



Extraction and transport of alkali metal ions through bulk liquid membranes by ethyleneglycoldiacetate

Varsha Gautam¹, Loni lokwani^{1*}, Sharda Sharma¹ and Uma Sharma²

¹PG Department of Chemistry, Govt. College, Kota, Rajasthan (India)

²School of Studies in Chemistry & Biochemistry, Vikram University, Ujjain, MP (India)

ABSTRACT

Extraction and facilitated transport of alkali metal ions have been studied using ethyleneglycoldiacetate as a carrier through bulk liquid membranes using dichloromethane, 1, 2-dichloroethane and chloroform. Picrate, dinitrophenolate and orthonitrophenolate have been used as anions. Higher extraction and transport values were observed for sodium ions. Picrate anion is found to be the best in comparison to dinitrophenolate and orthonitrophenolate. Liquid membranes provide applications in organic synthesis, photochemical energy conversion and isomer and isotope separation techniques.

Keywords: Extraction, Transport, Carrier, Alkali Metal Ions, Bulk liquid membranes.

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]. The effectiveness of a membrane separation study is determined by the flux of species through the membrane and by the selectivity of the membrane. Liquid membranes produce higher fluxes and selectivity [2]. 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 [3]. The ion transport through liquid membranes play an important role in stimulating biological membrane functions and separation technologies because of high transport efficiency, excellent selectivity and economic advantages of liquid membranes [4].

The phenomenon of ion transport across liquid membranes has received much attention in view of understanding biological membrane functions and developing this separation science methodology [5]. 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 [6].

The properties of liquid membranes make them useful in hydrometallurgy, medicine, biotechnology, environmental protection, in separation of amino acid, metal ion, and other mixtures [7]. It is well known that the membrane process have already been successfully applied in advanced components of analytical instruments (i.e. membrane sensors), biomedical and biotechnological applications, textile and pharmaceutical industry [8].

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 [9]. Complexation of cationic guests of linear and macrocyclic polyethers help the cation transport across the hydrophobic region of membranes [10].

In this paper we are reporting here the liquid-liquid extraction and carrier facilitated transport of Li^+ , Na^+ and K^+ picrates, dinitrophenolates and orthonitrophenolates through dichloromethane, 1,2-dichloroethane and chloroform bulk liquid membranes using ethyleneglycoldiacetate [figure 1] as an ionophore.

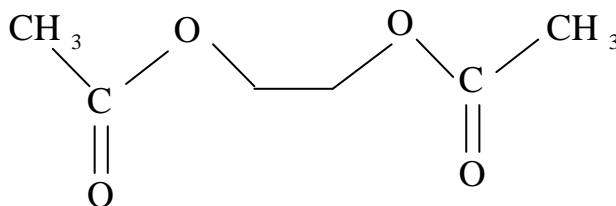


Fig. 1: Ethyleneglycoldiacetate [$\text{C}_6\text{H}_{10}\text{O}_4$]

EXPERIMENTAL SECTION

Materials

The metal salts (MX) in the form of picrate (Pic^-), dinitrophenolate (Dnp^-) and orthonitrophenolate (Onp^-) [$\text{MX}: \text{M}^+ = \text{Li}^+, \text{Na}^+$ and K^+ ; $\text{X}^- = \text{Pic}^-, \text{Dnp}^-$ and Onp^-] were prepared by the reported method [11]. Dichloromethane, 1,2-dichloroethane and chloroform were obtained from Merck and Qualigens and used without further purification. Analytical grade chemicals were used. Ionophore ethyleneglycoldiacetate was obtained from Aldrich.

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 and Melting point apparatus (MAC).

Liquid-liquid extraction studies

To investigate the carrier-facilitated extraction, 10 ml of 1.0×10^{-3} M aqueous salt solution was stirred with 10 ml of 1.0×10^{-3} M ionophore solution in bulk liquid membrane viz. CH_2Cl_2 , $\text{C}_2\text{H}_4\text{Cl}_2$ and CHCl_3 , in a covered small beaker using a magnetic stirrer (200 rpm) [12]. 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 founded 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 follows:

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

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 double distilled 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 follows:



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

$$J_M = \frac{C(\text{receiving}) \times V}{A \times t} \quad (2)$$

Where $C(\text{receiving})$ 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

The results of liquid- liquid extraction and transport studies with ethyleneglycoldiacetate are reported in **tables 2-4**. The selectivity of ionophore is shown in **table-3** and **figure 2-8**.

