

1,5,9,13-Tetraoxacyclohexadecane and Its 3,3,7,7,11,11,15,15-Octamethyl Derivative as Neutral Carriers for Lithium Ion through Artificial Membranes

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1,5,9,13-Tetraoxacyclohexadecane and its 3,3,7,7,11,11,15,15-octamethyl derivative have been synthesized and used as neutral carriers in membrane electrodes, the membrane consisting of the cyclic polyethers in tris(2-ethylhexyl)phosphate as plasticizer in a PVC matrix. Selectivities, working range and pH dependence have been studied. Lithium ion activities can be measured in the range 1 M to approximately 10^{-5} M, and the selectivities of lithium over ammonium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium and barium go from about 3 to 800.

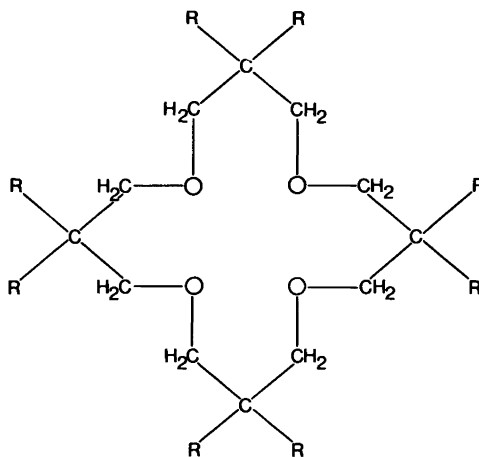
The conformational behaviour of the carriers in the membrane is discussed. The title compounds have different ring conformations depending on whether they are transporting Li^+ or not.

During the last decade much attention has been focused on the use of neutral carrier species as membrane components, having the capability to selectively extract ions from aqueous solution into a hydrophobic membrane phase and to transport these ions across such a barrier by carrier translocation. Different polyesters,¹ antibiotics^{2,3} and cyclic polyethers^{3–5} (crown ethers) have been investigated as neutral carriers. Some of them have shown to be quite useful together with different plasticizers as membrane components in ion selective membrane electrodes, especially for alkaline and alkaline earth ions.

Recently, Güggi *et al.*⁶ reported on the characteristics of a lithium ion selective electrode based on the neutral carrier *N,N'*-diheptyl-*N,N',5,5*-tetramethyl-3,7-dioxanonane diamide in tris(2-ethylhex-

yl)phosphate as membrane components in a polyvinyl chloride (PVC) matrix.

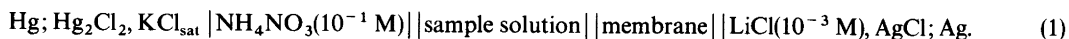
We have investigated the complexing ability between Li^+ and the crown ether 1,5,9,13-tetraoxacyclohexadecane (A) (Fig. 1) and its 3,3,7,7,11,11,15,15-octamethyl derivative (B) (Fig. 1) both by ^1H , ^{13}C and ^7Li NMR spectroscopy.⁷ It was of interest to determine if these crown ethers could act as neutral carriers in membranes. We here report on the characteristics of these neutral carriers for Li^+ in PVC membrane electrodes.



A: - R = - H

B: - R = - CH₃

Fig. 1. Structure of the neutral carriers investigated.



EXPERIMENTAL

Synthesis of neutral carriers. (A) and (B) were synthesized after a modified procedure⁷ originally described by Rose.⁸

Membrane preparation. The membranes were prepared according to Mascini and Pallozzi³ with the following composition: 180 mg PVC (Norvinyl PVC, S 2-70, Norsk Hydro A/S, Norway), 8.5 mg neutral carrier, 350 mg tris-(2-ethylhexyl)-phosphate (Merck).

Disks of 9 mm diameter and approx. 0.2 mm thickness were cut with a cork-borer and conditioned for 24 h in 1 M lithium chloride solution.

Electrode system. The membranes were incorporated into an Orion 93-19 electrode module with a silver-silver chloride internal reference electrode. The measurements were performed at 25 °C on a cell of the type given in eqn. (1).

