Binding of Organic Solutes to Poly(crown ethers) in Water

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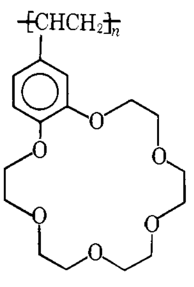
Abstract: Poly(vinylbenzo-18-crown-6), a polymer endowed with benzo-18-crown-6 ligands as pendant groups, behaves as a neutral polysoap when dissolved in water. It interacts hydrophobically with organic solutes such as picrate anions and methyl orange. Binding constants to the polymer were measured spectrophotometrically between 35 and 0 °C, and found to be considerably higher than reported for poly(vinylpyrrolidone) or bovine serum albumin. The thermodynamic binding parameters for the picrate anion are $\Delta H = -11.9$ kcal/mol, $\Delta S = -17$ eu, and for methyl orange $\Delta H = -3.9$ kcal/mol, $\Delta S = 9.7$ eu. The binding of anionic solutes can be enhanced electrostatically by charging the polymer with crown complexable cations, K^+ and Cs^+ being especially effective due to their high binding constants to the crown ether ligand. The maximum number of picrate anions bound to a polymer of DP $\simeq 200$ is about five to seven, depending on the temperature and the charge density on the polymer. Anions such as tetraphenylboron and dodecyl sulfate effectively compete with picrate for binding sites.

The ability of certain nonionic macromolecules to bind organic solutes of diverse chemical composition in aqueous solution has been well documented. Poly(vinylpyrrolidone) is especially effective and interacts with dodecyl sulfate, azo dyes, and a host of aromatic species,[1-7] although its affinity for substrates is still substantially less than that of bovine serum albumin, one of the natural polymers known for its strong affinity for a wide variety of molecules.[8-11] In many of these systems the interacting forces are hydrophobic in nature, but important contributions to the binding may arise from hydrogen bonding, charge transfer interactions, or electrostatic forces. The apolar interactions can often be enhanced by forcing the macromolecule into a more tightly coiled conformation, thereby reducing the swelling by water. This can be achieved by crosslinking the polymer,[12,13] a process that has also been carried out in the presence of solutes.[14] Another approach is the attachment of apolar side chains to the macromolecule. Such modified synthetic polymers often give very high binding constants with organic solutes.[15-17] Binding of ionic organic solutes can be increased by introducing charged groups into the polymer, e.g., through quaternization of nitrogen containing polymers.[14,17] Some of these polymers with apolar or charged moieties effectively catalyze reactions which are sensitive to the polarity of their environment.[18-21]

While exploring the cation binding properties of poly(vinylbenzo-18-crown-6),[22-24] it was observed that this neutral macromolecule when dissolved in water has a strong affinity for organic solutes.[25,26] The polymer, denoted by P18C6,



carries a crown ether ligand as pendant group, and becomes a polycation in solutions containing crown complexable cations.[22-24] The binding constants of cations to P18C6 in water are not high, at most in the order of 100 M^{-1}. On the other hand, the binding of organic solutes to P18C6 exceeds that of other homopolymers such as poly(vinylpyrrolidone) and even that of bovine serum albumin. Preliminary results[25] indicated that hydrophobic interactions played an important role in the binding of picrate anions and methyl orange, but that the affinity for these species could be enhanced by adding crown complexable cations such as K^+. In this paper the binding of these two solutes to P18C6 is now presented in more detail. Binding constants can be measured spectrophotometrically, since in both cases a significant change occurs in the optical absorption maximum of the respective solutes. Cation effects were also studied, especially with regard to the size of the binding site. The data are of importance in rationalizing catalytic effects which P18C6 was found to exert on reactions such as the decarboxylation of 6-nitrobenzisoxazole 3-carboxylate in water.[25-27]

Experimental Section

Materials. Picrate salts were prepared by neutralizing picric acid with the appropriate base. The salts were purified by recrystallization from ethanol.[28] Methyl orange (sodium salt), sodium dodecyl sulfate, sodium tetraphenylboron, and the alkali halides used in the experiments were all reagent grade materials. The synthesis of vinylbenzo-18-crown-6[22,28] and its radical polymerization in benzene with azobisisobutyronitrile[22] have previously been reported. The number average molecular weight of the polymer used in most experiments was 65 000. The polymer can be recovered from aqueous solute solutions by extraction with chloroform and washing the organic layer with water.