Effect of cation

From the results of extraction studies, it was observed that the ionophore is more selective for Na⁺ ion. The selectivity of Na⁺ ion is shown in **figure 2 & 4**. The complexation depends upon the diameter of metal cations as well as the diameter of pseudocyclic cavity of ionophore and on ion-ion interaction [14].

Table 2 Amount of cation extracted by ionophore ethyleneglycoldiacetate and distribution ratio in dichloromethane, 1,2-dichloroethane and chloroform membranes after 4 hrs.;

Metal salts concentration = 1×10^{-3} M, Ionophore concentration = 1×10^{-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	0.07	0.07	0.04	0.04	0.03	0.03
Li.Dnp	0.04	0.04	0.03	0.03	0.07	0.07
Li.Onp	0.17	0.15	0.10	0.08	0.12	0.10
Na.Pic	4.79	0.25	2.53	0.11	2.67	0.12
Na.Dnp	-	-	-	-	-	-
Na.Onp	2.07	0.06	0.39	0.01	7.83	0.31
K.Pic	-	-	-	-	0.31	0.06
K.Dnp	-	-	-	-	-	-
K.Onp	5.56	0.33	-	-	-	-

D_M = Distribution ratio

Table 3 Selectivity of Na⁺ over Li⁺ and K⁺ in Dichloromethane, 1,2 -dichloroethane and chloroform membranes impregnated with ethyleneglycoldiacetate (4hrs.)

Anion	CH ₂ Cl ₂		C ₂ H ₄ Cl ₂		CHCl ₃	
	Na ⁺ / Li ⁺	Na ⁺ / K ⁺	Na ⁺ / Li ⁺	Na ⁺ / K ⁺	Na ⁺ / Li ⁺	Na ⁺ / K ⁺
Pic ⁻	68.42	-	63.25	-	89	8.61
Dnp ⁻	-	-	-	-	-	-
Onp ⁻	12.17	0.37	3.9	-	65.25	-

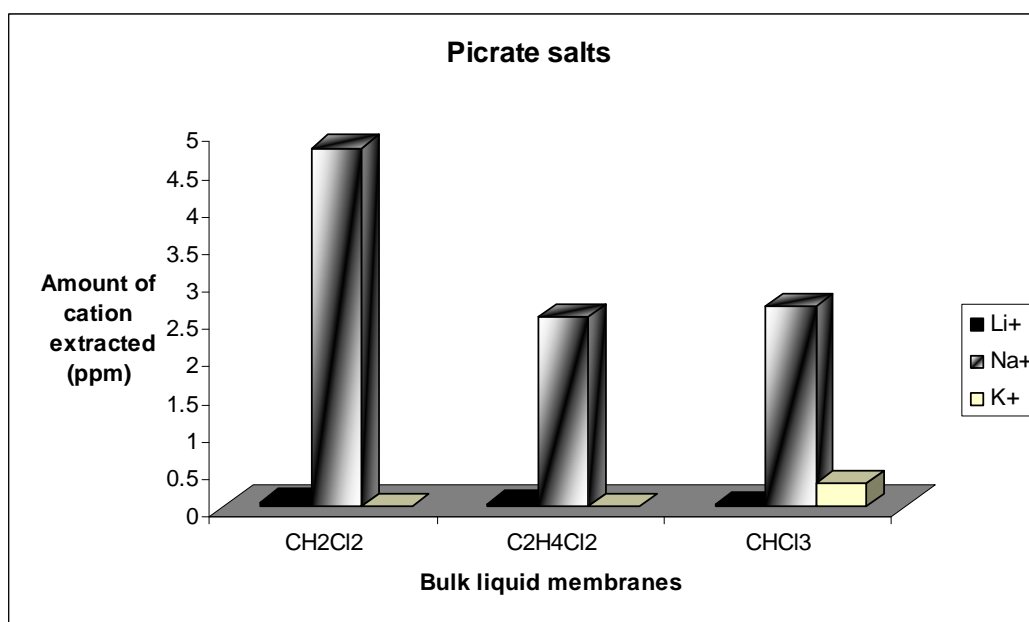


Fig. 2: Amount of cation extracted by ionophore ethyleneglycoldiacetate in dichloromethane, 1,2-dichloroethane and chloroform membranes using metal (Li⁺, Na⁺, and K⁺) picrates after 4 hrs.

