Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2017, 9(9):37-43

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Isolation and Characterization of Host Guest Complexes through Spectroscopy and Liquid –Liquid Extraction Studies

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ABSTRACT

A new method for the synthesis of Chromogenic ionophores; 4,4'–nitrophenyl-azo-O,O'-phenyl- 3, 6, 9-trioxaundecane-1, 10-dioate (R_1), bis-[4,4'-nitrophenyl-azo-naphthyl-(2,2-dioxydiethyl ether)] (R_2) and non-cyclic ionophores; 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) has been constructed and their interaction with lithium, sodium, potassium and calcium picrates has been studied. The Complexes were isolated in methanol and mixture of methanol and ethyl acetate. The stoichiometry of complexes was 1:1. Characterization of complexes was carried out by m.p., elemental analysis, IR, ^1H NMR, FAB mass analysis. The ionophore R_1 complexes with Na^+ and Ca^{++}, R_2 and R_5 with Li^+ and Mg^{++} respectively while R_3 and R_4 complexes with all metal ions. The same trend is observed in liquid –liquid extraction studies. As the supramolecular interaction between host and guest is temporary, non-covalent and required less energy to break interaction the selectivity / specificity of these ionophores will be utilized in construction of ion selective electrodes and as metal ion indicators.

Keywords: Chromogenic ionophores; Non-cyclic ionophores; Metal-ligand complexes; Stoichiometry selectivity

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INTRODUCTION

The crown ethers [1], cryptands [2] and podands [3] can interact with many guests including inorganic ions and neutral organic molecules through weak non-covalent interaction. The Chromogenic crown ethers have discovered by Nakamura et al. [4,5]. Nitrophenyl azo-15-crown-5 has been used as colorimetric regent for the determination of sodium and potassium [6]. The complexation properties of Chromogenic crown ethers [5,6] and non-cyclic ionophores (podands) have been investigated extensively. Interest in these compounds have been grown due to their importance in supramolecular chemistry [7] as they are selective for alkali, alkaline earth metal ions [8] and used as ion selective electrodes [9]. The complexing abilities of these ionophores can be increased by addition of aromatic end groups to simple glycols [10-12]. The aim of our work is to understand principles that are involved during complexation of these ionophores with metal ions i.e., stoichiometry of the complexes, effect of end group, chain length and charge of cation etc.

In this communication, we are reporting the synthesis of azo benzene bridged ionophores (R_1 and R_2) and non-cyclic ionophores (R_3-R_5) having naphthyl end groups with different chain length and isolation of their complexes with some alkali (Li^+, Na^+, K^+) and alkaline earth metal cations (Ca^{++}, Mg^{++}) in solid state and compared the M-L interation through liquid –liquid extraction studies.

