

Liquid-Liquid Extraction Study of Sodium and Potassium Ions by a Series of Non Cyclic Ionophores Composed of Furan Units

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Abstract

A new series of noncyclic ionophores containing two to four furan units (Ia to IIIb) *i.e.* 1,1-difurylthane (Ia), 2,5-bis(methylfurfuryl)furan (IIa) and 1,1'-ethylenedibis[5-(methylfurfuryl)furan] (IIIa), 2,2-difurylpropane (Ib), 2,5-bis(dimethylfurfuryl)furan (IIb), 2,2'-isopropylidenebis[5-(dimethylfurfuryl)furan] (IIIb) have been synthesized by the condensation of furan with acetaldehyde and acetone in ethanol separately in the presence of concentrated hydrochloric acid. These ionophores were used for the extraction of alkali metal ions from aqueous to organic phase in chloroform membrane using picrate, dinitrophenolate and orthonitrophenolate salts. All ionophores of series (a) and (b) extract K⁺ selectively over Na⁺ and ligands IIa and IIb show the best extraction efficiency for K⁺ among these series. Among anions, orthonitrophenolate is found to be the best in comparison to dinitrophenolate and picrate during extraction. Thus, we can control the extraction of cations by altering anion.

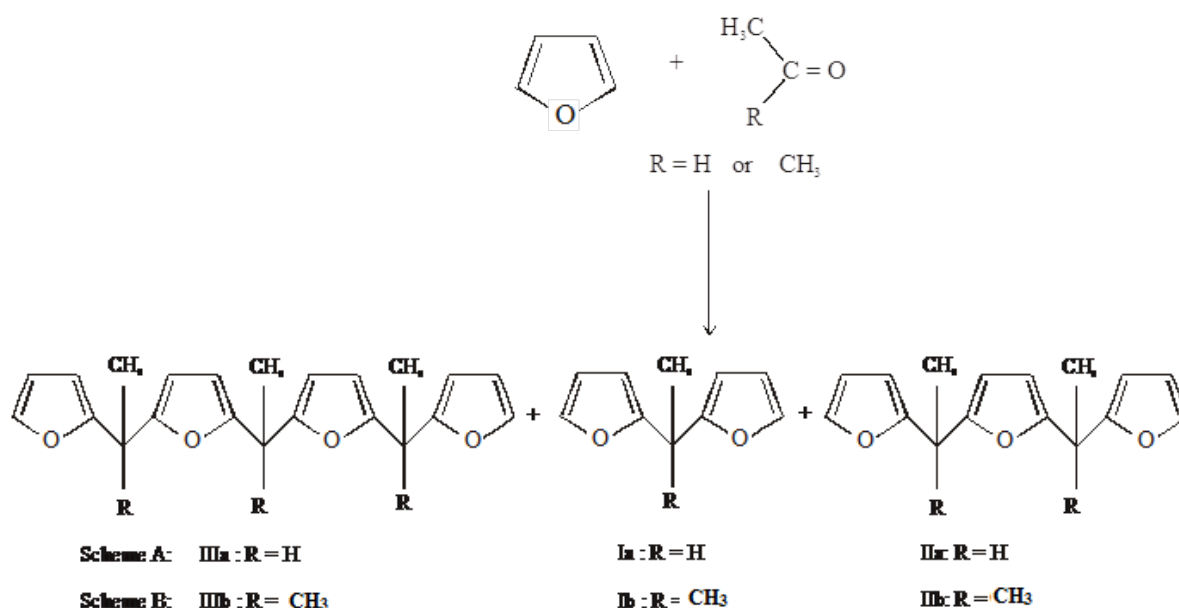
Keywords: Extraction; Noncyclic ionophores; Picrate; Dinitrophenolate; Orthonitrophenolate

