

Interaction of 1-pyrenebutyrate with poly(vinylbenzo-18-crown-6) and poly(vinylbenzogleyme) in water

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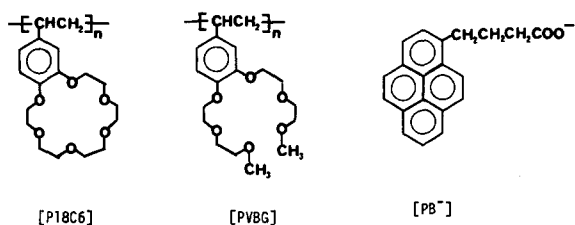
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Binding constants of 1-pyrenebutyrate (PB^-), 1-pyrenecarboxylate and 1-pyrenevalerate to the polysoap-type macromolecule poly(vinylbenzo-18-crown-6) (P18C6) and the poly(vinylbenzogleyme) PVBG (a polystyrene with two $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2$ -substituents at the 3 and 4 position of each benzene ring) were determined spectrophotometrically (λ_m 342 nm for free PB^- , 348 nm for polymer-bound PB^-). The binding appears to follow Langmuir adsorption behaviour. Interaction with P18C6 is enhanced on adding crown ether-complexable cations, which converts the neutral polymer into a polycation. The enhanced binding is chiefly caused by lower values of $1/n$ (minimum number of crown monomer units per bound PB^- molecule). This decreases at 25°C from $1/n=25$, for neutral P18C6, to 6.2 and 2.7 in the presence of 0.01 M CsCl and 0.1 M KCl, respectively. It is argued that the COO^- substituent of bound PB^- is probably located in the aqueous layer at the polymer-water interphase. Its presence close to the crown ligands enhances the binding of K^+ or Cs^+ cations to these ligands by forming crown-complexed ion pairs $\text{PB}^-, \text{M}^+ \cdots \text{P18C6}$. The typical excimer fluorescence emission peak of PB^- is observed when P18C6 in 0.1 M KCl is saturated with PB^- . Some of the binding measurements were carried out in ethanol-water mixtures.

(Keywords: poly(crown ether); pyrene butyrate; polysoap; polycations; interactions; hydrophobic)

INTRODUCTION

In aqueous solution, macromolecules composed of a polystyrene backbone to which crown ether ligands or short oligo-oxyethylene (glyme) chains are anchored often behave as typical polysoaps due to their tightly coiled conformation¹⁻⁸. The two best known examples are poly(vinylbenzo-18-crown-6) (P18C6) and the poly(vinylbenzogleyme) PVBG. Their structures are shown below.



Optical and fluorescent studies have demonstrated that a variety of organic solutes can be solubilized in the hydrophobic microdomains of the neutral polymers. These include picrate²⁻⁴, methylorange^{2,4}, 2-(4'-hydroxybenzeneazo)benzoate³, 8-anilino-naphthalene-1-sulphonate⁵, 2-p-toluidino-naphthalene-6-sulphonate⁵, auramine 0⁶ and 6-nitrobenzisoxazole-3-carboxylate⁷. The latter compound rapidly decarboxylates in its polymer-bound state.

Recently, the interaction of pyrene and other neutral arenes with P18C6 and PVBG was studied⁸. Pyrene compounds have been extensively used in the study of

micelles, proteins, synthetic macromolecules and colloidal particles⁹⁻¹⁶. Their fluorescence emission is relatively long-lived and sensitive to the polarity of the environment. Binding of pyrene to the hydrophobic domain of P18C6 or PVBG causes a significant bathochromic shift in the optical spectrum of this compound and the bound and free pyrene absorption maxima emerge as distinctly separate peaks⁸. It permits the measurement of binding constants and of thermodynamic binding parameters. This property of pyrene can also be utilized for many of its derivatives including ionic compounds. The latter are of particular interest in their interaction with P18C6 as the poly(crown ether) can be converted into a polycation by means of crown ether-complexable cations like K^+ , Cs^+ , Tl^+ or Ba^{2+} . This enhances the interaction with anionic solutes while that with cationic compounds like auramine 0 is decreased.

We have used 1-pyrenebutyrate (PB^-) and 1-pyrenebutyltrimethylammonium bromide (PN^+) to study the behaviour of ionic pyrene derivatives in aqueous solutions of P18C6 and PVBG, both in the absence and presence of inorganic salts. The two pyrene compounds have been used as fluorescent probes in a number of studies involving micelles, macromolecules and colloidal particles¹⁶⁻²⁰. This work describes our results for the binding of PB^- with neutral P18C6 and PVBG and with charged P18C6. The enhanced binding of PB^- to charged P18C6 appears to be largely the result of a strong increase in the maximum number of pyrenebutyrate anions that can be bound to P18C6 when the crown ligands of P18C6

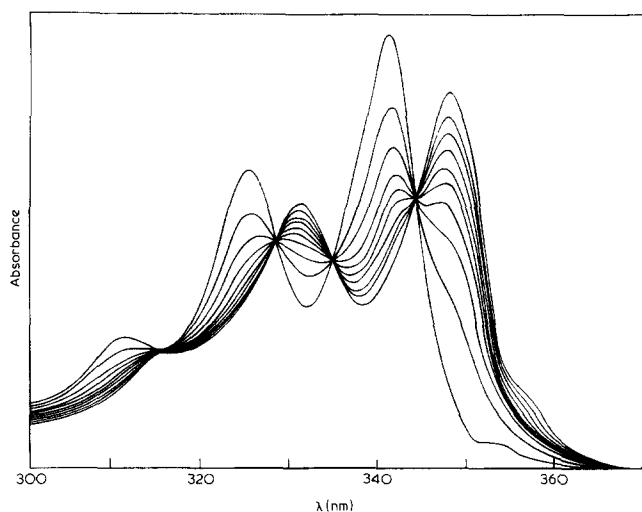


Figure 1 Change in optical spectrum of 1-pyrenebutyrate (PB^-) on binding to P18C6 or PVBG in water. Maxima at 332 and 348 nm for polymer-bound PB^- and at 326 and 341 nm for free PB^-

complex with cations like K^+ or Cs^+ . The effect of added ethanol was also studied. In addition, binding constants for 1-pyrenecarboxylate (PC^-) and 1-pyrenevalerate (PV^-) were determined to check the effect of side chain on the binding to P18C6.

