

# **Extraction and Bulk Liquid Membrane Transport of Alkali Metal Ions Facilitated by Tripropyleneglycolmonobutylether**

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**ABSTRACT:** In supramolecular chemistry, liquid membranes are frequently used to evaluate the complexation and transport properties of receptors. Tripropyleneglycolmonobutylether (TPGMBE) was used to study extractability and selectivity for alkali metal ions ( $\text{Li}^+$ ,  $\text{Na}^+$  &  $\text{K}^+$ ) using picrate ( $\text{Pic}^-$ ), dinitrophenolate ( $\text{Dnp}^-$ ) and orthonitrophenolate ( $\text{Onp}^-$ ) salts through various organic membranes viz. dichloromethane, 1,2-dichloroethane and chloroform. Higher extraction values were observed for  $\text{K}^+$  ions from picrate salts while  $\text{Li}^+$  ion shows maximum transport ability using  $\text{onp}^-$  as anion. Dichloromethane was found to be the best membrane for both extraction and transport processes. Liquid membrane technology provide applications in small and large separations, drug delivery and electrode sensing techniques etc.

**KEYWORDS:** Complexation, Alkali metal ions, Transport, Extraction and TPGMBE.

## **I. INTRODUCTION**

Separation phenomenon through molecular recognition of the host compound has been widely used by incorporation of ionophore into solvent extraction of liquid membranes [1]. The molecular recognition of  $\text{Na}^+$  and  $\text{K}^+$  ions by membrane-integrated ligands is one of the fundamental processes of living cells [2].

Complex formation is a very important process in which bonding interaction occurs. Molecular recognition is based on selective and specific complexation routes. This selective behavior is very important in the case of drug consumption in the body, where the drug selectivity and its selective interactions are vital [3]. Solvent extraction of metal has been extensively used in hydrometallurgical process. Metal salts usually are not soluble in organic solvents. Hence, this process required the introduction of an extractant that will combine with the metal ion to form an organic soluble species [4]. Membrane separation in bioreactors is one of the most attractive operations applied in biochemical processes [5]. Selective purification and concentration of metals in solution has primarily been achieved using liquid-liquid extraction techniques [6].

Carrier assisted transport through liquid membrane is one of the important applications of supramolecular chemistry. Non-cyclic ionophores (Podands) show binding and selectivity towards alkali and alkaline earth metal ions. This work investigates the use of synthetic carrier for the separation of metal ions [7]. Trans-membrane transport system using synthetically created membrane incorporating ionophores are biologically inspired in the sense that they mimic well-known biological process such as facilitated ion transport using ion channels like  $\text{Na}^+$  -  $\text{K}^+$  ion pumps [8]. Extraction studies were conducted to ascertain the occurrence or complexation between metal salt and the ionophore in solution state [9].

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In this paper, we are reporting here the liquid-liquid extraction and carrier facilitated transport of  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  picrates, dinitrophenolates and orthonitrophenolates by tripropyleneglycolmonobutylether through bulk liquid membrane system using dichloromethane, 1,2-dichloroethane and chloroform membranes.

## II. MATERIALS AND METHODS

### Materials

The metal salts (MX) in the form of picrate ( $\text{Pic}^-$ ), dinitrophenolate ( $\text{Dnp}^-$ ) and orthonitrophenolate ( $\text{Onp}^-$ ) [ $\text{MX}$ :  $\text{M}^+ = \text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ ;  $\text{X}^- = \text{Pic}^-$ ,  $\text{Dnp}^-$  and  $\text{Onp}^-$ ] were prepared by the reported method [10]. Dichloromethane, 1,2-dichloroethane and chloroform were obtained from Merck and Qualigens and used without further purification. Analytical grade chemicals were used. Ionophore tripropyleneglycolmonobutylether [figure 1] was purchased from Aldrich.

### Instruments

In all experiments, the instruments employed were digital flame photometer (Systronics – 128) for  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  estimation, magnetic stirrer (Model Remi – 2 MLH) and analytical balance (A X 200) of SHIMADZU Corporation, Japan and melting point apparatus (MAC).

