SELECTIVE TRANSPORT AND EXTRACTION OF ALKALI METAL CATIONS (Na$^+$ & K$^+$) THROUGH CHLOROFORM LIQUID MEMBRANE BY DIETHYLENE GLYCOL MONOBUTYL ETHER AND DIETHYLENE GLYCOL DIBUTYL ETHER

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Abstract

A liquid membrane containing diethylene glycol monobutyl ether (2) shows specificity for K$^+$ ion in transport while diethylene glycol dibutyl ether (1) was selective for Na$^+$ over K$^+$. As an extractant, ligand 2 exhibited pronounced extraction selectivity for K$^+$ over Na$^+$ in comparison with ligand 1.

Introduction

Podands are marked by their rapid complexation kinetics which make them particularly interesting for biological investigations [1]. For *in vitro* studies of membrane integrated phenomena liquid membranes can be used very effectively. The study reported here is an attempt to compare the capacity of podands '1' and '2' (Fig. 1) as extractant and carrier for the alkali metal cations (Na$^+$ & K$^+$) using metal picrate (M Pic) and metal dinitrophenolate (M Dnp) salts respectively. Results can be used to design specific synthetic carrier ionophores for understanding biological phenomenon as well as for separation techniques in industries.

Materials and Methods

All the alkali metal salts used in the present study were prepared as reported earlier [2]. All the podands were obtained from Fluka.

The liquid membrane system was adapted from the work of Kobuke *et al.* [3] and is similar in principle to the Schulmann Bridge [4] used by Cussler, Smid and other co-workers (Fig. 2). The source phase comprised of aqueous metal salt solution (1 × 10^{-3} M) whereas the receiving phase was simple deionized water. A chloroform layer containing 1 × 10^{-3} M '1' or '2' constitutes the membrane phase. The apparatus used was firmly sealed to prevent evaporation of the chloroform phase. At least
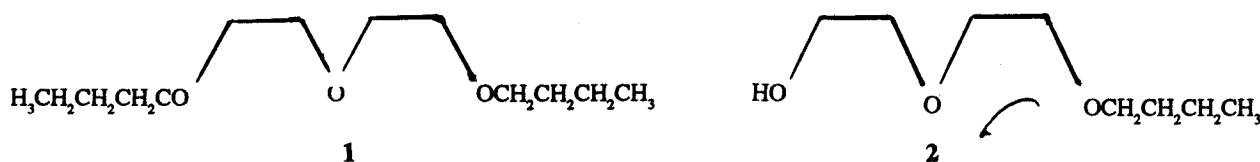

Figure 1

Keywords: Alkali metal cations (Na$^+$ & K$^+$); Extraction; Liquid membrane; Podands; Transport

a. Receiving phase
b. Source phase
c. Liquid membrane
   containing ligand
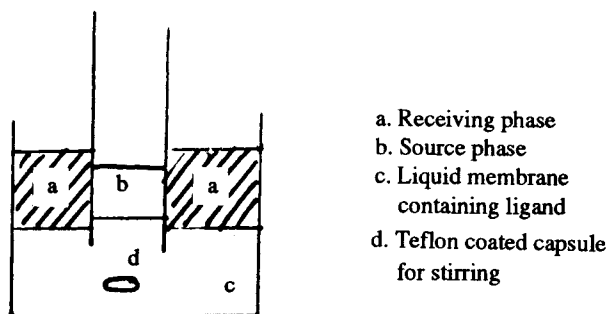d. Teflon coated capsule
   for stirring

Figure 2

three separate units were employed in the determination of cation transport for each salt-podand combination. One of these contained a blank membrane having no podand as carrier, while the other sets contained a carrier.

Samples were pipetted from receiving phase after 24 hours and were analyzed for cation (Na^+ & K^+) concentrations on an atomic absorption spectrophotometer. The results are summarized in Table 1.

Extraction studies were carried out by shaking a chloroform solution of the podand (1×10^{-3} M) with an equal volume of an aqueous solution of alkali metal salt

(1×10^{-3} M) for one hour in a beaker at room temperature. A magnetic stirrer driven at 600 rpm was used for shaking. The aqueous phase was separated and analyzed for the amount of cation extracted using atomic absorption spectrophotometer, whereas the organic phase was recovered and back reaction was studied by vigorously stirring (at 600 rpm) the solution with an equal volume of deionized water for a further hour. The results are summarized in Table 2. D_m and log K_{ex} were also calculated and are tabulated in Table 6.

