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Cation binding by thallium(I) selective crown ethers

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Contents

Abstract

The cation-binding abilities of crown ethers for thallium(I) ion are described.

Unsubstituted symmetrical and unsymmetrical crown-5 and crown-6 ethers usually possess high thallium(I) ion binding ability; however, its selectivity against alkali metal ions is not so high. Unsymmetrical benzo-type crown ethers possess high thallium(I) ion selectivity especially against potassium and rubidium ions. This review deals with the cation-binding ability/selectivity for thallium(I) ion against alkali metal ions evaluated from the solvent extraction of metal picrates and PVC membrane thallium(I) ion-selective electrodes based on crown ethers.

Keywords: Crown ether; Cation binding; Solvent extraction

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1. Introduction

The chemistry of crown ethers [1] has been extensively developed since Pedersen's pioneering work in 1967 [2], and a number of papers and books have been published to investigate and to review the attractive characteristics of crown ethers with respect to physical, organic, bioorganic, analytical, and polymer chemistry. Recently, it has shifted from simple monocyclic compounds [3] to more sophisticated structures involving lariat ether [4], cryptands [5], spherands [6], and other supramolecular systems [7]. The control of cation-binding ability of crown ethers especially has been the subject of more recent investigations, and a good deal of effort has been devoted to the complexation of alkali metal ions [1,5]. The heavy metal thallium(I) ion has a diameter of 3.00 Å [8], which is quite similar to those of potassium (2.76 Å) and rubidium (2.98 Å). However, separation of these metal ions by crown ethers has not yet been reported, probably because of the generally accepted hole-size concept [2]. Furthermore, in general, most crown ethers have higher cation-binding ability for thallium(I) than for potassium and rubidium. This is explained by the higher polarizability and the contribution of covalent bonding by the thallium(I) ion [9].

From the environmental and biological viewpoint, thallium poisoning is still a problem [10]. Thallium(I) is especially toxic in its bivalent compounds, e.g. sulfate (Tl_2SO_4), acetate (CH_3COOTl), and carbonate (Tl_2CO_3). The lethal dose of thallium(I) and its compounds is very low, and precautions must be taken when handling them because they are easily absorbed into the body by skin contact or ingestion. Furthermore, thallium(I) ion has been suggested as a probe for potassium ion in biological systems [11]. Thus, direct determination of thallium(I) in biological materials by analytical methods is of special interest; some spectrometric methods have already been reported [12].

We have reviewed complexation by crown ethers of low symmetry, and demonstrated the specific alkali metal ion selectivity of unsymmetrical crown ethers [13]. Compared with symmetrical crown ethers, crown ethers of low symmetry, possessing ($3m+n$)-crown-m skeletons showed lower cation-binding ability in general but exhibit drastically different and, in some cases, higher selectivities for specific cations. The application of crown ethers of low symmetry to ion-selective electrodes has also reported [14]. In this context, it is our special interest to investigate the thallium(I) ion binding behavior of crown ethers from the stand point of molecular symmetry and to describe the molecular design of highly thallium(I) selective crown ethers.

In this paper, we review the cation-binding behavior of the two major categories of crown ether, i.e. symmetrical and unsymmetrical. We discuss the cation-binding ability of crown ethers mainly from the data of solvent extraction experiments and PVC membrane electrodes based on these crown ethers.

It may be very difficult to explore the problem of thallium(I) selectivity from the present results, however, as the topic of thallium(I) selective crown ethers is new to crown ether chemistry. Ligand design, ligand conformation, electronic contribution, the nature of thallium(I), and complexation phenomena should be more carefully investigated from the crown ethers presented in this study.

2. Cation binding by crown ethers

2.1. Measurement techniques

A variety of measurement techniques for recording the cation-binding ability of crown ethers have been reported [15]. Notable among them are ion-selective electrode techniques, conductance methods, NMR methods, solvent extraction techniques, and calorimetry. In this paper, data obtained by solvent extraction techniques are presented for general discussion.

Furthermore, for the applications of crown compounds in analytical chemistry, the ion-selective electrode is a very important target. Recently, neutral carrier-type ion-selective electrodes have been extensively studied [14]. Some examples of thallium(I) ion-selective electrode based on crown ethers are also described in this paper.