### Methods

#### Liquid-liquid extraction studies

To investigate the carrier-facilitated extraction, 10 ml of  $1.0 \times 10^{-3}$  M aqueous salt solution was stirred with 10 ml of  $1.0 \times 10^{-3}$  M ionophore solution in bulk liquid membrane viz.  $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$  and  $\text{CHCl}_3$ , in a covered small beaker using a magnetic stirrer (200 rpm) [11]. 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 analyzed 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:

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

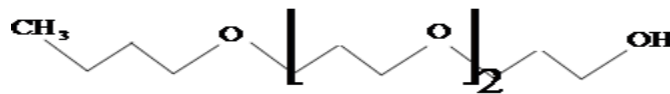


Fig. 1: Tripropyleneglycolmonobutylether ( $\text{C}_{13}\text{H}_{28}\text{O}_4$ )

#### Bulk liquid membrane transport studies

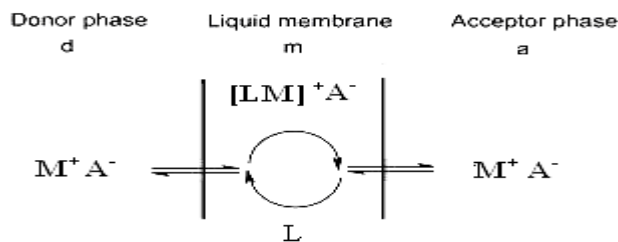
Transport experiments [12] were performed in a 'U' shape glass cell. 25 ml of the organic solution of ionophore was placed at the bottom of the 'U' tube to serve as liquid membrane. 10 ml of aqueous solution of metal salt was placed in one limb of the 'U' tube to serve as the source phase (SP) and 10 ml of double distilled water was placed in the other

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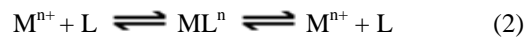
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limb of the 'U' tube to serve as the receiving phase (RP). The membrane phase was stirred for 24 hours. Amount of cation transported was analysed after 24 hours using digital flame photometer. The reaction mechanism of the transport can be expressed as **equation 2** and **figure 2**:



**Fig.2** Transport of metal ion through bulk liquid membrane



Where:  $M^+$  – Metal ion,  $L$  – Ligand,  $A^-$  – Anion and  $[LM]^+A^-$  – Lipophilic complex.

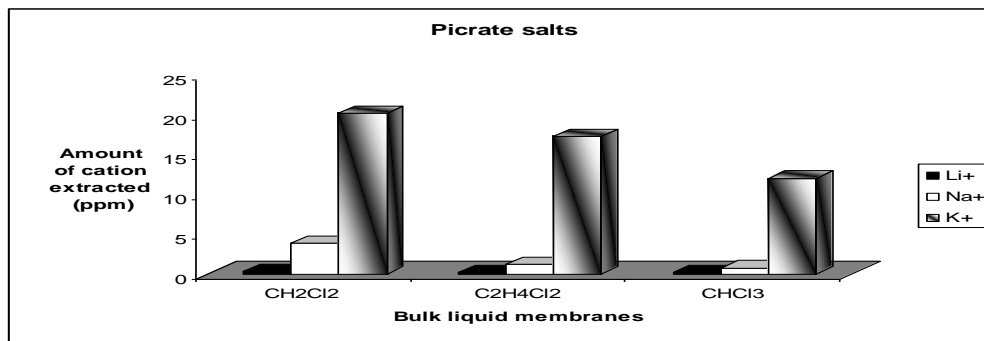
**Cation flux ( $J_M$ ) values were calculated using the relation:**

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

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

### III. RESULTS & DISCUSSION

The results of extraction and transport of alkali metal cations with tripropyleneglycolmonobutylether has been reported in **table 2-4** and cation selectivity shown in **figure 3-8**.



**Fig. 3:** Amount of cation extracted by ionophore tripropyleneglycolmonobutylether in dichloromethane, 1,2-dichloroethane and chloroform membranes using metal ( $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ) picrate salt after 4 hours.

