

Liquid-Liquid Extraction and Bulk Liquid Membrane Transport of Alkali Metal Ions through Various Organic Liquid Membranes Using Dipropyleneglycolmonomethylether

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Abstract: Podands are major class of supramolecular hosts having the possibility to form interesting complexes by forming pseudocyclic cavity exhibiting extractability and selectivity by trapping the metal ions. Dipropyleneglycolmonomethylether was used to study its carrier ability for alkali metal ions (Li^+ , Na^+ and K^+) using picrate (Pic^-), dinitrophenolate (Dnp^-) and orthonitrophenolate (Onp^-) salts through various organic solvents viz. 1,2-dichloroethane, chloroform and carbontetrachloride towards extraction and transport. Transport of Na^+ exceeds than K^+ and Li^+ . Thus, the development of the liquid-membrane ion selective electrodes owes much to the progress of supramolecular chemistry and has played an important role in bridging supramolecular chemistry with analytical chemistry, material technology, medicines, green chemistry, data storage and processing etc.

Keywords. Podands; extraction; transport; complexation; pseudocyclic.

1. Introduction

The separation of metal cations is not only a very important event in biological systems as well as in large scale industrial applications, and therefore, it is of a broad scientific interest. The separation of metals using liquid membrane has been subjected to extensive study by many researchers as reported¹⁻⁵ due to simple and continuous operation, high efficiency etc.⁶ Extraction and carrier facilitated transport of alkali and alkaline earth metal cations through bulk liquid membrane [BLM] are the most important issues in biochemistry. The selectivity in this technique is controlled by both the extraction/back extraction equilibrium at the interfaces and the kinetics of the transported species under a nonequilibrium mass transfer process.⁷

Liquid membrane soon became very popular in various fields due to their good selectivity and efficiency achieved by the presence of a mobile and selectively acting agent (a carrier).⁸ In recent years 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.⁹⁻¹³ In BLM system, a relatively thick layer of immiscible fluid is used to separate the feed and strip phases.¹⁴

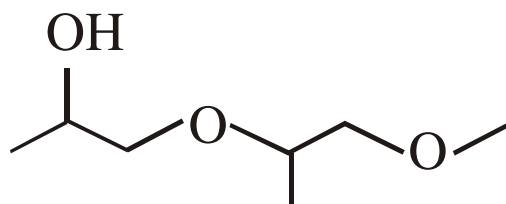
Podands¹⁵ offer a variety of interesting functions based on their specific bindings of organic guest species, They can act as carriers in ion extraction, membrane transport and phase transfer reactions.

In the present work, an attempt has been made to examine the efficiency of dipropyleneglycolmonomethylether as ionophore towards extraction and transport of alkali metal cations from picrate, dinitrophenolate and orthonitrophenolate as anions using viz. 1,2-dichloroethane, chloroform and carbontetrachloride.

2. Experimental section

Material and methods

The metal salts (MX) in the form of picrates (Pic⁻), dinitrophenolates (Dnp⁻) and orthonitro-phenolates (Onp⁻) [MX: M⁺ = Li⁺, Na⁺ and K⁺; X⁻ = Pic⁻, Dnp⁻ and Onp⁻] were prepared by reported method.¹⁶ Analytical grade chemicals were used. Ionophore dipropyleneglycolmonomethylether [DPGMME] [Scheme I] of Aldrich and 1,2-dichloroethane (DCE), chloroform and carbontetrachloride obtained from merck and qualigens and were used without further purification.



Scheme I: Dipropyleneglycolmonomethylether [CH₃(OC₃H₆)₂OH]

Liquid-liquid extraction

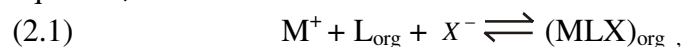
For extraction studies¹⁷ equal volume (50mL) of the aqueous solution of metal salt (Li⁺, Na⁺ and K⁺) and ionophore solution were vigorously stirred in a beaker for four hours on magnetic stirrer at 200 rpm.¹⁸ The amount of the metal ion in the aqueous phase was initially determined. After

four hours the amount of the metal ion in the depleted aqueous phase was determined using flame photometer for (Li^+ , Na^+ and K^+).