2.2. Solvent extraction of metal picrates

The solvent extraction of metal picrates has been employed as a convenient method for evaluating cation-binding ability of crown ethers, and, as far as monovalent cations are concerned, it affords quantitative binding constants compatible with those obtained in homogeneous phase complexation [16]. The solvent extraction of aqueous metal picrates were performed at 25 °C with crown ethers in dichloromethane. The percentage extractabilities (% Ex), defined as percentage picrate extracted into the organic phase, were measured. The extraction equilibrium constants K_{ex} and the complex stoichiometries n for $n:1$ crown ether–cation complexes were also determined [16].

That this extraction technique must be used with caution was discussed because the data obtained depend on several variables [15]: solvent, temperature, salt, and ionic strength. When the conditions of extraction are fixed, the data obtained give invaluable information [17]. The data presented in this paper are obtained under fixed and controlled conditions. Metal picrates are used as salts, and the dichloromethane–water system at 25 °C is adopted.

The overall extraction equilibrium between an aqueous solution of monovalent metal picrate (M^+A^-) and a dichloromethane solution of crown ether (CE) can be described for a $1:n$ crown ether–cation complex ($n=1, 2$) as follows [16]:

$$K_{ex}=[\mathrm{M(CE)}n\mathrm{A}]_{org}/[\mathrm{M}^+]_{aq}[\mathrm{A}^-]_{aq}[\mathrm{CE}]^n_{org} \quad (1)$$

where the subscripts aq and org refer to the aqueous and organic phases respectively. The distribution ratio D_M of a metal cation is expressed as follows:

$$D_M=[\mathrm{M(CE)}n\mathrm{A}]_{org}/[\mathrm{M}^+]_{aq} \quad (2)$$

From Eqs. (1) and (2), we obtain

$$K_{ex} = D_M/[A^-]_{aq}[CE]^n_{org} \tag{3}$$

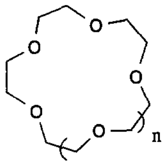
Modification of Eq. (3) results in the following equation:

$$\log (D_M/[A^-]_{aq}) = n \log[CE]_{org} + \log K_{ex} \tag{4}$$

Eq. (4) indicates that the plot of log $(D_M/[A^-]_{aq})$ as a function of log $[CE]_{org}$ should give a straight line with a slope of n ($n = 1$ or 2) and with log K_{ex} as the intercept.

3. 'Hole-size' concept

When we discuss the cation-binding ability of crown ethers, the complexation phenomena are initially considered using the 'hole-size' concept [2]. While the hole-size relationship fails to explain cation selectivity in flexible macrocycles and lariat ethers [15,18], the cation-selectivity in the solvent extraction of metal picrates can be rationalized in terms of this concept, indicating that the model is still valid at least in the solvent extraction experiment [19].



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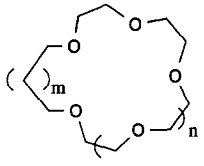

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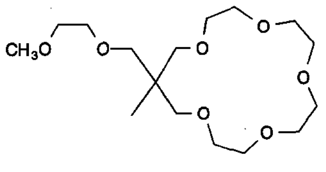

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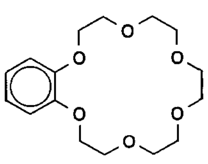

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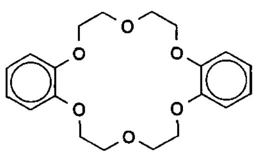

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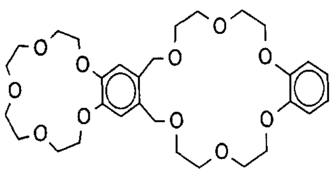
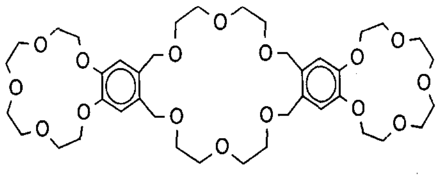


10



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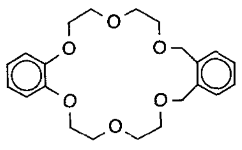

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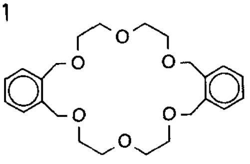

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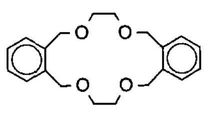

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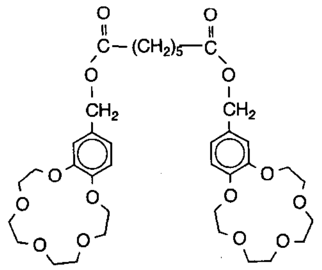

15

4. Crown ethers possessing high thallium(I) ion binding ability/selectivity

In this paper, typical symmetrical and unsymmetrical crown ethers, lariat ether, benzo-type crown ethers, bis-crown ether, and multi-loop crown ethers are presented for discussion.

