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Anion Dependence of Crown Ether Selectivities for Alkali Picrates and Sulfonates in Dioxane and Toluene. A Synergistic Effect

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Abstract. The binding constants, K_N, of sodium and potassium 8-anilinonaphthalene-1-sulfonate (ANS) and of sodium 5-dimethylamino-1-naphthalenesulfonate (DNS) to benzo-18-crown-6 bound to a 2% cross-linked polystyrene network (RN18C6) were measured spectrophotometrically in dioxane and the results compared with those obtained for picrate salts. The network RN18C6 was then used to measure in dioxane and toluene by a competition method the equilibrium constant, K, of the reaction $A^-M^+N + Cr \rightleftarrows A^-M^+Cr + N$. A^-M^+N denotes the ionic solute (ANS, DNS, methyl orange or picrate salt) bound to the network RN18C6 (N) and A^-M^+Cr is the solute bound to a soluble ligand Cr, where Cr represents a series of 18-crown-6 and 15-crown-5 compounds. Combining the K_N and K values the formation constants, K_L, of the crown ether complexes of the respective salts were obtained in dioxane. The data show a reversal in the complexation strength of the 18-crown-6 compounds in dioxane when sodium picrate is replaced by sodium ANS. The results were rationalized in terms of a synergistic effect exerted by dioxane, with dioxane forming a 1 : 1 dioxanate with the crown ion pair complex. This effect is especially strong with ANS and with a rigid planar crown ether like dibenzo-18-crown-6. The binding constants, K_N, of NaANS and NaDNS to RN18C6 in dioxane are nearly three times larger than for sodium picrate, and the same holds for the potassium salts. Differences in anion interactions with the network appear to be a plausible cause for the anion dependence of K_N.

Key words: Crown ether, binding constants, polystyrene, networks.

1. Introduction

In recent publications we have shown that crown ethers or linear polyethers (glyme) immobilized on polystyrene or polyacrylate resins can be used to measure affinities of all kinds of soluble ligands for ionic solutes in apolar solvents such as toluene, dioxane, or chloroform [1–4]. The method is based on the competing interaction of a network-bound crown ether or glyme, N, and a soluble ligand, L, for an ionic solute A^-M^+ according to the reaction

$$A^-M^+N + L \overset{K}{\rightleftarrows} A^-M^+L + N \qquad (1)$$

Thus, a relative scale of cation affinities of crown ethers, glymes, polyamines and other cation-binding ligands were obtained. Moreover, in solvents like dioxane [1] the binding constants, K_N, of ionic solutes to crown or glyme containing networks can be obtained directly. Their values, combined with the K value of a ligand, L, yields the complex formation constant, K_L, of the reaction $A^-M^+ + L$.

Crown ether selectivites towards cations in low polarity solvents have been obtained chiefly with the picrate chromophore as counterion because of its solubility in these media and its

convenient spectrophotometric properties. Ion pairing is prevalent in these solvents. Hence, crown complexes are formed with the ion pair, and the counteranion is expected to play an important role. Data on the anion dependence of crown ether selectivities are not abundant. Therefore, the competition method was used to measure K values of a series of 18-crown-6- and 15-crown-5-type crown ethers for 8-anilinonaphthalene-1-sulfonate (ANS) and some other sulfonates in toluene and dioxane. When compared with picrate salts, the results reveal some remarkable reversals in ligand affinities on changing the counterion, especially for the 18-crown-6 ligands with the sodium salts in dioxane.

2. Experimental

2.1. MATERIALS

Sodium and potassium 8-anilinonaphthalene-1-sulfonate (ANS) were prepared by neutralizing the acid in a 10 : 1 ethanol-water mixture. After solvent removal the solid was recrystallized from ethanol-benzene (5 : 1 v/v) and dried for 24 h in vacuo at 70°C. Sodium 5-dimethylamino-1-naphthalene sulfonate (DNS) was obtained by neutralizing the acid in a 1 : 1 ethanol-water mixture and drying the recrystallized solid for 24 h in vacuo at 100°C. Sodium methyl orange (MO) was an Aldrich product while pure anhydrous picrate salts (Pi) were available in our laboratory [1]. Dioxane was distilled from $LiAlH_4$ and toluene from calcium hydride.

The following crown ethers were used: 18-crown-6 (18C6), dicyclohexano-18-crown-6 (DCH18C6), 4′-methylbenzo-18-crown-6 (MB18C6), dibenzo-18-crown-6 (DB18C6), 4,4′-dimethyldibenzo-18-crown-6 (DMB18C6), 4,4′-di-*t*-butyldibenzo-18-crown-6 (DtBuB18C6), 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 4′-methylbenzo-15-crown-5 (MB15C5), and dibenzo-15-crown-5 (DB15C5). Compounds 18C6, DCH18C6, and 15C5 were acquired from Aldrich, while all other crown ethers were purified materials previously synthesized in our laboratory.

