EXTRACTION AND LIQUID MEMBRANE TRANSPORT OF SOME MAIN GROUP METAL IONS BY HEXAETHYLENE GLYCOL

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ABSTRACT

The extraction and carrier facilitated transport of Na^+, K^+, Mg^{2+} and Ca^{2+} picrates, dinitrophenolates, orthoniitrophenolates and thiocyanates were studied using hexaethylene glycol as a carrier through chloroform, 1,2, dichloroethane and carbon tetrachloride liquid membranes. K^+ and Ca^{2+} were selectively extracted into the organic phase, whereas no extraction of Na^+ and Mg^{2+} was observed. The selectivity for K^+ and Ca^{2+} was also observed using coexisting cations in the source phase. Na^+ is transported to a greater extent than K^+, whereas, the ionophore is an efficient carrier for the transport of both Mg^{2+} and Ca^{2+} ions. Poorer extraction and transport of cations were observed in CCl_4 than in $CHCl_3$ and CH_2ClCH_2Cl Higher extraction and transport of cations are observed for alkaline earth metal ions than alkali metal ions.

Interest in the development of new and improved tehniques for separation of ions and molecules has increased in recent years[1]. Much attention has been drawn towards the possible uses of liquid - liquid extraction[2] and membrane processes[3] in specific procedure for industrial and analytical importance. Several studies have shown that metal ions and molecules can be easily transported across liquid membrane by use of open chain equivalents of crown ethers[4] (podands). Besides host of possible commercial uses of liquid membrane systems may also be of much importance as models for cation transport across bio-membranes.

Keeping in view the above considerations we are reporting here extraction and carrier facilitated transport of Na^+, K^+, Mg^{2+} and Ca^{2+} picrates, dinitrophenolates, orthonitrophenolates and thiocyanates by hexaethylene glycol through $CHCl_3$, CH_2ClCH_2Cl and CCl_4 bulk liquid membrane systems.

RESULTS AND DISCUSSIONS

The blank experiments were carried out for extraction and transport studies for each salt in which membrane was devoid of carrier. No leakage of cation from source phase into organic layer was observed. All measurements were performed in duplicate to check reproducibility. Results are listed in Table 1 and 2. Relative amount of cations transported in $CHCl_3$, CH_2ClCH_2Cl and CCl_4 are shown in figures 1,2 and 3 respectively.

The results of extraction studies for single metal ion species indicate that ionophore extract only K^+ and Ca^{2+}. No extraction of Na^+ and Mg^{2+} was observed. This is expected because K^+ and Ca^{2+} hexaethylene glycol complexes are more stable than the corresponding Na^+ and Mg^{2+} ones, due to the larger chain length of hexaethylene glycol which is suitable for larger size[5] of K^+ and Ca^{2+} ions. This justifies the higher extraction of K^+ and Ca^{2+} by the ionophore. The competitive extraction of alkali metal ions (Na^+ and K^+) and alkaline earth metal ions (Mg^{2+} and Ca^{2+}) indicates that the ionophore also exhibits selectivity towards K^+ when Na^+ and K^+ exist together and towards Ca^{2+} when Mg^{2+} and Ca^{2+} exist together. This selectivity of hexaethylene glycol for K^+ and Ca^{2+} is almost comparable to that of the cyclic polyethers[6]. Interestingly, this trend is in line with the results obtained using a non-cyclic polyether containing the 3-carboxy-2-hydroxy phenyl group as one terminal group as a carrier through a $CHCl_3$ membrane, suitable to transport of alkaline earth metal ions but not alkali metal ions[7]

From the results of transport studies it is observed that a hexaethylene glycol is a better carrier for Na^+ than for K^+. This is expected because of the higher stability of K^+ hexaethylene glycol complexes

Table - 1 : Amount of cation extracted into an organic phase in 5 h using sodium, potassium, magnesium and calcium salts by hexaethylene glycol in chloroform, 1,2 dichloroethane and carbon tetrachloride

Source phase 10ml, 1.0 x 10^{-3} M metal salt in aqueous phase
Organic phase 10ml, 1.0 x 10^{-3} M ionophore in an organic solvent

