

**CARRIER-MEDIATED TRANSPORT OF  $\text{Ca}^{2+}$  BY TETRAETHYLENEGLYCOLDIACRYLATE USING BULK LIQUID MEMBRANE TECHNOLOGY****Poonam Ajwani<sup>1\*</sup>, Loni Lokwani<sup>2</sup>, Uma Sharma<sup>3</sup>**<sup>1</sup>Department of Chemistry, Jaipur Engineering College and Research Centre University, Jaipur-303905, Rajasthan, India.<sup>2</sup>Department of Chemistry, Govt. College, Kota-324001, Rajasthan, India.<sup>3</sup>School of Studies in Chemistry and Biochemistry, Vikram University, Ujjain-456010, MP, India.*\*Corresponding Author: Email: [poonamdec\\_14@rediffmail.com](mailto:poonamdec_14@rediffmail.com)*

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**ABSTRACT**

*Binding of metal ions through selective reagents are of special importance to broad areas of analytical chemistry and separation science. Bulk liquid membrane transport of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  was carried out through tetraethylene glycol diacrylate (TEGDAC) immersed in organic membrane viz. 1,2-dichloroethane, chloroform and carbon tetrachloride from picrate ( $\text{Pic}^-$ ), dinitrophenolate ( $\text{Dnp}^-$ ) and orthonitrophenolate ( $\text{Onp}^-$ ) salts. It was observed that the used podand has good efficiency to transport  $\text{Ca}^{2+}$  over other metal ions from its picrate salt. Variation in reduced concentration was also noted showing maximum at intermediate times. Transport ability of ligand and selectivity of  $\text{Na}^+$  over  $\text{K}^+$  were also observed by using coexisting picrate salts. The technique offers the advantages of active transport, possible usage of expensive carriers, high selectivity, low capital and operating cost in textile and food industry, hydrometallurgy, medicine, biotechnology and environment protection.*

**Keywords** – transport; carrier; picrate; selectivity; environment; separation.

**1. INTRODUCTION**

The mysterious chemical diversity of the cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) especially w.r.t. their membrane transport using natural as well as synthetic ionophores have attracted much attention and has been a challenge to a biochemist and to organic chemist.

The growth of applications based on membrane processes mimics the active sites in naturally occurring biological molecules and are very selective and sensitive sensors for analyzing the chemical composition of a medium, the environment or an organism through the determination of the concentration of the substances of interest. Chemical sensors could be used to detect individual molecules of a pollutant. The design and function of synthetic ionophores for recognition of metal ion are based on such diverse parameters as the structure and cavity size of the ligand, the stability and selectivity of its metal ion complexes.

The receptor properties of the podands make these compounds potentially very useful in the area of analytical chemistry *e.g.* ion selective electrodes, ion-channel sensors (ICSs), chemically modified electrodes (CMEs), solubilization of unusual species, cation transport, phase transfer catalysis, indicators, isotope separation etc.

The development of efficient and broad range sensing methods has important applications in the areas such as environmental control, quality checking or in the chemical characterization of an organism for medical diagnosis.

Present work deals with *in-vitro* studies of transport<sup>1</sup> studies of alkali and alkaline earth metal ions by TEGDac as a podand [Fig. 1]. Such studies will provide the knowledge of conformational changes of the ionophore by activation/deactivation which propose detailed mechanism for both binding and releasing property during transport through bulk liquid membranes and thus helps in development of better membrane separation technology. Recently, artificial liquid membrane has emerged as a novel and effective separation technique in the field of analytical chemistry due to specific complexation of guest molecule by the carrier<sup>2</sup>.

## 2. EXPERIMENTAL

### 2.1 Materials

Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, MgCO<sub>3</sub>, CaCO<sub>3</sub> and C<sub>2</sub>H<sub>5</sub>OH were obtained from Rankem and were used without further purification. Picric acid, 2,4-dinitrophenol and 2-nitrophenol were obtained from Loba and Himedia. 1,2-dichloroethane (DCE), chloroform and carbon tetrachloride were obtained from Loba and Qualigens. All metal salts prepared in solid form have been described earlier<sup>3</sup>.

### 2.2 Instrumentation

Metal estimation of Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup> and Ca<sup>2+</sup> was carried out by digital flame photometer (Systronics 128) and of Mg<sup>2+</sup> through atomic absorption spectrophotometer (Shimadzu 6300).

