Synthesis of New Non Cyclic Ionophores and Their Use in Extraction and Bulk Liquid Membrane Transport of Alkali Metal Ions

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Abstract

Separation phenomenon through molecular recognition of the host compound has widely been used by incorporation of ionophores into liquid membranes. New ionophores were synthesized and used to study their extractability and carrier ability for alkali (Li^+, Na^+ and K^+) metal ions using picrate, dinitrophenolate and orthonitrophenolate salts through dichloromethane, 1, 2-dichloroethane and chloroform membranes. Higher extraction and transport values were observed for K^+ ions from picrate salts through dichloromethane. The membrane process is successfully applied in advanced components of analytical instruments, biomedical and biological applications, textile and pharmaceutical industry.

Key words: Bulk liquid membrane, Alkali metal ions, Ionophore.

Introduction

Carrier-mediated transport of metal ions through bulk liquid membranes is not only interesting for its potential as a model for a biological membrane, but also for its potential applications to selective removal, concentration and purification of metal ions from their mixture [1]. Active research is recently in progress on the use of macrocyclic compounds as carriers in liquid membrane systems, in view of their capability of highly selective transport of metal ions [2]. Due to good selectivity and efficiency in presence of mobile and selectivity agent liquid membrane technology has taken a considerable, sophisticated attention in various fields over conventional techniques viz. in the cleaning of waste water by the removal of soluble metal species [3]. Membrane separation in bioreactors is one of the most attractive operations applied in biochemical processes [4]. Selective purification and concentration of metals in solution has primarily been achieved using liquid-liquid extraction techniques [5].

Liquid membrane extraction process has gained considerable interest in hydrometallurgical recovery of metal ions as well as removal of toxic metals from waste water generated by various metallurgical industries [6]. Chemists and chemical engineers would like to understand the mechanism of transport to that with the knowledge obtained they would be able to fabricate membranes of desired properties [7]. Ion transport through the liquid membrane plays an important role in stimulating biological membrane functions and separation technologies because of the high transport efficiency, excellent selectivity and economic advantages of the liquid membrane [8]. Complexation of cationic guests of linear and macrocyclic polyethers help the cation transport across the hydrophobic region of membranes [9].

Experimental work

Materials and instruments

The metal salts (MX) in the form of picrate (Pic^-), dinitrophenolate (Dnp^-) and orthonitrophenolate (Onp^-) [MX: $M^+ = Li^+$, Na^+ & K^+, $X^- = Pic^-$, Dnp^- & Onp^-] were prepared by the reported method [10]. Dichloromethane, 1, 2-dichloroethane and chloroform were purchased from Merck and Qualigens and used without further purification. Analytical grade chemicals were used. Ionophores 1-(4-Bromo phenyl)-2-(2-{2-[2-(4-bromo-phenyl)-2-oxo-ethoxy]-ethoxy}-ethoxy)-ethanone (A_1) and 1-(4-Bromo phenyl)-2-{2-[2-(2- butoxy-propoxy)-propoxy]-propoxy}-ethanone (A_2) were synthesized [11].

Instruments-

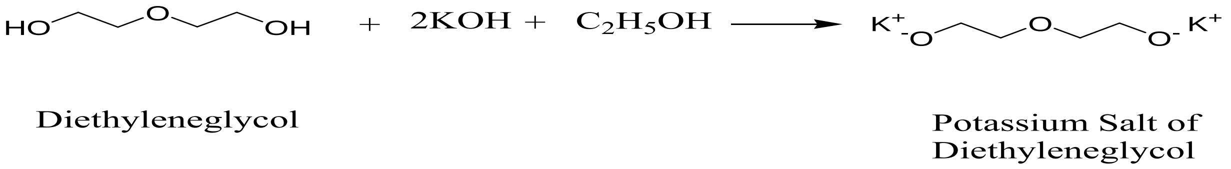
In all experiments, the instruments employed were digital flame photometer (systronics – 128) for Li^+, Na^+ and K^+ estimation, magnetic stirrer (Model Remi – 2 MLH) and analytical balance (A X 200) of SHIMADZU Corporation, Japan.

