Conductance Study of the Complexation of Diaza-Crown Ether Derivatives and Cryptand-Containing Polymers

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Abstract : Polysulfones containing cryptands in their backbones were prepared by the reaction of diaza-15-crown-5 and diaza-18-crown-6 with divinyl sulfone. And the ion-binding properties of low molecular weight phthalimidopropyl and aminopropyl derivatives of diaza crown ethers and their polymeric versions, polyamides were investigated by conductance measurements. Changes in solution conductance of alkali metal tetraphenylborates were measured in acetone and complex formation constants were estimated from these measurements. The log K_f values of aminopropyl derivatives of diaza-18-crown-6 for potassium ion was estimated to be larger than 5, exhibiting the highest selectivity. The decrease in equivalent conductance values were much larger with polymeric cryptands, and was about 40 ohm^{-1} cm^2 mol^{-1}. The break in the conductance curve was observed in the range of 2 and 3 of crown-to-cation ratio for polyamides, even though not clearly defined. The large cesium ion was not complexed by the polymers of 15-crown-5 ether moiety.

Introduction

In recent years there has been surging impetus in the research on the synthesis and properties of crown ethers of various structures[1]. Many attempts have also been made to modify the chemical structures and physical properties of these ligands in search for unusualb ut useful ion-binding properties[2]. One of these is the effort to construct polymeric crown ethers and a few polymers containing crown ethers have been reported[3].

When polymers were prepared directly from diaza-crown ethers by polycondensation reactions, the polymeric cryptands usually exhibited markedly decreased tendency to form complexes with metal ions. This decreased tendency is known to be due to the decreased electron-donating properties of nitrogens on the crown moiety by forming amide or urea linkagesi n the process of constituting polymers[4]. Thus it is of interest to prepare a polymer in which the crown ether moiety is left intact in the process of polymerization and to investigate the ion-binding properties of the resulting polymeric crown ethers.

We have already reported briefly the synthesisa nd ion-binding properties of various N, N'-disubstituted diaza-crown ethers[5,6] and cryptand-containing polyamide, polyimide, and polyurea prepared from the N,N'-bis(amino-

propyl)-diaza-crown-ethers and diaza-18-crown-6[7]. The present article describes synthesis of other cryptand-containing polysulfones, and ion-binding properties of polyamides are investigated in comparison with the results obtained with other systems.
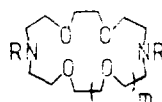
Experimental

Synthetic procedures for the preparation of phthalimidopropyl(2a and 2b) and aminopropyl (3a and 3b) derivatives and cryptand-containing polyamides 4a and 4b have been reported previously[7].

Preparation of polysulfones:

Polysulfones, 5a and 5b were prepared by the procedure analogous to that employed for the polyamide[7]. The reaction mixture obtained by the reaction of 1a and 1b with divinylsulfone was precipitated by pouring into dry ice-cooled diethyl ether and dried under vacuum. The percent polymer yield was about 90 %. The solution viscosity of the polymers were measured in chloroform, concentration of 0.5 g/dl, at 25°C by Cannon-Fenske capillary viscometer.
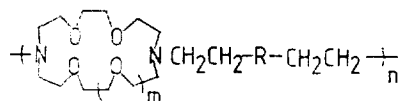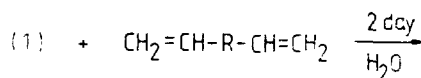
Conductance measurements:

Solution conductance of sodium, potassium, and cesium tetraphenylborate in acetone were measured. The sodium tetraphenylborate was recrystallized from aqueous acetone(acetone/water, 3 : 1 by v/v). Potassium and cesium salts were prepared by treating dilute aqueous solution of sodium tetraphenylborate with an equivalent amount of th erespective metal chlorides[8]. The relatively insoluble $KBPh_4$ and $CsBPh_4$ precipitated upon the reaction, and the separated and washed crystals were then purified by recrystallization from aqueous acetone. All these salts were dried by heating at 50°C under vacuum for 24h. Conductivities

(1) R = H
(2) R = (CH_2)_3 — [phthalimide]
(3) R = (CH_2)_3NH_2

(a) m = 0 , (b) m = 1

(1) + $CH_2=CH-R-CH=CH_2$ $\xrightarrow[H_2O]{2\ day}$

(4) R = $CONH-CH_2-NHCO$
(5) R = SO_2

were measured with a Yellow Springs Instruments Conductivity Bridge, Model 31, in a temperature-regulated water bath at $25\pm0.1°C$,