### 2.3 Procedure

Bulk liquid membrane transport experiment was carried out in a U-type<sup>4</sup> cell containing ionophore solution (25 ml), metal salt solution as a source phase (SP) (10 ml) in one end of tube and double distilled water as receiving phase (RP) (10 ml) in another end. Cation flux (J<sub>M</sub>) for transport studies was calculated by using the following eq.:

$$J_M = C_{(rec.)} V / At$$

where C<sub>(rec.)</sub> is concentration of cation in the receiving phase (mol/dm<sup>3</sup>), V is volume of receiving phase (mol/dm<sup>3</sup>), A is effective area of membrane (m<sup>2</sup>) and t is time in (s).

## 3. RESULTS AND DISCUSSION

We have carried out transport studies of alkali and alkaline earth metal cations (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) with TEGDac. The metal salt and ionophore concentration was varied from 1.0 x 10<sup>-1</sup> M to 1.0 x 10<sup>-6</sup> M for cations and the concentration of metal salt and ionophore was kept constant i.e. 1.0 x 10<sup>-3</sup> M.

The recommended mechanism for the liquid membrane transport technique is shown elsewhere<sup>5</sup> which contains two processes in a single stage in extraction of the metal ion from aqueous source phase to the hydrophobic organic membrane containing the host carrier with anion. This anion not only neutralizes the charged M<sup>Z+</sup> carrier complex but also induces a more lipophilic character to the metallic complex so that it can be readily extracted into the membrane phase. After complexation at the interface of source phase-membrane, the complex diffuses down its concentration gradient. The reextraction of this metal ion from the membrane to aqueous receiving phase occurs and the free carrier diffuses back across the membrane and cycle starts again. Hence, the overall

transport process consists of a mixture of diffusion steps and complexation/decomplexation reaction at two independent and possibly different interfaces<sup>6</sup>.

No detectable movement of cation from source phase into receiving phase was observed, suggesting that the transport of cations through the liquid membrane is carrier facilitated.

### **3.1 Effect of cation**

The ionophore shows maximum transport of  $\text{Ca}^{2+}$  in comparison to  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$ . The major difference between monovalent and divalent cations is not only the cation diameter but also the charge density. Divalent cations possess both a smaller size and a higher charge density than monovalent cations and this promises a stronger interaction with donor sites of the ligand.

$\text{Ca}^{2+}$ -ionophore interaction provides loose complex, which easily get dissociate at the membrane/receiving phase interface leading to more cation being transported into the aqueous receiving phase. It is also likely that the selectivity of  $\text{Na}^+$  [Table 1] and  $\text{Ca}^{2+}$  over  $\text{Li}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  is due to the greater lipophilicity of  $\text{Li}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$ . It can be explained by taking the fact that the amount of cation transported has the dependence on the amount release rather than the amount of cation uptake by ionophores<sup>7</sup>.

It was observed that the release of  $\text{Li}^+$  and  $\text{Mg}^{2+}$  takes place much slowly than uptake, allowing a much higher accumulation of both cations in the organic phase. The minimum transport behavior of  $\text{Li}^+$  and  $\text{Mg}^{2+}$  can be explained by assuming the smaller size and more charge density at the surface, which gets them solvated to a large extent than  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  by the formation of primary and secondary solvation spheres and hence bulkiness to it, due to which it gets tightly fit in pseudocyclic cavity<sup>8</sup> and lowers the chances to leave from ionophore in receiving phase. Thus, the amount of cation transported is inversely proportional to degree of solvation of cation in organic phase. Overall rate of transport depends upon the ratio  $K_{\text{complex}} / K_{\text{release}}$ .

The pseudocyclic cavity of ionophore requires some conformational changes to adopt cation which prefers the appropriate binding of  $\text{Na}^+$  in such a way that it gets released in receiving phase.

$\text{Na}$  complex has optimum stability with carrier while the carrier binding is too weak and unfavorable in case of  $\text{Li}$  complex results in insufficient amount of carrier transported. Binding of  $\text{K}^+$  complex with carrier is too tight and favorable, so the cation-carrier complex remains in organic phase at membrane-receiving phase interface which leads to the low amount of cation being transported into the receiving phase.

The observed trend for different cations across BLMs is;  $\text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Li}^+ \sim \text{Mg}^{2+}$ .

