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Extraction of alkali metal cations into various organic liquid membranes using dipropyleneglycoldibenzoate as carrier

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ABSTRACT

Extraction of Na^+, K^+ and Li^+ ions have been studied using dipropyleneglycoldibenzoate as carrier through organic liquid membranes viz. 1,2-dichloroethane, chloroform and carbontetrachloride. Picrates, dinitrophenolates and orthonitrophenolates have been used as anions. Higher extraction values were observed for Na^+ than K^+ and Li^+ from picrate salts in 1,2-dichloroethane. K^+ cation distributes itself to much extent among all cations. The results of extraction studies reveal that this selectivity can be used for fabrication of ion selective electrodes and sensors.

Keywords: Extractant, Complexation, liquid membrane, Podands.

INTRODUCTION

Separation phenomenon through molecular recognition of the host compound has widely been used by incorporation of ionophores into solvent extraction or liquid membranes [1-4]. Amongst the various extracting systems, liquid membrane technology for the separation process is increasingly being intensified which restricts lengthy extraction times, automation challenges and use of large organic solvents used in the traditional liquid-liquid extraction techniques [5]. A new modified process of solvent extraction is liquid membrane [6].

The extraction of analyte through ionophore can be controlled [7] by complex formation and their stability for the particular set of experimental conditions. The use of non cyclic polyethers can permit effective conformational changes in the binding of particular ion. Binding and selectivity of podands towards metal cations, and their enhanced complexation can be achieved by the addition of aromatic end groups to simple glycols [8] using bulk liquid membrane (BLM) and supported liquid membrane (SLM) for the separation [9] of Li^+, Na^+, K^+, Ca^{2+} and Mg^{2+}.

Along with the crown ethers and cryptands, the non cyclic polyethers are major class of supramolecular host. These receptors have the possibility to form interesting complexes by forming pseudocyclic cavity exhibiting extractability and selectivity by trapping the metal ions. Like the cyclic ionophore, the metal ion binding chemistry of non cyclic ionophores for extraction study, complexation is necessary between metallic ion and ionophore used in the study which is further affected by the anion present and size of cation. Use of proper mobile carrier in liquid membrane increases both flux and selectivity of the membrane. In the present study, dipropyleneglycoldibenzoate (DPGDB) has been shown to be a suitable carrier for extraction of alkali metal ions in liquid membrane. The complexation is characterized by favourable enthalpy and entropy change [10].

Due to good selectivity and efficiency in the presence of mobile and selectively agent, liquid membrane technology has taken a considerable, sophisticated attention in various fields [11] over conventional techniques viz. in the cleaning of waste water by the removal of soluble metal species [12], recovery of metals from ores and waste water [13]. For the efficient extraction through ionophore, its structural feature must be complementary with those of the guest [14].

Lipophilicity and thermodynamic stability also influence extraction efficiency in two phase solvent extraction experiment [15]**.** Solvent extraction processes based on simple organic complexing extractants are often used commercially for the recovery and purification of metal ions [16]. Low cost, excellent efficiency, high degree of selectivity obtained by the liquid membrane system demonstrate its potential applicability [17] to selective removal, concentration or purification of metals from mixtures.

In order to evaluate the potential of the DPGDB as ion carrier, liquid-liquid extraction of alkali metal cations (Li^+, Na^+ & K^+) from picrate, dinitrophenolate and orthonitrophenolate salts was conducted.

EXPERIMENTAL SECTION

Materials

The metal salts (MX) in the form of picrates (Pic^-), dinitrophenolates (Dnp^-) and orthonitrophenolates (Onp^-) [MX: M^+= Li^+, Na^+ and K^+; X^-= Pic^-, Dnp^-& Onp^-] were prepared by reported method [18]. 1,2-dichloroethane (DCE), chloroform and carbontetrachloride obtained from Merck and Qualigens and used without further purification. Analytical grade chemicals were used. Ionophore dipropyleneglycol-dibenzoate [Fig. 1] of Aldrich was used in the study.

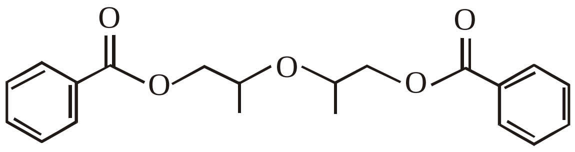

Fig.1 – Dipropyleneglycoldibenzoate [$(C_6H_5CO_2C_3H_6)_2O$]

Instruments

In experiment, the instruments employed were digital flamephotometer (systronics - 128) for Li^+, Na^+ and K^+ estimation, magnetic stirrer (Model Remi - 2 MLH) and analytical balance (A×200) of SHIMADZU Corporation, Japan and Melting point apparatus (MAC).

