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Estimation of Association Constants of Macrocyclic Ethers by Potentiometry. Part V. Na^+ Binding in Dioxane/Water (80/20)

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The various association constants, β_{nm} and K_{nm}, of NaCl and $NaClO_4$ with [12]crown-4, [15]crown-5, [18]crown-6, benzo[15]crown-5, benzo[12]crown-4, dibenzo[18]-crown-6 and dinaphtho[18]crown-6 have been estimated in a mixture of dioxane/water (80/20) using a sodium ion selective electrode (ISE). The constants have been estimated using $1/(K_{nm}[L_o]^{n+m-1}) = (1-nP')^n \times (1-mP')^m/P'$, where P', the mole fraction of complexed Na^+in the presence of identical cation/ligand concentrations, is obtained for different aggregation–dissociation possibilities. The association constants of the complexes are reported and discussed in terms of the multiple composition due to strong dioxane/water binding. The binding mechanism is shown to depend on the free cation and counter ion that are formed by different ratio macrocycle–metal complexes in dioxane/water (80/20) solutions.

Keywords: Macrocycles; Ion binding; Association constants; Potentiometry; ISE; Na^+

INTRODUCTION

The cation association of macrocycles in solution has been widely investigated [1,2]. However, the cationic interactions of macrocycles are still open to further investigation with respect to thermodynamic parameters and the binding mechanisms of coordination tendency and the radii of the cation as well as the size and conformational ability of the macrocycle [3–7].

We have been working on the cationic recognition of macrocycles using different methods [8–10]. In recent studies we have reported Na^+ and K^+complexing of some crown ethers in 50/50 dioxane/water using a sodium ion selective electrode (ISE) [11–15]. In the present work we have studied the association constants of NaCl and $NaClO_4$ complexing with [12]crown-4, [15]crown-5, [18]crown-6, benzo[15]crown-5, benzo[12]crown-4, dibenzo[18]-crown-6 and dinaphtho[18]crown-6 in a dioxane/water (80/20) solvent mixture using a sodium ISE. The binary water/dioxane mixture as solvent is used to enhance the power of macrocycle–cation interactions with the maximum solubility of the aromatic macrocyclics in the presence of the smallest amount of water.

Previously reported studies on the association constants of macrocycles with oxygen donor complexes used various experimental and calculation methods in different solvents [1–7,16–21]. We recently estimated the various association constants, β_{nm}, in an equilibrium with an n/m ratio of a macrocycle ether [L] and a cation $[A^+]$ to form a complex $[A_n{}^+L_m]$ in solutions with identical initial concentrations, $[A_o^+] = [L_o]$, using the linear regression analysis of an equation depending on the mole fraction, P', of the complex $[A_n{}^+L_m]$, see Eqs (1) and (2) [8–15].

$$nA^+ + mL \rightleftharpoons A_n^+L_m \tag{1}$$

$$\beta_{nm} = [A_n^+L_m]/[A^+]^n[L]^m \tag{2}$$

The mole fraction of a complexed ligand $P = [A_n^+L_m]/\{[A^+] - (1-m)[A_n^+L_m]\}$ is, in general, given by $P' = P/[1+(m-1)P]$ for simplicity [11–14]. Accordingly, the multiple association constants, β_{nm}, of a complex of n/m stoichiometry in solution can be obtained from the slope, $1/\beta_{nm}$, of the plot of $1/[A_o^+]^{n+m-1}$ versus $(1-nP')^n\ (1-mP')^m/P'$, Eq. (3). However, if $n = 1$, $m = 1$ and $P = P'$, then

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Eq. (4) is used, where $P = P'$ for a 1:1 association constant, K_{11} [8,9,11–14].

$$1/\beta_{nm}[\mathrm{L_o}]n^{+}m^{-1} = (1 - nP')^{n}(1 - mP')^{m}/P' \tag{3}$$

$$1/K_{11}[\mathrm{L_o}] = (1 - P')^{2}/P' \tag{4}$$

The complexation involves a stepwise process to reach the maximum stability of the complex structure; similarly, 2:1 and 3:2 (n:m) association constants K_{12} and K_{23} are given by Eqs. (5)–(8) [2–6].

