Interactions of Ions and Ion Pairs with Crown Ethers and Their Polymers

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ABSTRACT

The interactions of ions and ion pairs with crown ethers (macrocyclic polyethers) and their vinyl polymers were studied in aqueous and nonaqueous media by using optical spectroscopy, distribution equilibria, conductance, and viscosity. The polymers, poly(vinylbenzo-15-crown-5) and poly(vinylbenzo-18-crown-6), were found to be considerably more efficient than their monomeric analogs in binding those cations which have diameters larger than that of the crown cavity and which tend to form 2:1 crown-cation complexes. The stoichiometries of the complexes were determined by spectroscopy for fluorenyl ion pair salts in ethereal solvents and by conductance for inorganic salts in solvents such as acetone. The viscosity behavior of the polymers in the presence of salts resembles that of polyelectrolytes, with the reduced viscosity being strongly enhanced at low polymer-salt concentrations.

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INTRODUCTION

The cation binding properties of macrocyclic polyethers or crown ethers have been under active investigation for several years [1-15]. Many crystalline stoichiometric crown complexes of inorganic and organic salts have been isolated [1, 2]. The formation of complexes also frequently enhances the solubility of the salts in organic solvents. Addition of crown ethers to salt solutions often results in a strong increase in the anion reactivity [3], although it sometimes inhibits the reaction [4], depending on the role that the cation plays in the reaction mechanism. Another interesting feature is the ability of many crown ethers to promote ion transport across biological membranes by acting as ion carriers, similar to such antibiotics as monactin [5].

Several techniques, e.g., calorimetry [6], potentiometry [7], optical spectroscopy [8], proton and alkali NMR [8a, 9], IR spectroscopy [10], distribution equilibria [1, 5, 11], and conductance [12], have been utilized to study properties of crown ethers such as their selectivities in binding cations. Most cation–crown complexes in solution exhibit 1:1 stoichiometry, but 2:1 crown to cation ratios have also frequently been observed. This prompted us to prepare poly(vinylbenzo crown ethers) [13] and to compare their binding efficiencies and selectivities with those of the monomeric analogs.

This paper deals mainly with spectrophotometric measurements on ion pair equilibria in ethereal solvents in the presence of crown ethers and their polymers, and with data of crown/salt systems obtained from distribution equilibria, conductance, and viscosity studies.

EXPERIMENTAL

Preparation of the crown ethers used in this investigation has been described elsewhere [1, 8b]. The synthesis of the vinyl crown ethers and their conversion to high molecular weight polymers by radical and anionic polymerization has been published [14]. Experimental details relating to the extraction procedure have also been reported [1, 11]. The spectrophotometric techniques, in which the air- and moisture-sensitive fluorenyl carbanions are used as a probe to study the cation–crown interactions, have recently been described [8b, 15].

RESULTS AND DISCUSSION

Spectroscopic Measurements on Ion Pair Interactions with Crown Ethers and Their Polymers

Before discussing the poly(vinylbenzo crown ethers) it is illuminating to consider the results obtained in studies of ion pair interactions with

the monomeric crown ethers. The three crown ethers and the two
polymers most frequently used in our studies are
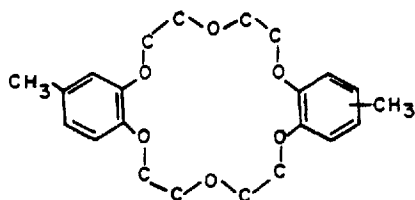
DB-18C6 (I)

15C5, n = 3 (II)

18C6, n = 4 (III)
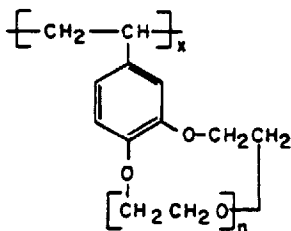
P15C5, n = 3 (IV)

P18C6, n = 4 (V)

where I = dimethyldibenzo-18-crown-6, II = 4'-methylbenzo-15-crown-5,
III = 4'-methylbenzo-18-crown-6, IV = poly(vinylbenzo-15-crown-5) and
V = poly(vinylbenzo-18-crown-6).

Ionic species associate to ion pairs in low dielectric constant
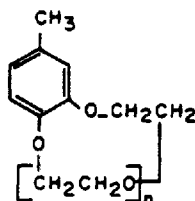media. At least two kinds of ion pair can often be found as chemically
distinct species, a contact or tight ion pair and a solvent separated
or loose ion pair. In the case of fluorenyl salts the two kinds of ion
pair have distinctly different absorption maxima, and their fractions
can be quantitatively determined [16]. The studies demonstrate a
strong dependence of the ion pair equilibrium on the nature of the
cation, the temperature, and the solvent.