Introduction

Numerous ionophores are responsible for the molecular recognition [1,2] in a biomembrane. Various types of podands, coronands and cryptands have been investigated as host molecules, which have the capacity to selectively extract guest ions from aqueous solution into a hydrophobic membrane phase by carrier translocation. New class of reagents namely crown compounds reported by Pedersen are fast emerging as potent extractants [3]. Macrocyclic polyethers have

drawn attention in both chemistry and biology to selective complexation of various metal cations [4,5]. These compounds are characterized by a hydrophilic cavity in their centres in which metal cations are selectively bound depending on their diameter. Recently open chain polyethers have attracted increasing attention because of their availability, fairly high effectiveness and possibility of regulating complex forming properties by altering their structure [6]. Incorporation of macrocyclic ligand into hydrophobic membrane to serve as a cation carrier offers a method to

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Scheme 1. Schematic representation of synthesis of ionophores (Ia to IIIb).

exploit the high cation selectivity [7,8] demonstrated by ligand molecules. The alkali and alkaline earth metal complexes are important in analytical, biochemical and pharmaceutical fields [9]. The extraction of alkali metal ions into organic media was studied using macroheterocycles containing tetrahydrofuran as a main constituent [10]. This extraction of alkali metal ions is strictly according to the cavity fit concept. The choice for further detailed work falls favourably on some open chain heterocycles. We have synthesized a series of linear oligomers containing two to four furan units. With this consideration, we are reporting here the liquid-liquid extraction of Na⁺ and K⁺ ions by a series of non cyclic ionophores composed of furan units in the presence of picrates (Pic⁻), 2,4-dinitrophenolates (Dnp⁻) and orthonitrophenolates (Onp⁻) as anions.

Extraction studies were conducted to ascertain the occurrence or complexation between metal salts (MX) and the ionophores in solution state [11]. In view of the recent interest in the preparation of macroheterocycles containing furan as a main constituent with a variation of ring size formed by the acid catalyzed condensation of carbonyl compounds with furan, we wish to report the capacity of the various ionophores to extract metal cations from an aqueous phase into an organic phase by complexation.

Material and Methods

All metal salts were prepared as reported earlier [12].

All the reagents were used of the analytical grade obtained from fluka, merck and used without purification. The solvent (chloroform) used was obtained from qualigens.

All the six ligands *i.e.* 1,1-difurylethane (Ia), 2,5-bis(methylfurfuryl) furan (IIa) and 1,1'-ethylenedibis[5-(methylfurfuryl)furan] (IIIa), 2,2-difurylpropane (Ib), 2,5-bis(dimethylfurfuryl)furan (IIb), 2,2'-isopropylidenebis[5-(dimethylfurfuryl)furan] (IIIb) were synthesized as reported earlier [10,13].

Synthesis of Ionophores

Scheme A: Synthesis of 1,1-difurylethane (Ia), 2,5-bis(methylfurfuryl) furan (IIa) and 1,1'-ethylenedibis[5-(methylfurfuryl)furan] (IIIa) [10]: These ligands (Scheme 1) were prepared by the addition of 22g (0.5 mol) of acetaldehyde to an ice cooled mixture of 68g (1.0 mol) of furan, 30 ml of ethanol and 20 ml of 35% hydrochloric acid with constant stirring. The addition required 30 min. and reaction was continued for 20 hrs at room temperature. The resulting dark green solution was diluted with ether and washed with sodium bicarbonate and then dried. After evaporation of solvents and unreacted furan, a mixture of Ia, IIa and IIIa was fractionally distilled to separate different oligomers.

The first fraction was obtained at temperature of 98°C and at pressure 21 mm Hg. To avoid impurities the first few mLs were discarded. The temperature was

increased upto 118°C and pressure was reduced to 0.1 mm Hg and the second fraction was obtained at this temperature. Again the temperature was increased upto 177.5°C and pressure was reduced to 0.03 mm Hg and third fraction was collected.

1,1-difurylethane (Ia): B.P. – 91°C (21 mm); yield-10.1 g.

IR (neat): 3125, 2985, 2940, 2885, 1585, 1500, 1445, 1365, 1310, 1240, 1230, 1175, 1150, 1010, 930, 910, 885, 805 and 735 cm^{-1} .

NMR (CDCl_3): δ 1.56 (d, 3H, $J = 7.0$ Hz, $-\text{CH}_3$), 4.19 (q, 1H, $J = 3.2, 1.8$ Hz, outside β -H of furan), 7.27 (d of d, 2H, $J = 1.8, 0.8$ Hz, α -H)

Mass spectrum: m/e (%): 162 (100), 148 (27), 91 (95), 77 (27), 65 (49).

