Substituent Effects on the Stability of Cation Complexes of 4′-Substituted Monobenzo Crown Ethers

R. Ungaro, B. El Haj, and J. Smid*

Contribution from the Chemistry Department, State University of New York, College of Environmental Science and Forestry, Syracuse, New York 13210.

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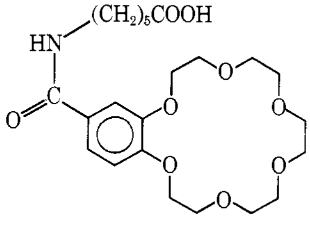
Abstract: Formation constants, *K*, and single ion conductances, Λ_c, of complexes of Na^+ and K^+ with a series of 4′-substituted monobenzo-15-crown-5 and monobenzo18-crown-6 ligands were determined conductometrically in acetone at 25 °C. For the complexes of Na^+ with benzo-15-crown-5 ligands a 25-fold difference in *K* is observed between the 4′-amino and 4′-nitro derivative. A good Hammett correlation is found by plotting log *K* vs. $\sigma_p^- + \sigma_m$ for nine 4′-derivatives, the ρ value being −0.45. The substituent effect in Na^+/benzo-18-crown-6 complexes is much smaller, and almost negligible for electron withdrawing substituents. No Hammet correlation is found. It is argued that in this system the pronounced difference in the diameters of cation and crown cavity causes the distance between the cation and the aromatic oxygen atoms to change as a function of the nature of the substituent, which in turn can induce conformational changes in the polyether ring. Substituent effects are somewhat larger for K^+/benzo-18-crown-6 complexes, but again no linear Hammett plot is obtained. In mixtures of K^+ with monobenzo-15-crown-5, 1:1 and 2:1 crown-cation complexes can exist simultaneously, and, although no *K* values could be calculated, substituent effects on the complexation are quite pronounced.

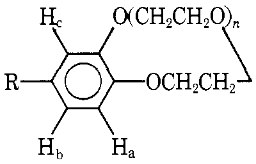
Since Pedersen's initial observations[1,2] on the affinity of macrocyclic polyethers to alkali and alkaline earth cations, several new types of ligands of similar structure have been synthesized to increase the stability of the cation-crown complex or to improve the cation selectivity of the ligand.[3,4] In several instances additional binding sites were attached to the crown ether in the form of neutral or ionic groups.[5,6] In studying one of these ligands, shown below we found that the complex formation constant of this 4′ derivative of monobenzo-18-crown-6 to K^+ ions in acetone was about eight times lower than that for 4′-methylbenzo-18-crown-6. It has been argued[2,7] that substitutions on the ring influence the complex stability to a lesser extent than a change in the ring size of the crown ether. However, recently reported data on the binding of 4,4′-dinitro- and 4,4′-diaminodibenzo-18-crown-6 to Na^+ in dimethylformamide revealed significant substituent effects.[8,9] Since additional binding sites are often attached to the crown ligand via a functional group[5,6] it is important to determine the effect that such a substituent exerts on the stability of the complex in order to properly evaluate the contribution of the additional binding site to the complex formation constant. A similar problem arises when comparing the binding characteristics of crown ligands attached to a macromolecule[10,11] with that of the crown ligand itself. In the case of the benzo crown ethers the ligand is attached to the polymer at the 4′ position, e.g., in the polymer derived from 4′-vinylbenzo-15-crown-5 or polymers derived from benzo-crown esters of methacrylic acid.



In this work we report the synthesis and complex formation constants to Na^+ and K^+ in acetone, of a series of 4′-substituted benzo-15-crown-5 and benzo-18-crown-6 ligands. The data, obtained by conductometry, reveal substituent effects which are often considerably larger than the ring size effect, especially for the system Na^+/benzo-15-crown-5, where a good Hammett relationship is found.