2,3-[4-(*N*-methylamino)methylbenzo]-1,4,7,10,13,16-hexaoxacyclooctadec-2-ene or 4′-(*N*-methylamino)methylbenzo-18-crown-6 (I). To 5.1 g of 4′-formylbenzo-18-crown-6 [5,6] in 50 ml benzene was added 800 mg methylamine in 9 ml benzene. Upon standing, water separated out. The mixture was then refluxed for 6 h using a water separator, and eventually the benzene evaporated, yielding an oil which crystallized on standing. The IR did not show any carbonyl. This residue was dissolved in 600 ml of absolute ethanol and stirred overnight with 600 mg $NaBH_4$. The mixture was then added to an equivalent amount of water and made weakly acidic with 50% acetic acid. Most of the ethanol was distilled off, the aqueous solution then made basic with NaOH and extracted with chloroform. The chloroform was dried with Na_2SO_4 and the solvent removed. The IR of the residue which was not further purified agreed with the expected product.

2.2. RN18C6 NETWORK

7.0 g chloromethylated polystyrene (Bio-Rad SX-2, 0.9 mequiv of Cl/g, 2% cross-linked, 200–400 mesh, porosity 5 ml/g in benzene) was treated with a 50 ml dimethylformamide solution of 5 g of I (about a 2× excess) and 600 mg $NaHCO_3$. The reaction mixture was stirred for seven days at 70°C, the resin then removed by filtration, washed with dimethylformamide and with dioxane-water mixtures and finally extracted with THF in a soxhlet [5]. The white powder was dried in vacuo at 80°C until constant weight. The total weight increase

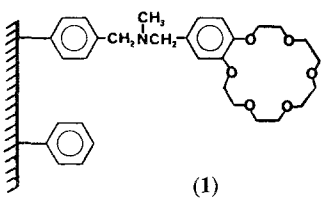
was close to the theoretical value, and incorporation of crown ether was indicated from the IR spectrum. The crown content of RN18C6 as determined by binding of potassium picrate in dioxane under saturation conditions (1) was found to be 0.70 meq/g [1].

2.3. MEASUREMENTS

The equilibrium constant, K, of the reaction A^-M^+, RN18C6 + $L \rightleftarrows A^-M^+L$ + RN18C6 was measured by adding first a sufficient amount of network (usually 1–5 mg) to the dioxane or toluene solution of A^-M^+ to bind most of this salt (in toluene, a small amount of ligand, L, was used to solubilize A^-M^+, hence all A^-M^+ is present in the form A^-M^+L). After reaching equilibrium, the unbound solute was measured spectrophotometrically. Known quantities of ligand L were now added to release the RN18C6-bound solute, and each time the concentration of A^-M^+L was measured after establishing equilibrium ($\approx$ 1 h). Molar absorptivities were determined for the salts and their complexes. In dioxane their values are: ε_m = 7300 for NaANS, λ_m 377 nm, and between 7700 and 8400 for the crown complexes; ε_m = 7100 for KANS, λ_m = 375 nm, and between 7200 and 8000 for the crown complexes; ε_m = 5100 for NaDNS, λ_m = 327 nm, and for the crown complexes ε_m = 5350–5480, λ_m = 319 nm; for NaMO, ε_m = 16,500, λ_m = 414 nm for both the free salt and its crown complexes. In toluene, NaANS crown complexes have ε_m = 7300 at λ_m = 377 nm, and for the potassium complexes ε_m = 7100, λ_m = 377 nm. Data for the picrate salts have been reported elsewhere [1]. Additional details of the competition method can be found in [1].

3. Results

The structure of the RN18C6 network (**1**) differs slightly from the benzo-18-crown-6-containing network R18C6 used for picrate salts in previous measurements [5] in that the



(1)

$-CH_2N(CH_3)CH_2-$ spacer is substituted for the $-CH_2OCH_2-$ group. The binding constants, K_N, of sodium ANS, DNS and Pi, and of potassium ANS and Pi to RN18C6 in dioxane were determined by equilibrating the respective salts with the resin at different salt concentrations (poor solubility of methyl orange in dioxane prevented us from determining its K_N value). The results were plotted in the form of a Klotz plot $1/R = 1/n + 1/nK_NA$, where $1/R$ denotes the ratio of total crown in the RN18C6 resin to bound solute, A is the concentration of free solute, K_N the intrinsic binding constant and $1/n$ the number of crown ligands in the crown-solute complex. The latter has a value of unity for the benzo-18-crown-6 complex with Na^+ and K^+. The plots shown in Figure 1 are similar to those previously obtained for picrate salts with R18C6 and other crown-containing networks [5]. Since $1/n$ = 1, the inverse of the slope equals K_N. Their values are listed in Table I, together with those for sodium and potassium picrate with R18C6, the standard deviation being about 5%. The latter are approximately 10% below those found with the RN18C6 resin. This means that the K value of the competition equilibrium (1) for a ligand L will be slightly lower when measured with

RN18C6 than with the resin R18C6 since $K = K_L/K_N$, K_L being the formation constant of the A^-M^+L complex in the solvent used. A similar behavior is expected in toluene. The insolubility of picrate salts in this solvent prevents a determination of K_N, but the K values of crown ethers with RN18C6 were found to be about 10% lower than with R18C6. For example, for the system KPi/MB18C6, K is 0.60 with R18C6 [1] and 0.53 with RN18C6 [7], while the respective values for KPi/18C6 are 4.09 [1] and 3.62 [7].