Results and Discussion

Transport and Extraction Studies

In blank experiments where chloroform membrane contained no carrier, no detectable amount of cation was found to be transported or extracted.

Results of the transport studies given in Table 1 show that the ligand 1 was selective for Na^+ over K^+ and the selectivity order is in the sequence $Na^+ > K^+$. But ligand 2 shows specificity for the transport of K^+ ion. Table 2 gives the results of extraction studies. It shows that ligand 2 exhibited pronounced extraction selectivity for K^+ in comparison with ligand 1. For both 1 & 2, selectivity is in the order $K^+ > Na^+$.

Maximum extraction of cation took place within the

Table 1. Amount of Na^+ and K^+ cation transported in 24 hours

Metal Salt	Ligand 1- % transport			Ligand 2 - % transport	
	Na^+	K^+	Na^+/K^+	Na^+	K^+
M Pic	10.87	0.19	56.32	0.00	0.39
M Dnp	6.52	0.13	50.15	0.00	0.26
M Onp	6.52	0.13	50.15	0.00	0.26

Reproducibility ±7%

Table 2. Amount of cation extracted into an organic phase in one hour

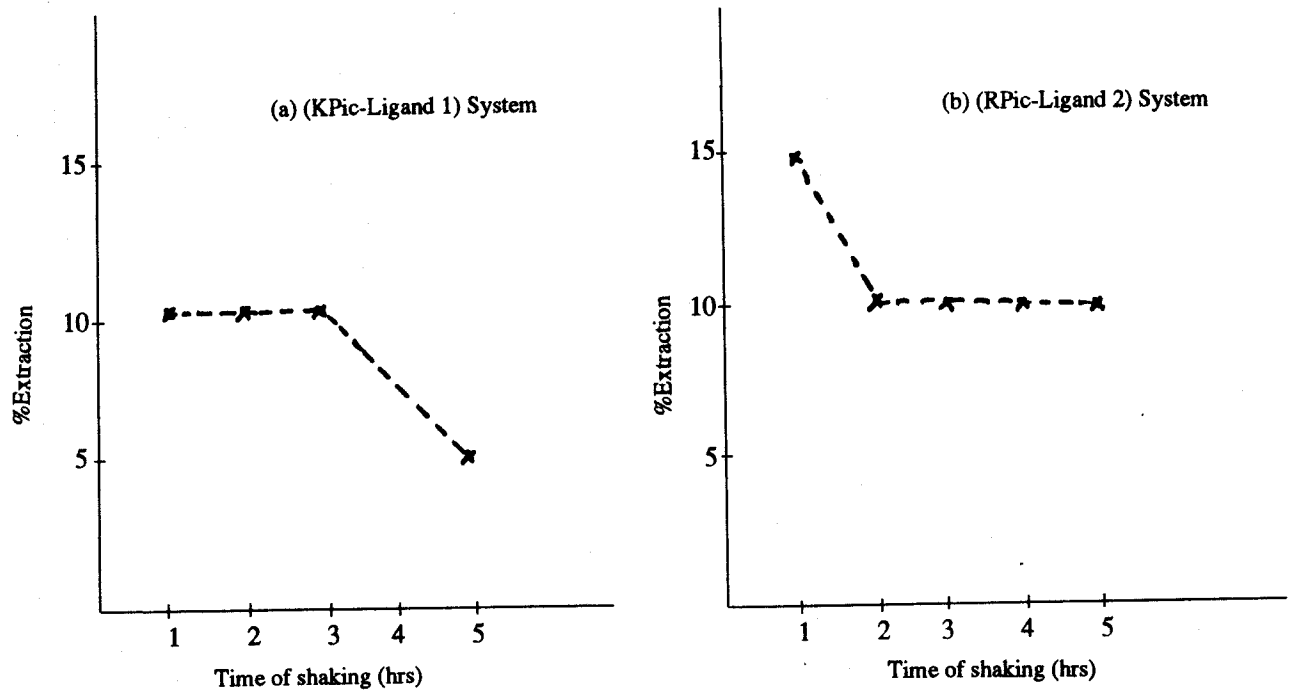| Metal Salt	Ligand 1- % extraction		Ligand 2 - % extraction	
	Na^+	K^+	Na^+	K^+
M Pic	0.00	7.5	0.00	15
M Dnp	0.00	0.00	0.00	15
M Onp	0.00	15	0.00	35