Synthesis of ionophores

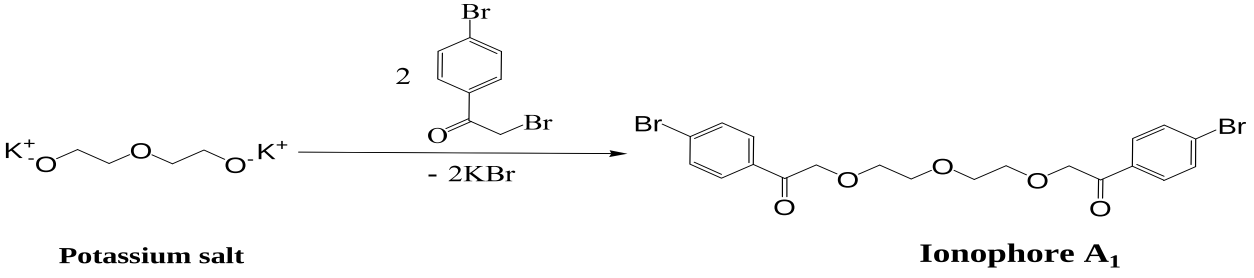
Synthesis of non cyclic ionophore 1-(4-Bromophenyl)-2-(2-{2-[2-(4-bromo-phenyl)-2-oxo-ethoxy]-ethoxy}-ethoxy)-ethanone (A_1)-

Diethyleneglycol (15.5 mmol, 1.46 ml) and KOH (31 mmol, 1.736 gm) were dissolved in ethanol (100 ml.). The mixture was refluxed for 4 hr. and then p-bromophenacylbromide (31 mmol, 8.649 gm) was added over a period of 50 min. the mixture was stirred for another 3 hr. at room temperature. The mixture was filtered and evaporated. The residue was dissolved in CHC_{l3} (150 ml.) and washed with aq. NaOH and then demineralised water. The organic layer was dried over MgS_{O4}, concentrated and purified by column chromatography over alumina. Yield: 4.80 gm (50%), Mol. Wt. 500. The synthesis of noncyclic ionophore was carried out by scheme 1 and scheme 2.

Scheme 1



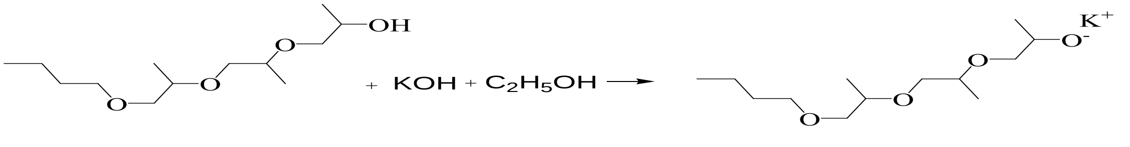
Scheme 2



Synthesis of non cyclic ionophore 1-(4-Bromo phenyl)-2-{2-[2-(2- butoxy-propoxy)-propoxy]-propoxy}-ethanone(A_2)-

Tripropyleneglycolmonobutylether (15.5 mmol, 4.12 ml) and KOH (15.5 mmol, 0.868 gm) were dissolved in ethanol (100 ml.). The mixture was refluxed for 4 hr. and then p-bromophenacylbromide (15.5 mmol, 4.3245 gm) was added over a period of 50 min. the mixture was stirred for another 3 hr. at room temp. The mixture was filtered and evaporated. The residue was dissolved in $CHCl_3$ (150 ml.) and washed with aq. NaOH and then DM water. The organic layer was dried over $MgSO_4$, concentrated and purified by chromatography over alumina. Yield: 4.62 gm (90 %), Molecular weight 445. The synthesis of noncyclic ionophore was carried out by scheme 1 and scheme 2.