Table 1. Amount of cation extracted using dipropyleneglycolmonomethylether as ionophore and distribution ratio across 1,2- dichloroethane, chloroform and carbontetrachloride membrane using metal salt after 4 h; Aqueous phase (50) ml of MX salt solution ($\text{conc}^n = 1 \times 10^{-3} \text{ M}$); Organic phase (50 ml).

Metal salts	1,2-dichloroethane		Chloroform		Carbontetrachloride	
	Amount of cation extracted (ppm)	D_M	Amount of cation extracted (ppm)	D_M	Amount of cation extracted (ppm)	D_M
Li.Pic	0.01	0.10	0.01	0.1	0.01	0.10
Li.Dnp	0.01	0.10	0.01	0.10	0.01	0.10
Li.Onp	0.00	-	0.00	-	0.00	-
Na.Pic	2.04	0.23	0.87	0.08	2.08	0.23
Na.Dnp	2.20	0.09	1.26	0.52	2.10	0.12
Na.Onp	2.93	0.10	0.31	0.01	0.21	0.006
K.Pic	0.97	1.58	0.62	1.02	0.48	0.78
K.Dnp	4.14	0.13	2.39	0.07	1.26	0.04
K.Onp	0.41	0.01	5.46	0.21	3.71	0.13

Back extraction was also studied *i.e.* after extraction, aqueous layer was separated and extraction further repeated by putting double distilled water over CHCl_3 layer for four hours. The amount of cation extracted in double distilled water was determined (Table 2) The equilibrium of metal-carrier complex in the aqueous and the organic phases is shown by the equation:¹⁹



$$(2.2) \quad K_{eq} = \frac{[\text{MLX}]_{\text{org}}}{[\text{M}^+][\text{L}]_{\text{org}}[\text{X}^-]}.$$

Distribution ratio of metal ion²⁰ was calculated as:

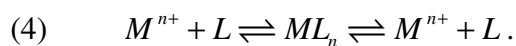
$$(2.3) \quad D_M = \frac{\text{Total concentration of metal ion in organic phase}}{\text{Total concentration of metal ion in aqueous phase}}.$$

Table 2. Amount of cation extracted and back extracted by using ionophore dipropyleneglycolmonomethylether in chloroform membrane 4 h; double distilled water (50ml); Organic phase (50 ml)

Metal ion	Amount of cation extracted (ppm)	Back extraction (ppm)
Li ⁺	0.01	-
Na ⁺	2.04	1.92
K ⁺	0.97	-

Bulk Liquid Membrane Transport

Transport experiments²¹ [Scheme II] 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 by magnetic stirrer 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:

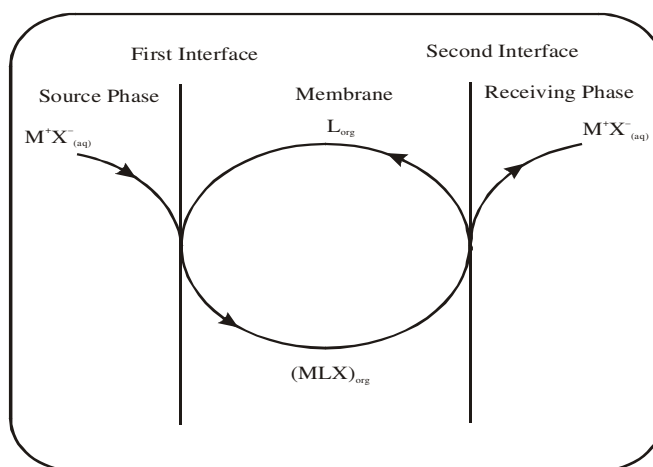


Cation flux (J_M) values were calculated using the relation:

$$(5) \quad J_M = \frac{C(\text{receiving}) \times V}{A \times t},$$

where $C(\text{receiving})$ is the concentration of cation in receiving phase (mol/dm³), V is the volume of receiving phase (dm³), A is the effective area of membrane (m²) and t is time (sec.).