Spectral Measurements. Binding of picrate salts and methyl orange was measured spectrophotometrically in a Cary 15 in the temperature range 0 to 35 °C. The picrate anion in water has its main absorption maximum at 355 nm, ϵ_m (25 °C) being 14 500. When completely transferred to the polymer domain (this can be accomplished by adding about a 150-fold excess of P18C6 to a 5×10^{-4} M picrate solution) the absorption maximum has shifted to 384 nm, ϵ_m (25 °C) 18 100. At intermediate ratios of P18C6 to picrate the fractions of free and bound solute can be computed from the recorded optical spectra and from the known spectra of the free and bound species. Methyl orange binding was measured in a similar way, the respective absorption maxima in water and the polymer domain being 465 nm, ϵ_m (25 °C) 24 700, and 435 nm, ϵ_m (25 °C) 21 540. The temperature dependence of the spectra of the free and bound species was taken into account in the calculations. To improve accuracy the fraction of bound solute as a function of P18C6 or solute concentration was varied as much as possible between 0.2 and 0.8 by a judicious choice of reagent concentrations.

Results and Discussion

The Polymer Solution. In spite of its polystyrene backbone, the water solubility of poly(vinylbenzo-18-crown-6) is quite high, 8.1 g/100 cm³ at 25 °C.[22] However, its intrinsic viscosity is only 0.107 at 25 °C for $M_n = 106\ 000$, the respective values in $CHCl_3$ and THF being 0.37 and 0.24.[22] The P18C6 solution

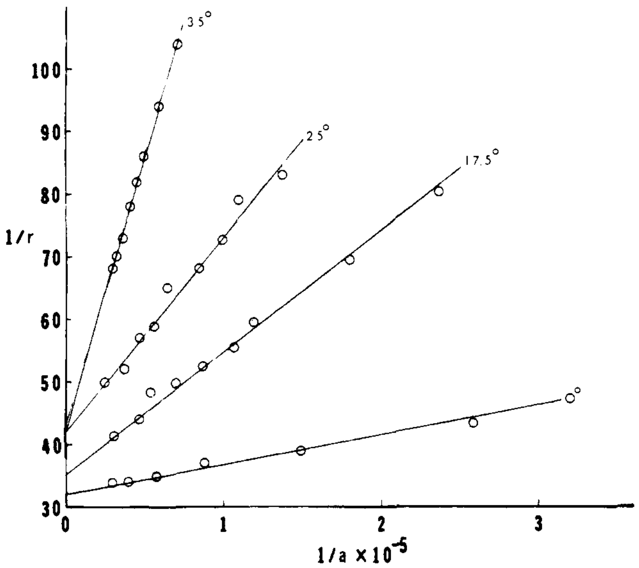


Figure 1. Plots of $1/r$ vs. $1/a$ for binding of sodium picrate to poly(vinylbenzo-18-crown-6) in water at 35, 25, 17.5, and 0 °C.

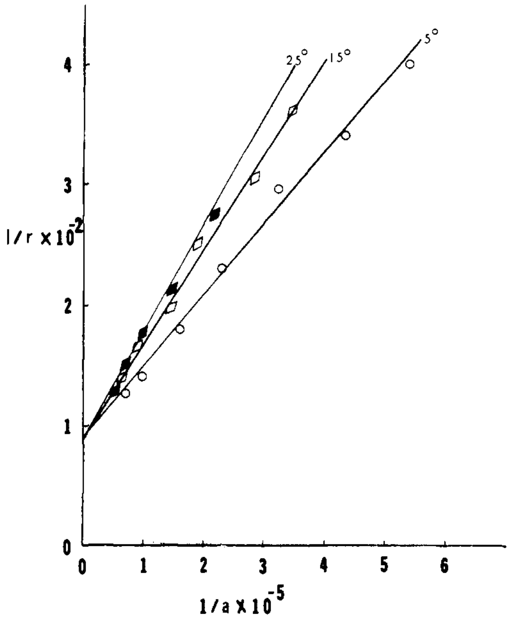


Figure 2. Plots of $1/r$ vs. $1/a$ for binding of methyl orange to poly(vinylbenzo-18-crown-6) in water at 25 (◆), 15 (◇), and 5 °C (○).

also exhibits inverse temperature solubility, a phenomenon observed for several water-soluble polymers, e.g., polyethylene glycol and many of its derivatives (for a recent discussion, see ref 29). Since the cloud point of the polymer is 37 °C, no binding studies could be carried out above this temperature.

The properties of P18C6 in water suggest that in this solvent the macromolecule is tightly coiled and may be regarded as a neutral polysoap, its apolar polystyrene backbone surrounded by hydrophilic 18-crown-6 moieties hydrogen bonded to neighboring water molecules. Crown complexable cations such as K^+ or Cs^+ can convert the neutral polymer into a polycation,[22] thereby enhancing its solubility. This permits the use of poly(crown ethers), which in the absence of such cations are poorly soluble in water, e.g., the benzo-18-crown-6 ester of polymethacrylic acid.[30] Although some expansion of the coiled P18C6 macromolecule in water is expected at high charge densities, the swelling apparently is small. It was found that the viscosity of a 1.5 g/100 cm^3 aqueous P18C6 solution increases by only 10% on addition of an equimolar quantity of KCl. It was calculated that under these conditions nearly half of the crown units contain a K^+ cation. For the same mixture in THF/MeOH the viscosity increased by at least a factor of 3.[22] In water, the charged P18C6 macromolecule, therefore, resembles a cationic micelle.