Method

For liquid-liquid extraction studies [19], 50 ml of 1.0 x 10^{-3} M aqueous salt solution was vigorously stirred with 50 ml of 1.0 x 10^{-3} M ionophore solution in BLM viz. CCl_4, $CHCl_3$ & $C_2H_4Cl_2$ in a small beaker using a magnetic stirrer (200rpm). The beaker was covered and kept in a thermostated incubator (25 ± 1^0C). The amount of cation in aqueous phase was initially determined before extraction was conducted using digital flame photometer. After every 1 hour of stirring the mixture was allowed to stand for 5 min. for separation of two phases. The depleted aqueous phase was removed and analysed for residual concentration of metal using digital flame photometer. The amount of cation extracted by the ionophore was found by determining its difference in aqueous phase before and after extraction. A blank experiment was also performed simultaneously with the same aqueous solution to determine the leakage of metal ion from aqueous to organic phase in absence of receptor. All measurements were performed in duplicate to check the reproducibility. Values of distribution ratio (D_M) were calculated as follows:

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

Back extraction experiments were also performed in double distilled water to check the back extraction of alkali metal ions using DPGDB in three membranes.

RESULTS AND DISCUSSION

The results of extraction of alkali metal cations after 4 hour with dipropyleneglycoldibenzoate reported in Tables 1-3 and Fig. 2-4. Extraction selectivity of ionophore is shown in Table 5. No extraction of metal ion was found in absence of ionophore.

Table 1- Amount of cation extracted by ionophore Dipropyleneglycoldibenzoate and distribution ratio across 1,2- dichloroethane membrane using metal salt during 4 h; Aqueous phase (50) ml of MX salt solution (conc^n = 1x 10^{-3} M); Organic phase (50 ml)

Metal cation	Pic^-		Dnp^-		Onp^-	
	Amount of cation extracted	D_M	Amount of cation extracted	D_M	Amount of cation extracted	D_M
Li^+	0.04	0.40	0.04	0.57	0.00	0.00
Na^+	17.40	1.85	8.30	1.02	15.60	2.17
K^+	3.40	5.67	5.60	0.17	16.66	0.74

No metal cation was detected in aqueous phase after back extraction which represents that ionophore does not show back extraction with metal ions.

Table 2- Amount of cation extracted by ionophore Dipropyleneglycoldibenzoate and distribution ratio across chloroform membrane using metal salt during 4 h; Aqueous phase (50) ml of MX salt solution (conc^n = 1x 10^{-3} M); Organic phase (50 ml)

Metal cation	Pic$^-$		Dnp$^-$		Onp$^-$	
	Amount of cation extracted	D_M	Amount of cation extracted	D_M	Amount of cation extracted	D_M
Li$^+$	0.01	0.08	0.01	0.10	0.00	0.00
Na$^+$	8.60	0.47	0.80	0.05	0.50	0.02
K$^+$	1.60	0.67	2.00	0.06	12.88	0.49

Table 3- Amount of cation extracted by ionophore Dipropyleneglycoldibenzoate and distribution ratio across carbontetrachloride membrane using metal salt during 4 h; Aqueous phase (50) ml of MX salt solution (conc^n = 1x 10^{-3} M); Organic phase (50 ml)

Metal cation	Pic$^-$		Dnp$^-$		Onp$^-$	
	Amount of cation extracted	D_M	Amount of cation extracted	D_M	Amount of cation extracted	D_M
Li$^+$	0.00	0.00	0.00	0.00	0.00	0.00
Na$^+$	1.60	0.06	2.55	0.16	2.00	0.09
K$^+$	1.60	0.67	2.00	0.06	2.86	0.08

Effect of cation

The trend for extraction of alkali metal ions with DPGDB is Na$^+$ > K$^+$ > Li$^+$. This selectivity can be explained on the basis of dipropylene chain of the ionophore, size as well as charge density of the metal cation. It is presumed that charge density of Na$^+$ shows more interaction with donor oxygen atoms and delocalization in aromatic rings of the ionophore. It may be assumed that due to the smallest size of Li$^+$, its charge density allows the solvation to a greater extent in aqueous solution and hence, pseudocyclic cavity of ligand becomes improper towards its accommodation and complexation. Hence, it shows minimum extraction.

