Effect of charge on anion and cation binding to poly(vinylbenzo-18-crown-6) in water

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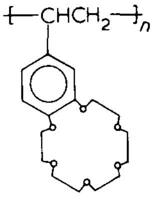
Complex formation constants, *K*, of cation to poly(vinylbenzo-18-crown-6) (P18C6) and to its monomeric analogue 4′-methylbenzo-18-crown-6 (MB18C6) were measured in water potentiometrically or spectrophotometrically. The constants for Na^+, K^+ and Cs^+ to P18C6, extrapolated to zero charge density, were found to be 2.4, 110 and 300 M^{-1}, respectively, and 27, 110 and ≈20 for MB18C6. Binding of K^+ and of picrate anions to P18C6 was measured as a function of the number of K^+ ions, *Z*, on the P18C6 chain. The charge effect (a decrease in K^+ binding with increasing *Z*, and an increase in picrate binding) can be reasonably well-described by assuming the macroion to be a solvent- and ion-impenetrable sphere, the potential of which can be calculated by using a Debye–Huckel approximation. A linear plot is predicted and found (at least for picrate binding) between ln*K* and *Z*, the slope yielding information on the radius of the P18C6 macroion. The cation effect on picrate binding to P18C6 was utilized to determine spectrophotometrically the order of binding of a series of cations to P18C6. The results were confirmed by using the dye, 2-(4′-hydroxybenzeneazo)benzoate which produces a much larger bathochromic shift on binding to P18C6 in water than does the picrate anion.

INTRODUCTION

Dissolved in water, the poly(vinylbenzo-18-crown-6) macromolecule assumes a compactly folded conformation, its properties resembling those of a micelle and/or a polysoap molecule[1–5]. The neutral polymer abbreviated in this paper as P18C6 strongly interacts with organic solutes such as picrate anions, tetraphenylboride and various dyes. The binding is partly hydrophobic in origin, but can be augmented for anionic solutes by addition of crown-complexable cations. By maniupulating the nature of the salt and its concentration, the anionic solute binding can be carefully controlled. The system was recently employed as a cation-controlled catalyst by binding the substance 6-nitrobenzisoxazole-3-carboxylate to P18C6; the decarboxylation of this substance is vastly accelerated when the compound is bound to an aprotic surface[3–6].



P18C6

In this paper we present data on the binding of cations and two anionic solutes to P18C6 in water. The relative binding capability of P18C6 with respect to a series of cations was measured spectrophotometrically, using picrate anions and the dye 2-(4′-hydroxybenzeneazo)benzoate (abbreviated as HAB) as optical probes. The optical spectrum of these anions changes on binding to P18C6. In addition, the binding of potassium and picrate ion was determined as a function of the number of K^+ ions bound to P18C6 macromolecule. An attempt was made to find a correlation between the respective binding constants and the number of charges on the polymer chain, using a Debye–Hückel approximation model and a treatment suggested by Killmann[7,8] for the binding of dyes to poly(vinyl pyrrolidone).

EXPERIMENTAL

Materials

The preparation of 4′-methylbenzo-18-crown-6 (MB18C6) and of 4′-vinylbenzo-18-crown-6, as well as the conversion of this monomer to the homopolymer P18C6 has been described elsewhere[1,9,10]. The DP_n of the polymer used in the cation binding experiments was 120; for picrate binding the DP_n was 200. The preparation of picrate salts was previously discussed[2], and 2-(4′-hydroxybenzeneazo)benzoic acid was acquired from Aldrich. Inorganic salts were reagent grade chlorides and nitrates.

Measurements

Complex formation constants of Na^+, K^+ and Cs^+ to MB18C6 and of Na^+ and K^+ to P18C6 were measured in water at 25°C by means of an Orion 801 potentiometer. A sodium ion-selective electrode (Corning No 476210) was used for Na^+, and a monovalent ion electrode (Corning No 476220) for K^+ and Cs^+. A calomel electrode served as reference. Measurements were carried out at constant crown concentration (10^{-2} M in terms of crown units) and at salt concentrations between 10^{-2} and 10^{-4}M. Calibration plots for the respective cations were linear in the 10^{-2} to 10^{-4}M

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Table 1 Binding constants of Na^+, K^+, and Cs^+ to 4'-methylbenzo-18-crown-6 and poly(vinylbenzo-18-crown-6) in water at 25°C[a]

	K (M^{-1})	
Cation	MB18C6	P18C6
Na^+	27	2.4 (2.8)[b]
K^+	110	110
Cs^+	≈20	300[b]

[a] Data for K^+ and Cs^+ with P18C6 reported in ref 14 are first binding constants, i.e. K_1 = 0.5 K; they were also measured at higher Z values

[b] Measured spectrophotometrically. All other values were determined by potentiometry

salt concentration range. The effect of ionic strength was determined by repeating the K^+ measurements in the presence of 0.1 and 0.5 M LiCl, Li^+ being a cation whose binding to P18C6 is negligibly small below 0.5 M.