Experimental Section

Synthesis of 4′-Substituted Monobenzo Crown Ethers. The general structure of the substituted benzo-15-crown-5 (n = 3) and benzo-18-crown-6 (n = 4) compounds is depicted below. The synthesis and physical properties of the unsubstituted benzo crown ethers and of the two 4′-methyl derivatives have been reported previously.[1,12] The prepartion of 4′-carboxybenzo-15-crown-5 and its methyl ester have also been described.[13]



2,3-(4′-Nitrobenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene or 4′-Nitrobenzo-15-crown-5 (I). The synthesis of this compound closely follows that reported for 4,4′-dinitrodibenzo-18-crown-6.[14] To 25 g (0.093 mol) of monobenzo-15-crown-5 (II) dissolved in a mixture of 350 ml of chloroform and 300 ml of acetic acid, 85 ml of nitric acid (70%) was added dropwise over a 30 min period. The mixture was stirred for 24 h at room temperature, then neutralized with aqueous Na_2CO_3 and the chloroform layer separated. The aqueous layer was extracted with $CHCl_3$, and the combined chloroform extracts were dried over $MgSO_4$. After evaporation of $CHCl_3$ a yellow solid was obtained which, upon recrystallization from ethanol, yielded 22.7 g (77%) of pure compound, mp 84–85 °C. NMR ($CDCl_3$) δ 3.6–4.4 (m, 16, $-CH_2-$), 6.8 (d, 1, H_a), 7.65 (d, 1, H_c), 7.8 (dd, 1, H_b, J_{ab} = 9 Hz, J_{bc} = 3 Hz).

Anal. Calcd for $C_{14}H_{19}NO_7$: C, 53.67; H, 6.11; N, 4.47. Found: C, 53.81; H, 6.06; N, 4.47.

2,3-(4′-Nitrobenzo)-1,4,7,10,13,16-hexaoxacyclohexa-deca-2-ene or 4′-Nitrobenzo-18-crown-6 (III). This compound was prepared from monobenzo-18-crown-6 (IV) according to the procedure described above for I. It was obtained in 56% yield after recrystallization from isopropyl alcohol, mp 70–72 °C. NMR ($CDCl_3$) δ 3.6–4.4 (m, 20, $-CH_2-$), 6.9 (d, 1, H_a, J_{ab} = 9 Hz), 7.7–8.1 (m, 2, $H_b + H_c$).

Anal. Calcd for $C_{16}H_{23}NO_8$: C, 53.78; H, 6.49; N, 3.92. Found: C, 53.61; H, 6.69; N, 3.84.

2,3-(3′,4′-Dinitrobenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene or 3′,4′-Dinitrobenzo-15-crown-5 (V). To 10 g (0.037 mol) of II dissolved in 200 ml of acetic acid was added 35 ml of 70% nitric acid, and the mixture refluxed for 24 h. After cooling, the solution was neutralized with Na_2CO_3 and 6.7 g of yellow product was recovered as described for I. Repeated recrystallization from ethanol until constant melting point yielded 3.5 g (20%) of light yellow crystals, mp 168 °C.[15] NMR ($CDCl_3$) δ 3.5–4.4 (m, 16, $-CH_2-$), 7.2 (s, 2, arom).

Anal. Calcd for $C_{14}H_{18}N_2O_9$: C, 46.93; H, 5.06; N, 7.82. Found: C, 46.69; H, 5.00; N, 7.55.

2,3-(4'-Aminobenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene or 4'-Aminobenzo-15-crown-5 (VI). A procedure reported for the synthesis of 4,4'-diaminodibenzo-18-crown-6[14] was modified. A solution of 19 g (0.06 mol) of 4'-nitrobenzo-15-crown-5 dissolved in 200 ml of freshly distilled dimethylformamide (DMF) was shaken for 1 h at room temperature in a Parr hydrogenator under a H_2 pressure of 25-35 psi in the presence of 2 g of 10% Pd/C. After the reaction was completed the catalyst was filtered off and the bulk of the solvent removed. Water (250 ml) was added, the mixture extracted with $CHCl_3$, the chloroform layer dried over $MgSO_4$, and the solvent distilled off. A brown oil remained which solidified upon standing. This material (18.4 g, 93%) was quite pure (NMR) but became dark on standing and was further purified by dissolving it in hot isopropyl alcohol, precipitating the dark oil impurities with petroleum ether, and cooling the solution to −10°. The pure 4'-amino compound had a mp of 73-74 °C. NMR ($CDCl_3$) δ 3.2-3.6 (s, broad, 2, NH_2), 3.65-4.2 (m, 16, $-CH_2-$), 6.1 (dd, 1, H_b, J_{ab} = 8 Hz, J_{bc} = 3 Hz), 6.2 (d, 1, H_c), 6.6 (d, 1, H_a).

