Ionophore synthesis for appropriate alkali metal ion extraction and transport

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Abstract

The dynamic character of host-guest chemistry confers the resulting constructions with fascinating stimuli-responsiveness. In the present study, we introduced the synthesized ionophore (podand) in membrane phase to promote the transfer of Na^+, K^+, Li^+ *as well as coexisting metal (*Na^+ *and* K^+*) salts. The experiments were performed to study the selectivity of one metal ion over another.*

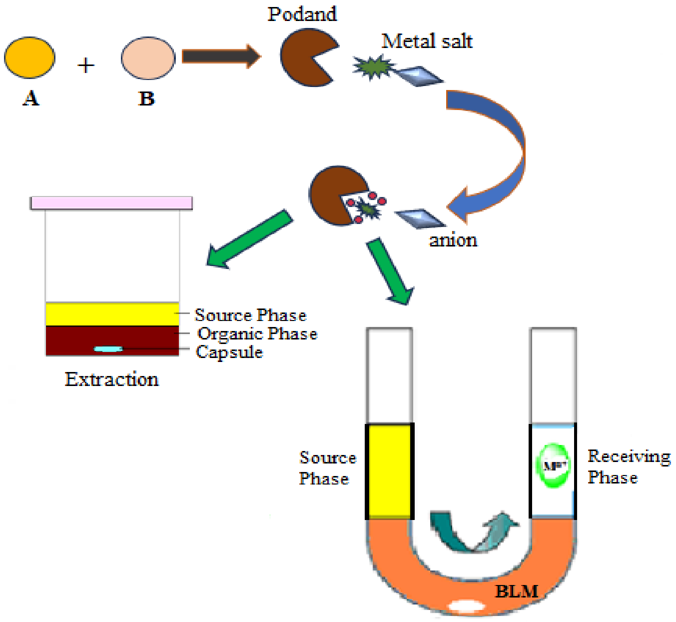
To choose the optimal parameter for a specific cation during extraction and transport, a variety of factors were taken into consideration including fluctuation in metal concentration, ionophore structure, type of anion and membrane effect. The results reveal that the concentration and type of ions, membrane type and associated anion alter the extraction and transport process from one phase to another phase.

Keywords: Dynamic, membrane, extraction, transport, ionophores

Introduction

Nature has created materials that handle chemical reactivity with particular uniqueness, productivity, all over the span of billions of years of progress. e.g. enzymes which may catalyze processes in their substrate-binding pockets. In these systems, the reaction takes place with the reactants dynamically contained in the enzyme binding site. The products are subsequently ejected, freeing the reaction site to host more reactions. The dynamic cavity of the host species plays a vital role in the transport of different metal ions on the fit concept, particularly with the development of materials with regard to chemical action having accuracy, efficiency and specificity.

Ionophores have the propensity to move ions through both natural and artificial membranes. This operates through complexation- decomplexation at the source (metal salt) - membrane and membrane-receiving phase (double distilled water). Ion transport across the membrane governs vital biological processes including signaling pathways, nerve impulse, muscle contraction and hormone regulation as therapeutic drug in cancer management. Various abnormalities in the human body may emerge through perturbations in the ion transport activity. The concept of artificial ionophores was introduced to imitate processes. The research delves into the application of metal-organic constructs as membrane transporters for ions, exploring their roles as carriers.



Graphical Abstract

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Ion transport through biological membranes[9,15] is crucial for various cellular functions like energy storage, cell signaling and pH regulation. Various techniques are used to predict the structure of active transporters within lipid bilayers and analytical methods like fluorescent indicators. Patch clamp measurements are employed to study ion transport processes. The field of synthetic ion transport is rapidly evolving, with a focus on diverse structures and stimuli-responsive systems, offering potential applications in therapeutics and diagnostics.

Metal-organic coordination complexes are gaining interest for their versatility in designing ion transport systems, providing opportunities for tailored structures with unique properties and functions[13]. By analyzing these factors, the research aims to understand the mechanisms influencing the extraction and transport of metal ions, providing insights into optimizing ionophore-based processes for efficient metal ion separation and transport.

The ionophores, in this case, have the ‘ion-recognizing system’ that is attached to the ‘signal-moiety’ through particular heteroatoms. The signal-moiety comprises of fused ring heterocycles, fused aromatics and substituted aromatics, which have a nitro or azo group. Chromogenic hosts[3] were designed to detect alkali and alkaline earth metal ions but exhibit varied pH response. The ionophores expose photo-responsive when subjected to artificial and natural light effects and, hence, can be employed in light-induced applications for metal ion extraction. The study aims to assess how the structure and concentration of non-cyclic ionophore having flexible nature and metal ion concentration with associated anion affect the metal ion extraction and transport[8,12.14].