Spectrophotometric measurements were carried out in the presence of picrate salts. Firstly, a solution is prepared containing 5 x 10^{-4} M P18C6, 1 x 10^{-5} M sodium picrate and 0.5 M LiCl (or 0.1 M LiCl). Under these conditions, Na^+ complexation to P18C6 can be neglected, while a fraction 0.55 of picrate anion is bound to P18C6. To determine the binding of a cation to P18C6, its chloride or nitrate salt is added to the above solution. The increase in picrate binding due to the cationic charge on P18C6 is now measured as a function of salt concentration by means of a Cary 15 spectrophotometer. The fraction of bound picrate is determined from the known spectra of the free picrate anion in water (λ_m = 354 nm, ϵ_m = 1.45 x 10^4) and the P18C6 bound anion (λ_m = 384 nm, ϵ_m = 1.81 x 10^4)[2]. Similar experiments were carried out with HAB. At pH = 6.45 this dye exhibits a large bathochromic shift on binding to P18C6, from λ_m = 347 nm, ϵ_m = 2.03 x 10^4 to λ_m = 494 nm, ϵ_m = 1.15 x 10^4.

RESULTS AND DISCUSSION

Potentiometric data

The dependence of the intrinsic cation binding constant, K, for K^+/P18C6 in water on the ratio, R, of bound K^+ over total crown units is shown in *Figure 1*. K was calculated from the expression

$$K = [\text{bound } M^+]/[\text{free } M^+]\,[\text{free sites}]$$

where [free sites] = 0.5 [total crown] − [bound K^+]. The factor 0.5 arises from the fact that even at high KCl content R does not exceed 0.5. Although K^+ only forms a 1:1 complex with MB18C6[9], extraction[11] and conductance experiments[12] on the K^+/P18C6 system have shown that the binding of K^+ to P18C6 drops sharply above $R \approx 0.5$, possibly because of electrostatic repulsion and steric interference. Also, polysalt complexes of different polyanions with K^+ charged P18C6 contain one anion per two crown units[13,14]. Only for high binding constants does R approach unity, e.g. in the binding of fluorenyl potassium to P18C6 in THF[15], or when the benzo-18-crown-6 units attached to the chain are spaced farther apart[11]. The factor 0.5 is not very precise (it may be as low as 0.4), but as long as R is kept below 0.2 small variations in this factor do not affect K significantly. A similar reasoning can be applied for Na^+ and Cs^+ binding. For the latter cation two crown ligands cooperate in the binding of this ion[1–3].

Table 1 compares the binding of Na^+, K^+ and Cs^+ to MB18C6 with that to P18C6. The order for MB18C6, $K^+ > Na^+ > Cs^+$, is the same as found for 18-crown-6[16] and for dibenzo-18-crown-6[17].

K values for the latter crown compound in a 0.1 M aqueous salt solution were reported to be 13.5 (Na^+), 44.2 (K^+), and 6.3 M^{-1} (Cs^+). The slightly higher K values for MB18C6 probably result from replacing two of the four aromatic ether oxygens by the more basic aliphatic oxygen atoms.

For 1:1 cation–crown complexes, the complex formation constants are not expected to change much after attaching the crown ligand to a polymer chain as long as neighbouring ligands or substituents do not participate or interfere in the cation binding. For example, extraction equilibrium constants for potassium picrate from water into chloroform are nearly identical for MB18C6 and a styrene copolymer containing 20 mol % of 4'-vinylbenzo-18-crown-6, and the constant for P18C6 is only slightly higher[11]. However, the binding of Na^+ to P18C6 in water is significantly lower than to the monomeric analogue MB18C6, although the values for K^+ are the same (*Table 1*). The low Na^+ binding to P18C6 can be understood if we assume that more hydration water must be removed to bind a cation to P18C6. With no adjacent crown ligands crowding in, a cation complexed to MB18C6 can retain a few water molecules. Since dehydration energies decrease in the order $Na^+ > K^+ > Cs^+$, the effect on K will be less for K^+ and Cs^+. Especially for the larger cations the loss of water may be partly compensated for by interaction of the cation with oxygen atoms of a neighbouring ligand. This is the reason for the higher binding constant of Cs^+ with P18C6, the Cs^+ being sandwiched inbetween two crown ligands.