Anal. Calcd for $C_{14}H_{21}NO_5$: C, 59.35; H, 7.47; N, 4.94. Found: C, 59.94; H, 7.48; N, 4.70.

2,3-(4'-Bromobenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene or 4'-Bromobenzo-15-crown-5 (VII). Under vigorous stirring, 20.5 g of *N*-bromosuccinimide was added to a solution of 30 g (0.11 mol) of II in 100 ml of CCl_4. After refluxing for 1 h the reaction mixture was cooled and filtered and the solid washed with CCl_4. The oily residue obtained after evaporation of the combined filtrates was recrystallized from *n*-heptane to yield 22.2 g (57%) of a white solid, mp 66-68 °C. NMR ($CDCl_3$) δ 3.7- 4.2 (m, 16, $-CH_2-$), 6.75 (d, 1, H_a, J_{ab} = 9 Hz), 6.9-7.2 (m, 2, $H_b + H_c$).

Anal. Calcd for $C_{14}H_{19}BrO_5$: C, 48.43; H, 5.52. Found: C, 48.46; H, 5.37.

2,3-(4'-Formylbenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene or 4'-Formylbenzo-15-crown-5 (VIII). Following Pedersen's procedure for the synthesis of II,[1] a solution of 9.5 g (0.069 mol) of 3,4-dihydroxybenzaldehyde (Aldrich) in 200 ml of N_2-purged *n*-butanol was charged with 5.85 g of NaOH in 15 ml of water, heated to reflux, and 15.9 g (0.068 mol) of 1,11-dichloro-3,6,9-trioxaundecane[1] dropwise added over a 10-min period. After 27 h of reflux the mixture was cooled, acidified with 18% HCl, and filtered, the solids washed with methanol, and the combined filtrates evaporated until no 1-butanol could be detected. The oily residue was continuously extracted with hot *n*-heptane, which upon cooling yielded white crystals. After recrystallization from *n*-heptane 8.0 g (40%) of **8** was obtained, mp 78-79°. NMR ($CDCl_3$) δ 3.7-4.3 (m, 16, $-CH_2-$), 6.95 (d, 1, H_a, J_{ab} = 9 Hz), 7.5 (d, 1, H_b), 7.40 (s, 1, H_c), 10.0 (s, 1, CHO).

Anal. Calcd for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 60.72; H, 6.95.

2,3-(4'-Formylbenzo)-1,4,7,10,13,16-hexaoxacyclohexadeca-2-ene or 4'-Formylbenzo-18-crown-6 (IX). This compound was prepared from 3,4-dihydroxybenzaldehyde and 1,14-dichloro-3,6,9,12-tetraoxatetradecane[1] by the same procedure as described for VIII. The product was obtained in 25% yield, mp 60-62 °C. NMR ($CDCl_3$) δ 3.6-4.4 (m, 20, $-CH_2-$), 7.08 (d, 1, H_a, J_{ab} = 9 Hz), 7.50 (s, 1, H_c), 7.50 (d, 1, H_b), 9.95 (s, 1, CHO).

Anal. Calcd for $C_{17}H_{24}O_7$: C, 59.99; H, 7.11. Found: C, 59.60; H, 7.20.

2,3-(4'-Carboxybenzo)-1,4,7,10,13,16-hexaoxacyclohexadeca-2-ene or 4'-Carboxybenzo-18-crown-6 (X). This compound was prepared in 80% yield following the method used for 4'-carboxybenzo-15-crown-5,[13] mp 118-120 °C. NMR ($CDCl_3$) δ 3.7-4.4 (m, 20, $-CH_2-$), 6.95 (d, 1, H_a, J_{ab} = 8.5 Hz), 7.6-7.9 (m, 2, $H_b + H_c$).

2,3-(4'-(*N*-*n*-butyl)-carboxamidobenzo)-1,4,7,10,13,16-hexaoxacyclohexadeca-2-ene or 4'-(*N*-*n*-butyl)carboxyamidobenzo-18-crown-6. To a mixture of 1.07 g of X in 25 ml of chloroform was added dropwise 2 ml of $SOCl_2$. The mixture was refluxed for 3 h, then evaporated to dryness under vacuum. An excess of *n*-butylamine (1 ml) in 30 ml of $CHCl_3$ was added, the mixture refluxed overnight, washed with water, and dried, and the solvent evaporated. After recrystallization of the product from 1:1 heptane/toluene, 1 g (83%) of white crystals was obtained, mp 97-98 °C. NMR ($CDCl_3$) δ 0.7-1.8 (m, 7, $n\text{-}C_3H_7$), 3.2-3.55 (m, 2, $N\text{-}CH_2$), 3.6-4.5 (m, 20, $-OCH_2-$), 6.2 (s, broad, NH), 6.85 (d, 1, H_a, J_{ab} = 8.5 Hz), 7.2-7.5 (m, 2, $H_b + H_c$).

