

TRANSPORT STUDIES OF ALKALI AND ALKALINE EARTH METAL IONS USING SYNTHESIZED OXO-CROWN ETHERS VIA POLYMER INCLUSION MEMBRANE

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Abstract

Transport studies of A⁺/A²⁺ through bulk liquid membrane have been reported earlier [1]. The same kind of studies have been extended using polymer inclusion membrane, using synthesized oxo-crown ethers as carrier. However, it was found that PIM offers less effective transport as compared to BLM. It suggests that in PIM, there is a restricted movement of ligand which is not capable of undergoing a conformational change to wrap the cation and hence to cause the transport. Conformational orientation is much feasible in BLM. Cation Selectivity is same in both membrane system.

Keywords: Pims, Bulk Liquid Membrane, Alkali and Alkaline Earth Metal Ions.

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Abbreviations

A⁺, Alkali metal ions; A²⁺, Alkaline earth metal ions; PIM, Polymer inclusion membrane; PVC, Poly vinyl chloride; CTA, Cellulose tri acetate; SX, Solvent extraction; 2-NPOE, 2- Nitrophenyl octyl ether; THF, Tetrahydrofuran; SEM, Scanning electron microscopy; FT-IR, Fourier Transform infrared; Pic⁻, Picrate anion (2,4,6, trinitrophenolates); I_a, I_b, and I_c, Acetoacetate diester of di, tri and tetra ethylene glycols respectively; J_m, Flux of flow of cation in mol/hour; r_m, ionic radai.

Introduction

Polymer inclusion membranes (PIMs) represent an emerging technology in chemistry, facilitating the secure and efficient separation of metallic and non-metallic ionic species, along with small organic molecules, from aqueous solutions [2,3]. PIMs employ a base polymer matrix, typically composed of poly(vinyl chloride, PVC) or ester-substituted cellulose derivatives like cellulose triacetate (CTA), wherein an extraction reagent is encapsulated. This encapsulation may include plasticizers and/or chemical modifiers. PIMs offer a safer alternative to conventional liquid–liquid extraction methods (commonly known as solvent extraction, SX), known for their reliance on significant quantities of toxic, volatile, and flammable chemicals. Researchers have successfully adapted existing SX technologies to PIM systems [4], and ongoing efforts focus on enhancing the understanding of the fundamental processes underlying PIM extraction and transport.

The functionality of PIM systems is rooted in carrier-facilitated transport, where the membrane selectively allows the passage of the target solute through the action of an extraction reagent. Typically, the target solute forms a reactive coupling with the extractant at the membrane–solution interface, subsequently undergoing transport into and through the membrane via the diffusion of the extractant–solute complex or ion-pair. Observable depletion of the solute in the aqueous phase

signifies its extraction into the membrane. The extraction process involves a synergy of physical diffusion processes within the membrane and chemical reaction kinetics at the membrane-solution interface, as extensively deliberated in prior studies [5]. In the present study, it was found that BLMs transport efficiency is much more effective with synthesized ligands.

Experimental

Chemicals and Reagents

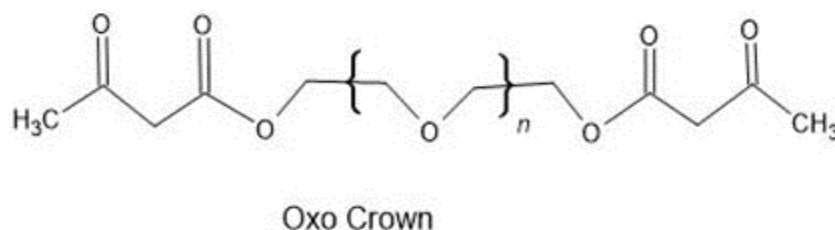
Diethylene glycol and Ethyl acetoacetate for ligand synthesis, Chloroform and Tetrahydrofuran were used as a solvent, Metal Picrates, Synthesized Ligands (as a carrier), PVC (as a base polymer), 2- NPOE (as a plasticizer) were used for membrane preparation. All of these chemicals were purchased from Sigma – Aldrich (USA) and were of analytical grade.

