

Systematic Transport Investigation on Alkali and Alkaline Earth Metal Ions using Selected Linear Oxo-Crown Ethers across Organic Liquid Membrane

Sourabh Muktibodh

Mata Jija bai govt. Girls Post Graduate College, Motitabela, Indore (M.P.) 452008

Abstract: Metal ion transport through organic liquid membrane, polymer inclusion membrane and PVC membrane is parallel to metal ion transport behavior in biological systems^{1-11, 21}. Therefore these are model membrane systems which may offer some understanding of actual biological systems. With these intentions systematic membrane studies using selected synthetic carrier is carried out. Two series of ligands were used in the present investigation. Metal ion transport of alkali and alkaline earth metal ions using these carriers and chloroform liquid membrane is thoroughly investigated. Several features of this dynamic process are observed. Synthetic macrocyclic compounds possessing limited number of donor atoms can successfully bring about transport process for fairly large number of instances. The phenyl incorporated mediators show less degree of transport efficiency than the corresponding non phenylated ones. Results are reported in terms of J_M value which is actually the flux of flow of cation across the membrane. It has been indicated that J_M value is directly proportional to the square of metal salt concentration in aqueous phase.

Keywords: Oxo-Crown ethers, transport, alkali metal ions, J_M value, organic liquid membrane

1. Introduction

The rapid developments in the synthesis of neutral macrocyclic compounds capable of complexing metal and organic ions has stimulated research efforts in many fields of chemistry. The pioneering work of Pedersen on macrocyclic polyethers or crown ethers was chiefly concerned with oxygen containing ring system and produced a series of powerful complexing agents for alkali and alkaline earth cations, as well as for primary alkali ammonium cations. The initial emphasis in ligand design was directed at selective complexation of metal cations, notably alkali and alkaline earth cation because of their importance in many chemical and biological processes.

The ion binding properties of crown ethers, cryptands and podands have been actively employed in diverse fields of chemistry. To the synthetic organic chemist the design and synthesis of these materials have been a challenging task, the phenomena exhibited by the often highly structured complexes resemble those underlying important biological processes such as enzyme catalysis and inhibition and material transport. The lipophilic character of many of the ligands suggested their use in mediated ion transport through membranes

Transport Studies

Transport investigations on alkali and alkaline earth metal cations mediated by synthetic ionophores is a rather recent trend. This approach has been utilized through the use of model non-polar membranes with source and receiving aqueous phases on either side of it. The main motivation of undertaking such studies has been to investigate behavior of alkali and alkaline earth metal cations under a degree of

parallelism on chemical principles for the natural environment. Natural environment is, of course, more complex than the model systems. Nevertheless, meaningful conclusions can be drawn on the basis of model transport experiments which may throw light on the transport patterns of the cation in the natural environment.

With this realization, we have carried out extensive transport investigations to appreciate the transport patterns of the cations and to examine the transport processes from different facets.

The transport mediators can be macrocyclic compounds or even the non-cyclic multidentates.¹⁸⁻²¹ The mediator is present exclusively in the non-polar phase and through contact of the cation present in the source phase, a complex between the transport mediator and the cation may be formed and this interface, de-complexation takes place and the metal can be made available the receiving phase. The transport process is thus a combination of complexation and compatible de-complexation. In this way the cation is made to pass through the non-polar environment in which it is otherwise unwilling to enter.

The presence of complexed species in the non-polar environment has been an important feature for complexation of alkali and alkali earth metal cations with the macrocyclic or non-cyclic multidentates. Use of this feature has been made in accomplishing transport process where the opposing factors are operative. The requirements of a species to exist in the polar environment such as an aqueous solution are drastically different from those of typically non-polar ones. What is truly remarkable here that the system, possesses in itself the two opposite components which allow their neutralization in different situations. The ionophore is

sufficiently hydrophobic to remain exclusively in the non-polar phase while it has adequate number of donor sites to account for the requirements of the cation.

