

# The association constants of $\text{Na}^+$ with dibenzo[3*n*]crown-*n* in THF/water using ISE

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Received 12 January 2004; received in revised form 24 March 2004; accepted 25 March 2004

Available online 20 July 2004

## Abstract

The  $\text{Na}^+$  association constants,  $K_{11}$  and  $\beta_{12}$ , of 1/1 and 1/2 stoichiometry of macrocycles of (1,2)dibenzo[15]crown-5, (1,3)dibenzo[18]crown-6, (1,4)dibenzo[21]crown-7, (2,3)dibenzo[21]crown-7, (2,4)dibenzo[24]-crown-8 and dicyclohexano[24]crown-8 were determined in THF/water, (50/50), mixtures. We used a *Methrom*  $\text{Na}^+$  ISE for the potentiometric measurements and applied the  $1/(\beta_{nm}[\text{A}_o^+]^{n+m-1} = (1 - nP_c)(1 - mP_c)/P_c$  equation where the  $P_c = P/[1 + (m - 1)P]$  and  $P$  is the mole fraction of the complexed cation,  $[\text{A}_n^+\text{L}_m]$  for association constants with linear best fit. Results were in well agreement with the macrocyclic size and cation radii relationships. Measurements showed the role of aromatic groups of macrocyclics in THF/water (50/50) which allowed the macrocyclic molecules more selectively bind  $\text{Na}^+$  compared to the associations those obtained in water.

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**Keywords:** Potentiometry; Ion selective electrodes; Macrocyclic ethers;  $\text{Na}^+$  ion complexes

## 1. Introduction

The Macrocyclic ethers have been known to form complexes with alkaline and alkali earth cations depending on the cation radii. The ion selectivity of such molecules have been studied mostly with potentiometry, using ion selective electrodes [1–10]. The association constants of  $\text{Na}^+$  and  $\text{K}^+$  with macrocyclic ethers have been determined using an ISE in water or dioxane/water recently which are properly accompanied with other analytical methods using the calculation way we reported [11,12].

We have so far determined the association constants precisely, using a practical formalism. Recently, common crown ether-cation associations studied by this way have given good results evidencing the cation radii-macrocyclic size relationships [13–16]. The calculation method is also quite applicable for the determination of association constants using NMR- $T_1$  measurements or steady state fluorescence emission spectroscopy of free and cation complexes of macrocyclic ethers [11,12].

The association constant,  $\beta_{nm}$ , of  $n:m$  ratio of a cation  $[\text{A}^+]$  and a ligand,  $[\text{L}]$  with experimental equivalent initial concentrations,  $[\text{A}_o^+] = [\text{L}_o]$ , to form a complex,  $[\text{A}_n^+\text{L}_m]$  could be calculated with Eqs. (1)–(3) depending on the mole fraction,  $P$  of the complex,  $[\text{A}_n^+\text{L}_m]$ . The mole fraction of a complexed ligand,  $P = [\text{A}_n^+\text{L}_m]/\{[\text{L}_o] - (1 - m)[\text{A}_n^+\text{L}_m]\}$ , however,  $P_c = P/[1 + (m - 1)P]$  of a *pseudo* mole fraction assignment is used to in Eqs. (3)–(5) to simplify the expressions [13–18].

$$n\text{A}^+ + m\text{L} \rightleftharpoons \text{A}_n^+\text{L}_m \quad (1)$$

$$\beta_{nm} = \frac{[\text{A}_n^+\text{L}_m]}{[\text{A}^+]^n [\text{L}]^m} \quad (2)$$

$$\frac{1}{\beta_{nm}[\text{A}_o^+]^{n+m-1}} = \frac{(1 - nP_c)^n (1 - mP_c)^m}{P_c} \quad (3)$$