Synthesis of Ligands (I_a, I_b, I_c)

0.66 mole diethylene glycol was thoroughly mixed with 2 mol of ethyl acetoacetate in a round bottom flask and was heated slowly for 4-6 hours at 180°C. The excess amount of ethyl acetoacetate was removed by the distillation under reduced pressure so as to avoid any possible decomposition at 180°C. A brown oily residue (I_a) i.e. acetoacetic diester of di ethylene glycol in the pure form was recovered from the distillation flask. The purity of these compound was confirmed by the IR spectroscopy using an FT-IR. The ligands do not contain any strong signal at 3500 cm⁻¹ indicating a complete esterification. The sharpness of signals also indicates the purity of sample. Some characteristic frequencies of IR are shown below;

1. Ligand I_a - 3500 cm⁻¹ (-OH), 1710 and 1725 cm⁻¹ (C=O , diketone)
2. Ligand I_b - 3420 cm⁻¹ (-OH), 1750 and 1720 cm⁻¹ (C=O , diketone), 1660 cm⁻¹ (enol, C=O)
3. Ligand I_c - 3440 cm⁻¹ (-OH), 1745 and 1720 cm⁻¹ (diketone), 1655 cm⁻¹ (enol, C=O)

Similar method was utilized for the synthesis of I_b and I_c ligands (Acetoacetic diester of tri and tetra ethylene glycols respectively). The chemical reactions involved in the above process can be depicted as following; here n = 1, 2, 3 for ligands I_a, I_b, I_c respectively.



Metal Picrates

Sodium and potassium picrates were prepared from picric acid and the corresponding metal hydroxide. The alkaline earth metal picrates (magnesium and calcium ions) were prepared from picric acid and the corresponding metal carbonates in hot water and the mixture was stirred for two hours. The solution was then evaporated to obtain dry metal picrate crystals.

Membrane Preparation

PIM was prepared by dissolving PVC (400 mg), Synthesized Carrier (0.1818 g) and 2- NPOE (0.3 ml as a plasticizer) in THF solvent and stirred magnetically for 2 hours and then solution was poured into a 9.0 cm diameter plate- bottom petri dish. The solvent was allowed to evaporate over 24 hours at room temperature and the resulting film was then carefully be flaked off the bottom of the petri dish and circular 2.5cm² pieces was cut from its central section and used in the experiments. PIMs of different thickness was prepared by reducing proportionally the total mass of polymer and Carriers.

SEM Analysis

Details about membrane morphology were studied through the utilization of Scanning Electron Microscopy, with images captured using a VEGA II SBH electron microscope manufactured by TESCAN. SEM was used to determine the appearance of membrane surface and cross section obtained image as shown in figure 1. Fig.1 shows cross section of PIM surface of PVC contains lumps and this show may incomplete melting of polymer. Carrier sometimes crystallize in the membrane during process. Some images show roughness of the film surface due to carrier (roughness was more visible).

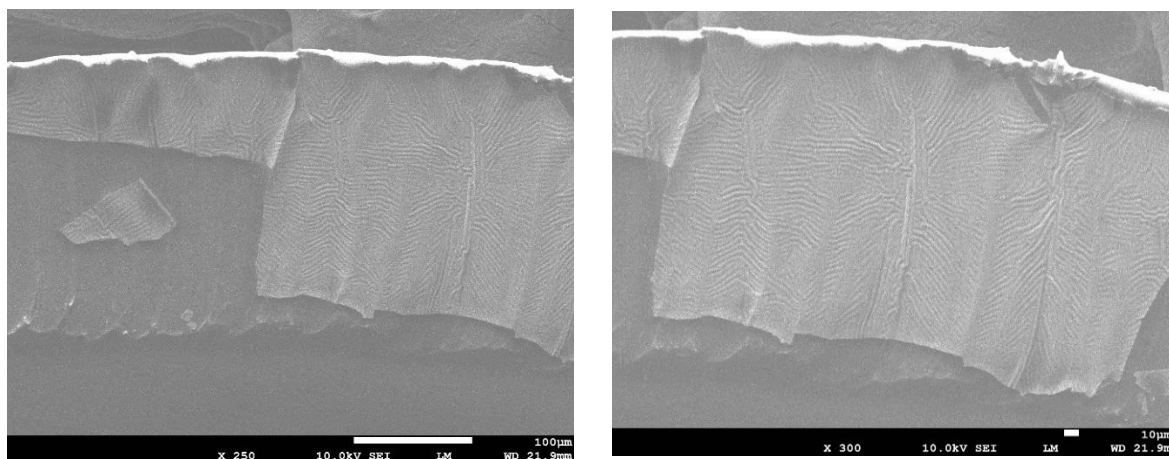


Fig.1 Cross-section of PVC membrane

Procedure involved in Bulk Liquid Membrane and Polymer Inclusion Membrane Transport