Material and Methods

Rankem provided carbonate salts of Li, Na, K and C_2H_5OH which were utilised without additional purification. Loba and Himedia chemicals (PicH, DnpH and OnpH) were used. $C_2H_4Cl_2$, $CHCl_3$, CCl_4, ethyl acetoacetate and acetonitrile were obtained from Qualigens.

Synthesis of dipropyleneglycolmonomethyletherbis (acetoacetate): Over the course of three hours, a combination of dipropylene glycol monomethylether (0.66mol) and ethyl acetoacetate (2.0mol) was progressively heated to 180˚C at atm. pressure. In this period, 68 ml of ethanol had been collected [Scheme 1]. Distillation was maintained at 20 mm after the ethanol ceased distilling which led to the accumulation of extra acetoacetate [B.P. 80˚C (20mm)]. With a 70% yield and 6% enol form, the remaining oily portion of the distillation pot was almost pure product (Host).

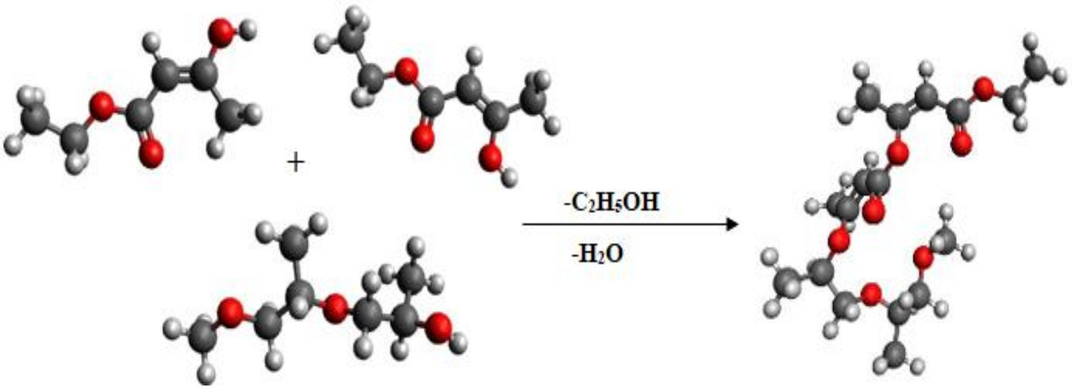
Extraction and transport experiments[6] were carried out by using picrate, dinitrophenolate and orthonitrophenolate salts of Li, Na and K metals. 1:1 ratio of organic solvent containing appropriate amount of ionophore and distilled water was stirred at 150 rpm. From 1.0×10^{-2} M to 1.0×10^{-4} M, the metal ion concentration was changed. However, using ionophores in extraction trials, the optimal concentration of metal salts was found to be 1.0×10^{-3} M. Table 1 shows the distribution ratio between the organic and aqueous phases as well as the measured amount of extracted metal ion at optimal concentration. After each 1 hr., 10 ml of water was analyzed for metal ion on flame photometer upto 4 hrs. Similarly, transport experiments[10,16] were done by using ‘U’ tube containing metal salt solution (source phase)-organic solvent (membrane)-distilled water (receiving phase) for 24 hrs. Then, receiving phase was analyzed for metal ion. Transport experiment was also performed using coexisting metal salts of Na and K. The results and cation flow [$J_M \times 10^{-9}$ (mol m^{-2} sec^{-})] are summarized in tables 2 and 3.

Results and Discussion

Characterization: The synthesized ionophore was characterized by IR, NMR and mass spectra [Fig. 1-3] indicating the proposed structure of podand.

Molecular formula: $C_{17}O_7H_{28}$

IR (neat): 3424.8 (OH), 1733.8 (C=O), 1457.1 (CH_3), 1252.4 (OCH_3),^1H NMR ($CDCl_3$) δ: 1.13-1.15 (enol, H-C=C), 3.4 (H-C-OCH_3), Mass spectra: Calc’d m/e: 344 (M^+), 299 (M^+- $C_2H_5O^{\cdot}$), 149 ($C_7H_{15}O_3^{\cdot}$) Found: 342.79, 297.18, 149.09.