The binding constant for K^+ changes from 110 M^{-1} for $R \to 0$ to about 40 M^{-1} when R reaches about 0.12, which, for a DP_n of 120, amounts to an average of 14 charges per chain (*Figure 1*). The effect of ionic strength is small. Measurements by Shchori *et al.* on the KCl binding to DB18C6[17] show that the binding constant slightly decreases with ionic strength, and this appears to be also the case in

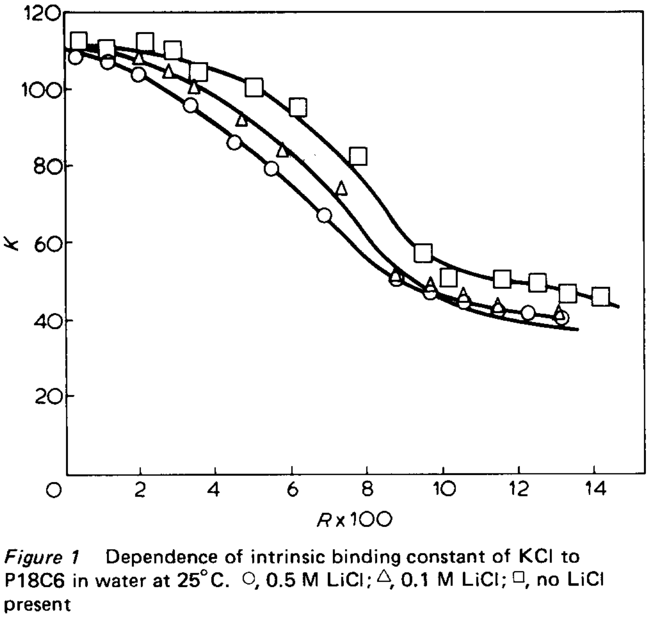


Figure 1 Dependence of intrinsic binding constant of KCl to P18C6 in water at 25°C. ○, 0.5 M LiCl; △, 0.1 M LiCl; □, no LiCl present

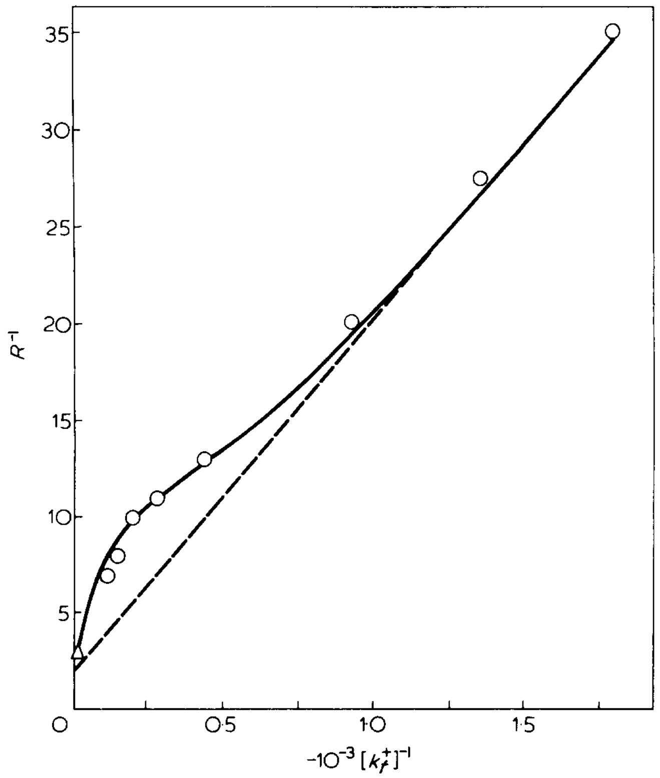


Figure 2 Plot of $1/R$ *versus* $1/[\text{free } K^+]$ for binding of KCl to P18C6 in water at 25°C. ○, 0.1 M LiCl; △, represents a number of points at [KCl] where saturation occurs

our system. The dependence of K on R levels off at higher R values. The charge dependence of K can also be observed by plotting the Langmuir adsorption isotherm in the form

$$1/R = 1/n + 1/nK\,[\text{free } K^+] \tag{1}$$

where $1/n$ is the number of crown ligands bound per cation. The deviation of this plot (*Figure 2*) from linearity implies an electrostatic repulsion effect on successive bindings of the K^+ ion. The limiting slope at $[\text{free } K^+] \rightarrow 0$ and the intercept $1/n = 2$ yields $K = 110\ M^{-1}$.

