provided the powder pattern of the never-dried paramylon as well as stimulating discussion on this subject.

Registry No. Curdlan hydrate, 86391-84-6; paramylon hydrate, 86391-86-8; (1→3)-β-D-glucan, 86391-85-7.

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Ion Binding Properties of Crown Ether Containing Network Polymers

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ABSTRACT: Binding of sodium, potassium, and cesium picrate and of sodium tetraphenylborate to network polymers containing pendant benzo-15-crown-5 and benzo-18-crown-6 ligands was measured spectrophotometrically in dioxane, tetrahydropyran, 2-methyltetrahydrofuran, and tetrahydrofuran as a function of ligand density in the network and the length of the chain connecting the crown ligand with the polystyrene backbone. The immobilized crown ether compounds were synthesized from 2% cross-linked chloromethylated polystyrene containing 0.7, 0.9, and 5 mequiv of Cl/g of polymer. For cation–crown ether combinations yielding only 1:1 complexes the salt binding to the crown network appears to follow Langmuir adsorption behavior close to the point of saturation even for networks containing as much as one crown ligand per two backbone monomer units. Where 1:1 and 2:1 crown–cation complexes can exist (e.g., benzo-15-crown-5 with K^+ or Cs^+ and benzo-18-crown-6 with Cs^+) both 1:1 and 2:1 crown–picrate ion pair complexes appear to exist in the network. A higher crown density in the network favors the 2:1 complexes, but they frequently convert into 1:1 complexes as the salt loading is increased to the point of saturation. Intrinsic binding constants for the picrate salts vary between 10^3 and 4×10^5 M^{-1}, depending on the specific cation–crown combination and the solvent. Increased density of crown ligands in the network invariably enhances the binding constant irregardless of whether 1:1 or 2:1 crown–picrate complexes are formed. Insertion of a $(CH_2)_{10}$ spacer between crown ligand and polystyrene backbone enhances binding constants by less than a factor 2. A change to the more bulky BPh_4 anion increases the binding constant for sodium ion to the benzo-15-crown-5 network in THF by at least a factor 15. The network polymers can also be utilized to measure binding constants of soluble ligands to salts in low-polarity media.

A considerable amount of work has been reported on the properties of polymers containing the cation-chelating crown ethers, cryptands, or podands (e.g., oligooxyethylenes) either as part of the polymer backbone or anchored to the chain as pendant ligands.[1] The use of insoluble supports such as polymeric networks, glass beads, or gels has led to the applications of these ligands as chromatographic stationary phases for separation of both ionic and neutral solutes and as heterogeneous anion-activating catalysts.[2-8] Most studies with immobilized crown ethers or similar ligands have focused on their role in enhancing rates and yields of reactions, especially under phase-transfer conditions, or in evaluating their effectiveness to separate solutes. However, quantitative information on the binding of ionic solutes to crown ether containing network polymers as a function of cation, counterion, solvent, ligand structure or content, and the spacing between polymer backbone and ligand is rather scarce.

This investigation, preliminary data of which were reported in a recent communication,[8] deals with the quantitative measurement of binding constants of alkali picrates

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to network polymers with pendant benzo-15-crown-5 and benzo-18-crown-6 ligands. The resins were derived from 2% cross-linked chloromethylated polystyrenes. The picrate anion functions as a sensitive spectrophotometric probe and permits the use of concentrations of ionic solutes as low as 10^{-5}–10^{-6} M. This minimizes formation of ionic aggregates higher than ion pairs in the low-polarity solvents in which these polymeric ligands are frequently employed as anion-activating catalysts. In our studies, ether-type solvents were used to facilitate solubilization of the picrate salts. The crown ether network polymers can also be utilized as an analytical tool to arrive at formation constants of complexes between ionic solutes and soluble ligands of any kind in solvents such as dioxane or tetrahydrofuran or to obtain a scale of ligand affinities toward such solutes in solvents like toluene or chloroform.

Experimental Section

Materials. 2,3-(4-Formylbenzo)-1,4,7,10,13-pentaoxacyclopentadec-2-ene or 4′-Formylbenzo-15-crown-5 (I). This compound was synthesized as outlined by Reinhoudt et al.,[9] using 3,4-dihydroxybenzaldehyde (Aldrich) and tetraethylene glycol ditosylate in dry acetonitrile containing anhydrous potassium fluoride. Pure product of mp 79–81 °C (lit.[10] mp 78–79 °C) was obtained in 54% yield after recrystallization from *n*-heptane. The same procedure was applied in the preparation of **2,3-(4-formylbenzo)-1,4,7,10,13,16-hexaoxacyclooctadec-2-ene** or **4′-formylbenzo-18-crown-6** (II), using pentaethylene glycol ditosylate. Pentaethylene glycol was synthesized as described in ref 11. The crown compound was obtained in 50% yield after recrystallization from ethyl ether, mp 65–66 °C (lit.[10] mp 60–62 °C).

2,3-[4-(Hydroxymethyl)benzo]-1,4,7,10,13-pentaoxacyclopentadec-2-ene or 4′-(Hydroxymethyl)benzo-15-crown-5 (III). To a well-stirred solution of 10 g (0.034 mol) of I in 250 mL of absolute ethanol was added 1.5 g of $NaBH_4$. After several minutes the reaction mixture became homogeneous and was stirred at room temperature for 24 h. The solution was then poured into an equal volume of H_2O, neutralized with dilute acetic acid, and extracted with $CHCl_3$. After washing with H_2O, drying over $MgSO_4$, and filtering, the $CHCl_3$ was evaporated and the residue allowed to crystallize. Recrystallization from ethyl ether afforded 8.6 g (85%) of III: mp 80 °C; NMR ($CDCl_3$) δ 3.10 (s, 1, OH), 4.00 (m, 16, CH_2), 4.60 (s, 2, CH_2OH), 6.90 (s, 3, aromatic). Anal. Calcd for $C_{15}H_{22}O_6$: C, 60.39; H, 7.43. Found: C, 59.82; H, 7.45. A similar procedure was used for the preparation of **2,3-[4-(hydroxymethyl)benzo]-1,4,7,10,13,16-hexaoxacyclooctadec-2-ene** or **4′-(hydroxymethyl)benzo-18-crown-6** (IV), starting from II. This product was obtained in 86% yield (mp 60 °C). NMR ($CDCl_3$) δ 2.35 (s, 1, OH), 4.00 (m, 20, CH_2), 4.60 (s, 2, CH_2OH), 6.90 (s, 3, aromatic). Anal. Calcd for $C_{17}H_{26}O_7$: C, 59.64; H, 7.65. Found: C, 59.82; H, 7.64.