Scheme 1: Synthesis of dipropyleneglycolmonomethyletherbis(acetoacetate)

Table 1
Amount of cation extracted into used bulk liquid membranes

Metal salts	1,2-dichloroethane ($C_2H_4Cl_2$)		Chloroform ($CHCl_3$)		Carbontetrachloride (CCl_4)	
	Cation extraction amount in ppm	D_M	Cation extraction amount in ppm	D_M	Cation extraction amount in ppm	D_M
Li.Pic	0.03	1.00	0.02	0.50	0.01	0.02
Li.Dnp	0.00	0.00	0.00	0.00	0.00	0.00
Li.Onp	0.00	0.00	0.00	0.00	0.00	0.00
Na.Pic	1.13	0.04	0.11	-	0.09	-
Na.Dnp	0.07	-	0.35	-	0.64	0.02
Na.Onp	0.70	0.03	1.26	0.05	0.17	-
K.Pic	1.64	0.03	0.69	0.01	0.45	-
K.Dnp	0.22	0.42	0.22	0.42	0.13	0.21
K.Onp	2.39	0.07	2.59	0.07	2.44	0.07

Table 2
Cation flux and ion transport in 24h host through different membranes

Metal salt	1,2-dichloroethane ($C_2H_4Cl_2$)		Chloroform ($CHCl_3$)		Carbontetrachloride (CCl_4)	
	Transported cation in ppm	Cation flow	Transported cation in ppm	Cation flow	Transported cation in ppm	Cation flow
LiPic	0.00	-	0.00	-	0.00	-
Li.Dnp	0.00	-	0.00	-	0.00	-
LiOnp	0.00	-	0.00	-	0.00	-
Na.Pic	1.41	3.68	1.32	3.45	1.25	3.26
Na.Dnp	1.30	4.14	0.38	1.21	0.64	2.04
Na.Onp	1.22	4.97	0.24	0.98	0.56	2.28
K.Pic	0.38	0.93	0.09	0.22	0.05	0.12
K.Dnp	0.28	0.83	0.08	0.24	0.04	0.12
K.Onp	0.15	0.56	0.05	0.19	0.03	0.11