When crown ethers are added to fluorenyl salts in ethereal solvents,
complex formation occurs, as is evident from the observed optical
changes. In systems where only 1:1 crown-ion pair complexes are
formed, at least two isomeric complexes can be found, i.e., a crown
complexed tight ion pair and a crown separated ion pair [8b],

$$F^-,M^+ + Cr \rightleftharpoons F^-,M^+,Cr \qquad\qquad K_1$$

$$F^-,M^+ + Cr \rightleftharpoons F^-,Cr,M^+ \qquad\qquad K_1'$$

$$F^-,M^+, Cr \rightleftharpoons F^-,Cr,M^+ \qquad\qquad K_2$$
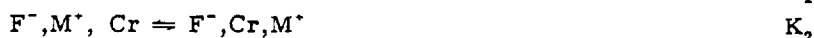
where Cr denotes a crown molecule, and F^- represents the fluorenyl carbanion. Hence a constant ratio of the two ion pair complexes is obtained at high crown concentrations. This behavior is depicted in Fig. 1 for a few systems. The constant K_2 decreases on changing to
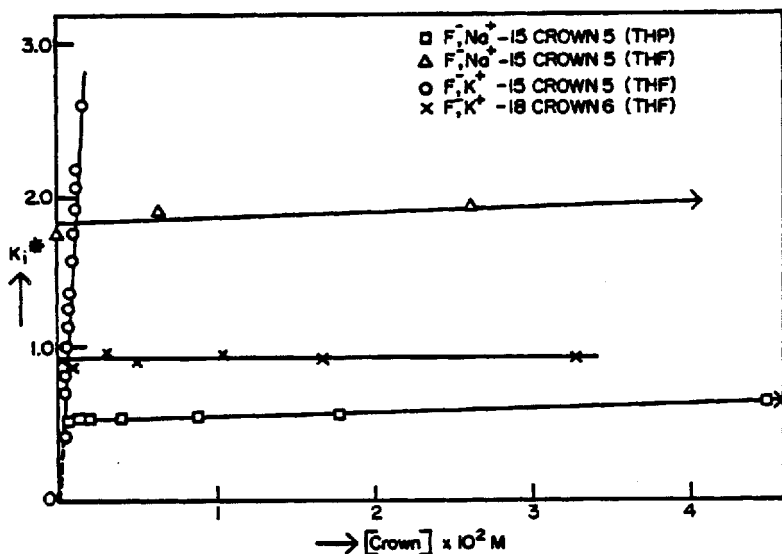
FIG. 1. Plot of the ratio R ($= K_i^*$) of separated over tight ion pairs in mixtures of fluorenyl salts and crown ethers.

less polar solvents. Actually, the equilibrium between the two isomeric complexes is better described by

$$F^-,M^+,Cr + nS \rightleftharpoons F^-,Cr,M^+,S_n$$
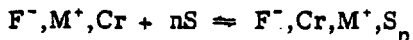
indicating that a few solvent molecules S are likely to interact with the cation as it protrudes from the crown cavity in the crown separated ion pair. Therefore, polar solvents such as THF favor the latter species. For example, the 15C5-F^-,Na$^+$ complex is predominantly a loose ion pair in THF, but in diethylether the spectrum of the complex resembles that of a tight ion pair. The size of the cation relative to that of the crown cavity is important in this respect. For example, 18C6 and DB-18C6 only form loose ion pairs with F^-,Na$^+$ in tetrahydropyran, but 15C5, which can barely accommodate the Na$^+$ ion, forms predominantly

tight ion pair complexes with F^-,Na^+ in this solvent [8b]. The anion, of course, also is of importance. Anions with less delocalized charges (e.g., alkoxides) are more difficult to separate and a tight ion pair complex is more favored. Some of the values of the different complexation constants are listed in Table 1.

A different behavior is observed in the system F^-,K^+-15C5 (see Fig. 1). Careful analysis of the data shows that, in addition to the two isomeric 1:1 complexes, a 2:1 crown separated ion pair is formed which has also been isolated in the solid state [8b].

$$F^-,K^+,C5 + C5 \rightleftharpoons F^-,C5,K^+,C5 \qquad\qquad K_3$$

The 2:1 crown cation complexes are particularly prevalent in systems where the cation is larger than the crown cavity, such as 15C5 with K^+, Rb^+, Cs^+, Ba^{2+}, and NH_4^+ or 18C6 with Cs^+. They are also found in solutions of free ions such as in methanol [7].

Divalent carbanion salts also form stable crown complexes [17] and again different kinds of ion pair complexes are found. For example, Ba^{2+}, F_2^{2-} in THF (a tight ion pair) forms a 1:1 complex with 18C6 and with DB-18C6. The optical spectra are identical to that of a mixture of equal fractions of tight and crown separated ion pairs. Addition of more than the equivalent amount of crown does not alter the spectrum. Species of the type F^-,Ba^{2+},Cr,F^- are apparently formed, and the Ba^{2+} may or may not oscillate between the two fluorenyl rings by passing through the crown cavity. Asymmetrically solvated species of this type have also been detected in other systems, e.g., in THF solutions of Sr^{2+},F_2^{2-} at low temperature [18].

When 15C5 is added to Ba^{2+},F_2^{2-} the tight ion pair absorption peak disappears and only the crown separated ion pair peak (λ_m 373 nm) remains, as the ratio 15C5/Ba^{2+} becomes larger than 2. The data show that a 2:1 complex is formed: Ba^{2+},F_2^{2-} + 2C5 $\rightleftharpoons$ F^-,$C5$,Ba^{2+},$C5$,F^-, the equilibrium constant being 1.6×10^8 $\underline{M}^{-2}$ [19].