2,3-[4-(Bromomethyl)benzo]-1,4,7,10,13-pentaoxacyclopentadec-2-ene or 4′-(Bromomethyl)benzo-15-crown-5 (V). This compound was synthesized by bromination of 6 g (0.0212 mol) of 4′-methylbenzo-15-crown-5[11] in CCl_4 using the method of Wong and Ng.[12] The compound, which is unstable at room temperature, was recrystallized but not recovered from its hexane solution and kept in the freezer. The estimated yield based on a previous run in which the compound was isolated is 80% (6.6 g).

2,3-[4-[[(10-Hydroxydecyl)oxy]methyl]benzo]-1,4,7,10,13-pentaoxacyclopentadec-2-ene or 4′-[[(10-Hydroxydecyl)oxy]methyl]benzo-15-crown-5 (VI). To 15 g (0.086 mol) of 1,10-decanediol (Aldrich) in 100 mL of THF was added 1 g of a 50% NaH in oil dispersion (0.02 mol of NaH), and the mixture was allowed to stir under N_2 at reflux for 1 h. About 6 g (0.015 mol) of V was then added and the reaction continued for 48 h. After cooling, the mixture was filtered and the THF removed. The solid residue was extracted with CCl_4, the extract dissolved in a 50/50 mixture of ethanol and water, the solution extracted with $CHCl_3$, and the extract washed with water. Solvent was removed from the combined CCl_4 and $CHCl_3$ extracts and the solid chromatographed on 30 g of neutral alumina (activity I) by elution with $CHCl_3$. After removal of solvent, the solid was further purified by HPLC using an ODS-2 column and a 35/65 water–ethanol solution. After solvent evaporation and extraction of the residue with hot hexane, 0.6 g of solid VI (yield 10%) of mp 42–43 °C was recovered by cooling the hexane solution in the freezer: mass spectrum, *m/e* 454 (M, 29%), 281 (M – $O(CH_2)_{10}OH$, 7.11%); NMR ($CDCl_3$) δ 1.40 (m, 16, CH_2), 3.50 (m, 2, CH_2), 4.42 (s, 2, CH_2), 6.90 (m, 3, aromatic).

Crown Ether Network Polymers. To a slurry of NaH (oil dispersion) in THF was added an equimolar amount of the appropriate hydroxy-containing crown ether III, IV, or VI under N_2. After stirring at room temperature for 0.5 h, H_2 evolution was complete, and the chloromethylated, cross-linked polystyrene was added in a ratio of crown alcohol to chlorine of 5:1 (3:1 for crown VI; excess crown alcohol can be recovered after the reaction by removing the solvent and recrystallizing the residue from ethyl ether). After refluxing for 48 h, the reaction mixture was cooled and filtered, and the solids were washed continuously with THF/H_2O mixtures (increasing the water content from 0 to 80%) to remove NaCl. The crown-substituted network was then continuously extracted in a Soxhlet with THF for 24 h and dried in vacuo to a constant weight. For the lower loaded crown networks Bio-Beads containing 0.9 mequiv of Cl/g were employed (Bio-Rad SX-2, 2% cross-linked, 200–400 mesh, porosity 5 mL/g in benzene). A 2% cross-linked Merrifield resin (Fluka, 200–400 mesh) containing 5 mequiv of Cl/g was used to make networks with high crown content. The network containing crown compound VI was made from a 2% cross-linked chloromethylated polystyrene containing 0.7 mequiv of Cl/g (Fluka, 200–400 mesh).

Network Analysis. The degree of substitution of Cl by a crown ligand was determined from the increase in the weight of the network after the reaction was completed, as well as by titrating the crown ether ligands with an alkali picrate in THF as solvent until saturation was achieved, i.e., until no more picrate was absorbed. Formation of a 1:1 crown–alkali picrate complex was ensured by using sodium picrate for the benzo-15-crown-5 networks and the potassium salt for resins with benzo-18-crown-6 (see Results and Discussion). The two methods of analysis agreed to within 5% and yielded degrees of substitution of 90–100% for networks with III and IV and 85% for the network with crown VI.

Measurements of Picrate Salt Binding. A small quantity of network (usually 1–5 mg) and 10 mL of picrate solution in dioxane, tetrahydropyran (THP), tetrahydrofuran (THF), or 2-methyltetrahydrofuran (MeTHF) were placed in a 50-mL round-bottom flask equipped with a fritted filter and optical cell. The system was thermostated and gently shaken until equilibrium was reached between bound and free picrate (about 20–40 min, depending on the solvent). The solution was then passed through the filter and the spectrum of unbound picrate recorded on a Cary 14 or Beckman Acta M VI spectrophotometer. After the solution was returned to the flask containing the network, the picrate concentration was increased by adding small aliquots of a concentrated picrate solution. Each time the concentration of unbound picrate was determined after reaching equilibrium. To minimize adherence of the network to the glass surface, the flask was silanized by treatment with a hexane solution containing 1% chlorotrimethylsilane and 1% 1,1,1,3,3,3-hexamethyldisilazane. The ether solvents were carefully distilled from sodium–potassium alloy. Picrate salts were obtained by neutralizing picric acid with the appropriate base in aqueous methanol, recrystallization of the salt from this solvent mixture, and drying the crystalline compounds for several days under vacuum at about 140 °C.