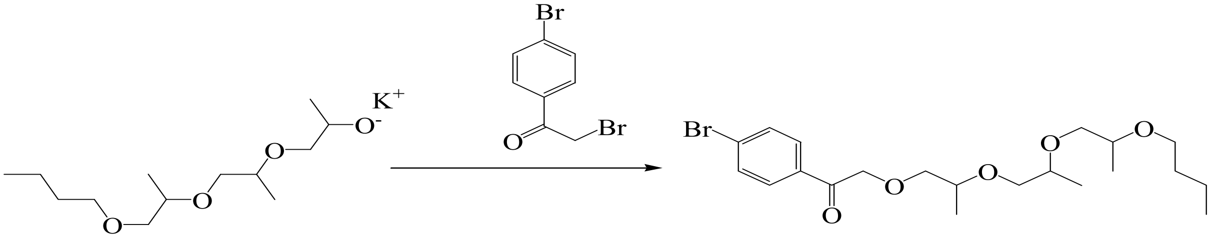
Scheme 1



Tripropyleneglycolmonobutylether

Potassium Salt of Tripropyleneglycolmonobutylether

Scheme 2



potassium salt

Ionophore A_2

Liquid-liquid extraction studies-

To investigate the carrier-facilitated extraction, [12] 10 ml of 1.0 x 10^{-3} M aqueous salt solution was stirred with 10 ml of 1.0 x 10^{-3} M ionophore solution, in bulk liquid membrane viz. CH_2Cl_2, $C_2H_4Cl_2$ and $CHCl_3$, in a covered small beaker using a magnetic stirrer (200 rpm). The amount of cation in aqueous phase was initially determined before extraction was conducted, using flame photometer. After 4 hours of stirring the mixture was allowed to stand for 5 min. for separation of two phases. The depleted aqueous phase was removed and analysed for residual concentration of metal ions using digital flame photometer. The amount of cation extracted by ionophore was found by determining its difference in aqueous phase before and after extraction. A blank experiment was also performed simultaneously with the same to determine the leakage of metal ion from aqueous to organic phase in the absence of carrier. All measurements were performed in duplicate to check the reproducibility. Values of distribution ratio (D_M) were calculated as equation 1:

$$D_M = \frac{\text{Total concentration of metal ion in organic phase}}{\text{Total concentration of metal ion in aqueous phase}} \qquad (1)$$

Bulk liquid membrane transport studies-

Transport experiments [13] were performed in a 'U' shape glass cell. 25 ml of the organic solution of ionophore was placed at the bottom of the '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 (SP) and 10 ml of demineralised water was placed in the other limb of the 'U' tube to serve as the receiving phase (RP). The membrane phase was stirred for 24 hours. Amount of cation transported was analysed after 24 hours by using flame photometer for (Li^+, Na^+ and K^+). The reaction mechanism of the transport can be expressed as equation 2:

$M^{n+} + L \rightleftharpoons ML^{n} \rightleftharpoons M^{n+} + L$ (2)

Cation flux (J_M) values were calculated using the relation in equation 3:

$$J_M = \frac{C\,(\text{receiving}) \times V}{A \times t} \quad (3)$$

Where C (receiving) is the concentration of cation in receiving phase (mol/dm^3), V is the volume of receiving phase (dm^3), A is the effective area of membrane (m^2) and t is time (sec.).

Results and discussion

Characterization of ionophores

Ionophore A_1

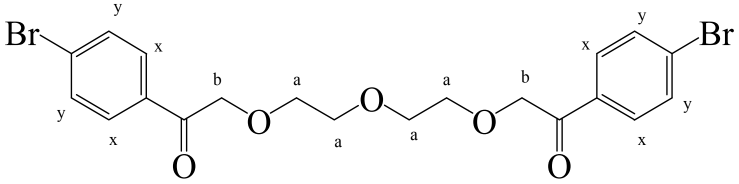


Figure 1

Ionophore A_1

Ionophore 1-(4-Bromo phenyl)-2-(2-{2-[2-(4-bromo-phenyl)-2-oxo-ethoxy]-ethoxy}-ethoxy)-ethanone (A_1) have been successfully synthesized by nucleophilic substitution on p-bromophenacylbromide showing in scheme 1 and 2. The structure of product has been confirmed by IR and ^{1}H NMR spectral analysis **(table 1).**

Table 1 Spectral data of ionophore A_1

Iono-phore	Molecular formula	Yield (%)	IR absorption band in cm^{-1}	^{1}H NMR absorption band in δ ppm
A_1	$C_{20}H_{20}O_5Br_2$	50%	3401,2956,1683.67, 1590,1351,1071	3.5 4.63 7.5-7.7

IR Spectra- In IR spectra of ionophore A_1, the –CO- group stretching absorption peak appears as a strong band in range of 1683-1667 cm^{-1}. This downfield shift is due to conjugation of carbonyl group with aryl group. The strong absorption band at 1590 cm^{-1} has been attributed to C=C stretching of aromatic moiety. The C-O-C stretching of glycol chain assigned to the absorption band at 1351 cm^{-1}. In the frequency region of 1351-1071 cm^{-1} ketonic ester group appeared. The broad band at 3401 cm^{-1} may be due to the presence of enolic –OH group. The presence of bands at 2956 cm^{-1} is due to stretching in C-H bonds.