As reported by Kobuke and Hanji [20], the extraction studies with macroheterocycles, the ionic diameter of metal cation and hole size of macroheterocycles are closely related and responsible for selective extraction, while our results show that in case of noncyclic ligands, this specificity and selectivity do not depend on hole size but on preferred pseudocyclic conformation and on other factors.

Ionophore shows maximum extraction for Na$^+$, which is somewhat similar for K$^+$, because it forms pseudo cavity due to ion-dipole interactions through the coordinating sites of ionophore.

Effect of anion

The extraction ability of ionophore must be carefully controlled with the companion anions [21]. Cation extraction can be altered by order of magnitude by proper anion selection. The mobility of cation-carrier-anion complex depends upon the characteristics of the anion. It was observed that more amount of metal ion was extracted from metal picrate salt than dinitrophenolate and orthonitrophenolate. It is due to quite consistency of charge delocalisation to much extent in picrate ring than dinitrophenolate and orthonitrophenolate ring.

Effect of membrane

Literature values for selected physical properties of the organic solvents used in the study are listed in Table 4.

Table 4 – Values of physical properties of solvents used in present studies

Solvent	Density (gm/cm^3)	Surface Tension (dyne/cm)	Viscosity (cP)	Solubility in H_2O, 20°C (% by wt.)	Dielectric Constant	Dipole Moment (Debye)
$C_2H_4Cl_2$	1.2521	32.20	0.887	0.81	10.36	1.20
$CHCl_3$	1.4891	26.70	0.596	0.81	4.81	1.01
CCl_4	1.5939	26.40	0.965	0.08	2.24	0.00

The observed order of solvents for the extraction of metal ions from aqueous solution is:
$C_2H_4Cl_2 > CHCl_3 > CCl_4$

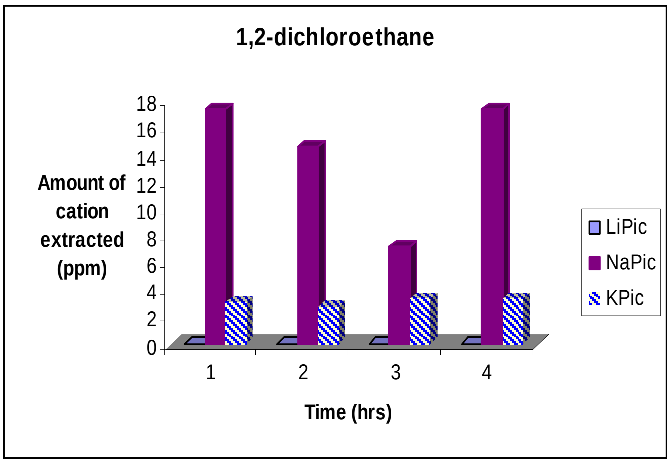

Fig. 2 – Amount of cation extracted by ionophore dipropyleneglycoldibenzoate across 1,2-dichloroethane membrane using metal picrate during 4 h; Aqueous phase (50) ml of MX salt solution (conc^n = 1x 10^{-3} M); Organic phase (50 ml)

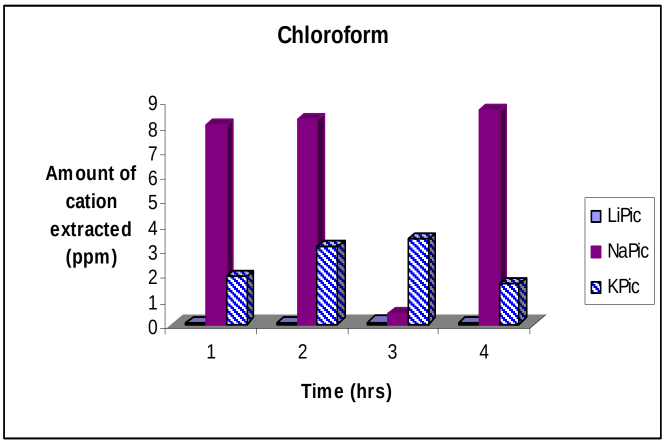

Fig. 3 – Amount of cation extracted by ionophore dipropyleneglycoldibenzoate across chloroform membrane using metal dinitrophenolate during 4 h; Aqueous phase (50) ml of MX salt solution (conc^n = 1x 10^{-3} M); Organic phase (50 ml)

The density and viscosity of solvent increases with an increase in chlorination while the dielectric constants, dipole moments and the mutual water-solvent solubility of the solvent decrease with an increase in chlorination [22]. The solvent with highest dipole moment will best solvate the ions from aqueous to organic phase during extraction. Carbon tetrachloride will have relatively thick water-free boundary layers that resist the flux of both ions and ligand for complexation. Polarity of 1,2-dichloroethane favours the dipole-ion interaction to bind the metal ion in pseudocyclic cavity.