The experimental data for Reaction (1) can be plotted in the form

$$(1/F_2) - 1 = K[(1/F_1) - 1] \tag{2}$$

where F_1 denotes the fraction of soluble ligand L bound to A^-M^+, and F_2 is the fraction of RN18C6-bound crown complexed to A^-M^+(1). In toluene the complex A^-M^+L is the only species present in solution. Hence, F_1 and F_2 can be easily calculated. In dioxane some free A^-M^+ is often present although sufficient network is used to bind most of the A^-M^+ before L is added. If no correction is made for the presence of A^-M^+, the value of $1/F_1$ will be too low, especially at low ligand concentration, since the optical spectrum measures the sum of A^-M^+ and A^-M^+L. However, the amount of free A^-M^+ can easily be computed from the expression $1/[A^-M^+] = K_N[(1/F_2) - 1]$ [1]. This correction was applied for all plots of Equation (2) where dioxane was the solvent. The results can also be plotted according to Equation (3)

$$[(1/F_2) - 1)]A_m = 1/K_N + KL \tag{3}$$

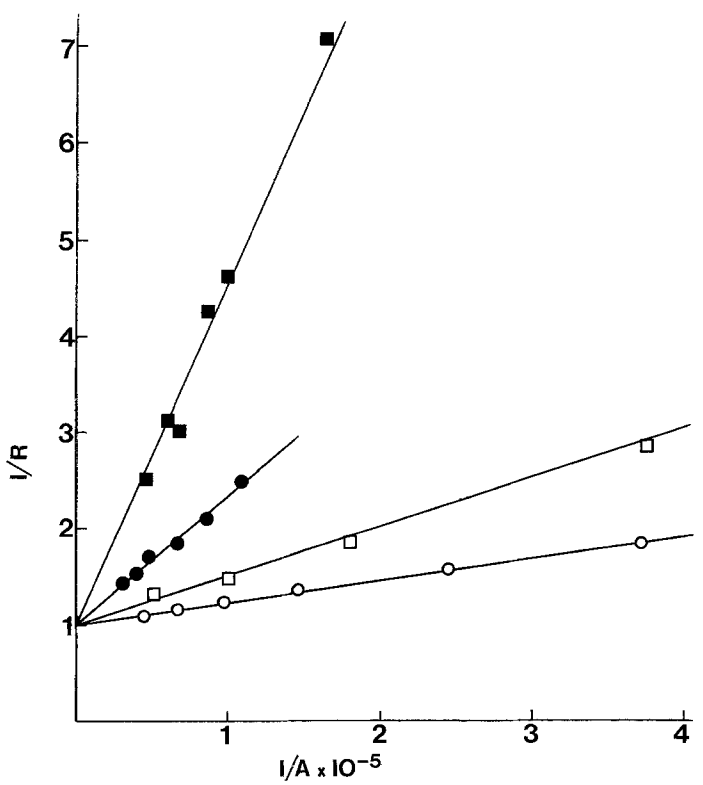


Fig. 1. Binding of sodium ANS (●), potassium ANS (○), sodium picrate (■) and potassium picrate (□) to the benzo-18-crown-16-containing polystyrene network RN18C6 in dioxane at 25°C.

Table I. Binding constants, K_N, of sodium and potassium ANS, DNS and picrate to RN18C6 and R18C6 in dioxane at 25°C

Network	Salt	$K_N \times 10^{-4}\ M^{-1}$	Reference
RN18C6	NaANS	7.46	[this work]
	NaDNS	9.3	[this work]
	NaPi	2.78	[this work]
	KANS	45.5	[this work]
	KPi	19.0	[this work]
R18C6	NaPi	2.58	[1]
	KPi	17.2	[1]

where A_m is the total salt concentration in solution ($A^-M^+ + A^-M^+L$) and the concentration of free ligand $L = L_0 - A_m + 1/K_N[(1/F_2 - 1)]$ [1], L_0 being the total concentration of added ligand. A plot of the left-hand side of Equation (3) versus L should yield a straight line with slope K and intercept $1/K_N$.

A number of representative plots of Equations (2) and (3) are shown in Figures 1–6. In plotting Equation (3) the known $1/K_N$ value of the system was taken as the intercept. K values derived from the slopes of the respective plots are collected in Table II. Standard deviations in these values average about 5%. Data obtained previously for some crown ether-picrate systems by means of the R18C6 network [1] are also included. They have been converted to give numbers based on RN18C6 in order to allow comparison with K values obtained directly with RN18C6. This was done by means of the relationship $K(RN18C6)/K(R18C6) = K_N(R18C6)/K_N(RN18C6)$ and using the K_N values of Table I.

