

EFFECT OF END GROUPS AND CHAIN LENGTH ON EXTRACTION OF LITHIUM ION BY A SERIES OF NON-CYCLIC IONOPHORES

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Abstract

A series of non-cyclic polyethers with different end groups and chain length were used for the extraction of lithium salt from aqueous into various organic phases *viz.* Chloroform, Carbon tetrachloride, 1,2-dichloroethane, to study the influence of structural variations within the extractant molecule upon the extraction selectivity and efficiency. The ionophores used were *viz.* DEG (I), DEGDME (II), DEGMBE (III), DEGDME (IV), DEGDDB (V), EE (VI), ME (VII), Cryptofix (VIII), TEG (IX), TrEG (X). The trend of extraction is IV > III > I \approx II > VI > VII > V > VIII \approx IX \approx X. The DEGDDB proved to be the most efficient extractant for the lithium ion.

Keywords: Lithium picrate; Liquid-liquid extraction; Ionophore

Introduction

New class of reagents namely crown compounds reported by Pedersen [1] are fast emerging as potential extractants. Initially the importance of these compounds were highlighted because of the fact that, they are good extractants for alkali and alkaline earth metals, and thus the separation of these metals by solvent extraction is possible.

Recently open chain polyethers have attracted increasing attention because of their availability [2] fairly high effectiveness and possibility of regulating complex forming properties by altering their structure. Wide applications are expected in selective separation of lithium ions and in monitoring Li⁺ selectivity in blood during therapy for manic depression psychosis [3]. Keeping in view, the above considerations we are

reporting here the liquid-liquid extraction of lithium ion [4] by a series of non-cyclic ionophores in the presence of picrate, 2,4-dinitrophenolate and orthonitrophenolate counterions. The influence of the structural factors of non-cyclic ionophores in lithium selectivity supplied an important concept and information in relation to the lithium selective electrode/ionophore [5].

Materials and Methods

All lithium salts as lithium picrate (LiPic), 2,4-dinitrophenolate (LiDnp) and orthonitrophenolate (LiOnp), were prepared as reported earlier [6]. All the reagents and ionophores used were of the analytical grade obtained from Fluka, Merck and used without further purification. The solvents used were obtained from Qualigens, dried and distilled before use.

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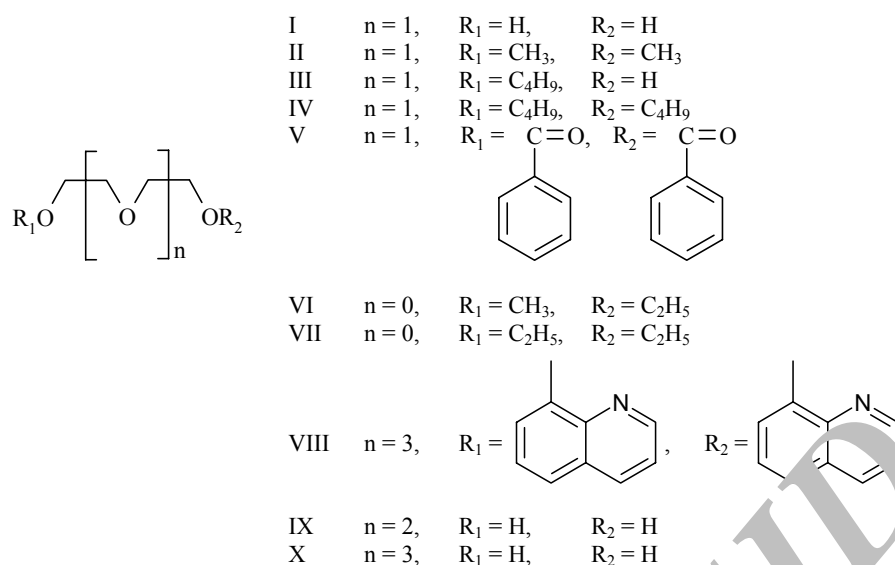


Figure 1. Ionophores used.