Picrate and Methyl Orange Binding to P18C6. The binding of picrate anion to P18C6 in water is accompanied by a shift of its absorption maximum from 355 to 384 nm. The latter spectrum resembles that reported for a picrate ion pair with its two opposing ions separated by a bis(crown ether) ligand,[31,32] or that of a free picrate anion in solvents such as acetone.[33] The absorption maximum of picrate solubilized in benzene by monobenzo-18-crown-6 or by P18C6 is at 356 nm, close to that found for crown ether complexed tight ion pairs in THF or $CHCl_3$.[23,31] The picrate, therefore, appears to be present in the apolar polymer core as a dehydrated free anion, although it is conceivable that as a result of the transfer a counterion becomes bound to the crown cavity on the surface of the polymer and may provide some of the needed binding energy.

The interaction of methyl orange with P18C6 results in a shift from 465 to 435 nm, similar to that observed with bovine serum albumin.[2,34] The hypsochromic shift has been attributed to polarity changes in the immediate vicinity of the bound species. The λ_m of methyl orange in benzene (with some ethanol present) is 420 nm,[2] but when the dye is dissolved directly in benzene by mixing with benzo-18-crown-6 the crown-complexed tight ion pair shows a λ_m 410 nm. The observed 435-nm band in our system may be that of the free anion, but this could not be established. Some of the more complex spectral changes observed for methyl orange binding to certain polymers[35] and apparently resulting from dye aggregation were not found in our system.

The interaction of picrate salts and methyl orange with P18C6 can be described by a rearranged form of the Langmuir isotherm, as suggested by Klotz,[8] i.e.,

$$1/r = 1/n + 1/nKa \qquad (1)$$

where in our system $1/r$ denotes the ratio of total crown monomer base units to bound solute and a is the free solute concentration. The constant n refers to the number of binding sites per mole of crown ether units; hence, $1/n$ represents the minimum number of crown units required to bind a solute molecule. Although no specific binding sites can be identified in our system, $1/n$ may be conveniently referred to as the size of the binding site. The constant K is the intrinsic binding constant, while the product nK is equal to the first binding constant, K_1.

Plots of $1/r$ vs. $1/a$ for sodium picrate and methyl orange are depicted in Figures 1 and 2. All plots show a reasonable linearity, but deviations at low crown to picrate ratios occur when potassium and, especially, cesium picrate are used. The intrinsic binding constants of K^+ and Cs^+ to the crown polymer are much higher than for Na^+, and some cations already are bound to the polymer at 5×10^{-4} M cation concentrations. This enhances the anion binding by electrostatic attraction. The charge density varies with the crown to picrate ratio, and increases at lower $1/a$ values. Hence, to study the hydrophobic contribution to the solute binding it is imperative to use the sodium, or even better the lithium salt. The binding of Li^+ to P18C6 is very weak, e.g., addition of 0.1 M LiCl does not affect the fraction of picrate anion bound to P18C6.

The binding constants and $1/n$ values, obtained by a least-squares analysis, are listed in Table I. The intrinsic binding constants, K (calculated from $K = K_1/n$), and the first binding constants, K_1, are given, the polymer concentration being expressed in moles per liter of monomer units. The relative errors in K and K_1 are 15% and 10%, respectively, and the error in $1/n$ is estimated to be 5%. $K_1{}^*$ refers to the first binding con-

Table I. Binding Constants of Sodium Picrate and Methyl Orange to Poly(vinylbenzo-18-crown-6) in Water[a]

Temp, °C	$K \times 10^{-3}$, M^{-1}	$K_1 \times 10^{-3}$, M^{-1}	$K_1^* \times 10^{-3}$, 10^5 g	$1/n$
		Sodium Picrate		
	$\Delta H = -11.9 \pm 1$ kcal/mol; $\Delta S = -17 \pm 4$ eu			
35	51	1.17	347	44
25	134	3.19	945	42
17.5	170	4.85	1430	35
0	673	20.9	6190	32
		Methyl Orange		
	$\Delta H = -3.9 \pm 0.2$ kcal/mol; $\Delta S = 9.7 \pm 1.5$ eu			
25	96	1.13	334	85
15	118	1.28	379	92
5	152	1.71	504	89

[a] The constants K, K_1, and K_1^* refer to the intrinsic binding constants in M^{-1}, the first binding constant in M^{-1} and the first binding constants expressed in 10^5 g of polymer, respectively. The ΔH and ΔS values, calculated from log K vs. $1/T$ plots, refer to the reaction: solute anion + P18C6 $\rightleftarrows$ P18C6 bound anion.