Results and Discussion

The structure of the respective crown ether networks and their coded names are shown in Chart I. The low-capacity networks R15C5 and R18C6, derived from a 0.9 mequiv of Cl/g of cross-linked chloromethylated polystyrene, contain about one benzocrown ether ligand per eleven styrene monomer units. The more highly substituted networks 5R15C5 and 5R18C6, synthesized from the 5 mequiv of Cl/g resin, have approximately one ligand per two monomer units. RD15C5, with the $(CH_2)_{10}$ spacer between the polymer backbone and the benzo-15-crown-5

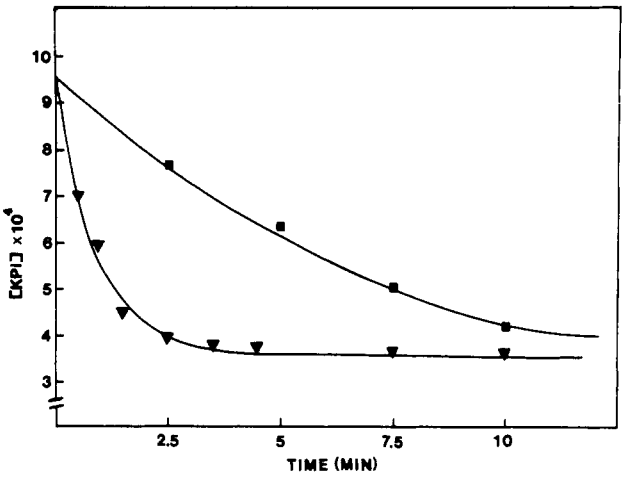
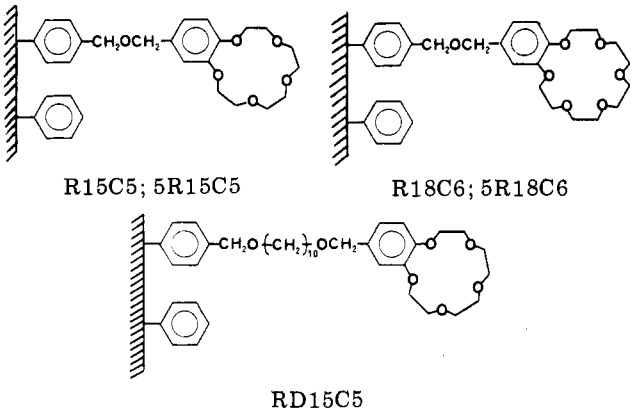


Figure 1. Rate of uptake of potassium picrate in a dry (■) and preswollen (▼) R18C6 network. Solvent THF.

Chart I



ligand, contains one ligand per thirteen monomer units.

The time necessary to reach equilibrium between bound and free picrate salt can be determined from its rate of uptake by the crown network. Figure 1 shows an example for potassium picrate with R18C6 in THF. The THF-preswollen network reaches equilibrium in about 10 min, while a nonswollen sample added to the picrate solution obviously requires more time. Solute diffusion into the polymer matrix depends on stirring rate, particle size, and other factors as demonstrated by phase-transfer catalysis studies.[13,14] In our system, the equilibration time was also found to be solvent dependent, the time being longer for dioxane and toluene than for THF or chlorobenzene. In all cases the picrate concentration reached a constant value in less than 40 min.

Picrate binding to the crown ether networks may be described in terms of the reaction

$$Cr^* + Pi^-,M^+ \underset{}{\overset{K_N}{\rightleftharpoons}} Pi^-,M^+,Cr^* \qquad (1)$$

where the asterisk refers to network-bound species. Cr* and Pi^-,M^+,Cr^* denote free crown ether sites and bound picrate, respectively, their concentrations being expressed in equivalents. Pi^-,M^+ is the unbound picrate in solution, the concentration of which is measured spectrophotometrically. If Cr_0^* is the total concentration of crown ligands and $1/n$ the number of ligands in the alkali picrate complex (in nearly all known cases of such complexes, $1/n$ equals one or two), then $Cr^* = Cr_0^* - [Pi^-,M^+,Cr^*]/n$. The bound picrate concentration is calculated by subtracting $[Pi^-,M^+]$ from the total picrate concentration, both expressed in equivalents. The intrinsic binding constant, K_N,

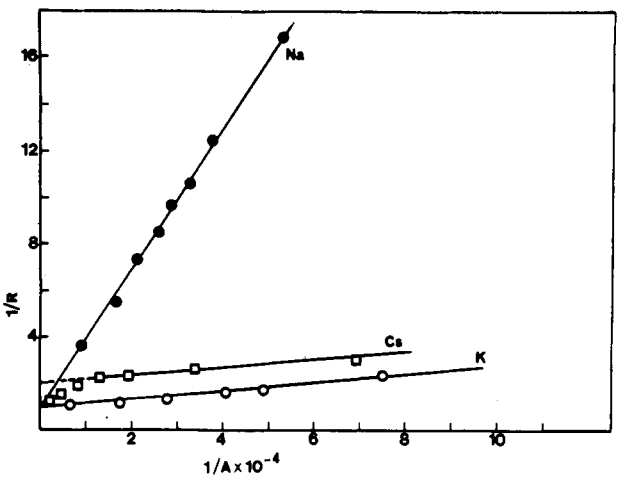


Figure 2. Binding of alkali picrates to R18C6 in THF at 25 °C.

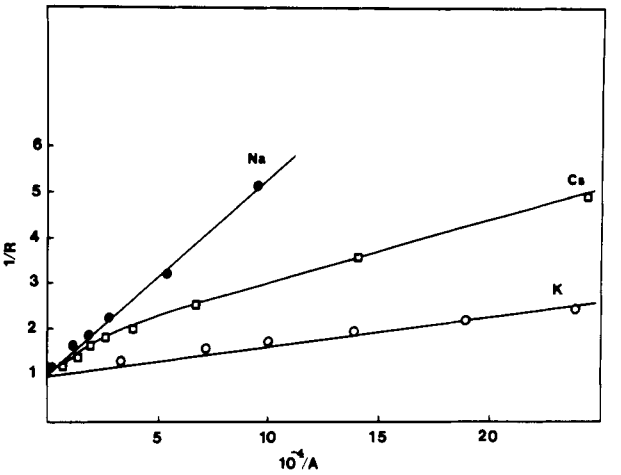


Figure 3. Binding of alkali picrates to R18C6 in dioxane at 25 °C.