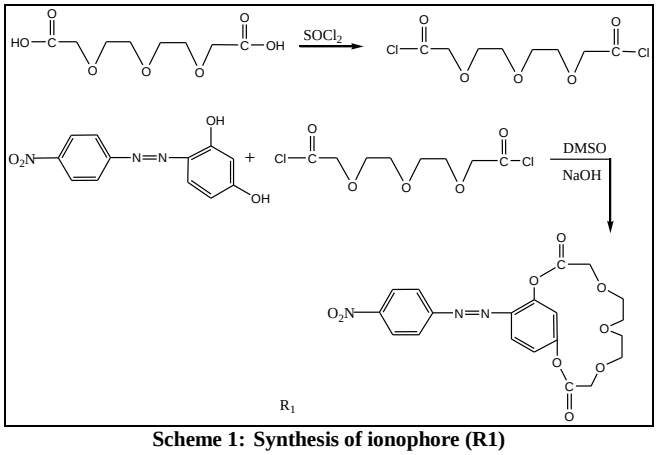
MATERIALS AND METHODS

The reagents used in the synthesis of ionophores (R_1-R_5) i.e., 4(4'-nitrophenyl-azo)-resorcinol, 4(4'-nitrophenyl-azo)-1-naphthol and 2-naphthol were purchased from Merck India and used as such while bis-(3,6,9-trioxaundecandioic) acid, 2,2'dichloro-diethylether, 1,11-dichloro-3, 6,9-trioxaundecane and bis-(1,2-chloroethoxy ethane) were purchased from FLUKA Switzerland. Methanol, 1-butanol, DMSO and $SOCl_2$ were purchased from Merck, India and used without purification. Hydrochloric acid, sodium hydroxide and Magnesium sulphate were purchased from Aldrich, USA.
The metal salts as Metal Picrates (MX: M^{n+} = Na^+, K^+, Ca^{++}, Mg^{++}, X^- = Pic^-) were prepared by reported method [13]. Melting points were determined by melting point apparatus (Boss 165). Elemental analysis (C, H, N) were obtained from CDRI Lucknow using elemental analyzer (Carlo Erba 1108). Metal ions were estimated by flame photometer (Systronics 121). IR spectra were recorded on FTIR spectrophotometer (Perkin Elmer 70836) and ^{1}H NMR spectra were recorded in $D_2O/CDCl_3$ using TMS as internal reference at CDRI Lucknow on NMR spectrophotometer (Varian 350) at 300 MHz.

Synthesis of Azo Benzene Bridged Ionophores R_1 and R_2

Preparation of ionophore (R_1); 4, 4'-nitrophenyl-azo-O, O'-phenyl-3, 6, 9-trioxaunde- cane 1, 10 dioate]:

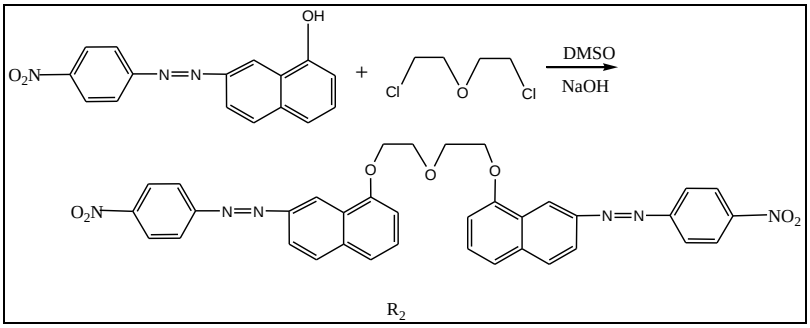
Synthesis of ionophore (R_1) has been carried out in two steps (Scheme 1):
Step I: Preparation of bis (3, 6, 9-trioxuandecandioic) acid chloride. A mixture (1:5) v/v of bis (3, 6, 9–trioxaundecandioic) acid (20 mL) and thionyl chloride (100 mL) was refluxed at 80°C for 6 h after refluxing, the product was distilled off at 70°C and characterized by TLC and spectral analysis.
Step II: 4(4'-nitrophenyl azo)-resorcinol 5.18 g (.019 mol) was dissolved in DMSO (25 mL) and NaOH 1.6 g (0.04 mol) in 20 mL water. The reaction mixture was stirred for 30 min. and bis-(3, 6, 9-trioxaundecandioic) acid chloride (5 mL) was added. The reaction mixture was refluxed at 80°C for 12 h. The product was neutralized by 4-5 drops of HCl (1M) and washed with deionised water. After this the product was vacuum filtered, recrystallized in methanol and characterized by mp, TLC and spectral analysis. Red solid (amorphous), m.p: 250°C, yield: 4.0 g (65%). FAB Mass: m/z 443 (molecular ion peak) calculated for $C_{30}H_{28}N_3O_{11;}$ M.Wt: (445).



Scheme 1: Synthesis of ionophore (R1)

Preparation of Ionophore (R_2); bis [4,4'-nitrophenyl-azo-napthyl (2,2'-dioxydiethyl ether)]
4(4'-nitrophenyl-azo)-1-naphthol 5.8 g (0.019 mol) was dissolved in DMSO (25 mL) and NaOH 0.8 g (0.02 mol) in 20 mL water. The reaction mixture was stirred for 30 minutes at room temperature and 2, 2'-dichloro diethyl ether 2 mL (0.013 mol) was added. The reaction mixture was refluxed at 80°C for 12 h. The product was neutralized by HCl (1M) and washed with deionised water. After this the product was vacuum filtered. The dark brown solid was recrystallized in methanol and characterized by mp, TLC and spectral analysis (Scheme 2).

Brown solid (amorphous), m.p: 270°C, Yield: 3.8 g (67%), FAB Mass: m/z 655(molecular ion peak) calculated for $C_{30}H_{28}N_3O_{11;}$ M.Wt: (656).