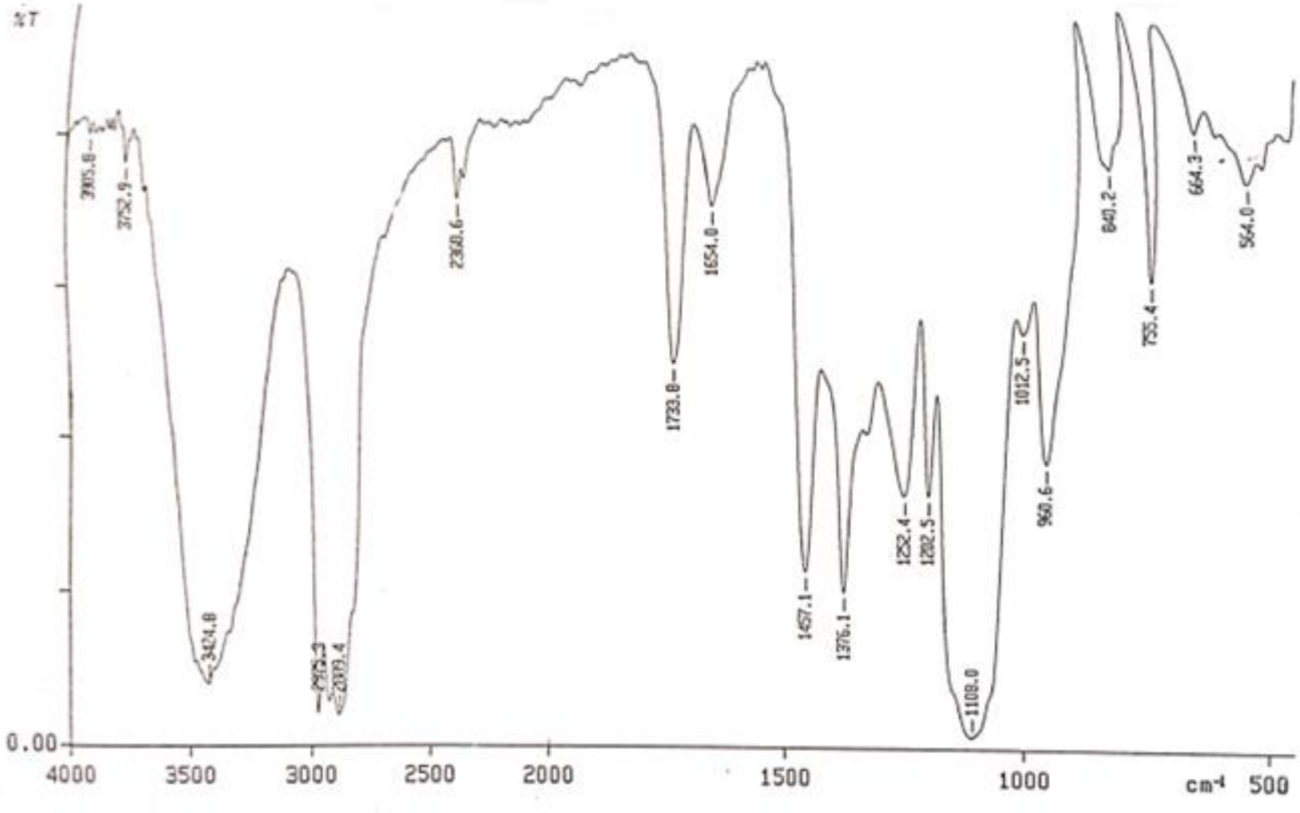


Fig. 1: Infra Red spectrum of synthesized host

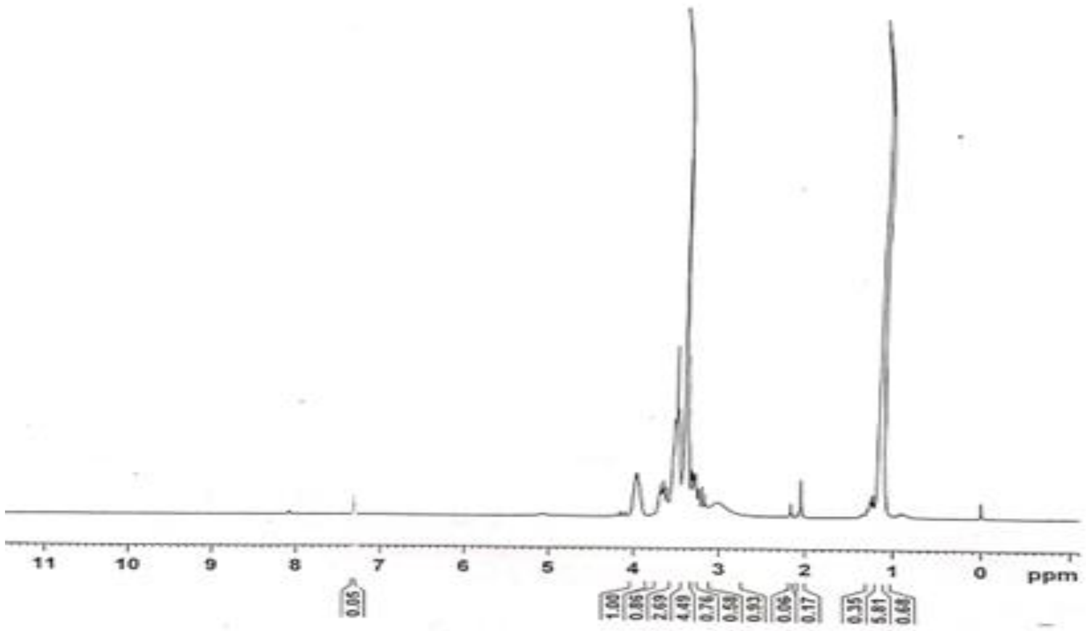


Fig. 2: PMR spectrum of synthesized host

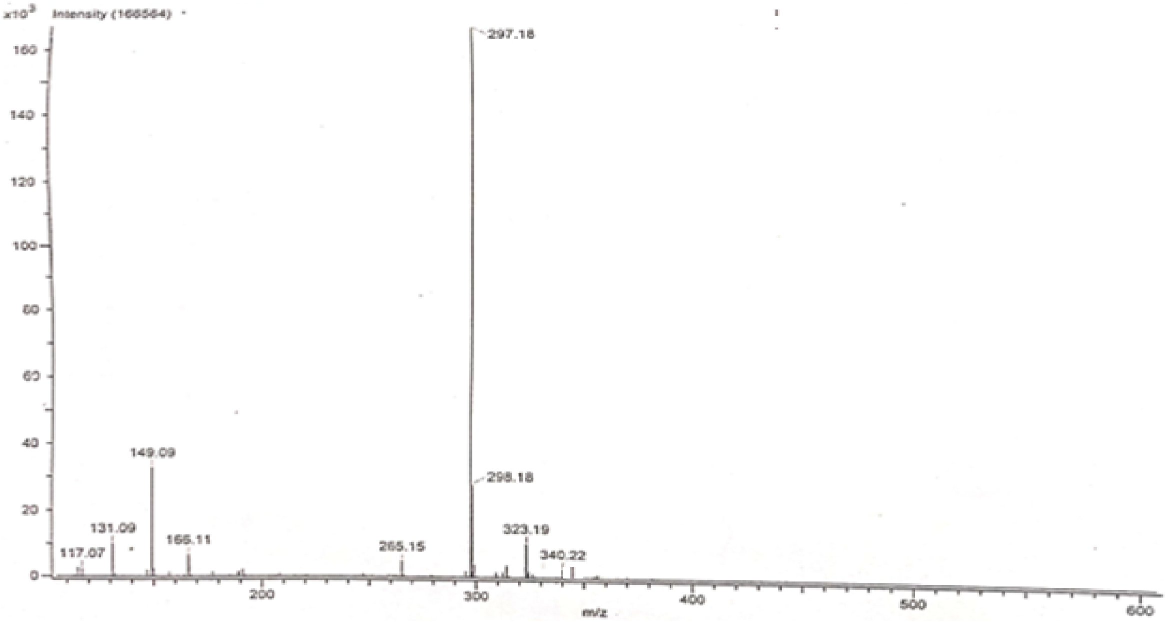


Fig. 3: Mass spectrum of synthesized host

Table 3
Amount of ion transport and cation flux in 24h using coexisting metal salts by host through different BLMs

Anion	BLM	Na^+		K^+	
		Transported cation in ppm	Cation flow	Transported cation in ppm	Cation flow
Picrate	$C_2H_4Cl_2$	0.42	1.1	0.09	0.22
	$CHCl_3$	0.35	0.91	0.23	0.56
	CCl_4	0.21	0.55	0.27	0.66
Dinitrophenolate	$C_2H_4Cl_2$	0.02	0.06	0.01	0.03
	$CHCl_3$	0..01	0.03	0.01	0.03
	CCl_4	0.00	0.00	0.00	-
Orthonitrophenolate	$C_2H_4Cl_2$	0.02	0.07	0.01	-
	$CHCl_3$	0.01	-	0.01	-
	CCl_4	0.56	6.02	0.03	4.81

Effect of type of metal: Using podand as the host, the perceived trend for alkali metal ion extraction[2] is: $K^+ > Na^+ > Li^+$ [Table 1]. The pseudocyclic cavity of the ionophore, as well as the metal cation's size along with charge density, may be responsible for this selectivity. As a result, it may be inferred that Li^+ has the lowest size and higher charge density permits more solvation in the aqua solution