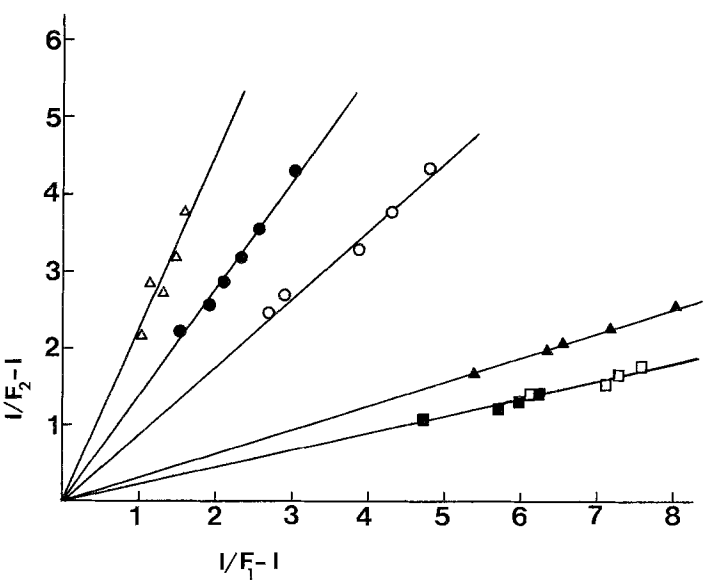


Fig. 2. Plots of Equation (2) for release of RN18C6-bound sodium ANS in dioxane on addition of DB18C6 (△), DMB18C6 (●), DtBuB18C6 (○), MB18C6 (▲), 18C6 (■) and DCH18C6 (□).

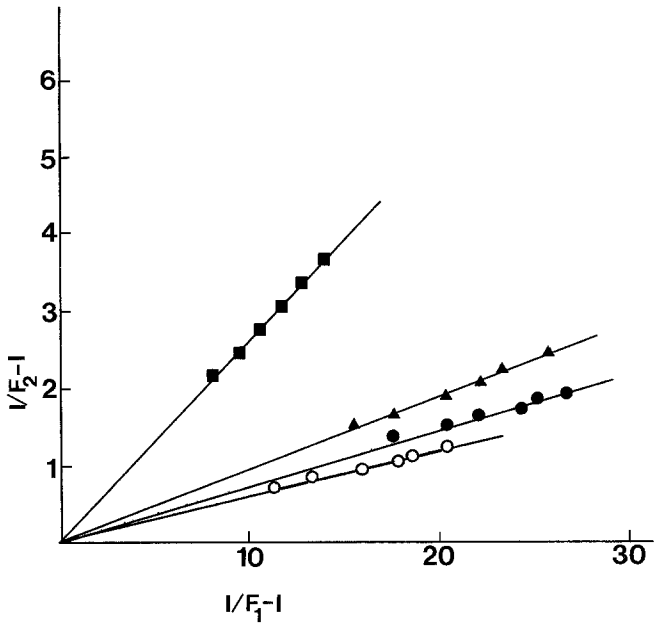


Fig. 3. Plots of Equation (2) for release of RN18C6-bound sodium ANS in toluene on addition of 18C6 (■), MB18C6 (▲), DMB18C6 (●) and DtBuB18C6 (○).

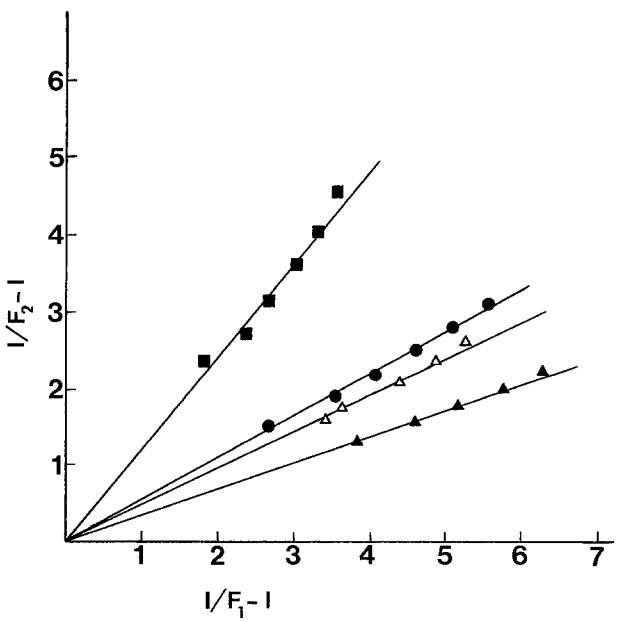


Fig. 4. Plots of Equation (2) for release of RN18C6-bound potassium ANS in dioxane on addition of 18C6 (■), DMB18C6 (●), DB18C6 (△) and MB18C6 (▲).