Anal. Calcd for $C_{21}H_{33}NO_7$: C, 61.30; H, 8.08; N, 3.40. Found: C, 61.38; H, 7.82; N, 3.15.

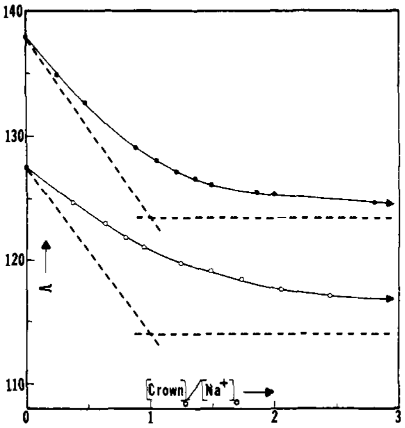


Figure 1. Equivalent conductance of sodium tetraphenylborate in acetone at 25 °C in the presence of crown ethers: ●, methylbenzo-18-crown-6, $[Na^+] = 5 \times 10^{-5}$ M; ○, methylbenzo-15-crown-5, $[Na^+] = 5 \times 10^{-4}$ M.

Conductance Measurements. Spectrograde acetone was purified by refluxing over Linde molecular sieve 5 A for 1 h, then twice distilled under nitrogen, collecting only middle fractions. Sodium tetraphenylborate (Fisher, 99.5% purity) was dried under vacuum for 24 h. The synthesis of the potassium salt has been described previously.[16] In experiments with benzo-15-crown-5 derivatives the salt concentration was kept constant at 5×10^{-4} M, and at 5×10^{-5} M in experiments with benzo-18-crown-6 compounds. In the former system crown ether could be added accurately as a solid. With the benzo-18-crown-6 derivatives aliquots of a solution with a crown to salt ratio of three to five were pipetted into a conductance cell (cell constant 0.0307 cm^{-1}) containing a known volume of salt solution of the same concentration as the crown-salt mixture. All transfer of solvent and preparation of samples were performed under dry nitrogen. Conductances were measured by means of a 1673 General Radio Corporation automatic capacitance bridge coupled with a 1672 digital control unit. Readings were recorded at 7 to 12 crown to salt ratios and corrected for solvent conductance (0.5-1 μmho). Conditions were chosen such that in all systems the fraction of complexed cations varied over a range of at least 0.2-0.8.

Results

Association to ion pairs in acetone at 25 °C is negligible for alkali tetraphenylborates below 10^{-3} M.[17] The drop in conductance on addition of crown can, therefore, be attributed to a lower mobility of the cation-crown complex, the change being sufficiently large to determine complex formation constants with reasonable accuracy.[9,18] In such systems the conductance Λ is given by

$$\Lambda = \alpha\Lambda_f + (1 - \alpha)\Lambda_c \qquad (1)$$

where Λ_f and Λ_c are the respective equivalent conductances of the free salt and its crown complex (it is assumed that only one crown complex is formed), and α denotes the fraction of free cations. The latter quantity and the complex formation constant, K, are related by the expression.[18]

$$\alpha = [-\{K(C_0 - A^-) + 1\} + (\{K(C_0 - A^-) + 1\}^2 + 4KA)^{-1/2}]/(2KA^-) \qquad (2)$$

where C_0 and A^- are the total concentrations of crown ether and salt, respectively. Since the salt concentration is kept constant, no corrections for interionic interactions are needed, assuming that changes in such interactions are negligible when the solvated cation is converted into a crown complexed cation.

