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New class of lithium ion selective crown ethers with bulky decalin subunits

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Contents

Abstract

Didecalino-14-crown-4 and decalino-14-crown-4 respectively show excellent extractability and high transport selectivity toward lithium ion. Decalino-14-crown-4 exhibits 1:1 (crown ether:cation mole ratio) stoichiometry on complexation with lithium and sodium ions, while benzo-14-crown-4 gives 1:1 complex with lithium ion and 2:1 complex with sodium ion. An electrode based on decalino-14-crown-4 shows the highest Li^+/Na^+ selectivity. Tetradecyldecalino-14-crown-4 is found to be the most practically valuable ionophore for lithium ion-selective electrode.

Keywords: 14-Crown-4; Crown ether; Complex; Ion-selective electrode

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1. Introduction

The most extensively investigated hosts are crown ethers which bind cations as well as neutral molecules by virtue of dipole–dipole interaction and/or hydrogen

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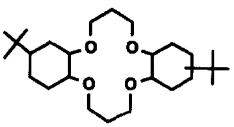
bonding. In view of their high complexation ability and versatility, simple *X*-crown-*Y* ($X=18$ and $Y=6$, $X=15$ and $Y=5$, and $X=14$ and $Y=4$, etc.) has been regarded as a prototype of this class of molecules, and by modifying *X*-crown-*Y* many crown ethers have so far been synthesized [1].

The selectivity of crown ethers toward alkali metal ions has generally been explained in terms of 'hole-size selectivity' of the crown ethers. For example, bis(*tert*-butylcyclohexano)-14-crown-4 (**1**), cyclohexano-15-crown-5 (**2**), and 18-crown-6 (**3**) undergo selective complexation with lithium, sodium, and potassium ions respectively [2–4].



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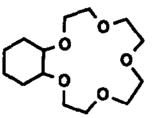

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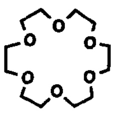

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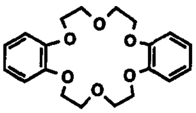
However, in the case of a flat crown ether, such as dibenzo-18-crown-6 (**4**), 'sandwich'-type 2:1 (crown ether:cation) or 'club-sandwich'-type 3:2 complex formation with large cations compared with its cavity size is a common feature (Fig. 1) [5]. Several sandwich-type structures have been confirmed by X-ray structure analyses, as exemplified by those complexes of 12-crown-4 (**5**) with lithium ion [6–12], **5** with sodium ion [13,14], benzo-15-crown-5 (**6**) with potassium ion [15], and tetramethyldibenzo-18-crown-6 (**7**) with cesium ion [16,17]. The sandwich-type complex formation is one of the factors which reduces the selectivity of crown ethers between cations.



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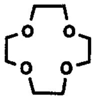

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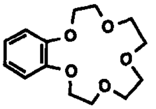

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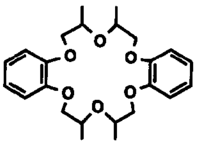

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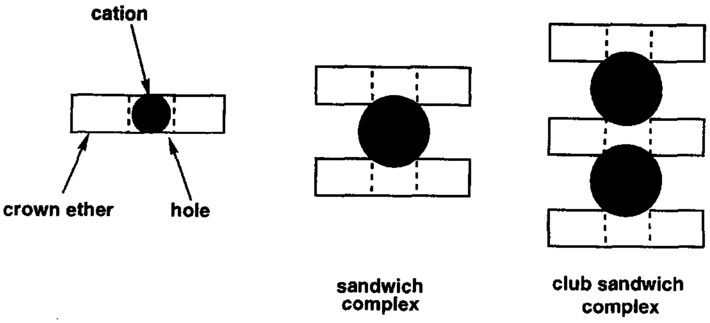


Fig. 1. Schematic representations of sandwich complexes. Reproduced from Ref. [5] with permission.