Table 1. Values of selected physical properties of the solvents used in the present studies

Solvent	Density (g/cm ³)	Surface Tension (dyn/cm ²)	Viscosity (c _p)	Solubility in H ₂ O, 20 °C (% by wt.)	Dielectric Constant	Dipole Moment (debye)
C ₂ H ₄ Cl ₂	1.2521	32.20	0.887	0.81	10.36	1.20
CHCl ₃	1.4891	26.70	0.56	0.81	4.81	1.01
CCl ₄	1.5939	26.40	0.95	0.08	2.24	0.00

Apparatus Section

In the experimental section we have used the spectralab motorless magnetic stirrer, thermostatic waterbath maintained at 25±1°C, Phillips 7700 double beam atomic absorption spectrophotometer.

Experimental Section

Liquid-Liquid Extraction

In the liquid-liquid extraction studies [7], 10 ml of 1.0 × 10⁻³ M aqueous Lithium salt solution was vigorously stirred with 10 ml of 1.0 × 10⁻³ M ionophores (Fig. 1) 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 4 h of stirring the mixture was allowed to stand for 5 min for the separation of two phases. The depleted aqueous solution was removed and analysed for the metal content using a Phillips 7700

double beam atomic absorption spectrophotometer. The amount of lithium extracted by the ionophore was found by determining its difference in aqueous phase before and after extraction. Values of distribution ratio (D_M) were calculated as follows [8]:

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

Results and Discussion

The blank experiments were carried out for extraction of lithium salt in which the membrane was devoid of carrier. No leakage of cation from source into the organic layer was observed. All measurements were performed in duplicate to check reproducibility.

Effect of Solvent

Literature values for selected physical properties of the solvents used in the present study are listed in Table 1 [9]. The order observed for extraction of Li⁺ ion is

$\text{CH}_2\text{ClCH}_2\text{Cl} > \text{CHCl}_3 > \text{CCl}_4$. The results shown in Table 2 and Figure 4, can be explained in terms of the physical properties of the solvent water system [10]. The solvent with highest dipole moment will best solvate the ions extracted to the organic phase so it is expected that dichloroethane will better extract the Li^+ ion.

Effect of End Groups and Chain Length

Among the series of non-cyclic ionophores (I to X) used for extraction of lithium ion, I to V are Diethylene glycol and its derivatives having different end groups, while ionophores X and VIII are simple glycol with larger chain length and quinoline end group respectively. The results of the extraction studies are given in Table 2 and Figure 2. The trend of extraction is $\text{IV} > \text{III} > \text{I} \approx \text{II} > \text{VI} > \text{VII} > \text{V} > \text{VIII} \approx \text{IX} \approx \text{X}$. The trend can be explained on the basis of end groups and chain length of the extractant. The ionophore IV having dibutyl group and small chain length shows maximum extraction, while longer chain length and rigid donor end group containing ionophores (VIII, IX and X) shows poor extraction [11].

Thus the adoptability of ionophore according to the size and charge density of the lithium ion is an important factor in case of non-cyclic ionophores. It was reported that among cyclic ionophores (14Crown4) was the best extractant for the lithium. Our observation shows that non-cyclic ionophores can be used for the extraction of lithium ion, provided that they possess suitable chain length.

Effect of Concentration Variation

Metal ion concentration

We have conducted different sets of experiments by varying the concentration of lithium salt (LiPic, LiDnp and LiOnp). The range selected is 1.0×10^{-2} M to 1.0×10^{-4} M for metal salts and ligand concentration was kept constant at 1.0×10^{-3} M. The values of D_M shown in Table 3 leads to the conclusion that optimum concentration is 1.0×10^{-3} M for lithium salts (Fig. 3).