$$[\mathrm{A^{+}L}] + [\mathrm{A^{+}}] \rightleftharpoons [\mathrm{A_2^{+}L}] \tag{5}$$

$$K_{12} = [\mathrm{A_2^{+}L}]/[\mathrm{A^{+}L}] + [\mathrm{A^{+}}] \tag{6}$$

$$[\mathrm{A_2^{+}L_2}] + [\mathrm{A^{+}}] \rightleftharpoons [\mathrm{A_3^{+}L_2}] \tag{7}$$

$$K_{23} = [\mathrm{A_3^{+}L_2}]/[\mathrm{A_2^{+}L_2}][\mathrm{A^{+}}] \tag{8}$$

The values of β_{mn} and K_{mn} of both association constants of the complexes can be estimated precisely using Eq. (3), where β_{mn} and K_{mn} define the constants of associations of the different steps of the complex formation.

$[\mathrm{A}_n^{+}\mathrm{L}_m]$ types of macrocyclic complexes are in equilibrium with multiple aggregations depending on the strength and polarity of the macrocycle that governs the association–dissociation mechanism. Thus, dissociations may involve, according to Eq. (9), a dissociative complex formation [5,6,12].

$$\begin{aligned} kn\,\mathrm{A^{+}} + km\,L &\rightleftharpoons (\mathrm{A}_n^{+}\mathrm{L}_m)_x \\ &\rightleftharpoons (\mathrm{A}_n^{+}\mathrm{L}_m)_{x-1} + \mathrm{A^{+}L} \rightleftharpoons \mathrm{A^{+}} + \mathrm{L} \end{aligned} \tag{9}$$

The estimation of association or dissociation constants can therefore be obtained with Eqs. (10)–(13) by measuring the free cation concentration in an equilibrium of the complexes in a solution, such as dioxane/water (80/20).

The dissociation of ion pairs may be given, accordingly, as outlined in the following equations, which in fact imply that the complex partners are dissociated but not exactly how they are associated [22,23]. As Eqs. (9) and (10) are not sufficient to explain the thermochemical parameters to be estimated, Eqs. (10)–(15) are proposed in support of our experimental results. Thus, an example is a 4:3 (n:m) associated complex of $(\mathrm{A_4^{+}L_3})$ that might be an aggregate of x times, $(\mathrm{A_4^{+}L_3})_x$. This could be partially dissociated in decimal concentration fragments, Eqs. (13)–(15).

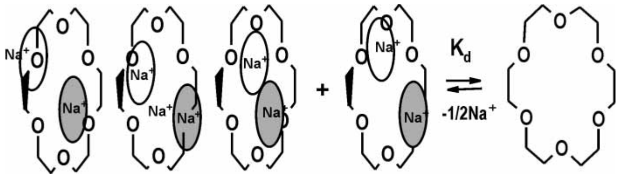


FIGURE 1 Illustration of the complex equilibrium of a 2:1 $\mathrm{Na^{+}}$/[18]crown-6 association forming the quadruple aggregated, four units of 2 × cation/macrocycle complex dissociation, Eq. (15).

$$n\mathrm{A^{+}} + m\mathrm{L} \rightleftharpoons \mathrm{A}_n^{+}\mathrm{L}_m \quad \text{and} \quad x\mathrm{A}_n^{+}\mathrm{L}_m \rightleftharpoons (\mathrm{A}_n^{+}\mathrm{L}_m)_x \tag{10}$$

$$\left(\mathrm{A}_n^{+}\mathrm{L}_m\right)_x \underset{K_{-\mathrm{d}}}{\overset{K_\mathrm{d}}{\rightleftharpoons}} \mathrm{A}^{+}_{n(x-1)}\mathrm{L}_{mx} + n\mathrm{A^{+}} \tag{11}$$

$$\mathrm{A}_n^{+}\mathrm{L}_m \rightleftharpoons n/x\,\mathrm{A^{+}} + 1/x\,(\mathrm{A}^{+}_{n(x-1)}\mathrm{L}_{mx}) \tag{12}$$