### **3.2 Effect of anion**

It has been reported earlier<sup>9</sup> that when uncharged ionophores are employed as carriers, the complexed cation carries its counter anion with it through the organic phase. The nature of associated counter anion should thus be a factor in determining the amount of cation transported<sup>10-12</sup>.

The trend of the effect of anion towards cation transport [Fig. 2-4] with all ligands is  $\text{Pic}^- > \text{Dnp}^- > \text{Onp}^-$ , but the amount transported is different. This is because that the charge on picrate anion is self-stabilized due to more delocalization of the charge than dinitrophenolates and orthonitrophenolates and hence less associated with the cations as well as picrate allows smaller Gibbs's free energy of hydration<sup>13</sup> and faster cation transport.

Due to higher charge density of  $\text{Li}^+$  and  $\text{Mg}^{2+}$ , they have a strong interaction with a higher charge density anion  $\text{Onp}^-$  ensuring less transport. While  $\text{Ca}^{2+}$  and  $\text{K}^+$  show the complexation with low charge density  $\text{Pic}^-$  anion and hence more transport of cation. The rate of cation transport is inversely related to the degree of solvation of the accompanying anion.

### 3.3 Effect of organic solvent

The degree of selectivity in transport is found to be strongly influenced by the identity of organic solvent. The physical and chemical properties of solvents are closely related to their structures and play important role in solute-solute and solute-solvent interactions in solutions. A solvent of low viscosity must be chosen to obtain the highest rate of transport in a particular system. Liquid membrane acts as a solvent for a transported solute whose transport is governed by its solubility in the membran<sup>14</sup>.

We observed the change in transport ability by replacing the membrane from 1,2-dichloroethane to chloroform and carbon tetrachloride. The observed ion transport ability of the ionophores in different solvents is: 1,2-dichloroethane > chloroform > carbon tetrachloride.

DCE membrane seemed to be more effective than chloroform and carbon tetrachloride. This may be due to the higher dipole moment of DCE which solvates ions the best. A fraction of C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> form 1,2-ethanediol in the presence of an aqueous M<sup>2+</sup> salt solution. It may act as a supporting ionophore with used non-cyclic ionophore and enhances the transport of cation across it towards receiving phase than other two membranes.

We found that CCl<sub>4</sub> does not provide a smooth flow of cations across membrane and produces a barrier to flow of cations.

The density and viscosity of solvents increase while dielectric constant, dipole moment and mutual water-solvent solubilities of the solvents decrease with an increase in chlorination. The decrease in mutual water-solvent solubilities suggests that interfacial boundary will be less distinct for CHCl<sub>3</sub> and C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> but very distinct for CCl<sub>4</sub>. The solvent with highest dipole moment will best solvate the cation transferred to the organic phase.

Higher viscosity of C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> restricts the diffusion of the M<sup>2+</sup>-ligand complex across the membrane, which is the rate determining step. It was reported that the concurrent increase in viscosity results in a steady decrease in the diffusivity of the carrier and also of the metal carrier-complex. The thickness of the boundary layers is a function of the rate at which the solvent is stirred, as well as its viscosity. No leakage of cation in the membrane was noted in the blank experiments. This indicates that the mode of transport is only carrier-facilitated.

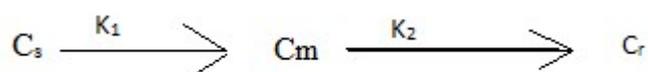
### 3.4 Effect of time on reduced concentration

The variation of the metal picrate concentration with time was directly measured in both source (C<sub>s</sub>) and receiving phases (C<sub>r</sub>). Due to practical reasons, the dimensionless reduced concentrations were used<sup>15</sup>.

$$R_s = C_s / C_{s0} ; R_m = C_m / C_{s0} ; R_r = C_r / C_{s0}$$

Where C<sub>s0</sub> is the initial Ca<sup>2+</sup> concentration in the source phase, while C<sub>s</sub>, C<sub>m</sub> and C<sub>r</sub> represent the Ca<sup>2+</sup> concentration in source, membrane and receiving phases respectively.