2. Experimental

2.1 Chemicals Used

- a) **Ligands:** - The non-cyclic Oxo "Crown" ligands were synthesized as reported earlier^{12-14, 22} (Fig-1& 2)
- b) **Solvents:** - Chloroform was used as membrane solvent and a set of comparisons for this purpose was provided by dichloromethane and carbontetrachloride solvents. All these three solvents were solvents were obtained from "FLUKA" and were distilled before use.
- c) **Metal picrates:** -Metal picrates were prepared by the method described^{16, 17}

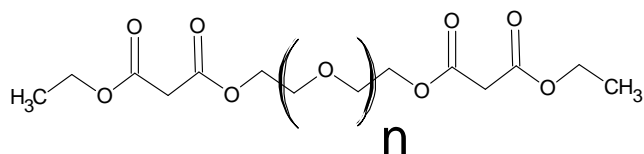


Figure 1: n=1, Ia n=2, Ib and n=3, Ic

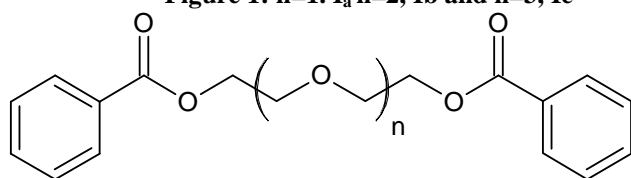


Figure 2: n=1, IIa n=2, IIb and n=3, IIc

3. Procedure

Liquid membrane experiments were conducted, as described.¹⁰⁻¹² A chloroform solution (100ml) containing 1.0×10^{-3} M of carrier was located at the bottom of 500 ml beaker. Suspended above the bottom of the beaker (below the chloroform surface) was a glass cylinder open at the both the ends which separated inner and outer areas. Atop the outer ring of chloroform was placed 40 ml of distilled, deionized water. Atop the chloroform, inside the cylinder was carefully kept 20 ml of salt solution. The three phases were agitated by a stirring bar located at bottom of beaker. The constant and reproducible stirring was provided by magnetic stirrer. The system was sealed at both the levels to minimize evaporation. Samples of 4ml were extracted by syringe at 12hrs intervals, for 48 hrs. resuming stirring five minutes after sample withdrawal. The experiment were conducted at room temperature. Samples were analyzed for cation content by the methods described by Kobuke et. Al.¹⁷ (anion determination spectrophotometrically) also by flame photometric technique and atomic absorption technique (where required). The results were recorded in terms of J_M (The net flux of metal cation across the membrane per hour).

Blank experiments were performed (no carrier present) for each source phase salt solution to determine membrane leakage. The amount of cation leakage varied with the cation but was always less than 1.0×10^{-8} mol/hour. The net transport by carrier mechanism has been expressed as the

difference of apparent rate from blank experiments for certain cations where membrane shows higher leakage.

4. Results and Discussion

These J_M values are listed in Table 7 for two broad types of ligands. Table 1to 6 describes the pattern of obtaining J_M values. and the bar digram at the end describes the selectivity of the carrier for particular type of cation.

The J_M trends show conspicuous variations in the transport for different cations. The value can be as high as 292.8×10^{-7} mol/hour (for K^+ mediated by I_C) or as low as 0.25×10^{-7} mol/hour (for Cs^+ mediated by I_b). The J_M values greater than 100×10^{-7} mol/hour are for Li^+ mediated by I_a , Na^+ mediated by I_c , Li^+ mediated by I_c , Rb^+ mediated by I_C and Li^+ mediated by II_C . The systems displaying no detectable transport after 48 hours of experimentation are $Cs^+ - I_b$, and $Mg^{2+} - II_C$. The ligand I_a is unique in that it brings about successfully the transport process for all the eight cation under consideration, whereas the ligand II_b shows the shortest range of feasibility of the transport process.