Mol formula: $\text{C}_{10}\text{H}_{10}\text{O}_2$: Calc'd: C, 74.06, H, 6.21; O, 19.73.

Found: C, 73.95; H, 5.98; O, 19.70.

2,5-bis(methylfurfuryl)furan (IIa): B.P. - 115°C (0.1 mm); yield -12.4g

IR (neat): 3120, 2980, 2940, 1590, 1550, 1500, 1450, 1370, 1230, 1170, 1150, 1010, 950, 915, 885, 805, 790 and 735 cm^{-1}

NMR (CDCl_3): δ 1.54 (d, 6H, $J = 7.0$ Hz, $-\text{CH}_3$), 4.15 (q, 2H, $J = 7.0$ Hz, $-\text{CH}$), 5.90 (d, 2H, $J = 0.4$ Hz, central furan), 5.98 (d of t, 2H, $J = 3.2, 0.8$ Hz, inside β -H of terminal furan), 7.27 (d of d, 2H, $J = 3.2, 1.8, 0.3$ Hz, outside β -H of terminal furan), 7.27 (d of d, 2H, $J = 1.8, 0.8$ Hz, α -H)

Mass spectrum: m/e (%): 256 (100), 242 (30), 241 (190), 161 (68), 141 (30), 113 (27), 105 (58), 95 (66), 81 (51), 77 (34).

Mol. Formula: $\text{C}_{16}\text{H}_{16}\text{O}_3$: Calc'd: C, 74.98, H, 6.29; O, 18.73.

Found: C, 74.99; H, 6.38; O, 18.43.

1,1'-ethylenedibis[5-(methylfurfuryl)furan]

(IIIa): B.P. – 166.5°C (0.03 mm); yield -7.4g

IR (neat): 3120, 2980, 2940, 2880, 1700, 1585, 1545, 1500, 1445, 1370, 1300, 1295, 1235, 1170, 1150, 1055, 1010, 965, 950, 915, 885, 790 and 735 cm^{-1} .

NMR (CDCl_3): δ 1.52 (d, 3H, $J = 7.2$ Hz, central $-\text{CH}_3$), 1.54 (d, 6H, $J = 7.2$ Hz, terminal $-\text{CH}_3$), 4.11 (q, 1H, $J = 7.2$ Hz, central $-\text{CH}$), 4.16 (q, 2H, $J = 7.2$ Hz, terminal $-\text{CH}$), 5.88 (AB quartet, 4H, $J = 3.2$ Hz, inside furan), 5.99 (d of t, 2H, $J = 3.2, 0.8$ Hz, inside β -H of terminal furan), 6.25 (d of d, 2H, $J = 3.2, 1.8$ Hz, outside β -H of terminal furan), 7.28 (d of d, 2H, $J = 1.8, 0.8$ Hz, α -H).

Mass spectrum: m/e (%): 351 (100), 350 (440), 336 (140), 335 (130), 189 (170).

Mol. Formula: $\text{C}_{22}\text{H}_{22}\text{O}_4$: Calc'd: C, 75.41, H, 6.33; O, 18.26.

Found: C, 75.51; H, 6.47; O, 18.36.

Scheme B: Synthesis of 2,2-difurylpropane (Ib), 2,5-bis(dimethylfurfuryl)furan(IIb),2,2'-isopropylidenebis[5-(dimethylfurfuryl)furan] (IIIb) [13]: In a three necked flask fitted with a reflux condenser and stirrer 340g (5.0 mols) of furan, 150 ml of absolute ethanol and 100 ml of 37% hydrochloric acid solution were placed. To this mixture 146g (2.5 moles) of

Table 1. Amount of cation extracted into an organic phase (chloroform) in 1 hr.by ionophore Ia to IIIb using M.Pic salt

Ionophore	Amount of cation extracted (mg/L)		Selectivity (K^+/Na^+)
	Na^+	K^+	
Ia	2.00	2.50	1.25
IIa	0.00	10.00	–
IIIa	6.00	9.00	1.50
Ib	2.00	15.00	7.50
IIb	0.00	17.50	–
IIIb	6.00	15.00	2.50