The association constant,  $\beta_{nm}$  of a complex of  $n/m$  stoichiometry in a solution is obtained from the slope of  $1/[\text{A}_o^+]^{n+m-1}$  versus  $(1 - nP_c)^n (1 - mP_c)^m / P_c$  using Eq. (3). However, if  $n = 1$ ,  $m = 1$  and  $P = P_c$  then Eq. (4) is obtained for 1/1, ( $n/m$ ), association,  $K_{11}$ . This is the only reported way of estimation of association constants with a linear relationship depending on the initial concentration of

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### Nomenclature

$[A_o^+]$	initial concentration of a cation
$[L_o]$	initial concentration of a ligand
$K_{11}$	(1/1) ratio of ligand/cation association constant
$P$	mole fraction of the complexed cation
$P_c$	pseudo mole fraction of the complexed cation, $P_c = P/[1 + (m - 1)P]$
$\beta_{12}$	(2/1) ratio of ligand/cation association constant

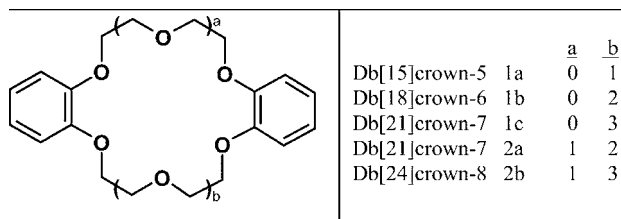
any complexing sites. Then 1/2 type of cation/ligand, ( $n/m$ ) association were estimated using Eq. (5).

$$\frac{1}{K_{11}[A_o^+]} = \frac{(1 - P)^2}{P} \quad (4)$$

$$\frac{1}{\beta_{12}[A_o^+]^2} = \frac{(1 - P_c)(1 - 2P_c)^2}{P_c} \quad (5)$$

## 2. Experimental

We estimated the association constants of NaCl complexes of crown ethers, **1a–2b**, (Scheme 1) which were available to us, [19,20] in THF/water, (50/50) binary mixture with potentiometry using a  $Na^+$  ISE. The chemicals were from FLUKA and used without further purification. THF was from MERCK and mixed with double distilled water to prepare analytical samples in THF/water (50/50). The free  $Na^+$  as well as the equivalent amounts of the crown ether/ $Na^+$  mixture of samples were arranged with an electronic pipette (SCHOTT, T80/20) of 0.01 ml of volumetric steps (see Table 1 and Fig. 1). The appropriate amounts of aliquots, were add into a thermostated cell (50 mL) containing 25.00 mL THF/water, (50/50 (v/v)) that was equipped with a  $Na^+$  ISE electrode (METROHM-model 6.0501.100) and a double junction reference electrode (SCHOTT-B2220),  $Ag^+/AgCl$ /(Tris-hydroxymethylaminomethane) and set to 25 °C (using PT 1000). The measurement of mV ( $\pm 0.05$  mV using PC program) of each aliquot was carried out with a millivoltmeter, (SCHOTT, model CG-804). Association constants of 1/1 and 1/2 stoichiometry, ( $n/m$ ), of cation/ligand complexes were calculated from the inverse of the slope of the best fitting plot of  $1/[A_o^+]^{n+m-1}$ , sum of power of inverse of cation concentration, versus



Scheme 1. Macrocyclic ethers studied in the work.