Due to material balance, R<sub>s</sub> + R<sub>m</sub> + R<sub>r</sub> = 1; so the kinetic behavior of the consecutive irreversible first order reaction can be described as follows:



K<sub>1</sub> and K<sub>2</sub> are membrane entrance and exit rate constants respectively. Variation in reduced concentration [Table 2] reveals that R<sub>s</sub> decreases exponentially with time accompanied by a simultaneously increase of R<sub>r</sub>; while R<sub>m</sub> presents maximum at intermediate time [Fig. 5].

### **3.5 Effect of carrier concentration**

The influence of carrier concentration in the organic phase on the transport efficiency of metal cations was studied. The transport efficiency was increased with the concentration of ionophore as carrier up to the optimum value ( $1 \times 10^{-3}$ ), after while transport efficiency decreases. It may be due to the adsorption of surface active species at the liquid-liquid interface that can produce an interfacial resistance, which reduces the mass transfer rate of other compounds across the interface<sup>16</sup>.

### **3.6 Effect of pH**

pH of source and receiving phase also influence on the transport efficiency of  $\text{Ca}^{2+}$  from its picrate salt and it was found that maximum transport of  $\text{Ca}^{2+}$  occurs at pH 5.0 through 1,2-dichloroethane [Fig. 6]. This pH may be attributed to the fact that higher pH values could result in the hydrolysis of the metal ion and lower pH value caused the protonation of ionophore which may hinder the accommodation of metallic ion in its pseudocyclic cavity at source phase-membrane interface.

### **3.7 Effect of temperature**

The effect of temperature on the reduced concentration of  $\text{Ca}^{2+}$  ions in receiving phase through 1,2-dichloroethane membrane containing  $1 \times 10^{-3}\text{M}$  carrier concentration was examined [Table 3] at 293K, 298K, 303K, 308K and 313K (200rpm). It was observed that maximum transport of  $\text{Ca}^{2+}$  occurs at 303K [Fig. 7]. It can be attributed by the fact that below 303K, complexation of  $\text{Ca}^{2+}$  with carrier at SP-membrane interface is much but its decomplexation at membrane-RP interface is quite low while at higher temperature complexation at first interface is low due to breakage of interaction between cation and carrier results in quite low releasing power of ionophore.

### **3.8 Competitive Transport**

The amount of cation transported with ionophore using co-existing salts of alkali metal ions ( $\text{M}^+ = \text{Na}^+$  and  $\text{K}^+$ ;  $\text{X}^- = \text{Pic}^-$ ,  $\text{Dnp}^-$  and  $\text{Onp}^-$ ) was observed as described under experimental section. The results indicate that both ionophores exhibit selectivity towards  $\text{Na}^+$  over  $\text{K}^+$  using picrate salts in 1,2-dichloroethane.

From Table 4, it is observed that selectivity decreased when binary mixtures of ( $\text{Na}^+$  and  $\text{K}^+$ ) salts were used in source phase [Fig. 8]. The reason for decreased selectivity in coexisting cations is due to the competition between both ions. TEGDAc is suitable carrier for cation which provides pseudocyclic conformation in such a way that complexation and decomplexation at source phase/membrane and receiving phase/membrane interfaces occur respectively.

## **4. CONCLUSION**

Carrier-mediated transport has been proved to be an alternative tool in various analytical fields. Ionophore used has the selectivity towards  $\text{Ca}^{2+}$  and the study could be used to explore the possibility of designing a new specific carrier for metal ion selective electrodes, drug delivery and drug designing etc.

## **5. ACKNOWLEDGEMENT**

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**Table 1:** Amount of cation transported in 24h by TEGDac through 1, 2-dichloroethane, chloroform and carbon tetrachloride membranes.

Metal salt concentration =  $1 \times 10^{-3}$  M; Ionophore concentration =  $1 \times 10^{-3}$  M