EXPERIMENTAL

Materials

1-Pyrenebutyric acid (4-(1-pyrenyl)butanoic acid), an Aldrich product, was recrystallized three times from ethanol. 1-Pyrenevaleric acid and 1-pyrenecarboxylic acid were acquired from Molecular Probes, Inc., and also recrystallized from ethanol. The syntheses of the two polymers P18C6 and PVBG have been reported elsewhere^{4,21}. The number average molecular weights of the two polymers, determined by high speed membrane osmometry, were 110 000 for P18C6 ($\text{DP}_n=325$) and 50 000 for PVBG ($\text{DP}_n=150$). Inorganic salts used were all reagent-grade compounds.

Polymer concentrations were determined from the weight of added polymer or from the 280 nm absorption maximum (ϵ_m 2950) of the benzocrown or benzoglyme ligand²². Solutions of the pyrene carboxylates were obtained by dissolving a known quantity of the corresponding acid in water using a slight excess of lithium hydroxide. The Li^+ ions do not bind to P18C6 in water below 0.1 M of this cation. The carboxylate concentration was calculated from the 341 nm (ϵ_m 41 000) absorption maximum. This peak shifts to 348 nm (ϵ_m 36 000) for the polymer-bound species. Binding experiments were carried out by keeping the concentration of pyrene compound constant and varying the polymer concentration, or *vice versa*.

All spectra were recorded on a Beckman Acta VI spectrophotometer using a thermostatically controlled cell. Concentrations of bound and free solute in the mixture were computed from the known spectra of the individual species. Experimental conditions as to solute and polymer concentrations are given in the Figure captions. In a number of experiments, known quantities of salts or ethanol were added.

RESULTS

Figure 1 depicts the changes in the optical spectrum of an aqueous solution of PB^- on adding P18C6. The appearance of well-defined isobestic points implies the presence of a polymer-bound species (λ_m 332 and 348 nm) in equilibrium with free PB^- (λ_m 326 and 341 nm). Similar changes occur when PVBG is added, or when PC^- or PV^- are used instead of PB^- . The spectral changes resemble those reported for pyrene in the presence of P18C6 or PVBG⁸ except for the bathochromic shift of the two absorption peaks resulting from the presence of a 1-substituent.

Analysis of the spectra yield the fractions of free and bound solute. The data are then plotted using the Klotz expression²³ of the Langmuir adsorption isotherm, $1/R = 1/n + 1/nKA$, where $1/R$ denotes the ratio of the concentration of polymer (expressed in terms of monomer base units) to that of bound solute, A represents the free solute concentration, K is the intrinsic binding constant, $1/n$ the minimum number of monomer base units per polymer-bound solute molecule, and $K_1 = nK$ is the first binding constant. Examples of such plots for the system PB^- -P18C6 between 10° and 35°C are shown in Figure 2. The open symbols on these plots refer to experiments at constant $[\text{PB}^-]$ while for the closed symbols $[\text{P18C6}]$ was kept constant. The two sets of data for each temperature fall on the same linear plot (see also subsequent Figures). The data at constant $[\text{P18C6}]$ generally yield points closer to the saturation value $1/R = 1/n$. This facilitates the determination of $1/n$ by extrapolation of the plots and, consequently, improves the accuracy of the K values. Linear plots were also obtained for PB^- with PVBG and for PC^- and PV^- with P18C6. The latter three systems were only studied at 25°C.

Addition of sufficient K^+ or Cs^+ ions converts P18C6 into a cation-charged poly(crown ether). This strongly enhances the binding of anionic solutes such as PB^- . Figure 3 shows binding plots for the system PB^- -P18C6 in the presence of 0.01 and 0.1 M KCl, the latter at two different concentrations of P18C6. The $1/R$ vs. $1/\text{PB}^-$ plots are again linear, but they and the $1/R$ vs. PB^- plots clearly reveal that much lower $1/R$ values are reached than in the absence of K^+ ions. Temperature dependent

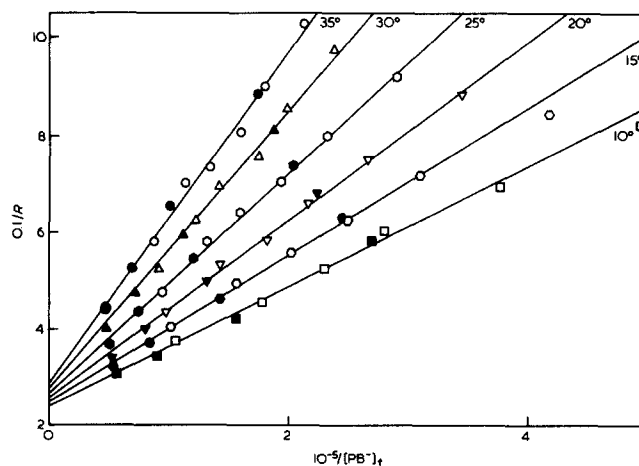


Figure 2 Temperature dependence of the binding of 1-pyrenebutyrate (PB^-) to P18C6 in water. Open symbols: $[\text{PB}^-] = 1.5 \times 10^{-5}$ M; $[\text{P18C6}] = 2 \times 10^{-4} - 1 \times 10^{-3}$ M. Closed symbols: $[\text{P18C6}] = 3.5 \times 10^{-4}$ M; $[\text{PB}^-] = 8 \times 10^{-6} - 3 \times 10^{-5}$ M