Transport experiments of mixed salts (Na⁺ and K⁺) and by using picric acid in the receiving phase was also performed. Blank experiments were also carried out²² for transport studies of the metal salts in which membrane was devoid of carrier. All the measurements were performed in duplicate to check the reproducibility.



Scheme II: Representation of metal ion transport from source aqueous phase to receiving aqueous phase through bulk liquid membrane impregnated with ionophore [L]

Table 3. Amount of cation transported after 24h using lithium, sodium and potassium salts by dipropyleneglycolmonomethylether in 1,2-dichloroethane, chloroform and carbontetrachloride

Metal salt	$C_2H_4Cl_2$		$CHCl_3$		CCl_4	
	Cation transported (ppm)	Cation flux $J_M \times 10^{-9}$ ($mol\ m^{-2}\ sec^{-1}$)	Cation transported (ppm)	Cation flux $J_M \times 10^{-9}$ ($mol\ m^{-2}\ sec^{-1}$)	Cation transported (ppm)	Cation flux $J_M \times 10^{-9}$ ($mol\ m^{-2}\ sec^{-1}$)
Li.Pic	0.05	0.14	0.00	-	0.00	-
Li.Dnp	0.00	-	0.00	-	0.00	-
Li.Onp	0.00	-	0.00	-	0.00	-
Na.Pic	0.07	0.18	0.09	0.23	0.98	2.56
Na.Dnp	1.30	4.13	1.05	3.34	0.65	2.07
Na.Onp	0.07	0.28	0.04	0.16	0.04	0.16
K.Pic	0.03	0.07	0.05	0.10	0.37	0.91
K.Dnp	0.01	0.03	0.01	0.03	0.08	0.24
K.Onp	0.05	0.18	0.21	0.78	0.05	0.18

Table 4. Amount of cation transported after 24h using coexisting sodium and potassium salts by dipropylene glycol monomethylether in 1,2-dichloroethane, chloroform and carbontetrachloride

Anions	DCE		CHCl ₃		CCl ₄	
	Na ⁺	K ⁺	Na ⁺	K ⁺	Na ⁺	K ⁺
Picrate	0.45	0.00	0.38	0.04	0.35	0.28
Dinitrophenolate	0.07	0.00	0.05	0.00	0.04	0.02
Orthonitrophenolate	0.23	0.00	0.02	0.06	0.10	0.09

3.Results and discussion

The results of extraction and transport of alkali metal cations with dipropylene glycol monomethylether are reported in Tables 1-4 and Fig. 1-4. No transport of metal ion was found in the absence of ionophore.

The results of extraction studies for single metal ion revealed the selective extraction of K⁺ into organic membrane over Na⁺ and Li⁺. The overall specificity and selectivity of the ligand can be explained on solvation behaviour of cations. As the K⁺ is known to be less solvated due to large size, results in its more extraction while due to high solvation of Na⁺ and Li⁺ in polar medium, they tend to remain in the source aqueous phase.

It was observed that overall amount of cation extracted is maximum with Dnp⁻ and Onp⁻. This is in accordance to the hydrophobicity of the anion which follows the order: Pic⁻ < Dnp⁻ ≈ Onp⁻, and hence respective salts have more solubility in the organic membrane.