^{1}H NMR Spectra- All 'a' protons of ethylene group gives four peaks of triplet at 3.4-3.6 ppm. There are two peaks of singlet which has been observed due to 'b' protons of –CH_2-CO- group at 4.4-4.8 ppm. The x and y protons of aromatic moiety shows their multiplets at 7.5-7.7 ppm in aromatic region.

3.1.2 Ionophore A_2

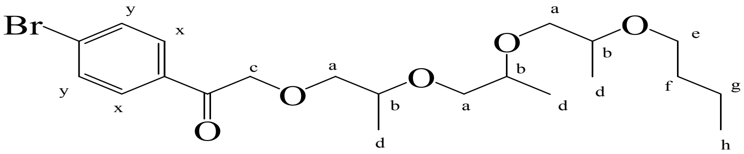


Figure 2

Ionophore A_2

Ionophore 1-(4-Bromo phenyl)-2-{2-[2-(2- butoxy-propoxy)-propoxy]-propoxy}-ethanone (A_2) have been successfully synthesized by nucleophilic substitution on p-bromophenacylbromide in scheme 1 and 2. The structure of product has been confirmed by IR and ^{1}H NMR spectral analysis **(table 2).**

Table 2 Spectral data of ionophore A_2

Iono-phore	Molecular formula	Yield (%)	IR absorption band in cm^{-1}	^{1}H NMR absorption band in δ ppm
A_2	$C_{21}H_{33}O_5Br$	90	3448,2932 1705,15871458,1011	3.5, 3.34, 1.4, 1.3, 0.96, 4.6, 7.5-7.7

IR Spectra- In IR spectra of ionophore A_2, there is a broad band observed at 3448 cm^{-1}, which shows the presence of enolic –OH group. The band at 2932 cm^{-1} observed due to C-H stretching. The C=O stretching for keton was obtained at 1705 cm^{-1}. Bands at 1587 and 1011 cm^{-1} were obtained due to C=C stretching in aromatic moiety and C-O-C stretching in glycol chain respectively. The bending of C-H bond was obtained at 1458 cm^{-1}.

^{1}H NMR Spectra- In NMR spectra all three 'a' protons give peaks on 3.50 ppm. The presence of 'b' and'd' protons assigned at 3.34 and 1.21 ppm respectively. There is a sharp singlet peak at 4.63 of 'c' protons of –CO-CH_2- group. The 'x' and 'y' protons of aromatic moiety give their multiplets at 7.5-7.7 ppm. Peaks of 'e', 'f', 'g' and 'h' protons obtained at 3.37, 1.46, 1.33 and 0.96 respectively.

Effect of cation

It has been observed that A_1 and A_2 are good carriers for K^+ ions. Peak selectivity for K^+ is shown in **figure 3-6** and **tables 3-6**. Such complexation depends upon the relative size of diameter of the pseudocyclic cavity of the ionophore as well as the diameter of the cation [14]. The selectivity of these ligands for K^+ can be explained on the solvation behavior of Na^+ and K^+ ions. K^+ ion is known to be less solvated than Na^+ due to large size, results in its more extraction, while due to high solvation of Na^+ and Li^+ ions in polar medium, they tend to remain in the source aqueous phase [15]. This selectivity and specificity is not depending on the cavity size of macroheterocycles [16] but on the preferred pseudocyclic conformation and solvation of cation.