A broad conclusion from the results is that alkaline earth cations display a transport process of much lower efficiency than alkali cations. This is keeping with the fact that in natural systems also these cations behave semi mobile. The lower efficiency of the transport process of alkaline earth cations may be related, at least in part, to the blockade of the cation by two anions so that the initial interaction between the cation and the ligand may not work out quite successfully. Moreover, in the entire process of diffusion across the non-polar membrane, the cation has to drag along itself two counter anions, thus having an adverse bearing on the mobility. Nevertheless, the transport behavior of Ba^{2+} as mediated by I_C and II_C is very much remarkable and stands distinguished from the other results of the related cations. Of the six possible transport mediators, Mg^{2+} exhibits transport by I_a , I_b , II_a and II_b . In no case, however, the transport efficiency can be termed as high. Mg^{2+} is known to be a strongly solventphilic cation and in order to make it transported, the transport mediator has to overcome solventphilicity of this cation. The ligand having greater number of donor sites such as I_C and II_C apparently fail to perform this aspect, while those having relatively lower number of donor sites I_a , I_b , II_a and II_b succeed in making Mg^{2+} transported. On the other hand, Ca^{2+} has been considered to be profoundly anionphilic i.e. more involved with anion than expected on the basis of its charge density. Only II_a does not succeed in causing transport of Ca^{2+} , while all other five ligands display transport process of some magnitude. The charge density of Ca^{2+} is no doubt lower than that of Mg^{2+} and accordingly the donor atom inviting ability of this cation should, in principle, be lesser than that could have been exercised by Mg^{2+} . The message conveyed by transport data of Ca^{2+} is that under appropriate conditions Ca^{2+} participated in the transport process, though not effectively, and despite prolonged stirring the transport pattern for Ca^{2+} cannot be drastically changed.

The major difference between the series of mono and divalent cation is also of energy of hydration. The divalent cation possess much higher free energy of hydration (ΔG°) than the monovalent ones, $\Delta G^\circ(\text{H}_2\text{O})$ values are 68 to 114 Kcalmole⁻¹ while 314 to 454 Kcalmole⁻¹ for the divalent ones. This does not immediately mean that the cation of higher hydration energy encounters greater difficulty upon complexation with a ligand, since the higher hydration energy also promises stronger interaction with the donor oxygen atoms of the ligand as well as water molecules. The major difficulty for the divalent cations to be extracted into the organic phase may originate from the incomplete dehydration of the cation.

Among the alkali cations, Li⁺ is known to be a solventphilic cation. However, Solventphilicity of this cations is of lower magnitude than that possessed by Mg²⁺. This is evidenced by partial presence of water molecules in the interaction sphere of Li⁺ which continues to retain some contacts with the counter anion in the solid state. In the periodic table also, the diagonal relationship between Li⁺ and Mg²⁺ has been stressed. Both I_a and II_a display significant transport for Li⁺ which goes on decreasing progressively as I_a is replaced by I_b or I_c, or II_a is replaced by II_b or II_c. The progressive decrease is indicative of the progressive non-compatibility of the transport mediator with increase in the number of donor sites. The non-compatibility in no case, however, becomes uncontrolled so that non feasibility of transport is never noticed for Li⁺ for the experiments performed in our work.

Na⁺ is expected to be an anionphilic cation with anionphilicity of lower magnitude than that of Ca²⁺. Nevertheless, the transport behavior of Na⁺ is drastically different from the exhibited by Ca²⁺. Indeed in three of the six cases of transport behavior of Na⁺, J_M (1 x 10⁻⁷ mol/hour) is greater than 100 and in the fourth case too, it approaches around 100. This behavior of Na⁺ obviously calls for a closer look. It appears that Na⁺ continues to be an anionphilic cation but this anionphilicity of Na⁺ does not adversely affect the complexation process to a large extent. Moreover, the favored transport process may be a consequence of the extraction into the membrane and appropriate de-extraction from the membrane. For the two sets of ligands, interestingly, I_b and II_b display more favored transport. It appears quite likely that after having materialized the first component of transport viz, extraction, the anionphilicity of Na⁺ may even assist the diffusion phenomenon of the complexed species across the membrane.

Potassium (K⁺) has been a preferred cation in the selectivity sequence for many ligands. There are no reasons why the ligands studied in the present work should not display favorable complexation towards K⁺. Remarkably K⁺ displays extreme behavior for transport indicating critical susceptibility of the nature of transport mediator. The ability of I_a, I_b, II_b to fulfill the coordinative requirements of the cation is, no doubt, lesser than that possessed by I_c or II_c. Consequently, the poor performance displayed by I_a, I_b, II_a and II_b cannot be attributed to just profound complexation and weak decomplexation. On the contrary, it appears that none of I_a, I_b, II_a and II_b fulfills the coordinative requirements

of K⁺ adequately and, therefore, extraction into the membrane may not be sufficient magnitude. Despite low transport observed for several K⁺ systems in our work, transport of K⁺ by I_c is the most favored one.