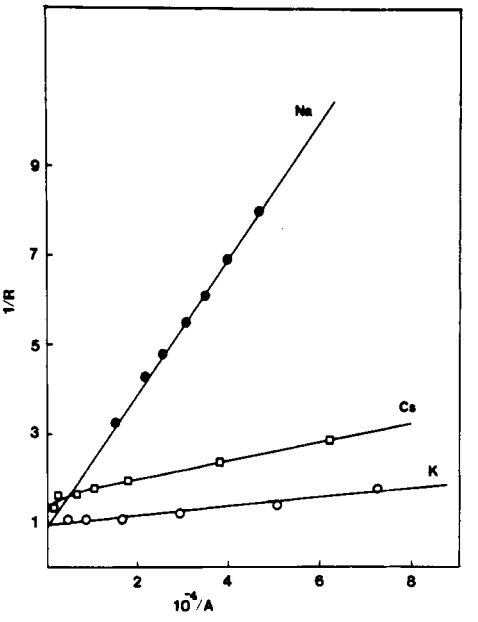


Figure 4. Binding of alkali picrates to 5R18C6 in THF at 25 °C.

for reaction 1 can be calculated by plotting the data according to the familiar Klotz equation[15]

$$1/R = 1/n + 1/nK_NA \qquad (2)$$

where $1/R = Cr_0^*/[Pi^-,M^+,Cr^*]$ and A is the concentration of unbound picrate.

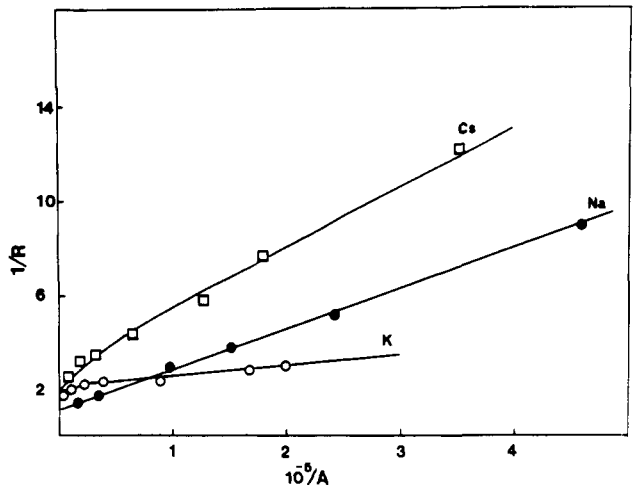


Figure 5. Binding of alkali picrates to 5R15C5 in dioxane at 25 °C.

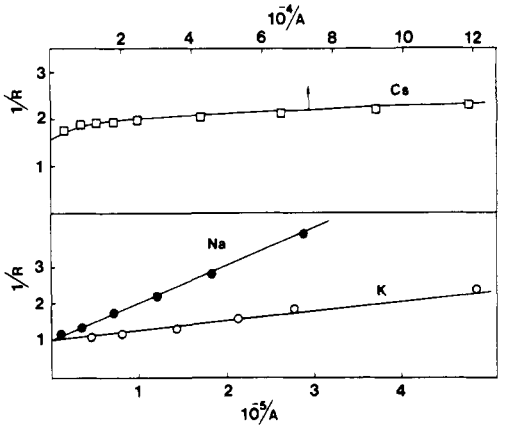


Figure 6. Binding of alkali picrates to 5R18C6 in dioxane at 25 °C.

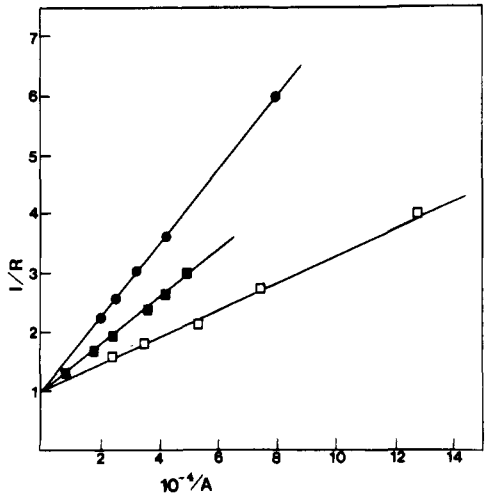


Figure 7. Binding of alkali picrates to R15C5. Systems: (●) Na^+/THP; (□) K^+/MeTHF; (■) Na^+/MeTHF. T = 25 °C.

Stoichiometry of the Network-Bound Picrate Complexes. Plots of $1/R$ vs. $1/A$ for alkali picrates with several networks in different solvents are depicted in Figures 2–9. Linear relationships are found in those systems where cation and crown are known to form complexes of 1:1 stoichiometry and where 2:1 crown–cation complexes are unlikely to form. This is the case for sodium picrate with all five networks in the four solvents used and for potassium picrate with the two benzo-18-crown-6 networks R18C6 and 5R18C6. For 1:1 complexes the plots should

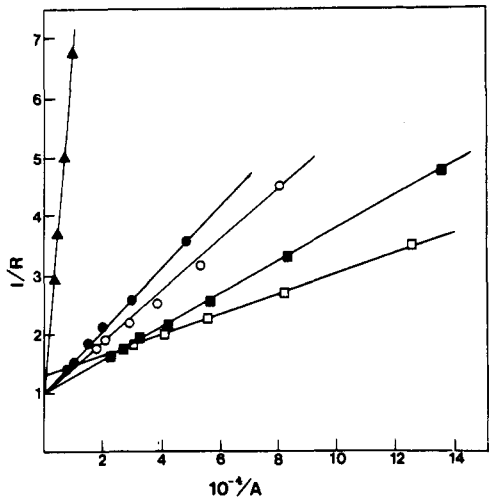


Figure 8. Binding of alkali picrates to RD15C5. Systems: (●) Na^+/THP; (○) K^+/THP; (■) Na^+/MeTHF; (□) K^+/MeTHF; (▲) Na^+/THF. T = 25 °C.