Cation selectivities of crown ethers have been reported by a number of investigators. In water and methanol the dicyclohexyl-18-crown-6 has a selectivity order K^+ > Rb^+ > Cs^+ > Na^+ > Li^+ [6a, 7]. This order is expected to depend on the solvent medium, as solvent molecules are competing with the crown for the cation. For example, one finds spectrophotometrically that on addition of an equivalent amount of F^-,Na^+ to the F^-,DB-18C6,K^+ complex, the crown molecule is transferred to F^-,Na^+, at least when THF is the solvent. In the more basic oxetane, the crown remains around the K^+ ion. In this latter solvent, fluorenyl sodium is a loose ion pair compared to a tight ion pair in THF.

Ion pair interactions of poly crown ethers with fluorenyl salts can be studied spectrophotometrically in the same manner as described for the monomeric crown ethers. Concentrations must be kept low to prevent

TABLE 1. Complex Formation Constants of Crown Ethers with Fluorenyl Ion Pairs in Tetrahydrofuran (THF) and Tetrahydropyran (THP) at 25°C[a]

Ion pair	Crown	Solvent	$K_1 \times 10^{-3}$ (M^{-1})	K_2	K_3 (M^{-1})	$K_1 \times 10^{-3}$ (M^{-1})
F⁻,Na⁺	15C5	THF	9.2	1.8	3.5	16.5
		THP	>20	0.52	2.8	>10
	18C6	THF				> 20,000
		THP				> 40,000
	DB-18C6	THP				> 40,000
F⁻,K⁺	15C5	THF	~5	~0.2	1840	~1
	18C6	THF	> 10	0.93		> 9
	18C6	THP	> 10	0.55		> 5.5
	DC-18C6 A[b]	THF	> 30	1.80		> 54
	DC-18C6 B[b]	THF	> 40	0.80		> 32

[a]Values are taken from Ref. 8b.
[b]Dicyclohexyl-18-crown-6, isomers A and B; see Refs. 7 and 8b.

precipitation of the charged polymers in the low dielectric constant
media. Titrations are carried out under vacuum by adding a fluorenyl-
crown solution from a buret to a fluorenyl solution of approximately
the same concentration but containing no crown ether [8b, 15]. The
conversion of tight to crown separated ion pairs is followed spectro-
photometrically. Let n be the number of crown moieties bound to a
cation, then

$$n = [Cr]_{bound}/[F^-,Cr,M^+]$$

and

$$[Cr]_{free} = [Cr]_0 - n[F^-,Cr,M^+]$$

Experimentally, one determines the ratio R of crown separated to
contact ion pairs, i.e., $R = [F^-,Cr,M^+]/[F^-,M^+]$. Combined with the
above relationships, one finds

$$\frac{[Cr]_0}{R} = \frac{1}{K} + n[F^-,M^+]$$

where K is the equilibrium constant of the reaction $F^-,M^+ + (nCr) \rightleftharpoons$
F^-,nCr,M^+ (it is implicitly assumed that for $n > 1$ closely neighboring
crown moieties are involved in complexing a cation). Hence a plot of the
ratio of the total crown concentration over R vs the concentration of
tight ion pairs should yield K and the number of crown units bound per
cation. The results of a few such experiments are shown in Fig. 2. It
is interesting to observe that slopes of unity are found for F^-,Na^+ with
both P15C5 and P18C6, but a slope of 2 is found for F^-,K^+ with P15C5.
This is consistent with results obtained for the monomeric crown
analogs, with F^-,Na^+ forming 1:1 complexes with 15C5 and 18C6,
respectively, while F^-,K^+ yields a stable 2:1 complex with 15C5. The
equilibrium constant is approximately 3.5×10^4 M^{-1} for F^-,Na^+-P15C5
and $> 1 \times 10^5$ M^{-1} for F^-,Na^+-P18C6 and F^-,K^+-P15C5. The conditions
under which the experiments were carried out did not permit us to
establish whether K varies with the number of ion pairs bound per chain.