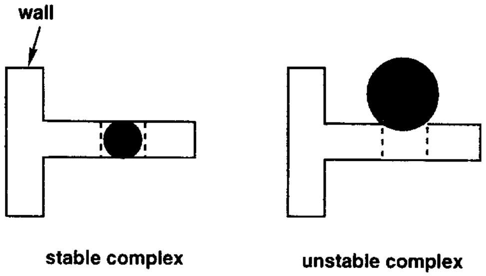
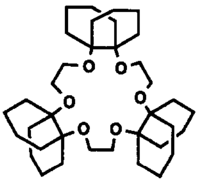


Fig. 2. Schematic representations of 1:1 (crown ether:cation) complexes of bulky crown ethers.

Our basic idea for the molecular design of highly selective crown ethers is that the introduction of bulky subunits in a crown ether ring would suppress the formation of a sandwich-type complex with a cation whose diameter is larger than the cavity size of the crown ether (Fig. 2). Consequently, the high selectivity inherent in the crown ether due to the size-fit between cation and cavity would be preserved. In order to prove this idea, we chose the aliphatic decalin subunit as an effective steric barrier. As the first example, we designed a new class of crown ether, tridecalino-18-crown-6 (**8**), having three bulky decalin subunits, as a potassium ion selective crown ether [18].



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Indeed, crown ether **8** exhibited high complexation ability as well as excellent selectivity toward potassium ion, as expected. Space-filling molecular model (CPK) examination suggests that the incorporated three decalin subunits are almost perpendicular to the crown ether ring and provide the definite steric barriers which spread out above and below the axial direction of the crown ether, constructing a beautiful 'cylindrical' architecture in which the top and bottom spaces are left open (Fig. 3). The height of the 'decalin wall' is estimated as about 8.8 Å. In this molecule, the formation of a sandwich-type complex would be perfectly suppressed by the steric hindrance of the bulky decalin subunits, preserving the high selectivity toward potassium ion inherent of the 18-crown-6 itself. In addition, strong complexation is also expected because the coordination site is well surrounded by the three decalin subunits. Therefore, the coordinated cation in the center of the crown ether is buried deeply in the lipophilic atmosphere, and the cation is shielded from attack by solvent molecules or anions in the decomplexation process.

Much attention has been focused on lithium from the viewpoint of actual and potential use with wide applicability from material science to medical and clinical

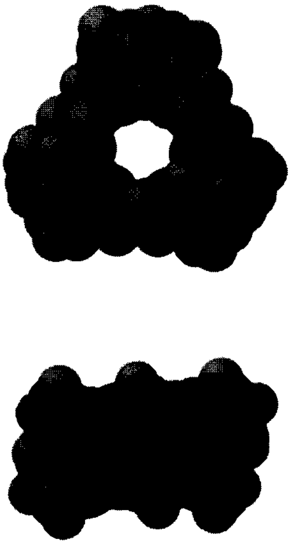
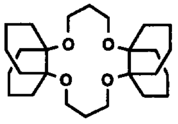


Fig. 3. Computer generated molecular model of crown ether **8**. Top view (above) and side view (below).

sciences [19]. Especially, the growing demand of lithium as a vital source for tritium has arisen in the field of material science [20–22]. In connection with supplying this demand, much effort has been paid to the technique for extracting or concentrating lithium ion from hot spring water or sea water [23]. However, little is known about designing an ionophore showing high selectivity for lithium ion, not only because lithium ion has a small ionic diameter and is strongly hydrated in water, but also because sodium ion is much more abundant in nature.

We planned to prepare a highly lithium ion selective ionophore by applying our decalin wall strategy to the 14-crown-4 system which should inherently be lithium ion selective. We designed a new class of crown ethers, didecalino-14-crown-4 (**9**) and decalino-14-crown-4 (**10**), in the expectation of forming a strong and efficient ionophore for lithium ion [24,25].



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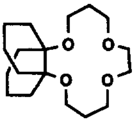

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Herein, we report recent results on lithium ion selective ionophore based on the decalin wall strategy; syntheses, alkali metal ion selectivity, X-ray molecular structure analyses of lithium ion complexes, and application to the lithium ion-selective electrodes of decalino-14-crown-4 derivatives are discussed.