Metal salt	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>		CHCl <sub>3</sub>		CCl <sub>4</sub>	
	Cation transported (ppm)	Cation flux $J_M \times 10^{-9}$ (mol m <sup>-2</sup> sec <sup>-1</sup> )	Cation transported (ppm)	Cation flux $J_M \times 10^{-9}$ (mol m <sup>-2</sup> sec <sup>-1</sup> )	Cation transported (ppm)	Cation flux $J_M \times 10^{-9}$ (mol m <sup>-2</sup> sec <sup>-1</sup> )
Na.Pic	0.92	2.40	0.31	0.81	0.29	0.79
Na.Dnp	0.38	1.21	0.47	1.50	0.27	0.86
Na.Onp	0.23	0.94	0.25	1.02	0.30	1.22
K.Pic	0.25	0.61	0.18	0.44	0.09	0.22
K.Dnp	0.11	0.32	0.07	0.21	0.06	0.18
K.Onp	0.07	0.26	0.02	0.07	0.01	0.04
LiPic	0.00	-	0.00	-	0.00	-
Li.Dnp	0.00	-	0.00	-	0.00	-
LiOnp	0.00	-	0.00	-	0.00	-
Mg(Pic) <sub>2</sub>	0.00	-	0.00	-	0.00	-
Mg(Dnp) <sub>2</sub>	0.00	-	0.00	-	0.00	-
Mg(Onp) <sub>2</sub>	0.00	-	0.00	-	0.00	-
Ca(Pic) <sub>2</sub>	1.58	2.09	1.45	1.92	1.39	1.97
Ca(Dnp) <sub>2</sub>	1.05	1.69	0.97	1.57	0.45	0.73
Ca(Onp) <sub>2</sub>	0.54	1.12	0.43	0.89	0.42	0.87

**Table 2:** Reduced concentration of Ca<sup>2+</sup> present in source, 1,2-dichloroethane membrane and receiving phases in various intervals

Metal salt concentration =  $1 \times 10^{-3}$  M; Ionophore concentration =  $1 \times 10^{-3}$  M

Time (hrs.)	R <sub>s</sub>	R <sub>m</sub>	R <sub>r</sub>
0	1.00	0.00	0.00
4	0.75	0.06	0.19
8	0.47	0.15	0.38
12	0.29	0.18	0.53
16	0.24	0.12	0.64
20	0.16	0.09	0.75
24	0.14	0.05	0.81

**Table 3:** Reduced concentration of Ca<sup>2+</sup> in receiving phase at different temperatures in various intervals

Metal salt concentration =  $1 \times 10^{-3}$  M; Ionophore concentration =  $1 \times 10^{-3}$  M

Time (hrs.)	293K	298K	303K	308K	313K
4	0.02	0.03	0.06	0.05	0.03
8	0.07	0.11	0.15	0.12	0.08
12	0.1	0.15	0.18	0.16	0.13
16	0.06	0.08	0.12	0.09	0.08
20	0.02	0.05	0.09	0.06	0.03
24	0.01	0.02	0.05	0.04	0.01

**Table 4:** Amount of cation transported in 24h using coexisting metal picrate salts by TEGDac through 1,2-dichloroethane, chloroform and carbon tetrachloride membranes.

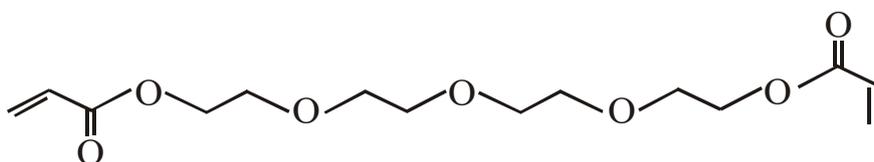
Metal salt concentration =  $1 \times 10^{-3}$  M; Ionophore concentration =  $1 \times 10^{-3}$  M

BLM	Na <sup>+</sup>		K <sup>+</sup>	
	Cation transported (ppm)	Cation flux $J_M \times 10^{-9}$ (mol m <sup>-2</sup> sec <sup>-1</sup> )	Cation transported (ppm)	Cation flux $J_M \times 10^{-9}$ (mol m <sup>-2</sup> sec <sup>-1</sup> )
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	0.58	1.51	0.18	0.44
CHCl <sub>3</sub>	0.15	0.39	0.13	0.32
CCl <sub>4</sub>	0.17	0.44	0.05	0.12