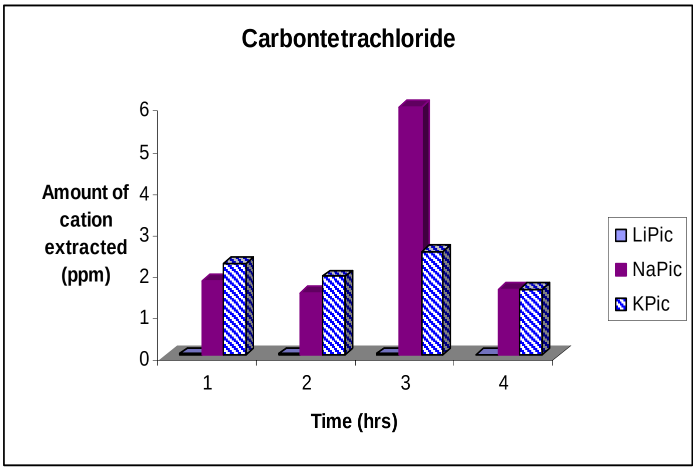

Fig. 4 – Amount of cation extracted by ionophore dipropyleneglycoldibenzoate across carbontetrachloride membrane using metal picrate during 4 h; Aqueous phase (50) ml of MX salt solution (conc^n = 1x 10^{-3} M); Organic phase (50 ml)

Table 5 – Representation of selectivity of Na$^+$ over K$^+$ and Li$^+$ in 1,2- dichloroethane, chloroform and carbontetrachloride membranes impregnated with Dipropyleneglycoldibenzoate (4 h)

Anion	DCE		$CHCl_3$		CCl_4	
	Na^+/K^+	Na^+/Li^+	Na^+/K^+	Na^+/Li^+	Na^+/K^+	Na^+/Li^+
Pic^-	5.11	435	5.37	860	1	-
Dnp^-	1.48	207.50	0.4	80	1.27	-
Onp^-	0.94	-	0.04	-	0.70	-

Effect of time

We have estimated the concentration of metal ion extraction with DPGDB after each hour upto 4 h from the obtained results; we can predict that no considerable change occurs in the metal concentration during extraction.

Distribution Ratio (D_M)

D_M is much more for K^+ when counter anion is picrate that indicates that K^+ has the maximum tendency to distribute itself in between two phases taken for study [Fig. 5]. But it is comparatively more for Na^+ in its dinitrophenolate and orthonitrophenolate salts.

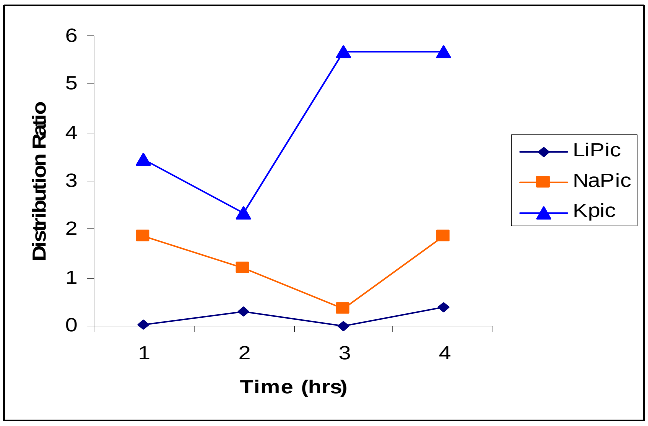

Fig. 5 – Distribution ratio of cations in between organic (1,2-dichloroethane) and aqueous phases using metal picrate during 4 h by using dipropyleneglycoldibenzoate; Aqueous phase (50) ml of MX salt solution (conc^n = 1x 10^{-3} M); Organic phase (50 ml)

CONCLUSION

The study demonstrates that the efficiency of an ionophore to extract a specific cation across a liquid membrane depends on rate of uptake. A lipophilic envelope is formed around a cation through ionophore by using donor sites to extract it into organic membrane. The study demonstrates that DPGDB has been shown to be suitable carrier ability for extraction of Na^+ over K^+ and Li^+. Thus, the results presented and discussed here show that different membrane systems containing a carrier can be used to accomplish separation of elements. Ionophore has found potential application for the design of ion selective electrodes.

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