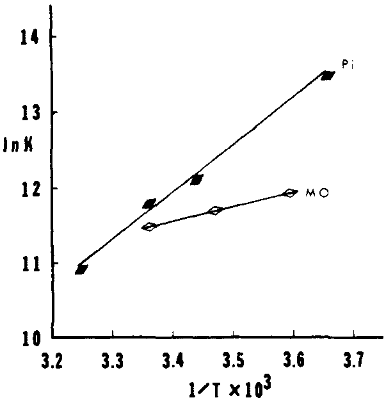


Figure 3. Temperature dependence of the binding constants of sodium picrate (◆) and methyl orange (◇) to P18C6 in water.

stant expressed in 10^5 g of polymer, a unit frequently used in the literature to compare binding capacities of various polymers. The enthalpy and entropy of binding were computed from the log K vs. $1/T$ plots depicted in Figure 3: for picrate binding, $\Delta H = -11.9 \pm 1$ kcal/mol, $\Delta S = -17 \pm 4$ eu, and for methyl orange binding, $\Delta H = -3.9 \pm 0.2$ kcal/mol, $\Delta S = 9.7 \pm 1.5$ eu.

The affinity of P18C6 for organic solutes compares favorably with that of poly(vinylpyrrolidone) or bovine serum albumin. For the latter two macromolecules the respective K_1^* values at 25 °C for methyl orange are 2.7×10^4 and 6.1×10^4 (expressed in 10^5 g of polymer and determined by equilibrium dialysis).[2] The corresponding value for P18C6 is 3.3×10^5. This is also higher than found for some of the modified polymers, e.g., $K_1^* = 1.45 \times 10^5$ for cross-linked polylysine[13] or for some of the polycations endowed with apolar side chains.[17] Only incorporation of long apolar side chains in the macromolecule produces affinities higher than found for P18C6, e.g., when lauryl groups are attached to polyethylenimine[16] or to polycations.[17] However, the effectiveness of P18C6 can be dramatically increased by adding cations, as shown later.

Binding constants of picrate salts to serum bovine albumin[36-39] are more difficult to interpret, since some authors report two binding constants associated with two different binding sites.[37] A table of solute binding constants given in ref 36 lists for picrate $K_1^* = 2.3 \times 10^5$ at 25 °C and $K_1^* = 2.8 \times 10^5$ at 1 °C (computed for 10^5 g of polymer). Our values for P18C6 are 9.4×10^5 (25 °C) and 61.9×10^5 (0 °C), respectively. Teresi and Luck[39] report $K_1^* = 1.9 \times 10^6$ at 5 °C, our value being 3.8×10^6 (calculated from $\Delta H = -11.9$ kcal/mol). A maximum of six picrate anions are bound to a protein molecule of mol wt = 70 000,[39] the same as found for P18C6 at 0 °C. No significance should be attached to this, since the structures of the two polymers are entirely different. Actually, Andersson et al.[37] report two binding constants at 5 °C, i.e., $K_1^* \simeq 4 \times 10^6$ and $\simeq 3 \times 10^5$ (both are first binding constants in 10^5 g of polymer), with only two picrate anions bound per protein molecule for each type of binding site. Equilibrium dialysis was used in all these measurements.

No binding constant for picrate anion to poly(vinylpyrrolidone) has been reported. However, we could determine by dialysis[25] that, given a set of identical conditions, P18C6 binds 75% picrate while poly(vinylpyrrolidone) yielded only 5% binding. The latter polymer does not shift the spectrum of picrate.

The enthalpy of -3.9 kcal/mol and entropy of 9.7 eu for binding of methyl orange to P18C6 are comparable to the values reported for bovine serum albumin ($\Delta H = -3.5$ kcal/mol and $\Delta S = 10$ eu) and poly(vinylpyrrolidone) ($\Delta H = -2.3$ kcal/mol and $\Delta S = 12$ eu). The entropy increase indicates that the interaction is hydrophobic in nature. Corrected for the "cratic" term of 7.98 eu (which accounts for the reduction of solute species in the binding process, see ref 1), the entropy gain is 18 eu. On the other hand, the rather large exothermic binding enthalpy for picrate anions suggests that the interaction between this solute and P18C6 involves van der Waals forces. The three electron-withdrawing nitro groups in the solute and the two electron-donating aromatic oxygen atoms in the crown ligand are contributing factors in augmenting the interaction. The binding enthalpy of 6-nitrobenzisoxazole 3-carboxylate to P18C6, obtained from kinetic data, is equal to -11.8 kcal/mol, ΔS being -28 eu.[25,27] Hydrophobic interactions resulting in considerable negative ΔH and ΔS values have sometimes been referred to as "nonclassical".[35] The binding enthalpies of several aromatic carboxylates to poly(vinylpyrrolidone) are in the order of -3 to -5 kcal/mol,[1] and the association of p-nitrophenolate to α-cyclodextrin has a $\Delta H = -7.2$ kcal/mol.[40] Stronger exothermic binding processes have been reported for dyes and other hydrophobic substances.[35]