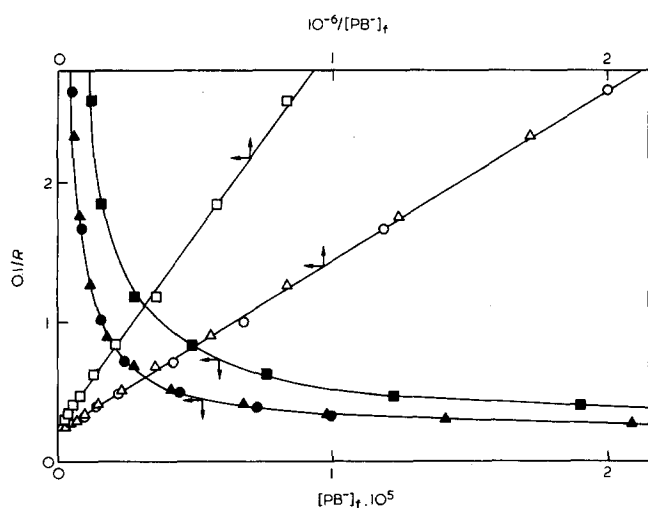


Figure 3 Binding of 1-pyrenebutyrate (PB^-) to P18C6 in the presence of 0.01 M KCl (\square , \blacksquare) and 0.1 M KCl (\circ , \triangle , \bullet , \blacktriangle). $[\text{PB}^-] = 4 \times 10^{-6} - 8 \times 10^{-5}$ M; Circles and squares: $[\text{P18C6}] = 2 \times 10^{-4}$ M; triangles: $[\text{P18C6}] = 1 \times 10^{-4}$ M

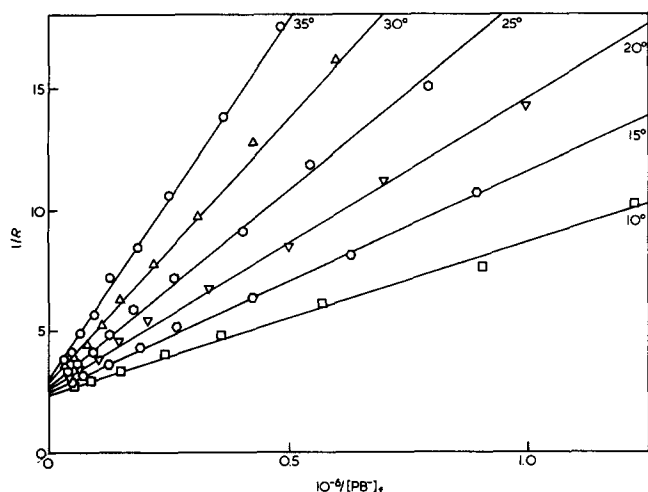


Figure 4 Temperature dependence of the binding of 1-pyrenebutyrate (PB^-) to P18C6 in water in the presence of 0.1 M KCl. $[\text{P18C6}] = 8 \times 10^{-5}$ M; $[\text{PB}^-] = 7 \times 10^{-6} - 5 \times 10^{-5}$ M

measurements were carried out in the presence of 0.1 M KCl and 0.01 M CsCl to obtain the thermodynamic parameters for these systems. The Klotz plots are shown in Figures 4 and 5.

For each system the slope and intercept of the appropriate plot were determined by least square analysis yielding the K_1 and $1/n$ values. The intrinsic binding constants were then computed from the expression $K = K_1/n$. The latter constants are sensitive to errors in the extrapolation of the Klotz plots when determining $1/n$. As with other solutes³ the quantity $1/n$ appears to decrease with temperature. For example, in the absence of salt $1/n$ for PB^- equals 28 at 35°C, and 25 at 10°C. Corresponding values in the presence of salts are 3.0 and 2.4 with 0.1 M KCl, and 6.5 and 5.7 with 0.01 M CsCl. Values of $1/n$ at temperatures between 10° and 35°C were calculated by assuming a proportional increase of $1/n$ with temperature (the plots of Figures 2–5 were drawn by using thus calculated intercept values). Least square analysis yielded an average standard deviation of 5% for the K_1 values, while K values have an accuracy of about

10%. Constants for the various systems are collected in Table I. Included are the binding enthalpies and entropies which were calculated from the van't Hoff plots of the intrinsic binding constants (Figure 6).