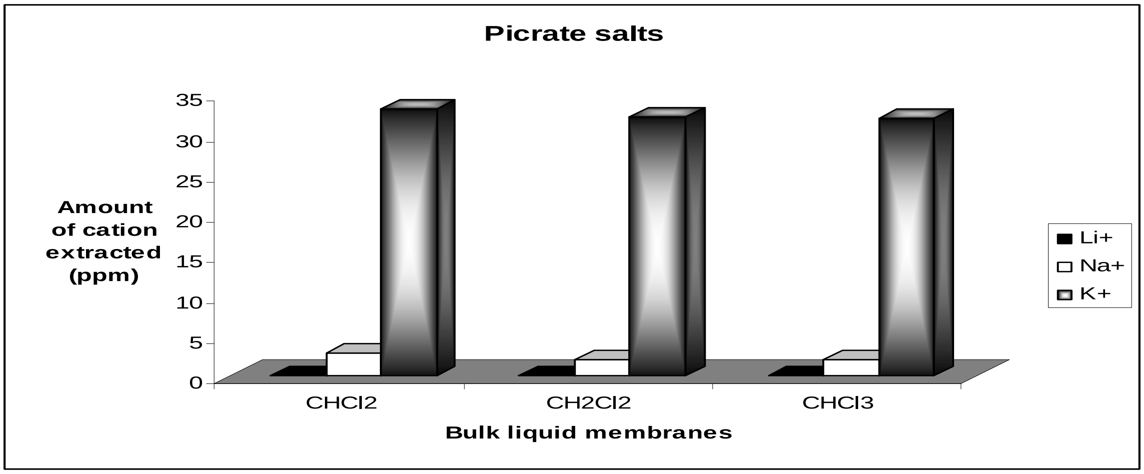


Fig. 3 Amount of cation extracted by ionophore A_1 in dichloromethane, 1,2-dichloroethane and chloroform membranes using metal (Li^+, Na^+, and K^+) picrate salt after 4 hrs.

In transport studies, K^+ ions are transported to a greater extent. This is because the amount of cation transported is dependent on the amount of release rather than the amount of uptake by ionophore [17]. Since, all solvation spheres are removed around the metal ion during complexation, so the binding of Li^+ (1.20 Å) in pseudocyclic cavity is very poor which becomes more preferred for K^+ (2.66 Å) and Na^+ (1.90 Å) cations.

Table 3 Amount of cation extracted by non cyclic ionophores in dichloromethane, 1,2-dichloroethane and chloroform membranes using metal salts after 4 hrs.;
Metal salts concentration = 1X 10^{-3} M, Ionophore concentration = $1X10^{-3}$ M

Metal salts	Dichloromethane		1,2-dichloroethane		Chloroform	
	Amount of cation extracted (ppm) Ionophore A_1	Amount of cation extracted (ppm) Ionophore A_2	Amount of cation extracted (ppm) Ionophore A_1	Amount of cation extracted (ppm) Ionophore A_2	Amount of cation extracted (ppm) Ionophore A_1	Amount of cation extracted (ppm) Ionophore A_2
Li.Pic	-	0.23	-	-	-	1.72
Li.Dnp	-	-	-	0.80	-	-
Li.Onp	-	-	-	-	0.51	0.51
Na.Pic	2.83	10.24	2.01	10.12	2.00	1.64
Na.Dnp	2.60	0.91	2.00	0.91	2.00	-
Na.Onp	2.00	0.59	1.89	0.11	1.88	-
K.Pic	33.12	16.01	32.12	15.46	32.00	11.14
K.Dnp	19.01	13.01	18.57	12.96	18.43	12.00
K.Onp	17.17	10.41	16.01	10.09	15.93	10.01

Table 4 Distribution ratio of metal ions in dichloromethane, 1,2-dichloroethane and chloroform membranes using metal salts after 4 hrs.;

Metal salts	Dichloromethane		1,2-dichloroethane		Chloroform	
	D_M Ionophore A_1	D_M Ionophore A_2	D_M Ionophore A_1	D_M Ionophore A_2	D_M Ionophore A_1	D_M Ionophore A_2
Li.Pic	-	0.01	-	-	-	0.09
Li.Dnp	-	-	-	0.04	-	-
Li.Onp	-	-	-	-	-	0.01
Na.Pic	1.26	3.09	0.65	2.95	0.65	0.13
Na.Dnp	1.39	0.26	1.23	0.26	1.23	-
Na.Onp	0.49	0.02	0.45	-	0.45	-
K.Pic	15.69	11.35	10.32	7.88	10.01	1.77
K.Dnp	2.71	4.33	2.49	4.24	2.43	2.99
K.Onp	9.86	2.06	5.52	1.87	5.34	1.83