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**Table-2**

Amount of cation extracted by ionophore tripropyleneglycolmonobutylether and distribution ratio in dichloromethane, 1,2-dichloroethane and chloroform using metal salts after 4 hrs.

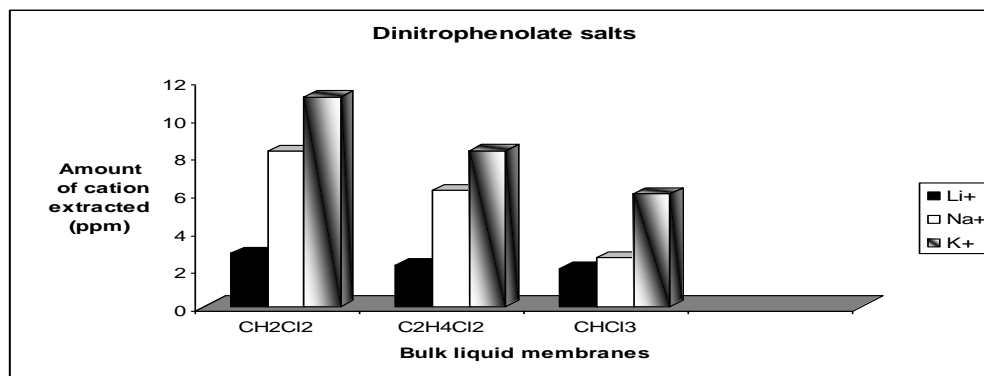
Metal salts concentration =  $1 \times 10^{-3}$  M, Ionophore concentration =  $1 \times 10^{-3}$  M

Metal salts	Dichloromethane		1,2-dichloroethane		Chloroform	
	Amount of cation extracted (ppm)	$D_M$	Amount of cation extracted (ppm)	$D_M$	Amount of cation extracted (ppm)	$D_M$
Li.Pic	0.32	0.19	0.21	0.11	0.20	0.11
Li.Dnp	2.83	1.27	2.19	0.76	2.03	0.67
Li.Onp	0.24	0.13	0.34	0.19	0.34	0.19
Na.Pic	3.84	0.18	1.16	0.05	0.74	0.03
Na.Dnp	8.23	0.46	6.14	0.31	2.58	0.11
Na.Onp	14	0.94	8.69	0.43	5.88	0.25
K.Pic	20.17	2.38	17.25	1.51	12	0.72
K.Dnp	11.12	3.07	8.24	1.26	5.98	0.68
K.Ono	19.68	1.17	17.72	0.94	8.86	0.32

### Effect of cation

From the results, it was observed that the ionophore is effective extractant for alkali metal cations and exhibit extraction selectivity for  $K^+$  over  $Na^+$  and  $Li^+$ . No size fit concept was observed in the noncyclic ionophores. They can form pseudocyclic cavity.

The complexation of metal ion in the pseudocyclic cavity of ionophore is depending on the diameter of metal ion as well as on the size of pseudocyclic cavity. The size of pseudocyclic cavity of the ionophore is suitable for  $K^+$  (2.66 Å) than  $Li^+$  (1.20 Å) and  $Na^+$  (1.90 Å) and  $K^+$  is less solvated than  $Li^+$  and  $Na^+$  [13]. Therefore, it is extracted more readily by the ionophore.