Spectrophotometric measurements

The cation dependence of picrate binding to P18C6 is shown in *Figure 3*. To avoid saturation the ratio crown to picrate in all experiments was at least a factor 40^2. With no salt present (except LiCl to assure constant ionic strength) a fraction 0.55 of picrate is bound to P18C6. More picrate becomes bound when P18C6 is charged with cations. If it is assumed that the charge effect does not depend on the nature of the bound cation, then the increase in the fraction of bound picrates at comparable salt concentrations should, for a series of monovalent cations, reflect the binding ability of P18C6 for such cations. The data of *Table 2*, giving the fraction of bound picrate at 10^{-2} M salt concentration, reveals that the cation binding constant increases in the order

$$Li^+ \ll Na^+ \approx C_2H_5\overset{+}{N}H_3 < NH_4^+ < Ag^+ < K^+ < Rb^+ < Cs^+$$

This, at least for the alkali cations, corresponds to the decrease in their dehydration energies. The same holds for the alkaline earth cations.

The effect of ionic strength on picrate binding is small, and the increase in the fraction of bound picrate from 0.45 (the fraction of picrate bound when [picrate] = 10^{-5} and [P18C6] = 5×10^{-4}, and no LiCl or other salts are present) to 0.55 on addition of 0.5 M LiCl can nearly all be accounted for as coming from impurities present in the LiCl (Na^+, K^+, Ba^{2+}, Pb^{2+}, the 0.003% K^+ impurity listed on the label can already enhance the picrate binding from 0.45 to 0.49). Note also that for the same fraction of bound cations, Ba^{2+} is twice as effective in increasing the electrostatic potential than K^+, although at higher R values the stronger repulsion between Ba^{2+} cations is likely to decrease $K(Ba^{2+})$ as a function of R more rapidly than $K(K^+)$ (see *Figure 3*). The decrease in picrate binding on addition of Zn^{2+} or Cd^{2+} is peculiar. Formation of $M^{2+}Pi^-$ ion pairs could cause such an effect, but this was not further checked.

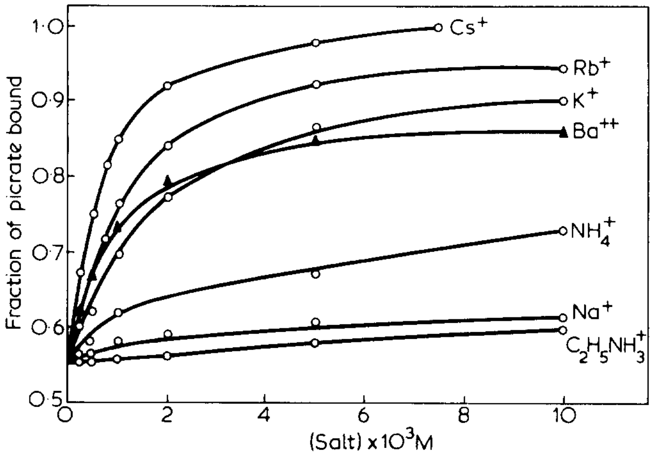


Figure 3 Effect of crown complexable cations on the fraction of picrate bound to P18C6 in water at 25°C. [P18C6] = 5×10^{-4} M; [Picrate] = 1×10^{-5} M

Table 2 Cation effect on binding of picrate and 2-(4′-hydroxybenzeneazo)benzoate (HAB) to P18C6 in water (25°C)[a]

Cation	Fraction of picrate bound $[M^+] = 10^{-2}$ M		Fraction of HAB Bound $[M^+] = 10^{-1}$ M
		0.5 M LiCl	
–	0.45	0.55	0.03
Li	0.45		0.031
Na	0.53	0.61	0.095
$C_2H_5NH_3$		0.60	0.088
NH_4	0.70	0.73	0.136
Ag	0.74		
Tl			0.20
K	0.92	0.91	0.38
Rb		0.98	0.29
Cs	1.0[b]	1.0[b]	0.79
Zn	0.36		
Cd	0.36		
Mg		0.55	
Ca		0.57	
Sr		0.70	0.127
Pb[c]	0.71		
Hg[c]	0.79		
Ba	0.85	0.86	0.263