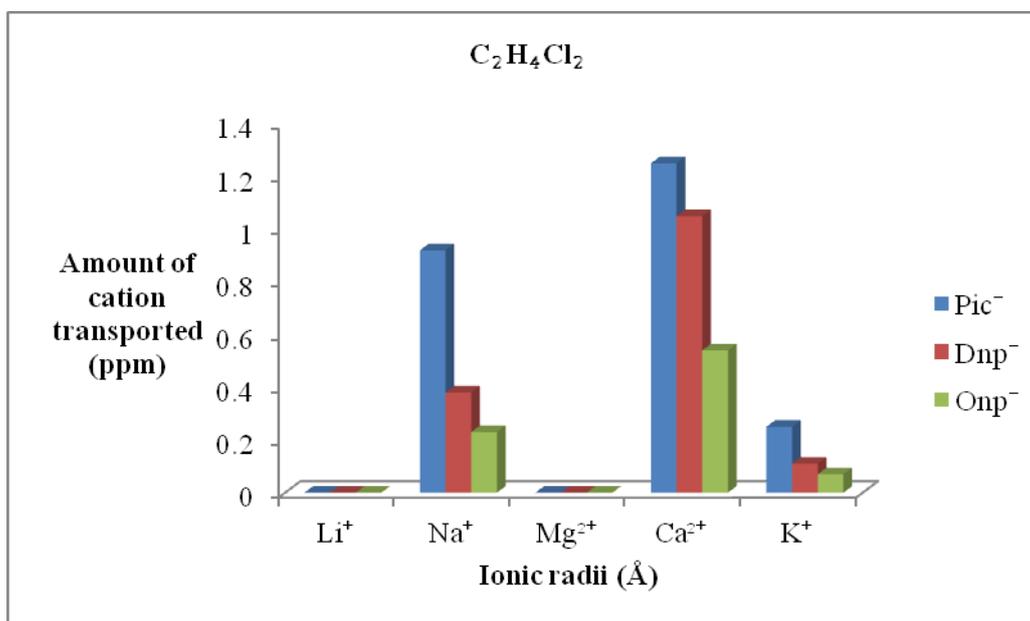
**Table 5:** Selectivity of Na<sup>+</sup> over K<sup>+</sup> in 24h using single and coexisting picrate salts into 1,2- dichloroethane, chloroform and carbon tetrachloride membranes containing TEGDac.

Metal salt concentration =  $1 \times 10^{-3}$  M; Ionophore concentration =  $1 \times 10^{-3}$  M

Ionophore	DCE		CHCl <sub>3</sub>		CCl <sub>4</sub>	
	Single	Binary	Single	Binary	Single	Binary
TEGDac	3.68	4.61	1.72	3.69	3.22	3.4