2. Molecular design

Molecular model examination suggests that, in the case of crown ether **9**, the crown ether has a small cavity (about 1.2 Å) and decalin subunits construct bulky walls in both sides of the crown ether (Fig. 4). Lithium ion coordinated in the crown ether would be buried deeply in the lipophilic atmosphere of the two decalin subunits. This crown ether would, therefore, extract lithium ion effectively. In contrast, in the case of crown ether **10**, one decalin subunit in the crown ether ring constructs a bulky wall on one side, while the opposite side of the crown ether ring remains relatively unhindered (Fig. 5). Accordingly, crown ether **10** would be a good example for an ion selective ionophore, because it satisfies the indispensable conditions as an ion-selective ionophore: i.e. the balance between complexation and decomplexation abilities and high lipophilicity for efficient recycle of ionophore.

3. Synthesis

The target crown ethers **9** and **10** were easily synthesized from *cis*-1,6-dihydroxy-bicyclo[4.4.0]decane (decalin diol) (**11**) and its monobenzyl ether **12** respectively, as shown in Schemes 1 and 2 [24,25]. Reaction of decalin diol **11** with 1,10-dichloro-4,7-dioxadecane (**13**) in the presence of NaOH as a base and $LiClO_4$ as a template in dimethyl sulfoxide gave crown ether **10** as shown in Scheme 1. Reaction of alcohol **12** and allyl bromide followed by hydroboration oxidation and tosylation yielded tosylate **14**. Reaction of tosylate **14** and alcohol **12** followed by hydrogenolysis provided didecalino-diol **15**. Cyclization of didecalino-diol **15** with

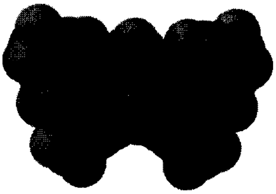


Fig. 4. Side view of computer generated molecular model of crown ether **9**.

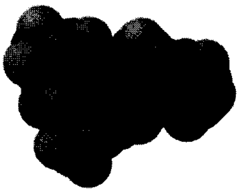
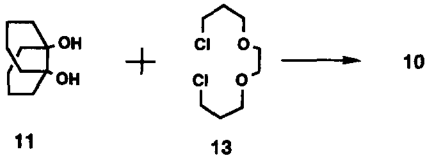
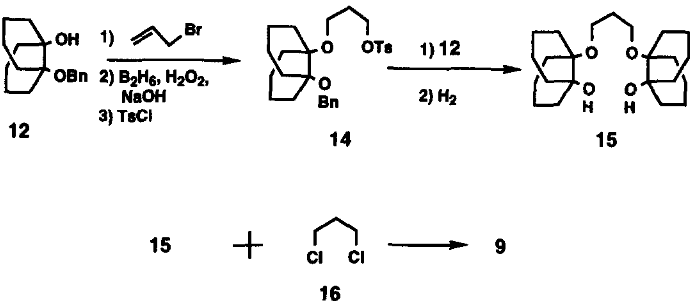


Fig. 5. Side view of computer generated molecular model of crown ether **10**.

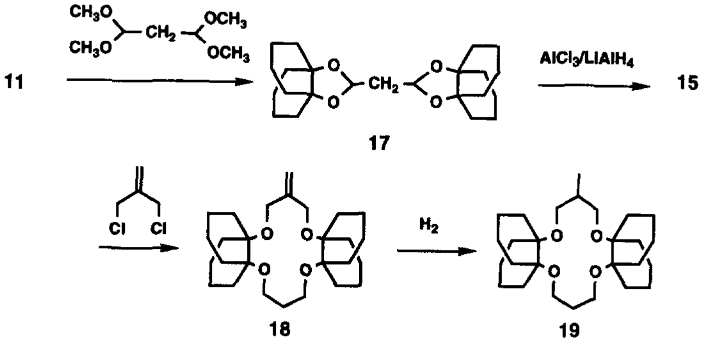


Scheme 1.



Scheme 2.

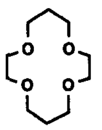
1,3-dichloropropane (**16**) gave crown ether **9**. Recently, Sachleben et al. [26] reported an effective synthesis for methyldidecalino-14-crown-4 (**19**) according to Scheme 3. The key reaction is the reductive ring-opening of bisacetal **17** which is prepared by the reaction of decalin diol **11** and 1,1,3,3-tetramethoxypropane. The reaction proceeded in excellent yields to provide the intermediate diol-diether **15**. The cyclization of **15** with methallyl dichloride followed by hydrogenation of the double bond gave crown ether **19** in a good yield.