The liquid membrane transport technique contains two processes in a single stage in extraction of the metal ion from aqueous source phase to the membrane containing the carrier and reextraction of this metal ion from the membrane to the aqueous receiving phase. Hence, the overall transport process consists of a mixture of diffusion steps and complexation/decomplexation reactions at two independent and possibly different interfaces.²³ From the results of transport studies, it can be concluded that DPGMME is better carrier for Na⁺ than K⁺ and Li⁺. The transport ability of receptor is based upon the release of ion rather than uptake.²⁴ Na complex has optimum stability (log K=3.9 MeOH) with carrier while in case of Li complex with carrier, the binding is too weak and unfavourable, so insufficient amount of carrier transported. The transport results indicate that the ionophore exhibits the selectivity towards Na⁺. In case of K⁺ complex with carrier, binding is too tight and favourable (log K=4.3 MeOH), so the cation-carrier complex remains in the organic phase at

membrane-receiving phase interface which leads to the low amount of cation being transported into the RP.

Table 4 shows the transport of coexisting metal cations (Na^+ and K^+). The ionophore retains the exclusive selectivity for Na^+ than K^+ in single cation as well as in binary mixture. DPGMME transports Na^+ more than K^+ in single cation transport system, while this selectivity increases in binary mixture. This discrimination may be explained on the basis of release of more amount of Na^+ from the source phase to the receiving phase due to distortion in pseudocyclic cavity when K^+ is present together. The extent of distortion is sufficient to encapsulate the K^+ . So, K^+ does not release in a sufficient amount to the receiving phase.

Results of the studies revealed that extraction and transport both are favourable when counter anion is dinitrophenolate.

The competitive transport of Na^+ and K^+ by using co-existing cationic salts indicates that the ionophore also exhibits selectivity towards Na^+ over K^+ using picrate salts.

The trend of organic solvents used for extraction and transport experiments is $\text{ClCH}_2\text{CH}_2\text{Cl} > \text{CHCl}_3 > \text{CCl}_4$.

DCE membrane seems to be more effective than chloroform and carbotetrachloride. This may be due to the higher dipole moment of DCE which solvates ions the best.²⁴ We found that CCl_4 does not provide a smooth flow of the cations across the membrane and produces a barrier to flow of cations as compared to CHCl_3 and $\text{C}_2\text{H}_4\text{Cl}_2$ with ionophore. No leakage of cation in the membrane was noted in the blank experiments. This indicates that the mode of transport is only carrier-facilitated.

The behaviour of metal ions (Na^+ and K^+) during extraction and coexisting metal transport was reversed in CCl_4 than other two membranes. It is probably due to the fact that complexation of Na^+ in CCl_4 occurs more strongly than K^+ . So, it does not release in a sufficient amount in transport when both ions coexist. No optimum pH was observed for extraction and transport of cations.

4. Conclusion

The present study demonstrates that the ionophore dipropyleneglycolmonomethylether is an excellent carrier for selective and efficient extraction and transport of alkali metal ions. The presence of dinitrophenolate moiety with metal ion facilitates the efficiency of ionophore. The results indicate the potential use of ionophore in biomedical applications, for the construction of ion selective electrodes and in different areas of separations and environmental chemistry for the removal of metal ions from waste water.

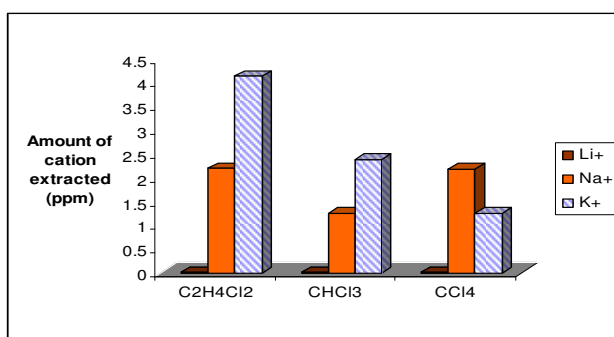


Fig.1 Amount of cation extracted by ionophore dipropyleneglycolmonomethylether across 1,2-dichloroethane, chloroform and carbontetrachloride membranes using metal dinitrophenolate; Aqueous phase I (source phase) 50 ml of MX salt solution ($\text{conc}^n = 1 \times 10^{-3} \text{ M}$); Organic phase (50 ml); Ionophore ($\text{conc}^n = 1 \times 10^{-3} \text{ M}$)