Metal salts concentration = 1X 10^{-3} M, Ionophore concentration = $1X10^{-3}$ M

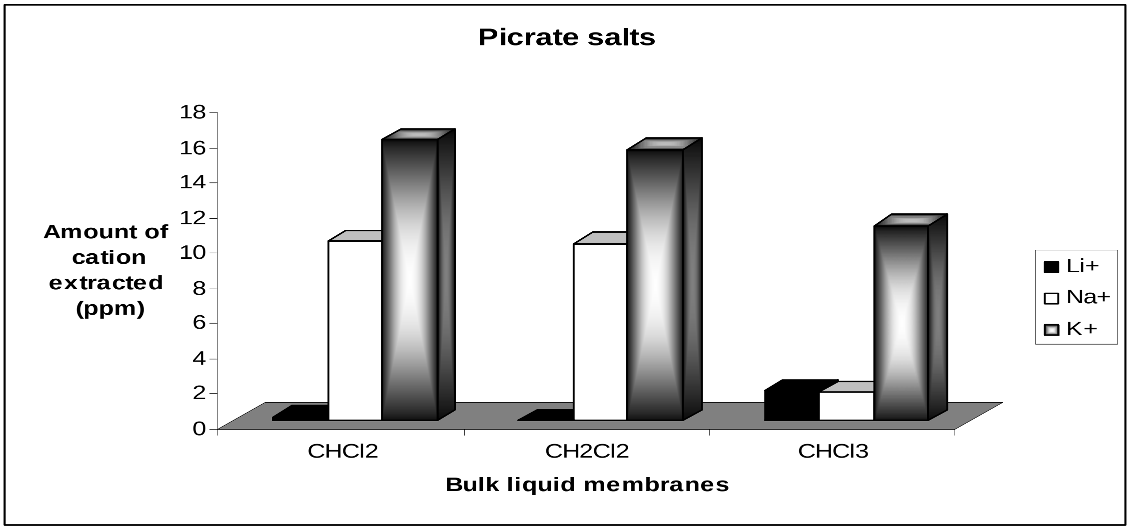


Fig. 4 Amount of cation extracted by ionophore A_2 in dichloromethane, 1,2-dichloroethane and chloroform membranes using metal (Li^+, Na^+, and K^+) picrate salt after 4 hrs.

Effect of anion

The extraction and transport of metal ions through membranes is depending on the nature of anion. All cations are highly extracted and transported when the counter anion is picrate in case of Na^+ and K^+, but it was found least with Li^+. Because picrate is a self stabilized [18] anion due to more delocalization of electrons. Hence, it releases the metal ion easily in comparison to dinitrophenolate and orthonitrophenolate. Thus we can control the extraction of cations by altering anion. Ionophore A_1 fails to transport Li^+ using all anions Pic^-, Dnp^- and Onp^-, while A_2 transport $K^+ > Na^+ > Li^+$.

Table 5 Amount of cation transported by non cyclic ionophores across dichloromethane, 1,2-dichloroethane and chloroform membranes using alkali metal salts after 24 hrs.
Metal salts concentration = 1X 10^{-3} M, Ionophore concentration = $1X10^{-3}$ M

Metal salts	Dichloromethane		1,2-dichloroethane		Chloroform	
	Amount of cation transported (ppm) Ionophore A_1	Amount of cation transported (ppm) Ionophore A_2	Amount of cation transported (ppm) Ionophore A_1	Amount of cation transported (ppm) Ionophore A_2	Amount of cation transported (ppm) Ionophore A_1	Amount of cation transported (ppm) Ionophore A_2
Li.Pic	-	0.51	-	0.46	-	0.45
Li.Dnp	-	0.33	-	0.25	-	0.20
Li.Onp	-	0.05	-	0.05	-	0.05
Na.Pic	8.44	24.89	7.01	24.50	6.92	24.13
Na.Dnp	6.90	22.01	6.23	22.00	6.20	21.63
Na.Onp	5.44	15.09	5.23	15.01	5.01	14.63
K.Pic	18.17	32.01	18.00	32.01	17.50	31.00
K.Dnp	17.46	28.96	17.01	28.90	17.01	28.80
K.Onp	16.32	27.09	16.23	27.01	16.20	27.01

Nature of ionophore-

Ionophore A_1 having two rigid aromatic end groups but small chain length and ionophore A_2 have larger chain length and one rigid aromatic end group. As reported that end groups and chain length of ionophore affects the amount of cation extracted, transported and also the selectivity of the metal ions [19].