4.1. Unsubstituted crown ethers (1–6), and lariat 16-crown-5 (7)

The cation-binding abilities of unsubstituted crown ethers (**1–6**) and lariat 16-crown-5 (**7**) are discussed in terms of their extraction equilibrium constants K_{ex} [16,19,20] shown in Table 1. The cavity sizes of the crown ethers used in this study are shown in Table 2.

Table 1

Estimated cavity sizes of some crown ethers by CPK molecular models and some relevant cation diameters

Crown ether	Cavity diameter (Å)	Cation diameter[a] (Å)	
15-Crown-5 (**1**)	1.7	Na^+	2.04
16-Crown-5 (**3**)	1.8	K^+	2.76
17-Crown-5 (**4**)	2.0	Rb^+	2.98
18-Crown-6 (**2**)	2.6	Cs^+	3.40
19-Crown-6 (**5**)	2.8	Ag^+	2.30
20-Crown-6 (**6**)	3.3	Tl^+	3.00
Dibenzo-18-crown-6 (**9**)	2.4		
Dibenzo-20-crown-6 (**12**)	2.8		
Dibenzo-22-crown-6 (**13**)	3.7		

[a] Ref. [8].

Table 2

Extraction equilibrium constants (K_{ex}) with some crown ethers[a]

Compound	log K_{ex}[b]						Selectivity[c]	
	Na^+	K^+	Rb^+	Cs^+	Ag^+	Tl^+	Tl^+/K^+	Tl^+/Rb^+
1	4.52	4.40	4.29	3.74	5.00	5.08	4.8	6.2
2	3.89	6.20	5.96	5.17	5.09	6.71	3.2	5.6
3	4.55	3.65	3.52	3.14	5.25	4.63	9.6	12.9
4	3.39	3.45	3.12	3.01	4.40	4.13	4.8	10.2
5	3.46	4.68	4.58	4.01	4.24	5.28	4.0	5.0
6	2.95	4.40	4.64	4.55	4.08	5.45	11.2	6.5
7	4.57	3.39	3.24	2.86	4.91	4.26	7.4	10.5
8	3.32	5.52	4.95	4.53	4.63	5.85	2.1	7.9
9	2.81	4.84	4.43	4.08	3.74	5.02	1.5	3.9
12	2.32	3.43	3.35	3.23	3.14	4.37	8.7	10.5
13	2.04	2.82	2.96	3.22	3.19	4.41	38.9	28.2
14	ND[d]	1.86	1.93	ND[d]	3.44	3.75	77.6	66.0

[a] Dichloromethane–water system at 25 °C. [b] Values for 1:1 crown ether–cation complex; error <0.05. [c] Relative cation selectivity determined by K_{ex}. [d] Not determined. Sources: from Refs. [16,17, 19,20,23].

15-Crown-5 (**1**) and 18-crown-6 (**2**) have a symmetric skeleton, and (**2**) had the higher K_{ex} values for all cations employed other than those of (**1**). 15-Crown-5 (**1**) and 18-crown-6 (**2**) had the highest K_{ex} value and selectivity for Tl^+. The K_{ex} value of (**2**) (cavity size 2.6 Å) for Tl^+ (cation diameter 3.00 Å) was higher than that of (**1**) (1.7 Å), which is explicable using the hole-size concept. However, the high K_{ex} value of (**1**) for Tl^+ cannot be explained by this concept, considering the cation diameter of the alkali metal ions, though the nature of alkali metal ions and heavy metal ions (Ag^+ and Tl^+) may explain the result; however, until now, no comprehensive study on this point has been reported.

Unsymmetrical crown-5 ethers (16-crown-5 (**3**), and 17-crown-5 (**4**)), and crown-6 ethers (19-crown-6 (**5**), and 20-crown-6 (**6**)) had lower K_{ex} values than those of the corresponding symmetrical crown ethers, (**1**) and (**2**). In general, the results also showed that the K_{ex} values decreased with increasing methylene chain length of the crown ether ring; e.g. for K_{ex} values of K^+: (**1**)>(**3**)>(**4**) and (**2**)>(**5**)>(**6**).