[a] [Picrate] = 10^{-5} M; [P18C6]/[Picrate] = 50; [HAB] = 5×10^{-5} M; [P18C6]/[HAB] = 160

[b] All Picrate anions are bound at [CsCl] = 7.5×10^{-3} M

[c] Solution becomes cloudy

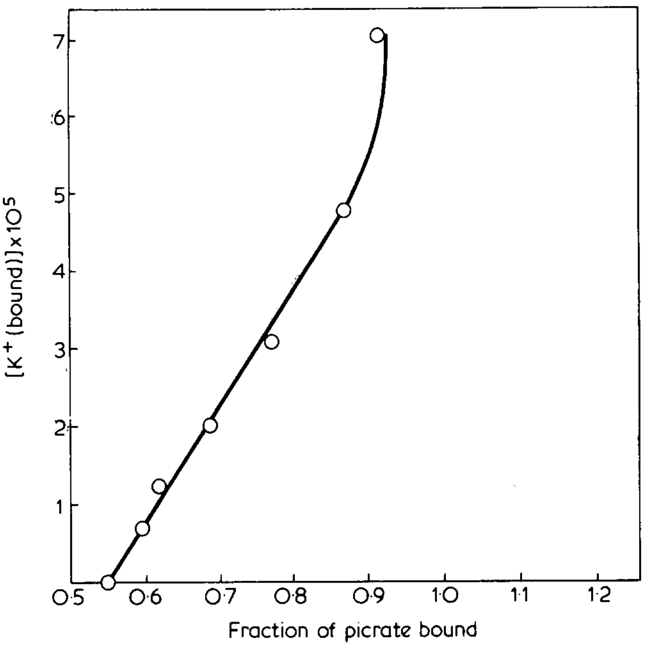
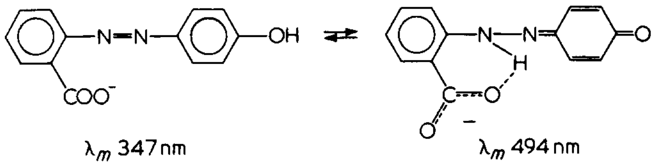


Figure 4 Concentration of K$^+$ ion bound to P18C6 as a function of the fraction of picrate anion bound to P18C6 in water at 25°C with 0.1 M LiCl present

The high fraction of picrate bound to neutral P18C6 makes this anion less attractive as a probe to determine the cation binding to P18C6. For this reason we investigated the dye 2-(4′-hydroxybenzeneazo)benzoate (HAB) and the cation effect on the binding of this anion to P18C6. At pH 6.45 the monoanion changes from the azo form in water (λ_m = 347 nm) to the hydrazone form (λ_m = 494 nm) in an organic medium or when bound to cationic detergents or serum albumin[18,19].



At a ratio P18C6/HAB = 200 only a fraction 0.03 of HAB is bound to neutral P18C6, but this increases on charging the macromolecule, and in the presence of 0.1 M CsCl all HAB is bound, i.e. no azo form can be detected. At a ratio P18C6/HAB equal to 160 a fraction of 0.8 was bound. Apparently, a large excess of crown units is required to accommodate one dye molecule. The fraction of HAB bound to P18C6 at 0.1 M salt concentration and for P18C6/HAB = 200 is recorded in *Table 2*. Except for Rb$^+$, the effect of cation binding on HAB follows the same pattern as observed for picrate anions.

Complex formation constants of cations to P18C6 can be determined from picrate or HAB binding experiments if the assumption is made that the increase in the anion binding solely depends on the number of complexed cations on the chain and not on their type. Since for K$^+$ the dependence of K on R = [bound K$^+$]/[total crown] is known from potentiometric measurements, a calibration curve can be constructed by plotting the [bound K$^+$] *versus* the fraction of picrate bound, using *Figure 3*. This turns out to be close to a straight line between a fraction of 0.55 (no M$^+$ present) and 0.85 of picrate bound (see *Figure 4*). The effect of any cation M$^+$ on picrate binding can be determined as a function of [M$^+$] (*Figure 3*). From the calibration plot in *Figure 4* the relationship between [P18C6], [M$^+$], and [bound M$^+$] can now be found, hence the complex formation constant of M$^+$ to P18C6 can be calculated. Results for Cs$^+$ yield a value $K = 300\ M^{-1}$ at low R, and, as also found for K$^+$ (*Figure 1*), decreasing at higher charge density of the chain. The value for Na$^+$ was found to be 2.8 M^{-1}, close to the potentiometric value of 2.4 M^{-1} (*Table 1*).