The complexation of K^+ (2.66 Å) is very poor than Na^+ (1.90Å) and Li^+ (1.20Å) which suggests that the overall selectivity of ionophore is for Na^+ and Li^+ in comparison to K^+ .

In transport studies, Na^+ ion is 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 [15].

Effect of anion

The extraction and transport of metal ions through membranes is depending on the nature of anion. In case of extraction, metal picrates and orthonitrophenolates are more selective to extract Na^+ only, while with dinitrophenolates the extraction of Li^+ is higher.

Sodium picrate is highly transported by ionophore, which suggests that picrate is a self stabilized anion due to more delocalization of electrons. Hence, it releases the metal ion easily in comparison to dinitrophenolate and orthonitrophenolate.

Table 4 Amount of cation transported by ionophore ethyleneglycol diacetate across dichloromethane, 1,2- dichloroethane and chloroform membranes after 24 hrs.

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

Metal salts	Dichloromethane		1,2-dichloroethane		Chloroform	
	Amount of Cation Transported (ppm)	Cation flux $J_M \times 10^{-9}$ ($\text{mol m}^{-2} \text{sec}^{-1}$)	Amount of Cation Transported (ppm)	Cation flux $J_M \times 10^{-9}$ ($\text{mol m}^{-2} \text{sec}^{-1}$)	Amount of Cation Transported (ppm)	Cation flux $J_M \times 10^{-9}$ ($\text{mol m}^{-2} \text{sec}^{-1}$)
Li.Pic	0.88	0.24	0.91	0.25	0.87	0.24
Li.Dnp	0.98	0.33	0.94	0.32	0.93	0.31
Li.Onp	0.91	0.40	0.91	0.40	0.91	0.40
Na.Pic	3.86	0.98	2.82	0.72	3.37	0.85
Na.Dnp	2.64	0.78	2.03	0.64	2.00	0.63
Na.Onp	1.64	0.65	1.39	0.57	1.91	0.72
K.Pic	-	-	-	-	-	-
K.Dnp	-	-	-	-	-	-
K.Onp	-	-	-	-	-	-

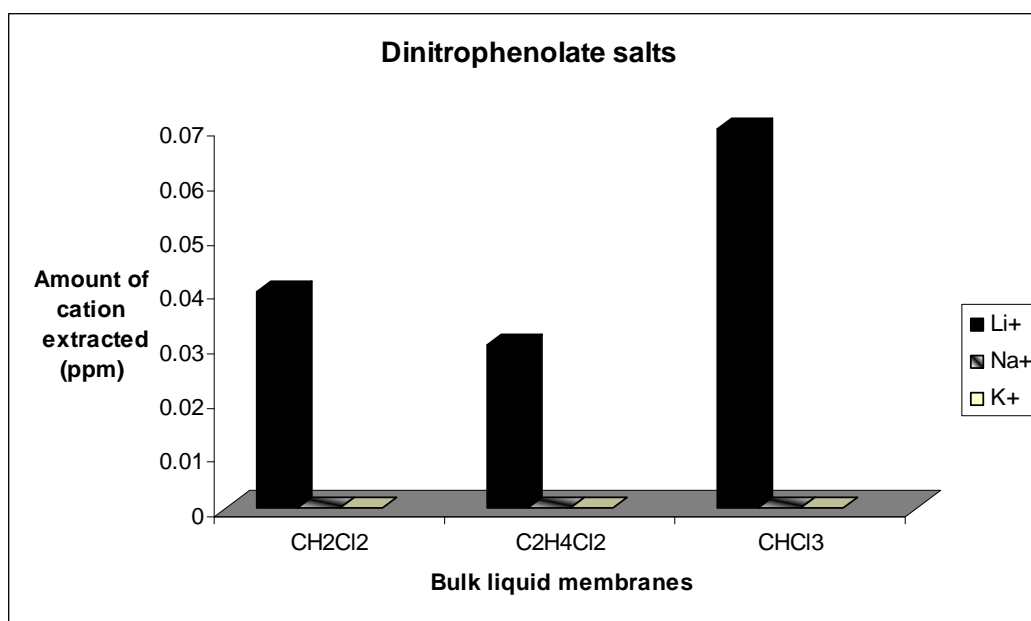


Fig. 3: Amount of cation extracted by ionophore ethyleneglycol diacetate in dichloromethane, 1,2-dichloroethane and chloroform membranes using metal (Li^+ , Na^+ , and K^+) dinitrophenolates after 4 hrs.