Two examples of plots of Λ vs. the ratio of total crown to total salt are depicted in Figure 1 and reveal a smooth de-

Table I. Formation Constants of Complexes of Na^+ and 4′-Substituted Benzo-15-crown-5 in Acetone at 25 °C. $[NaBPh_4] = 5 \times 10^{-4}$ M

4′-Subst.	Λ_c[a]	Stand. dev Λ_c	Λ_c^+	Λ_f^+/Λ_c^+[a]	M_r, cm^3/mol	$10^{-3}K$, M^{-1}	Stand. dev ($K \times 10^{-3}$)	$\sigma_p + \sigma_m$[b]	$\sigma_p^- + \sigma_m$[b]
NH_2	111.3	0.23	55.1	1.29	5.42	8.21	0.8	−0.82	−0.82
CH_3	114.0	0.39	57.8	1.23	5.65	3.96	0.44	−0.24	−0.24
H	115.5	0.37	59.3	1.20	1.03	3.44	0.47	0	0
Br	111.9	0.28	55.7	1.28	8.88	2.05	0.13	0.62	0.62
COOH	107.0	0.24	50.8	1.40	6.93	1.61	0.06	0.77	1.08
$COOCH_3$	108.4	0.29	52.2	1.36	12.87	1.23	0.05	0.79	1.10
CHO	110.9	0.32	54.7	1.30	6.88	1.11	0.05	0.79	1.34
NO_2	108.2	0.61	52.0	1.37	7.36	0.365	0.02	1.50	1.94
3′,4′-dinitro	103.1	1.61	46.9	1.52	—	0.15	0.02	3.00	—

[a] Λ_c values expressed in $ohm^{-1}\ cm^2\ equiv^{-1}$; Λ_f at 5×10^{-4} M $NaBPh_4$ is 127.4 ± 0.3; $\Lambda_f^+ = 71.1$. [b] σ_p and σ_m values were taken from ref 28, σ_p^- values from ref 29.

Table II. Formation Constants of Complexes of Na^+ and K^+ with 4′-Substituted Benzo-18-crown-6 in Acetone at 25 °C. $[Salt] = 5 \times 10^{-5}$ M

	Na^+				K^+			
4′-Subst.	Λ_c[a]	Stand. dev. (Λ_c)	$10^{-5}K$, M^{-1}	Stand. dev. ($K \times 10^{-5}$)	Λ_c[a]	Stand. dev. (Λ_c)	$10^{-5}K$, M^{-1}	Stand. dev ($K \times 10^{-5}$)
CH_3	123.2	0.16	1.23	0.09	123.9	0.49	3.83	1.37
H	122.8	0.35	0.52	0.05	124.7	0.47	1.27	0.30
CHO	123.7	0.99	0.39	0.09	122.4	0.53	0.77	0.13
$CONHC_4H_9$[b]	113.0	0.42	0.32	0.02	112.0	0.89	0.56	0.09
NO_2	121.8	0.19	0.47	0.02	120.0	0.50	0.63	0.08

[a] Λ_c in $ohm^{-1}\ cm^2\ equiv^{-1}$; Λ_f at 5×10^{-5} M $NaBPh_4 = 137.5 \pm 0.5$; Λ_f at 5×10^{-5} M $KBPh_4 = 137.9 \pm 0.3$. [b] No σ values for CONHR could be found in the literature. The $\sigma_p + \sigma_m$ for $CONH_2$ is 0.66 and $\sigma_p^- + \sigma_m = 0.90$.[28,29]

crease of Λ as the crown concentration increases. The crown content was sufficiently low ($< 5 \times 10^{-3}$ M) to avoid corrections for viscosity changes. Points at high crown to salt ratios were used to obtain an estimate of Λ_c (too high ratios may result in formation of 2:1 crown–cation complexes for Na^+/benzo-15-crown-5 derivatives[12,18]). These Λ_c estimates were then used in calculating estimated values for K from the expression: $K = (\Lambda_f - \Lambda)[\text{crown}]/(\Lambda - \Lambda_c)$ where $[\text{crown}] = C_0 - A^-(\Lambda_f - \Lambda)/(\Lambda_f - \Lambda_c)$.[9] The actual K and Λ_c values were obtained by a nonlinear least-squares analysis.[18,19] They are listed in Tables I and II, together with their standard deviations.