In ring-enlarged crown-6 ethers, the K_{ex} value of ring-enlarged 20-crown-6 (**6**) (3.3 Å) for Tl^+ was higher than that of 19-crown-6 (**5**) (2.7 Å), which is in accordance with the hole-size concept; for K_{ex} values of Tl^+: (**2**)>(**6**)>(**5**). The relationship between the cavity size of the crown ether and Tl^+ selectivity (Tl^+/K^+ and Tl^+/Rb^+) is not clear from the K_{ex} values; however, unsymmetrical crown ethers might show higher Tl^+ selectivity than symmetrical crown ethers.

Lariat ethers [4] have been designed to enhance the cation-binding ability of common crown ethers by introducing a side arm carrying extra donor group(s). A number of lariat 16-crown-5 ethers possessing a variety of single or double side arm(s) were synthesized by our group [19]. Lariat 16-crown-5 (**7**) was designed to enhance the cation-binding ability and selectivity for Na^+ and Ag^+ over any other crown-5. High Tl^+ selectivity was also obtained from (**7**); however, compared with those of 16-crown-5 (**3**), the effect of the side-arm upon Tl^+ selectivity was not obtained.

4.2. Benzo-type crown ethers

Benzo-18-crown-6 (**8**) and dibenzo-18-crown-6 (**9**) with symmetric skeletons showed the highest cation-binding ability K_{ex} for Tl^+ among the cations employed [17] as shown in Table 2. Owing to the influence of the basicity of the oxygen atoms [2], the K_{ex} values of (**8**) and (**9**) are lower than those of 18-crown-6 (**2**). However, the Tl^+ selectivity over K^+ and Rb^+ is not as high as those of (**2**). Unsymmetric benzo-crown-6 ethers might also be potential candidates for a Tl^+ selective crown ether; this is described in Section 4.4.

4.3. Di- and tri-loop crown ethers

A particular kind of crown ether is the multisite crown ether. They make possible oligonuclear complexes with several different cations. As a new type of multisite crown ether, di- and tri-loop crown ethers based on a spiro junction have been synthesized [21]. These ligands have a perpendicular orientation of the crown compartments around the spiro centers which may cause steric hindrance upon complexation. A coplanar orientation of crown compartments and no steric hindrance were needed in this type of compound. Thus, di- and tri-loop crown ethers, (**11**) and (**12**), having aromatic junctions have been synthesized, and the cation-binding abilities of the compounds were evaluated by solvent extraction (Table 3) [22].

From the extraction experiments shown in Table 3, the cooperative effects of neighboring binding sites, the multiplicity, and the symmetry of the crown ether were discussed. Compounds (**10**) and (**11**) showed the highest cation-binding abilities

Table 3
Solvent extraction of aqueous metal picrates with some crown ethers[a]

Compound	Extractability (%)[b]					
	Na^+	K^+	Rb^+	Cs^+	Ag^+	Tl^+
9	0.8	23.6	15.1	7.9	4.3	30.8
10	2.7	6.2	4.6	3.4	6.1	18.3
11	4.9	30.4	27.3	11.5	10.2	30.7
12	0.3	2.4	2.2	1.9	1.5	14.6
13	0.2	0.9	1.2	2.2	1.9	16.6

[a] Temperature 25 °C; aqueous phase (5 ml), [picrate] = 3.0 mM; organic phase (CH_2Cl_2, 5 ml), [crown ether subunit] = 3.0 mM. [b] Defined as percent picrate extracted into the organic phase. Average of two independent runs. Source: from Ref. [22].

for Tl^+, and higher Tl^+ selectivity over K^+ and Rb^+ was obtained compared with dibenzo-18-crown-6 (**9**). The extraction data might not bear quantitative discussion, however, as unexpected results were obtained from the constituent monocyclic crown ethers (**12**) and (**13**), which were the skeleton of the centers of (**10**) and (**11**).