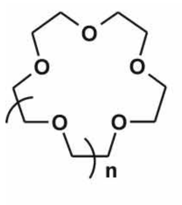
$$K_{-\mathrm{d}} = [\mathrm{A}_n^{+}\mathrm{L}_m]/[\mathrm{A^{+}}]^{n/x}[\mathrm{A}^{+}_{n(x-1)}\mathrm{L}_{mx}]^{1/x} \tag{13}$$

$$\begin{gathered} K_{-\mathrm{d}} = [\mathrm{A_2^{+}L_3}]/[\mathrm{A^{+}}]^{2/3}[\mathrm{A_9^{+}L_9}]^{1/3} \\ \text{if } x = 3,\ n = 2,\ m = 3 \end{gathered} \tag{14}$$

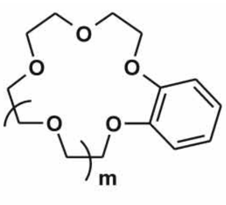
$$\begin{gathered} K_{-\mathrm{d}} = [\mathrm{A_2^{+}L}]/[\mathrm{A^{+}}]^{2/4}[\mathrm{A_6^{+}L_4}]^{1/4} \\ \text{if } x = 4,\ n = 2,\ m = 1 \end{gathered} \tag{15}$$

The experimental results in the present work have thus been explained by such a mechanism of dissociative complexation. A 6-oxygen macrocycle caused $k = 4$, of multiple $\mathrm{Na^{+}}$/[18]crown-6 association could give the free cation equilibrium as described in Fig. 1. Accordingly, depending on the macrocyclic size as well as its relevant conformation, the six electrons of [18]crown-4 may be shared by sodium metal ions, which may be exchanged due to metal coordination ability [2–6].

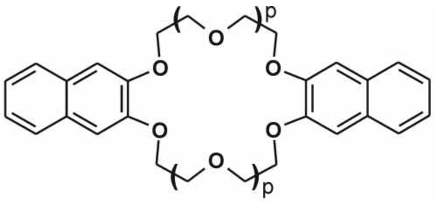
The association constants of existing $\mathrm{Na^{+}}$ complexes in dioxane/water (80/20) with [18] crown-4 (**III**), [15]crown-5 (**II**) and [12]crown-4 (**I**), as well as their naphtho (**VI** and **VII**) and benzo (**VIII** and **IX**) derivatives, are displayed and discussed.



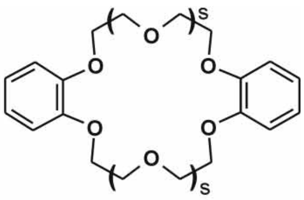
I (n=0)
II (n=1)
III (n=2)



IV (m=1)
V (m=1)



VI (p=1)
VII (p=2)



VIII (s=1)
IX (s=2)

EXPERIMENTAL

The chemicals were obtained from FLUKA and used without further purification. Dibenzo[18]-crown-6 (**VIII**), dinaphtho[18]crown-6 (**VI**) and dinaphtho[24]-crown-8 (**VII**) were synthesized according to Pedersen's methods [15]. The association–dissociation constants were estimated using an Na^+ ISE in dioxane/water (80/20) (v/v) [11–14]. Dioxane was purified on metallic sodium and then mixed with deionized water. The free Na^+ and also the equivalent amounts of the macrocycle/Na^+ mixture of 15–20 samples prepared in volumetric flasks were measured in a thermostated cell that was equipped with a combined glass electrode from Orion (model Ross).

The mV data (± 0.5 mV) were obtained with an Orion millivoltmeter, model 920 A (Tables I and II) [5,7–9]. The association constants, $K_{-\mathrm{dk}}$, of inverse of dissociation K_{dk}, were calculated from the slope of the simulated best-fitting line of the maximum Pearson correlation coefficient, R^2, of Eq. (3) or (11) (see Figs 2 and 3). The y-intercept of the straight line is definitely under consideration for the mechanism and the stoichiometry (see Tables III and IV).