RSD: $\text{Na}^+ = 2.73$; $\text{K}^+ = 5.48$

Table 2. Amount of cation extracted into an organic phase (chloroform) in 1 hr.by ionophore Ia to IIIb using M.Dnp salt

Ionophore	Amount of cation extracted (mg/L)		Selectivity (K^+/Na^+)
	Na^+	K^+	
Ia	8.00	22.50	2.81
IIa	4.00	40.00	10.00
IIIa	8.00	35.00	4.37
Ib	6.00	32.50	5.42
IIb	6.00	42.50	7.08
IIIb	10.00	37.50	3.75

RSD: $\text{Na}^+ = 2.10$; $\text{K}^+ = 7.07$

Table 3. Amount of cation extracted into an organic phase (chloroform) in 1 hr.by ionophore Ia to IIIb using M.Onp salt

Ionophore	Amount of cation extracted (mg/L)		Selectivity (K^+/Na^+)
	Na^+	K^+	
Ia	8.00	40.00	5.00
IIa	10.00	40.00	4.00
IIIa	10.00	40.00	4.00
Ib	10.00	40.00	4.00
IIb	12.00	40.00	3.33
IIIb	12.00	40.00	3.33

RSD: $\text{Na}^+ = 1.51$; $\text{K}^+ = 0.00$

acetone was added dropwise while stirring. The addition of acetone was completed after 35 minutes. No heat was evolved but the reaction mixture slowly took on a reddish tinge. Stirring was continued for 18 hours at room temperature. When stirring was stopped the mixture separated into two phases. The upper pink aqueous phase was separated from the lower orange organic phase. The organic phase was washed with 5% aqueous sodium bicarbonate, dried over magnesium sulfate and fractionally distilled under diminished pressure.

The same procedure was used to separate the different oligomers of (b) series as described in the separation of (a) series ligands.

2,2-difurylpropane (Ib): B.P. – 74.5°C (5-6 mm); yield – 32.1g and had density 1.043.

IR (neat): 3110, 2965, 2935, 2830, 1580, 1449, 1565, 1440, 1380, 1275, 1240, 1225, 1215, 1150, 1115, 1095, 1090, 1070, 1005, 955, 925, 885, 865, 820, 805, 725, 990 and 595 cm^{-1} .

MR_D: Calc'd: 51.16, Found: 49.43.

Molecular Weight: 176, Found: 189

Mol. Formula: C₁₁H₁₂O₂; Calc'd: C, 74.0; H, 6.87; O, 23.13.

Found: C, 74.9; H, 7.09; O, 18.01.

2,5-bis(dimethylfurfuryl)furan (IIb): B.P. – 121.5°C (1 mm); yield -14.2g

IR (neat): 3105, 2970, 2930, 2835, 1500, 1460, 1385, 1365, 1270, 1240, 1215, 1205, 1160, 1110, 1090, 1065, 1010, 960, 930, 885, 810, 785, 730 and 595 cm^{-1} .

Molecular Weight: 284, Found: 285

Mol. Formula: C₁₈H₂₀O₃; Calc'd: C, 76.1, H, 7.09; O, 16.81.

Found: C, 75.8; H, 6.94; O, 17.26.

2,2'-isopropylidenebis[5-(dimethylfurfuryl)furan] (IIIb): B.P. – 165°C (1 mm); yield -10.2g and had density = 1.030

IR (neat): 3100, 2970, 2930, 2835, 1505, 1465, 1380, 1360, 1270, 1206, 1160, 1120, 1115, 1060, 1015, 955, 925, 890, 790, 735 and 600 cm^{-1} .

MR_D: Calc'd: 116.1, Found: 115.1.

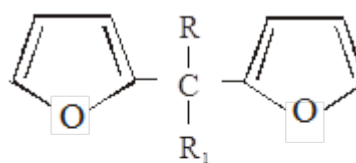
Molecular Weight: 392, Found: 418

Mol. Formula: C₂₆H₂₈O₄. Calc'd: C, 76.5, H, 7.19; O, 16.31.