Scheme 2: Preparation of ionophore (R2)

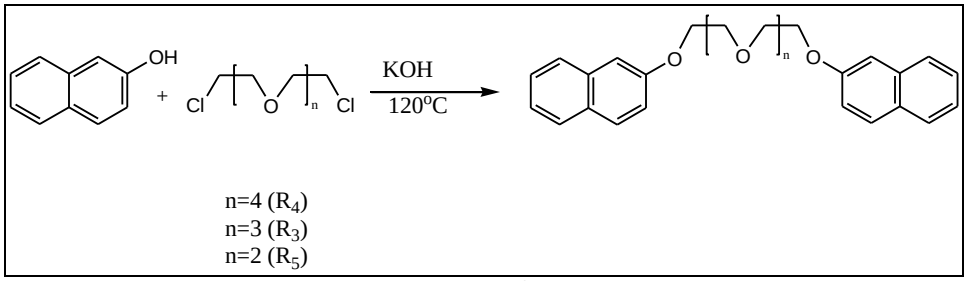
Synthesis of Non-cyclic Ionophores (R_3-R_5)

Preparation of ionophore R_3; 1, 8-bis (2-naphthyloxy)-3, 6-di-oxaoctane:

In 150 mL of boiling 1-butanol solution 2-naphthol 8.64 g (.06 mol), KOH 3.36 g (0.6 mol) and bis (1, 2-chloro ethoxy ethane) 4.68 mL (.030 mol) were added one by one. The reaction mixture was refluxed at 120^{o}C for 20 h. After this fine precipitates (KCl) formed were filtered off, the solution was evaporated to dryness under vaccum. The residue was taken up in chloroform and washed several times with dilute NaOH and deionized water. The organic phase was separated, dried over $MgSO_4$ and concentrated by distillation under vaccum (Scheme 3).

m.p: 54^{o}C; Brown solid; yield: 6.5 g (50%), FAB Mass: m/z 402(molecular ion peak) calculated for ($C_{26}H_{26}O_4$) M.Wt; (402).

Synthesis of ionophore R_4 and R_5 was done by refluxing 1,11 dichloro-3,6,9 trioxaundecane 4.74 mL (0.29 mol) and 2,2'-dichloro diethyl ether 3.8 mL (0.02 mol) as above procedure.



Scheme 3: Synthesis of ionophore R_3

Ionophore R_4; 1, 11-bis (2-naphthyloxy)- 3,6,9-trioxaundecane:

m.p: 80^{o}C; White shiny crystals; yield: 5 g (41.6%), FAB Mass: m/z 446 (molecular ion peak) calculated for ($C_{28}H_{30}O_5$) M. Wt.; (446).

Ionophore R_5; 1, 5-bis (2-naphthyloxy) -3-oxapentane:

m.p: 132^{o}C; White crystalline solid; yield: 4.0 g (33.4%), FAB Mass: m/z 356 (molecular ion peak) calculated for ($C_{24}H_{26}O_3$) M. Wt.; (356).

Isolation Studies

The isolation studies were performed by mixing metal salt with ionophore in 1:1, 1:2 (M: L) ratio in methanol. The mixture was warmed on a water bath and then allowed to crystallize at room temperature. Crystallization generally occurs within two to three days. Initially complexes were characterized by melting points. The crystals were vacuum filtered and recrystallized from the same solvent from which they had been isolated. If distinct melting point was not obtained, solvents variation have been done by using different solvents i.e. isopropanol, ethyl acetate, acetonitrile, mixture methanol + ethyl acetate, carbon-tetrachloride and dichloromethane etc. The stoichiometry of the complexes was determined by elemental

analysis (C, H, N) and metal estimation were done by using flame photometer (Li^+, Na^+, K^+, Ca^{++}) and spectrophotometer (Mg^{++}).

$$D_m = \frac{\text{Total conc. of cation in organic phase}}{\text{Total conc. of cation in aqueous phase}}$$

Extraction Studies: **Liquid Liquid Extraction**

In the liquid -liquid extraction [13]. studies, 10 ml of 1.0×10^{-2} M aqueous metal salt solution was vigorously stirred with 10 ml of 1.0×10^{-4} M ionophore solution in nitrobenzene in a 50ml 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 minutes for the separation of two phases. The depleted aqueous solution was removed and analyzed for metal content by flame photometer. (Li^+, Na^+, K^+, Ca^{++}) and spectrophotometer (Mg^{++}). The amount of metal ion extracted by ionophore was found by measuring its difference in aqueous phase before and after extraction [14,15].