The ammonium nitrate solution was connected to the sample solution *via* an ammonium nitrate agar bridge (Bacto-agar, Difco Laboratories, Detroit,

Michigan) to minimize the liquid junction potentials.⁹ The sample solutions were unbuffered.

Selectivity coefficients and activity coefficients. In the same way as by Güggi *et al.*⁶ selectivity coefficients were determined by the separate solution technique on 10⁻¹ M aqueous solutions of the chlorides using the relationship (2), where R ; gas

$$\log k_{\text{LiM}} = \frac{(E_2 - E_1)F}{2.303RT} - \log a_{\text{M}^{z+}}^{1/z} + \log a_{\text{Li}^+} \quad (2)$$

constant; a ; ion activities; T ; absolute temperature; z ; charge of the interfering ion; F ; Faraday constant; E_1 ; EMF of the cell assembly, the sample being a LiCl solution of analytical concentration 10⁻¹ M; E_2 ; EMF of the cell assembly, the sample being a 10⁻¹ M solution of the chloride of the interfering cation.

The activity coefficients for sodium and calcium were calculated from eqns. (3) and (4),^{6,10} where I is the ionic strength. For all other cations the

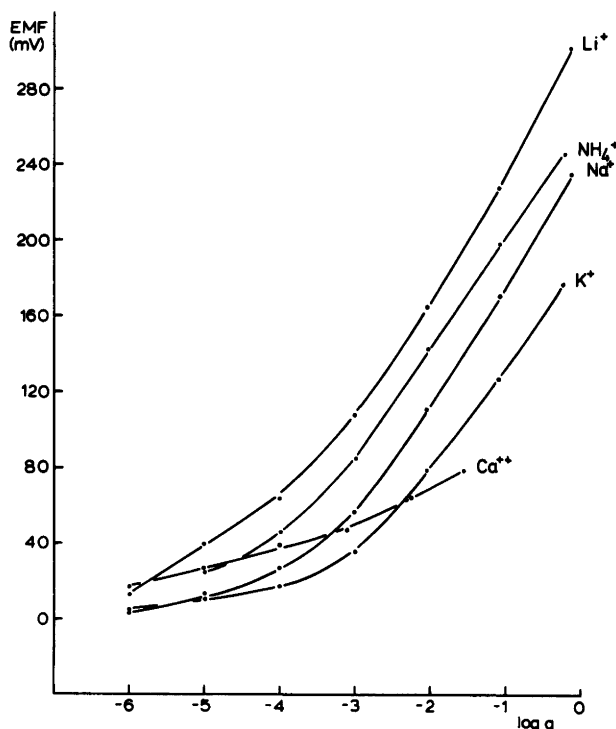


Fig. 2. EMF response of cell (1) to aqueous solutions of the chlorides of Li⁺, NH₄⁺, Na⁺, K⁺ and Ca⁺⁺ using neutral carrier A (Fig. 1) as a membrane component.

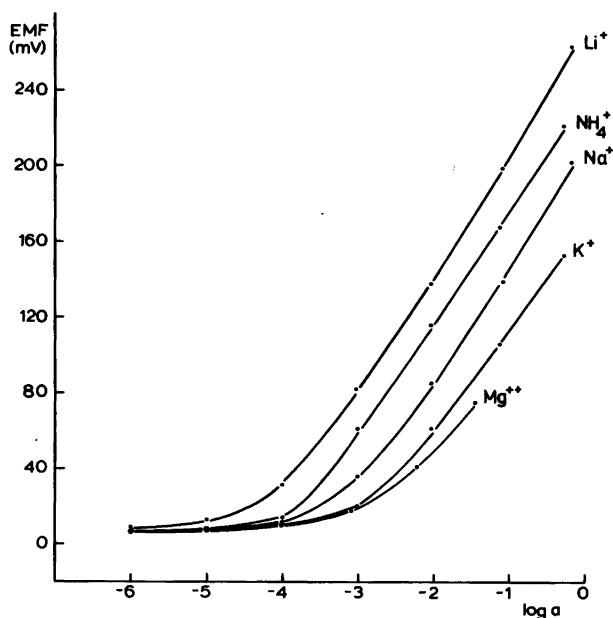


Fig. 3. EMF response of cell (1) to aqueous solutions of the chlorides of Li^+ , NH_4^+ , Na^+ , K^+ and Mg^{++} using neutral carrier B (Fig. 1) as a membrane component.