Positive entropies associated with hydrophobic interactions have been attributed to structure breaking effects resulting from transfer of the hydrophobic solute to the less polar polymer domain. More polar solutes such as picrate anions and the nitrocarboxylate should give a smaller entropy gain. Moreover, binding to hydrophobic regions of a polymer also contributes to a positive entropy change if such binding occurs at the polymer/water interphase. In our system the observed spectral change for the picrate anion implies that the solute is most likely buried inside the polymer core. Also, the rate constant of decarboxylation of 6-nitrobenzisoxazole 3-carboxylate bound to P18C6 domain is close to that found in benzene,[27] suggesting that also this solute is not located at the polymer/water interphase. Therefore, binding of these solutes probably does not affect this interphase, and no positive entropy contribution from this source occurs. Even if anion solubilization is accompanied by the binding of a counterion to an adjacent crown moiety as suggested earlier, it probably would lower the entropy of the overall process. Alkali ion binding to cryptates[41] and crown ethers[42] in water is frequently accompanied by a loss in entropy of as much as -27 eu, depending on the nature of ligand and cation. Hence, the thermodynamic parameters found for picrate binding to P18C6 appear reasonable.

The sizes of the binding sites, $1/n$ (Table I), were obtained as the intercepts of the plots of Figure 1. The same values can be obtained directly by measuring the fraction of picrate bound under saturation conditions, i.e., by increasing picrate at constant [P18C6]. The value $1/n = 42$ at 25 °C means that

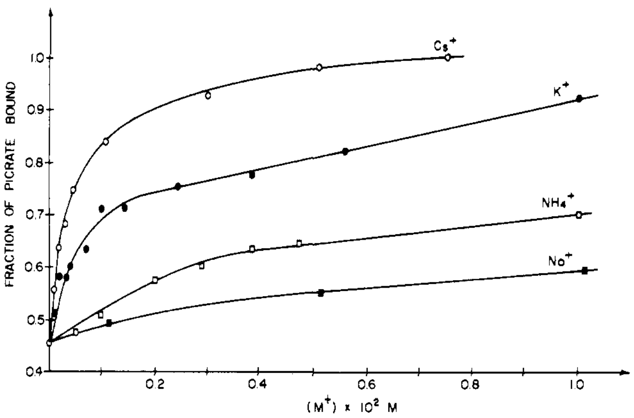


Figure 4. Effect of cation on the fraction of picrate bound to P18C6: [P18C6] = 5×10^{-4} M: [picrate] = 1×10^{-5} M.

for M_n = 65 000 a maximum of five picrate anions can be bound to a P18C6 molecule. For methyl orange $1/n$ = 85, which gives on the average 2.5 molecules of this dye per polymer chain. Bovine serum albumin (mol wt 70 000) binds 22 methyl orange molecules per chain.[8] For poly(vinylpyrrolidone) $1/n$ is about 10, irrespective of the solute,[1] although the extrapolation of the binding plots was not always accurate.

It is not clear what determines the value of $1/n$ in the P18C6 system, but solute size may be a factor. If the compact polymer core is to accommodate a number of solute molecules it must expand to some degree. This requires less energy for a small molecule. It is interesting to note that for picrate anions $1/n$ decreases from 44 at 35 °C to 32 at 0 °C; i.e., the polymer chain binds on the average 4.5 picrate anions at 35 °C and 6.5 at 0 °C. The increase may result from a slight chain expansion at lower temperatures, as expected for polymers which exhibit inverse temperature solubility. Indeed, measurements show that the intrinsic viscosity of P18C6 in water (M_n = 133 000) increases from 0.11 at 25 °C to 0.13 at 0 °C. The size of the binding site also decreases on charging the P18C6 chain (see below), and chain expansion, although small (see earlier discussion), may again be responsible. Changes of $1/n$ with temperature for methyl orange are probably within the experimental error.

Effect of Added Salts. The addition of crown complexable cations is expected to promote the binding of anionic solutes, and results of such studies are shown in Figure 4. Conditions were chosen such that about 45% picrate anions were bound in the absence of salt ([picrate sodium] = 1×10^{-5} M, [P18C6] = 5×10^{-4} M; the ratio P18C6/solute should always exceed the value $1/n$ in order to avoid saturation of the binding sites). It is obvious that the increase in solute binding depends on the nature of the cation, with the cation binding constant to P18C6 expected to be the determining factor.