Ligand concentration variation

The amount of lithium extracted by the ligand at different concentration is shown in Table 4. The lithium ion concentration was kept constant 1.0×10^{-3} M. The range selected for ligand concentration variation is 1.0×10^{-5} to 1.0×10^{-3} M. The optimum concentration is 1.0×10^{-3} M for ligand.

Effect of Time

We have estimated the amount of lithium extracted with the ionophores I to X after every 30 min time interval up to 240 min. On the basis of observations shown in Table 5, we can predict that longer chain length ionophores having rigid end groups, show no change in amount of lithium ion extracted, while ionophores which possess small chain length and flexible end groups show regular uptake and release of the Li^+ [16]. These observations further verify the role of chain length and end group in the extraction of metal ion (Fig. 5).

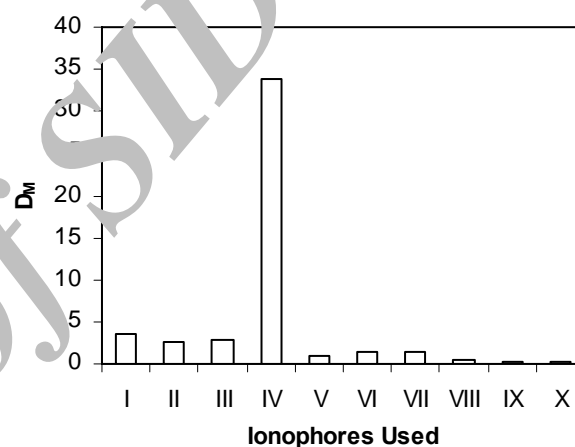


Figure 2. Amount of Lithium ion extracted (D_M) with ionophore I to X at 1.0×10^{-3} M concentration of lithium picrate.

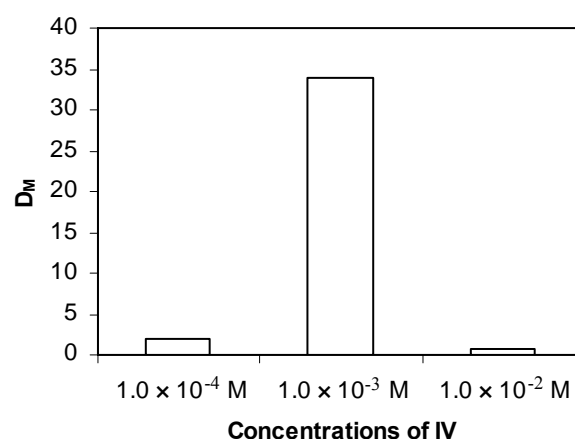


Figure 3. Amount of lithium ion extracted (D_M) into an organic phase by using diethyleneglycol dibutyl ether (IV) at different concentration.

Table 2. Amount of Li^+ ion extracted into an organic phase in 4 h by series of ionophores in CHCl_3 , CCl_4 , $\text{CH}_2\text{ClCH}_2\text{Cl}$
Metal Salt Concentration and Ionophore Concentration = 1.0×10^{-3} M