Scheme 3.

4. Extraction and transport of lithium ion

With a view to estimating the complexation and extraction ability of crown ethers **9** and **10**, extraction experiments of alkali metal picrates were carried out in dichloromethane–water system [24,25]. As shown in Table 1, crown ether **9** showed quantitative extraction toward lithium ion under the conditions using tenfold excess crown ether relative to lithium picrate. Even under the conditions using an equimolar amount of crown ether relative to lithium picrate, crown ether **9** still exhibits good extractability toward lithium ion. Crown ether **10** also showed high extractability toward lithium ion. Moreover, the Li^+/Na^+ selectivity of **10** is high compared with those of the reference crown ethers, **1**, parent 14-crown-4 (**20**) [2], and decalino-stilbeno-14-crown-4 (**21**). These results clearly demonstrate that crown ether **9** is a highly effective extractant for lithium ion.



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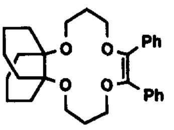


21

Next, in order to know the transport selectivity of crown ether **10**, the competitive transport of alkali metal picrates through chloroform membrane was examined using the double glass cell where two aqueous phases were separated by chloroform membrane [25]. As shown in Fig. 6, crown ether **10** transported Li^+ much more effectively than the reference compounds **20** and **21**; the rate of Li^+ transport using **10** is about ten-times faster than those using **20** and **21**. Crown ether **10** did not transport K^+, Rb^+, and Cs^+ at all. The Li^+/Na^+ selectivity of **10** was determined to be about 20. As a result, crown ether **10** having one decalin subunit is proved to be an effective and selective ionophore for lithium ion.

Table 1
Extraction of alkali metal picrates in the water–dichloromethane system by crown ethers **1**, **9**, **10**, **20** and **21**[a]

Crown ether	Extractability/%				
	Li^+	Na^+	K^+	Rb^+	Cs^+
9	ca. 100	20			
9	(24)	(3)	(<1)	(<1)	(<1)
10	81	5	1	1	1
21	13	3	3	3	3
1[b]	11.9	4.7	0.4	—	ca. 0
20	11	1	<1	<1	<1

[a] [Crown ether] = 7.0×10^{-4} M, [picric acid] = 7.0×10^{-5} M, [alkali metal hydroxide] = 0.1 M. The values in parentheses were obtained under the conditions of [crown ether] = 7.0×10^{-5} M, [picric acid] = 7.0×10^{-5} M, and [alkali metal hydroxide] = 0.1 M. [b] See Ref. [2].

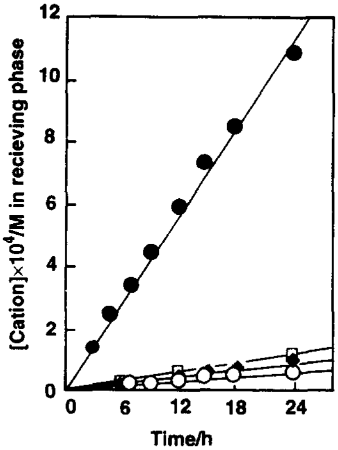


Fig. 6. Competitive transport of alkali metal ions through a chloroform membrane containing ionophores **10**, **20**, and **21**. Plots for transport of Li^+ by ● **10**, □ **20**, and ◆ **21**. Plot for competitive transport of Na^+ by ○ **10**. K^+, Rb^+, and Cs^+ were not transported at all by **10**. Reproduced from Ref. [25] with permission.