Experimental procedure to obtain the formation constants of crown ether complexes with metal ions is as follows[9]. Acetonesoultion of the alkali metal tetraphenylborate ($10^{-3}M$, 50ml)was first placed in the cell and conductance of the solution was measured. Then the aliquots of crown ether solution were pipetted into the cell, until the total concentration of crown ether was about three to five times those of the alkali metal tetraphenylborate. Conductance of the solution in the cell was measured after each addition of crown ether solution. From the measurements of conductance a plot of equivalent conductance against [crown]/[salt] was obtained for each crown ether-salt system. For small values of $K_f[M^+]$ a smooth curve was obtained and from this curve the complex formation constants K_f were calculated.

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Results and Discussion

Preparation of polysulfones:

Addition reaction of primary or secondary amines to vinyl double bonds activated by electron attracting groups are well known[10]. In this reaction, nitrogen is always bound to the carbon at the β-position to the activating group. Thus obtained polymers have cryptands and sulfone functions regularly arranged along the main chains. The polymerization is a nucleophilic polyaddition undergoing in an ionic mechanism, and takes place free from any significant secondary reactions[11]. Diaza-crown ethers serve also as the basic catalyst for this reaction and no other catalyst was used.

Table 1 gives the inherent viscosities and melting points of polysulfones and polyamides. The polysulfones were freely soluble in ethyl alcohol and chloroform but insoluble in aliphatic hydrocarbons. In their IR spectra polysulfones exhibited two characteristic absorption bands of sulfone group at 1300 and 1130 cm^{-1}. NMR spectrum of polysulfone is relatively simple and O-CH$_2$-protons, —SO$_2$CH$_2$-protons, and NCH$_2$-protons give three main peaks cen-

Table 1. Syntheses of Cryptand-Containing Polysulfones and Polyamides

Polymer	Solvent	Reaction time (hr)	Yield (%)	η_{ink} (dl/g)^a	T_m (°C)^b
4a	H$_2$O	48	90	0.35	113
4b	//	//	100	0.42	—^{c}
5a	//	//	80	0.19	—^{c}
5b	//	//	90	0.27	50

a. Concentration of 0.5g/dl in chloroform at 25 °C.
b. Melting point of the polymer; measured with a DSC-1B of Perkin-Elmer.
c. T_m could not be determined with any accuracy

tered at 3.6 ppm, 3.2ppm, and 2.6—3.0 ppm respectively.

Conductance Measurements

Derivatives of diaza-crown ethers:

Coordination of a crown molecule to a cation affects its ionic mobility. As a result, the conductivity of a salt solution changes upon the addition of the crown ethers. In the present case, conductivity measurements were performed on acetone solutions of sodium, potassium, and cesium tetraphenylborates complexed by derivatives of cryptands at 25°C. The concentration employed mostly was 10^{-3}M.

The equivalent conductance, Λ vs $[Cr]_t/[M]_t$ plots for alkali metal tetraphenylborates complexed by 3b are given in Figure 1, where $[Cr]_t$ and $[M]_t$ are the total concentrations of 3b and the alkali metal ion, respectively. The Λ vs $[Cr]_t/[M]_t$ plots show a gradual decrease in values with the increase in 3b concentration.
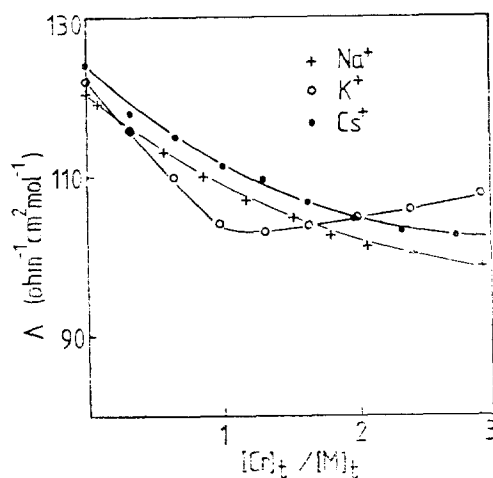
As the plot shows, an apparent break was

Fig. 1. Equivalent conductance of metal tetraphenylborate in the presence of 3b in acetone at 25°C.