Experiments involving liquid membranes were conducted following the described procedures [6,7]. In a 500 ml beaker, a chloroform solution (100 ml) containing a 1.0×10^{-3} M carrier was positioned at the bottom. A glass cylinder, open at both ends, was suspended just below the chloroform surface, creating inner and outer areas. On the outer ring of chloroform, 40 ml of distilled, deionized water was placed, while inside the cylinder, 20 ml of salt solution was carefully added. A stirring bar at the beaker's bottom facilitated constant and reproducible stirring through a magnetic stirrer. The system was sealed at both levels to minimize evaporation. Samples of 4 ml were extracted at 12-hour intervals over 48 hours using a syringe, with stirring resumed five minutes after each withdrawal. The experiments were conducted at room temperature. Cation content in the samples was analyzed using methods outlined by Kobuke et al.[8], involving anion determination spectrophotometrically, flame photometric technique, and atomic absorption technique where necessary. Results were documented in terms of J_m , representing the net flux of metal cation across the membrane per hour. Blank experiments, without the carrier, were

conducted for each source phase salt solution to identify membrane leakage. Cation leakage varied with the cation but consistently remained below 1.0×10^{-8} mol/hour.

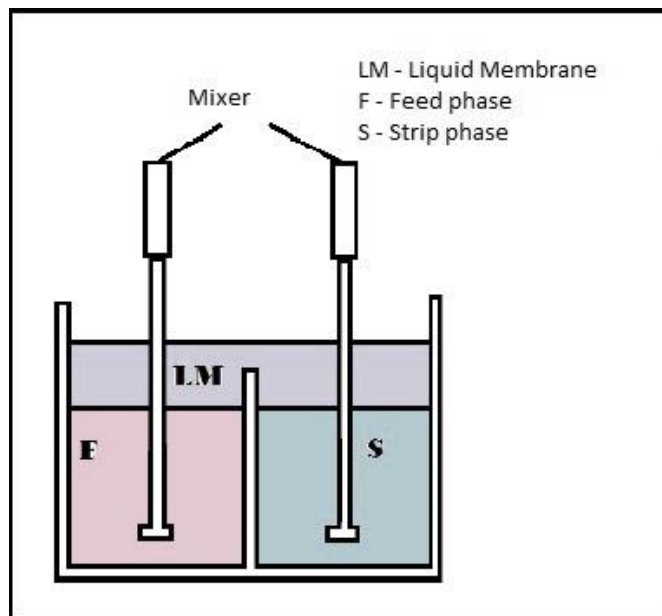


Fig.2 Schematic diagram of bulk liquid membrane

The experimentation on metal transport (PIM) employed a glass cell, delineated in Figure3, comprising two compartments with a maximum capacity of 100 ml each, separated by the PIM. In the feed compartment, a solution of metal picrates was placed, while the strip compartment held distilled water, both compartments having an identical volume of 100 ml. Each compartment featured a vertical mechanical stirrer set at a stirring speed of 800 rpm, a rate determined as effective in minimizing the boundary layer thickness. The experiments initiated with the activation of stirring motors in both cell compartments. The membrane's exposed area measured 2.5 cm^2 . All trials were conducted in a thermostat, maintaining a constant temperature of 25°C . The experiments spanned 7 days, with 0.5 mL of the solution extracted from the strip compartment every 24 hours for the determination of A^+/A^{2+} ion flux through the membrane.



Fig.3 Polymer Inclusion Membrane set up

Results and Discussion

The results of entire range of transport studies through bulk liquid membranes performed with three ligands I_a , I_b , and I_c already studied by the author [9] are given in tables (1,2,3). This provides the picture of the mode in which J_m was worked out for the series of cations through variations in the time allowed for performing and evaluating the transport process. The variation of time in the transport process has been done in the slab mode i.e. 12 hours, 24 hours, 36 hours, 48 hours.