Using a slightly different titration procedure, one can add aliquots
of a fluorenyl salt in THF to a THF solution of crown ether or its
polymer, each time measuring the absorbance at the λ_m of the crown
separated ion pair. If the complex formation constant is high, a sharp
break is observed at the equivalent point, from which the stoichiometry
of the complex can be calculated. The data are plotted as VA_λ/ℓ vs V_t,
where A_λ is the measured absorbance at the absorption maximum of
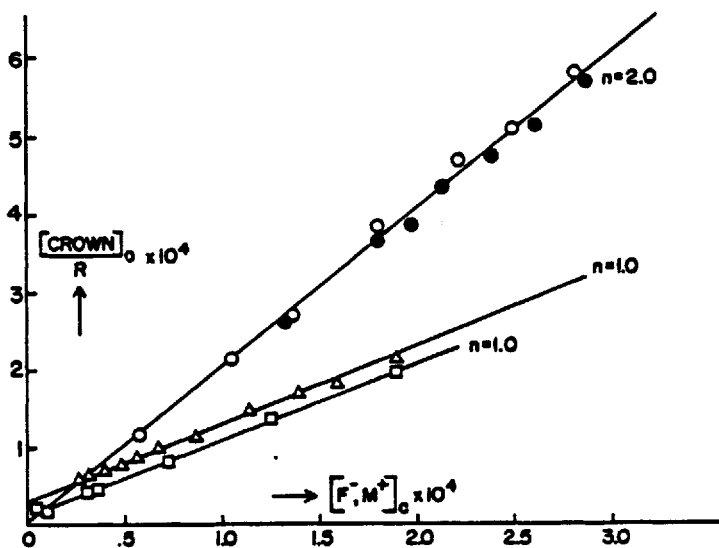
FIG. 2. Plot of $[Cr]_0/R$ vs $[F^-,M^+]_c$ in THF at $25°$ for F^-,Na^+-P15C5 ($\triangle$), F^-,Na^+-P18C6 ($\square$) and F^-,K^+-P15C5 [$\circ$, $\bullet$].

the crown separated fluorenyl ion pair, ℓ is the optical cell length, V_t the volume of the added titrant, and $V = V_t + V_0$, V_0 being the initial volume of the crown ether solution. Such a plot results in two straight lines intersecting at the equivalence point [15]. Some examples involving barium fluorenyl are shown in Fig. 3, and Table 2 gives the stoichiometry of some of the complexes calculated from the equivalence point. Again we observe a 1:1 stoichiometry for Na^+ with both P15C5 and P18C6, and also for K^+ with P18C6, but a 2:1 crown/cation ratio for K^+ and Ba^{2+} with P15C5. Actually, for the 1:1 complexes the observed crown/cation ratio is closer to 1.2, which probably means that a complete saturation of the polymer chain with cations is difficult, possibly due to steric hindrance or cation-cation repulsions between the closely packed cation-crown complexes. With 2:1 complexes (K^+-P15C5,Ba^{2+}-P15C5) the ratio crown/cation at the equivalence point appears to be between 2.3-2.5. Steric hindrance and electrostatic repulsion in these systems should be less than in the saturated 1:1 systems, and it is therefore more likely that the higher ratios are due to a statistical factor. Flory [20] has calculated that in selecting at random pairs of consecutive substituents of a macromolecule with structural units of the type $-CH_2CHX-$, 13.5% of
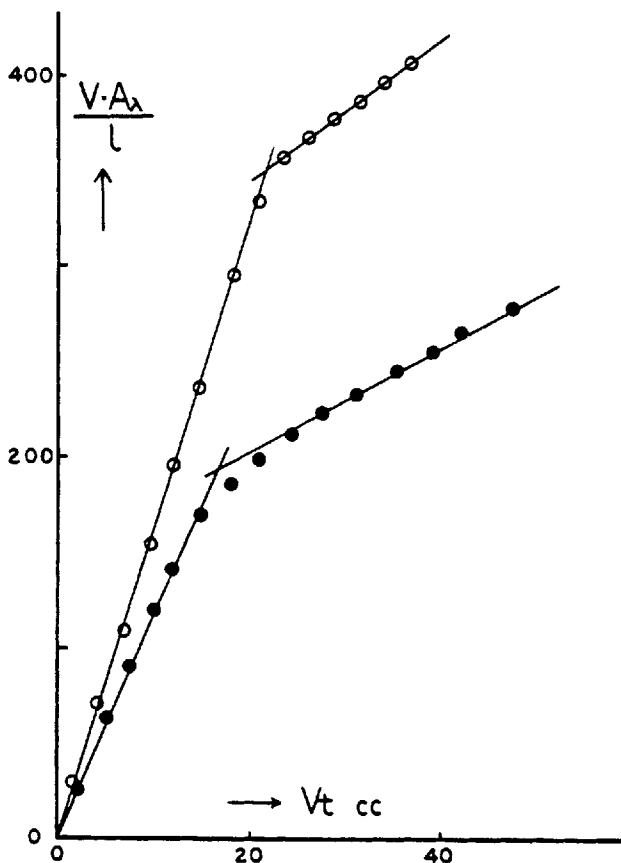
FIG. 3. Titration of poly(vinylbenzo-15-crown-5) and poly(vinyl-benzo-18-crown-6) with barium difluorenyl in THF at 25°C. The absorbance A_λ refers to the absorption maximum of the crown separated ion pair (λ_m 373 nm). V_t = volume of Ba^{2+}, F_2^{-2} added; V = total volume; l = cell length.

unpaired substituents will be left. This calculation strictly applies only to irreversible reactions [20], e.g., the reactions of aldehydes with poly(vinyl alcohol). The complexing of cations to poly(vinyl crown ethers) is a reversible process, and the binding sites are continuously rearranging. However, complete saturation, i.e., a ratio of crown ether

