

THE CARRIER FACILITATED TRANSPORT OF THE LITHIUM IONS BY A SERIES OF NON-CYCLIC SYNTHETIC IONOPHORES

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Abstract

The carrier facilitated transport of lithium picrate was studied using a series of non-cyclic polyethers containing different end groups and chain lengths through Bulk Liquid Membrane (BLM) and Supported Liquid Membrane (SLM) systems. The various membrane supports used are viz. PTFE, cellulose nitrate, and dialysis membrane and onion membrane. The amount of Li^+ transported depends upon the structure of the ionophores and membrane supports used. The amount of Li^+ ion transported follows the trend $V \gg IV \approx III \approx II > I > VI > VII > VIII = IX$ in the BLMs studies. Diethylene glycol dibenzoate proved to be the most efficient carrier for the transport of the lithium ion through liquid membrane systems.

Keywords: Lithium; Diethyleneglycol; Triethyleneglycol; Tetraethyleneglycol; LiPic

Introduction

A systematic investigation of the factors which influence the rate of transport of cations across various liquid membrane systems viz. Bulk liquid membrane [1], supported liquid membrane [2] and emulsion liquid membrane system using a series of non-cyclic ionophores [3] was carried out. The main disadvantage of the bulk liquid membrane [4] system is the large quantity of the carrier relative to the membrane effective area, where phase transfer can take place. Consequently, in supported liquid membrane system [5,6], the carrier in organic solvents immobilized in thin porous microfiltration films, which separates two aqueous phases. These systems resemble the biological membranes in which natural ionophores facilitate selective transport of the metal ion [7].

Since the monitoring of Li^+ activity in blood is very important during the lithium therapy of patients

suffering from manic depressive psychosis [8], many research efforts are presently being focused on the design of electrically neutral carriers for the Li^+ selective liquid membrane electrodes.

The rate of lithium transport through membranes by a series of non-cyclic ionophores has been shown to be influenced by the structural variations of the ionophores and membrane systems. We have reported earlier the systematic study of these effects during extraction [9] and also the effect of solvent variation [10]. The present investigation is the study of carrier facilitated transport of lithium Picrate (LiPic) by DEG (I), DEGDME (II), DEGMBE (III), DEGDBE (IV), DEGDB (V), ME (VI), EE (VII), TrEG (VIII), TEG (IX), through liquid membrane systems and also supported liquid membrane systems using PTFE, cellulose nitrate, dialysis membrane and onion membrane as supports.

The results can be used to explore the possibility in designing a new and specific carrier for lithium ion

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selective electrodes [10].

Experimental

The LiPic was prepared as reported earlier [11]. All the ionophores were obtained from Fluka used without further purification. Analytical grade chemicals and solvents were used for all the experiments. Chloroform used was obtained from Qualigents, which was dried and distilled before use. The membrane support was prepared by impregnating various supports viz. PTFE, cellulose nitrate, dialysis membrane and onion membrane with ionophore solution in CHCl_3 for 24 h.

Transport Studies

Bulk liquid membrane studies-Transport measurements were performed in a U-tube glass cell [12] placed in a thermostated incubator ($25 \pm 1^\circ\text{C}$). The 1.0×10^{-3} M carriers in 25 ml of organic solvent were placed in the bottom of the U-tube serving as the membrane. 10 ml of 1.0×10^{-3} M aqueous metal salt solution was placed in one limb of the U-tube serving as source phase (S.P.) and 10 ml of double distilled water was placed in another limb of the U-tube, which served as the receiving phase (R.P.). The two aqueous i.e. source and receiving phases are floating on the organic membrane phase, respectively, in the two limbs of the U-tube. The membrane phase was constantly stirred using magnetic stirrer (100 rpm). The samples were withdrawn from the receiving phase after 24 h and analyzed for the amount of the cation transported using Philips 7700 double beam atomic absorption spectrophotometer. Cation flux (J_M) values were calculated using the relation [13].

$$J_M = \frac{C_{(\text{receiving})} \times V}{A \times t}$$

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

Supported Liquid Membrane Studies

The membrane was positioned between the two cylindrical half cells. One cell compartment contained an aqueous solution of LiPic, 50 ml of 1.0×10^{-3} M (source phase) and the other cell contained the receiving phase 50 ml, double distilled water separately by the membrane having an effective diameter of 1 cm. Both the phase were stirred on magnetic stirrer at 100 rpm at room temperature for 24 h. The sample was

withdrawn from the receiving phase after 24 h and analyzed for lithium using atomic absorption spectrophotometer. Cation flux (J_M) values were calculated as described above.