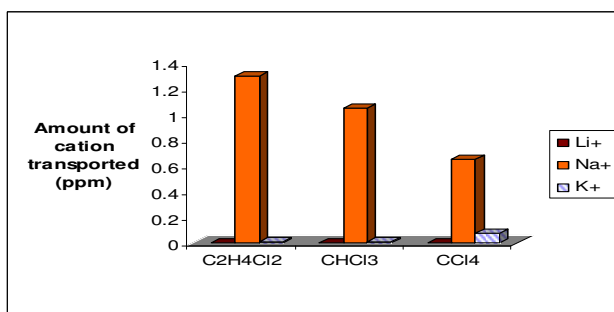


Fig.2 Amount of cation transported by ionophore dipropyleneglycolmonomethylether across 1,2-dichloroethane, chloroform and carbontetrachloride membranes using metal dinitrophenolate; Aqueous phase I (source phase) 10 ml of MX salt solution ($\text{conc}^n = 1 \times 10^{-3} \text{ M}$); Organic phase (25 ml); Ionophore ($\text{conc}^n = 1 \times 10^{-3} \text{ M}$); Aqueous phase II (receiving phase) 10 ml of double distilled water

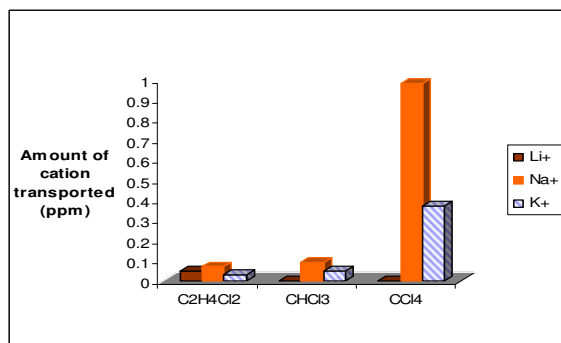


Fig.3 Amount of cation transported by ionophore dipropyleneglycolmonomethylether across 1,2-dichloroethane, chloroform and carbontetrachloride membranes using metal picrate; Aqueous phase I (source phase) 10 ml of MX salt solution ($\text{conc}^n = 1 \times 10^{-3} \text{ M}$); Organic phase (25 ml); Ionophore ($\text{conc}^n = 1 \times 10^{-3} \text{ M}$); Aqueous phase II (receiving phase) 10 ml of double distilled water

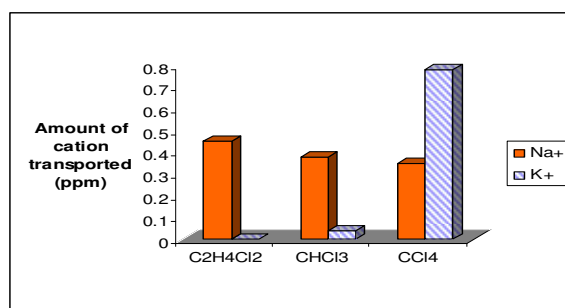


Fig.4 Amount of coexisting cations ($\text{Na}^+ + \text{K}^+$) transported by ionophore dipropyleneglycolmonomethylether across 1,2-dichloroethane, chloroform and carbontetrachloride membranes using metal picrate; Aqueous phase I (source phase) (5+5) ml of MX salt solution ($\text{conc}^n = 1 \times 10^{-3} \text{ M}$); Organic phase (25 ml); Ionophore ($\text{conc}^n = 1 \times 10^{-3} \text{ M}$); Aqueous phase II (receiving phase) 10 ml of double distilled water

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