TABLE 2. Ratios of Crown to Cation in Crown Complexes of Fluorenyl
Ion Pairs as determined from Titration Experiments (see Fig. 3).
Solvent THF, T = 25°C

| Ion pair	Crown ether			
	15C5	P15C5	18C6	P18C6
F^-,Na^+	1.0^a	1.16	1.0^a	-
F^-,K^+	1.96	2.4^b	1.0^a	1.22
2,3-Benzo-F^-,K^+		2.45		
F^-,Cs^+				2.20
Ba^{2+},F_2^{2-}	2.0	2.20	0.98	~1.4

^{a}See Ref. 8b.
^{b}This is an average value (2.4 ± 0.1) from three experiments, using
different concentrations of F^-,K^+.

to cation equal to 2, is difficult to achieve because it involves a consider-
able loss of entropy. The extent to which this ratio deviates from the sta-
tistical value of 2.31 will be a function of the complex formation constant.

DISTRIBUTION EQUILIBRIA

Pedersen [1] developed an extraction procedure which provides a
means for a quick qualitative comparison of cation binding efficiencies
of crown ethers. An aqueous solution of a picrate salt ($\sim 10^{-4}$ $\underline{M}$) con-
taining 0.1 or 0.01 $\underline{M}$ base is shaken with an equal volume of an im-
miscible organic solvent (CH_2Cl_2) in which crown ether is dissolved.
The crown ether solubilizes the picrate salt in the organic solvent,
and the amount transferred is measured spectrophotometrically. The
overall heterogeneous reaction describing the salt partition is given
by

$$M_{aq}^+ + A_{aq}^- + Cr^* \rightleftharpoons M^+,Cr,P^{-*} \qquad\qquad K_e$$
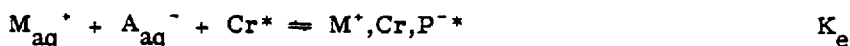
with the added complication that at low picrate concentration the
complexed ion pairs in the organic phase are partially dissociated [7]
(the asterisk refers to species in the organic phase). The fundamental

equilibria underlying the overall reaction have been analyzed by
Eisenman [5] and Frensdorff [7]:

$$M_{aq}^+ + Cr_{aq} \rightleftharpoons M^+,Cr_{aq} \qquad K_s$$

$$Cr^* \rightleftharpoons Cr_{aq} \qquad P_e$$

$$M^+,Cr_{aq} + A_{aq}^- \rightleftharpoons M^+,Cr,A^- {}^* \qquad P_c$$
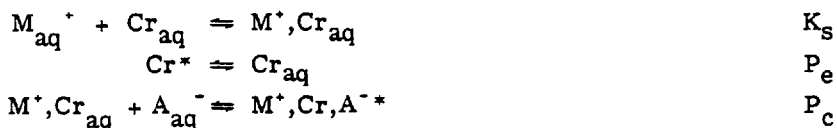
The overall equilibrium constant K_e is given by $K_e = K_s P_e P_c$. Observed differences in the K_e value of various systems may, therefore, result from differences in the complex formation constant K_s and/or from variations in the partition coefficients P_e and P_c.

A set of extraction data obtained at 0.01 $\underline{M}$ base concentration and at a crown ether to picrate ratio of 3 is shown in Table 3 (in each crown-cation system the extractions were performed at five different crown to cation ratios). The results, expressed as percent of total picrate salt transferred to the organic phase, demonstrate that the polymer is a more effective extracting agent, especially in systems which tend to form stable 2:1 crown-cation complexes. If it is assumed that no ion pair dissociation occurs in the organic phase, and that only 1:1 crown-cation complexes are formed, the following expression for K_e can be derived:

$$K_e = \frac{\alpha}{a^+ (1 - \alpha)(Cr_0/A_0 - \alpha) A_0}$$

where a^+ is the activity of the cation in the aqueous phase, Cr_0 and A_0 are the total concentrations of crown ether and picric acid, respectively, and α denotes the fraction of picrate salt transferred to the organic phase. It is also assumed in the derivation that $Cr^* \gg Cr_{aq} + M^+,Cr_{aq}$, which certainly holds in the H_2O-CH_2Cl_2 system.

The calculated K_e values are collected in Table 4. They actually represent apparent K_e values, since dissociation of ion pairs is neglected, and a trend of K_e with α (or with the ratio Cr_0/A_0) is often noticeable. A more detailed account of these experiments, including calculation of dissociation constants, has been published [14]. However, the apparent K_e values do provide us with a reasonably good qualitative comparison of the extraction capabilities of the different crown species.

TABLE 3. Complexation of Cations to Poly(vinylbenzo-15-crown-5)
and Poly(vinylbenzo-18-crown-6) as Compared to Their Monomeric
Analogs[a]

	Percent picrate salt extracted[b]			
Cation	15C5	P15C5[c]	18C6	P18C6[c]
Li^+	<1	3.0	<1	2.0
Na^+	1.6	9.5	3.0	9.0
K^+	4.9	54.6	44.4	69.4
Rb^+	2.5	53.1	23.2	55.4
Cs^+	<1	25.2	14.5	63.9
Ba^{2+}	<1	4.0	2.7	16.7
NH_4^+	<1	10.8	1.5	12.0

[a]Concentration of picric acid, 7.0×10^{-5} $\underline{M}$; macrocyclic polyether,
21×10^{-5} $\underline{M}$; metal hydroxide, 0.01 $\underline{M}$.
[b]Based on total amount of picric acid.
[c]Concentrations of the polymers are expressed as concentration of
crown units.

