

Transport of alkali metal cations through liquid membrane using non-cyclic synthetic ionophores

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Furan and acetaldehyde have been condensed in ethanol in the presence of conc. HCl to get linear oligomers possessing tetrahydrofuran units. A series of synthetic ionophores is synthesized with the introduction of different end groups at the terminal positions of tetraethylene glycol. For the transport of Na^+ and K^+ , 3, 4 exhibit selectivity for Na^+ over K^+ , while 1, 2 and 5, 6 show greater transport ability with no selectivity through liquid membrane. From the results of ion transport study, relationship between the structure and transport ability is discussed.

Alkali metal cations (Na^+ , K^+) play vital role in bio-systems. Some of the natural ionophores, e.g., actins, nigericin and monensin possess tetrahydrofuran units and have potential ability for carrying an ion across a biological membrane. Recently, appreciable interactions between oxyethylene units and alkali metal ions have been shown by the complex formation of synthetic acyclic oligoethylene glycols and their derivatives with alkali metal salts¹.

In this study, the synthetic acyclic ionophore tetraethylene glycol and its derivatives having acetoacetate, ethyl benzoate and quinolyl end groups and tetrahydrofuran units (Fig. 1, 1-6) have been synthesized. They have been used as the carriers and their abilities for selective ion transportation examined.

Experimental

Alkali metal picrates were prepared as reported earlier². Ionophores 1 and 3 were obtained from Fluka. Ionophores 2, 4, 5 and 6 were synthesized^{3,4} according to Schemes 1-3.

Preparation of tetraethylene glycol bis(acetoacetate) (2) and tetraethylene glycol bis(ethylbenzoate) (3)

A mixture of ethyl acetoacetate (2.0 ml) and tetraethylene glycol (0.66 mol) was stirred and heated slowly over a period of 3 hr to 180°C at atmospheric pressure. During this period 68 ml of ethanol was

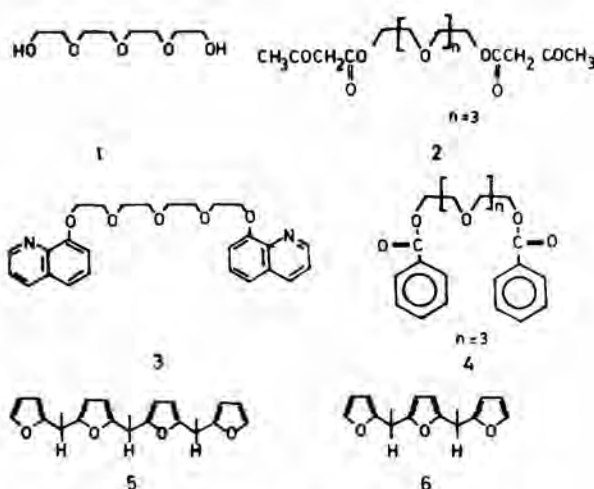
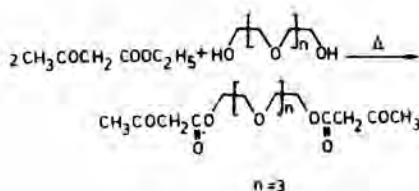
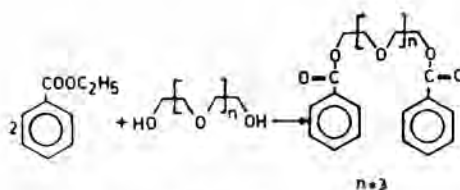


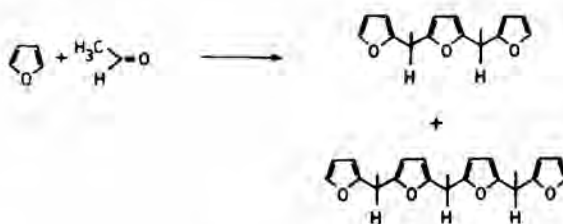
Fig. 1—Ionophores 1-6 used in the present study.



Scheme-1



Scheme-2



Scheme-3

collected. Once ethanol ceased to distil off, distillation was continued at 20 mm, leading to the collection of excess ethyl acetoacetate. The oily residue in the distillation pot was nearly pure (**2**) (87% yield); its ^1H NMR spectrum showed signals at δ 2.25 (s, 6CH_3), 3.42 (s, 4CH_2), 3.59 (s, 8OCH_2), 3.64 (m, 4OCH_2) and 4.24 (m, 4 ester OCH_2). Because of decomposition of **2** at elevated temperature, no exact mass spectral molecular weight determination was possible.

For (**3**), ethyl benzoate (2.0 mol) and tetraethylene glycol (0.66 mol) were stirred and heated over a period of 3 hr to 210°C at atm pressure. After removing excess ethyl benzoate under reduced pressure, the residue in pot was characterised. Its ^1H NMR spectrum showed signals at δ 4.07 ($-\text{COOPh}$), 3.59 (s, 9OCH_2) and 1.48 (s, C_6H_5). No exact mass spectral analysis was possible.