A more systematic assessment of the effect of P18C6-bound cation on the binding of PB^- to a charged poly(crown ether) was obtained from sets of experiments each of which was carried out at a constant but different concentration of CsCl varying between 5×10^{-5} and 0.01 M. The results are given in Figure 7 as plots of $1/R$ vs. $[\text{PB}^-]$ while the Klotz plots are shown in Figure 8. Under identical conditions of $[\text{P18C6}]$ and $[\text{PB}^-]$, $1/R$ decreases at increasing concentrations of CsCl. Both plots reveal a dramatic enhancement in the maximum capacity of P18C6 for binding PB^- , i.e., under saturation conditions ($1/R = 1/n$) much more PB^- can be bound to P18C6 with CsCl present even at 5×10^{-5} M of this salt. For example, while in the absence of salt $1/n$ at 25°C equals 25 (Table I, the value being slightly lower in the experiment shown in Figure 8), it decreases to $1/n = 6$ in the presence of 0.01 M CsCl. Note also that at CsCl concentrations below 10^{-3} M the $1/R$ vs. $1/\text{PB}^-$ plots curve downward as the PB^- concentration is increased.

The effect of the type of added cation (Li^+ , Na^+ , K^+ , Cs^+) on the binding of PB^- to P18C6 is given in Figure 9. The Figure also shows that for the poly(vinylbenzoglyme) the increase in bound PB^- is very small even when Cs^+ is added.

Finally, several experiments were carried out in mixtures of water and ethanol to determine the effect of a solvent that destroys the polysoap-type properties of P18C6 or PVBG. The results are shown in Figure 10 for one system without salt and for two systems with 0.1 M CsCl and different concentrations of P18C6. Since the fraction of PB^- bound is a function of both $[\text{P18C6}]$ and $[\text{CsCl}]$, different amounts of ethanol are needed to cause a decrease in the fraction of bound PB^- as calculated from the change in optical spectrum (the spectra of free PB^- in water and ethanol are identical). At 8×10^{-4} M P18C6 and 0.1 M CsCl nearly all PB^- remains bound close to

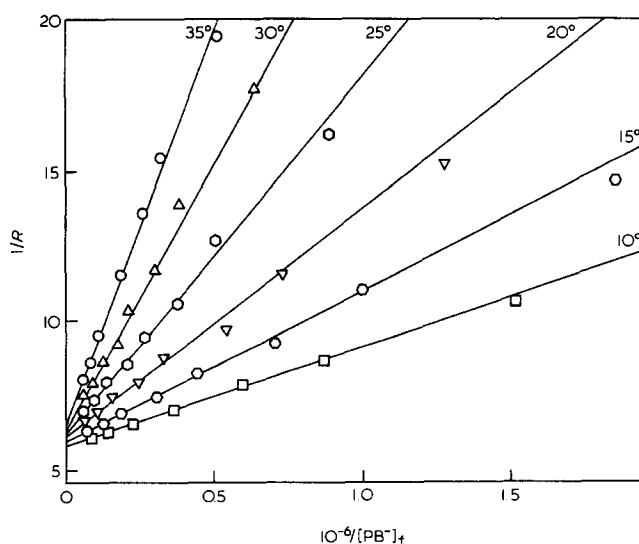
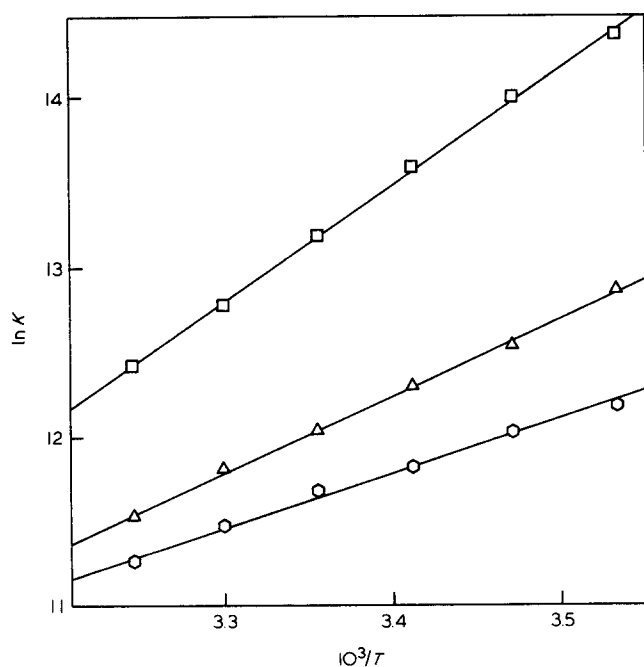


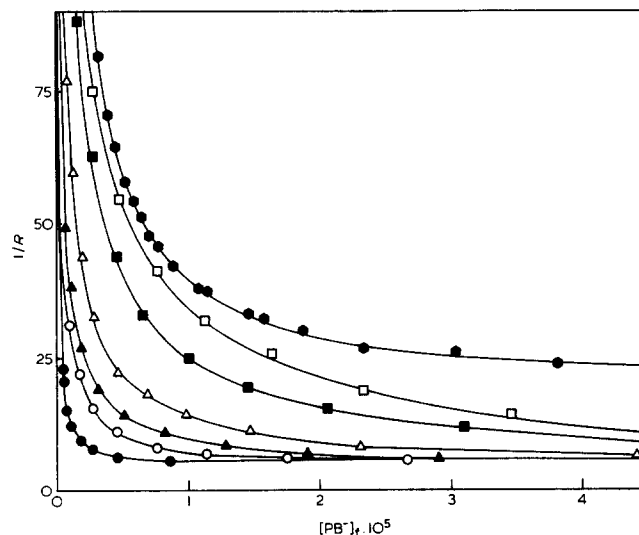
Figure 5 Temperature dependence of the binding of 1-pyrenebutyrate (PB^-) to P18C6 in water in the presence of 0.01 M CsCl. $[\text{P18C6}] = 8 \times 10^{-5}$ M; $[\text{PB}^-] = 6 \times 10^{-6} - 3 \times 10^{-5}$ M