The J_m values thus obtained are reflective of the flux of the flow of cation across the membrane. These J_m values are listed in the table (4). The values of $\log J_m$ vs r_m (ionic radius) for I_a , I_b and I_c have been given in table (5).

The J_m values show conspicuous variations in the transport for different cations. The value is high (292.8×10^{-7} mol/hour) for K^+ mediated by I_c . Na^+ is anticipated to be a cation with an anionophilicity lower in magnitude compared to Ca^{2+} . However, the transport behavior of Na^+ significantly differs from that of Ca^{2+} . Furthermore, the favored transport process may result from the extraction into the membrane and proper de-extraction from the membrane. Notably, in the case of the two sets of ligands, I_b exhibits more favorable transport. It seems probable that, after accomplishing the initial transport component, i.e., extraction, the anionophilicity of Na^+ might even facilitate the diffusion of the complexed species across the membrane.

Potassium (K^+) has traditionally been a preferred cation in the selectivity sequence for many ligands. There is no apparent reason why the ligands studied in this work should not exhibit favorable complexation towards K^+ . Interestingly, K^+ displays distinctive transport behavior, indicating the critical susceptibility of the nature of the transport mediator. While I_a and I_b may have a lesser ability to fulfill the coordinative requirements of the cation than I_c , their poor performance cannot be solely attributed to profound complexation and weak decomplexation. On the contrary, it seems that neither I_a nor I_b adequately fulfill the coordinative requirements of K^+ , making extraction into the membrane insufficient. Despite observing low transport for several K^+ systems, the transport of K^+ by I_c is the most favored.

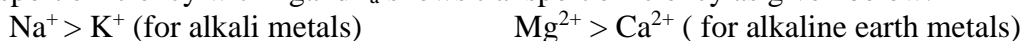
Mg^{2+} is recognized as a strongly solventphilic cation, requiring the transport mediator to overcome its solventphilicity. Ligand with a greater number of donor sites, such as I_c appear to fail in this

aspect, while those with a relatively lower number of donor sites, I_a and I_b, succeed in transporting Mg²⁺. In contrast, Ca²⁺ is considered profoundly anionphilic, more involved with anions than expected based on its charge density. All ligands display some magnitude of the transport process in the case of calcium. The charge density of Ca²⁺ is indeed lower than that of Mg²⁺, and the transport data for Ca²⁺ suggests its participation in the process, although not as effectively, and the transport pattern for Ca²⁺ remains relatively unchanged despite prolonged stirring.

The varying chain length and the number of donor sites impact the efficiency and pattern of complexation. The overall transport process becomes efficient with an increased availability of donor sites in a series of transport carriers, as observed in I_a, I_b, and I_c, when the co-coordinative requirements of the cation are adequately met.

A broad inference from the results is that alkaline earth cations exhibit a transport process of much lower efficiency compared to alkali cations. This aligns with the behavior of these cations as semi-mobile in natural systems. The lower efficiency of the transport process for alkaline earth cations may be partly attributed to the cation being blocked by two anions, hindering the successful initial interaction between the cation and the ligand. Additionally, throughout the diffusion process across the nonpolar membrane, the cation must drag along two counter anions, adversely affecting its mobility.

The transport efficiency with ligand I_a shows transport efficiency as given below.



The transport efficiency with ligand I_b shows transport efficiency as given below.



The transport order in case of ligand I_c is K⁺ > Na⁺ and Mg²⁺ > Ca²⁺.

Table 1: The Pattern of obtaining J_m by ligand I_a

Cation	Metal Transported (in moles) After				
	12hrs.	24hrs.	36hrs.	48hrs.	J _m x 10 ⁷ mol/hrs.
Na ⁺	0.9 x 10 ⁻⁵	1.50 x 10 ⁻⁵	2.40 x 10 ⁻⁵	3.0 x 10 ⁻⁵	63
K ⁺	1.7 x 10 ⁻⁶	2.35 x 10 ⁻⁶	3.53 x 10 ⁻⁶	4.7 x 10 ⁻⁶	0.98
Mg ²⁺	1.2 x 10 ⁻⁵	2.50 x 10 ⁻⁵	3.70 x 10 ⁻⁵	5.0 x 10 ⁻⁵	10.26
Ca ²⁺	1.0 x 10 ⁻⁶	2.10 x 10 ⁻⁶	3.20 x 10 ⁻⁶	4.2 x 10 ⁻⁶	0.88