observed in the case of potassium salt at $[Cr]_t/[M]_t$ ratio of around one, whereas smooth curves were obtained for sodium and cesium salt. Generally, when a crown compound complexes strongly with certain metal cation, all the crown ether added will be converted to the complex and Λ will decrease proportionally to the ratio of $[Cr]_t/[M]_t$. When excess amount of crown ether is present Λ value will remain constant. Accordingly the plots of Λ vs $[Cr]_t/[M]_t$ are usually straight lines with rather sharp breaks at a crown-to-salt ratio equal to the composition of the complex. This is the case of $K^+/3b$ system. However, a slow increase rather than a constant Λ value was observed after the breaking point, probably due to the small residual conductivity of the titrant 3b itself. A steady decrease observed in the case of sodium and cesium salt is indicative of that the complex formation was not so effective as compared to potassium salt. This is somewhat contrary to the results obtained from solvent extraction and transport experiments in that the 3b derivative exhibited high but non-selective complexation behavior[4,5]. In the latter experiments we determined the salt concentration only by measuring picrate concentrations in each phase, and not by direct cation analysis. With ligands containing amino functions there is certain risk that we may actually have the ligands in the protonated form, and not the cation complex[12]. Compounds 3a and 3b contain as many as four amino functions and are further characterized by having the side-chain amino function which can be stabilized in the protonated form by hydrogen bonding to the ring amino function[13]. If it is actually picric acid that is extracted, it is obvious that one fails to observe any cation selectivity.

Another possibility is that the amino groups of the crown ether could interact directly with the picrate anion. There is an instance in which the $-NH_2\cdots Pic^-$ type of bonding was reported in $M(Pic^-)_2$ (Ethylene diamine)$_2$ complexes[14].

On these premises it may be speculated that certain interaction other than strong complexation by cyclic ether portion, such as direct interaction between amino group and large lipophilic counter-ion is operative to some extent in the solvent extraction and transport phenomena. However, the exact nature of such interaction is yet to be investigated.

Cryptand-containing polyamides:

The conductometric titrations of metal salts with cryptand-containing polyamides were carried out under the same condition. Polysulfones could not be subjected to the present study because of their poor solubility in acetone. The Λ vs $[Cr]_t/[M]_t$ plots for 4a and 4b are given in Figure 2 and 3.

As expected, the decrease in Λ values were much larger in the case of polymers. Mobility of an ion complexed with the polymeric cryptand would be much smaller than those of the low molecular weight crown ethers[15]. The decreased leveled-off Λ values were about 40 ohm^{-1} cm^2 mol^{-1} for Na$^+$/4a and K$^+$/4b. Also notable was that the equivalent conductance did not become constant even after the 1 : 1 stoichiometry of crown to cation ratio was reached, probably because the redistribution of charges occur when more polymer was added to the cation-saturated polymers[16]. However, the break in the conductance curve was still observed at the crown-to-salt ratio greater than one, i.e., in the range of 2 and 3. The same results were also obtained for KBPh$_4$ with 4b and this may be due to the difficulty in obtaining a fully cation-saturated polymer
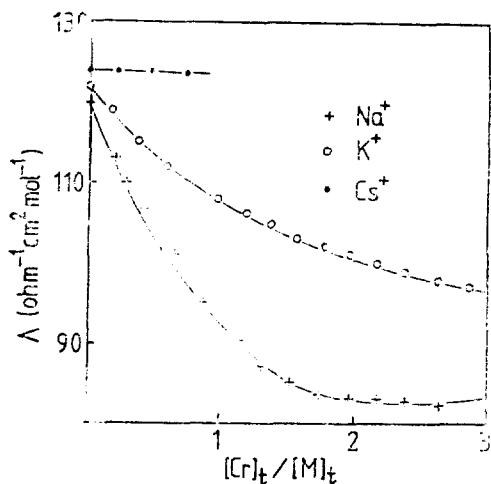
Fig. 2. Equivalent conductance of metal tetraphenylborate in the presence of polyamide 4a in acetone at 25°C
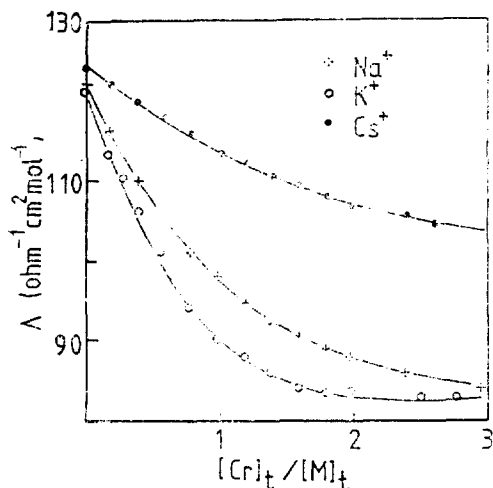

Fig. 3. Equivalent conductance of metal tetraphenylborate in the presence of polyamide 4b in acetone at 25°C.

with the cryptand-containing polymers[16].