Rb⁺ and Cs⁺ are genuine low charge density cations and accordingly their ligand inviting ability is not of very high order. Nevertheless, I_c succeeds in displaying considerable transport. The behavior of Rb⁺ in terms of transport is more versatile than of K⁺. This is borne out by the fact that Rb⁺ displays favored transport with I_c and II_c, poor transport with I_a, I_b and II_a and no transport at all with II_b. Thus the behavior of Rb⁺ is obviously an extension of the susceptibility feature displayed by K⁺. On the other hand, Cs⁺ in no case reaches the upper margin of transport. It either displays poor transport (I_a, I_c, II_a and II_c) or no transport at all. This comes out to be the extract of J_M values obtained for two sets of ligands I_a, I_b, I_c and II_a, II_b, II_c reported in Table 7 collectively.

In many cases, the transport increased linearly with respect to time, so that the jump in transport from 12 hours to 24 hours was almost equal to that noticed for the successive 12 hours intervals. This is broadly in agreement with the findings reported by other workers also. Nevertheless, some notable exceptions can be traced. The most in-consistent transport rise (other than the systems showing delayed start of transport) was exhibited by K⁺ and Rb⁺ mediated by I_a (table-7) and also by K⁺ mediated by I_c. Interestingly, Na⁺ also displayed inconsistent transport rise. This can be broadly attributed to susceptibility of the respective cations manifested in the transport behavior according to the experimental condition.

The ligands, in the present experimentation, II_a, II_b and II_c appear to be more hydrophobic than I_a, I_b or I_c. This factor should contribute to increased retention of II_a, II_b or II_c relative to that exhibited by I_a, I_b or I_c. Attachment of phenyl nuclei at the terminal position has electronic implications also. It is not surprising, therefore, that II_a, II_b and II_c display relatively reduced transport efficiency than that exhibited by I_a, I_b or I_c. This is because the electron withdrawing phenyl groups, placed at the terminal position are causing reduced electron density at the donor atoms and consequently display lower complexing efficiency than otherwise. It also establishes the compensation of the advantage conferred by the increased number of carbon atom with respect to hydrophobicity.

The variation in the chain length along with the number of donor sites has a bearing on complexation efficiency and pattern. Complexation and accompanying de-complexation decide the fate of transport. Thus in a not-so-favored transport, it may so happen that complexation may be strong enough to drive the cation into the membrane but de-complexation may not be so intense so as to force the exit of the cation from the membrane. With the increased availability of donor sites in a series of transport carriers, as noticed for I_a, I_b and I_c, the overall transport process becomes efficient if the co-coordinative requirements of the cation are just adequately met. This implies that with the suitable variation in the environment such as interaction with the

excess water molecules, de-complexation can be brought about successfully, resulting in a significant impact on the transport. For a high charge density cation like Li^+ , not all the donor atoms may be required to participate in the interaction sphere around the cation and hence some additional donor sites may be left un-utilized during the entire process. With I_a for example, Li^+ in all likelihood may not require the two terminal carbonyl groups for meeting the co-coordinative requirement of its own. On the other hand a low charge density cation such as K^+ , which by itself has lower donor atom inviting ability than a high charge density cation may require the use of almost all donor atoms present in the transport carrier. Eventually each transport carrier has to wrap around the cation either moderately or exhaustively, and to make available the donor atoms for interaction with the cation while projecting the hydrophobic part towards the outside as much as possible.

Of all the six transport mediators studied in this work II_b appears to be most "choosy". This statement can be justified by the fact that out of the eight cations subjected to transport through this mediator, only five responded viz Li^+ , Na^+ and K^+ (among M^+) and Mg^{2+} and Ca^{2+} (among M^{2+}) Table (14). The cations rejected for transport by this ligand of course, do not display a general favored transport efficiency (with the exception of Rb^+ and Ba^{2+} for I_c and II_c). The transport process can be visualized to be a sort of negotiation between the cation and transport mediator. Although, the K^+ - I_c negotiation emerges out to be most successful (as evidenced by the highest transport efficiency), the contribution of I_c cannot be underestimated to that of K^+ .