Potentiometric measurements[43] in water yield binding constants of Na^+ and K^+ to P18C6 of 1.2 and 35 M^{-1}, respectively (the latter value actually decreases from 55 to 20 M^{-1} as the number of K^+ ions attached to P18C6 increases). This explains the different effects of Na^+ and K^+ on the picrate binding. The Li^+ cation in water apparently does not bind to P18C6, since addition of 0.1 M LiCl to the P18C6-picrate solution did not alter the fraction of picrate bound. On the other hand, cesium cations are very effective. The intrinsic binding constant for picrate anions changes from 1.34×10^5 M^{-1} in the absence of salt (see Table I) to 3.1×10^6 M^{-1} on the addition of 2×10^{-3} M CsCl (see Figure 3; the fraction bound at this concentration is 0.9, hence $K = K_1/n = 42 \times 9/[(5 \times 10^{-4}) - (42 \times 0.9 \times 10^{-5})]$), assuming $1/n$ is not affected by the charge density on the polymer.

The binding constant of Cs^+ to P18C6 could not be measured potentiometrically because of poor electrode sensitivity, but it can be calculated with reasonable accuracy from the cation effect on the picrate binding. Let us assume that on addition of a cation, M^+, the increase in picrate binding is determined only by the charge density on the polymer, irrespective of the nature of M^+. At any total concentration of M^+ the fraction of picrate bound can be determined and from a calibration curve with KCl it can be established at which concentration of KCl a similar increase in picrate binding is obtained with K^+. Since the binding constant of K^+ to P18C6 is known, one can then calculate the fraction of M^+ bound to P18C6, and, hence, the binding constant. This procedure yielded for Na^+ a binding constant of 1.4 M^{-1}, in reasonable agreement with the potentiometric value 1.2 M^{-1}. The binding constant for Cs^+ was found to be 110 M^{-1}. The method is useful with cations for which a potentiometric measurement is difficult. Binding studies of cations such as Ag^+, Hg^{2+}, and Pb^{2+} by this procedure are presently being pursued.

The high binding constant of Cs^+ to P18C6 results from its tendency to form 2:1 crown/cation complexes with the 18-crown-6 moiety, especially when these ligands are in close proximity such as in P18C6. This was confirmed from extraction[22,23] and conductance studies[21] in nonaqueous solvents. The respective binding constants for Na^+, K^+, and Cs^+ to P18C6, i.e., 1.2, 35, and 110 M^{-1}, are quite different from those for the monomeric crown analogue 4′-methylbenzo-18-crown-6. The latter values are 27 (Na^+), 110 (K^+), and 20 M^{-1} (Cs^+).[43] The higher value for Cs^+/P18C6 may be attributed to the fact that in water 4′-methylbenzo-18-crown-6 itself does not form a 2:1 complex with Cs^+. The lower binding constant for K^+ to P18C6, and especially for Na^+, may be attributed to differences in the desolvation requirements of cation binding. For the monomeric crown some water molecules remain attached to the cation in the crown complex, but this may be difficult in the crowded polymer chain.

The high affinity of picrate anions to a charged P18C6 chain is a result of favorable interactions between the bound anion and the crown complexed cations located near the polymer/water interphase. Such interactions are also apparent from the increased reactivity of P18C6 bound 6-nitrobenzisoxazole 3-carboxylate.[27] The decarboxylation rate constant of the bound solute is more than quadrupled on addition of Cs^+ ions, presumably because the complexed cations stabilize the transition state of the reacting solute. However, it should be stressed that for picrate anions the optical spectrum on addition of cations remains identical with that of a free anion or crown separated ion pair, hence the anion does not associate intimately with the cation. Experiments are in progress to quantitatively correlate binding constant and charge density. The latter may be expressed in terms of the fraction of cation containing crown ligands, which can be measured potentiometrically.

Charge density also affects the size of the binding site, $1/n$. At a P18C6/picrate ratio of 20 the ratio $1/r$, on addition of KCl or CsCl, drops below the value $1/n$ = 42 found in the absence of salt to a constant value of 30 at 0.02 M KCl or 0.01 M CsCl (see Figure 5). Hence, the maximum number of picrate anions bound per chain of 200 monomer units at 25 °C changes from 5 to an average of 6.5. This increase may be attributed to a slight expansion of the polymer coil as demonstrated by a 10% increase in the intrinsic viscosity of the polymer solution on addition of KCl.