Ionophore	Li Salt	CHCl_3		$\text{CH}_2\text{ClCH}_2\text{Cl}$		CCl_4	
		Cation extracted $\mu\text{g/ml} (\times 10^{-3})$	D_M	Cation extracted $\mu\text{g/ml} (\times 10^{-3})$	D_M	Cation extracted $\mu\text{g/ml} (\times 10^{-3})$	D_M
I	LiPic	7.857	3.66	7.421	2.87	3.510	0.54
	LiDnp	8.581	1.41	8.011	4.02	3.123	0.46
	LiOnp	6.345	1.73	7.789	3.53	3.600	0.42
II	LiPic	7.141	2.49	8.423	5.32	2.100	0.26
	LiDnp	5.570	1.25	7.927	3.91	–	–
	LiOnp	6.579	1.91	7.912	3.91	–	–
III	LiPic	7.428	2.87	8.927	3.25	3.980	0.66
	LiDnp	7.428	2.87	9.012	3.25	3.900	0.63
	LiOnp	8.851	7.66	9.000	9.10	2.570	0.34
IV	LiPic	9.714	33.96	9.751	39.00	6.010	1.50
	LiDnp	9.714	33.96	9.751	39.00	6.980	2.31
	LiOnp	9.579	22.31	9.731	36.00	8.017	4.02
V	LiPic	5.000	1.00	7.010	4.02	5.000	1.00
	LiDnp	3.579	0.58	7.210	2.58	–	–
	LiOnp	5.000	1.00	7.293	2.69	–	–
VI	LiPic	5.000	1.33	8.012	4.02	2.890	1.16
	LiDnp	4.250	0.73	8.000	4.00	1.000	0.11
	LiOnp	4.070	0.98	7.790	3.52	2.010	0.25
VII	LiPic	7.000	1.51	8.573	4.990	–	–
	LiDnp	6.420	1.79	6.500	1.85	–	–
	LiOnp	7.857	3.65	5.540	1.24	1.920	0.23
VIII	LiPic	3.570	0.55	5.000	1.00	3.540	0.52
	LiDnp	2.570	0.34	3.500	0.53	–	–
	LiOnp	3.500	0.50	3.142	0.45	2.920	0.40
IX	LiPic	2.140	0.27	3.010	0.43	–	–
	LiDnp	2.140	0.27	5.010	1.00	–	–
	LiOnp	1.890	0.23	5.000	1.00	1.000	0.11
X	LiPic	2.140	0.27	4.892	0.95	3.140	0.45
	LiDnp	–	–	4.000	0.66	–	–
	LiOnp	–	–	2.510	0.28	–	–

Table 3. Amount of Li⁺ ion extracted into an organic phase in 4 h by a series of ionophores in chloroform