RESULTS AND DISCUSSION

By simple, cheap and convenient methods the ionophores were synthesized. The physical properties, analytical data of ionophores (R_1-R_5) and their complexes are given in Tables 1-3. The complexes were isolated in methanol and mixture of methanol + ethyl acetate and characterized by m.p. and spectral analysis. Metal estimation and elemental analysis indicates that the isolated complexes are of 1:1 stoichiometry.

Table 1: Physical characteristics and analytical data of isolated complexes of metal salts with ionophores (R_1-R_5)

Metal Salt	IP	M:L	Solvent	m.p.°C	Yield (%)	Molecular Formula	Elemental Analysis (%) C H N M				
NaPic	R_1	1:01	MeOH	273	42	$C_{26}H_{21}O_{16}N_9Na$	F	70	3.5	28.01	4.3
							C	70.11	4.7	28.31	5.4
$Ca(Pic)_2$	R_1	1:01	MeOH	225	39	$C_{32}H_{23}O_{23}N_9Ca$	F	86.25	4.92	27.5	8
							C	86.29	5.16	28.51	8.9
LiPic	R_2	1:01	MeOH	152	48.23	$C_{44}H_{32}O_{21}N_{12}Li$	F	78.02	4.04	25.2	3.62
							C	80.36	4.8	5.57	3.65
NaPic	R_3	1:01	Ethyl acetate+ MeOH	68	45	$C_{32}H_{28}O_{11}N_3Na$	F	57.8	3.72	7.2	3.3
							C	58.2	4.2	6.4	3.5
KPic	R_3	1:01	Ethyl acetate+ MeOH	70	47	$C_{32}H_{28}O_{11}N_3K$	F	57.4	4	6.4	5
							C	57.3	4.1	6.2	5.8
$Ca(Pic)_2$	R_3	1:01	Ethyl acetate + MeOH	72	40	$C_{38}H_{30}O_{18}N_6Ca$	F	51	3	9	4.16
							C	57.73	3.3	9.3	0.18
NaPic	R_4	1:01	Ethyl acetate+ MeOH	41	42.2	$C_{34}H_{32}O_{12}N_3Na$	F	58.5	4.5	6.02	3.2
							C	50.8	4.6	6.9	3.2
KPic	R_4	1:01	Ethyl acetate+ MeOH	45	48	$C_{34}H_{33}O_{12}N_3K$	F	57.2	4.4	5.8	5.4
							C	57.8	4.6	5.9	5.2
$Ca(Pic)_2$	R_4	1:01	Ethyl acetate+ MeOH	60	44.2	$C_{40}H_{34}O_{26}N_6Ca$	F	50.8	3.8	8 .20	4
							C	50.8	3.6	8.9	4.2
$Mg(Pic)_2$	R_5	1:01	MeOH	85	41	$C_{36}H_{28}O_{13}N_6Mg$	F	57.3	3	7.2	3.3
							C	57	3.7	7.4	3.2

The isolation results reveals that ionophore R_1 complexes with sodium and calcium picrates while the ionophore R_2 complexes with lithium picrate (Table 1). These results are supported by liquid –liquid extraction in the liquid -liquid study Ionophore R1 extracts sodium and calcium at greater extent while transport less. The IR spectra of ionophores R_1 and R_2 are shown in Table 2. The characteristic IR peaks of ionophore R_1 at 3074 cm^{-1}, 2865 cm^{-1} (C-H), 1718 cm,$^{-1}$ (Ar-COO-),1596 cm^{-1} (N=N), 1251 cm^{-1} (Ar-O-CH_2) and 1109 cm^{-1} (CH_2-O-CH_2) are shifted towards lower frequency in metal complexes.