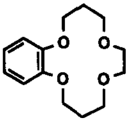
5. Stoichiometric selectivity on complexation

To probe whether or not the stoichiometry of complexation of **10** with alkali metal ions is definitely 1 : 1 (crown ether: cation mole ratio), complexes were prepared and their stoichiometry was determined by elemental analyses [27]. Crystalline complexes were prepared by the reaction of lithium and sodium salts with either an equimolar or two molar amounts of **10**, as shown in Table 2. A similar reaction was undertaken with benzo-14-crown-4 (**22**) for comparison. Crown ether **10**, having one decalin subunit, gave only 1 : 1 complexes with both lithium and sodium ions regardless of the relative amount of the reactants. No sandwich-type complex was observed. In contrast, crown ether **22**, being a flat molecule, gave a 1 : 1 complex with lithium

Table 2
Stoichiometry and yields of crystalline complexes of crown ethers **10** and **22** with lithium and sodium salts

Crown ether	Salt	Mole ratio of reactant (crown ether : cation)	Mole ratio of complexes (crown ether : cation)	Yield/%
10	$LiClO_4$	1:1	1:1	86
10	$LiClO_4$	2:1	1:1	97
10	$NaClO_4$	1:1	1:1	64
10	$NaClO_4$	2:1	1:1	93
22	LiNCS	1:1	1:1	72
22	LiNCS	2:1	1:1	75
22	$NaClO_4$	1:1	2:1	99
22	$NaClO_4$	2:1	2:1	85

ion even in the presence of excess **22**; interestingly, it only formed a 2 : 1 complex with sodium ion even when equimolar amounts of **22** and $NaClO_4$ were used. The sandwich structure of the 2 : 1 complex $\mathbf{22}_2$–$NaClO_4$ was confirmed by X-ray structure analysis as will be discussed in the next section [27]. These results clearly demonstrate that introduction of a decalin subunit in the crown ether caused 1 : 1 stoichiometric selectivity in complexation with lithium and sodium ions.



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6. Molecular structures of crown ether–lithium ion complexes

X-ray structure analysis of **10**–lithium picrate complex was investigated as shown in Fig. 7 [27]. The bulky decalin subunit spreads out above and below the crown ether ring and constructs a definite steric barrier to the axial direction of the crown ether. The plane defined by four ethereal oxygen atoms of the crown ether is planar within 0.04 Å. The decalin subunit is inclined relative to the O_4 plane, and the lithium ion is situated 0.70 Å above the O_4 plane. The oxygen atom of the phenolate anion coordinates from the upper direction to form a five-coordinate square pyramidal lithium ion, which is quite normal in the lithium ion complexes of

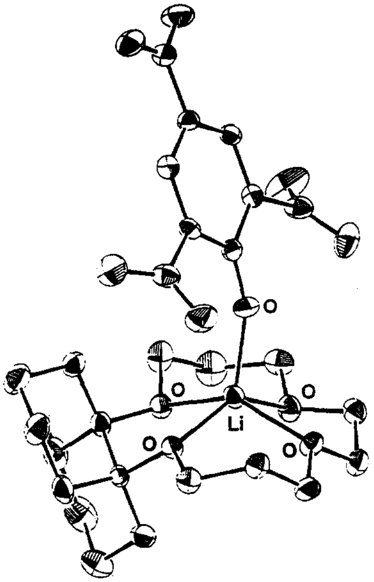


Fig. 7. ORTEP drawing of the **10**–lithium picrate complex. Hydrogen atoms are omitted for clarity.

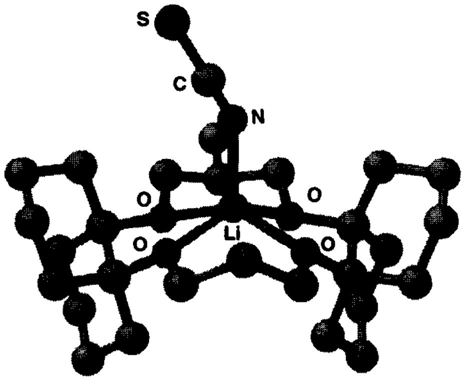


Fig. 8. Molecular structure of the **19**–LiNCS complex. The molecular structure reported is redrafted because of easy comparison with the molecular structure of the **10**–lithium picrate complex in Fig. 7.

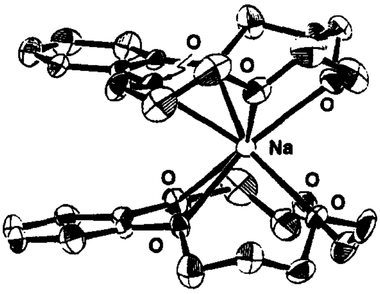


Fig. 9. ORTEP drawing of the **22**$_2$–$NaClO_4$ complex. Hydrogen atoms and perchlorate anion are omitted for clarity.