Results and Discussion

The blank experiments were carried out for BLM and SLM transport studies for lithium salt in which the membrane was devoid of carrier. No leakage of cations from source into the organic layer was observed. All measurements were performed in duplicate to check the reproducibility. Among the series of non-cyclic ionophores (I to IX) used for transport of lithium ion, I to V are diethylene glycol and its derivatives having different end groups, while VIII and IX are simple glycol with larger chain lengths. The results of BLM and SLM studies are shown in Tables 1 to 3.

The order of transport of cation in BLM is $V \gg IV \approx III \approx II > I > VI > VII > VIII = IX$. The highest transport of lithium were observed with ionophore (V) which has stable pseudocavity due to rigid aromatic end groups, as compared to others, to hold the cation and carry it through the organic membrane. Due to the smaller size and high charge density of lithium ion it gets self encapsulated into the pseudocavity and hence shows maximum transport. The ionophore containing diethylene chain shows maximum transport in comparison to ionophores containing tetra, tri and mono ethylene chain lengths, respectively [10].

We have conducted different sets of experiments by varying the concentration of the lithium salt. The ranges selected is 1.0×10^{-1} to 1.0×10^{-4} M for the metal salt and 1.0×10^{-3} to 1.0×10^{-5} M for the ionophores. The values of J_M are listed in Tables 1 and 2, leads to the conclusion that the optimum concentration is 1.0×10^{-2} M for metal salt and 1.0×10^{-3} for ionophores.

Results of SLM studies are listed in Tables 3. The transport of lithium salts was measured under the conditions of 1.0×10^{-3} M ionophores and 1.0×10^{-2} M lithium salt concentration. The ionophore VI and VII, which are smaller in size and less hydrophobic, show minimum transport. We have found that ionophore IX, which contains a higher chain length and therefore more hydrophobicity, shows more transport of Li^+ in comparison to ionophores I and VIII, respectively.

The ionophore (V) provides membrane stability due to presence of hydrophobic aryl end groups and hence shows maximum transport. The membrane nature also plays an important role during transport of lithium ion; cellulose nitrate membrane, which is polar shows maximum transport, but PTFE, which is non-polar in nature shows no transport. Dialysis membrane and

onion membrane shows transport of Li^+ to the same extent.

Table 1. Amount of Li^+ ion transported after 24 h using lithium picrate by a series of ionophores in chloroform at different lithium ion concentrations. Membrane: $1.0 \times 10^{-3} \text{ M}$ carrier in 25 ml organic solvent. Receiving Phase: 10 ml double distilled water

Ionophore	Lithium Ion Concentration					
	$1.0 \times 10^{-4} \text{ M}$		$1.0 \times 10^{-3} \text{ M}$		$1.0 \times 10^{-2} \text{ M}$	
	Cation Transported (ppm)	$J_M \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$	Cation Transported (ppm)	$J_M \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$	Cation Transported (ppm)	$J_M \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$
I	—	—	4.59	2.34	3.12	1.58
II	—	—	4.32	2.19	4.93	2.76
III	—	—	3.23	1.62	5.23	3.45
IV	1.05	0.75	4.91	2.92	7.01	3.97
V	1.23	0.92	8.21	4.19	19.32	11.02
VI	—	—	2.80	1.43	3.31	1.64
VII	—	—	2.10	1.41	3.21	1.68
VIII	—	—	1.12	0.63	—	—
IX	—	—	—	—	—	—