4.4. Unsymmetrical dibenzo-crown ethers

Dibenzo-20-crown-6 (**12**) and dibenzo-22-crown-6 (**13**) were synthesized to evaluate the complexation properties of multisite crown ethers (**10**) and (**11**) [22]. As shown in Table 3, unsymmetrical crown ethers (**12**) and (**13**) showed lower extractabilities in general than the more symmetric dibenzo-18-crown-6 (**9**), and showed the highest extractability for Tl^+. A more quantitative discussion was made from the K_{ex} values [23] shown in Table 2. The K_{ex} values for Tl^+ were less sensitive to the methylene chain length than the alkali metal ions. Thus, for the first time, higher Tl^+ selectivity with reference to alkali metal cations has been observed for unsymmetrical dibenzo-crown-6 ethers. Although the cation diameters of K^+, Rb^+, and Tl^+ are similar, higher Tl^+/K^+ and Tl^+/Rb^+ selectivities were determined for (**12**) and (**13**). This result is rather unexpected considering the simple structure of the crown ethers. A more surprising result was reported from the extraction data of dibenzo-16-crown-4 (**14**) [24]. The smaller unsymmetrical dibenzo-16-crown-4 (**14**) showed quite low cation-binding abilities for alkali metal cations. However, because the decrease of the K_{ex} value for Tl^+ was smaller, this species exhibits the highest Tl^+/K^+ selectivity among dibenzo-crown ethers and all crown ethers used in this study. Thus, unsymmetrical dibenzo-crown ethers could be promising candidates for Tl^+ selective crown ethers.

Using ^1H and ^{13}C NMR spectroscopy and ^{13}C relaxation time (T_1) measurements, the higher Tl^+ selectivity of (**13**) compared with (**9**) and (**12**) was investigated [25]. The conformational changes of these crown ethers caused by complexation with K^+ and Tl^+ ions in acetonitrile–d_3 were determined by ^1H and ^{13}C NMR spectroscopies. In addition, ^{13}C relaxation time (T_1) measurements were obtained to reveal the changes in molecular motion for the dibenzo-crown ethers. The results might explain the reason why (**13**) possesses a higher Tl^+ selectivity over K^+. Since (**13**) has a much larger cavity (3.7 Å) than the diameter of Tl^+ (3.00 Å) and K^+ (2.76 Å), a considerable conformational change should occur when all six oxygen donor atoms in (**13**) interact with the metal(I) ion. When (**13**) interacts with K^+ to form the complex, it should be more highly strained than the complex with Tl^+. This proposition is supported by the fact that the shift to higher field for the position of the methylene protons next to the benzene ring of (**13**) is much larger with K^+ than Tl^+.

5. Polymer membrane thallium(I)-selective electrodes based on dibenzo-crown ethers

Ion-selective electrodes are one of the most convenient and reliable analytical tools for estimating metal-ion concentrations. There have only been a few reports on liquid-membrane thallium(I)-selective electrodes (Tl^+-ISEs) [26]. They need to be improved with regard both to their low selectivities against alkali metal ions and to pH dependence. Recently, thallium(I)-selective electrodes based on polythiamacrocycles have been reported [27]; however, Tl^+ selectivity against K^+ and Rb^+ was not investigated.

In ion-selective electrodes, the membrane potential between an internal filling solution of a constant concentration of primary cation (I) and a measuring solution of the primary cation and an interfering cation (J) is given by Eq. (5) (the so-called Nicolsky–Eisenman equation) [14]

$$E=E_o+RT/z_IF\ \ln\left[a_I+\sum_J K_{IJ}^{Pot}a_J(z_I/z_J)\right] \tag{5}$$

where E_o is a constant, R is the gas constant, T is the thermodynamic temperature, F is the Faraday constant, a is the activity, and z_I, z_J are the electric charges of the I and J ions.

The factor K_{IJ}^{Pot} is referred to as the potentiometric selectivity coefficient, and the values of the selectivity coefficient are determined by a mixed solution method in the present study. Finally, K_{IJ}^{Pot} is computed from the equation $K_{IJ}^{Pot}=a_Ia_J(z_I/z_J)$.

PVC membrane Tl^+-ISEs based on bis(crown ether)s containing the benzo-15-crown-5 moiety (**15**) have been reported previously [28]. This electrode exhibited good slope and linearity of calibration plots, and the electrode response was stable over a wide pH range; however, the Tl^+ selectivity against K^+ for (**15**) was fairly poor.