which causes the ligand's pseudocyclic cavity to behave improperly when it comes to complexation and accommodation. Larger size and lower charge density of K^+ allow[1,7] it to fit in the ionophoric cavity with more efficiency and increases resistance while passing across the membrane and further slows down transport [Table 2].

Effect of type of associated anion: The presence of nitro groups greatly affects the complex and the mobility of the cation carrier/anion complex upon which an extraction is performed. Because of its greater solubility and stronger binding affinity, picrate anion is more effective than dinitrophenolate and orthonitrophenolate when it comes to the extraction and transport of species employing ionophores in bulk liquid membranes [Fig. 4-6]. Picrate's negative charge density is increased by its three nitro groups, which also boost its propensity to remove electrons. The extraction procedure is more effective as a result of this high negative charge's more robust interaction with metal cations.

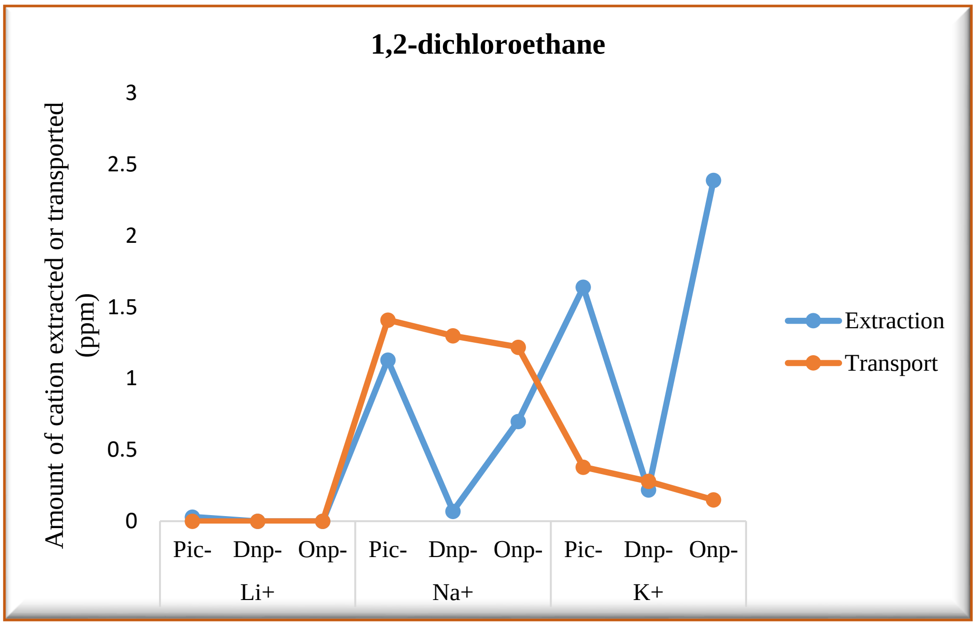


Fig. 4: Impact of counter ion on amount of cation extracted and transported by synthesized ionophphore in 1,2- dichloroethane