The conductances of the tetraphenylborate solutions in the absence of crown ethers agree with the literature values, e.g., $\Lambda(NaBPh_4)$ at 5×10^{-4} M in acetone at 25 °C is 127.4 ± 0.3 as compared to 127.0 found by Evans.[17] The computed Λ_c values are within 1% of those obtained directly at high crown to salt ratios. The standard deviations in the K values are below 10% for Na^+ with benzo-15-crown-5 ligands, and somewhat higher in a number of benzo-18-crown-6 systems where K is much higher and the method less accurate.

To evaluate the change in cation mobility on addition of crown as a function of the nature of the 4′-substituent, it is more realistic to compare Λ_c^+ values. These can be found from the relationship $\Lambda_c^+ = \Lambda_c - \Lambda^-(BPh_4)$, where $\Lambda^-(BPh_4)$ at 5×10^{-4} M can be obtained by interpolation of Λ values reported for triisoamylbutyl tetraphenylborate in acetone,[17] assuming that the relationship $\Lambda_0^+ = \Lambda_0^-$ found for this salt[20] also holds for the equivalent conductances at 5×10^{-4} M, i.e., $\Lambda^+ = \Lambda^-$. One finds $\Lambda^-(BPh_4)$ at 5×10^{-4} M = 56.2. The calculated Λ_c^+ values as well as the ratios Λ_f^+/Λ^+ are given in Table I.

Discussion

Inspection of Table I reveals that single ion conductances, Λ_c^+, and formation constants, K, of Na^+ complexes with benzo-15-crown-5 ligands show a pronounced dependence on the nature of the 4′-substituent in the crown. The diameter of the crown ring (1.7–2.2 Å, ref 2) is such that the Na^+ cation (1.96 Å) fits tightly in the crown cavity. When associated with an anion the sodium frequently is found to protrude from the benzo-15-crown-5 cavity, such as in solid complexes of sodium iodide and benzo-15-crown-5[21] or in crown complexed tight ion pairs with fluorenylsodium in tetrahydropyran[12] or with sodium picrate in tetrahydrofuran or chloroform.[11] It is possible that with the free Na^+ ion the cation is more in the center of the cavity, and associated on each side of the ring with an acetone molecule, although a more asymmetric solvation complex is certainly not excluded. The presence of acetone in the complex is likely on account of the large drop in Λ^+ on addition of crown (without crown the single ion conductance of Na^+ in acetone is comparable to that of $N^+(C_3H_7)_4$, see ref 17).

The ratios Λ_f^+/Λ_c^+ roughly parallel the steric bulkiness of the substituents as expressed by the steric molar refractivity coefficients, M_r, given in Table I,[22] at least for the less polar substituents such as CH_3, Br, or $COOCH_3$ (another rough correlation exists with the functional group contributions to the van der Waals radii reported by Bondi, see ref 23). However, the correlation fails for polar substituents, probably because interactions with solvent dipoles tend to lower the mobility of the cation–crown complexes. The largest deviations in Λ_c^+ are found with the NH_2 and COOH groups, the most likely cause being hydrogen bonding between acetone and amino[24] or carboxylic substituents[25] which would further decrease the mobility.

Turning now to the formation constants, we observe a nearly 25-fold difference in K between the 4′-amino- and 4′-nitrobenzo-15-crown-5. Little is known about substituent effects on interactions between aromatic ether oxygens and electron deficient species, but the effect observed in our system is most likely caused by the changing basicity of the two aromatic ether oxygens. It is known that the chemical shift of the side chain protons of 1-substituted 3,4-methylenedioxybenzenes can be correlated with the Hammett σ_m and σ_p constants.[26] Also, the strength of alkali ion interactions with ethers is known to depend on the basicity of the ether oxygen.[27] We, therefore, plotted log K vs, $\sigma_p + \sigma_m$ (values taken from ref 28) as shown in Figure 2. The value $2(\sigma_p + \sigma_m)$ was used for the 3′,4′-dinitro compound on the basis of the additivity rule.[28] Although the correlation is reasonable (correlation coefficient $r = 0.979$, standard deviation $s = 0.11$), the formation constants of crown derivatives with substituents that withdraw electrons by a resonance effect appear to deviate. If such an effect is exerted on the binding sites, it is expected to be more pronounced with the free crown ligand than with the complex, since in the latter case electron delocalization from the aromatic ether oxygens is diminished by the close proximity of the cation. The overall effect tends to lower the formation constant K. It suggests, of course, the use of σ_p^- values (taken from ref 29) and the resulting plot of log K vs. $\sigma_p^- + \sigma_m$ is slightly better (see Figure 2) than the previous plot, with $r = 0.989$ and $s = 0.083$. The $2(\sigma_p + \sigma_m)$ value was taken for the dinitro compound as substituents ortho to a p-nitro group are known to significantly reduce the resonance effect of this group by preventing it from lying in the plane of the ring.[30]