GENERAL DISCUSSION

The electrostatic free energy, W_{el}, of placing charges on a macromolecule depends on the electrostatic potential ψ. The latter parameter in turn is a function of the number and distribution of the charges on the chain. Expressions for ψ have been derived by assuming that the chain approaches one of three models[20]: (a) a compactly-folded spherical particle which is partly or fully impenetrable to solvent; (b) a charged cylindrically-shaped rod, or (c) a flexible linear polyelectrolyte in which the electrostatic energy is minimized by rotation of charged segments. In all three cases W_{el} is given by $W_{el} = BZ^2e^2$, where Ze is the average charge on the macroion and B depends on the particular model appropriate for the polyelectrolyte system[20].

It has been argued that to a first approximation the P18C6 macromolecule in water may be regarded as a compactly-folded particle with physical properties that resemble globular proteins or non-ionic detergents. Its $[\eta]$ at 25°C (M_n = 110000) equals 10.7 ml g^{-1} [1], far below the 40–100 ml g^{-1} value for random coils[20] and closer to the 3.5–5 ml g^{-1} for globular proteins[20] and micelles of non-ionic detergents[21]. The spectrum of P18C6-bound methyl orange[2] is nearly identical to that of the same dye bound to bovine serum albumin[22] or certain polysoap molecules[23,24], and not to that of methyl orange bound to the water swollen poly(vinyl pyrrolidone) macromolecule[25,26]. The spectrum of the latter methyl orange is identical to that in water. These and other facts suggest a P18C6 macromolecule to be a more or less water-impenetrable particle, compactly folded (its cloudpoint is only 37°C), with many of its crown rings hydrogen bonded to water molecules at the water–polymer interface[2]. Most of the crown-complexed cations, therefore, may be located at the surface of the macroion. The close proximity of the ligands promotes a rapid cation transfer between crown units[27,28] similar to that recently observed in surfactants containing terminal cryptand ligands[29]. Therefore, in the calculations we have made the assumption that P18C6 in water is a spherical macroion, nearly impenetrable to solvent and mobile ions, with bound K$^+$ ions evenly distributed over the surface.

The electrostatic potential $\psi = \psi(Z)$ on a macroion modifies the activation energy of adsorption or desorption of an ion that complexes with this macroion by a term $z_i e\psi$, where z_i is the charge on the approaching ion[7,8]. If in our system K_0 denotes the intrinsic binding constant of the picrate or M$^+$ ion to neutral P18C6 ($\psi = 0$), then the binding constant K of these solutes to charged P18C6 is given by:

$$K = K_1 \exp(-E_{el}/NkT) = K_1 \exp(-2z_i e\psi/kT) \qquad (2)$$

where z_i is -1 for picrate anions and $+1$ for M$^+$ binding, N being Avogadro's number. The potential ψ may be obtained from the Debye–Hückel approximation for the potential of a spherical, solvent-impenetrable macroion of charge Ze and radius b in aqueous solution of ionic strength I.

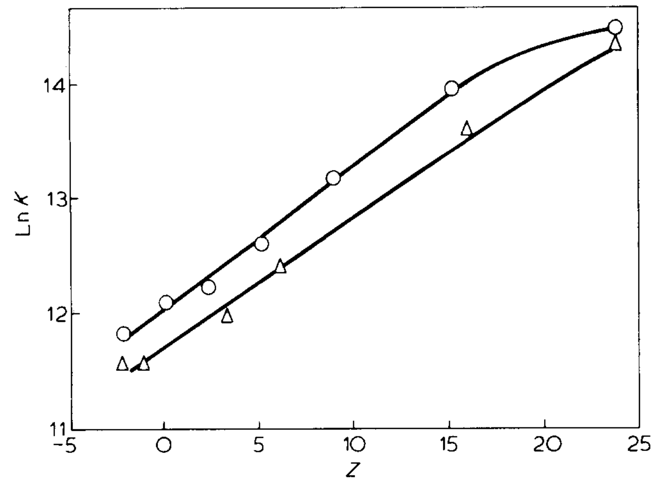


Figure 5 Plot of ln*K* *versus* the number, *Z*, of K^+ ions bound to a P18C6 chain in the binding of picrate anions to P18C6 in water at 25°C in the presence of 0.1 M LiCl