$$\log \gamma_{\text{Na}} = \frac{-0.51I^{\frac{1}{2}}}{1+1.30I^{\frac{1}{2}}} + 0.06I \quad (3) \quad -\log \gamma_i = Az^2 \frac{I^{\frac{1}{2}}}{1+BbI^{\frac{1}{2}}} \quad (5)$$

$$\log \gamma_{\text{Ca}} = \frac{-2.04I^{\frac{1}{2}}}{1+1.55I^{\frac{1}{2}}} + 0.2I \quad (4)$$

activity coefficients were calculated according to the form (5) of Debye-Huckel equation¹¹

A and B were taken to be 0.509 and 0.328, respectively, and b denotes the effective size of the hydrated ion.¹¹

Reagents. De-ionized water and chemicals from Merck (*pro analysis*) were used throughout the investigation.

Table 1. Electrode selectivity coefficients, k_{LiM} , determined by the separate solution technique on 10^{-1} M aqueous solutions of the chlorides.

	Carrier (A)		Carrier (B)	
	k_{LiM}	$1/k_{\text{LiM}}$	k_{LiM}	$1/k_{\text{LiM}}$
Li^+	1.0	1.0	1.0	1.0
H^+	4.7	0.2	3.5	0.3
NH_4^+	3.4×10^{-1}	3	3.2×10^{-1}	3
Na^+	1.0×10^{-1}	10	9.9×10^{-1}	10
K^+	2.0×10^{-2}	50	2.9×10^{-2}	35
Rb^+	1.4×10^{-2}	72	1.5×10^{-2}	67
Cs^+	1.3×10^{-2}	77	1.4×10^{-2}	71
Mg^{++}	1.7×10^{-3}	590	3.5×10^{-3}	286
Ca^{++}	1.4×10^{-3}	715	9.5×10^{-3}	105
Sr^{++}	1.2×10^{-3}	830	1.4×10^{-3}	715
Ba^{++}	1.2×10^{-3}	830	1.6×10^{-3}	625

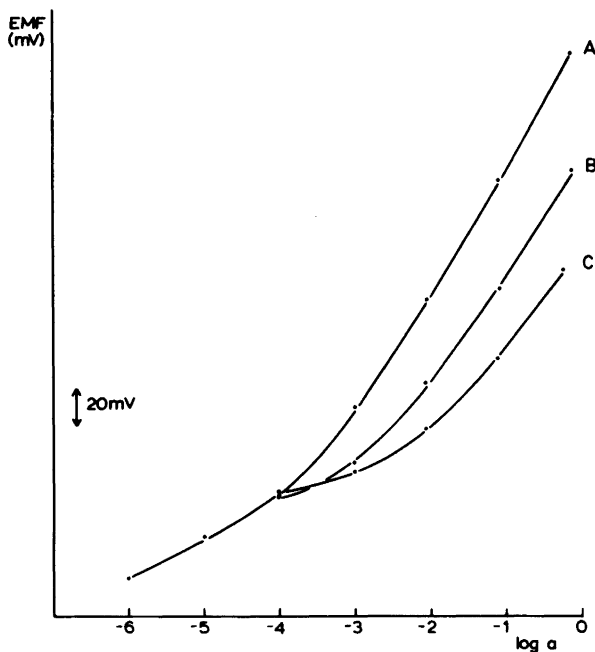


Fig. 4. EMF response of cell (1) to aqueous solutions of the chlorides of: A, Li^+ only; B, Na^+ with $[\text{Li}^+] = 10^{-4} \text{ M}$ as background; C, K^+ with $[\text{Li}^+] = 10^{-4} \text{ M}$ as background. Neutral carrier A (Fig. 1) used as membrane component.