Table 1 First (K_1) and intrinsic (K) binding constants of 1-pyrenebutyrate, 1-pyrenecarboxylate and 1-pyrenevalerate to P18C6 and PVBG in water in the absence and presence of CsCl or KCl

T (°C)	K_1 ($\times 10^{-3} \text{ M}^{-1}$)	K ($\times 10^{-4} \text{ M}^{-1}$)	$1/n$	
1-Pyrenebutyrate/P18C6				
				<i>No salt</i>
35	2.92	7.9	27	
30	3.51	9.1	26	
25	4.43	11.0	25	$\Delta H = -6.0 \text{ kcal mol}^{-1}$
20	5.38	12.9	24	$\Delta S = 3.2 \text{ e.u.}$
15	6.67	15.7	23.5	
10	8.05	18.5	23	
				<i>0.01 M CsCl</i>
35	38.0	24.7	6.5	
30	55.8	35.5	6.3	
25	83.5	53.0	6.2	$\Delta H = -13.5 \text{ kcal mol}^{-1}$
20	131	79.3	6.0	$\Delta S = -19 \text{ e.u.}$
15	197	116	5.9	
10	296	170	5.7	
				<i>0.1 M KCl</i>
35	33.8	10.1	3.0	
30	45.9	13.3	2.9	
25	62.0	16.7	2.7	$\Delta H = -9.0 \text{ kcal mol}^{-1}$
20	83.3	21.7	2.6	$\Delta S = -6.3 \text{ e.u.}$
15	111	27.7	2.5	
10	160	38.6	2.4	
1-Pyrenebutyrate/PVBG				
25°	6.4	19	30	
1-Pyrenecarboxylate/P18C6				
25°	0.85	0.85	10	
25° (0.1 M CsCl)	13	5.2	4	
1-Pyrenevalerate/P18C6				
25°	5.7	8.0	14	


Figure 6 Temperature dependence of the binding constants of 1-pyrenebutyrate (PB^-) to P18C6 in water. (\circ), no salt; (\triangle), 0.1 M KCl; (\square), 0.01 M CsCl

20% ethanol, but this changes rapidly as more ethanol is added, and with 60% ethanol the spectrum of PB^- has become identical to that of free PB^- in water.


Figure 7 Effect of CsCl on the binding of 1-pyrenebutyrate (PB^-) to P18C6 in water at 25°C. [P18C6] is constant in each experiment but differs (between 8×10^{-5} and $2.4 \times 10^{-4} \text{ M}$) for each concentration of CsCl. [PB^-] = 4×10^{-6} – $9 \times 10^{-5} \text{ M}$. [CsCl] = 0 (\bullet), $5 \times 10^{-5} \text{ M}$ (\square), 10^{-4} M (\blacksquare), $2.5 \times 10^{-4} \text{ M}$ (\triangle), $5 \times 10^{-4} \text{ M}$ (\blacktriangle), 10^{-3} M (\circ) and 10^{-2} M (\bullet). Binding saturation occurs when $1/R$ reaches a constant value

DISCUSSION

The tightly coiled conformations of P18C6 and PVBG in water cause the two polymers to behave as polysoap-type macromolecules, and their hydrophobic domains are

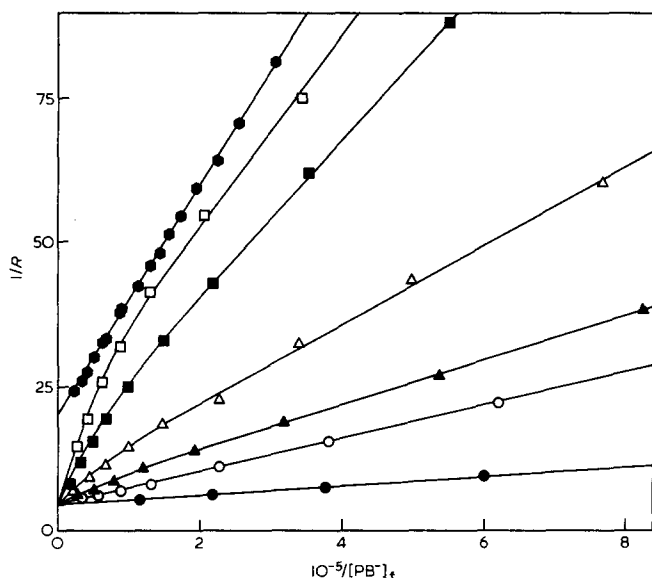


Figure 8 Binding plots of 1-pyrenebutyrate to P18C6 in water at 25°C in the presence of CsCl. [CsCl]=0 (○), 5×10^{-5} M (□), 10^{-4} M (■), 2.5×10^{-4} M (△), 5×10^{-4} M (▲), 10^{-3} M (○), 10^{-2} M (●). Concentrations of polymer and solute, see Figure 7