Table 1

Potentiometric data of  $Na^+/1c$  complex at 25 °C in THF/water, Fig. 2

$[A_o^+] 10^3$ M/L	$\log$ $[A_o^+]$	mV (free)	MV (compl)	$P_c$	$(1 - P_c)^2/P_c$	$1/[A_o^+]$ L/M
1.38	-2.86	1293.0	1285.0	0.052	17.9	724.64
1.67	-2.78	1342.0	1323.0	0.058	15.4	598.80
1.94	-2.71	1385.0	1367.0	0.063	13.8	515.46
2.19	-2.66	1415.0	1392.0	0.068	12.8	456.62
2.40	-2.62	1440.0	1419.0	0.072	12.0	416.67
2.69	-2.57	1465.0	1441.0	0.076	11.2	371.75
2.90	-2.54	1482.0	1458.0	0.079	10.8	344.83
3.06	-2.51	1498.0	1475.0	0.082	10.4	326.80
3.24	-2.49	1510.0	1489.0	0.083	10.1	308.64
3.42	-2.47	1525.0	1501.0	0.085	9.8	292.40
3.60	-2.44	1537.0	1513.0	0.087	9.6	277.78
3.75	-2.43	1547.0	1523.0	0.089	9.4	266.67
3.90	-2.41	1557.0	1533.0	0.090	9.2	256.41
4.05	-2.39	1566.0	1541.0	0.092	9.0	246.91
4.19	-2.38	1575.0	1550.0	0.093	8.9	238.66
4.32	-2.36	1581.0	1556.0	0.094	8.7	231.48

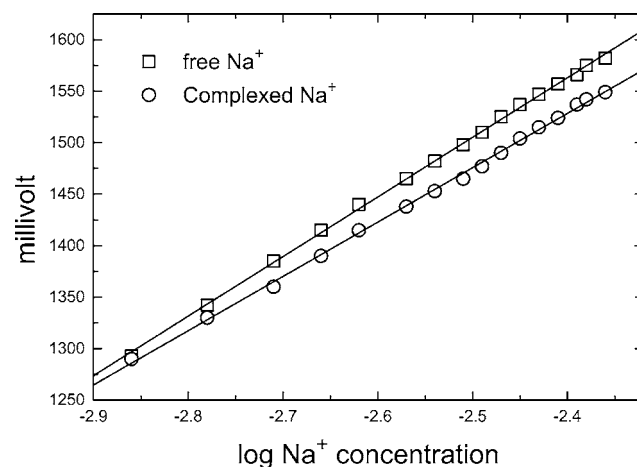


Fig. 1. The plot of  $\log [Na^+]$  and  $1c/Na^+$  (2/1) complex vs. ISE potential.

$(1 - nP_c)^n(1 - mP_c)^m/P_c$  where  $P_c = P/[1 + (m - 1)P]$ , Figs. 2 and 3. The mole fraction of the complexed cation,  $P$  is calculated from the differences of the free (without crown ether for cation calibration) and uncomplexed cation

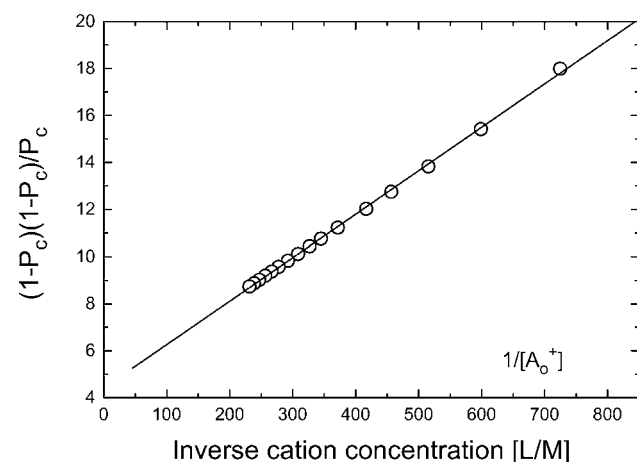


Fig. 2. The (1:1)  $Na^+$  complex formation plot of **1c** according to Eq. (4).