Taking account of the higher Tl^+ selectivity for unsymmetrical dibenzo-crown-6 ethers (**12**) and (**13**) obtained from extraction experiments, polymer membrane thallium(I)-selective electrodes based on dibenzo-crown-6 ethers (**9**, **12**, and **13**) and dibenzo-16-crown-4 (**14**) were prepared and reported in a preliminary communication [24,29]. The selectivity coefficients for alkali, alkaline earth, and heavy-metal cations (log $K_{Tl,M}^{Pot}$), determined by the mixed solution method, are shown in Fig. 1 and Table 4. As expected, the electrodes based on (**13**) and (**14**) exhibited higher Tl^+/K^+ and Tl^+/Rb^+ selectivities than the symmetrical dibenzo-18-crown-6 (**9**).

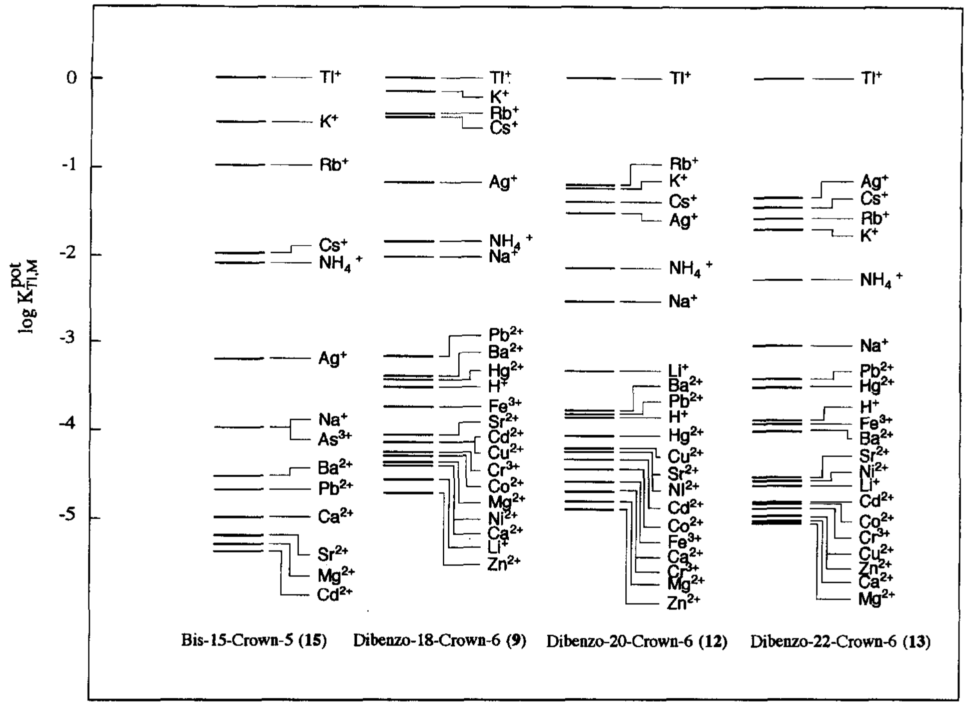

Fig. 1. Selectivity coefficients for thallium(I) ion-selective electrodes based on (**9**), (**12**), (**13**), and (**15**). Source: from Refs. [28,29].

Table 4
Selectivity coefficients for thallium(I) ion-selective electrodes based on **13**, **14** and **15**

Electrode	log $K^{Pot}_{T,M}$				Selectivity[a]			
	Na^+	K^+	Rb^+	Ag^+	Tl^+/Na^+	Tl^+/K^+	Tl^+/Rb^+	$Tl^+/Ag+$
13	−3.05	−1.73	−1.60	−1.37	1120	54	40	23
14	−3.43	−2.12	−2.11	−0.85	2690	132	129	7
15	−4.00	−0.52	−1.00	−3.22	10000	3	10	1660

[a] Potentiometric selectivity coefficient ($1/K_{TlM}$) for Tl^+ over Na^+, K^+, Rb^+ and Ag^+. Sources: from Refs. [24,28,29].

The Tl^+/K^+ and Tl^+/Rb^+ selectivity was improved by more than one order of magnitude compared with the bis(crown ether)-type electrode based on (**15**), while (**15**) showed excellent Tl^+/Na^+ and Tl^+/Ag^+ selectivity.

Further investigations are now in progress toward elucidating the selectivities of unsymmetrical dibenzo-crown ethers used in Tl^+ sensing by the method of solvent extraction and polymer supported ion-selective electrodes based on crown ethers.

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