As can be seen from Figure 2, the cesium ion was not complexed by 4a and any change in conductance was not observed. With cesium salt and 15-membered cryptand-containing 4a a 2 : 1 sandwich-type of complex formation was not expected to occur, because the ap-

proach of two crown moiety situated in the polymer backbone to the favorable conformation for the cooperative ion-binding is not likely[17].
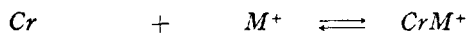
Complex Formation Constants(K_f)

The complexation reaction between a crown ether and a metal ion, and the complex formation constant, K_f, can be expressed as follows:
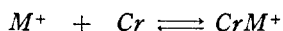
$$M^+ + Cr \rightleftharpoons CrM^+$$
$$K_f(CrM^+) = [CrM^+]/[Cr][M^+]$$

In the present case, the determination of formation constants was based on the conductometric titration of alkali metal tetraphenylborate with crown ethers.

The decrease in conductance under these conditions can be explained by assuming that the following equilibrium exists in solution:

$$Cr + M^+ \rightleftharpoons CrM^+$$
$$[Cr]_t-(1-\alpha)[M]_t \quad \alpha[M]_t \quad (1-\alpha)[M]_t$$

where M^+, Cr and α are an alkali metal ion, cryptand and the fraction of free alkali metal Ions. Accordingly, the complex fomation constant, $K_f(CrM^+)$, is defined as frollows:

$$K_f(CrM^+) = [CrM^+]/[M^+][Cr] = (1-\alpha)/\alpha[Cr]$$

and can be transformed into

$$K_f(CrM^+) = (\Lambda_{MBPh_4}-\Lambda)/(\Lambda-\Lambda_{MCrBPh_4})[Cr]$$

where $[Cr] = [Cr]_t-[M]_t(\Lambda_{MBPh_4}-\Lambda)/(\Lambda_{MBPh_4}-\Lambda_{MCrBPh_4})$,

where Λ_{MBPh_4} and Λ_{MCrBPh_4} are the equivalent conductance of alkali metal tetraphenylborate and alkali metal tetraphenylborate complex of crown ether respectively[18].

The procedure for obtaining the $K_f(CrM^+)$ values is as follows[18,19]: The Λ_{MCrBPh_4} value is estimated from the Λ values at the points of large$[Cr]_t$ to $[M]_t$ ratios. Using this Λ_{MCrBPh_4} value, the $K_f(CrM^+)$ value in Equation 1 can be calculated. The actual $K_f(CrM^+)$ and Λ_{MCrBPh_4} values are calculated by a nonlinear least-square analysis using

Table 2. Formation Constants of Complexes of Alkali Metal Tetraphenylborates and Derivatives of Diaza-crown Ethers[a]

Compound	log $K_f(CrM^+)$		
	Na$^+$	K$^+$	Cs$^+$
1a	3.8	3.0	—[b]
2a	4.2	3.5	—[b]
3a	>4.7[c]	4.2	2.3
4a	3.7	3.1	—[b]
1b	3.8	4.2	2.3
2b	4.6	>4.7[c]	4.1
3b	4.4	>5.3[c]	4.9
4b	3.4	4.2	2.9

a In acetone at 25°C, [MBPh$_4$]=10^{-3}M.
b Too small to determine precisely.
c Too large to determine precisely by the present method.

Marquardt regression algorithm[20].

The calculated values of formation constants for the substituted cryptands are given in Table 2. In the case of Cs^+/1a-derivative systems, except 3a, since hardly any change in Λ was observed in spite of an increase in the crown ether concentration, the conductometric determination of the complex formation constant was not applicable.

The low and high molecular weight cryptands investigated in the present study showed selectivity towards cations to a considerable degree. It may be seen from Table 2 that substituted 1b complexes selectively with potassium ion and 1a preferentially with sodium ion. The complex formation constants increase generally in the order of unsubstituted<phthalimidoalkyl<aminoalkyl derivatives. The comparison of the data on the polyamide with low molecular weight analogs reveal that complexation is much less efficient with the former, owing to the much larger steric hindrance imposed by the polymer chain and also to the difficulty of obtaining ion-saturated

form with polymers. As the complex formation constants are concerned, polyamides behaved similarly to the unsubstituted diaza-crown ethers.

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