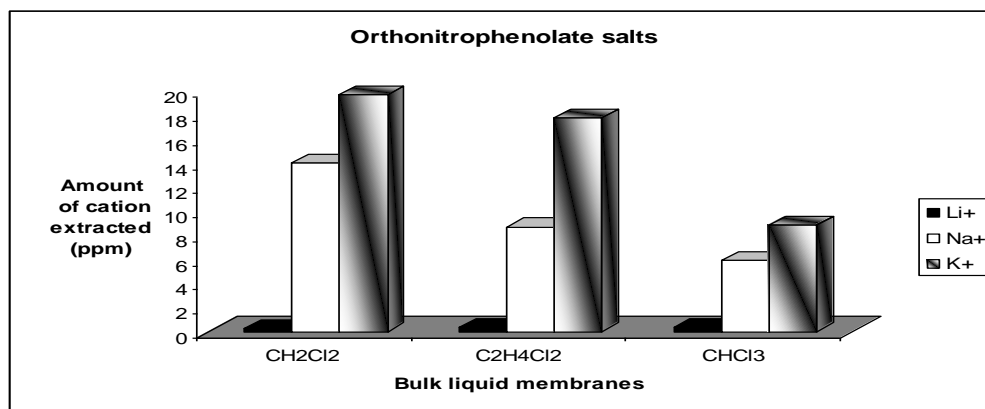
**Fig. 4:** Amount of cation extracted by ionophore tripropyleneglycolmonobutylether in dichloromethane, 1,2-dichloroethane and chloroform membranes using metal ( $Li^+$ ,  $Na^+$ , and  $K^+$ ) dinitrophenolate salt after 4 hours.

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From the results of transport studies, it was observed that ionophore tripropyleneglycolmonobutylether is better carrier for  $\text{Li}^+$  and  $\text{Na}^+$  in comparison to  $\text{K}^+$ . Due to the smaller size and high charge density of  $\text{Li}^+$  ion, it gets self-encapsulated into the pseudocavity and hence show maximum transport.



**Fig. 5:** Amount of cation extracted by ionophore tripropyleneglycolmonobutylether in dichloromethane, 1,2-dichloroethane and chloroform membranes using metal ( $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ) orthonitrophenolate salt after 4 hours.

**Table-3**

Selectivity of  $\text{K}^+$  ions over  $\text{Li}^+$  and  $\text{Na}^+$  ions in dichloromethane, 1,2- dichloroethane and chloroform membranes impregnated with tripropyleneglycolmonobutylether (after 4 hrs.)

Anion	Dichloromethane		1,2-dichloroethane		Chloroform	
	$\text{K}^+/\text{Li}^+$	$\text{K}^+/\text{Na}^+$	$\text{K}^+/\text{Li}^+$	$\text{K}^+/\text{Na}^+$	$\text{K}^+/\text{Li}^+$	$\text{K}^+/\text{Na}^+$
Pic-	63.03	5.25	82.14	14.88	60	16.21
Dnp-	3.92	1.35	3.76	1.34	8.01	2.31
Onp-	82	1.40	52.11	2.03	26.05	1.50

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**Table-4**

Amount of cation transported by ionophore tripropyleneglycolmonobutylether across dichloromethane, 1,2-dichloroethane and chloroform using alkali metal salts after 24 hrs.

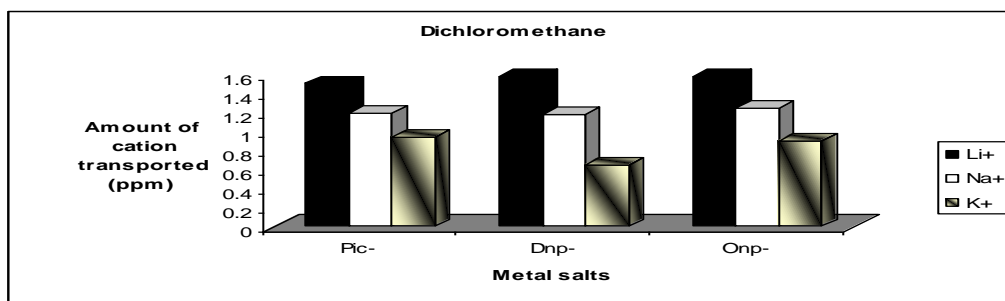
Metal salts concentration =  $1 \times 10^{-3}$  M, Ionophore concentration =  $1 \times 10^{-3}$  M