S. No.	Metal Salt	$CHCl_3$		CH_2ClCH_2Cl		CCl_4	
		Cation extracted ppm	D_M	Cation extracted ppm	D_M	Cation extracted ppm	D_M
1.	NaPic	00	00	00	00	00	00
2.	NaDnp	00	00	00	00	00	00
3.	NaOnp	00	00	00	00	00	00
4.	NaSCN	00	00	00	00	00	00
5.	KPic	05	0.14	10	0.15	00	00
6.	KDnp	05	0.16	35	0.77	00	00
7.	KOnp	05	0.14	10	0.14	00	00
8.	KSCN	00	00	00	00	10	0.33
9.	$Mg(Pic)_2$	00	00	00	00	00	00
10.	$Mg(Dnp)_2$	00	00	00	00	00	00
11.	$Mg(Onp)_2$	00	00	00	00	00	00
12.	$Ca(Pic)_2$	08	0.02	35	0.27	04	0.25
13.	$Ca(Dnp)_2$	18	0.04	09	0.07	00	00
14.	$Ca(Onp)_2$	39	0.23	15	0.24	06	0.04

Table - 2 : Amount of cation transported after 24 h using sodium, potassium, magnesium and calcium salts by hexaethylene glycol in chloroform, 1,2 dichloroethane and carbon tetrachloride

Source phase 10ml, 1.0 x 10^{-3} M metal salt in aqueous phase
Membrane 1.0 x 10^{-3} M ionophore in 25ml organic solvent
Receiving Phase 10ml, double distilled water

S. No.	Metal Salt	$CHCl_3$		CH_2ClCH_2Cl		CCl_4	
		Cation transported ppm	J_M x (10^{-8}) mol/m²/s	Cation transported ppm	J_M x (10^{-8}) mol/m²/s	Cation transported ppm	J_M x (10^{-8}) mol/m²/s
1.	NaPic	02	4.43	5.5	12.1	03	6.64
2.	NaDnp	0.5	1.10	7.5	16.6	02	4.43
3.	NaOnp	3.5	7.75	7.5	16.6	02	4.43
4.	NaSCN	1.5	3.32	1.5	3.32	2.5	5.54
5.	KPic	2.41	3.13	2.25	2.94	3.1	4.05
6.	KDnp	0.91	1.17	1.95	2.54	0.65	0.84
7.	KOnp	0.75	0.98	2.1	2.74	0.60	0.78
8.	KSCN	1.4	1.82	0.8	1.04	0.55	0.71
9.	$Mg(Pic)_2$	20	42.4	20	42.4	19	40.3
10.	$Mg(Dnp)_2$	03	6.37	13	27.6	17	36.1
11.	$Mg(Onp)_2$	16	33.9	15	31.8	13	27.6
12.	$Ca(Pic)_2$	19	24.2	10	12.7	19	24.2
13.	$Ca(Dnp)_2$	15	19.1	12	15.2	51	64.9
14.	$Ca(Onp)_2$	14	17.8	16	20.3	58	73.9

than that of Na^{+} ones[8]. Na^{+} forms a lesser stable complex with the ionophore which is easily dissociated at the membrane receiving phase interface leading to more cations being transported into the aqueous phase. The ionophore showed almost the same transport ability for both Mg^{2+} and Ca^{2+} ions.

There was no effect seen when changing the counter-anion on the extraction of cations, whereas, anions played an important role in their transport. Increased transport is observed for picrates, dinitrophenolates and orthonitrophenolates, whereas, negligible transport is observed for thiocyanates. The lipophilicity of the anion might play an important role here.

In the present investigations, it is found that the order of solvents for extraction of cation is $CH_2CtCH_2Cl > CHCl_3 > CCl_4$ and for transport of cations is $CHCl_3 \cong CH_2ClCH_2Cl > CCl_4$. Poorer extraction and transport of cations was observed in CCl_4 than in $CHCl_3$ and CH_2ClCH_2Cl [9]. This may due to the low dipole moment of CCl_4 and higher charge density than that of others. The solvent with higher dipole moment will best solvate the ions transferred into the organic phase consequently, it is expected that $CHCl_3$ and CH_2ClCH_2Cl will extract the cations into the membrane complex to a greater extent.

Higher extraction and transport values are observed for alkaline earth metal ions than alkali metal ions. The major difference between monovalent and divalent cations is not only the cation diameter but also free energy of hydration. The divalent cations possesses much higher free energy of hydration than monovalent cations and this promises stronger interaction with donor oxygen atoms of ligand as well as water molecule.

No optimum pH is observed for extraction and transport of cations.

A comparison with our earlier results[10] shows that the amount of cation transported increases when hexaethyelene glycol is used as a carrier. This is due to increase in chain length of donor atoms.

In conclusion, selectivity of hexaethylene glycol for K^{+} and Ca^{2+} during extraction is observed. Suitable modifications and variation of parameters can lead to the effective separation techniques and useful for the design of ion selective electrodes[11]. Further investigations concerning to new non-cyclic polyethers exhibiting cation selectivity are in progress.