Table 2: Selected Infrared data of complexes (in cm^{-1})

IP	Complex	(Ar-CH)	(COO)	(N=N)	(Ar-O-CH_2)	(CH_2-O-CH_2)	Ar-ring	Shift in IR peaks toward lower frequency
R_1		3050	1718	1597	1251	1109	989	
		2865						
	NaPic.R_1	3024	1633	1557	1200	1060	937	26 (C-H), 75 (-COO-) 39 (N=N), 51 (Ar-C-O),49 (R-C-O), 52 (Ar C-H)
	$Ca(Pic)_2.R_1$	3020	1634	1561	1209	1107	987	30 (C-H), 74 (C-OO-), 35 (N=N), 47 (Ar-C O), 02 (R-C-O), 02 (Ar C-H)
R_2		3074	-	1597	1225	1108	978	
	LiPic.R_2	3070	-	1560	1220	1108	970	04 (C-H), 37 (N=N), 05 (Ar-C-O), 08 (Ar- C-H)
R_3		2924	-	-	1253	1114	967	
	NaPic. R_3	2872				1055		
		2901	-	-	1255	1067	967	23,14 (C-H), 03 (Ar-C O), 47, 02 (R-C-O),
		2868				1053		
	KPic.R_3	2900	-	-	1255	1066	963	24 (C-H), 48 (Ar-C O), 04, (R-C-O), 04 (Ar -C-H)
						1051		
	$Ca(Pic)_2.R_3$	2900	-	-	1255	1667	958	24 (C-H), 03 (Ar-C-O), 47 (R-C-O), 09 (Ar C-H)
		2860				1053		
R_4		3056	-	-	1255	1184	967	
	NaPic.R_4	2900				1052		
		2924	-	-	1259	1078	967	32 (C-H), 04 (Ar-C O), 16 (R-C-O)
	KPicR_4	2853				1059		
		2923	-	-	1245	1079	967	33 (C-H),10 (Ar-C O), 15 02 (R-C-O)
		2852				1052		
	$Ca(Pic)_2R_4$	2940	-	-	1238	1108	967	16 (C-H),17 (Ar-C O), 02 (R-C-O)
		2892				1052		
R_5	$Mg(Pic)_2R_5$	3056	-	-	1260	1080	968	
		2949				1056		
						1020		
		3025	-	-	1260	1050	960	31 (C-H), 06, 10 (R-CO)
		2950				1070		

It is observed that IR peaks of R_1 at 1596 cm^{-1} (N=N), 1251 cm^{-1} (Ar-O-CH_2) and 1109 cm^{-1} (CH_2-O-CH_2) are shifted to 1557 cm^{-1}, 1200 cm^{-1}, 1060 cm^{-1} in sodium picrate-R_1 and 1560 cm^{-1}, 1209 cm^{-1}, 1107 cm^{-1} in calcium picrate-R_1 complex. The shift ($\Delta\nu$) of IR peaks towards lower frequency in NaPic-R_1 complex due to azo group (N=N), aromatic C-O (Ar-O-CH_2) and aliphatic C-O stretching (CH_2-O-CH_2) is 39 cm^{-1} , 51 cm^{-1} and 49 cm^{-1} and in CaPic-R_1 complex is 35 cm^{-1} (N=N), 42 cm^{-1} (Ar-O-CH_2), 02 cm^{-1} (CH_2-O-CH_2).

From the results, it is found that the extent of shifting of IR peaks towards lower frequency is greater in NaPic-R_1 complex, which indicates greater interaction of ionophore R_1 with sodium picrate. The selectivity of ionophore R_1 can be explained by cavity fit concept [10], it may be suggested that the ionic radius of Na^+ (0.97Å) and Ca^{++} (0.98 Å) matches with the cavity size of R_1. The results are further supported by ^{1}H NMR spectral data (Table 3). The proton signals in ionophore R_1 at δ 3.30 (CH_2-O-CH_2), δ 4.86 (CH_2-COO-Ar), 6.3- 8.3 (Aromatic C-H) shifted slightly downfield in the metal complexes, which shows non covalent interaction of Na^+ and Ca^{++} ions with ionophore R_1.

Ionophore R_2 complexes with lithium picrate. The characteristic IR peaks of ionophore R_2 at 3024 cm^{-1} (C-H), 1597 cm^{-1} (N=N), 1225 cm^{-1} (Ar-O-CH_2) and 1108 cm^{-1} (CH_2-O-CH_2) are shifted towards lower frequency in metal complexes. Due to short chain length (di-ethylene glycol oxygen donor binding sites) ionophore R_2 complexes with small size and high charge density lithium ion, in the same trend ionophore R_2 extract lithium at greater extent. The results are further supported by ^{1}H NMR spectral data (Table 3). The proton signals in ionophore R_2 at δ 3.29 (CH_2-O-CH_2), δ 3.60 (CH_2-O-Ar), 7.3-7.8 (Aromatic C-H) are shifted downfield in the metal complexes, which show interaction of Li^+ ions with ionophore.