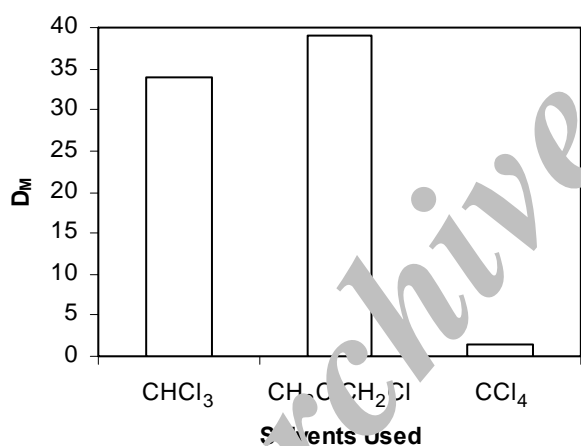
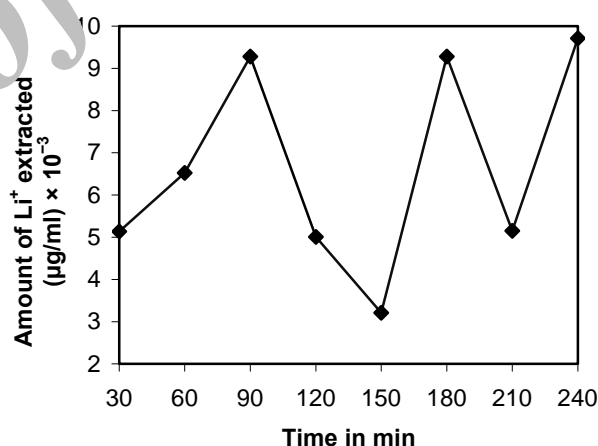
Ionophore	Li Salt	Metal Concentration					
		1.0×10^{-4} M		1.0×10^{-3} M		1.0×10^{-2} M	
		Cation extracted $\mu\text{g/ml} (\times 10^{-4})$	D_M	Cation extracted $\mu\text{g/ml} (\times 10^{-3})$	D_M	Cation extracted $\mu\text{g/ml} (\times 10^{-2})$	D_M
I	LiPic	7.143	2.50	7.857	3.66	1.127	0.12
	LiDnp	–	–	5.850	1.41	1.281	0.14
	LiOnp	–	–	6.340	1.73	1.400	0.16
II	LiPic	2.571	0.39	7.141	2.49	1.127	0.12
	LiDnp	–	–	5.571	1.25	1.841	0.22
	LiOnp	–	–	6.572	1.91	1.127	0.12
III	LiPic	5.327	1.13	7.428	2.87	2.557	0.34
	LiDnp	3.243	0.48	7.428	2.87	2.710	0.37
	LiOnp	–	–	8.851	3.05	1.412	0.16
IV	LiPic	6.714	2.04	9.714	3.96	4.425	0.79
	LiDnp	6.714	2.04	9.714	3.96	4.425	0.79
	LiOnp	6.613	1.95	5.571	22.31	4.982	0.81
V	LiPic	3.327	0.49	5.000	1.00	1.859	0.22
	LiDnp	5.857	1.41	5.571	0.55	1.594	0.18
	LiOnp	–	–	5.000	1.00	3.012	0.43
VI	LiPic	3.590	0.56	5.812	1.38	3.598	0.56
	LiDnp	–	–	4.251	0.73	1.854	0.22
	LiOnp	4.127	0.70	4.936	0.98	1.412	0.16
VII	LiPic	4.289	0.72	6.000	1.50	1.127	0.12
	LiDnp	–	–	6.421	1.79	1.841	0.22
	LiOnp	–	–	7.857	3.65	1.281	0.14
VIII	LiPic	–	–	3.576	0.55	2.559	0.34
	LiDnp	–	–	2.573	0.34	–	–
	LiOnp	3.256	0.48	3.500	0.50	1.856	0.24
IX	LiPic	–	–	2.140	0.27	–	–
	LiDnp	4.428	0.78	2.140	0.27	1.400	0.16
	LiOnp	–	–	1.890	0.23	2.752	0.37
X	LiPic	–	–	2.140	0.27	1.856	0.24
	LiDnp	–	–	–	–	2.752	0.37
	LiOnp	–	–	–	–	1.485	0.11

Table 4. Amount of Li⁺ ion extracted into an organic phase in 4 h by a series of ionophores in chloroform

Ionophore	Li Salt	Ligand Concentration					
		1.0×10^{-5} M		1.0×10^{-4} M		1.0×10^{-3} M	
		Cation extracted $\mu\text{g/ml} (\times 10^{-3})$	D_M	Cation extracted $\mu\text{g/ml} (\times 10^{-3})$	D_M	Cation extracted $\mu\text{g/ml} (\times 10^{-3})$	D_M
I	LiPic	2.141	0.27	3.653	0.57	7.857	3.66
	LiDnp	2.159	0.28	5.125	1.05	5.851	1.42
	LiOnp	2.981	0.42	5.125	1.05	6.341	1.73
II	LiPic	1.892	0.23	3.653	0.57	7.141	2.49
	LiDnp	2.141	0.27	6.289	1.69	5.570	1.25
	LiOnp	1.892	0.23	4.289	0.95	6.578	1.91
III	LiPic	3.500	0.53	–	–	7.428	2.87
	LiDnp	3.500	0.53	4.592	0.94	7.428	2.87
	LiOnp	2.131	0.27	4.892	0.95	8.851	33.96
IV	LiPic	4.251	0.73	6.992	2.32	9.714	33.96
	LiDnp	4.251	0.73	6.992	2.32	9.714	24.31
	LiOnp	4.251	0.73	6.289	1.69	9.579	1.00
V	LiPic	4.525	0.82	5.000	1.00	5.000	0.55
	LiDnp	3.571	0.55	6.000	1.50	3.570	1.00
	LiOnp	2.571	0.34	5.851	1.38	5.000	1.38
VI	LiPic	2.571	0.34	–	–	5.810	0.73
	LiDnp	1.892	0.23	–	–	4.250	0.98
	LiOnp	2.141	0.23	5.851	1.38	4.970	1.50
VII	LiPic	2.131	0.27	–	–	6.000	1.79
	LiDnp	1.892	0.23	3.652	0.57	4.400	3.65
	LiOnp	–	–	–	–	7.857	0.55
VIII	LiPic	–	–	–	–	3.570	0.33
	LiDnp	–	–	6.000	1.50	2.570	0.50
	LiOnp	–	–	5.851	1.38	3.500	0.27
IX	LiPic	–	–	–	–	2.410	0.27
	LiDnp	–	–	3.653	0.57	2.140	0.27
	LiOnp	–	–	–	–	1.809	0.23
X	LiPic	–	–	–	–	2.140	0.27
	LiDnp	–	–	–	–	–	–
	LiOnp	–	–	–	–	–	–