Reproducibility ±7%

Figure 3

Table 3. Simple transport studies

a) Ligand 1-conc.variation
[NaPic]= 1×10^{-3} M

[1] (M)	Cation trans-ported (ppm)
10^{-1}	1
10^{-2}	1.5
10^{-3}	2.5
10^{-4}	1.0
10^{-5}	1.0

b) Picrate conc. variation
[1]= 1×10^{-3} M

[NaPic] (M)	Cation trans-ported (ppm)
10^{-1}	0.5
10^{-2}	0.5
10^{-3}	2.5
10^{-4}	0.5
10^{-5}	0

c) Ligand 1-conc.variation
[KPic]= 1×10^{-3} M

[1] (M)	Cation trans-ported (ppm)
10^{-1}	0
10^{-2}	0.025
10^{-3}	0.075
10^{-4}	0
10^{-5}	0.025

d) Picrate conc. variation
[1]= 1×10^{-3} M

[KPic] (M)	Cation trans-ported (ppm)
10^{-1}	-
10^{-2}	-
10^{-3}	0.075
10^{-4}	0.025
10^{-5}	0.025

first one hour indicating that the time for attaining equilibrium is one hour (Fig. 3 (a) & (b)). For back reaction studies, aliquots from the loaded organic phase were withdrawn and subsequently back extracted for about one hour with the same volume of the strippant which is deionized water in the present study. Extraction studies were conducted at stirring efficiency varying from 400-600 rpm. No notable difference could be observed.

Effect of Anions

The concentrations of Na$^+$ and K$^+$ ions transported were determined by using various anions (Pic$^-$, Dnp$^-$ and Onp$^-$). Maximum amount of transport was observed when counter anion was Pic$^-$. Maximum extraction of cations took place when the counter anion was Onp$^-$. The maximal metal (K$^+$) loading of the organic phase for ligands 1 and 2 was 38.5% and 89.7% respectively when counter anion was Onp$^-$. When Pic$^-$ was used as the counter anion, the metal loading (K$^+$) was only 19.5% and 38.5% for ligands 1 and 2 respectively.

Effect of Concentration Variation

For optimizing concentration for transport and extraction studies, we have conducted different sets of experiments by varying the concentration of metal salt (M Pic, M Dnp, M Onp where M= Na$^+$ or K$^+$) and ionophore ('1' or '2'). The range selected varied from 1×10^{-1} M to 1 $\times10^{-5}$ M. Results for NaPic-ligand 1 and KPic-ligand 1 systems are given as examples in Tables 3(a), (b), (c) and (d). The results led to the conclusion that optimum concentration was 1×10^{-3} M.

Effect of End Groups

Ligand 1 showed pronounced transport selectivity for Na$^+$ while ligand 2 was selective for K$^+$. But both ligands 1 & 2 extracted K$^+$ ion selectively over Na$^+$. Thus, a reversal in selectivity was observed in extraction studies.

A team in our laboratory conducted transport and extraction studies with diethylene glycol and its derivatives (viz. diglyme, diethylene glycol dibenzoate) [5]. On comparing the amount of cation extracted by the above mentioned ligands with that of ligands '1' & '2', it was observed that ligand 2 is the best extractant for K$^+$ ion. The terminal butyl group is bulkier in comparison to glycol and causes steric hinderance in the molecule, thus reducing ligand flexibility.

Cation-ligand complex, formed because of the conformational changes undergone by the end groups of ligand 2, is more stable and the pseudocyclic cavity is suitable for the size of K$^+$ ion.