This potential at the surface of the macroion is given by[20]:

$$\psi = Ze/Db' \tag{3}$$

where D is the bulk dielectric constant and $1/b'$ is given by:

$$1/b' = 1/b - \kappa/(1 + \kappa a) \tag{4}$$

The parameter a in equation (4) is the distance of closest approach of the mobile ions (LiCl) to the macroion and κ is given by:

$$\kappa = (8\pi Ne^2/1000\,DkT)^{0.5}I^{0.5} \tag{5}$$

Combining equations (2) and (3) yields:

$$\ln K = \ln K_0 - 2wz_iZ \tag{6}$$

where w has the same meaning as in the thermodynamic treatment of ion binding to macromolecules (see ref 20, p 539), i.e., for a spherical macroion:

$$w = e^2/DkTb' \tag{7}$$

A plot of ln*K* *versus* *Z* (or *versus* *R*, since $R = Z/DP_n$) should yield a straight line with slope $2z_iw$ from which the radius b of the P18C6 macroion can be derived. Z can be determined from the relationship between added KCl and R as obtained from potentiometric data, and the DP_n of the polymers (see Experimental). Z is corrected for the number of picrate anions bound. This varies from an average of 2.3 to 3.5 per chain, depending on the amount of picrate bound. The correction barely affects the slope of the plot.

The results for picrate binding, shown in *Figure 5*, demonstrate a reasonable linearity between ln*K* and *Z* up to $Z \approx 25$ (90% of picrate bound). More scattering is observed in the absence of LiCl, partly because the ionic strength varies from 0.0001 to 0.1. The slope of *Figure 5* yields a radius b of 34.5 ± 1.5 Å for the P18C6 macromolecule in 0.1 M LiCl ($1/\kappa$ = 9.6 Å) and a radius of 29 ± 1.5 Å in 0.5 M LiCl ($1/\kappa$ = 4.3 Å). The linearity of ln*K* and *Z* suggests that the radius of the macroion is not highly susceptible to changes in its charge density. This is confirmed from viscosity measurements of P18C6 in water. The intrinsic viscosity of a 1.4% P18C6 solution in water increases only 10% on addition of 0.04 M KCl, while under similar conditions $[\eta]$ increases by a factor 3 when the solvent is THF/MeOH[1].

The variation of the macroion radius with LiCl concentration suggests that some contraction or expansion occurs on varying the ionic strength. But it should be pointed out that the assumed model and calculations may be rather crude. For example, the use of the bulk dielectric constant is questionable. Moreover, the macroion is not likely to be perfectly spherical. Also, the picrate anion may be located more in the inner core of the macroion rather than on its surface. Nevertheless, the calculated radius of the macroion is not unreasonable. Applying the expression $V_h = (4/3)\pi b^3 = M[\eta]/2.5\,N$ (ref 20) for the hydrodynamic volume of a spherical particle and using the value $[\eta]$ = 6.7 ml g^{-1} found for P18C6 of DP_n = 200 in water, a value for b = 41 Å is obtained for the neutral P18C6 macromolecule. The b value from picrate measurements appears too low, possibly because the picrate anions may not be adsorbed on the surface but deeper inside the particle.

A plot of ln*K* vs. *Z* for K^+ binding to P18C6 deviates from linearity at low and high *Z* values. *Figure 6* indicates that *K* levels off at higher *Z* to a constant value. Killmann[7,8] observed similar behaviour for dye binding to poly(vinyl pyrrolidone). Data in methanol for the latter system reveal that a constant binding constant is reached when the electrostatic attraction energy exceeds the thermal energy 2*kT* of the two ions involved, i.e. under conditions where, according to Bjerrum's theory, ion pairing is favoured. Anion binding under these conditions is accompanied by specific counterion binding (see also Manning, ref 30). When applied to our system, monovalent counterion binding should occur when $E_{el} = 2e\psi = 2kT$, or when $Z = DbkT/e^2$. In water at 25°C the term e^2/DkT equals 7.1 Å. Hence, counterion binding is expected when $Z = b'/7.1$, or when $Z = 2/S$ where $S = 14.3/b'$ represents the slope of the ln*K* vs. *Z* plots of *Figures 5* and *6*.