The ratio $1/r$ remains constant at 30 between 0.02 and 0.1 M KCl, but increases to 35 at 0.5 M KCl and to 39 at 1 M KCl (Figure 5). CsCl only gives a small increase to 32 at 1 M CsCl. The increase in $1/r$ at high KCl concentration also occurs for sodium 2-cyano-5-nitrophenolate, the decarboxylation product of 6-nitrobenzisoxazole 3-carboxylate.[27] The cause of the in-

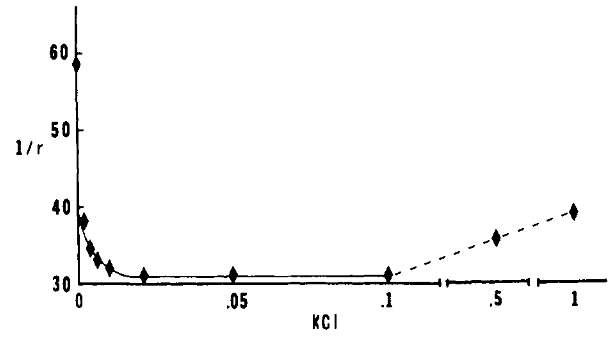


Figure 5. Effect of KCl on the ratio total crown to picrate bound (1/*r*): [P18C6] = 8.5 × 10^{-4} M; [picrate] = 4.2 × 10^{-5} M.

crease in 1/*r* may be due to either a decrease in the maximum number of anions that can be bound to a polymer chain, or to a lower binding constant. To distinguish between these two possibilities, KCl was added to a solution containing P18C6 and picrate in a 50:1 ratio. At about 0.02 M KCl all picrate anions were bound, but above 0.1 M KCl the picrate spectrum revealed a hypsochromic shift, suggesting release of solute molecules. This observation implies that the intrinsic binding constant, *K*, is decreasing. No spectral shift should have occurred if the size of the binding site had increased, since the ratio P18C6/picrate = 50 would have been sufficient to accommodate a change of 1/*n* from 30 to 39. The high Cl^- content is not a factor, as 1/*r* remains constant at 30 on addition of 1 M LiCl.

A decrease in the intrinsic binding constant at high KCl content may be the result of a peculiar behavior of the K^+/P18C6 system observed in several of our studies.[22-24] Although K^+ forms a 1:1 complex with a benzo-18-crown-6 ligand, the binding constant of K^+ to P18C6 drops drastically when more than 40-50% crown units contain a potassium ion, due to steric hindrance and/or electrostatic repulsion.[23] Apparently, only at high KCl concentrations can more K^+ cations be forced onto the P18C6 chain. In tetrahydrofuran, the ratio of bound K^+ to total crown approaches unity,[44] but in this solvent the binding constant of K^+ to P18C6 is higher than in water by at least four powers of 10. If in water more K^+ cations become bound to P18C6 at very high KCl concentration, a considerable chain expansion may result from electrostatic repulsion or for steric reasons, and the system may lose its micellar properties. Viscosity measurements may show whether this suggestion is correct. High cesium chloride concentrations do not yield this increase in 1/*r* since the ratio of bound cation to total crown ligands never exceeds 0.5, the large Cs^+ cation being sandwiched in between two crown ligands.

Other organic anions such as BPh_4^- and $C_{12}H_{25}SO_3^-$ compete with picrate anions for binding sites. Figure 6 shows that even small quantities of such anions can drastically decrease the amount of picrate bound to P18C6. The intrinsic binding constants of BPh_4^- and dodecyl sulfate may be calculated by assuming two independent competitive binding equilibria in the mixture solute/picrate/P18C6. However, no constant values were obtained, indicating that the system is more complex. As mentioned earlier, Cl^- has no effect on the binding even at 1 M concentration, but addition of 1 M $LiClO_4$ at 25 °C causes the polymer to precipitate. This may be associated with the structure breaking effect of ClO_4^- as recently reported for the binding of methyl orange to poly(vinylpyrrolidone).[45]

Addition of organic solvents lowers the binding constant of picrate to P18C6. Mixing ethanol with an aqueous mixture of picrate and P18C6 reduces the fraction of bound picrate from 0.75 in water to 0.58 in 11% v/v ethanol to 0.27 in 25% ethanol and binding disappears above 40% ethanol. The decrease in bound picrate is proportional to the increase in alcohol content. The alcohol most likely solvates the polymer molecule and eventually destroys its micellar character.

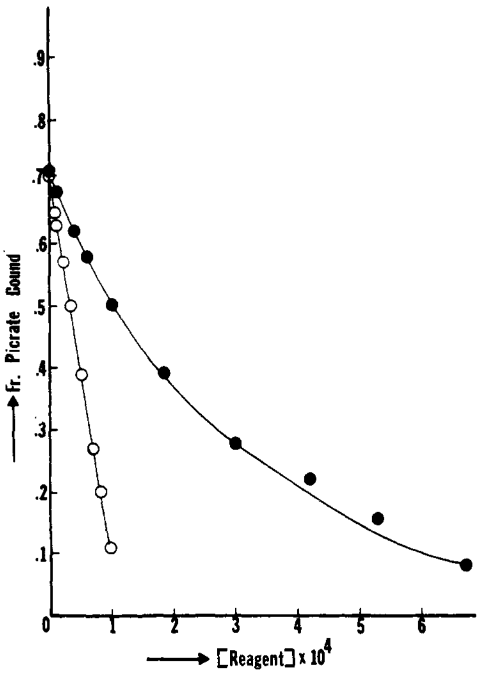


Figure 6. Effect of sodium tetraphenylboron (○) and sodium dodecyl sulfate (●) on the fraction of picrate bound to P18C6: [P18C6] = 2 × 10^{-3} M; [picrate] = 3 × 10^{-5} M.