RESULTS AND DISCUSSION

This paper describes the estimation of the potentiometric association constants, $K_{-\mathrm{dk}}$, of NaCl and $NaClO_4$ complexing with macrocycles in a dioxane/water (80/20) binary mixture using an Na^+ ISE. The study of the macrocyclic ether–cation interactions using Eqs. (3)–(11) showed that the mechanism of cationic interactions of the oxygen dipoles clearly involves both associative and dissociative interactions [1–12].

TABLE I The 0.28/0.56 association data of [18]crown-6/Na^+in dioxane/water

$[A_o^+]$* (mol l^{-1})	Log $[A_o^+]$	Salt mV†	Comp. mV‡	Mol. fr., P§	$(1-nP)^n/P$¶	$1/[A_o^+]^{m+n-1}$
0.00138	−2.8604	37.00	26.30	0.769	0.885	0.349
0.00166	−2.7799	40.50	29.70	0.755	0.911	0.359
0.00194	−2.7122	43.00	32.20	0.742	0.934	0.368
0.00219	−2.6596	45.00	34.20	0.733	0.952	0.375
0.00242	−2.6162	47.40	36.00	0.724	0.968	0.381
0.00265	−2.5768	49.00	37.80	0.717	0.982	0.387
0.00286	−2.5436	50.00	39.30	0.711	0.995	0.392
0.00306	−2.5143	51.50	40.80	0.705	1.006	0.396
0.00324	−2.4895	52.30	42.00	0.701	1.015	0.400
0.00342	−2.4660	53.30	43.00	0.696	1.024	0.406
0.00359	−2.4449	54.00	44.00	0.693	1.032	0.409
0.00375	−2.4260	55.00	45.00	0.689	1.040	0.409
0.00390	−2.4089	55.40	45.70	0.686	1.047	0.412
0.00405	−2.3925	56.30	46.20	0.683	1.054	0.414
0.00419	−2.3778	57.00	46.70	0.680	1.060	0.416
0.00432	−2.3645	57.75	47.10	0.678	1.065	0.418

*Concentration of the [18]crown-6/NaCl solutions. †mV of NaCl solutions. ‡mV of complex solutions. §Mole fraction, P, of complex. ¶Calculated fraction ratios.

TABLE II The 0.95/0.95 association data of [12]crown-4 with Na^+ in dioxane/water

$[A_o^+]$* (mol l^{-1})	Log $[A_o^+]$	Salt mV†	Comp. MV‡	Mol. fr., P§	$(1-nP)^n/P$¶	$1/[A_o^+]^{m+n-1}$
0.00138	−2.8604	37.00	28.00	0.411	0.947	375
0.00166	−2.7799	40.50	29.00	0.445	0.789	317
0.00194	−2.7122	43.00	31.50	0.473	0.681	276
0.00219	−2.6596	45.00	33.00	0.493	0.611	247
0.00242	−2.6162	47.40	34.40	0.509	0.559	226
0.00265	−2.5768	49.00	35.50	0.523	0.518	208
0.00286	−2.5436	50.00	36.50	0.535	0.485	194
0.00306	−2.5143	51.50	37.40	0.545	0.486	183
0.00324	−2.4895	52.30	38.20	0.554	0.437	174
0.00342	−2.4660	53.30	38.90	0.562	0.418	165
0.00359	−2.4449	54.00	39.30	0.568	0.402	159
0.00375	−2.4260	55.00	39.90	0.575	0.388	152
0.00390	−2.4089	55.40	40.40	0.580	0.377	147
0.00405	−2.3925	56.00	40.90	0.585	0.365	142
0.00419	−2.3778	56.30	41.40	0.590	0.356	138
0.00432	−2.3645	57.40	41.80	0.594	0.347	134

*Concentration of the [18]crown-6/NaCl solutions. †mV of NaCl solutions. ‡mV of complex solutions. §Mole fraction, P, of complex. ¶Calculated fraction ratios.