14-crown-4 derivatives [28]. The 14-crown-4 ring adopts a pseudo-chair conformation. 'V'-shape decalin barriers, a normal five-coordinate square pyramidal geometry of the lithium ion, and a pseudo-chair geometry of the 14-crown-4 ring were also observed for the **19**–lithium thiocyanate complex (Fig. 8) [29].

In contrast to **10**, crown ether **22** formed a sandwich-type 2:1 complex with sodium ion (Fig. 9) [27]. Sodium ion is coordinated by eight oxygen atoms and is situated 1.55 Å above the mean plane of the four oxygen atoms of a crown ether to form an eight-coordinate square antiprism geometry. The 14-membered ring has a pseudo-boat configuration, in which both central methylene groups of the trimethylene bridge bend toward the direction of the cation. It is noteworthy that two 14-crown-4 rings of the complex have a head-to-head geometry, in contrast to the head-to-tail geometry of the **6**$_2$–KI complex [15].

7. Ionophore for lithium ion-selective electrodes

There has been much interest in lithium ion-selective electrodes using neutral carriers in environmental, medical, and clinical fields because they are the most convenient and practical tools for analysis of lithium concentration [30,31]. A number of synthetic ionophores have so far been synthesized and some of them have shown high selectivity for lithium ion against the most abundant sodium ion [32–36]. Since crown ethers with four oxygen atoms are known to exhibit lithium ion selectivity, several 12-crown-4, 14-crown-4, and 16-crown-4 derivatives have so far been applied to the ionophores of the lithium ion-selective electrodes [37–41]. However, such electrodes were not satisfactory in the Li^+/Na^+ selectivity. We applied the decalino-14-crown-4 (**10**) as an ionophore for the lithium ion-selective electrode [42]. We also investigated the relationship between structures of the related 14-crown-4 derivatives and ion-selectivity of the electrodes [43].

Ion-selective membranes were composed of ionophore, membrane solvent, potassium tetrakis(*p*-chlorophenyl) borate as a lipophilic anion, and polyvinyl chloride as a binder. The composition of the electrochemical cell system was

Ag; AgCl, KCl soln|NH_4NO_3 soln|test soln|membrane|LiCl soln, AgCl; Ag

As shown in Fig. 10, the electrode containing crown ether **10** as an ionophore is found to be one of the best lithium ion-selective electrode system so far known [42]. In this system, the membrane solvent also has an important effect on lithium ion selectivity. Low polarity solvents such as bis(butylpentyl) adipate (BBPA) ($\varepsilon = 4$, ε: dielectric constant) and bis(2-ethylhexyl) phthalate (BEHP) ($\varepsilon = 4$) gave better Li^+/Na^+ selectivity than high polarity solvents such as 2-nitrophenyl octyl ether (NPOE) ($\varepsilon = 24$) and 2-nitrophenyl phenyl ether (NPPE) ($\varepsilon = 24$). The electrode with BBPA, especially, showed one of the highest Li^+/Na^+ selectivities about 2000 ($\log K^{pot}_{Li,Na} = -3.3$) and a linear Nernstian response slope ranging from 1×10^{-6} to 1 M of Li^+.

Although crown ether **10** showed excellent lithium ion selectivity in the membrane

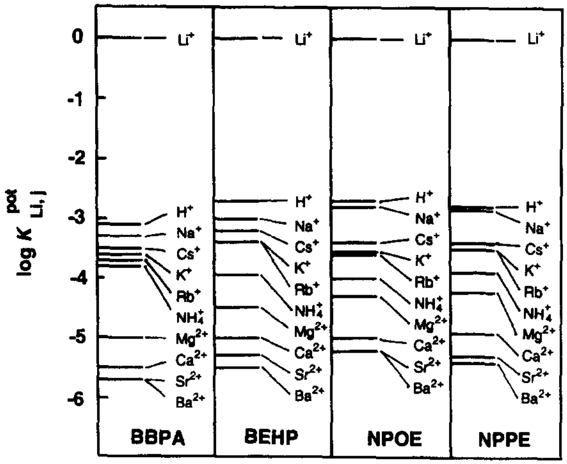
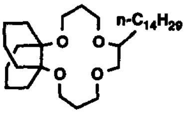