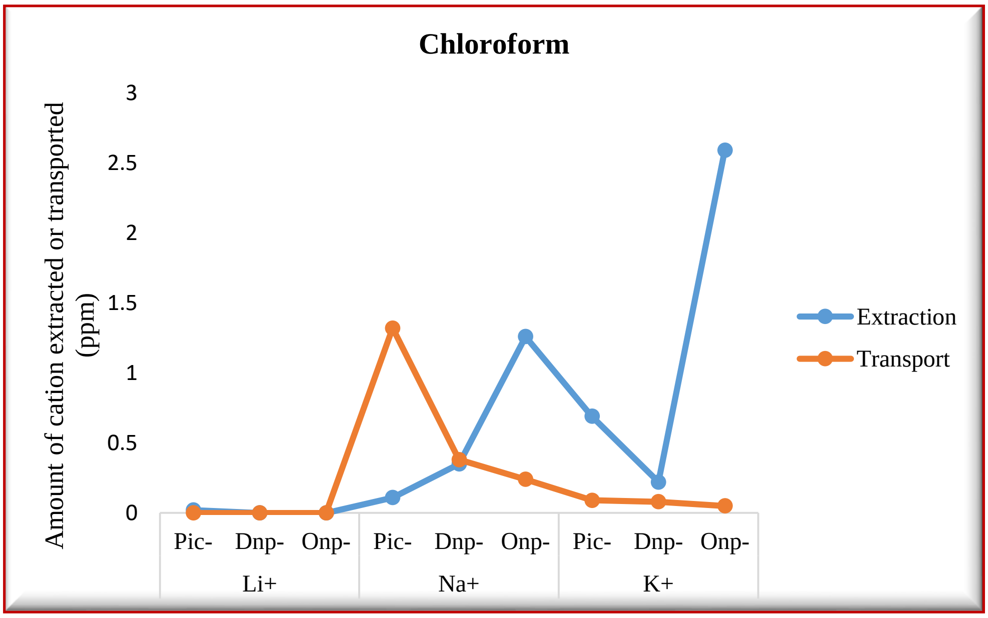


Fig. 5: Impact of counter ion on amount of cation extracted and transported by synthesized ionophphore in chloroform

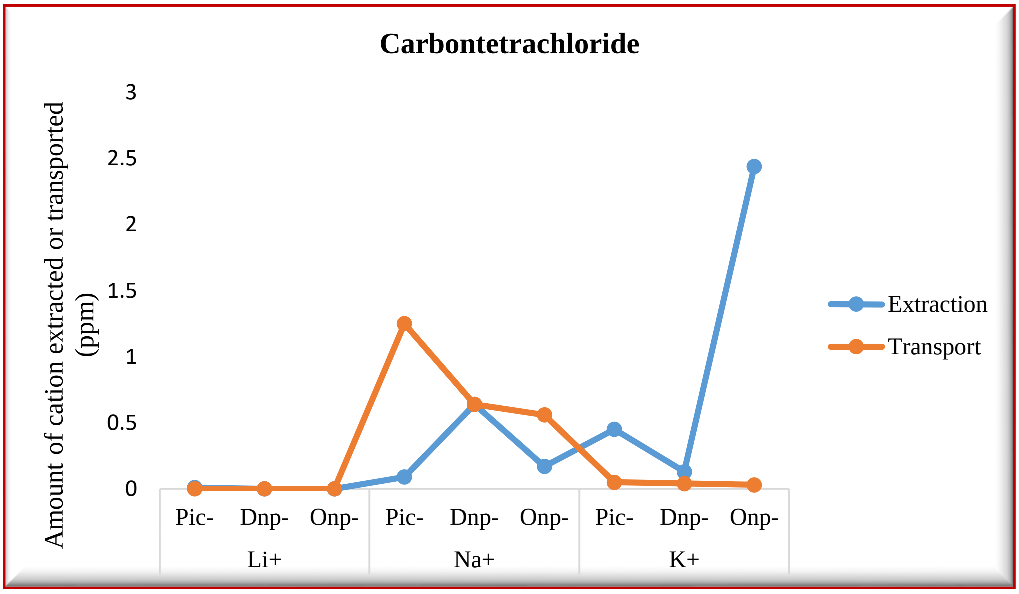


Fig. 6: Impact of counter ion on amount of cation transported by synthesized ionophphore in carbontetrachloride