Table 3: Selected ^{1}H NMR of complexes (in ppm)

Complexes	Proton signals in ionophores (R_1-R_5)	Proton signals in complexes (R_1-R_5)
NaPic.R_1	3.30 (s, 4H) (-CH_2-O-CH_2), 4.86 (s,4H) (CH_2-COO-Ar), 6.3-8.3 (m,7H) (aromatic C-H)	3.29 (s,4H) (-CH_2-O-CH_2), 4.86 (s,4H) (CH_2- COO-Ar), 8.8 (s, 7H) (aromatic C-H)
Ca(Pic)$_2$.R_1	3.30 (s,4H) (-CH_2-O-CH_2), 4.86 (s,4H) (-CH_2 -COO-Ar), 6.3-8.3 (m,7H) (aromatic C-H)	3.34 (s,4H) (-CH_2-O-CH_2), 4.89 (s,4H) (CH_2-COO-Ar), 8.8 (s,7H) (aromatic C-H)
LiPic.R_2	3.29 (d,4H) (-CH_2-O-CH_2) ,3.6 (t,4H) (-CH_2-O-Ar),7.8-8.7 (m,12H) (aromatic C-H)	3.34 (s,4H) (CH_2-O-CH_2), 4.8 (s,4H) (-CH_2-O-Ar), 7.8-8.7 (s,12H) (aromatic C-H)
NaPic.R_3	3.80 (s,4H) (-CH_2-O-CH_2) 3.93 (t,4H) (O-CH_2-CH_2-O-Ar),4.22(CH_2-O-Ar)7.11-7.75 (m,14H) (naphthyl C-H)	3.84 (s,4H) (CH_2-O-CH_2), 3.92 (t,4H) (O-CH_2-CH_2-O-Ar), 4.23 (CH_2-O-Ar), 7.12-7.75 (m,14H) (naphthyl C-H)
KPic.R_3	3.80 (s,4H)(-CH_2-O-CH_2), 3.93 (t,4H)	3.88 (s,4H) (-CH_2-O-CH_2) 3.93 (t,4H)
	(O-CH_2-CH_2-O-Ar),4.22 (CH_2-O-Ar), 7.11-7.75 (m,14H) (naphthyl C-H)	(O-CH_2-CH_2-O-Ar), 4.24 (CH_2-O-Ar), 7.11-7.75 (m,14H) (naphthyl C-H)
CaPic.R_3	3.80 (s,4H) (-CH_2-O-CH_2) , 3.93 (t,4H)	3.82 (s,4H) (-CH_2-O-CH_2) 3.93 (t,4H)
	(O-CH_2-CH_2-O-Ar),4.22 (CH_2-O-Ar), 7.11-7.75 (m,14H) (naphthyl C-H)	(O-CH_2-CH_2-O-Ar), 4.22 (CH_2-O-Ar), 7.11-7.75 (m,14H) (naphthyl C-H)
NaPic.R_4	3.79 (m,8H) (-CH_2-O-CH_2), 3.90 (t,4H) (O-CH_2-CH_2-O-Ar),4.23 (CH_2-O-Ar), 7.11-7.75 (m,14H) (naphthyl C-H)	3.82 (m,8H) (-CH_2-O-CH_2), 3.93 (t,4H) (O-CH_2-CH_2-O-Ar), 4.25 (CH_2-O-Ar),7.13-7.75 (m,14H) (naphthyl C-H)
KPic.R_4	3.79 (m,8H) (-CH_2-O-CH_2), 3.90(t,4H) (O-CH_2-CH_2-O-Ar),4.23(CH_2-O-Ar), 7.11-7.75 (m,14H) (naphthyl C-H)	3.85 (m,8H) (-CH_2-O-CH_2), 3.96 (t, 4H) (O-CH_2-CH_2-O-Ar), 4.25 (CH_2-O-Ar), 7.11-7.77 (m,14H) (naphthyl C-H)
Ca(Pic)$_2$.R_4	3.79 (m,8H) (-CH_2-O-CH_2), 3.90 (t,4H) (O-CH_2-CH_2-O-Ar),4.23 (CH_2-O-Ar), 7.11-7.75 (m,14H) (naphthyl C-H)	3.82 (m,8H) (-CH_2-O-CH_2), 3.95 (t,4H) (O-CH_2-CH_2-O-Ar),4.30 (CH_2-O-Ar),7.11 .75 (m, 14H) (naphthyl C-H)
Mg(Pic)$_2$.R_5	3.58 (s,4H) (-CH_2-O-CH_2), 4.12 (CH_2-O-Ar), 7.11-7.75 (m,14H) (naphthyl C-H)	3.60 (s,4H) (-CH_2-O-CH_2), 4.18 (CH_2-O-Ar), 7.11 -7.75 (m,14H) (naphthyl C-H)