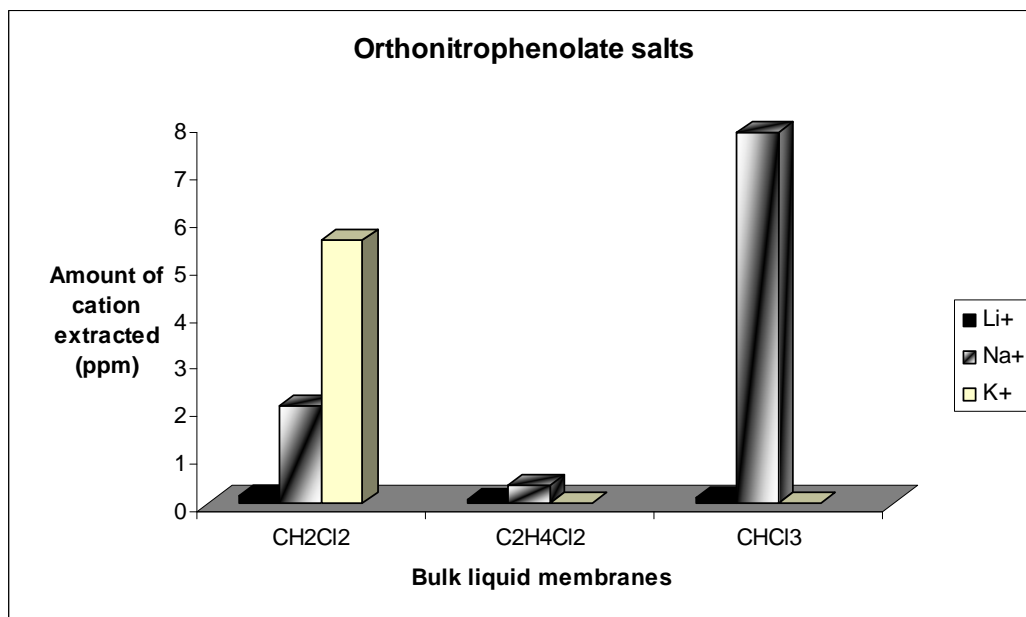


Fig. 4: Amount of cation extracted by ionophore ethyleneglycoldiacetate in dichloromethane, 1,2-dichloroethane and chloroform membranes using metal (Li⁺, Na⁺, and K⁺) orthonitrophenolates after 4 hrs.