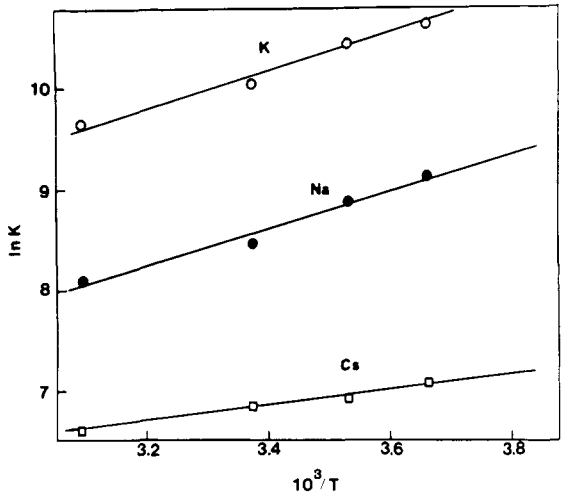


Figure 9. Temperature dependence of the binding constants of alkali picrates to R15C5 in THF.

yield intercepts of $1/n = 1$, and in those systems where data were obtained close to the point of site saturation (low $1/R$ values; see plots in Figures 3 and 5–8), the lines clearly intersect at $1/n$ equal or very close to unity. Hence, for all these systems a value $1/n = 1$ was taken as the intercept and used in the calculation of K_N.

Stable, sandwich-type 2:1 crown–cation complexes, in addition to 1:1 complexes, are frequently encountered when the cation diameter is larger than that of the crown cavity. An example is benzo-15-crown-5 with K^+ or Cs^+ and benzo-18-crown-6 with Cs^+.[16,18] The stability of complexes with 2:1 stoichiometry is significantly enhanced when the two crown ligands are linked by a short chain as in the bis(crown ethers) or anchored to the same polymer backbone as in the linear poly(crown ethers).[12,19–23] When complexes of both 1:1 and 2:1 stoichiometry can exist in the networks, the shape of the $1/R$ vs. $1/A$ plots will depend on their relative amounts as a function of the degree of site binding. For potassium picrate with R15C5 in THF, MeTHF, or THP and with RD15C5 in THP, the $1/R$ vs. $1/A$ plots are linear with an intercept close to unity (Figures 7 and 8). Apparently, 1:1 complexes are more stable than 2:1 complexes in these systems over the entire range of $1/R$ values. For potassium picrate with 5R15C5 in THF and dioxane, and with R15C5 in dioxane, and for most of the cesium picrate systems, the binding plots exhibit a linear portion at high $1/R$ values with an extrap-

Table I
Intrinsic Binding Constants, K_N, of Alkali Picrates to Immobilized Crown Ethers in Ether-Type Solvents (T = 25 °C)[a]

	$K_N \times 10^{-3}$, M^{-1}										
	sodium				potassium				cesium		
network	THF	MeTHF	THP	dioxane	THF	MeTHF	THP	dioxane	THF	MeTHF	dioxane
R15C5	1.66	22.8	16.6	15.5	20.8	43.3	15.2	220*	1.3		(3.5*)
5R15C5	2.20			58.0	79*			350*	(55*)		66*
R18C6	3.41			25.8	54			172	125*		(150)
5R18C6	6.80			97.0	100			258	(96*)		410*
RD15C5	1.60	36.5	18.9			59.4	26.7			24.4	

[a] Values with an asterisk were calculated by using $1/n$ = 2. For all other constants $1/n$ equals unity. Bracketed values were derived from plots that were slightly curved (see text).

olated intercept close to $1/n$ = 2 (Figures 2–5). However, close to the point of saturation (low $1/R$ values), the plots tend to curve downward and appear to intercept the $1/R$ axis close to unity. Apparently, salt binding initially yields 2:1 complexes, but on forcing more picrate into the network, these complexes are converted into 1:1 complexes according to the reaction

$$Pi^-,Cr^*,M^+,Cr^* + Pi^-,M^+ \rightleftarrows 2Pi^-,M^+,Cr^* \quad (3)$$

When the 2:1 complex of a particular ion pair–crown combination is much more stable than the 1:1 complex, a linear $1/R$–$1/A$ plot with $1/n$ = 2 should be obtained. This appears to be the case for cesium picrate with R15C5 and 5R18C6 (Figure 6) and possibly with 5R15C5 (Figure 5), all in dioxane. For RD15C5/Pi^-,K^+/MeTHF (Figure 8) a linear plot is found that extrapolates to $1/n$ = 1.3. This situation may arise when the stability of the 1:1 and 2:1 complexes are comparable. However, even in this RD15C5 system the plot may still curve downward to $1/R$ = 1 if more picrate had been added.

Linearity of the Binding Plots. Equation 1 describes the case where salt binding follows a Langmuir isotherm. It is well recognized that the linearity of the Klotz plot obscures deviations from Langmuir adsorption in regions approaching the saturation point, that is, at high $1/A$ values, where the data tend to become compressed on the Klotz plot.[24,25] However, the near-perfect linearity in systems where only 1:1 complexes are formed suggests that significant deviations from linearity resulting from cooperative effects do not occur. This is even the case for the high-capacity networks 5R15C5 and 5R18C6 (see, for example, Figures 5 and 6 for sodium picrate). Apparently, contributions to the binding caused by intra- or intermolecular interaction forces between bound picrate ion pairs do not appear to be significant in our work. Therefore, deviations from linearity in systems where both 2:1 and 1:1 complexes can exist are most likely not caused by cooperative effects involving bound ion pairs, but by conversion of 2:1 into 1:1 complexes as more salt is forced into the network.