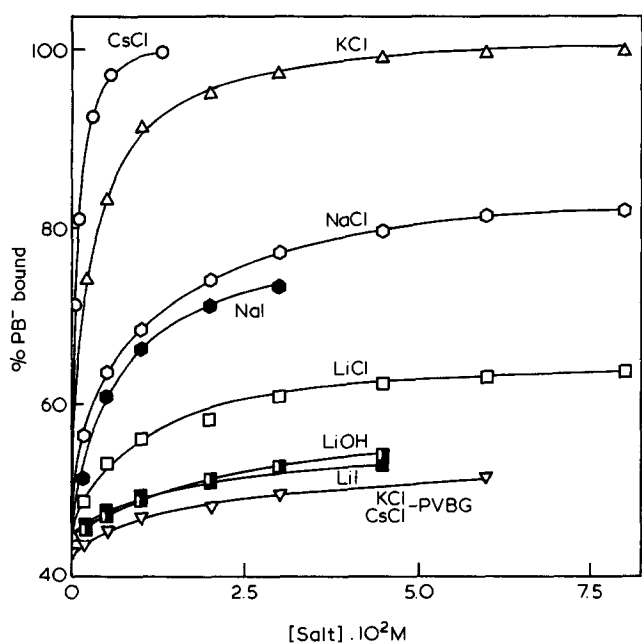


Figure 9 Effect of salts on the binding of 1-pyrenebutyrate (PB^-) to P18C6 and PVBG in water at 25°C. $[\text{PB}^-] = 2 \times 10^{-5}$ M; $[\text{P18C6}] = 2.5 \times 10^{-4}$ M; $[\text{PVBG}] = 3 \times 10^{-4}$ M

able to solubilize a variety of ionic solutes¹⁻⁷. The binding of pyrene to these two polymers is accompanied by a shift in its 334 nm absorption maximum to 341 nm for the polymer-bound species⁸. Other maxima exhibit similar bathochromic shifts. The shifts resemble those shown in Figure 1 for the 326 and 341 nm peaks of PB^- , PC^- and PV^- , and that of the pyrene derivative 1-pyrenebutyltrimethylammonium bromide²⁴. Bathochromic shifts were also observed for PB^- bound to proteins²⁵ and micelles¹⁸. The shifts do not merely result from a change in the polarity of the pyrene environment, since spectra of pyrene in cyclohexane or heptane are identical to those in water or ethanol. Significant spectral changes occur when pyrene is surrounded by polarizable

molecules. Spectral shifts of PB^- on binding to proteins, and the accompanying hypochromicities (between 10 and 50%, depending on the protein used) have been attributed to possible stacking of pyrene with the nucleotide bases²⁵. A similar suggestion was made to rationalize shifts for DNA-bound pyrene²⁶. The shifts in λ_m for PB^- bound to P18C6 or to PVBG are identical to those reported for the protein poly-A, but the 15% hypochromicity for our polymers is less. In our system the pyrene moiety may be intercalated between two benzocrown ligands or embedded in a rather loosely organized cavity⁸.

The Klotz plots for PB^- , PC^- and PV^- all exhibit reasonable linearity, implying that binding to P18C6 or PVBG is essentially governed by statistical factors. Other solutes studied previously with these two polymers also show this Langmuir adsorption behaviour¹, although it is realized that in this type of plot deviations from this behaviour may be obscured due to the compression of data points at low $1/R$ and $1/\text{PB}^-$ values. However, $1/n$ values for neutral P18C6 and for PVBG are 10 or higher (Table I). Hence, even at saturation the average distance between bound anionic solutes appears to be large enough to minimize repulsion effects. Much lower $1/n$ values are found in the presence of CsCl and especially KCl, and deviation from Langmuir behaviour close to the point of saturation may well exist in these systems due to the closer proximity of bound solute molecules.

The binding constants for the pyrene/P18C6 system ($K_1 = 2.9 \times 10^4 \text{ M}^{-1}$, $K = 2.9 \times 10^5 \text{ M}^{-1}$, $1/n = 10$, see Ref 8) considerably exceed those for PB^- , PC^- or PV^- (Table I). The first binding constant actually represents a partition coefficient for the solute between polymer

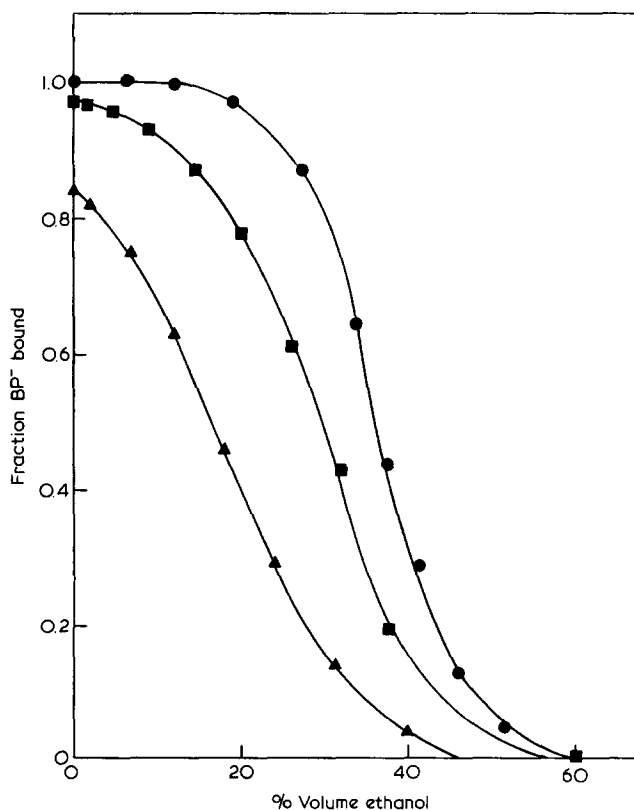


Figure 10 Effect of added ethanol on the fraction of 1-pyrenebutyrate (PB^-) bound to P18C6 in water. (▲) $[\text{P18C6}] = 1.6 \times 10^{-3}$ M, no salt present; (■) $[\text{P18C6}] = 2.67 \times 10^{-4}$ M, 0.1 M CsCl; (●) $[\text{P18C6}] = 8 \times 10^{-4}$ M, 0.1 M CsCl

domain and water. The more water soluble pyrene carboxylates, relative to pyrene at least, favour the water and are expected to yield lower K_1 values. The increase in K_1 in the order $PC^- < PB^- < PV^-$ appears to be reasonable based on the increase in the size of the hydrophobic side chain. The binding constant of PB^- to PVBG is slightly higher than that to neutral P18C6. This was also found for pyrene⁸ and for all other solutes previously studied with the exception of the cationic fluorophore auramine O¹.