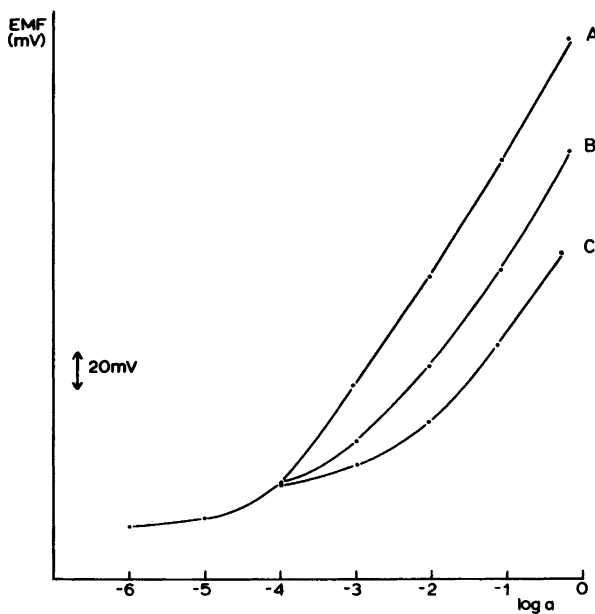


Fig. 5. EMF response of cell (1) to aqueous solutions of the chlorides of: A, Li^+ only; B, Na^+ with $[\text{Li}^+] = 10^{-4} \text{ M}$ as background; C, K^+ with $[\text{Li}^+] = 10^{-4} \text{ M}$ as background. Neutral carrier B (Fig. 1) used as membrane component.

RESULTS

The response of cell (1) to Li^+ , NH_4^+ , Na^+ , K^+ and Ca^{++} using (A) as the neutral carrier is shown in Fig. 2. The response of the same cell to Li^+ , NH_4^+ , Na^+ , K^+ and Mg^{++} using (B) as the neutral carrier is shown in Fig. 3. The EMF readings are not corrected for changes in the liquid junction potential by Henderson's equation.^{12,13} The uncertainties in the EMF readings should be comparable to those estimated by others using the same kind of experimental setup.^{3,4}

As shown in Figs. 2 and 3, the response is linear over the activity range 10^{-4} to 1 M for both (A) and (B), with nearly Nernstian slopes of 59 mV per activity decade for a monovalent ion at 25 °C. The membranes can also be used at lower concentrations. The electrodes also react in a near Nernstian fashion in different concentration regions for NH_4^+ , K^+ and Na^+ . This indicates that the electrodes can change from lithium ion response to an interfering

ion response depending upon the relative concentrations. This is illustrated in Figs. 4 and 5 where EMF readings for NaCl and KCl solutions in the concentration region 10^{-4} to 1 M with a constant background of 10^{-4} M LiCl are shown together with the readings for pure LiCl solution. The electrodes change rapidly, and reproducibly, from a lithium ion response to an interfering ion response during a single experiment and indicate a high rate of ion-replacement in both carriers. The same kind of behaviour has been found for other PVC membrane electrodes using crown ethers as neutral carriers.³

Selectivity coefficients obtained by the separate solution technique on 10^{-1} M solutions of the chlorides are indicated in Fig. 6 together with results from a glass electrode¹⁴ and investigations by Güggi *et al.*⁶ on their neutral carrier PVC membrane electrode. The selectivity coefficients are listed in Table 1. The present electrodes based on the neutral carriers (A) and (B) give better selectivity for lithium