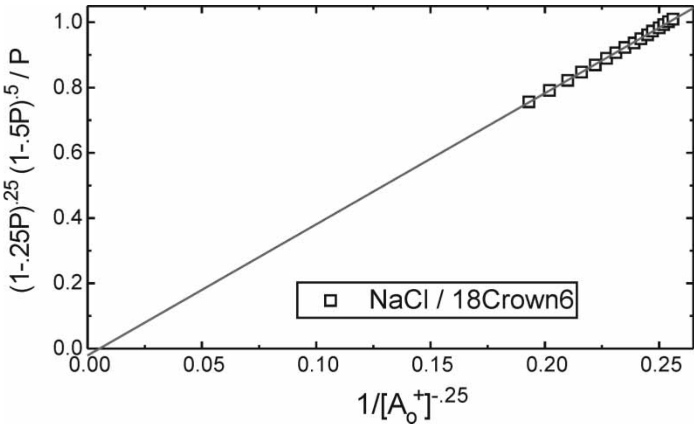


FIGURE 2 Plot to estimate the 0.50:0.25 molar ratio of the association constant of NaCl/[18]crown-6 in dioxane/water (80/20) at 25°C.

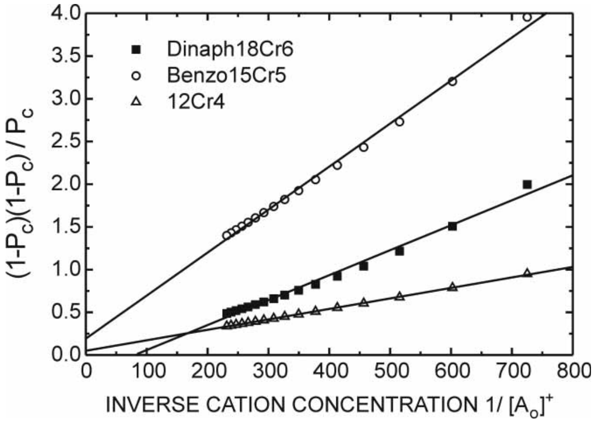


FIGURE 3 Plots to estimate the 1:1 association constant of NaCl/macrocycles in dioxane/water (80/20) at 25°C. Note that the dinaphtho[18]crown-6 is not exactly a 1:1 ratio in this concentration range, as the *y*-intercept does not pass through the origin (Table II).

We report the binding data of 1:1 common complexes (Fig. 3), according to Eq. (3), as well as the Na$^+$ partial dissociation data of the aliphatic macrocycles (**I–III**), using Eq. (11) (see Fig. 2) [8,22,23].

In the present work, the results indicate that the dissociative mechanism depends on the structures, the association ratios (*n*:*m*), and the power of the complexed ion pair interactions. The relevant oxygen numbers affected the ligand–cation exchange rate and the coordination ability of the cation, like potassium, and the electron delocalization of the counter ion may cause the higher associations with lower binding entropy [5].

The maximum stability of the multiple complexes of Na$^+$ with [15]crown-5 and [18]crown-6 in dioxane/water (80/20) was displayed, indicating the successful use of the calculation method (Fig. 3). [12]Crown-4 displayed strong 1:2 (*n*:*m*) NaClO$_4$ binding, although further associations are negligible due to the counter ion while Na$^+$Cl$^-$ forms a 1:1 stable complex (Tables III and IV) [7,10,11,21]. The results depend partially on the counter anions, Cl$^-$ and ClO$_4^-$, because of the 20% water in the solvent, and the large amount of dioxane in the composition increased the association constants and caused the aggregation. However, even higher amounts of dioxane may alter the junction potential of the reference electrode of water body [8–11].

Macrocycles with aromatic moieties have shown fairly small associations due not only to electron-withdrawing π electrons but also to the bulky aromatic rings that hinder the further association of a molecular complex $[A_n^+L_m]_k$. The higher stoichiometry of ligand–cation interactions, however, involving larger free energies, $-\Delta G$, were explained recently in terms of enthalpy–entropy

TABLE III NaCl association constants, $K_{-\mathrm{dk}}$, in water/dioxane (80/20) at 25°C