Table 2: The Pattern of obtaining J_m by ligand I_b

Cation	Metal Transported (in moles) After				
	12hrs.	24hrs.	36hrs.	48hrs.	J _m x 10 ⁷ mol/hrs.
Na ⁺	2.25 x 10 ⁻⁴	4.50 x 10 ⁻⁴	2.40 x 10 ⁻⁴	3.0 x 10 ⁻⁴	187.60
K ⁺	1.53 x 10 ⁻⁵	3.00 x 10 ⁻⁵	3.53 x 10 ⁻⁵	4.7 x 10 ⁻⁵	12.80
Mg ²⁺	1.71 x 10 ⁻⁶	3.40 x 10 ⁻⁶	3.70 x 10 ⁻⁶	5.0 x 10 ⁻⁶	1.42
Ca ²⁺	4.56 x 10 ⁻⁶	9.42 x 10 ⁻⁶	3.20 x 10 ⁻⁶	4.2 x 10 ⁻⁶	3.80



Table 3: The Pattern of obtaining J_m by ligand I_c

Cation	Metal Transported (in moles) After				
	12hrs.	24hrs.	36hrs.	48hrs.	$J_m \times 10^7$ mol/hrs.
Na ⁺	1.32×10^{-4}	2.64×10^{-4}	4.00×10^{-4}	5.28×10^{-4}	110.00
K ⁺	3.50×10^{-4}	7.00×10^{-4}	10.52×10^{-4}	12.21×10^{-4}	292.80
Mg ²⁺	-	-	-	-	-
Ca ²⁺	2.67×10^{-6}	3.53×10^{-6}	8.00×10^{-6}	10.72×10^{-6}	2.23

$[M^{+}Pic^{-}] = 2 \times 10^{-3} M$ $[oxo\ crown] = 1 \times 10^{-3} M$

Table 5: Log J_m vs r_m for ligands I_a, I_b and I_c (BLM)

Cation	Log J_m for			
	r_m	I _a	I _b	I _c
Na ⁺	1.02	-5.20	-4.70	-5.01
K ⁺	1.38	-7.00	-5.90	-4.52
Mg ²⁺	0.72	-6.00	-6.84	-
Ca ²⁺	1.00	-7.05	-6.42	-6.65