Table 6 Cation flux across dichloromethane, 1,2-dichloroethane and chloroform membranes using alkali metal salts after 24 hrs.

Metal salts	Dichloromethane		1,2-dichloroethane		Chloroform	
	Cation flux J_M X10^{-9} (mol m^{-2} sec^{-}) A_1	Cation flux J_M X10^{-9} (mol m^{-2} sec^{-}) A_2	Cation flux J_M X10^{-9} (mol m^{-2} sec^{-}) A_1	Cation flux J_M X10^{-9} (mol m^{-2} sec^{-}) A_2	Cation flux J_M X10^{-9} (mol m^{-2} sec^{-}) A_1	Cation flux J_M X10^{-9} (mol m^{-2} sec^{-}) A_2
Li.Pic	-	0.14	-	0.12	-	0.12
Li.Dnp	-	0.11	-	0.08	-	0.06
Li.Onp	-	0.02	-	0.02	-	0.02
Na.Pic	2.20	6.49	1.83	6.39	1.80	6.29
Na.Dnp	2.19	7.00	1.98	6.99	1.97	6.88
Na,Onp	2.21	6.14	2.12	6.10	2.03	5.95
K.Pic	4.45	7.85	4.41	7.85	4.29	7.60
K.Dnp	5.15	8.54	5.02	8.53	5.02	8.51
K.Onp	6.04	1.00	6.00	9.99	5.99	9.99

Metal salts concentration = 1X 10^{-3} M, Ionophore concentration = 1X10^{-3} M

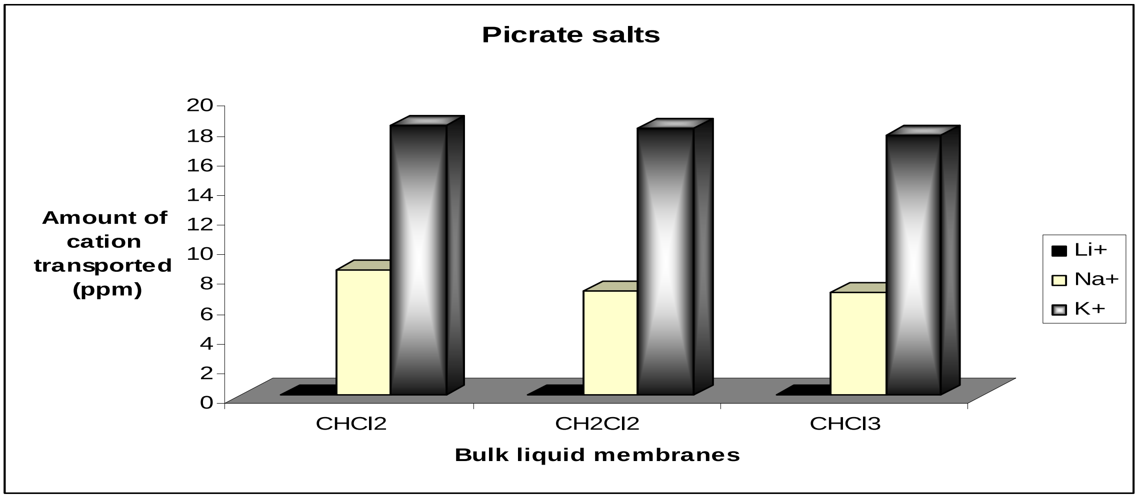


Fig. 5 Amount of cation transported by ionophore A_1 in dichloromethane, 1,2-dichloroethane and chloroform membranes using metal (Li^+, Na^+, and K^+) picrate salt after 4 hrs

Ionophore A_1 shows highest selectivity towards K^+ ions due to its suitable pseudocyclic cavity and ionic radii of K^+ ions and it contains double aromatic moiety which shows an aromatic π- stacking interaction with metal ions. Na^+ ions are transported by A_2 to a greater extent than A_1 due to more ion-ion interaction between Na^+ and donating atom in their pseudocyclic cavity. The amount of cation transported by both the ionophores is different. The overall facts show that the selectivity of metal ions by ionophore depends on the chain length and end group of ionophore.