Metal salts	Dichloromethane		1,2-dichloroethane		Chloroform	
	Amount of cation transported (ppm)	Cation flux $J_M \times 10^{-9}$ (mol $m^{-2}$ sec $^{-1}$ )	Amount of cation transported (ppm)	Cation flux $J_M \times 10^{-9}$ (mol $m^{-2}$ sec $^{-1}$ )	Amount of cation transported (ppm)	Cation flux $J_M \times 10^{-9}$ (mol $m^{-2}$ sec $^{-1}$ )
Li.Pic	1.52	0.41	1.50	0.41	1.49	0.41
Li.Dnp	1.59	0.54	1.54	0.53	1.54	0.53
Li.Onp	1.59	0.71	1.56	0.70	1.58	0.71
Na.Pic	1.20	0.31	1.23	0.32	2.58	0.67
Na.Dnp	1.19	0.37	1.18	0.37	1.57	0.49
Na.Onp	1.26	0.51	2.05	0.83	2.38	0.96
K.Pic	0.95	0.23	0.83	0.20	0.87	0.21
K.Dnp	0.65	0.19	0.52	0.15	0.52	0.15
K.Onp	0.97	0.33	0.88	0.32	0.89	0.32

### Effect of anion

The mobility of cation-carrier-anion complex depends upon the characteristics of the anion. In extraction studies,  $K^+$  ions were found to be at a greater extent when counter anion was picrate. Picrate is self-stabilized anion due to more delocalization of electrons on the aromatic ring. Hence, it releases  $K^+$  ions easily in the organic phase and shows maximum extraction [14]. In case of  $Li^+$  and  $Na^+$  metal ions, lithium dinitrophenolate and sodium orthonitrophenolate were extracted in greater extent in all membranes.

The overall amount of  $M^+$  ion transported is maximum with orthonitrophenolates. Results are shown in **figure 6-8**. The ligand incorporates the metal ion into its cavity, and the counter anion is coordinated in the axial position forming a lipophilic neutral complex that is suitable for transfer into the organic phase. Thus, the degree of transport increases with increasing hydrophobicity of the anion. Order of hydrophobicity: picrate < dinitrophenolate < orthonitrophenolate.

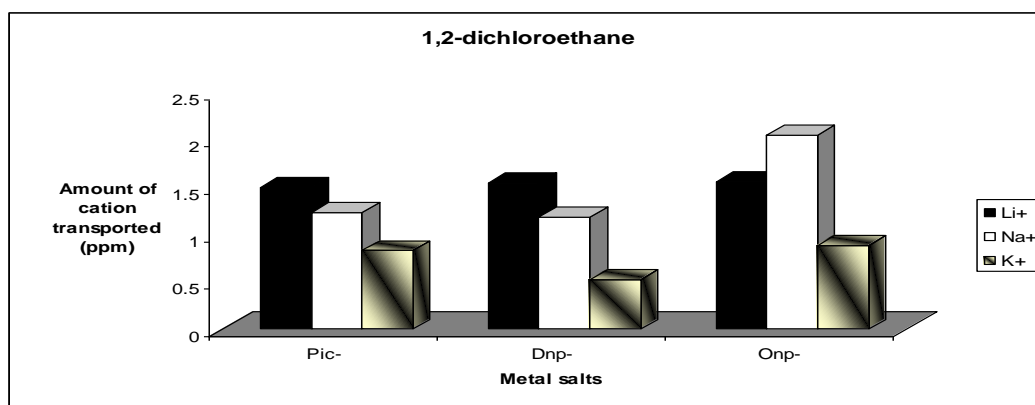


**Fig. 6:** Amount of cation transported by ionophore tripropyleneglycolmonobutylether across dichloromethane membrane using metal ( $Li^+$ ,  $Na^+$ , and  $K^+$ ) salt after 24 hours.