Fig. 10. Selectivity coefficients ($\log K^{pot}_{Li,j}$, j is the interfering cation) of the PVC-matrix membrane electrodes based on crown ether **10** with different membrane solvents obtained by the fixed interference method. Reproduced from Ref. [42] with permission.

electrode system as described above, it is desirable for practical purposes to prepare ionophores with larger lipophilicity. For this purpose, Suzuki et al. [43] planned to introduce a long alkyl chain, an *n*-tetradecyl group, at the ethano bridge of crown ether **10** to furnish tetradecyldecalino-14-crown-4 (**23**). Crown ether **23** and reference compounds **24**, **25**, and **26** were synthesized according to a method similar to that described for **10**. The excellent Li^+/Na^+ selectivity of the electrode using crown ether **10** (log $K^{pot}_{Li,Na} = -3.3$ by the fixed interference method) was scarcely reduced by the long *n*-tetradecyl chain, exhibiting excellent Li^+/Na^+ selectivity with the electrode using **23** (log $K^{pot}_{Li,Na} = -3.0$ by the separation solution method and log $K^{pot}_{Li,Na} = -3.1$ by the fixed interference method) and over 1000 selectivity against all other alkali metal ions examined. Electrodes using crown ethers **24**, **25**, and **26** also showed high Li^+/Na^+ selectivity (log $K^{pot}_{Li,Na} = -2.6$, -2.8, and -2.9 respectively) (Fig. 11). High lipophilicity was successfully introduced into ionophore **10** to furnish **23**–**26** without appreciably reducing the high Li^+/Na^+ selectivity of **10**.



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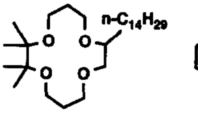

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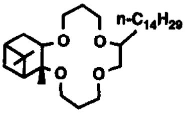

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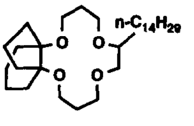

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Crown ethers **27**–**33** were also synthesized and their ion selectivities as electrodes were investigated by Suzuki et al. [43]. Electrodes based on crown ethers **27**, **28**, **29**, and **30** having two bulky subunits on both ethano bridges showed a relatively lower selectivity toward Li^+ than that based on crown ether **23**, as can be seen in Fig. 12. The observed small e.m.f. values and slow response to Li^+ of the electrodes

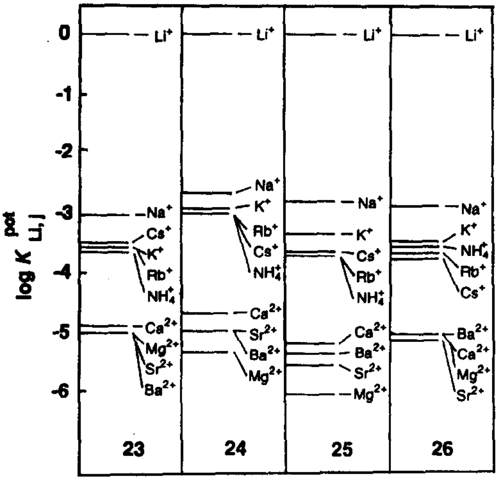


Fig. 11. Selectivity coefficients (log $K^{pot}_{Li,j}$, *j* is the interfering cation) of the PVC-matrix membrane electrodes based on crown ether **23**–**26** by the separation solution method. Reproduced from Ref. [43] with permission.