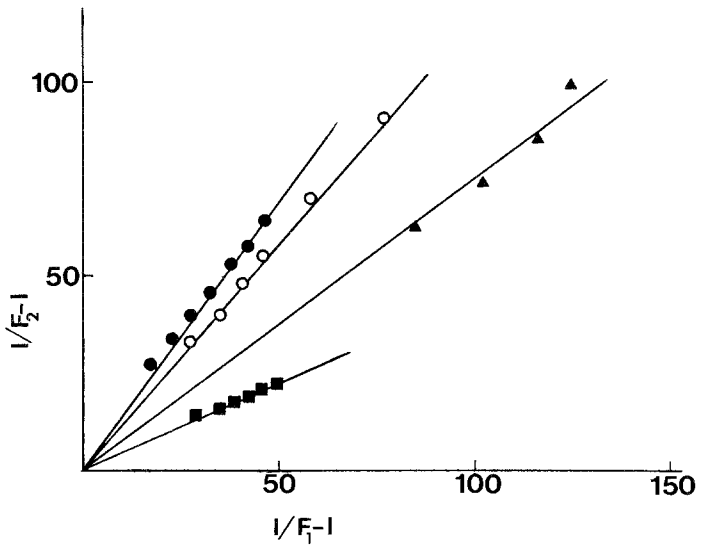


Fig. 5. Plots of Equation (2) for release of RN18C6-bound sodium methyl orange in dioxane on addition of DMB18C6 (●), DtBuB18C6 (○), MB18C6 (▲) and 18C6 (■).

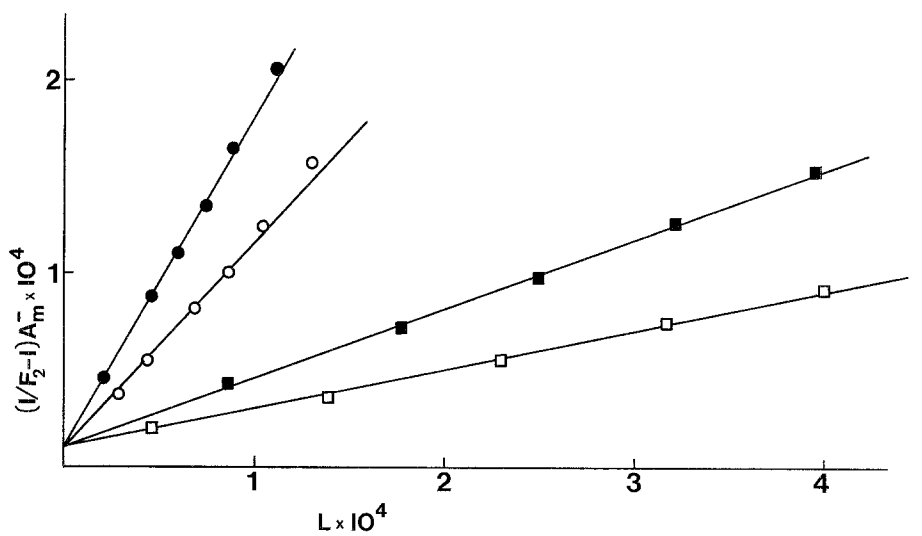


Fig. 6 Plots of Equation (3) for release of RN18C6-bound sodium DNS in dioxane on addition of DMB18C6 (●), DtBuB18C6 (○), 18C6 (■) and DCH18C6 (□).

The formation constants, K_L, of the $A^- M^+ L$ complexes in dioxane can be calculated from the expression $K_L = KK_N$. Their values are given in Table III. For comparing selectivities of a series of ligands with respect to a particular ion or ion pair either K or K_L values can be used. Only the latter permit a comparison between the interaction of a particular ligand with various salts.

Table II. Equilibrium constants, K, of the reaction A^-M^+, RN18C6 + L $\rightleftarrows$ A^-M^+L + RN18C6 for sodium and potassium ANS, DNS, methyl orange and picrate in dioxane and toluene at 25°C

	Dioxane						Toluene	
	ANS		Pi		DNS	MO	ANS	Pi
Ligand (L)	Na^+	K^+	Na^+	K^+	Na^+	Na^+	Na^+	Na^+
18C6	0.23	1.20	1.24[a]	5.09[a]	0.35	0.45	0.25	1.13[a]
DCH18C6	0.23	0.50	0.93[a]	2.83[a]	0.20			1.11[a]
MB18C6	0.32	0.32	0.72[a]	0.82[a]	0.38	0.71	0.094	0.60[a]
DtBuB18C6	0.87	0.35	0.51	0.41	1.06	1.20	0.060	0.095
DMB18C6	1.41	0.55	0.49	0.54[a]	1.70	1.40	0.073	0.112[a]
DB18C6	2.27	0.47	0.68	0.41			0.100	0.074
15C5	0.073	0.0059	2.6[a]					
MB15C5	0.056	0.0147	0.69[a]		0.15			1.75
B15C5	0.048	0.0052					0.167	0.75
DB15C5	0.011	0.0014						

[a] These values were calculated from data obtained previously with a different benzo-18-crown-6 network (R18C6, see reference [1], and the results-section of this paper).