**Fig. 1:** Tetraethylene glycol diacrylate



**Fig. 2 :**

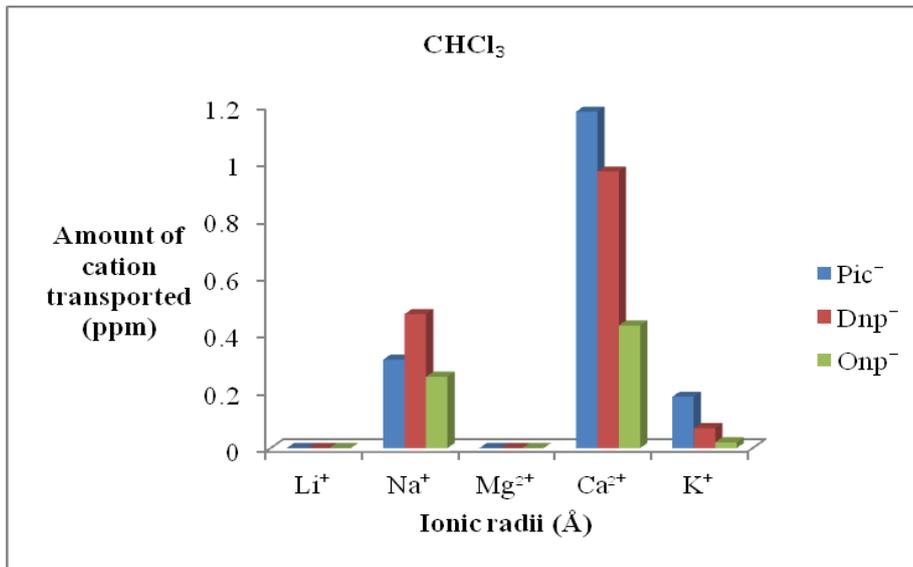


Fig. 3

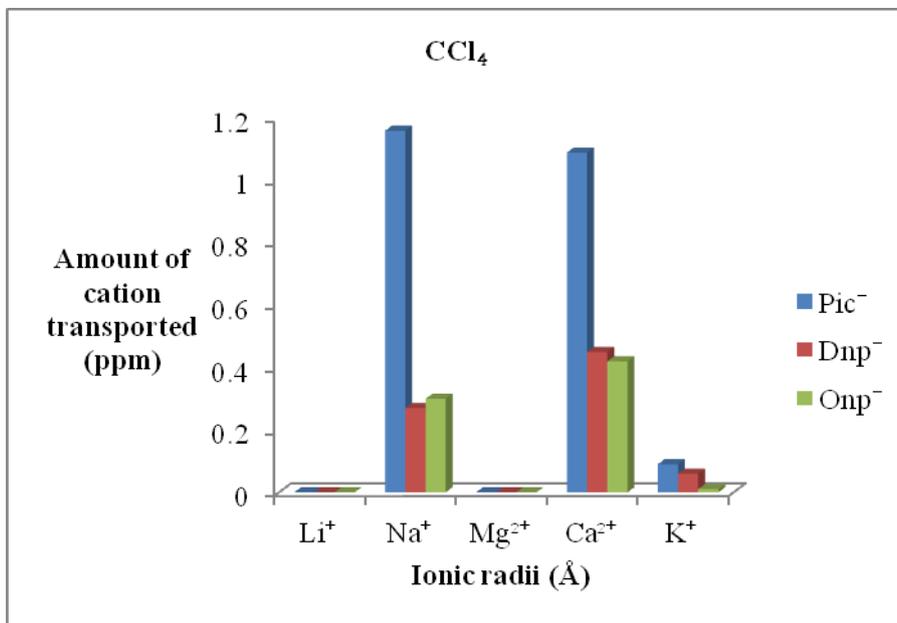


Fig. 4

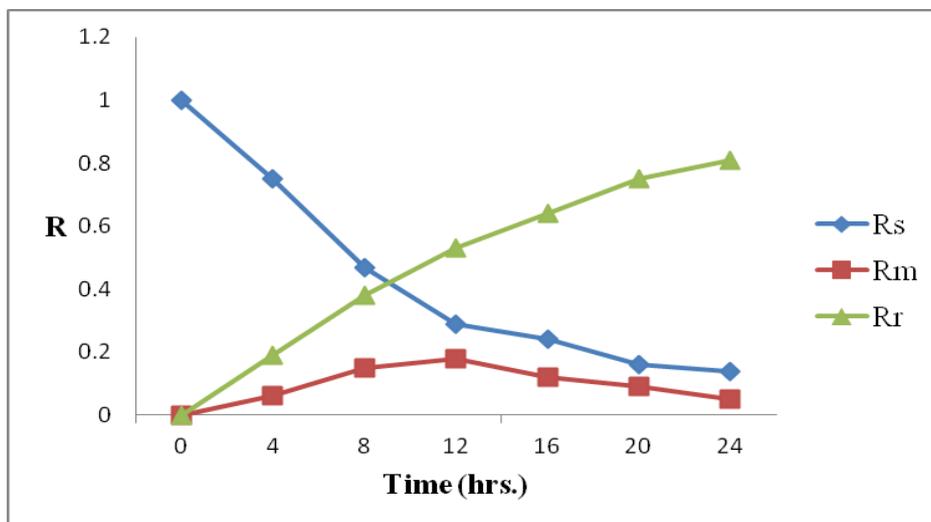