We have isolated complexes of non-cyclic ionophore R_3, R_4 with Na^+, K^+, Ca^{++} and R_5 with Mg^{++}(Metal Picrates). Ionophores R_3, R_4 and R_5 have rigid naphthyl end group and varying tri, tetra and diethylene glycol chain length respectively (Scheme 3). When these results were compared with liquid –liquid ectravtionn Ionophores R_3, R_4 and R_5 extracts potassium at greater extent (Table 4) The results shown in Table 1 indicate that complexing tendency is enhanced in ionophore R_3 and R_4. From IR spectra of complexes, it is observed that characteristic IR peaks of ionophores due to C-H stretching, Ar-O-CH_2 and CH_2 –O-CH_2 are shifted towards lower frequency in complexes (Table 2).

The interaction of these ionophores (R_3-R_5) with metal salts is further supported by ^{1}H NMR spectral data. The proton signals in ionophores (R_3-R_5) at δ 3.52 -3.80 (CH_2-O-CH_2), δ 3.90-3.93 (-O-CH_2-O-CH_2 -Ar), δ 4.12-4.22 (O-CH_2-Ar), δ 7.11 -7.75 (naphthyl C-H) are found to be shifted slightly downfield in the complexes (Table 2).

On the basis of IR and ^{1}H NMR spectral data, it is suggested that during complexation ionophores (R_3-R_5) adopt pseudo cavity conformation. Ionophore R_3 and R_4 has four and five oxygen donor binding sites. Due to the flexible chain length ionophores R_3 and R_4 complex with Na^+, K^+ and Ca^{2+} metal ions. Ionophore R_5 has short chain length (three oxygen donor binding sites) complexes with Mg^+ ions. The pseudocavity

conformation of non-cyclic ionophores (R_3-R_5) is the driving force for the metal ion complexation and due to the increment in chain length from diethylene to tetra ethylene, the selectivity changes from small size cation to larger size cations [6].

Table 4: Amount of metal cations extracted into an organic phase in 4 h by ionophores (R_1–R_5) in chloroform Metal salt concentration = 1×10^{-2} M; ionophore concentration = 1×10^{-3} M

Metal salts		Amount of cations extracted (in ppm) by ionophores			
	R_1	R_2	R_3	R_4	R_5
LiPic	1.6	11	—	5.3	5.8
NaPic	12	2.7	16	4.2	1.8
KPic	7	4	95	26	20.5
$Ca(Pic)_2$	15	5	—	12	7.5
$Mg(Pic)_2$	—	—	4	6	—

CONCLUSION

We have synthesized different end group bearing ionophores; azo benzene bridged ionophores (R_1 and R_2) and 2-naphthol derived podands (R_3-R_5). From the results, it was found that the complexing abilities of ionophores (R_1-R_5) have been affected on varying end groups and chain length. Ionophore R_1 is selective for Na^+ and Ca^{++} As like Nitrophenyl azo-15-crown-5, ionophore R_1 (Scheme I) may be used as extraction colorimetric regent for the determination of these ions while R_2 is specific for Li^+. Ionophore R_3 and R_4 having different chain length adopt pseudocyclic conformation and complexes with all metal cations and selectivity is lost while due to short chain length R_5 is specific for Mg^{++}ions. As the supramolecular interaction between host and guest is temporary, non-covalent and required less energy to break interaction the selectivity / specificity of these ionophores will be utilized in construction of ion selective electrodes and as metal ion indicators.

ACKNOWLEDGEMENTS

The authors would like to thank Madhyapradesh Council of Science and Technology Bhopal, India for financial assistance for the project no. 1082/CST/R&D/2012 and support of SAIF Punjab for spectral analysis is also acknowledged.

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