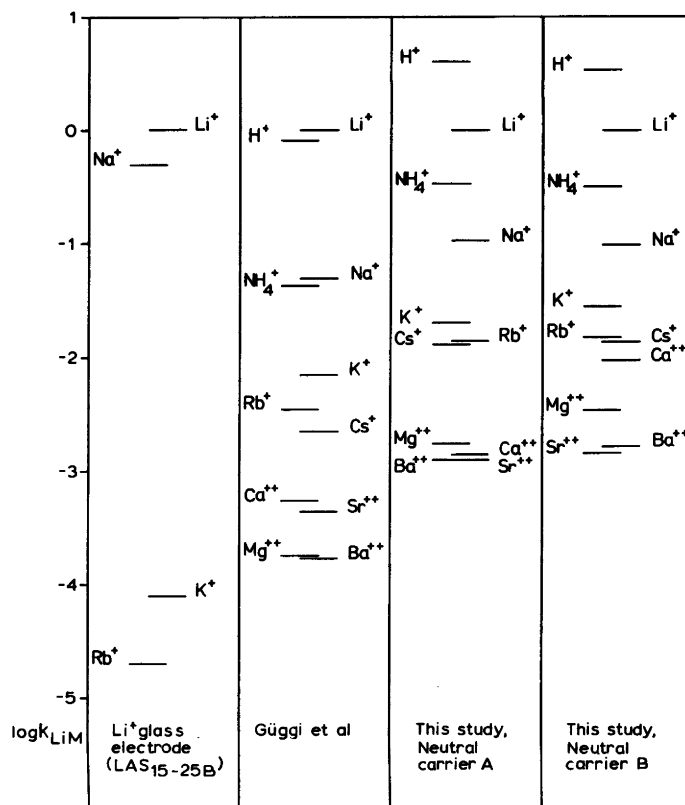


Fig. 6. Selectivity coefficients obtained by the separate solution technique on 10^{-1} M solutions of the chlorides. (See Refs. 6 and 14).

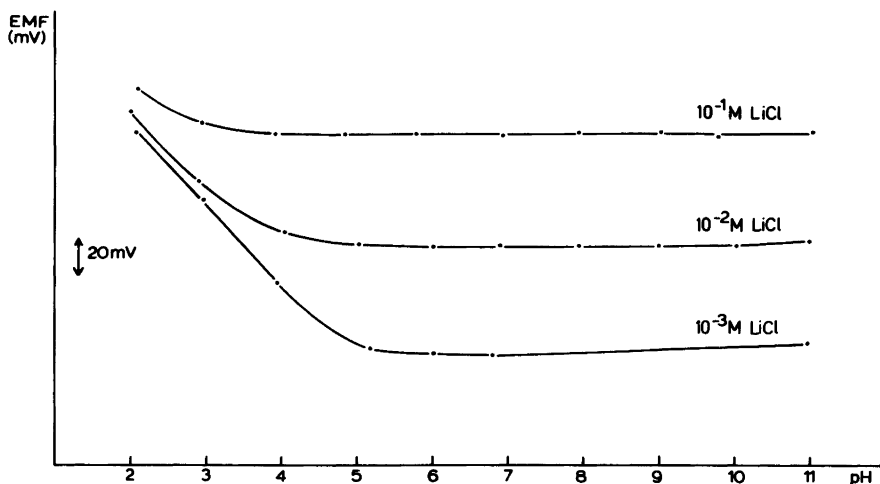


Fig. 7. EMF response of cell (1) for different LiCl concentrations as a function of pH. Neutral carrier A (Fig. 1) used as membrane component, HCl and KOH used to change the pH value.

to sodium than can be obtained with the glass electrode, but the selectivities are not as good as those found by Guggi *et al.*⁶ using the neutral carrier *N,N'*-diheptyl-*N,N',5,5*-tetramethyl-3,7-dioxanonane diamide.

Attempts were made to prepare membranes with plasticizers other than tris(2-ethylhexyl)phosphate, especially because the octamethyl derivative carrier was rather sparingly soluble in this medium, and sometimes the carrier crystallized in the PVC matrix. Plasticizers such as tributylphosphate, di-

buthylphthalate, diphenylether, nitrobenzene and didecylphthalate were investigated, but did not give good results. We think that further attempts should be made to find a more suitable plasticizer for the neutral carrier (B), *i.e.* a more hydrophobic plasticizer where solubility and mobility of the carrier would be enhanced.