It should be stressed that we have assumed ion pairs to be the predominant species in all these systems (eq 1 and 3). In THF, the solvent of highest dielectric constant, the dissociation constant of sodium picrate at 25 °C is 1.05×10^{-8} M[26] and for potassium picrate 9.2×10^{-8} M.[19] In this solvent, the concentration of unbound picrate in our experiments was never lower than 10^{-5} M. Therefore, the fraction of free ions was always less than 0.1 and much less than 0.1 in THP, MeTHF, or dioxane. Spectral evidence also rules out the presence of a significant fraction of free ions. Crown complexes of picrate salts have much higher dissociation constants (in the order of 10^{-5} M for crown-separated picrate ion pairs in THF; see ref 19), but their very high concentration in the network prevents their dissociation. In media of higher dielectric constants, free ion dissociation of unbound salt would most likely cause the binding plots to curve upward at high $1/A$ values, since increased ionization will shift the equilibrium $A^-,M^+,Cr^* \rightleftarrows A^-,M^+ + Cr^* \rightleftarrows A^- + M^+ + Cr^*$ to the right. In solvents of very low polarity, ion pairs may associate into higher aggregates and this again would cause nonlinear binding behavior. Apparently, this does not occur in our systems but could be a problem at higher salt concentrations. The use of sensitive spectrophotometric probes such as picrate salts permits measurements at low salt concentration and minimizes formation of ion pair aggregates.

The lack of significant ion pair–ion pair interactions within the salt-loaded network may be surprising at first sight. Even if swelling increases the network volume by a factor 10, the salt concentration in the network would still exceed 0.1 M. Solutions of oxyanion pairs (e.g., phenoxides and ketyls) are known to aggregate in ethereal solvents at these concentrations. And while crown ligands tend to break down such aggregates, crown complexes of fluorenyl carbanion pairs were found to form aggregates in MeTHF and THP at concentrations above 10^{-3} M.[27] However, ion pairs of the type A^-,M^+,Cr with the ligand complexed externally to the tight A^-,M^+ ion pair are much less susceptible to aggregation than crown-complexed loose ion pairs A^-,Cr,M^+.[27] Spectral data for picrate salt–crown complexes in ether-type solvents demonstrate that most 1:1 complexes are of the type Pi^-,M^+,Cr, especially when the solvent polarity decreases.[18,19] Their presence in our network would decrease ion pair–ion pair interactions. Moreover, in spite of the expected chain flexibility in 2% cross-linked networks, the polymer-bound ion pairs are restricted in their mobility. Data on fluorenyl ion pairs connected by a short chain[28,29] or bound to a polymer[30] have shown that intramolecular ion pair–ion pair interactions are weak unless the two ion pairs are in very close proximity. Intermolecular ion pair–ion pair interactions would cause the chains in the network to collapse on one another. This would limit salt accessibility to the ligands. The fact that equilibrium is reached equally rapid close to the point of network saturation by salt even in the high-capacity networks also suggests that ionic interactions within the networks do not constitute an important factor in our measurements.

Binding Constants. Intrinsic binding constants (K_N = slope/n) computed from the respective binding plots are collected in Table I. For cation–crown systems that only form 1:1 complexes, $1/n$ was taken as unity. Where both 1:1 and 2:1 complexes can exist, $1/n$ = 2 was used in the case of linear plots that clearly intercept at $1/R$ = 2 or when the plot contains a distinctly linear portion at higher $1/R$ values with an extrapolated intercept $1/R$ = 2. These K_N values are marked in Table I with an asterisk and describe salt binding to these systems under conditions where Cr_0* is at least twice the equivalent of bound picrate. When more picrate is bound, 1:1 complexes can form ac-

cording to reaction 3. A few systems (e.g., R18C6/Pi^-,-Cs^+/dioxane) yield a slightly curved plot over the entire $1/R$ range, probably as a result of a change in the relative amounts of 1:1 and 2:1 complexes. In these cases, K_N was computed from the best straight line with $1/n = 1$ or 2, depending on whether the intercept was closer to 1 or 2. These K_N values are bracketed in Table I. They are less accurate, but since the curvature is small, they represent a reasonable approximation for comparing the salt binding in these systems with those where linear relationships are found.

Effect of Solvent. The data of Table I demonstrate that binding constants and, therefore, network selectivities for picrate salt binding are solvent sensitive and depend on whether the systems form predominantly 1:1 or 2:1 crown–cation complexes. As expected, a good cation-coordinating solvent like THF will lower K_N values, but the decrease depends on the nature of the cation. Complexation of a crown ligand to the externally solvated tight picrate ion pair, Pi^-,M^+,S_n, requires removal of part or all of the solvent molecules, S. This is energetically less favorable when M^+ is a small cation and S a strong cation-binding solvent. Hence, differences in K_N values between THF and dioxane are largest for Pi^-,Na^+ (a factor 8–25) and are small for Pi^-,Cs^+. The effect on the potassium salt is less than a factor 3, at least for networks where 1:1 complexes are formed. Interactions with ether-type solvents decrease in the order $Na^+ > K^+ > Cs^+$, and mobility data reveal little specific interaction with the Cs^+ cation even in THF.[31] Differences in K_N values for Pi^-,Na^+ in MeTHF, THP, and dioxane are comparatively small. Although MeTHF is more basic than THP, binding constants in the former solvent are all higher. They may reflect steric effects in the interaction of MeTHF and the ion pairs. K_N values are probably also affected by differences in network swelling by the respective solvents, as this may change the polarity inside the swollen network.

Solvent release on salt complexing to the crown networks is also implied from thermodynamic data. Measurements of alkali picrate binding to R15C5 in THF between 50 and 0 °C yield linear van't Hoff plots (Figure 9) with ΔH values (in kcal/mol) of −2.7 (Na^+), −3.5 (K^+), and −1.6 (Cs^+) and ΔS values (in (cal/deg)/mol) of 6.6 (Na^+), 8.4 (K^+), and 8.2 (Cs^+). The positive entropy change for the complex formation (reaction 1) points to the release of solvent molecules.