*Preparation of 1,1-ethylidene bis-5-(methylfurfuryl)furan (**5**) and 2,5-bis-(methylfurfuryl)furan (**6**)*

To an ice-cooled mixture of 68 g (1.0 mol) of furan, 30 ml of ethanol and 20 ml of 35% hydrochloric acid, 22 g (0.5 mol) of acetaldehyde was added with stirring. The addition required 30 min and the reaction was continued for 20 hr at room temperature. The resulting dark green solution was diluted with ether, washed with sodium carbonate and dried. After evaporation of solvents and unreacted furan, a mixture of **5** and **6** was fractionally distilled.

[**6**]-b.p. $114\text{--}116^\circ\text{C}$ (0.1 mm), yield 20.1 g. ^1H NMR (CDCl_3): δ 1.54 (d, 6H), 4.15 (q, 2H), 5.90 (d, 2H). Mass spectrum m/z (%) 250 (100), 242 (30), 241 (190), 161 (68), 141 (30), 113 (23), 105 (58), 95 (66), 81 (57), 77 (34).

[**5**]-b.p. $165\text{--}168^\circ\text{C}$ (0.03 mm) yield 8.0 g. ^1H NMR (CDCl_3): δ 1.52 (d, 3H), 1.54 (d, 6H), 4.11 (q, 1H), 4.16 (q, 2H), 5.99 (d, 2H, inside $\beta\text{--H}$ of terminal furan), 6.25 (d, 2H outside $\beta\text{--H}$ of terminal furan) and 7.28 (d, 2H, $\alpha\text{--H}$). Mass spectrum m/z (%) 35 (100), 350 (450), 336 (140), 335 (130), 189 (170).

The transportation study of alkali metal cations was carried out using three sets of apparatus⁵ identical with that shown schematically in Fig. 2. In addition, a blank experiment was performed for each salt in which the membrane contained no carrier. No detectable amount of cation across the chloroform membrane was found in blank experiments.

A chloroform solution (350 ml) containing $1.0 \times 10^{-3} M$ carrier was located at the bottom of a

Table 1—Amount of Na^+ and K^+ cation transported using metal picrates with ionophores **1–6** through CHCl_3 membrane after 24 hr

[S.P.: metal picrate ($1.0 \times 10^{-2} M$), R.P.: distilled water, membrane phase: $1.0 \times 10^{-3} M$ ionophore in CHCl_3]

Ionophore	Transported cation (%)		Total (%)	Selectivity Na^+/K^+
	Na^+	K^+		
1	90	40	130	2.25
2	20	6.0	26	3.3
3	28	2.0	30	14.5
4	25	3.0	28	8.3
5	44	34	78	1.2
6	32	17	49	1.8
Control	0	0	0	

Reproducibility: $\pm 7\%$

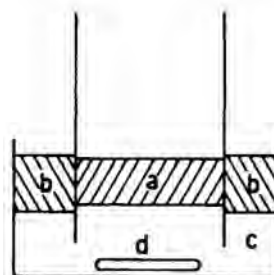


Fig. 2—The liquid membrane cell used for the transportation study. [(a) source phase, (b) receiving phase, (c) membrane phase and (d) magnetic stirrer].

120×65 mm glass beaker. Atop this layer there were two water phases separated by a glass cylinder open at both ends and fixed with the help of rubber sole. The inner phase comprised alkali metal picrate solution 42 ml ($1.0 \times 10^{-2} M$) serving as a cation source and outer phase comprised doubly distilled water (168 ml) serving as receiving phase. The three phases were agitated constantly by a magnetic stirrer which provided constant and reproducible stirring. The system was sealed to minimize evaporation. The vessels were maintained at $25 \pm 1^\circ\text{C}$ in a copper bath, in which water at 25°C was circulated continuously from a thermostat. Samples were withdrawn from the outer receiving phase by a syringe after 24 hr and analysed for cation content using a Perkin Elmer model 2380 atomic absorption spectrophotometer.

Results and discussion

Amounts of cation transported by various synthetic ionophores 1-6 after 24 hr are listed in Table 1. Na^+ selective ion transport was observed with ionophores 3 and 4 while 1, 2, 5 and 6 exhibited more transport ability but less selectivity. Presence of hydrophobic tetrahydrofuran units in 5, 6 and aromatic donor end groups in 3 and 4 decreases their solubilities in the aqueous medium and reduces the flexibility of the oxyethylene chain. In addition, the pseudocyclic conformation of ligand and stability of complexes are greatly enhanced by the π electrons of the aromatic donor end groups⁶ in ionophores 3, 4; ionophore 3 adopts pseudocyclic conformation as was reported in case of its RbI complex⁷. The inner cavity size (dia. 2.9 Å) of 3 was estimated to be of the order of ionic radius of K^+ (1.33 Å) while Na^+ ion is smaller in size, forms less stable complex and is transported more efficiently and selectively by 3. Highest transport ability was observed with simple glycols and linear oligomers of tetrahydrofuran units, as these ionophores can

adopt more easily according to the size of both cations and thus selectivity is lost.

These results indicate that the nature of end group and flexibility of ionophore are very important factors for the ion transportation ability and selectivity. We can design an effective and selective carrier by altering end groups for the efficient separation of certain cation species.

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