Table III. Formation constants, K_L, for crown ether complexes of sodium ANS, DNS, and picrate and for potassium ANS and picrate in dioxane at 25°C

	$K_L \times 10^{-4}\ M^{-1}$				
Crown ether	NaANS	KANS	NaPi	KPi	NaDNS
18C6	1.72	54.6	3.46	96.7	3.24
DCH18C6	1.72	22.8	2.58	53.8	1.85
MB18C6	2.39	14.6	2.00	15.6	3.52
DtBuB18C6	6.49	15.9	1.42	7.8	9.82
DMB18C6	10.5	25.0	1.36[a]	10.2	15.7
DB18C6	16.9	21.4	1.89	7.8	
15C5	0.54	0.27	7.22		
MB15C5	0.43	0.67	1.91		1.39
B15C5	0.36	0.24			
DB15C5	0.082	0.064			

[a] The K_L value reported previously for this system [1] was too low due to an impure sample of DMB18C6 [4].

4. Discussion

Formation constants of crown ether or cryptand complexes with ion pairs in apolar media are frequently too high to measure directly. In such systems the competitive equilibrium method using ligands immobilized on solvent-swollen networks is very effective. This is especially the case when the transformation of the ion pair solute A^-M^+ into a crown ether complex is not accompanied by a shift in the optical spectrum of A^-. Since no spectral shifts occur on complexing ANS or DNS with crown ethers, the method is especially appropriate for these solutes.

The data of Table I reveal that the binding constants of sodium and potassium ANS to RN18C6 exceed those of the corresponding picrate salts by about a factor of 2.5. The K_N for sodium DNS is more than thrice that of sodium picrate. This anion dependence on the binding constant of a *network-bound* crown ether to ion pairs with a common cation is also evident with *soluble* crown ethers. While the formation constants, K_L, for MB18C6 complexes with NaANS and NaPi in dioxane are nearly the same, the K_L for the DMB18C6 complex with NaANS is nine times higher than that for NaPi, and the K_L for the 15C5 complex with NaANS is 13 times *less* than for NaPi. In fact, the most striking result of our studies is the reversal in the affinities of 18-crown-6-type ligands for NaANS and NaPi in dioxane (K or K_L values in Tables II and III). The complexing ability of these ligands for NaANS increases in the order 18C6 = DCH18C6 < MB18C6 < DtBuB18C6 < DB18C6, the total difference in K_L (or K) being a factor of 10. For NaPi the sequence is DMB18C6 ≈ DtBuB18C6 < DB18C6 ≈ MB18C6 < DCH18C6 < 18C6, the total spread in K_L values being only a factor of 2.5. With minor variations the complexation order with NaDNS and NaMO resembles that of NaANS. DB18C6 and DMB18C6 in dioxane are much better complexing agents for the three sodium sulfonates than is 18C6, while the reverse is true when picrate is the counter anion. The reversal in the order of complexation in dioxane is not found with the potassium salts. However, while for KPi the K_L with 18C6 is 12 times higher than that with DB18C6, the difference is only a factor of 2.5 for KANS. The complexation sequence for the 18-crown-6 compounds in toluene (Table II) is the same for NaANS and NaPi. For the latter salt 18C6 is better than DB18C6 by a factor of 15.

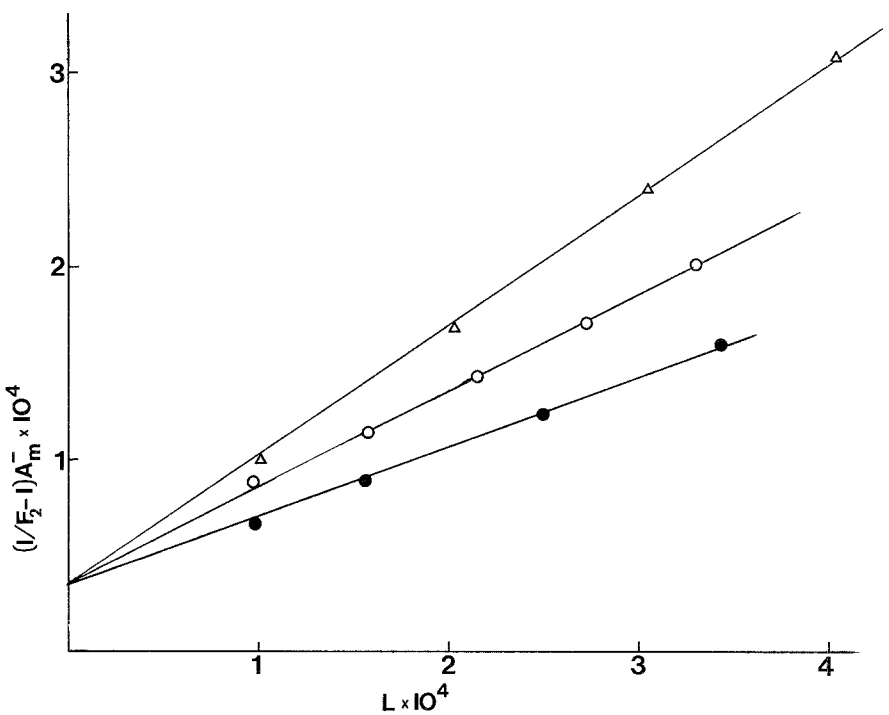


Fig. 7. Plots of Equation (3) for release of RN18C6-bound sodium picrate in dioxane on addition of DB18C6 (△), DtBuB18C6 (○) and DMB18C6 (●).