The assumption of a 1:1 stoichiometry for the crown-cation complex
is probably not correct for the K^+-15C5 system. Assuming a 2:1
15C5-K^+ complex, the expression for K_e changes to

$$K_e = \frac{\alpha}{a^+ (1 - \alpha)(Cr_0/A_0 - 2\alpha)^2 A_0^2}$$

Calculations based on this expression yield apparent K_e values
which decrease with increasing crown concentrations. However, if
corrections are made for dissociation of the ion pair complex, using
the expressions derived by Frensdorff, we obtain $K_e = (11.2 \pm 0.5) \times 10^{\prime}$
$\underline{M}^{-3}$ with $K_{diss} = 4.0 \times 10^{-5}$ $\underline{M}$. The value for K_{diss} is close to that
found by Frensdorff for the dicyclohexyl-18-crown-6 complex of
potassium picrate [7]. The constancy of K_e is evidence for the forma-
tion of a 2:1 complex, and is consistent with our spectrophotometric

TABLE 4. Apparent K_e values[a] of Poly(vinylbenzo-15-crown-5)[b] and Poly(vinylbenzo-18-crown-6)[b] and their monomeric analogs. Solvents: H_2O-CH_2Cl_2; Concn base 0.01 $\underline{M}$.

| | $K_e \times 10^{-3}$ $\underline{M}$ | | | | | |
	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$	NH$_4^+$
15C5	-	8.6	35[c]	16	7.6	-
P15C5	19	59	1730	1630	260	73
18C6	-	15	530	170	97	7.2
P18C6	12	50	1160	1000	2150	87

[a]K_e values are calculated on the assumption that the 1:1 complex is not dissociated in CH_2Cl_2. The standard deviation for all K_e values is less than 40%.

[b]K_e values for polymers refer to samples of M_n = 110,000 prepared by radical polymerization.

[c]When calculated on the basis of a 2:1 crown-K$^+$ complex and correcting for ion pair dissociation, one finds $K_e = (11.2 \pm 0.5) \times 10^6$ $\underline{M}^{-3}$, $K_{diss} = 4 \times 10^{-5}$ $\underline{M}$.

data on ion pair-crown equilibria in THF, where fluorenyl potassium forms stable 1:2 complexes with 15C5.

In those poly crown ethers where cation coordination is likely to involve two crown moieties (i.e., P15C5 with K$^+$, Rb$^+$, Cs$^+$, Ba^{2+}, and NH$_4^+$, and P18C6 and Cs$^+$) the term $(Cr_o/A_o - \alpha)$ in the expression for K_e should be replaced by $(Cr_o/A_o - 2\alpha)$, assuming again that the two crown units on the polymer chain are not too far apart.

To further analyze the causes for the different K_e values, we determined the partition coefficients P_e for the four crown species [7, 14], and obtained the following values: $P_e = 5.1 \times 10^{-4}$ (15C5), 0.11×10^{-4} (P15C5), 19×10^{-4} (18C6), and 0.073×10^{-4} (P18C6). The lower P_e values for the polymers are not unexpected, and would tend to make the two polymers less effective in extracting the cations. Potentiometric measurements are presently being carried out to obtain the respective K_s values [21]. Preliminary data reveal that for Na$^+$

ions the K_s values for 15C5 and P15C5 in a mixture of equal volumes
of THF and H_2O are nearly identical, and the same holds for 18C6 and
P18C6. Both monomeric crown ethers are known to form only 1:1
complexes with Na^+ ions. However, the K_s value for K^+-P15C5 is
approximately 15 times that of K^+-15C5, and this higher value can be
expected if the cation complexes with two crown ethers. Judging
from these P_e and K_s values, much of the observed differences in the
extraction equilibrium constants K_e are due to the P_c factor. Ap-
parently, P_c differences between monomer and polymer cation complexes
are much more pronounced than the known variations in the P_e values.
The importance of the complex partition coefficient was also stressed
by Frensdorff [7].
      More cations can be forced into the organic phase by increasing
the picric acid concentration in the aqueous phase at constant crown
concentration. Experiments of this type may be used to obtain the
maximum cation to crown ratio attainable for the poly crown ethers.
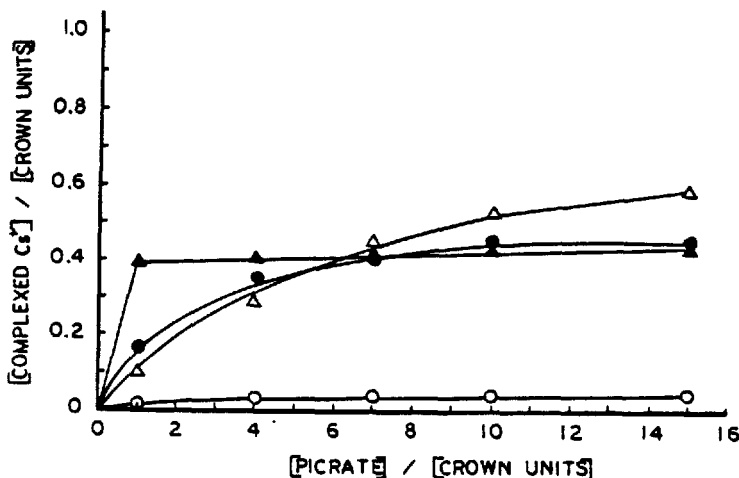Some of the results are graphically depicted in Fig. 4. for the Cs^+ ion.

