231–248 (1984)

3. Koreyta, J.: Ions Electrodes and Membranes, pp. 137–141. Wiley, New York (1982)

4. Faridbod, F., Ganjali, M.R., Dinarvand, R., Norouz, P.: Developments in the field of conducting and non-conducting polymer based potentiometric membrane sensors for ions over the past decade. Sensors. **8**, 2331–2341 (2008)

5. Petrovic, T.T., Jonsson, J.A.: Application of SLM extraction of investigation of metal–humic acid bindings. Desalination. **148**, 247 (2002)

6. Kocherginsky, N.M., Qian, Y., Seelam, L.: Recent advances in supported liquid membrane technology. Sep. Purif. Technol. **53**, 171–177 (2007)

7. Kocherginsky, N.M., Qian, Y.: Big carrousel mechanism of copper removal from ammoniacal wastewater through supported liquid membrane. Sep. Purif. Technol. **54**, 104–116 (2007)

8. Yang, Q., Kocherginsky, N.M.: Copper recovery and spent ammoniacal etchant regeneration based on hollow fiber supported liquid membrane technology: from bench-scale to pilot-scale tests. J. Memb. Sci. **286**, 301–309 (2006)

9. Yang, Q., Kocherginsky, N.M.: Copper removal from ammoniacal wastewater through a hollow fiber supported liquid membrane system: modeling and experimental verification. J. Memb. Sci. **297**, 121–129 (2007)

10. Tummler, B., Maass, G., Vogtle, F., Weber, E.: Open chain polyethers: influence of aromatic donor end groups on thermodynamics and kinetics of alkali metal ion complex formation. J. Am. Chem. Soc. **101**, 2588–2599 (1979)

11. Bhatnagar, M., Sharma, U.: Effect of end groups and chain length on extraction of lithium ion by a series of non cyclic ionophores. J. Sci. I. Rep. Iran **14**(4), 333–336 (2003)

12. Singh, R., Mehta, R., Kumar, V.: Simultaneous removal of copper, nickel and zinc metal ions using bulk liquid membrane system. Desalination. **272**, 170–173 (2011)

13. Tomar, J., Sharma, U.: Design and Synthesis of azobenzene bridged photoresponsive ionophores and their application in extraction and liquid membrane transport of main group metal ions (Li^+, Na^+, K^+, Ca^{2+}). J. Main Group Metal Chem. **29**(3), 119–126 (2006)

14. Tomar, J., Chauhan, P. S., Sharma, U.: Isolation and characterization of chromogenic metal–ionophore complexes. Tetrahedron Lett. **314**, 2160–2165 (2011)

15. Tomar, J., Bhatanagar, M., Sharma, U.: Isolation and characterization of complexes of alkali and alkaline earth metal cations with synthetic podands. Proc. Natl. Acad. Sci. USA **76**, 1–4 (2007)

16. Mishra, D., Sharma, U.: Carrier mediated transport of some main group metal ions across various organic liquid membranes. J. Sep. Sci. Technol. **34**(15), 3113–3124 (1999)

17. Awasthy, A., Bhatanagar, M., Joshi, N., Sharma, U.: Effect of side arm chain length of redox ionophores on uptake of some metal ions. Indian J. Chem. **45A**, 1170–1172 (2006)

18. Mishra, D., Sharma, U.: Influence of halocarbon solvents on carrier mediated cation transport through bulk liquid membranes. Indian J. Chem. **3**, 245–249 (1996)

19. Awasthy, A., Bhatanagar, M., Tomar, J., Sharma, U.: Design and synthesis of redox switched lariat ethers and their application for transport of alkali and alkaline earth metal cations across supported liquid membrane. J. Bioinorg. Chem. Appl **2006**, 1–4 (2006)

20. Raizada, P., Vyas, V., Sharma, U.: Liquid membrane extraction and transport of amino acids using calix[6]rene. Indian J. Chem. Technol. **17**, 267–273 (2010)

21. Huang, L.T., Hsu, P.S., Chen, S.C., Lai, J.Y.: Por size control of PTFE membrane by stretch operation with asymmetric heating system. Desalination. **233**, 64–72 (2008)

22. Vogel A. I.: A Text Book of Quantitative Inorganic Analysis, 4th edn. Longmans Green and Co., London (1986)

23. Izatt, R., Clark, G.A., Bradshaw, J.S., Lamb, J.D., Christansen, J.J.: Macrocycle-facilitated transport of ions in liquid membrane systems. J. Sep. Purif. Methods **15**, 21 (1986)

24. Nakamura, H., Nishida, H., Takagi, M., Ueno, K.: Chromogenic crown ethers reagents for spectrophotometric determination of sodium and potassium. Anal. Chem. Acta **139**, 219–227 (1982)

25. Tomar, J., Awasthy, A., Sharma, U.: Synthetic ionophores for separation of Li^+, Na^+, K^+, Ca^{2+} & Mg^{2+} metal ions using liquid membrane technology. Desalination **232**, 102–109 (2008)