Table 5. Amount of lithium extracted ($\mu\text{g/ml}$) per 30 min by ionophores using concentration of lithium picrate (1.0×10^{-3} M) and ionophores concentration (1.0×10^{-3} M)

Ionophores	Time in minute							
	30	60	90	120	150	180	210	240
	Cation extracted ($\mu\text{g/ml} \times 10^{-3}$)	Cation extracted ($\mu\text{g/ml} \times 10^{-3}$)	Cation extracted ($\mu\text{g/ml} \times 10^{-3}$)	Cation extracted ($\mu\text{g/ml} \times 10^{-3}$)	Cation extracted ($\mu\text{g/ml} \times 10^{-3}$)	Cation extracted ($\mu\text{g/ml} \times 10^{-3}$)	Cation extracted ($\mu\text{g/ml} \times 10^{-3}$)	Cation extracted ($\mu\text{g/ml} \times 10^{-3}$)
I	0.80	6.42	6.55	3.07	6.48	2.24	6.21	7.85
II	0.72	6.55	2.38	7.87	7.92	7.97	7.90	5.85
III	0.30	5.12	7.92	8.60	8.60	7.92	6.42	7.42
IV	5.14	6.52	9.28	5.01	3.21	9.28	5.12	9.71
V	0.82	6.55	3.07	4.12	2.01	1.13	3.15	5.00
VI	0.62	1.99	5.21	1.89	2.89	1.73	4.32	5.81
VII	0.57	3.52	1.85	4.32	4.32	4.32	4.32	6.00
VIII	0.30	2.14	1.92	1.85	–	–	–	3.57
IX	0.21	2.14	2.14	–	–	2.14	–	2.14
X	–	1.85	–	2.14	–	–	–	2.14

**Figure 4.** Amount of Lithium ion extracted (D_M) into an organic phase by using diethyleneglycol dibutyl ether in chloroform, 1,2-dichloroethane and carbon tetrachloride.**Figure 5.** Amount of Lithium ion extracted ($\mu\text{g/ml} \times 10^{-3}$) vs. time in minutes.

Li^+ picrate concentration = 1.0×10^{-3} M

Diethyleneglycol dibutyl ether = 1.0×10^{-3} M

Effect of pH

As an extension of these studies we have investigated the effect of pH on extraction. The pH range of LiX ($X = \text{Pic, Dnp, Onp}$) is 5-8. It is observed that amount of Li^+ extraction enhanced with the decrease in pH of aqueous phase.

Conclusion

The structural variation is the most decisive factor in determining the extraction selectivity and efficiency. The results reported here lead to the conclusion that the non-cyclic ionophore IV having dibutyl group and diethylene chain are good extractant for Li^+ ion and it

provides good potential for development of Li⁺ ion specific receptors which can help in monitoring of lithium concentration in human body.

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