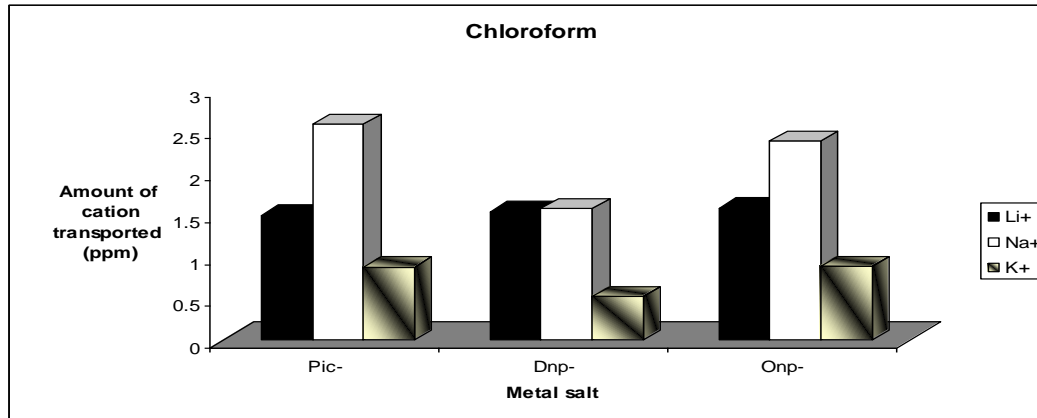
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**Fig. 7:** Amount of cation transported by ionophore tripropyleneglycolmonobutylether across 1,2-dichloroethane membrane using metal ( $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ) salt after 24 hours.



**Fig. 8:** Amount of cation transported by ionophore tripropyleneglycolmonobutylether across chloroform membrane using metal ( $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ) salt after 24 hours.

### Distribution ratio ( $D_M$ )

$D_M$  is much higher for  $\text{K}^+$  ions when the counter anion is picrate, which indicates that  $\text{K}^+$  has the maximum tendency to distribute itself between two phases taken for the study. Highest  $D_M$  values were observed in dichloromethane, which have highest dipole moments among all three bulk liquid membranes.

Decreasing order of  $D_M$  values is observed as -

Dichloromethane > 1, 2-dichloroethane > chloroform

### Effect of membrane

The extraction and transport of metal ions is greatly influenced by the nature of the organic solvents used. The literature values for selected physical properties of the organic solvents are listed in **table 1**.

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**Table 1**  
Literature values for selected physical properties of the organic solvents

Solvent	Density (gm/ cm <sup>3</sup> )	Surface tension (dyne/cm)	Visco sity (cP)	Solubility in water (% by Wt.)	Dielectric constant	Dipole moment (debye)
CH <sub>2</sub> Cl <sub>2</sub>	1.325	28.12	0.413	1.60	8.93	1.60
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	1.2521	32.20	0.887	0.81	10.36	1.20
CHCl <sub>3</sub>	1.4891	26.70	0.596	0.81	4.81	1.01

It was found that dichloromethane membrane provides a better medium for extraction of metal ions by the ionophore. This is due to the highest dipole moment and lowest viscosity of dichloromethane among all three solvents. The observed order of solvents for the extraction of cations is:

Dichloromethane > 1,2-dichloroethane > chloroform.

The observed order of solvents for the transport of cations is:

CH<sub>2</sub>Cl<sub>2</sub> > CHCl<sub>3</sub> ≈ C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>.

## IV. CONCLUSION

The present study demonstrates that the ionophore tripropyleneglycolmonobutylether is an excellent carrier for extraction and transport of alkali metal ions. Extraction of metal ion depends upon the nature of anion, metal-ligand interactions and conformation of ionophore used. It was observed from the studies that this ionophore is good extractant for K<sup>+</sup> ions from picrate salt while during transport studies it is better carrier for Li<sup>+</sup> ions from orthonitrophenolate salts. The selectivity observed for K<sup>+</sup> ions among these biologically important ions (Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>) may also be of much importance as models for cation transport across biomembrane. It provides good applications for the development of Li<sup>+</sup> ion specific receptors, which can help in monitoring of lithium concentration in human body and in ion selective electrode.

## ACKNOWLEDGEMENT

We are thankful to the University Grant Commission, New Delhi for the financial support in the form of minor research project. We are also thankful to Department of Science & Technology, New Delhi for providing the instrumental facilities to the Department of Chemistry, Government College, Kota (India) under FIST programme.

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