This is so because K^+ turns out to be a poor negotiator for each of I_a , I_b , II_a and II_b . However I_c continues to negotiate successfully even for Na^+ and K^+ ; this behavior of I_c finds some parallelism in that of II_c for a general good behavior towards Na^+ , K^+ and Rb^+ . It therefore follows that I_c , and to a great extent II_c also bear optimum transport mediator requirements so that unless the cation is very much "demanding", it has chances of being transported to a fairly high extent.

Interestingly, I_c displays the widest range in the transport efficiency which is closely followed by II_c . On the other hand I_a displays the transport range which has not been "stretched" to the corresponding extent. The transport mediator I_a displays a fairly wide range in transport efficiency with the order being.

$\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ (for M^+) and $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Ba}^{2+}$ (for M^{2+})

The mediator I_b displays a relatively wider range in transport efficiency than that exhibited by I_a , because herein, there is even a single case of no transport observed (Cs^+). The most preferred cation is now Na^+ rather than Li^+ and the transport order works out to be

$\text{Na}^+ > \text{Li}^+ > \text{K}^+ > \text{Rb}^+$ (for M^+), and $\text{Ca}^{2+} < \text{Mg}^{2+}$ and Ba^{2+} (for M^{2+}).

The carrier I_c is distinct in transport efficiency in that three cations display J_M greater than 100×10^{-7} mol/hour. The most preferred cation is now K^+ rather than Li^+ or Na^+ the overall transport order is $\text{K}^+ > \text{Rb}^+ > \text{Na}^+ > \text{Cs}^+ > \text{Li}^+$ and

$\text{Ba}^{2+} > \text{Ca}^{2+}$. A notable point about the transport behavior shown by I_c is that for M^+ , the disparity in the two successive cation for a given transport sequence is not of very high order. (Except Cs^+ vis-o-vis). This observation corroborates the realization that high transport efficiency is not necessarily a guarantee for high transport selectivity.

The carrier II_a displays a rather compressed range of transport efficiency. The high transport efficiency exhibited by this mediator matches the level of the 3rd preferred cation of I_c . This sharp contrast indicates the relatively less suitability of this mediator with regard to the transport phenomenon. The transport order works out to be:

$\text{Li}^+ > \text{Na}^+ > \text{Rb}^+ > \text{K}^+ > \text{Cs}^+$ (for M^+)

The transport mediator displays a restricted transport feasibility for only some of the cation investigated. Nevertheless, the highest transport efficiency displayed by the ligand (shown towards Na^+) is greater than that exhibited by II_a (shown towards Li^+). The transport efficiency work out to be in the following order:

$\text{Na}^+ > \text{Li}^+ > \text{K}^+$ (for M^+) and $\text{Ca}^{2+} > \text{Mg}^{2+}$ (for M^{2+})

The transport mediator II_c transport all the studied cations except Mg^{2+} . The extent of transport efficiency by II_c is next only to I_c . Herein the transport order works out to be: $\text{K}^+ > \text{Rb}^+ > \text{Na}^+ > \text{Cs}^+ > \text{Li}^+$ and $\text{Ba}^{2+} > \text{Ca}^{2+}$

The greater transport efficiency displayed by Rb^+ than that of Na^+ is not a general phenomenon, and has been observed only for I_c and II_c .

From overall consideration it follows that the ligand I_a and II_a have a greatest preference for Li^+ , the ligands I_b and II_b have greatest preference for Na^+ while the ligands I_c and II_c display a distinct preference for K^+ . This may be broadly understood in terms of ligand flexibility and an apparent pseudocavity concept. Wherein the enhanced encircling provided by the ligand frame work tends to look for an increased ionic radius of the cation. The increase in encircling frame work is, of course accompanied by an increase in number of donor sites.