The ρ value for the complex formation equilibrium was found to be −0.45. A change in medium is likely to affect ρ. Solvent molecules may interact with the binding sites of the free crown ether, especially protic solvents. Also, since some of them are attached to the cation in the complex, they are likely to affect the position of the cation relative to that of the two aromatic oxygens. It is the distance between the cation and these oxygens atoms that determines the magnitude of the substituent effect. A variable distance in a series of substituted benzo-crown ether complexes will probably cause the Hammett relationship to fail. This may be one of the reasons for the peculiar behavior of the 4′-substituted benzo-18-crown-6 compounds with Na^+. While the presence of four instead of three aliphatic oxygen atoms is expected to reduce to substituent effect on complexation, another difference with the 15-crown-5 cavity is the larger diameter of the 18-crown-6 cavity (2.6–3.2 Å, see ref 2) with respect to the Na^+ cation. The cation is likely to be preferentially attracted to the more basic aliphatic oxygen atoms, especially in derivatives with electron withdrawing substituents. Note that the formation constants for the nitro-, formyl- and butylcarboxamidobenzo crown ethers with Na^+ are nearly identical and almost equal to that of the nonsubstituted benzo-18-crown-6 (Table II). Only the methyl derivative shows a 2.5-fold increase in K, probably because the cation now moves closer to the two aromatic oxygens. Another factor may be the increased flexibility of the 18-crown-6 ring as compared to the more rigid benzo-15-crown-5 cavity. As the cation shifts under the influence of a 4′-substituent, the ring conformation in the complex adjusts itself, and under such conditions it is unlikely that a Hammett relationship will be found. It is also interesting that the Λ_c^+ values do not appear to follow the same pattern as observed for the 15-crown-5 compounds. This again may indicate that small conformational changes in the Na^+-benzo-18-crown-6 complex occur on varying the 4′-substituent. An anomolous substituent effect was also found in the series 4,4′-dinitro-, 4,4′-diamino-, and nonsubstituted dibenzo-18-crown-6 on complexation with Na^+ in DMF,[9] and was attributed to conformational changes in the diamino compound due to interactions between the two NH_2 groups.

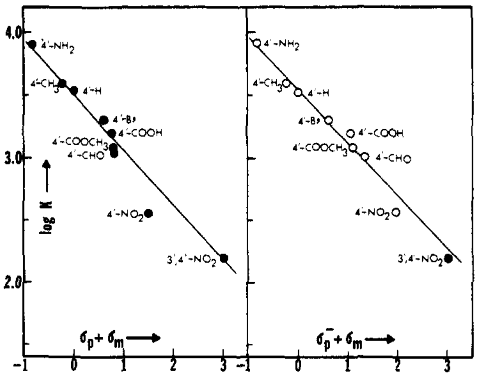


Figure 2. Hammett plot for complexation of Na^+ with substituted benzo-15-crown-5 compounds in acetone at 25 °C: (a) log K (complex formation constant) vs. $\sigma_p + \sigma_m$; $\rho = -0.47$; corr. coeff, $r = 0.978$; stand. dev, $s = 0.11$; (b) log K vs. $\sigma_p^- + \sigma_m$; $\rho = -0.45$; $r = 0.989$; $s = 0.082$.

The K^+ ion (2.6 Å) fits more tightly into the benzo-18-crown-6 cavity. However, while the log K values do change with the σ values of the substituents in the expected direction, no linear correlation is found. This again could be attributed to the more flexible structure of the benzo-18-crown-6. Note also the poor selectivity of this crown with respect to sodium and potassium in acetone. Selectivity, of course, not only depends on the structure of the crown ether but also on solvent–cation interactions. In methanol and water the 18-crown-6 ligand prefers K^+, although the selectivity with respect to K^+ and Na^+ varies significantly with the nature of the substituent attached to the polyether ring.[2] Also, in transporting a mixture of potassium and sodium picrate from one aqueous phase to another across a chloroform layer containing benzo-18-crown-6, the selectivity ratio K^+/Na^+ is more than 100.[11] On the other hand, Na^+ is preferred in solvents such as tetrahydrofuran.[31] Apparently, acetone (and also acetonitrile, see ref 18) is a solvent in which differences between solvent–cation interactions for Na^+ and K^+ approximately balance those between interactions of benzo-18-crown-6 and the two cations.