FIG. 4. Determination of maximum ratio of complexed Cs^+ cations
to crown units in complexes of P15C5/Cs^+ and of P18C6/Cs^+ from
extraction experiments in the presence of excess picric acid; [crown] =
7.10^{-5} $\underline{M}$; [base] = 0.1 $\underline{M}$; (○) 15C5; (●) P-15C5; (△) 18C6; (▲) P18C6.

Even at high picrate to crown ratios the ratio of complexed cation to crown for both P15C5 and P18C6 never exceeds 0.5, indicating that two crown ethers are engaged in the complexing with Cs^+ ion. The same is observed for K^+-P15C5 [13] and Rb^+-P15C5, but the ratio goes up to at least 0.7 for K^+-P18C6, the cavity of the 18C6 being large enough to accommodate the K^+ cation.

CONDUCTANCE AND VISCOSITY MEASUREMENTS

Coordination of a crown molecule to a cation is likely to affect its ionic mobility. As a result, the conductance of a salt solution is expected to change on addition of crown ether. This simple tool was used by Pedersen and Frensdorff [12] to determine the stoichiometry of crown salt complexes. Assuming complete dissociation of the salt and a high complex formation constant (i.e., all crown ether added is converted to the complex), one can show that at constant salt concentration the observed Λ is nearly proportional to the ratio [crown]/[salt]. When excess crown is added, Λ becomes constant, and the breaking point yields the stoichiometry of the complex.

The decrease in Λ is much larger on addition of poly(crown ethers), as the mobility of the macro ion will be low. Also, the equivalent conductance often does not become constant after the stoichiometric crown to cation ratio has been reached, since a redistribution of charges occurs when more poly(crown ether) is added to the cation-saturated polymer. However, the break in the conductance curve still exists.

A number of conductivity experiments were carried out at 0.001 M salt concentrations (chlorides and tetraphenyl borides were used). After each addition of a small quantity of crown ether the conductance was determined at 25.0°C, using a General Radio Co. 1673 automatic capacitance bridge. Some of the results are graphically shown in Fig. 5 for $KBPh_4$ in acetone with 15C5 and P15C5, respectively. In this solvent ($\epsilon = 20$) the tetraphenylboron salt at 10^{-3} M is virtually completely dissociated into the free ions. As the plot shows, a clear break is observed at a 15C5/$KBPh_4$ ratio of 2, a stoichiometry that is consistent with spectrophotometric and extraction data on other K^+/15C5 systems. The same ratio is found for $KBPh_4$ with P15C5, although the break is not as sharp. This may be due to the problem of obtaining a fully cation saturated polymer with K^+-P15C5, as pointed out earlier. For $CsBPh_4$ and P18C6 in acetone a break in the conductance plot is also observed at a 2:1 crown to cation ratio, but for the monomeric 18C6 the 2:1 complex with Cs^+ appears to be much less stable and a distinct break is noticeable at a 1:1 crown to cation ratio.
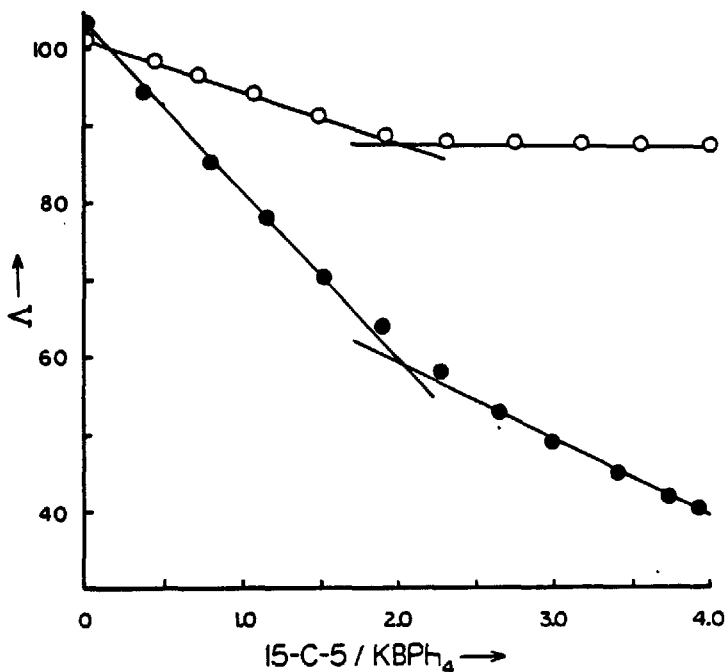
FIG. 5. Plot of equivalent conductance Λ vs the ratio [crown] /[salt] in acetone at 25°C for the systems $K^+,BPh_4^- - 15C5$ (o) and $K^+,BPh_4^- - P15C5$ (•). $[K^+,BPh_4^-] = 10^{-3}$ M.