Finally, the P18C6/picrate complex in water can be precipitated with polyanions such as sodium carboxymethylcellulose in the presence of KCl. The two polymers, with K^+ cations bound to P18C6, form an insoluble polysalt complex[43] and after centrifugation nearly all picrate anions have been removed from the aqueous solution. This is direct evidence that the solute was present in P18C6.

Conclusion

Poly(vinylbenzo-18-crown-6) acts as a neutral polysoap when dissolved in water, and powerfully interacts hydrophobically with organic solutes such as picrate anions and methyl orange. Binding constants can be dramatically increased by complexing the crown ligands with cations. The binding then becomes cation specific, Cs^+ and K^+ being especially effective due to their high binding constants to P18C6. The polymer/salt solutions also effectively catalyze reactions of organic solutes whose rates are enhanced when the reactant is transferred to an aprotic environment. It may be anticipated that binding of anionic solutes to other neutral polysoaps can be enhanced by incorporating through copolymerization crown ligands into such polymers. These polymers can be converted into polycations on addition of electrolytes. An attempt was made to incorporate crown ligands into polymers containing catalytic sites, such as pyridine units, for the hydrolysis of reactive esters. Addition of crown complexable cations changes the polymer into a polycation which then can bind a reactive ester endowed with an anionic substituent. Once bound the hydrolysis of the ester can be catalyzed by the pyridine moieties or by other basic residues on the chain.[46] Significant rate enhancements were observed in these systems as compared to those not containing crown ligands.

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Spectroscopic Study of the $Tc_2Cl_8{}^{3-}$ Ion

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Abstract: The visible spectrum of the $Tc_2Cl_8{}^{3-}$ ion in aqueous hydrochloric acid has been recorded. A band between 6000 and 8000 cm^{-1} has been recorded also at 5 K using a pressed CsI pellet. The latter band shows vibrational structure, with an origin at 5900 cm^{-1}, and its intensity is insensitive to temperature. A scattered wave $X\alpha$-SCF calculation previously reported for the ground state of the $Tc_2Cl_8{}^{3-}$ ion has been extended to afford predictions of the electronic spectrum. The band originating at 5900 cm^{-1} is assigned as the $\delta \rightarrow \delta^*$ band, for which the calculated energy is 6050 cm^{-1}. Assignments of other transitions are suggested and discussed. All observed bands can be convincingly assigned with good numerical agreement. For the first time the position of a $\delta \rightarrow \delta^*$ transition is accurately predicted; the reason for this is discussed. The generally satisfactory agreement between the observed and calculated spectra validates the description of bonding.

The $Tc_2Cl_8{}^{3-}$ ion was prepared[3] prior to the recognition[4] of the existence of quadruple bonds, and its similarity to the $Re_2Cl_8{}^{2-}$ ion immediately led to crystallographic investigation[5,6] of its structure. The structure, by its analogy to that of $Re_2Cl_8{}^{2-}$ [6] (as well as that of $Mo_2Cl_8{}^{4-}$ [7]), leads naturally to its formulation as a species with eight electrons forming a Tc–Tc quadruple bond plus one more electron occupying a nonbonding or weakly antibonding orbital. A study of its EPR spectrum[8] suggested that this "excess" electron occupies the δ^* orbital, thus, in effect, reducing the Tc–Tc bond order to 3.5. This $\sigma^2\pi^4\delta^2\delta^*$ configuration has been suggested by a CNDO calculation,[9] by a Fenske–Hall calculation,[10] and, more significantly, is supported by a SCF-$X\alpha$-SW calculation.[11]

In order to make a stringent test of the bonding description produced by the SCF-$X\alpha$-SW calculation, the results have been used as the basis for predicting the electronic spectrum of $Tc_2Cl_8{}^{3-}$ and the spectrum has been measured experimentally. In this report the calculated and measured spectra are reported and compared.

Experimental Section

Spectroscopic Measurements. Salts of the $Tc_2Cl_8{}^{3-}$ ion were prepared according to literature procedures.[3,5,6] Solutions were prepared in thoroughly deoxygenated aqueous HCl to avoid contamination by $TcCl_6{}^{2-}$. The spectrum of that species, which is the only observed[5] oxidation product of $Tc_2Cl_8{}^{3-}$, was recorded by us, found to be in good agreement with that in the literature,[12] and we were thus able to be