Macrocycle	$[L]^m/[A^+]^n$	$\ln K_{-\mathrm{dk}}$	$-\Delta G^{\theta}$ (kJ mol^{-1})	R^2	*y*-intercept
[12]crown-4	0.95/0.95	6.01	14.82	0.999	0.037
[15]crown-5	0.50/1.00	5.64	13.92	0.999	−0.002
[18]crown-6	0.28/0.56	0.95	2.34	0.999	−0.018
Bz[15]crown-5	1.00/1.00	5.35	13.22	0.997	−0.197
Bz[18]crown-6	1.00/1.00	5.29	13.05	0.998	−0.020
Db[18]crown-6	1.00/1.00	4.68	11.55	0.996	0.200
Dn[24]crown-8	1.00/1.00	2.98	16.92	0.999	0.456
Dn[18]crown-6	1.00/1.00	6.46	15.94	0.999	0.033
Db[24]crown-8	1.00/1.00	5.62	13.86	0.999	−0.075
Db[24]crown-8	1.10/2.00	11.69	28.83	0.999	−0.220

TABLE IV $NaClO_4$ association constants, $K_{-\mathrm{dk}}$, in water/dioxane (80/20) at 25°C

Macrocycle	$[L]^m/[A^+]^n$	$\ln K_{-\mathrm{dk}}$	$-\Delta G^{\theta}$ (kJ mol^{-1})	R^2	y-intercept
[12]crown-4	2.00/1.00	8.79	21.70	0.999	0.533
[15]crown-5	0.75/1.00	4.19	10.33	0.999	0.018
[18]crown-6	1.00/1.00	6.46	15.93	0.999	0.033
[18]crown-6	0.50/1.00	3.13	7.72	0.997	− 0.465
Bz[15]crown-5	0.75/1.00	2.46	6.08	0.999	− 0.185
Db[18]crown-6	1.00/1.00	4.68	11.54	0.999	0.258
Db[18]crown-6	1.00/1.50	7.73	19.018	0.999	0.610
Dn[18]crown-6	1.00/1.00	4.44	10.95	0.999	0.247

compensations [5]. This was also observed in ^{13}C NMR dipole–dipole relaxation rate studies of the estimation of the stability of macrocycle–cation complexes [7,12,16].

The complex stoichiometry is affected by the solvent, such as water or methanol–water, and the binding power is the lowest, forming only 1:1 or 2:1 complexes [1–4]. In 80/20 dioxane/water, the stability of the complex is higher than that obtained in 50/50 dioxane/water as more aggregation is involved [8–11,22,23]. The results have particularly shown that a certain macrocycle size in less polar solvents, such as dioxane, is capable of encapsulating more than one Na^+.

The resulting association constants in dioxane/water are, therefore, fairly high compared to water as solvent as the hydration of the macrocycle partially breaks down the mechanism, Eqs. (5)–(8).

The consecutive exchanges of the oxygen–metal bonds take place along with solvent–metal interactions. Small macrocycles result in small K_{nm} values and are likely to form more stable 2:1 (m:n) systems together with 1:1 complexes, like [12] crown-4. The ratios 1:2 or 2:3 (m:n) of complexes such as [15]crown-5/Na^+ are fairly strong and more common as the strong interactions involve more degrees of aggregation, x. It is noteworthy that large rings like benzo[24]crown-8 (**IX**) have exhibited both remarkable 1:2 (m:n) association as well as the 1:1 because of the size and flexibility of the macrocycle, which causes very rapid exchange between the cations (Tables III and IV).

Equilibrium constants are mostly decided experimentally by the total $[A^+]$ originated from the any type of dissociation. In contrast to expectations, the K_{nm} or β_{nm} values found for the 1:1 ratio are smaller than the β_{nm} for the 1:2, and even smaller than K_{nm} or β_{nm} for 3:2 ratio complexes found with Eqs. (3) and (4) (see references cited in Ref. [5]). The metal–ligand coordination of more than 60–100 kcal mol^{-1} is in fact very different from the ion–oxygen dipole interactions of 20–30 kcal l^{-1} as explained by the Eigen–Winkler-like mechanism in this work.

The results do, however, reveal the necessity of using linear regression analysis of the relevant relationships and cationic selectivity. This is the best method to estimate the composition of the complex for the thermodynamic quantities.

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