Found: C, 76.4; H, 7.26; O, 16.34.

Apparatus

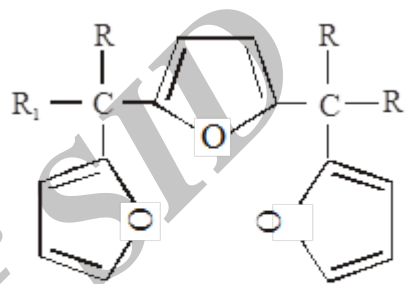
The instrument used for Na⁺ and K⁺ estimation was Systronics 128 digital flame photometer and we have used the spectralab motorless magnetic stirrer, thermostatic water bath maintained at 25±1°C.



Ia : R₁ = H, R = CH₃

Ib : R₁ = R = CH₃

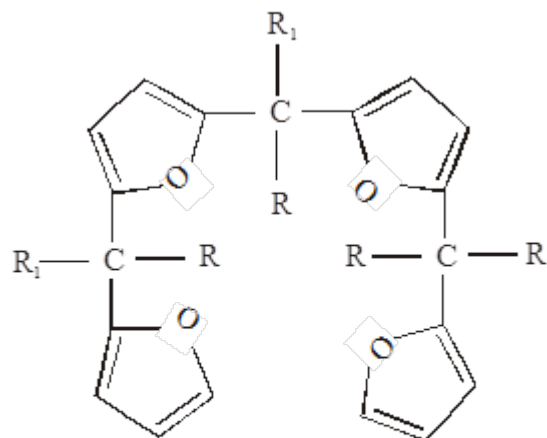
Scheme 2. 1,1-difurylpropane (Ia) and 2,2-difurylpropane (Ib).



IIa : R₁ = H, R = CH₃

IIb : R₁ = R = CH₃

Scheme 3. 2,5-bis(methylfurfuryl)furan (IIa) and 2,5-bis(dimethylfurfuryl)furan (IIb).



IIIa : R₁ = H, R = CH₃

IIIb : R₁ = R = CH₃

Scheme 4. 1,1'-ethylenedibis[5-(methylfurfuryl)furan] (IIIa) and 2,2'-isopropylidenebis[5-(dimethylfurfuryl)furan].

Liquid-Liquid Extraction Study

An aqueous metal salt (MX) solution (1×10^{-3} M) was vigorously stirred at 200 rpm with an ionophore solution (1×10^{-3} M) in chloroform in a small beaker, with a teflon coating capsule [14]. The amount of M^+ in the organic phase was determined before the extraction was conducted. The beaker was firmly sealed to minimize evaporation. After one hour of stirring the mixture was allowed to stand for one hour to separate the two phases. The aqueous phase was separated and analysed for the amount of cation extracted. Cations Na^+ and K^+ were estimated by flame photometer. The actual amount of M^+ estimated by various ionophores was determined by determining the difference in amount of M^+ in the aqueous phase before and after the extraction. No extraction was detected in absence of ionophore.

Results and Discussion

From the results given in Table 1-3, it was observed that all six ligands [Schemes 2-4] are effective extractants for alkali metal cations and exhibit extraction selectivity for K^+ over Na^+ . Peak selectivity for K^+ is shown by ligands IIa and IIb.

The overall specificity and selectivity of these ligands for K^+ can be explained on the solvation behaviour of Na^+ and K^+ as the Na^+ is known to be more solvated in polar medium than K^+ and remains in the aqueous phase.

Maximum extraction of K^+ with ligands IIa and IIb can be explained on the basis of conformational changes in the ligands. This selectivity and specificity is not dependent on cavity size of macroheterocycles as reported by Kobuke et al. [10], but on the preferred pseudocyclic conformation and solvation of cations. In trimers (IIa and IIb), the groups R and R_1 found outside the plane of pseudocavity [Scheme 3] and the interior cavity found is suitable for bigger cation K^+ and thus extract it to a greater extent. While in tetramers (IIIa and IIIb) [Scheme 4] because of increased no. of furan units, the preferred conformation is having groups (R and R_1) inside the pseudocavity and reduced the flexibility and hence, less space is available for metal cation to accommodate. So, the smaller cation Na^+ will preferably taken by IIIa and IIIb in comparison to other oligomers.