EXPERIMENTAL

Hexaethylene glycol was obtained from Aldrich. Analytical grade chemicals and solvents were used for all experiments. Metal picrates (MPic), dinitrophenolates (MDnp), orthonitrophenolates (MOnp) were prepared as reported earlier[12]

Extraction Studies : For extraction[13], the 10 ml of 1.0 x 10^{3} M aqueous metal salt solution was vigorously stirred with 10 ml of 1.0 x 10^{3} M ionophore solution in an organic solvent in a small beaker using magnetic stirrer (100 rpm). The beaker was covered and kept in a thermostated incubator (25 ± 1°C). The amount of cation in aqueous phase was initially determined. After 5 hours of stirring the mixture was allowed to stand for 5 minutes for the separation of two phases. The depleted aqueous phase was removed and analysed for metal content using a Philips 7700 double beam atomic absorption spectrophotometer. The amount of cation extracted by the ionophore was found by determining its difference in aqueous phase before and after extraction. Values of distribution ratio were calculated as follows[11]

$$D_M = \frac{\text{Total concentration of metal ion in organic phase}}{\text{Total concentration of metal ion in aqueous phase}}$$

Transport measurements : Transport experiments were performed in a U-tube glass cell[15] placed in a thermostated incubator (25 ± 1°C). The 1.0 x 10^{-3} M carrier in 25 ml of organic solvent was placed in the bottom of the U-tube serving as the membrane. 10 ml of 1.0 x 10^{3} M aqueous metal salt solution was placed in one limb of the U-tube serving as source phase 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 phase i.e. source and receiving phases 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 receiving phase after 24 hours and analysed for cation transported using atomic absorption spectrophotometer.

Fig.1 : Amount of alkali and alkaline earth metal ions tansported using hexaethylene glycol in chloroform

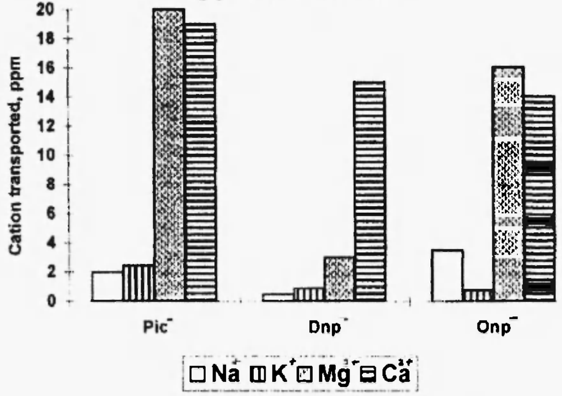


Fig.2 : Amount of alkali and alkaline earth metal ions tansported using hexaethylene glycol in 1,2 dichloroethane

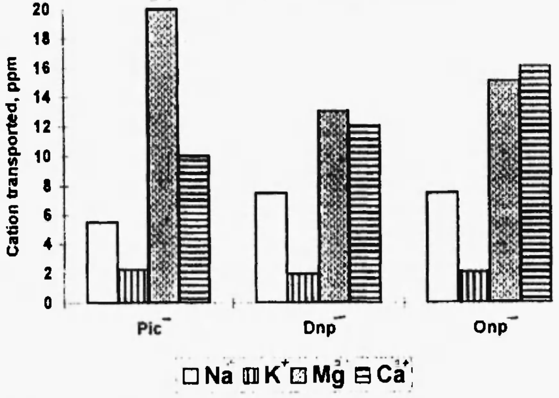
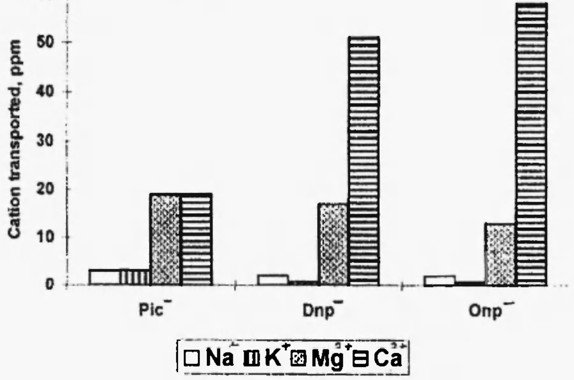


Fig.3 : Amount of alkali and alkaline earth metal ions tansported using hexaethylene glycol in carbontetrachloride



Cation flux values were calculated by using the relation[16]

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

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

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