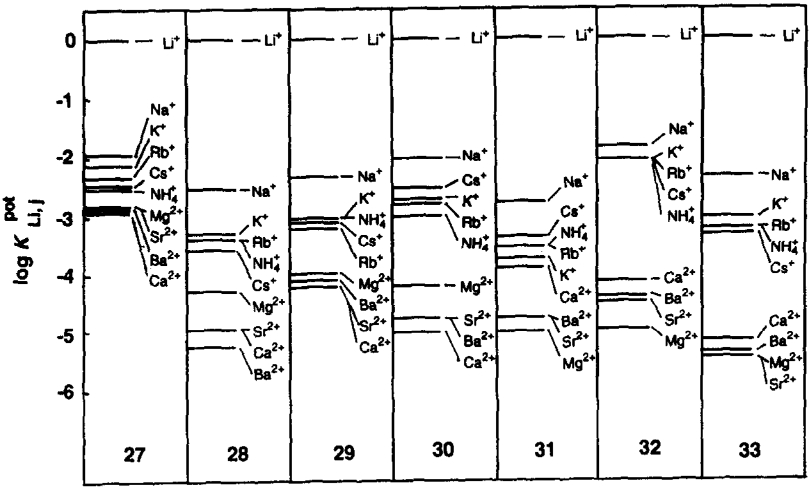
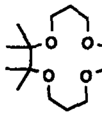
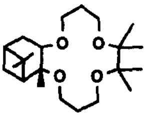
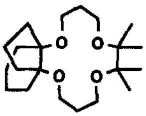


Fig. 12. Selectivity coefficients (log $K^{pot}_{Li,j}$, j is the interfering cation) of the PVC-matrix membrane electrodes based on crown ether **27**–**33** by the separation solution method. Reproduced from Ref. [43] with permission.

based on crown ethers **27**, **28**, **29**, **30** indicate that slow kinetic reactions occur in complexation of the crown ethers with Li$^+$. The electrode based on **31** showed good selectivity toward Li$^+$ while electrodes using **32** and **33** with the bulky subunits at the trimethylene bridges of the crown ether ring exhibited lower selectivity to Li$^+$. These results show that the 14-crown-4 derivatives with two bulky subunits on both sides of ethano bridges, except for **31**, are unsuitable for lithium ion-selective ionophore, because too many bulky subunits cause lower Li$^+$/Na$^+$ selectivity.


27


28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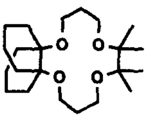
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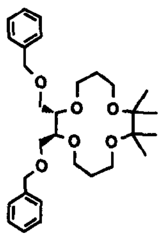
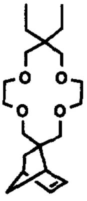
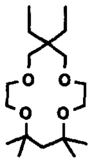

31


32


33

As for practical use, the electrode based on crown ether **23** can determine 0.5 mM

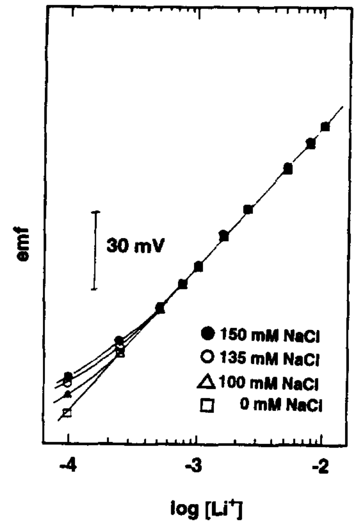


Fig. 13. Typical Li^+ response curves of the electrodes based on crown ether **10** with different Na^+ background concentrations. Reproduced from Ref. [43] with permission.

Li^+ with an error between 1.7% and 3.4% in cases where the background Na^+ concentration varies in the range from 130 to 150 mM and from 100 to 150 mM respectively. A linear Nernstian response is observed in the concentration ranges from 2×10^{-6} to 1 M Li^+ when no interfering ion is present and up to 1 mM Li^+ when the test samples contain 150 mM Na^+, as shown in Fig. 13. In conclusion, crown ether **23** presently offers the best lithium ion selective electrode yet known.

8. Concluding remarks

Rational design of new crown ethers inspired by molecular model examination has provided us with didecalino-14-crown-4 (**9**), decalino-14-crown-4 (**10**), and tetradecyldecalino-14-crown-4 (**23**). Crown ether **9** was found to be a highly effective lithium ion-selective extractant. Crown ether **10** was found to be one of the best ionophores for the lithium ion-selective electrode, and crown ether **23** bearing a long alkyl chain was the most practically valuable ionophore; the Li^+/Na^+ selectivities were 2000 and 1300 respectively.

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