In trying to rationalize these complexation data it should be remembered that formation constants of ion pair-crown ether complexes not only depend on the nature and structure of the cation, ligand and solvent but also on that of the anion. Effective interaction with the crown ether binding sites often requires penetration of the cation into the crown ether cavity, or a wrapping of the ligand around the cation. This necessitates a stretching of the interionic ion pair distance, a process which is favored when the anion is more charge delocalized. Cation penetration into the crown ring will be hindered when bulky substituents close to the anionic site interfere with the crown ether molecule, as might be expected to occur in picrate salts.

We propose that the reversal in the complexation order of the 18-crown-6 ligands with the three sodium sulfonates *vis à vis* sodium picrate in dioxane is the result of a synergistic effect exerted by dioxane as it interacts with the ion pair-crown ether complex. In earlier work dealing with the structure of crown ether complexes of fluorenyl salts in ethereal solvents we demonstrated by optical spectroscopy and other means the existence of crown ether-complexed tight and loose ion pairs denoted by A^-M^+Cr and A^-CrM^+ [8,9]. The ratio A^-CrM^+/A^-M^+Cr of the two isomeric complexes strongly varies with solvent. For the system sodium fluorenyl – MB15C5 its value at 25°C is zero in ethyl ether (i.e., only tight ion pairs), 0.52 in tetrahydropyran and 1.8 in tetrahydrofuran. The shift to crown-complexed loose ion pairs is caused by the interaction of one or more solvent molecules with the cation of the A^-CrM^+ complex.

$$A^-CrM^+ + nS \rightleftarrows A^-CrM^+S_n \tag{4}$$

The formation of the solvated species $A^-CrM^+S_n$ is facilitated when the cation can easily penetrate the crown cavity. When the crown is externally complexed to the ion pair as in A^-M^+Cr the solvent cannot come sufficiently close to the cation. Cation penetration is difficult when the diameter of the cation exceeds that of the crown cavity. In such cases formation of sandwich-type 2 : 1 crown-ion pair complexes, A^-CrM^+Cr, often occurs at higher crown concentrations. This is observed for complexes of 15-crown-5-type ligands with potassium fluorenyl [9] and potassium picrate [10]. Cation-solvent interactions are stronger for small cations, one reason why MB18C6 and fluorenyl sodium in THF form only loose crown-complexed ion pairs, while a mixture of tight and loose ion pairs are found with the potassium salt [9].

Spectral changes for the alkali picrates on complexing crown ethers provide some information on the structure of the ion pair complex [10]. The absorption maximum λ_m for NaPi in dioxane is 347 nm and for KPi 349 nm. The crown-complex separated ion pair has its λ_m at 377–380 nm [9,11]. The complexes of NaPi and KPi with the 18-crown-6-type compounds in dioxane or toluene all have their absorption maximum at 360 nm while those of 15C5 and MB15C5 with NaPi in dioxane are reported to be at 352 nm [1]. Apparently very little stretching of the interionic ion pair distance takes place in the tight ion pair of Pi^-Na^+ on complexing a crown ether with a 15-crown-5 cavity. More stretching occurs when an 18-crown-6 type ligand is used, but it is considerably less than for a loose ion pair. No spectral changes are found on complexing ANS, DNS or MO with crown ethers, hence, optical spectroscopy in these systems does not provide information on changes in ion pair structures. Dipole moment measurements in octanoic acid on crown ether complexes with potassium-p-toluenesulfonate show an increase in the K^+TsO^- distance of 0.5 Å for the complex with DB18C6 and of only 0.15 Å for that with cyclohexyl-15-crown-5 [12]. It appears that in low polarity solvents crown-complexed tight ion pairs are the predominant species with picrate and sulfonate salts, although partial ion separation is evident.

Let us now return to the proposed rationalization of the reversal in the complexation order of 18-crown-6-type ligands in dioxane. Since dioxane is a good alkali ion binding solvent it favors formation of $A^- CrM^+ S_n$-type complexes where S now is dioxane. The formation of these complexes promotes the release of salt from the network as Equilibrium (1) is shifted further to the right. As argued, dioxane complexation with the cation will be facilitated in systems where the cation can penetrate the crown cavity. This is likely to be an easier process with a rather rigid, planar crown ether like DB18C6 than with the more flexible 18C6. The latter crown compound is more wrapped around the cation, and the oxygen binding sites all have similar basicities. This is not the case with DB18C6, and the cation may prefer a dioxane oxygen atom as one of its binding sites. The restricted motions in DB18C6 will keep this crown in a rather planar conformation, and stretching of the $A^- M^+$ ion pair distance need not be large in order for the cation to penetrate and bind a dioxane molecule. Hence, the synergistic effect of dioxane is expected to increase in the order 18C6 < MB18C6 < DB18C6. We expect it to be larger for the sulfonates since the bulky ortho-nitro substituents in the picrate anion interfere with the cation penetration in the crown cavity, and prevents the close approach of a dioxane molecule. Since dioxane interaction with the K^+ ion is weaker than with the smaller Na^+ ion the synergistic effect found with NaANS is much less pronounced for KANS. No reversal in complexing power of the crown ethers was found for KANS *vis à vis* *K*Pi, but the effect of dioxane is not nil since the K_L for KANS with DB18C6 is only 2.5 times less than for 18C6, while for Pi*K* the difference is a factor of 12.