The transport behavior of Ba^{2+} is conspicuously different from that of Mg^{2+} or Ca^{2+} . Firstly, neither for Mg^{2+} nor for Ca^{2+} I_c and II_c display favored transport. Both these mediators, however, display significant transport efficiency towards Ba^{2+} . This disparity in transport pattern can be rationalized in terms of greater donor atom requirement of Ba^{2+} , than that of Mg^{2+} or Ca^{2+} . Secondly the extent of transport shown by Ba^{2+} is much higher at the same carrier concentration. This trend of transport behavior of M^{2+} is in sharp contrast to M^+ . Among M^{2+} the lowest charge density cation (Ba^{2+}) displays the reasonable transport efficiency provided the carrier fulfills the co-coordinative requirement of the cation. On the other hand, for M^+ , as will be evident from the following paragraphs. The lowest charge density to Cs^+ is not the cation of choice with regard the transport efficiency. It follows, therefore, that the mere numerical value of charge density is not important, but the inherent interactive characteristics, which are related to charge density are of considerable importance. Thus Cs^+ is rather an inert cation while Ba^{2+} is not so.

It is exciting to know that the behavior of all cations investigated in our work does not show concordance with each other. This is so because the intrinsic interactive requirements of a cation are distinctly different from that of the others. Consequently, some cations behave consciously as “demanding” cations whereas others are somewhat “less demanding” In essence the transport process is a consequence of the „contract“ between the cation and carrier. The successful operation of this contract depends on the extent of meeting the requirement of the cation by the mediator and vice versa. Any disproportionation in the mutual affinity may project one of the partners as a “demanding” partner.

The foremost guiding point in assessment of “demanding” cations is the point of start of this transport process versus other cations. In our work the cations Li^+ and Na^+ responded to the transport process right at the minimum concentration chosen for the present work $\text{Vis}, 0.1 \times 10^{-3} \text{ M}$. This, however, does not imply that the interactive requirements of Na^+ and Li^+ are same. A justification for this statement is obviously provided by different magnitudes of the transport displayed at the same concentration.

The solventphilic Mg^{2+} is apparently more demanding than Li^+ or Na^+ . It “refuses” to be transported at the lowest concentration level but at the next concentration level the process of transport eventually materializes. The cation K^+ , Rb^+ , Cs^+ , Ca^{2+} and Ba^{2+} are apparently even more demanding than Li^+ , Na^+ or Mg^{2+} . All the five cation display a little or no transport (transport less than $5 \times 10^{-8} \text{ mol/hour}$) can be concentration levels. However, in the successive concentration level they cease to dictate their terms beyond a certain limit.

The concentration level 1.0×10^{-3} has been deliberately chosen for comparative assessment of transport efficiency under common reaction conditions. This concentration level has the advantage of meeting the transport requirements of all cations in almost all conditions. Nevertheless, some instances of non-feasibility of transport have been noticed even at this concentration. These are $\text{Cs}^+ - \text{II}_a$, $\text{Ca}^{2+} - \text{II}_a$, $\text{Ba}^{2+} - \text{II}_a$, $\text{Rb}^+ - \text{II}_b$, $\text{Ba}^{2+} - \text{II}_b$ and $\text{Mg}^{2+} - \text{II}_c$ combinations. The lesser extent of transport shown by M^{++} relative to the corresponding M^+ has already been emphasized and is also viewed from a surmounting of these combinations not responding to the transport process. Interestingly, none of these six combinations involve I_a , I_b or I_c indicating that the greater efficiency of the set I carriers overcome the hurdles presented by any factor in the transport process.

Cation	Metal transported (in moles) after (by I_a)				$\text{J}_M \times 10^7 \text{ mol/hour}$
	12 hours	24hours	36 hours	48 hours	
Li^+	1.70E-04	3.43E-04	5.20E-04	6.50E-04	142
Na^+	0.9×10^{-5}	1.50E-05	2.40E-05	3.00E-05	63
K^+	1.70E-06	2.35E-06	2.53E-06	4.70E-06	0.98
Rb^+	1.00E-06	2.06E-06	3.10E-06	4.10E-06	0.86
Cs^+	1.00E-06	2.00E-06	3.10E-06	4.20E-06	0.87
Mg^{2+}	1.20E-05	2.00E-05	3.70E-05	5.00E-06	10.26
Ca^{2+}	1.00E-06	2.10E-06	3.20E-06	4.20E-06	0.88
Ba^{2+}	0	1.7×10^{-6}	2.60E-06	3.50E-06	0.73