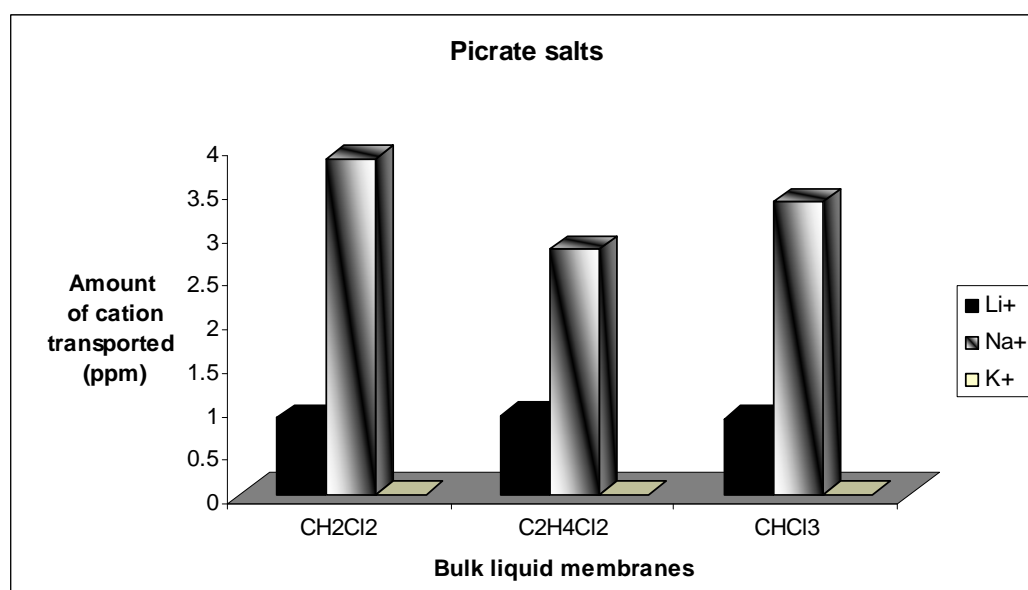


Fig. 5 Amount of cation transported by ionophore ethyleneglycoldiacetate across dichloromethane, 1,2-dichloroethane and chloroform membranes using metal (Li⁺, Na⁺, and K⁺) picrates after 24 hrs.

Effect of Diluents

The extraction and transport of metal ions is greatly influenced by the nature of the organic solvent used. The literature values for selected physical properties of the organic solvents are listed in **table 5**.

Table 5 Values of physical properties of solvents used in present studies

Solvent	Density (gm/cm ³)	Surface tension (dyne/cm)	Viscosity (cP)	Solubility in water (% by Wt.)	Dielectric constant	Dipole moment (debye)
CH ₂ Cl ₂	1.325	28.12	0.413	1.60	8.93	1.60
C ₂ H ₄ Cl 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

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

Dichloromethane > chloroform > 1, 2- dichloroethane.

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 and chloroform are better solvents for the extraction and transport of metal ions.

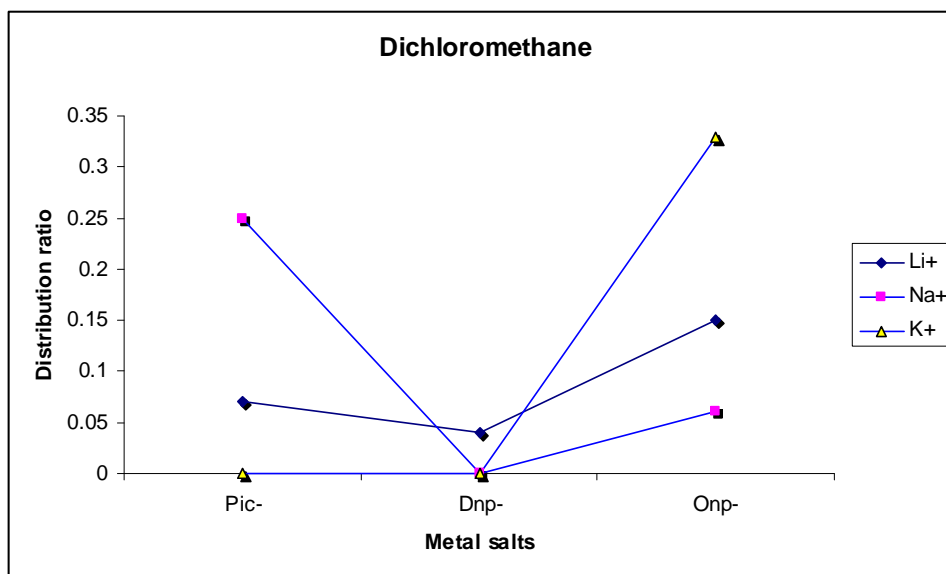


Fig. 6: Distribution ratio of metal ions in between aqueous (metal salt) phase and organic phase (dichloromethane) using ionophore ethyleneglycoldiacetate after 4 hrs.

Distribution ratio (D_M)

D_M is much higher for Na^+ when counter anion is picrate, which indicates that Na^+ has the maximum tendency to distribute itself between two phases taken for study in all three bulk liquid membranes.