The synergistic effect in the 15-crown-5 series is apparently less significant than for the 18-crown-6 compounds. The formation constant of the DB15C5 complex with NaANS is about six times less than that with 15C5, and the order in K_L values is not very different from that found for *K*ANS. The smaller size of the 15-crown-5 cavity makes cation penetration more difficult. Addition of excess 15-crown-5-type compound often results in the formation of 2 : 1 crown-separated ion pair complexes, especially for potassium salts. This causes the $1/F_2 - 1$ vs $1/F_1 - 1$ plots to curve upward at high crown concentrations as reported for *K*Pi in dioxane with MB15C5 [1]. Under our experimental conditions no such plots were found with *K*ANS. This may suggest that *K*ANS is a tighter ion pair than *K*Pi, making it more difficult to stretch the interionic ion pair distance on complexation with a crown ether. It could also explain the larger K_L values for the 15-crown-5 complexes of NaPi as compared to NaANS.

Synergistic effects involving crown ethers and other ion-binding additives have been reported in a few other studies. For example, tributylphosphate is claimed to enhance the extraction of rubidium and cesium picrate into benzene by 15C5 and 12C4 [13]. Another system concerns the extraction of alkali metals into benzene with a mixture of a crown ether and an apolar liquid cation exchanger such as di(2-ethylhexyl)phosphoric acid [14]. The synergistic effect of the crown compound was found to be optimal for those ions which best fitted the crown cavity. Because of the complexity of extraction systems, a quantitative evaluation of synergistic effects is easier to obtain with the competition method. We have recently carried out experiments in which at constant concentration of DB18C6 increasing quantities of dioxane were added to the system RN18C6/NaANS/DB18C6 in toluene. While in the absence of DB18C6 the added dioxane did not release the RN18C6-bound NaANS into the toluene, with DB18C6 present dioxane caused a rapid increase in the amount of NaANS released from the network in the form of a 1 : 1 dioxanate of the DB18C6 complex of NaANS. The formation constant of this complex (Equilibrium (4)) was found to be 3.5 M^{-1}. Other complexing agents such as tetrahydrofuran or dimethylsulfoxide are also being explored. The detailed results of these studies will be reported elsewhere.

In an earlier publication on the complexation of picrate salts to soluble and immobilized crown ethers our results suggested that the formation constant of a crown-salt complex is not greatly changed by anchoring the crown ether to a network such as cross-linked polystyrene. For example, the K values for RN18C6/MB18C6 in either dioxane or toluene for both NaPi and KPi all fall between 0.5 and 1.0, (Table II and [1]). The similarity in the crown structures of MB18C6 and RN18C6 (or R18C6) made this result plausible. However, the result for NaANS and KANS suggest that the above conclusion cannot be generalized. K for RN18C6/MB18C6 is 0.32 for NaANS and KANS in dioxane and only 0.094 for NaANS in toluene! Table I shows that the low K values for NaANS and KANS in dioxane result from their higher binding constants to RN18C6. We already alluded to this result at the start of our discussion without attempting an explanation. Since K_N values are higher by about the same factor for NaANS, KANS and NaDNS we suspect that the enhanced binding is caused by a difference in the interactions between the respective anions with the polystyrene network. Recent measurements in which MB18C6 was replaced by a linear random copolymer of styrene and vinylbenzo-18-crown-6 (10 : 1 molar ratio) as soluble ligand showed some increase in the K value for NaANS, especially in dioxane (a factor of 1.7) while that for KPi remained nearly the same. Hence, incorporation of the crown into a linear polystyrene chain has some effect on the NaANS binding constant, but it is not sufficient to explain the entire increase in K_N, or the low K value in toluene for MB18C6. Interionic interactions between resin-bound ion pairs would also increase K_N, but measurements at different degrees of salt saturation of the resin did not affect the linearity of the $1/F_2 - 1$ vs $1/F_1 - 1$ plots or the K values from these plots. It may be that the ANS molecule can be partially inserted in between the monomer units of the polystyrene backbone and some additional stability derived from this. However, measurements with other alkali salts are needed to find a more satisfactory explanation for the anion effect on the K_N values. A larger interionic ion pair distance will increase K_N. This is the reason for the high K_N of $NaBPh_4$ to R18C6 in dioxane which was reported to be at least fifteen times larger than for NaPi [5]. Conductance measurements on crown complexes of NaANS and NaPi in ethereal solvents may provide better information on the interionic ion pair distance in these species.

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