Cation	Metal transported (in moles) after (by I_b)				$\text{J}_M \times 10^7 \text{ mol/hour}$
	12 hours	24hours	36 hours	48 hours	
Li^+	3.9×10^{-5}	3.43×10^{-4}	5.2×10^{-4}	6.5×10^{-4}	32.5
Na^+	2.25×10^{-4}	1.5×10^{-5}	2.4×10^{-5}	3.0×10^{-5}	187.6
K^+	1.53×10^{-5}	2.35×10^{-6}	2.53×10^{-6}	4.7×10^{-6}	12.8
Rb^+	0	1.60×10^{-6}	2.40×10^{-6}	3.31×10^{-6}	0.69
Cs^+	0	0	0	0	0
Mg^{2+}	1.71×10^{-6}	3.40×10^{-6}	5.12×10^{-6}	6.82×10^{-6}	1.42
Ca^{2+}	4.56×10^{-6}	9.42×10^{-6}	1.40×10^6	1.82×10^{-6}	3.8
Ba^{2+}	0	1.75×10^{-6}	2.63×10^{-6}	3.50×10^{-6}	0.73

Cation	Metal transported (in moles) after (by I_c)				$\text{J}_M \times 10^7 \text{ mol/hour}$
	12 hours	24hours	36 hours	48 hours	
Li^+	3.80×10^{-6}	7.70×10^{-6}	11.5×10^{-6}	1.50×10^{-6}	3.2
Na^+	1.32×10^{-4}	2.64×10^{-4}	4.00×10^{-4}	5.28×10^{-4}	110
K^+	3.50×10^{-4}	7.00×10^{-4}	10.52×10^{-4}	12.21×10^{-4}	292.8
Rb^+	1.90×10^{-4}	3.83×10^{-4}	5.70×10^{-4}	7.61×10^{-4}	159.6
Cs^+	1.50×10^{-5}	3.70×10^{-5}	4.60×10^{-5}	6.1×10^{-5}	12.8
Mg^{2+}	0	0	0	0	0
Ca^{2+}	2.67×10^{-6}	3.53×10^{-6}	8.00×10^{-6}	10.72×10^{-6}	2.23
Ba^{2+}	8.67×10^{-4}	1.73×10^{-4}	2.60×10^{-4}	3.50×10^{-4}	72.3

Cation	Metal transported (in moles) after (by II_a)				$\text{J}_M \times 10^7 \text{ mol/hour}$
	12 hours	24hours	36 hours	48 hours	
Li^+	1.26×10^{-4}	2.70×10^{-4}	3.80×10^{-4}	5.00×10^{-4}	105.3
Na^+	6.21×10^{-5}	1.32×10^{-4}	2.10×10^{-4}	2.50×10^{-4}	51.3
K^+	0	1.54×10^{-6}	2.40×10^{-6}	2.70×10^{-6}	0.64
Rb^+	0	1.54×10^{-6}	2.51×10^{-6}	3.10×10^{-6}	0.73
Cs^+	0	0	2.00×10^{-6}	2.80×10^{-6}	0.5
Mg^{2+}	1.20×10^{-5}	2.5×10^{-5}	3.50×10^{-5}	4.70×10^{-5}	9.7
Ca^{2+}	0	0	0	0	0
Ba^{2+}	0	0	0	0	0