Effect of Crown Structure and Crown Content. Inspection of Table I reveals that binding constants for the high-capacity networks 5R15C5 and 5R18C6 are invariably higher than those of their low-capacity analogues R15C5 and R18C6, irrespective of whether the networks form 1:1 or 2:1 crown–picrate complexes. Data on bis(crown ethers) and linear poly(crown ethers) show that the stability of 2:1 complexes relative to that of the 1:1 complex increases as the spacing between crown ligands is decreased.[19,21] Table I shows that potassium picrate forms 1:1 complexes with R15C5, where crown ligands on the same chain are separated by 11 styrene units on the average. Only in dioxane does binding of Pi^-,K^+ to R15C5 result in 2:1 complexes, at least at low $1/R$ values. The reason for this is not immediately obvious, although it is worth pointing out that the time necessary to reach binding equilibrium in dioxane is longer than in the other solvents. This may suggest that network swelling in this solvent is less extensive, resulting in a decreased distance between ligands. It should also be noted that a random distribution of crown ligands in a R15C5 or R18C6 network yields a considerable fraction of crown ligands that are spaced apart by only a few styrene monomer units. If binding to such "bis(crown ether)" units is high, formation of 2:1 complexes at low degrees of saturation (high $1/R$ values) may still be the prevailing binding mode in these networks. In RD15C5, crown ligands are separated by two $(CH_2)_{10}$ spacers in addition to about thirteen styrene units, and Pi^-,K^+ in this network appears to form only 1:1 complexes in both MeTHF and THP.

When R15C5 is replaced by 5R15C5, the average distance between crown units on a chain is substantially reduced. This favors formation of 2:1 complexes, as it increases their stability.[21] In dioxane, K_N is increased by a factor 1.6, and in THF by a factor 4. In the latter solvent, the change from R15C5 to 5R15C5 is accompanied by a change in the stoichiometry of the crown–picrate complex from 1:1 to 2:1, although at high saturation the 2:1 complexes are converted back into 1:1 tight ion pair complexes (eq 3). The increase in K_N on changing R15C5 into 5R15C5 is especially large for cesium picrate, viz., a factor 40 in THF and nearly 20 in dioxane. This is due to the low stability of Cs^+ complexes with one benzo-15-crown-5 ligand, while the larger interionic ion pair distance in Pi^-,Cs^+ as compared to the potassium ion pair facilitates its separation to a 2:1 crown-separated ion pair. The increase in K_N for the cesium salt is much less when R18C6 is replaced by 5R18C6. Both networks form 2:1 complexes with Pi^-,Cs^+, although close to the point of saturation R18C6 appears to form 1:1 complexes.

"*Intramolecular*" cooperation involving two neighboring crown ligands is probably the predominant mode of formation of a 2:1 crown–picrate ion pair complex, especially when the ligands are not spaced too far apart. This was found to be the case in THF solutions of potassium picrate and linear copolymers of styrene and vinylbenzo-15-crown-5.[21] However, "*intermolecular*" complexation involving two crown ligands on different chain segments and resulting in increased cross-link density cannot be excluded. Such complexes were detected in concentrated methyl ethyl ketone solutions of the above copolymers in the presence of K^+ ions as evidenced by large viscosity increases.[21]

The networks with high crown ligand density also give higher binding constants with picrate salts when only *1:1* complexes are formed. The increase is only a factor 1.4 for sodium picrate in THF when R15C5 is replaced by 5R15C5, but a fourfold increased is observed in dioxane. The same increase is obtained with sodium picrate in THF when 5R18C6 is substituted for R18C6. Enhanced binding as a function of the crown content of a macromolecular chain was also suggested from extraction data in $CHCl_3$–H_2O mixtures for picrate salts that form 1:1 complexes with linear copolymers of styrene and vinylbenzocrown ethers.[32] It should be stressed that the increase in K_N for networks with high crown content does not result from cooperative interactions between the larger number of bound ion pairs. In that case, the Klotz plots would depict nonlinearity, and this is not observed in these systems. The change from one crown ligand per eleven monomer units in the low-capacity networks to about one ligand per two monomer units in the resins with high crown density constitutes a rather drastic change in the microenvironment in the vicinity of a crown binding site. While salt binding results from a specific interaction between crown ligand and the cation of the picrate ion pair, the microenvironment around the cation–crown complex will affect the value of the binding constant in a manner similar to the effect of solvent on the stability of a soluble picrate–crown complex or to the effect of comonomer substituents

on the binding of picrate salts to linear copolymers endowed with pendant crown ether ligands. For example, closer spacing between crown ligands in the high-capacity networks could result in increased specific interactions between the π clouds of the picrate anion associated with the crown–cation complex and that of a neighboring benzocrown ether moiety. Also, additional oxygen binding sites supplied by an adjacent empty crown ligand may contribute to the stability of a crown–cation complex. Similar factors may play a role in changing the spacer length between ligand and polymer backbone. Results for RD15C5 indicate that in comparison to R15C5 the insertion of a $(CH_2)_{10}$ spacer between a benzo-15-crown-5 ligand and the polystyrene backbone increases the K_N for 1:1 complex formation by a factor less than 2. Binding enhancement could be the result of decreased interference between neighboring crown ligands and the picrate anion associated with the crown-bound cation, a change in the mobility of the binding site or in the swelling behavior of the network, or possibly other factors. Increased spacer length has been reported to improve the catalytic effects of anion-activating crown ether networks used in phase-transfer reactions.[31] Better accessibility of the catalytic site and changes in the microenvironment of the crown-bound reactants have been advanced as reasons for the improved catalysis.

Effect of Anion. Formation constants of ion pair–crown ether complexes are affected by the interionic ion pair distance, which varies with the size and structure of the anion associated with the cation.[1] To determine the anion effect on cation complexation to a crown ether network, sodium tetraphenylborate was complexed to 5R18C6 in THF as solvent. However, the 270-nm absorption band of BPh_4^- has a low extinction coefficient. This, coupled with the expected high complexation constant (forcing the use of a low salt concentration), makes it difficult to determine K_N directly by optical spectroscopy. In such a case, a salt with a more favorable spectrum and for which the binding constant to the network is known can be used in competition with borate salt. In our experiment, sodium picrate in THF was first bound to the network. Aliquots of $NaBPh_4$ were then added, forcing the picrate out of the network. Each time the amount of released picrate in the THF solution was measured.