Calculation of D$_m$ and log K$_{ex}$

The D$_m$ and log K$_{ex}$ values were calculated by

considering the following equilibrium.

$$M_{aq}^{m+} + m\ A_{aq}^- + n\ \text{Podand org.} \xrightarrow{K_{ex}} [M(Podand)_n (A)_m]$$
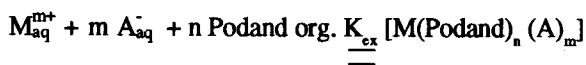
Maximum extraction of the metal ions occurred at a pH range of 6.5-7.8. The equilibrium constant [6] will be given by the following equation:

$$K_{ex} = \frac{[M(Podand)_n\ A_m]_{org}}{[M^{m+}]_{aq}\ [A^-]_{aq}^m\ [Podand]_{org}^n} \tag{1}$$

Distribution Coefficient [7]

$$D_m = \frac{\text{Total conc. of metal ion in org. phase}}{\text{Total conc. of metal ion in aq. phase}}$$
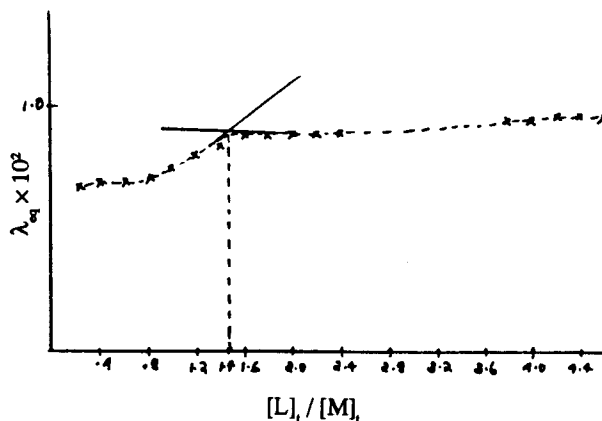
i.e. $\dfrac{[M(Podand)_n\ A_m]_{org}}{[M^{m+}]_{aq}}$

Figure 4. λ_{eq} vs [L]$_t$/[M]$_t$ plot for NaPic complex with Ligand-1 in methanol at 25°C

Table 4

[Ligand] = 1×10^{-3}M   [M Pic] = 1×10^{-3} M

Ligands	Amount of cation extracted in ppm	
	Na$^+$	K$^+$
*Diethylene glycol	3	3.2
*Diglyme	1	5
*Diethylene glycol dibenzoate	15	15
1	0	7.5
2	0	15.00

*Ref.4

Therefore, from equation (1)

$$K_{ex} = \frac{D_m}{[A^-]_{aq}^m \, [Podand]_{org}^n}$$ (2)

On rearranging equation (2),

$$\log \frac{D_m}{[A^-]^m} = n \log [Podand]_{org} + \log K_{ex}$$

We have determined the value of 'm' and 'n' for all the M salt-ligand systems by the conductometric method [7]. The conductance measurements were made on conductivity bridge of Systronics (model no. 304). A cell having a cell constant of one was used. Experimental procedure was the same as described by Takeda[8]. The data for the NaPic-ligand 1 system is given as an example in Table 5. λ_{eq} vs $[L]_t/[M]_t$ plot is shown in Fig. 4. As the graph indicates that a 1:1 complex is formed, m= 1 and n= 1. This stoichiometry was used for the calculation of log K_{ex} and D_m values for

Table 5. $[L]_t/[M]_t$ and λ_{eq} values of NaPic/Ligand 1 system

$[L]_t/[M]_t$	$\lambda_{eq} \times 10^2$
0.2000	0.9129
0.5996	0.9216
1.0000	0.9351
1.4002	0.9578
1.8053	0.9676
2.2007	0.9701
2.6020	0.9704
3.0007	0.9753

$[L]_t$ and $[M]_t$ -- Total ligand and metal concentrations. λ_{eq} -- Equivalent conductance.

Table 6. D_m and log K_{ex} values of KX/Podand system in chloroform X= Pic, Dnp or Onp

Ligand	D_m			log K_{ex}		
	M Pic	M Dnp	M Onp	M Pic	M Dnp	M Onp
1	0.375	-	0.25	5.57	3.00	5.40
2	0.429	0.429	0.875	5.63	5.63	5.94

K_{ion}^+ (Table 6).

The results considered here lead to the conclusion that the podand with a 'butyl' and a 'hydroxyl' end group works as a good carrier and extractant for Na$^+$ and K$^+$. When compared to the podands with 'hydroxyl' or 'methoxy' end groups [9], diethylene glycol monobutyl ether shows highest discrimination between Na$^+$ and K$^+$.

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