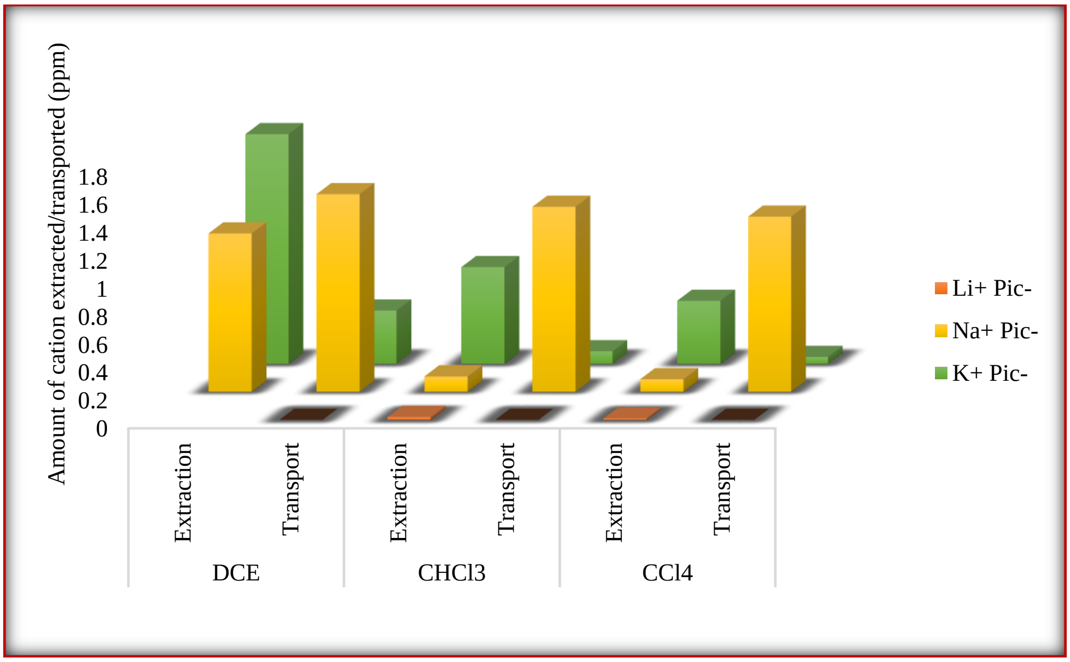


Fig. 7: Impact of various bulk liquid membranes on cation extraction amount using picrate salts

It is known that the extraction of alkali metal ion with ionophore is: $Onp^- > Pic^- > Dnp^-$. Moreover, picrate's strong electron-withdrawing nitro group makes it more soluble in bulk liquid membranes. Because of its increased solubility, the picrate anion may easily form a complex with the ionophore, allowing for more effective transport across the membrane [Table 2].

Effect of type of membrane: It was discovered that chloroform and 1, 2-dichloroethane were suitable solvents for the extraction of metal ions. Ionophores in different organic solvents remove cations from metal picrate salts in the following ways [Fig. 7-9]:

1, 2-dichloroethane > chloroform > carbontetrachloride

It may be simply understood by asserting that the dielectric constant in non-polar solvents is relatively small. Consequently, in organic solvents, the association of a metal anion pair is also favored, although it dissociates in high dielectric constants. It is evident that the thick, water-free border layers of carbon tetrachloride prevent ions and ligands from refluxing. CCl_4 shows more transport of Na^+ in case of using coexisting metal orthonitophenolate [Table 3].

The density and viscosity of the solvent rise with inreasing chlorination. On the other hand, when the chlorination is high, the solvents' mutual water solvent solubility, dielectric constants and dipole moments[4] all fall. Solvents having the highest dipole moment would be the most effective at removing ions from the aqueous phase and transferring them into the organic phase. 1,2-dichloroethane's polarity exhibits a dipole-ion interaction that is advantageous. It can therefore be bound by the metal ion in the pseudocyclic cavity. For certain salts, more metal ions were extracted in carbon tetrachloride and chloroform than in 1, 2-dichloroethane[11].

Conclusion

It is shown from the data obtained that the synthesised ionophore's pseudocyclic cavity provides a great way to access metal ions from the picrate salt in DCE such as Na^+ and K^+. This selectivity is essential in biological and chemical processes where precise ion regulation is crucial. The study of cation extraction and transport by ionophores is essential for progress and sustainability in the sectors of energy, agriculture, healthcare, environmental protection and industrial operations. This study contributes to the development of diagnostic tools, optimizes targeted medication delivery and improves therapies for illnesses associated to ion imbalance.