Two equilibria must be considered:

$$Pi^-,Na^+ + Cr^* \overset{K_N}{\rightleftharpoons} Pi^-,Na^+,Cr^* \quad (4)$$

$$BPh_4^-,Na^+ + Cr^* \overset{K_1}{\rightleftharpoons} BPh_4^-,Na^+,Cr^* \quad (5)$$

The K_N value for equilibrium 4 is that of the Pi^-,Na^+/5R18C6/THF system reported in Table I. The ratio of the two binding constants K_N and K_1 is given by

$$\frac{K_1}{K_N} = \frac{(B_0 - B)P_f}{P_b B} \quad (6)$$

where B_0 is the total borate concentration, B and P_f are the respective concentrations of free borate and free picrate in the solution, and P_b denotes the concentration of bound picrate. Assuming 1:1 complexes (as is the case for Na^+ with 5R18C6), the concentration of free sites (in equivalents) is given by

$$[Cr^*] = [Cr_0^*] - P_b - (B_0 - B) \quad (7)$$

Solving eq 6 yields

$$B = \frac{K_N B_0 P_f}{K_N P_f + K_1 P_b} \quad (8)$$

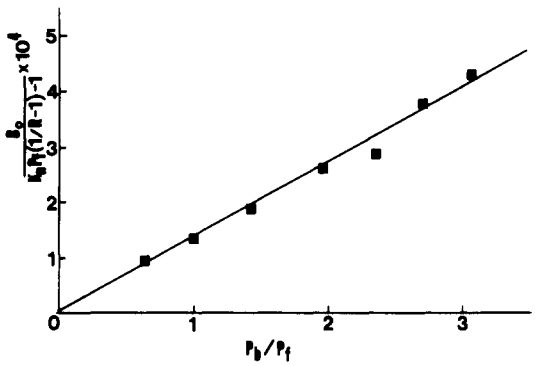


Figure 10. Competitive binding of sodium tetraphenylborate and sodium picrate to 5R18C6 in THF. T = 25 °C.

Substituting this expression for B into eq 7 and replacing $[Cr^*]$ by $P_b/K_N P_f$ (see eq 4), one finds

$$\frac{P_b}{K_N P_f} = [Cr_0^*] - P_b - \frac{K_1 P_b B_0}{K_N P_f + K_1 P_b} \quad (9)$$

Dividing eq 9 by P_b and rearranging yield

$$\frac{[Cr_0^*]}{P_b} - 1 - \frac{1}{K_N P_f} = \frac{K_1 B_0}{K_N P_f + K_1 P_b} \quad (10)$$

and

$$\frac{K_N P_b P_f}{K_N P_f [Cr_0^*] - K_N P_b P_f - P_b} = \frac{K_N P_f}{K_1 B_0} + \frac{P_b}{B_0} \quad (11)$$

Equation 11 can be further rearranged to the expression

$$\frac{B_0}{K_N P_f (1/R - 1) - 1} = \frac{1}{K_1} + \frac{P_b}{K_N P_f} \quad (12)$$

where $1/R = [Cr_0^*]/P_b$. By measuring the free picrate concentration, P_f, the bound picrate, P_b, can be computed for any value of B_0. A plot of the left-hand side of eq 12 vs. P_b/P_f should yield a straight line with slope $1/K_N$ and intercept $1/K_1$. Figure 10 shows that a linear relationship is indeed obtained, with $K_N = 6.5 \times 10^3$ M^{-1} (as compared to 6.8×10^3 M^{-1} from direct measurements; see Table I), but the intercept is too small to determine K_1 with any accuracy. However, K_1 appears to exceed the value 10^5 M^{-1}. This is a factor 15 larger than the binding constant for sodium picrate. The higher value for sodium tetraphenylborate is to be expected on account of the higher electric field strength of the cation as a result of the large interionic distance. More accurate intercepts, and, therefore, K_1 values should be obtained by choosing the proper combination of salts such that K_N and K_1 will differ by a smaller factor.

Two important observations pertinent to the use of immobilized crown ethers as anion-activating catalysts should be stressed. First, the high-capacity networks 5R15C5 and 5R18C6 may not only yield higher binding constants with ionic solutes but also favor formation of 2:1 crown–separated ion pair complexes in systems where such complexes compete with the formation of 1:1 crown–complexed tight ion pairs. Since the latter are often much less reactive than loose ion pairs, the catalytic effect of a high-capacity network may exceed that of an identical crown ether network of lower capacity. Second, under saturation conditions, the catalytic activity of the network may decrease if this leads to conversion of 2:1 crown–separated ion pairs into 1:1 crown–complexed tight ion pairs as observed in a number of network–picrate systems. Of course, differences in the microenvironment around the bound

reactant as well as its distance from neighboring substituents on the chain are additional factors determining reactivity differences between low- and high-capacity networks (see also ref 14 and 34).

Finally, crown ether networks can be used effectively in determining binding constants of soluble ligands to solutes in low-polarity media. When adding a ligand, L, to a picrate-containing crown ether network in a solvent such as dioxane or toluene, picrate will be released according to the reaction

$$Pi^-,M^+,Cr^* + L \overset{K}{\rightleftharpoons} Pi^-,M^+,L + Cr^* \qquad (13)$$

It can be easily shown that $K = K_L/K_N$, where K_N is defined as in eq 1 and K_L is the formation constant for the reaction $Pi^-,M^+ + L \rightleftharpoons Pi^-,M^+,L$ in the solvent used. Hence, if K_N is known, K_L can be determined for a variety of ligands. Even if K_N cannot be determined, for example, when toluene is the solvent, K values for a series of ligands still provide a scale of binding efficiencies of such ligands with respect to the solute used. An important result of these measurements is the observation that for a low-capacity network such as R18C6 the formation constant of a 1:1 picrate ion pair complex with the immobilized crown ether is not very different from that found for the same complex but with the crown ligand free in solution. Details of this work, some of which was reported in a preliminary communication,[8] have recently been published.[35]

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