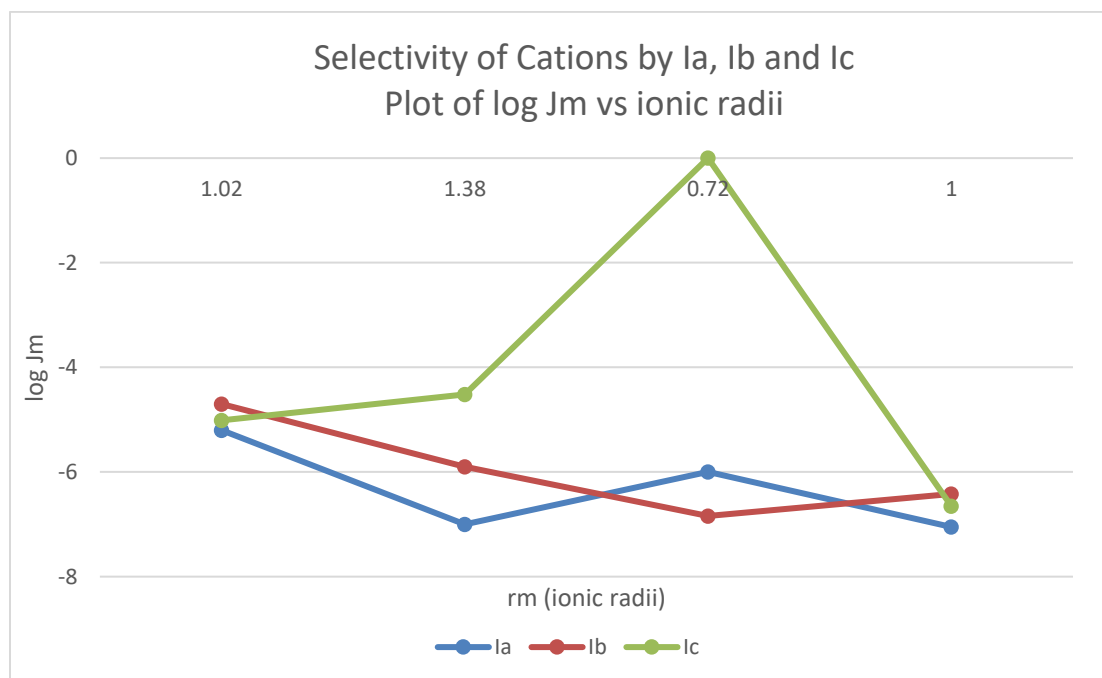


Fig.4 Selectivity of Cations by I_a, I_b and I_c (BLM)

Table 4: Flux of cation across the membrane (BLM)

Cation	-G ⁰ Kcal/mol (Hydration Energy)	$J_m \times 10^7$ mol/ hour Carrier		
		I _a	I _b	I _c
Na ⁺	98	63.00	187.6	110.00

K ⁺	81	0.98	12.80	292.80
Mg ²⁺	454	10.26	1.42	-
Ca ²⁺	379	0.88	3.80	2.23

$$[M^+Pic^-] = 2 \times 10^{-3} \text{ M} \quad [oxo \text{ crown}] = 1 \times 10^{-3} \text{ M}$$

While bulk liquid membranes have demonstrated efficiency in transporting certain cations, the effectiveness of polymer inclusion membranes (PIM) for the same purpose appears to be limited in this particular study. The ligands, specifically the acetoacetic diester of di, tri, and tetraethylene glycols, encounter challenges in undergoing the necessary conformational changes required to envelop cations but selectivity is same as shown in bulk liquid membrane.

In the case of PIM, the movement of ligands is inherently constrained, particularly due to the synthesized oxo-crown ethers acting as carriers. This restricted flexibility hinders the ligands' ability to adapt to the essential conformational changes necessary for effectively wrapping around cations and facilitating their transport.

In contrast, bulk liquid membranes provide a more favorable environment for ligands to undergo the required conformational changes. The increased freedom of movement allows ligands to efficiently envelop cations, enabling their effective transport through the membrane.

In essence, the limited movement of ligands within polymer inclusion membranes poses a hindrance to the required conformational changes, resulting in less effective cation transport compared to bulk liquid membranes. The conformational feasibility provided by bulk liquid membranes emerges as a crucial factor contributing to the efficient transport of cations in this specific study as compared to polymer inclusion membrane.

Table 6: Flux of cation across the membrane (PIM)

Cation	-G ⁰ Kcal/mol (Hydration Energy)	J _m x 10 ⁷ mol/ hour Carrier		
		I _a	I _b	I _c
Na ⁺	98	50.4	150.08	86.9
K ⁺	81	0.784	10.24	234.24
Mg ²⁺	454	8.208	1.136	-
Ca ²⁺	379	0.704	3.04	1.784

$$[M^+Pic^-] = 2 \times 10^{-3} \text{ M} \quad [oxo \text{ crown}] = 1 \times 10^{-3} \text{ M}$$

Table 7: Log J_m vs r_m for ligands I_a, I_b and I_c (PIM)

Cation	Log J _m for			
	r _m	I _a	I _b	I _c
Na ⁺	1.02	-5.29	-4.82	-5.06
K ⁺	1.38	-7.10	-5.98	-4.63
Mg ²⁺	0.72	-6.08	-6.94	-
Ca ²⁺	1.00	-7.15	-6.51	-6.74