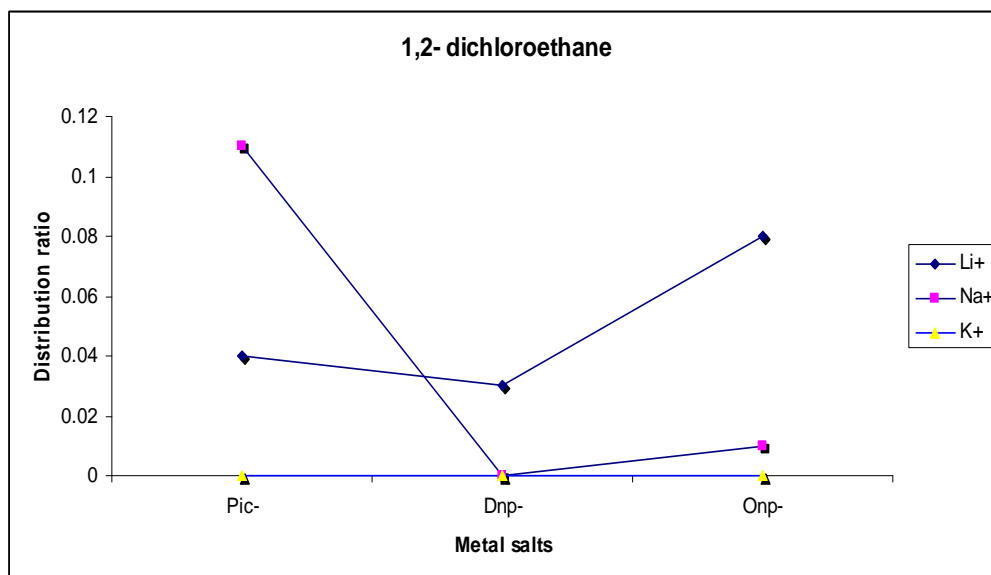


Fig. 7: Distribution ratio of metal ions in between aqueous (metal salt) phase and organic phase (1,2-dichloroethane) using ionophore ethyleneglycoldiacetate after 4 hrs

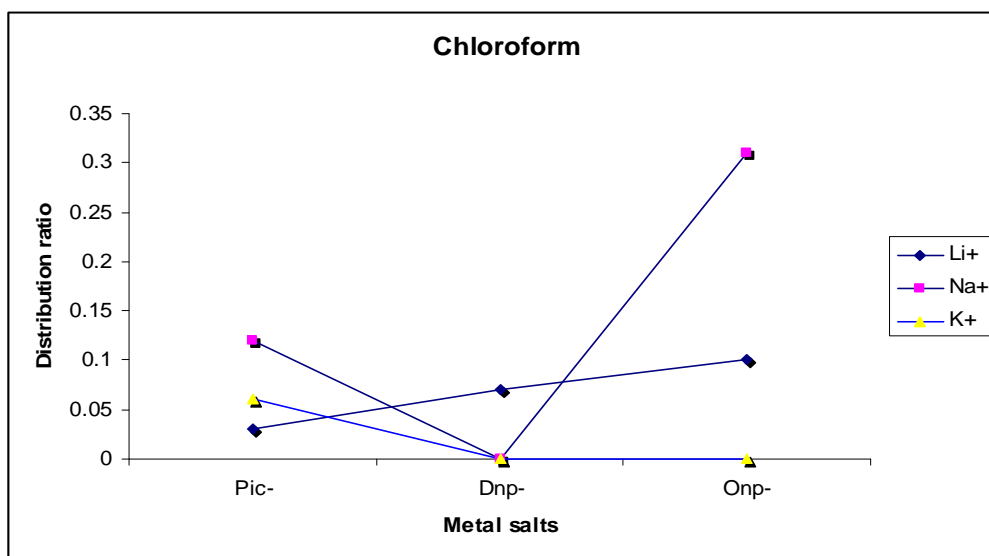


Fig. 8: Distribution ratio of metal ions in between aqueous (metal salt) phase and organic phase (chloroform) using ionophore ethyleneglycoldiacetate after 4 hrs.

CONCLUSION

In this paper, the carrier facilitated transport and extraction of metal ions through bulk liquid membranes was investigated using ethyleneglycoldiacetate as a carrier. The pseudocyclic cavity of the ionophore prefers the binding of Na^+ when the counter anions are picrates and orthonitrophenolates. While with dinitrophenolate salts, the extraction of Li^+ ion is higher. 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.

Acknowledgement

Financial assistance from University Grant Commission, New Delhi in the form of minor research project is gratefully acknowledged. We are also thankful to Department of Science and Technology, New Delhi for providing the instrumental facilities to the Department of Chemistry, Government College, Kota (India) under FIST programme.

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