Figs. 7 and 8 show the EMF readings for different lithium chloride solutions as a function of pH. The readings are constant in a wide region of the pH scale, but at low pH values there is serious inter-

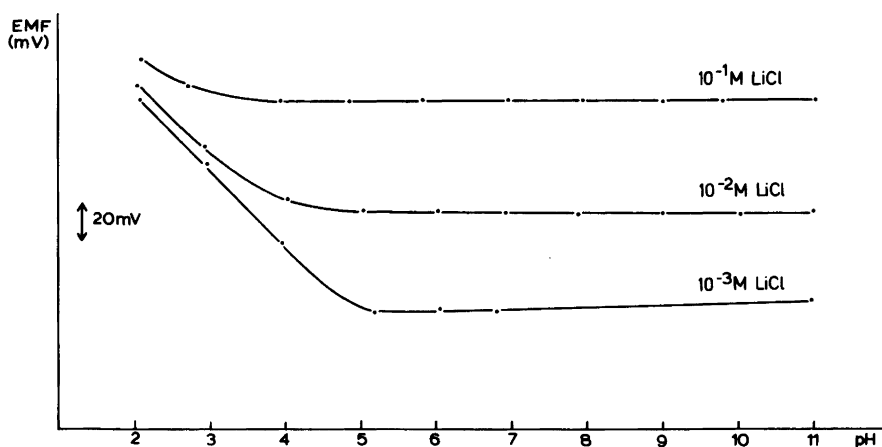


Fig. 8. EMF response of cell (1) for different LiCl concentrations as a function of pH. Neutral carrier B (Fig. 1) used as membrane component, HCl and KOH used to change the pH value.

ference with H^+ ions. This is to be expected according to the selectivity coefficients measured in 10^{-1} M solutions (Fig. 6 and Table 1).

Guggi *et al.*⁶ pointed out that an anion interference of 5 mV was observed for SCN^- compared to Cl^- in 10^{-1} M solutions. The same kind of behaviour is observed in the two membranes investigated in this work. The response time for both electrodes is in the order of a few seconds both in concentrated and dilute solutions, and the lifetime of the membranes is substantial, as is found for other PVC membranes. The uncertainty in the EMF readings is ± 0.15 mV. Stirring the solutions has very little effect upon the EMF readings.

DISCUSSION

The interactions between ligand binding sites and cations are normally analyzed into several energy contributions, mostly in electrostatic terms. An excellent review article by Lehn¹⁵ deals with the various factors influencing complexation. A number of factors influence cation selectivity. For inorganic cations the following factors are important: charge, size, electronic structure and associated ions or counterions. The most important factors for the ligand are cavity size, donor atom type and number, ring conformation and ring substituents. Some data also indicate that the type of polymer used may change the selectivity drastically.¹⁶

Winkler¹⁷ has pointed out that in the case of lithium, which has a very high field density at the surface, the energy required to strip off the inner hydration shell of four water molecules is 510 kJ mol^{-1} ($122 \text{ Kcal mol}^{-1}$) and that the interaction of any acceptor ligand with the cation must be very favourable to compete with this hydration energy. However, individual water molecules in this shell have a very high rate of substitution by ligands and Winkler suggests that the optimal acceptor would be one which substitutes water molecules in a step-wise fashion and was itself flexible enough to change conformation sequentially to a more compact structure. We think we have two such compounds at hand.

The conformational situation for ligands (A) and (B) has been discussed in the preceding article⁷ both with and without Li^+ present. We believe that the following situation exists when (A) and (B) are transporting Li^+ through the so-called solid-liquid membrane: the ring conformation of (A) and (B) in

the membrane without Li^+ present is as depicted in Fig. 1 in the preceding article.⁷ On the membrane surface the carriers (A) and (B) substitute one of the four inner water molecules around Li^+ with an ether oxygen. The closed unoccupied oxygens in the ring are facing away from the incoming Li^+ , now with three water molecules. A successive inward rotation of oxygens can now substitute one water molecule after the other, and the final ring conformation of the ligand is as depicted in Fig. 3 in the preceding article.⁷ The activation energies for these conformational changes are also discussed in detail in that article.⁷ The complex can now diffuse across the membrane. The ligands in the complexed form have a much more hydrophobic exterior than the uncomplexed square form. The release action of Li^+ at the opposite boundary on the membrane is likely to be the reverse of what has been described above.

If the description as given above is correct, then the compounds (A) and (B) meet the criteria set forth by Winkler for good carriers.¹⁷

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