Conductances have also been measured in media of lower polarity, such as THF or $CHCl_3$-MeOH (9:1 by volume). Ion pairs are pre-dominant in these solvents and the conductance usually goes up on addition of crown ethers [12] due to an increase in the ion pair dissoci-ation. A break in the conductance plot is again observed in many systems at crown to cation ratios of 1 or 2. Details of these measure-ments will be published elsewhere.

The binding of ion or ion pairs to poly(crown ethers) should have a pronounced effect on the conformation of the macromolecule. To check this the viscosity of the polymer solution in the presence and absence of salt was measured with an Ubbelohde viscometer at 25°C as a function of polymer concentration. The solvent consisted of a mixture of equal volumes of THF and MeOH. The results are graphically de-picted in Fig. 6.
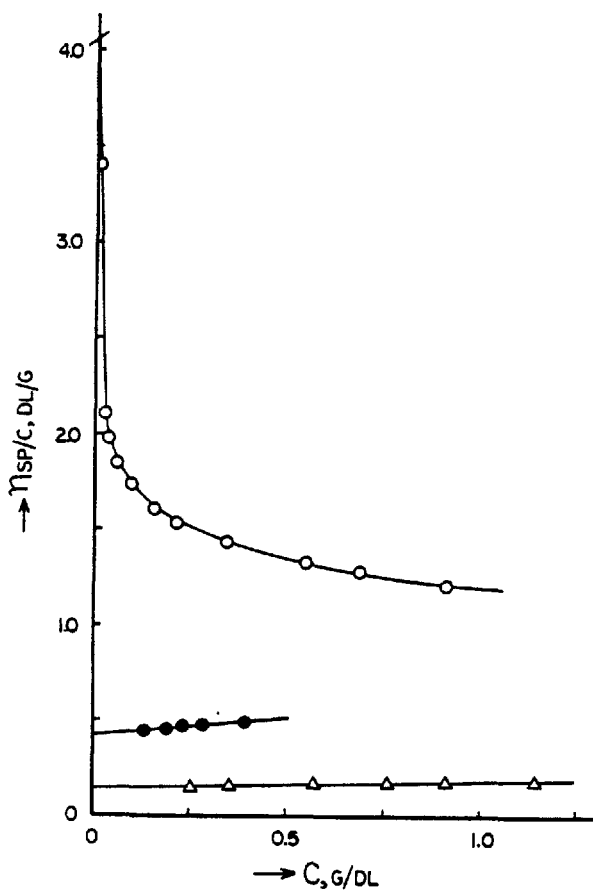
FIG. 6. Plot of reduced viscosity vs concentration of P-15C5 in a mixture of THF-methanol (50-50 volume) in the absence and presence of salt: ($\triangle$) no salt present; ($\circ$) KBr, constant ratio of [KBr]/[crown] = 0.5: ($\bullet$) KBr; salt concentration is kept constant; initial ratio KBr/crown = 3.

In the absence of salt the poly(vinylbenzo-15-crown-5) (M_n = 110,000) gives a normal plot of reduced viscosity vs polymer concentration, $[\eta]$ being 0.15. However, a mixture of P15C5 and KBr (ratio KBr:crown = 0.5) has a much higher viscosity than the same polymer solution in the absence of KBr. On dilution with solvent the reduced

viscosity increases rather drastically and a curve typical of that found for polyelectrolytes is obtained [22]. The strong increase at low polymer concentrations is not observed when the ionic strength is kept constant (initial ratio KBr:crown = 3, see Fig. 6), although the reduced viscosity is still considerably higher than in the absence of salt. The often observed linear relationship between c/η_{sp} and

$c^{1/2}$ for polyelectrolytes [22] is not strictly obeyed in our case. It may be that ion pairing occurs at higher polymer salt concentrations. Also, at very low concentrations the cation-crown complex may dissociate, and the charged polymer becomes neutral again. This may be the reason that no upward turn in the viscosity curve was found for P15C5-KBr in a 50-50 THF-H_2O mixture. Another system that shows a similar behavior in THF-MeOH as KBr-P15C5 is P18C6 with either KBr or CsCl.

In conclusion, it appears that the poly(vinyl crown ethers) represent convenient systems to study ion or ion pair interactions with neutral macromolecules in both aqueous and nonaqueous media. A variety of techniques are available to obtain the stoichiometry of the complexes and to determine cation binding selectivities and complexation constants. We are presently preparing random and block copolymers of the vinyl crown ethers with different monomers to study both inter and intramolecular ion binding. It should also be of interest to study ionic reactions that are promoted by these polymers through binding of the respective reactants.

ACKNOWLEDGMENTS

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