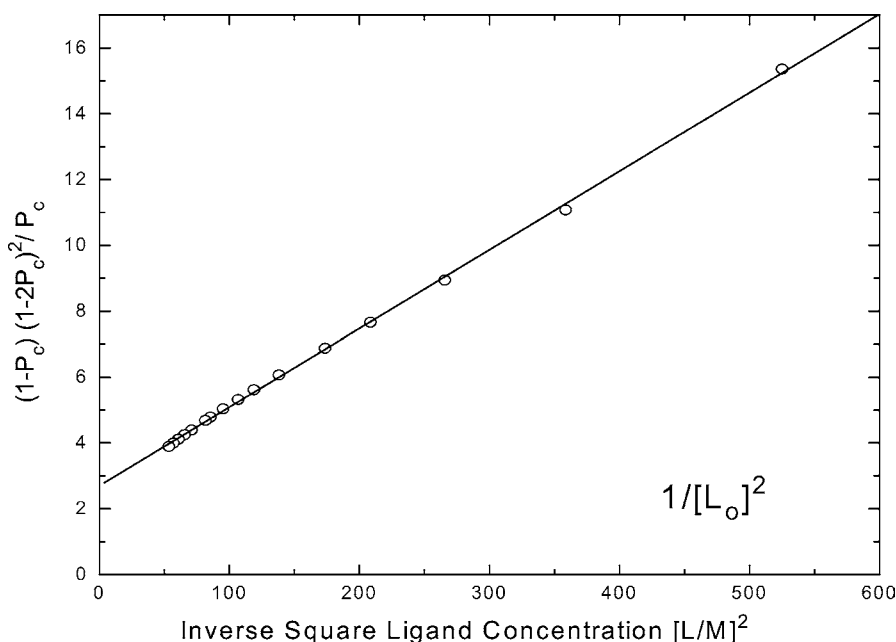


Fig. 3. The (2:1) Na<sup>+</sup> complex formation plot of **1c** according to Eq. (5).

(with crown ether but not complexed) concentrations obtained with ISE measurements, (see Table 1). The maximum correlation coefficient,  $R^2$  and the smallest y-intercept of the straight line of the plot of Eqs. (4) and (5) are obtained regarding the stoichiometry and the ion binding mechanism.

### 3. Results and discussion

The association constants of macrocyclic ethers have been studied by different authors using ISE and various ISE systems in methanol, propylene glycol, acetonitrile as well as water using different calculation programs mostly from Eq. (2) which requires several data points of a non-linear best fit [2–8]. The calculation methods are important due to the chemical cation selectivity or the use of high amount of material in technology. The estimation of thermodynamic constants requires a linear best fit with unknown activity coefficients of ion solutions, in particular, due to formation of ion pairs depending on concentrations in nonhydroxylic solutions. We have studied the associa-

tion constant measurements with ISE in mixtures of water with water miscible ethers, like dioxane or THF and used Eqs. (3)–(5) for calculations [11–20]. Cation binding role of macrocyclic ethers were investigated with commercial ISE electrodes designed to work in water. This is the why we still keep water in the medium to study on cation binding. We used glass type electrodes in binary mixtures with single and double junction reference electrodes. In this work Tris-hydroxymethylaminomethane was used in the reference electrode which gave good results at low ion concentrations, Table 1.

Recently we reported the synthesis of **1a–2b**, and their cationic recognition using fluorescence spectroscopy in acetonitrile [19,20]. In the present work the cation complexing of **1a–1c** and **2a, 2b** were investigated using a Na<sup>+</sup> ISE in a mixture of water/THF (50/50). The measured electrode potentials, mV, of NaCl solutions of the different concentrations,  $[A_o^+]$ , without and with compounds **1a–1c** and **2a, 2b**, of macrocyclic ether concentrations,  $[L_o]$ , in THF/water, (50/50) gave 1/1 and 1/2 ratio of cation/ligand association constants of Na<sup>+</sup> by using Eqs. (4) and (5). The study of macrocyclic ether–cation interactions showed the mecha-

Table 2  
Na<sup>+</sup>/dibenzocrown ether (1:1) association data, Eq. (4)