Although the selectivity remains same of K^+ by altering the anion, the overall amount of M^+ ion extracted is maximum with orthonitrophenolate (Figs. 1-3). This is in accordance with the hydrophobicity of the anion, which increases in the order: $Pic^- < Dnp^- < Onp^-$, and hence metallic salts have more solubility in chloroform. In case of $K.Onp$, the complete extraction

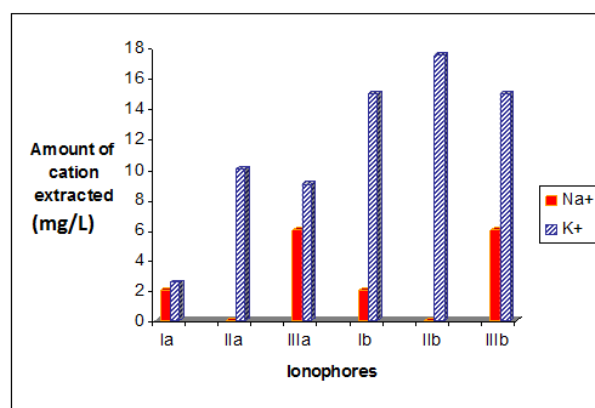


Figure 1. Amount of cation extracted by ionophores (Ia to IIIb) across chloroform membrane using metal picrate salts during 1h; Aqueous phase (50) ml of MX salt solution ($conc^n = 1 \times 10^{-3}$ M); Organic phase (50) ml.

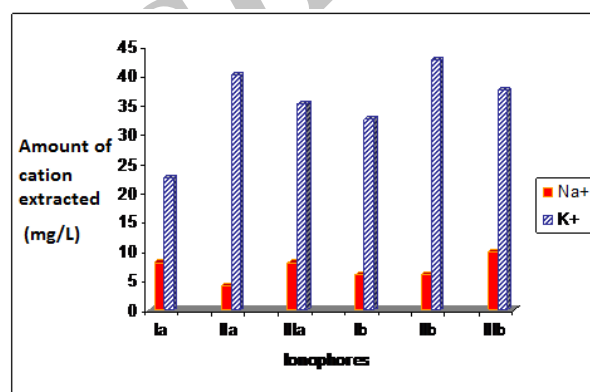


Figure 2. Amount of cation extracted by ionophores (Ia to IIIb) across chloroform membrane using metal dinitrophenolate salts during 1h; Aqueous phase (50) ml of MX salt solution ($conc^n = 1 \times 10^{-3}$ M); Organic phase (50) ml.

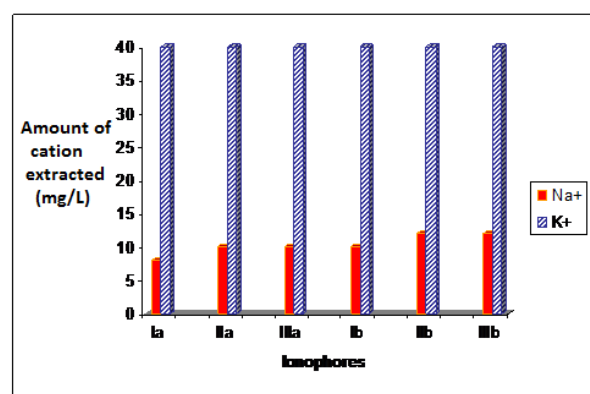


Figure 3. Amount of cation extracted by ionophores (Ia to IIIb) across chloroform membrane using metal orthonitrophenolate salts during 1h; Aqueous phase (50) ml of MX salt solution ($conc^n = 1 \times 10^{-3}$ M); Organic phase (50) ml.

of cation, along with the anion is observed and phase gets decolourised during extraction. Although the selectivity order is same for all the ligands *i.e.* $K^+ > Na^+$, but the extent of metal extraction efficiency is different. Thus, the extraction efficiencies for the ionophores of both the series a and b remain high and independent of the nature of group R. Extraction of metal ion depends upon the nature of anions, metal-ligand interactions and conformation of ionophores used.

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