Ionophores enhance the effectiveness of medications and improve patient outcomes by promoting selective ion transport across cell membranes. Ionophore studies are therefore important to medicine because they have the potential to transform diagnosis and therapy approaches, which will improve patient outcomes and advance medical science.

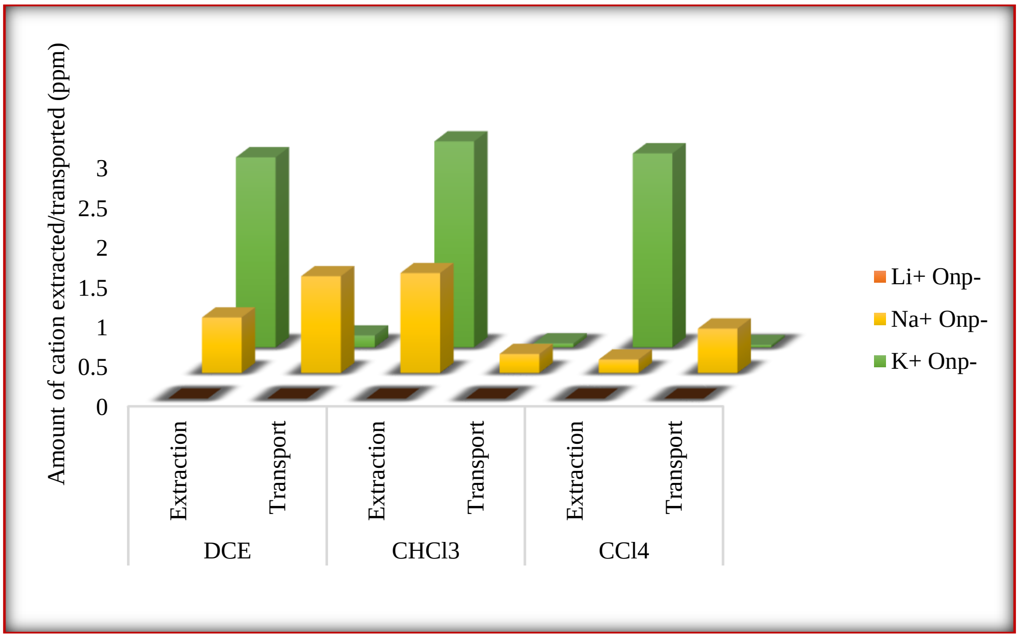


Fig. 8: Impact of various bulk liquid membranes on cation extraction amount using orthonitrophenolate salts

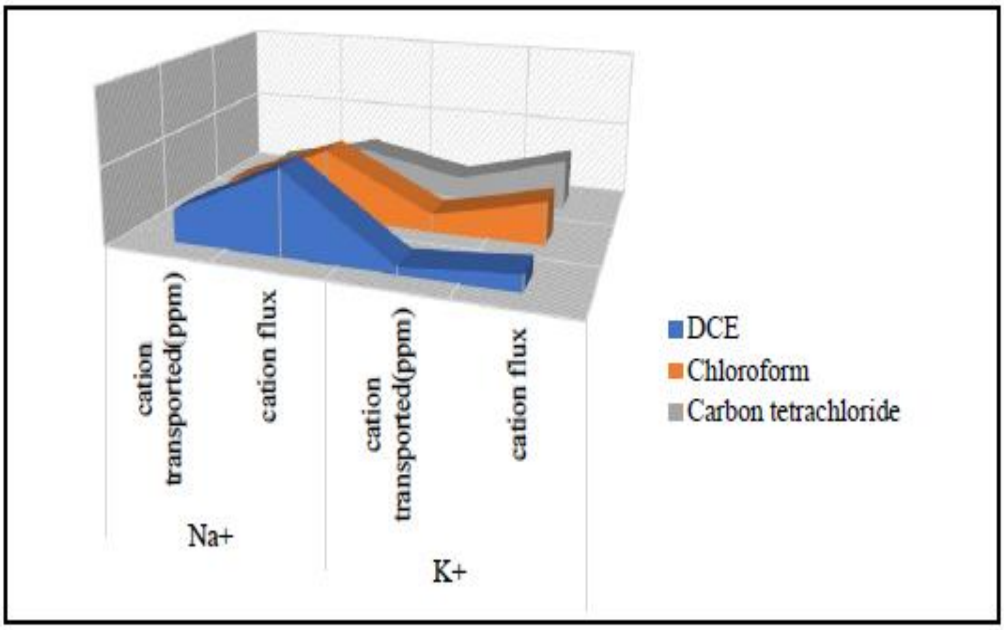


Fig. 9: Amount of cation released and cation flow in a day using coexisting metal picrate salts via host impregnated in various BLMs

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