Macrocyclic ether	log $K_{11}$	ln $K_{11}$	$-\Delta G$ (kJ mol <sup>-1</sup> )	Correlation coefficient ( $R^2$ )	y-intercept
Dibenzo[15]crown-5 <b>1a</b>	1.88	4.33	10.67	0.9986	2.83
Dibenzo[18]crown-6 <b>1b</b>	2.27	5.23	12.89	0.9983	0.92
Dibenzo[21]crown-7 <b>1c</b>	1.83	4.21	10.39	0.9977	1.39
Dibenzo[21]crown-7 <b>2a</b>	2.58	5.94	14.64	0.9987	1.30
Dibenzo[24]crown-8 <b>2b</b>	2.11	4.86	11.98	0.9982	1.17
Dicyclohexyl[24]crown-8	2.05	4.72	11.63	0.9998	3.97
[18]Crown-6	2.56	5.89	14.53	0.9938	–0.014

Table 3

Na<sup>+</sup>/dibenzocrown ether (1:2) association data, Eq. (5)

Macrocyclic ether	log $\beta_{12}$	ln $\beta_{12}$	– $\Delta G$ (kJ mol <sup>–1</sup> )	Correlation coefficient ( $R^2$ )	y-intercept
Dibenzo[15]crown-5 <b>1a</b>	3.78	8.71	21.47	0.9707	9.45
Dibenzo[18]crown-6 <b>1b</b>	5.28	12.14	29.96	0.9777	3.50
Dibenzo[21]crown-7 <b>1c</b>	4.67	10.74	26.50	0.9988	6.96
Dibenzo[21]crown-7 <b>2a</b>	7.14	16.43	40.52	0.9974	0.10
Dibenzo[24]crown-8 <b>2b</b>	4.68	10.76	26.00	0.9983	0.45
Dicyclohexyl[24]crown-8	5.60	12.90	31.81	0.9812	1.23
[18]Crown-6	5.75	13.24	32.75	0.9996	0.17

nism of cation complex association involving a dissociative binding due to the strong interactions. We observed, that the  $\beta_{12}$  values are larger than the  $K_{11}$  [9–15], Tables 2 and 3. The roles of crowns have been reported before but not outlined with the examples of potentiometric complexes [4–9].

The several types of dibenzo crown ethers have been studied [9,10]. However, the molecules of **1a–2b** are less known as we reported recently [19,20]. In general, Na<sup>+</sup> complexes were favoured for six oxygen ligand, **1b**, due to the coordination of Na<sup>+</sup> THF/water, Table 2. To compare the results Na<sup>+</sup>/1/1 ratio of [18]crown-6 complex was also studied at similar conditions and log  $K_{11} = 2.56$  was obtained which is even higher than the log  $K_{11} = 2.27$  of **1b**. However, five oxygen dibenzocrown, **1a**, as a strained structure, [21] displayed log  $K_{11} = 1.88$ . We also observed in dioxane/water that [18]crown-6 was more effective to Na<sup>+</sup> than [15]crown-5 for both 1/1 and 1/2 complexes [14–17].

Na<sup>+</sup> binding results were interesting with dibenzo[21]crown-7 derivatives, **1c** and **2a** where log  $K_{11} = 1.88$  of **1c** is smaller than log  $K_{11} = 2.58$  of **2a**, Figs. 2 and 3. This shows the role of flexibility of the macrocyclic backbone that forms more stable complexes even if the macrocyclics are large which was reported before [3,4]. Accordingly **2a** displayed the strongest 1/2 complexing effect of log  $\beta_{12} = 7.14$ . The results, for comprehension, were furnished with the 1/1 and 1/2 association constants of dicyclohexyl[24]crown-8 which displayed the role of flexible eight oxygen non-aromatic macrocycle to bind the Na<sup>+</sup>, although, the log  $K_{11} = 2.05$  is lesser than log  $K_{11} = 2.11$  of compound **2b** of similar macrocycle ring size [19,20]. The all of the log  $\beta_{12}$  values are larger than log  $K_{11}$  evidencing the stability of multiple sandwich types of complexes [9,10].

## Acknowledgements

This work was kindly supported by TUBITAK, project no TBAG-2026.

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