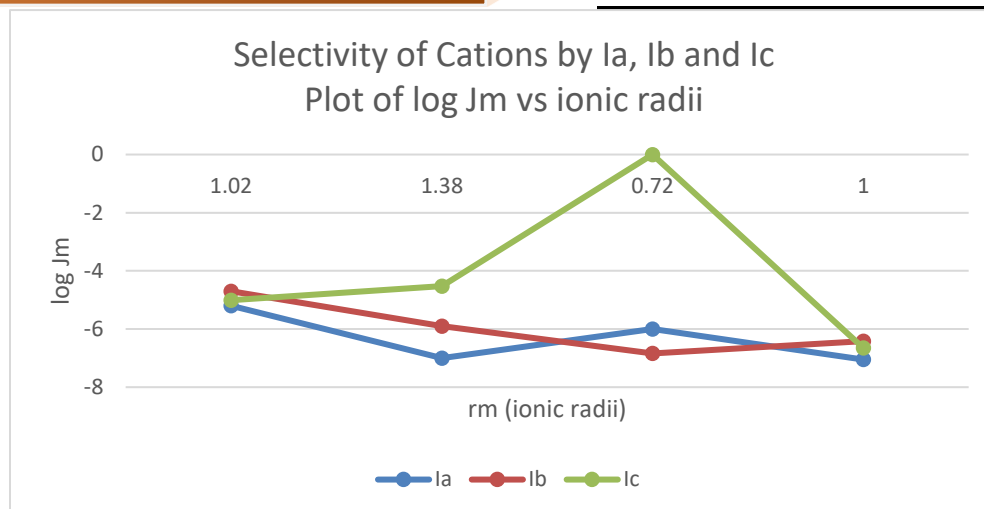


Fig.5 Selectivity of Cations by Ia, Ib and Ic (PIM)

Conclusion

In this research paper, we have described the transport studies of alkali and alkaline earth metal ions through polymer inclusion membrane using synthesized ligands Ia, Ib, and Ic, Acetoacetate diester of di, tri and tetra ethylene glycols respectively and we have compared it with bulk liquid membrane transport, which has already been studied by the author. We found in this study that cations are transported more easily through bulk liquid membrane as compared to polymer inclusion membrane because in PIM, there is a restricted movement of ligand which is not capable of undergoing a conformational change to wrap the cation and hence to cause the transport. Conformational orientation is much feasible in BLM. Cation Selectivity is same in both membrane system.

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References

1. Muktibodh, S. Systematic Transport Investigation on Alkali and Alkaline Earth Metal Ions using Selected Linear Oxo-Crown Ethers across Organic Liquid Membrane. *Int. J. Sci. Res.* 2015, 4, 1001-1006.
2. O'Rourke, M.; Cattrall, R.W.; Kolev, S.D.; Potter, I.D. The extraction and transport of organic molecules using polymer inclusion membranes. *Solvent Extr. Res. Dev. Jpn.* 2009, 16, 1-12.
3. Nghiem, L.D.; Mornane, P.; Potter, I.D.; Perera, J.M.; Cattrall, R.W.; Kolev, S.D. Extraction and transport of metal ions and small organic compounds using polymer inclusion membranes. *J. Membr. Sci.* 2006, 281, 7-41.
4. Vasudevan, T.; Das, S.; Debnath, A.K.; Pandey, A.K. Facilitated transport of europium (III) ions across fixed-site membrane. *J. Membr. Sci.* 2009, 342, 113-120.
5. St John, A.M.; Cattrall, R.W., Kolev, S.D. Extraction of uranium (VI) from sulfate solutions using a polymer inclusion membrane containing di- (2- ethylhexyl) phosphoric acid. *J. Membr. Sci.* 2010, 364, 354-361.
6. Tayeb, R.; Fontas, C.; Dhahbi, M.; Tingry, S.; Seta, P. Cd (II) transport across supported liquid membranes and polymeric plasticized membranes mediated by Lasalocid A. *Sep. Purif. Technol.* 2005, 42, 189-193.

7. Thunhorst, K.L.; Noble, R.D.; Bowman, C.N. Properties of the transport of alkali metal salts through polymorphic membranes containing benzo-18-crown-6 crown ether functional groups. *J. Membr. Sci.* 1999, 156, 293-302.
8. Kobuke, Y.; Hanji, K.; Horiguchi, K.; Asada, M.; Nakayama, Y.; Furukawa, J. Macrocyclic ligands composed of tetrahydrofuran for selective transport of monovalent cations through liquid membranes. 1976, 98, 7414-7419.
9. Muktibodh, S. Systematic Transport Investigation on Alkali and Alkaline Earth Metal Ions using Selected Linear Oxo-Crown Ethers across Organic Liquid Membrane. *Int. J. Sci. Res.* 2015, 4, 1001-1006.