Effect of cations

The fraction of P18C6-bound PB^- can be dramatically increased by adding those cations that in water can complex to the benzocrown ether ligands of P18C6. The cationic charge on the P18C6 chain will, of course, depend on the nature and concentration of added cation. The behaviour shown in *Figure 9* is similar to that obtained for anionic solutes such as picrate, TNS or ANS^{1-3,5}. The effectiveness of added cations to enhance PB^- binding to P18C6 decreases in the order $Cs^+ > K^+ > Na^+ \gg Li^+$. This sequence reflects the trend in the binding constants of these cations to P18C6: $K = 300 M^{-1}$ for Cs^+ , $110 M^{-1}$ for K^+ , $2.4 M^{-1}$ for Na^+ and negligibly small for Li^+ . Lithium salts, especially LiCl, slightly increase the binding, but this may at least in part be due to small amounts of impurities in these salts, e.g., Ba^{2+} and Pb^{2+} . The presence of electrolytes in the aqueous phase may also affect the conformations of the two polymers. Even the binding to PVBG is somewhat increased on adding salts, although the interaction of alkali ions with this polymer in water is very weak. It probably remains essentially a neutral macromolecule even in the presence of KCl or CsCl. Note also that the effect of counterion is not significant in the P18C6 system. Sodium chloride and iodide differ little in increasing PB^- binding (*Figure 9*). Generally, the cation effect decreases when the counterion of the added salt is less hydrophilic. Counterion binding to the P18C6 polycation becomes more effective and this reduces the electrostatic interaction with the anionic solute. Large hydrophobic counterions merely replace the bound solute due to competitive binding. For example, adding $10^{-4} M NaBPh_4$ to a mixture of PB^- and P18C6 in which 75% PB^- is bound reduced binding of this solute to 35%.

Linearity of the Klotz plots is maintained in the presence of 0.01 M and 0.1 M KCl and of 0.01 M CsCl (*Figures 3-5*). At these salt concentrations a fraction of crown ligands close to 0.5 is complexed to a K^+ or Cs^+ cation (it probably does not exceed 0.5 since Cs^+ forms a 2:1 crown-cation complex with P18C6 and for the 1:1 complex with K^+ electrostatic repulsion decreases the binding constant to P18C6 when too many K^+ ions become polymer-bound, see Ref 3. *Table 1* shows that at 25°C K_1 increases by a factor 19 on adding 0.01 M CsCl and by a factor 14 with 0.1 M KCl. The increase for PC^- with 0.1 M CsCl is a factor 15.

The increase in the intrinsic binding constants, K , on adding salts are considerably smaller than those in K_1 due to the decrease in $1/n$. In fact, the most important conclusion from this study is the observation that the maximum binding capacity of P18C6 for PB^- or PC^- is dramatically increased on adding KCl or CsCl. For example, with our poly(crown ether) of $DP_n = 325$, a maximum number of 13 PB^- molecules ($1/n = 25$) can be

bound to neutral P18C6 at 25°C. This increases to 52 ($1/n = 6.2$) when 0.01 M CsCl is added and to 120 ($1/n = 2.7$) in the presence of 0.1 M KCl. For PC^- and PV^- the $1/n$ values with neutral P18C6 are lower than for PB^- (10 and 14, respectively), but also for PC^- $1/n$ decreases from 10 to 4 on adding 0.1 M CsCl.

The behaviour of PB^- contrasts that of picrate anions. For the latter solute, $1/n$ decreases only moderately, from 42 for neutral P18C6 to about 30 in the presence of up to 1 M CsCl or 0.1 M KCl². The increased binding of picrate anion as a function of the charge density of P18C6 was described in terms of an electrostatic interaction which is superimposed onto the largely hydrophobic interaction between this anion and neutral P18C6^{2,3}. For PB^- , such an electrostatic contribution certainly exists in solutions of P18C6 with 0.1 M KCl or with 0.01 M CsCl where P18C6 is a highly charged polycation. However, the low $1/n$ values may suggest a different sequence of events with this anion especially when considering the results at low concentrations of CsCl (*Figures 7 and 8*). Below $10^{-3} M$ CsCl the Klotz plots for the PB^- -P18C6 system appear to be linear in the region where comparatively few PB^- molecules are bound. However, at high PB^- concentration the plots are curved and appear to intercept the $1/R$ axis close to the $1/n = 6$ value obtained above $10^{-3} M$ CsCl concentration. This is the case even for $5 \times 10^{-5} M$ or $1 \times 10^{-4} M$ CsCl where under our conditions ($[P18C6] \cong 10^{-4} M$) only a very small fraction of the crown ligands of P18C6 contain a Cs^+ ion. This also means that at these CsCl concentrations electrostatic interaction between P18C6 and anionic solute is very small and could not explain the accelerated increase in bound PB^- at high PB^- concentrations.