Table 2. Amount of Li^+ ion transported after 24 h using lithium picrate by varying the concentrations of ionophore in chloroform. Source Phase: $1.0 \times 10^{-2} \text{ M}$ LiPic in aqueous phase, Receiving Phase: 10 ml double distilled water

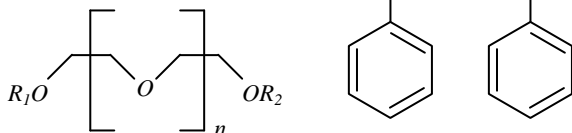
Ionophore	Ionophore Concentration					
	$1.0 \times 10^{-4} \text{ M}$		$1.0 \times 10^{-3} \text{ M}$		$1.0 \times 10^{-2} \text{ M}$	
	Cation Transported (ppm)	$J_M \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$	Cation Transported (ppm)	$J_M \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$	Cation Transported (ppm)	$J_M \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$
I	9.12	4.72	12.13	6.16	5.51	2.28
II	12.10	6.61	13.12	6.68	5.51	2.28
III	13.13	6.66	15.89	8.10	5.00	2.55
IV	14.29	7.28	15.23	7.76	7.01	3.57
V	15.19	7.74	17.79	9.11	—	—
VI	5.13	2.61	8.01	4.08	—	—
VII	6.92	3.52	—	—	—	—
VIII	—	—	7.89	4.02	—	—
IX	—	—	—	—	—	—

Table 3. Amount of Li^+ transported after 24 h using lithium picrate by a series of ionophore through SLM. Source Phase: 50 ml $1.0 \times 10^{-2} \text{ M}$ lithium salt in aqueous phase; Membrane: $1.0 \times 10^{-3} \text{ M}$ carrier in chloroform, Receiving Phase: double distilled water, 50 ml

Ionophores	Membrane							
	Dialysis membrane		Cellulose nitrate		Onion membrane		PTFE	
	Cation Transported (ppm)	$J_M \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$	Cation Transported (ppm)	$J_M \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$	Cation Transported (ppm)	$J_M \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$	Cation Transported (ppm)	$J_M \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$
I	3.093	7.88	5.936	15.02	3.210	8.21	—	—
II	4.512	11.50	10.312	26.26	12.12	30.89	—	—
III	4.923	12.50	9.896	25.04	5.312	13.54	—	—
IV	4.123	10.51	13.312	33.04	7.521	19.17	—	—
V	6.857	17.49	19.939	50.165	3.597	9.17	—	—
VI	2.120	5.08	7.895	20.02	3.125	7.96	—	—
VII	2.121	5.08	5.012	12.55	3.000	7.64	—	—

VIII	3.237	8.25	6.423	16.27	—	—	—	—
IX	4.705	12.40	7.989	20.07	—	—	—	—

- I $n = 1, R_1 = H, R_2 = H$
 II $n = 1, R_1 = CH_3, R_2 = CH_3$
 III $n = 1, R_1 = C_4H_9, R_2 = H$
 IV $n = 1, R_1 = C_4H_9, R_2 = C_4H_9$
 V $n = 1, R_1 = C=O, R_2 = C=O$



- VI $n = 0, R_1 = CH_3, R_2 = C_2H_5$
 VII $n = 0, R_1 = C_2H_5, R_2 = C_2H_5$
 VIII $n = 2, R_1 = H, R_2 = H$
 IX $n = 3, R_1 = H, R_2 = H$

Figure 1. Ionophores used for BLM and SLM studies.

Conclusion

The results reported here lead to the conclusion that end groups and chain length of the ionophore significantly contribute to the selective transport of lithium ion. The selective and specific transport of Li⁺ through SLMs was achieved using cellulose nitrate membrane. The selectivity of ionophore (V) is retained in both membrane systems. End group and chain lengths are the governing factors for the transport of lithium ion in spite of the membrane systems used. It provides good potential for the development of Li⁺ ion specific receptors which can help in monitoring of lithium concentration in human body and also in ion selective electrode.

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