The slope of the ln*K* vs *Z* plot for K^+ binding is 0.08 ± 0.01 (neglecting the first two points and those above Z = 10). This means that counterion binding should occur at $Z \approx 25$. Enough KCl was added to reach Z = 15 (*Figure 6*), hence, *K* should decrease still more before reaching a constant value. The slope S = 0.08 yields b = 33.2 Å for the K^+ charged macroion. From the hydrodynamic volume expression (see above) and the measured $[\eta]$ = 4.4 ml g^{-1} for a P18C6 molecule of DP_n = 120 a radius of 31 Å for the neutral P18C6 molecule is calculated. The K^+ cation probably binds more on the surface of the crown polymer, and the K^+ binding data, therefore, may provide more accu-

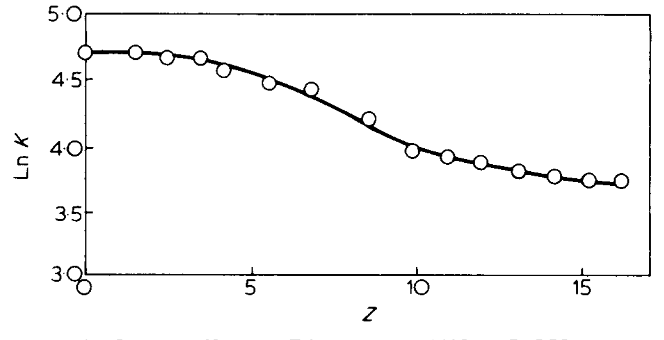


Figure 6 Plot of ln*K* *versus* *Z* for binding of KCl to P18C6 in water at 25°C, 0.1 M LiCl present

rate information on the radius of the macroion than the picrate binding experiments.

The slope S of the ln$K$ vs. Z plot for Ba^{2+} absorption should be $-4w$, z_i being 2 for Ba^{2+}. Hence, the binding constant for Ba^{2+} declines as a function of $[BaCl_2]$ more rapidly than the binding constant of K^+ as a function of [KCl], assuming comparable K_0 values for the two cations. No Ba^{2+} binding constants were determined, but *Figure 3* shows that the increase in picrate binding as a function of salt concentration slows down more rapidly for Ba^{2+} than for K^+, a consequence of the more rapid decrease in the Ba^{2+} binding constant.

At the crossover point (*Figure 3*) of the K^+ and Ba^{2+} curves ([Salt] = 3.5×10^{-3} M) the total charge on P18C6 should be the same for the Ba^{2+} as for the K^+ charged macroion, i.e. twice as many K^+ ions are bound at this salt concentration as Ba^{2+} ions. Since $K = \theta/(1-\theta)[\text{free } M^+]$ (where θ is the fraction of crown units complexed to a cation), and $[\text{free } M^+] \approx [KCl]_0 = [BaCl_2]_0 = 3.5 \times 10^{-3}$ M one finds that at the crossover point $K(Ba^{2+}) \approx 0.4\,K(K^+)$. The ratio $\ln\,[K(K^+)/K(Ba^{2+})]$ equals $\ln[K_0(K^+)/K_0(Ba^{2+})] + 2wZ$, and at 0.0035 KCl Z is equal to 16. Since for K^+ we found $w = 0.04$ the ratio $K_0(Ba^{2+})/K_0(K^+)$ equals 1.5, i.e. Ba^{2+} in water binds stronger to neutral P18C6 than K^+. If picrate binding as a function of Ba^{2+} or K^+ concentration had been compared at 10^{-2} M salt concentration, the reverse conclusion could have been drawn. Therefore, the effect of different cations on the adsorption of HAB to P18C6 (*Table 2*) may not always yield the correct order for the intrinsic binding constants of the respective cations to neutral P18C6 when comparing mono- and divalent cations. The results with HAB as optical probe were compared at 0.1 M salt concentration, and the polymer under these conditions is already considerably charged.

Interpretation of binding data could possibly be refined by minimizing solvent and ion penetration into the coiled polymer. This may be achieved by incorporating hydrophobic monomers into the chain. Copolymers of equal molar quantities of 4′-vinylbenzo-18-crown-6 and styrene are poorly soluble in water, and an amount of 10 or 20 mol % of styrene may add sufficient hydrophobicity to significantly reduce solvent penetration. Spacing between crown ligands can also be varied by copolymerization of vinylbenzocrown ethers with vinylbenzoglymes, styrene monomers in which short poly(ethylene oxide) chains (n = 2 to 8) are attached to the benzene ring[31]. Some of the homopolymers of the latter monomers are water soluble and also exhibit polysoap character, with strong adsorption of picrate anions accompanied by a spectral change similar to that found with P18C6. Another improvement would be the use of carefully fractionated polymer samples.

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