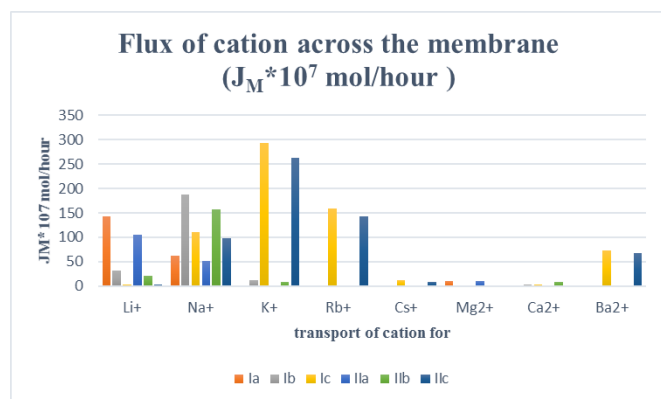
Cation	Metal transported (in moles) after (by II_b)				$\text{J}_M \times 10^7 \text{ mol/hour}$
	12 hours	24hours	36 hours	48 hours	
Li^+	2.60×10^{-5}	5.28×10^{-5}	8.20×10^{-5}	10.70×10^{-5}	2
Na^+	2.00×10^{-4}	2.50×10^{-4}	3.50×10^{-4}	4.40×10^{-5}	97.3
K^+	3.20×10^{-5}	6.50×10^{-5}	9.50×10^{-5}	13.00×10^{-5}	263
Rb^+	1.70×10^{-6}	3.50×10^{-6}	6.30×10^{-6}	7.00×10^{-6}	142.7
Cs^+	1.0×10^{-6}	2.20×10^{-5}	3.13×10^{-5}	4.00×10^{-5}	8.7
Mg^{2+}	0	0	0	0	0
Ca^{2+}	2.10×10^{-6}	4.28×10^{-6}	6.20×10^{-6}	7.80×10^{-6}	1.7
Ba^{2+}	8.2	2.00×10^{-6}	2.50×10^{-6}	3.10×10^{-6}	67.2

Cation	Metal transported (in moles) after (by II_c)				$\text{J}_M \times 10^7 \text{ mol/hour}$
	12 hours	24hours	36 hours	48 hours	
Li^+	2.60E-05	5.28E-05	8.20E-05	4.70E-05	2
Na^+	2.00×10^{-4}	2.50×10^{-4}	3.50×10^{-4}	4.40×10^{-5}	97.3
K^+	3.20×10^{-5}	6.50×10^{-5}	9.50×10^{-5}	13.00×10^{-5}	263
Rb^+	1.70×10^{-6}	3.50×10^{-6}	6.30×10^{-6}	7.00×10^{-6}	142.7
Cs^+	1.0×10^{-6}	2.20×10^{-5}	3.13×10^{-5}	4.00×10^{-5}	8.7
Mg^{2+}	0	0	0	0	0
Ca^{2+}	2.10×10^{-6}	4.26×10^{-6}	6.20×10^{-6}	7.80×10^{-6}	1.7
Ba^{2+}	8.2	2.00×10^{-6}	2.50×10^{-6}	3.10×10^{-6}	67.2

Cation	$\text{G}^0 (\text{H}_2\text{O}) \text{ Kcal/mol}$	$\text{J}_M \times 10^7 \text{ mol/hour}$						
		NegativeHydration	Carrier			Carrier		
			I_a	I_b	I_c	II_a	II_b	II_c
Li^+	63	142	32.5	3.2	105.3	21.7	2.2	
Na^+	98	63	187.6	110	51.3	157.8	97.3	
K^+	81	0.98	12.8	292.8	0.64	8.7	263	
Rb^+	76	0.86	0.69	159.6	0.73	0	142.7	
Cs^+	68	0.87	0	12.8	0.52	0	8.7	
Mg^{2+}	454	10.26	1.42	0	9.7	0.67	0	
Ca^{2+}	379	0.88	3.8	2.23	0	8.35	1.7	
Ba^{2+}	340	0.73	0.73	72.3	0	0	67.2	

In no case the order reversal in transport efficiency with increase in carrier concentration has been noticed; which is consistent with the normal pattern of transport. In other words the cation transport to a greater extent than the

neighboring cation continues to do so despite increases in carrier concentration. This observation together with the linearity in metal transport concentration give strength to the realization that the process is not a normal kinetic one governed by the rate law where the concentration decreases exponentially with respect to time, instead the process is genuine carrier facilitated one where the complexation and de-complexation at two different interfaces are complimentary to each other.



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Author Profile



Sourabh Muktibodh received his Master's, M.Phil. and Ph.D. degrees in Chemistry from school of studies in Chemistry, Vikram University Ujjain (M.P). His major field of interest in research is Crown- Ether chemistry although he has some publications in chemical kinetics and environmental chemistry. He has about 25 years of experience in teaching Physical Chemistry, spectroscopy and Group theory for post-graduate and graduate students. Presently he is professor of chemistry in a higher Education department of Govt. of Madhya Pradesh.