Binding of PB^- ion pairs

To account for the different behaviour of PB^- and picrate anions it should be pointed out that the delocalized picrate anion is probably located more in the hydrophobic interior of the coiled P18C6 macromolecule. The optical spectrum of P18C6-bound picrate is identical to that of a free picrate anion in aprotic solvents like acetone or tetrahydrofuran². While P18C6-bound Cs^+ or K^+ ions enhance the binding of picrate to P18C6, the spectrum is not changed and there is no evidence of ion pairing between bound anions and cations in the polymer coil. However, the strong hydrogen bond between COO^- and water may cause the COO^- substituent of P18C6-bound PB^- to protrude into the aqueous layer at the polymer-water interphase. Most of the crown ligands also lie at this interphase, since P18C6 is kept in solution by hydrogen bonding between water molecules and the crown ether oxygen atoms as indicated by the inverse temperature solubility of this polymer². The presence of a COO^- group close to a crown ring may well enhance the binding of K^+ or Cs^+ cations to the ligand by forming an ion pair $COO^-, M^+ \cdots crown$. The overall binding process of PB^- to P18C6 should then be described by the reaction $PB^- + M^+ + P18C6 \rightleftharpoons P18C6 \cdots M^+, PB^-$ rather than by a process that only involves the free PB^- anion. Under the conditions of our experiments, there were always sufficient cations available to pair with bound PB^- ions even for $[CsCl] = 5 \times 10^{-5} M$.

At the point of saturation a P18C6 chain in 0.1 M KCl contains, on the average, one bound PB^- molecule per 2.7 crown monomer base units. To accommodate so many

solute molecules it is likely that nearly all PB^- molecules are bound close to the polymer-water interphase, possibly with the planar pyrene sandwiched inbetween the benzocrown ligands. The close proximity of the bound PB^- molecules in this system also causes the PB^- fluorescence spectrum to exhibit a distinct excimer emission maximum at 480 nm in addition to the monomer emission spectrum arising from the presence of excess free PB^- in the water phase. No excimer emission is found in the PB^- -P18C6 system with 0.01 M CsCl. With CsCl 1/n does not decrease below the value six, hence, the average distance between bound PB^- molecules is larger than in 0.1 M KCl solutions. This is consistent with earlier observations that no excimer emission peaks are found when pyrene itself is solubilized in P18C6 although the polymer coil may contain as many as twenty pyrene molecules⁸. Unlike with micelles, diffusion of bound solute molecules in a P18C6 coil is highly restricted and this prevents formation of excimers⁸.

Ground state interaction between bound PC^- molecules in P18C6-0.1 M CsCl (1/n=4) is suggested by the observation that the 348 nm absorption peak for PC^- bound to neutral P18C6 is replaced by a peak at 352 nm. This maximum is the same as that found for 2:3 complexes between 1-pyrenebutyltrimethylammonium (PN^+) and BPh_4^- ²⁴. In these complexes, formed in aqueous media at very low concentrations of the components, the λ_m of the 341 nm PN^+ peak has shifted to 352 nm while the fluorescence emission spectrum only depicts the excimer maximum.

The binding of neutral pyrene to P18C6 was reported to be enhanced by nearly a factor three on adding CsCl, while KCl had little effect⁸. It was argued that Cs^+ ions, by forming 2:1 crown-cation complexes with the benzocrown ligands, may produce intramolecular crosslinks in a P18C6 coil. This in turn may cause the coil to contract and provide an even more hydrophobic environment for the pyrene moiety⁸. It is possible that some of the increase in the binding of PB^- or PC^- to Cs^+ -charged P18C6 originates from this special effect.

The binding enthalpy and entropy for PB^- with neutral P18C6 ($\Delta H = -6$ kcal mol⁻¹, $\Delta S = +3.2$ eu, see Table I) are close to those for pyrene ($\Delta H = -6$ kcal mol⁻¹, $\Delta S = 1$ eu, see Ref. 8). This also suggests that the COO^- end of P18C6-bound PB^- remains surrounded by water molecules. The ΔH and ΔS values are more negative in PB^- -P18C6 solutions containing CsCl or KCl (Table I). If the binding of PB^- to P18C6 involves simultaneous complex formation between cation and crown ligand, then the latter reaction must also be taken into consideration. While the thermodynamic parameters for the binding of cations to P18C6 in water are not available, it is known that the binding of K^+ or Cs^+ ions to crown ethers or cryptands in water or ethanol generally is exothermic with negative entropies^{27,28}. However, other factors may affect ΔH and ΔS for PB^- binding to P18C6 in the presence of salts (conformational changes in the coil, coulombic interactions if ion pairs are formed, etc.), and not sufficient information is available to satisfactorily explain the observed trend.

Finally, Figure 10 shows that considerable quantities of ethanol can be added to an aqueous mixture of PB^- -P18C6 before binding is prevented, especially when the polymer coil is charged. The polysoap-type character of P18C6 decreases in water-ethanol mixtures due to coil

expansion. At the same time the solubility of PB^- in the aqueous phase will increase with ethanol content. It is not certain whether the change in the spectrum of PB^- into that of free PB^- on adding ethanol accurately measures the amount of PB^- released from the polymer domain. Earlier dialysis measurements on solutions of P18C6-picrate in water-ethanol mixtures appear to imply that the solute can remain bound while the optical spectrum already changes². Fluorescence studies in similar systems but with TNS as solute appear to confirm this⁵. The optical shifts could result from water penetration into the expanding coil when ethanol is added while the solute remains bound, at least as long as the ethanol content is not too high. A more detailed study is needed to resolve this problem for PB^- , and to determine at what alcohol content the PB^- is actually released.

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