Fig. 5

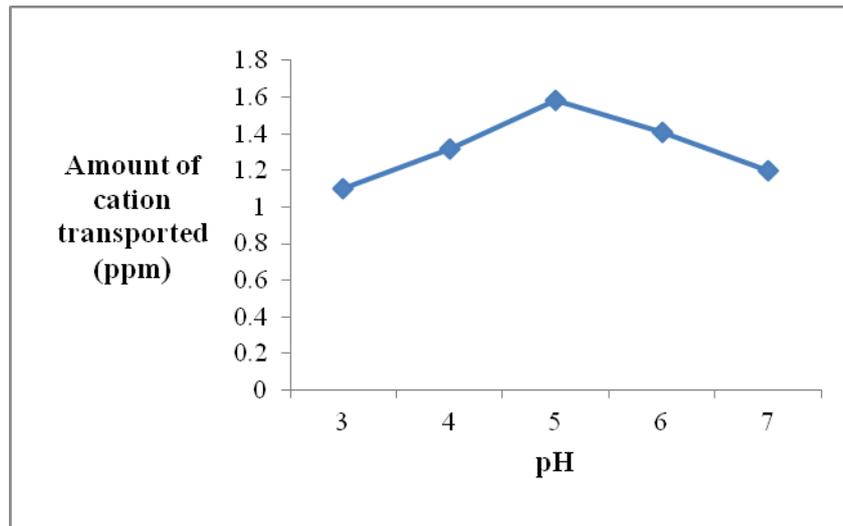


Fig. 6

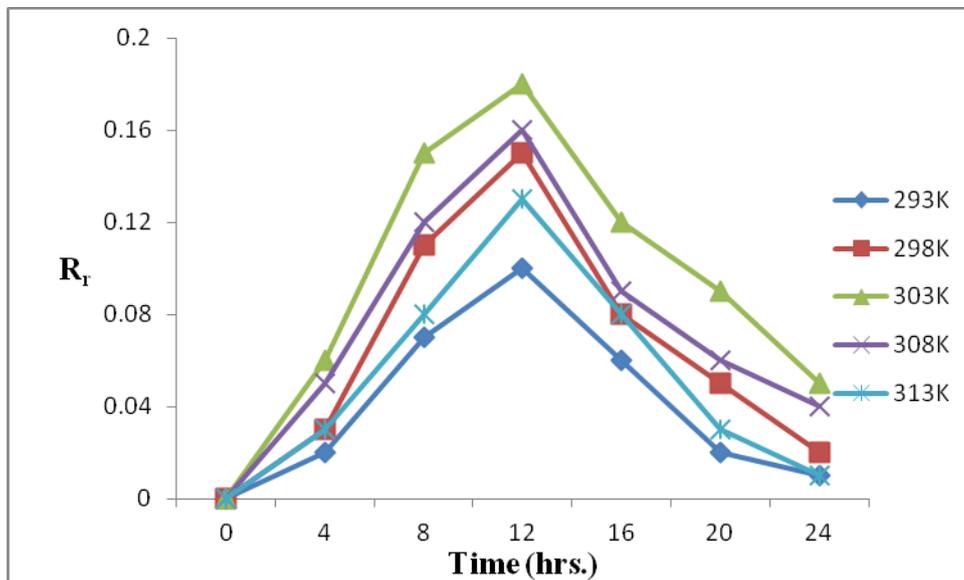


Fig. 7

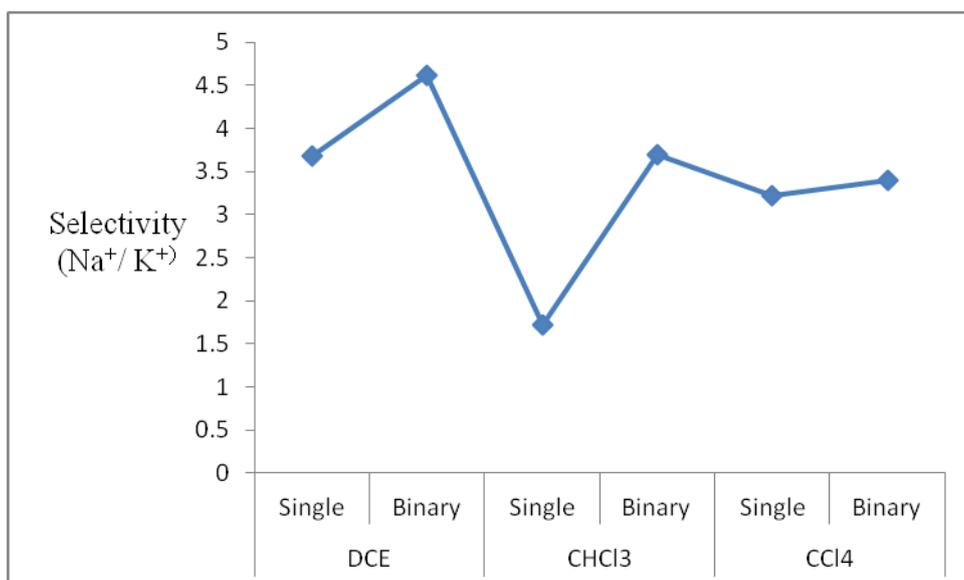


Fig. 8

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