Complex formation was also studied conductometrically for K^+ with benzo-15-crown-5 and its 4′-amino and 4′-nitro derivative. Again the plots of Λ vs. the crown to salt ratios are smooth curves, but the total drop in the equivalent conductance is considerably larger than for Na^+. For example, $\Lambda_f - \Lambda_c$ for 4′-aminobenzo-15-crown-5 with K^+ was found to be 22.0 for K^+ and 16.0 for Na^+. This is not surprising since K^+ is known to form stable 2:1 crown–cation complexes with benzo-15-crown-5 compounds.[2,12] When calculated on the basis of either a 1:1 or 2:1 complex, the K values show a strong dependence on the crown to cation ratio. It is likely that the two complexes are present simultaneously in acetone, as was also observed in methanol,[2] and this complicates the calculation since two Λ_c^+ values are needed to determine K_1 and K_2. Although more data are needed to obtain the two formation constants, the decrease in Λ shows the expected dependence on the nature of the 4′-substituent, the effect being quite pronounced. That would not be surprising since in the 2:1 complex four aromatic oxygen atoms are interacting with the cation, the basicity of each one being susceptible to a change in the 4′-substituent.

In conclusion, we have shown that a change in the 4′-substituent for benzo-15-crown-5 can cause a significant change in the complex formation constant. The effect may be as large as that caused by a change in the structure of the polyether ring. A Hammett correlation was found for the Na^+-benzo-15-crown-5 system, but no such relationship exists with the benzo-18-crown-6 compounds. The results show that caution must be applied in extrapolating substituent effects found in one system to other crown–cation combinations.

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Chemically Induced Dynamic Electron Polarization. Ionic Strength and Radical Concentration Dependence[1]

A. D. Trifunac

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439.

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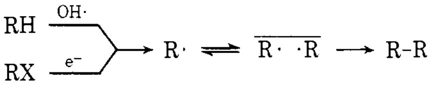
Abstract: The ionic strength effect on the polarization of radicals from radiolysis of acetate and malonate solutions is moderate. It appears that this effect is more pronounced at lower ionic strength. These findings are in qualitative agreement with theoretical predictions of Pedersen and Freed. It was also observed that polarization enhancement is independent of radical concentration.

Introduction

The intriguing question in the experimental study of the chemically induced dynamic electron polarization (CIDEP) phenomenon is whether this effect can be used to study intimate details of radical-radical interaction in solution. Of particular interest is to find out if larger and thus more experimentally accessible manifestations of various interradical interactions are reflected in the observables of a polarization study.

A brief outline of the current view of the magnetic polarization phenomena as it applies to the CIDEP of radicals produced by pulse radiolysis follows.



The radicals in a typical aqueous system are produced either by OH· abstraction reaction or hydrated electron reaction, where X is usually halogen. The addition of an OH· scavenger or e_{aq}^- scavenger can eliminate either of these two reactions. The use of N_2O effects conversion of e_{aq}^- to OH·, giving a clear-cut reaction system. Whether e_{aq}^- or OH· is the precursor can be determined by the study of initial relative signal intensities in the EPR spectrum of the radical in question. Our submicrosecond time-resolved EPR study of radicals from acetate and halo acetates is illustrative on this point.[2]

The radicals once produced encounter and undergo spin-selective reaction. Usually the singlet-state radical pairs preferentially react, leaving the excess of radical pairs with triplet-spin character. These remaining radicals undergo diffusive displacements, at which time singlet-triplet mixing can occur.[3] The polarization process is completed by the exchange (J) when the radicals are close enough (re-encounter). Any change in attraction or repulsion between radicals may have an effect on the electron-spin polarization, which is generated in the region where radicals are attracted or repulsed. In their recent theoretical work, Pedersen and Freed consider the effect of ionic interaction among charged radicals.[6] The effect of the ionic strength of the solution on the polarization of radicals depends on the size of exchange (J). The effect of the Coulomb force on the polarization is smaller for larger values of ex-