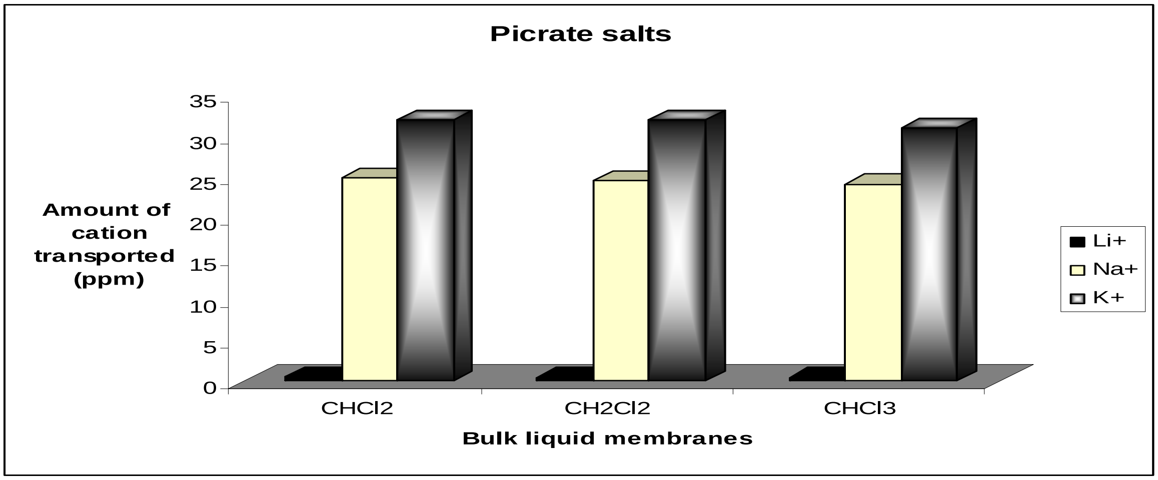


Fig. 6 Amount of cation transported by ionophore A_2 in dichloromethane, 1,2-dichloroethane and chloroform membranes using metal (Li^+, Na^+, and K^+) picrate salt after 4 hrs.

Distribution ratio (D_M)

D_M is much higher for K^+ when the counter anion is picrate, which indicates that K^+ has the maximum tendency to distribute itself between two phases taken for the study in all three bulk liquid membranes. The values of distribution ratio were slightly higher in solvent of higher polarity.
Order of polarity: dichloromethane > 1, 2-dichloroethane > chloroform.

Effect of diluents

The trend of organic solvents used for extraction and transport experiments is $CH_2Cl_2 > C_2H_4Cl_2 > CHCl_3$.The solvent with the lowest viscosity and highest dipole moment will best solvate the ions transferred to the organic phase. So it is inferred that dichloromethane is best solvent for the extraction and transport of metal ions. The literature values for selected physical properties of the organic solvents are listed in **table 7**.

Table 7 Literature values for selected physical properties of the organic solvents

Solvent	Density (gm/cm3)	Surface tension (dyne/cm)	Viscosity (cP)	Solubility in water (% by Wt.)	Dielectric constant	Dipole moment (debye)
CH_2Cl_2	1.325	28.12	0.413	1.60	8.93	1.60
$C_2H_4Cl_2$	1.2521	32.20	0.887	0.81	10.36	1.20
$CHCl_3$	1.4891	26.70	0.596	0.81	4.81	1.01

Conclusion

In this paper, the carrier facilitated transport and extraction of metal ions through bulk liquid membranes was investigated using newly synthesized ionophores as carriers. The pseudocyclic cavity of the ionophore prefers the binding of K^+ when the counter anions were picrate. The amount of cation extracted and transported depends upon the structure of the ionophore, end groups, number of donor sites, flexibility of chain length, ionophore concentration, charge density and size of the metal ion. Carrier mediated transport and extraction of metal ions through bulk liquid membranes is not only interesting for its potential applications but also for selective removal, concentration and purification of metal ions from their mixtures. Besides commercial uses, the selectivity observed among these biologically important ion pairs may also be of much importance as models for cation transport across biomembranes. The potassium cation is the major cation in intracellular fluids and it is essential for nerve and heart functions.

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