

# Potentiometric study of complexation of phenylaza-15-crown-5, 4-nitrobenzo-15-crown-5 and dibenzopyridino-18-crown-6 and other derivative of 18-crowns-6 with Na<sup>+</sup> ion in methanol

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**Abstract** The complexation reaction of phenylaza-15-crown-5, and 4-nitrobenzo-15-crown-5, benzo-15-crown-5 and dibenzopyridino-18-crown-6, benzo-18-crown-6, dicyclohexyl-18-crown-6 (cis and trans), and 18-crown-6 with Na<sup>+</sup> ion in methanol have been studied by potentiometric method. The Na<sup>+</sup> ion-selective electrode has been used both as indicator and reference electrode. The stoichiometry and stability constants of complexes of these crown ethers with sodium ion were evaluated by MINIQUAD program. The major trend of stability of resulting complexes of these macrocycle with Na<sup>+</sup> ion varied in the order DCY18C6 > DB18C6 > 18C6 > DBPY18C6 > phenylaza-15C5 > benzo-15C5 > 4-nitrobenzo-15C5. The obtained results in particular stability constant of complexes of DBPY18C6, phenylaza-15C5 and 4-nitrobenzo-15C5 with sodium ion in comparison with other crowns ether are novel, and interesting.

**Keywords** Complexation · Sodium ion-selective electrode (Na<sup>+</sup>-ISE) · Dibenzopyridino-18C6 · Phenylaza-15C5 · 4-Nitrobenzo-15C5 · Methanol

## Introduction

The major advantages of primary synthesized crown ether are their strong affinity for alkali and alkali earth metal ions [1–5]. The primary crown ethers which contain only oxygen binding sites have high tendency toward the alkali

metal ions [1–3]. This event changes drastically the chemistry of alkali metal ions. Up to know, many various derivatives of crown ethers have been synthesized [1–5]. Among these new derivatives crown ethers, the reports about the behaviour of phenylaza-15-crown-5, 4-nitrobenzo-15-crown-5, and dibenzopyridino-18-crown-6 are quite sparse [1–6]. The situation of sodium ion among the alkali metal ion, because of its biological, vital, pharmaceutical and industrial applications, is unique [7]. The complexations of crown ethers with sodium ion were studied with various techniques [4, 5, 8]. The literature reviews show many reports about complexation of ordinary crown ethers with sodium ion [4, 5, 8]. Currently, our research group has been interested in the chemistry of dibenzopyridino-18-crown-6 with several metal ions [9–13]. So, we have been interested to consider the behaviour of these crown ethers with sodium ion in a systematic manner. For this purpose, we have designed the study of the familiar series of 18-crown-6 and 15-crown-5 with Na<sup>+</sup> in methanol. Since the ion-selective electrode is simple, facile, and accurate analytical tool for potentiometric studies [14], we have stimulated using Na<sup>+</sup> ion-selective electrode as a probe in methanol in this study. Throughout the discussion of the results, we have considered the effect of the substituted group on the stability of resulting complexes.

## Experimental

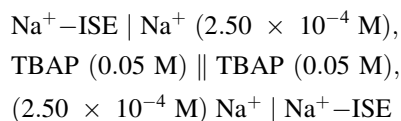
Reagent grade 18-crown-6 (18C6, **I**), benzo-18-crown-6 (DB18C6, **II**), dicyclohexyl-18-crown-6 (DCY18C6, **III**), dibenzopyridino-18-crown-6 (DBPY18C6, **IV**), benzo-15-crown-5 (B15C5, **V**), phenylaza-15-crown-5 (PhA15C5, **VI**), 4-nitrobenzo-15-crown-5 (NB15C5, **VII**) and sodium

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nitrate (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over  $P_2O_5$  (Scheme 1). Absolute methanol (Merck) was used as solvent. Tetrabutylammonium perchlorate (TBAP) was prepared from the 1:1 mixture of reagent grade perchloric acid and tetrabutylammonium bromide (both from Merck). The resulting TBAP salt was recrystallized three times from triply distilled deionised water and dried at 110 °C for 72 h. The stock solution of crown ethers (0.02 M) and sodium nitrate (0.01 M) were prepared and kept under dark.

A concentration cell was used for monitoring the concentration of sodium ion during the potentiometric titration of  $Na^+$  ion with a solution of the each crown ethers [15, 16]. The concentration of free sodium ion was measured with a glass sodium ion-selective electrode (Metrohm). The reference electrode was also a sodium ion-selective electrode, immersed in a known solution of  $NaNO_3$  ( $2.50 \times 10^{-4}$  M) in methanol and separated from the test solution by a salt bridge containing 0.1 M TBAP in the same solvent. The emf of the cell was measured with a digital voltmeter (model 624 Metrohm). In all experiments, the cell was thermostated at the desired temperature  $25 \pm 0.1$  °C, using a Huber thermostat. All titrations were carried out using a Metrohm electronic burette with a

precision of  $\pm 0.001$  ml. In all experiments, the ionic strength was kept constant at  $I = 0.05$  M using TBAP as supporting electrolyte. The schematic diagram of the cell is shown as:



To evaluate the stability constants, the following procedure was conducted. The sodium ion-selective electrode was placed in the reaction vessel containing 20 mL of 0.05 M TBAP in methanol. The reference compartment contained 0.05 M TBAP and  $2.50 \times 10^{-4}$  M sodium nitrates in the same solvent. First, a concentrated sodium nitrate (0.01 M) was added gradually until a  $Na^+$  ion concentration of  $2.50 \times 10^{-4}$  M was achieved, and the cell potential was measured. Plot of emf versus  $\log [Na^+]$  was strictly linear (slope: 58.9 mV/decade, intercept: 215 mV and  $r$ : 0.9980) at 25 °C.

## Results and discussion

The stability constant of the  $Na^+$ -crown ether complex ( $K_{Na}$  of Eq. 1), can be determined by simple potentiometric titration of a solution of  $Na^+$  ion with a solution of crown ether, and monitoring the equilibrium concentration of sodium ion.

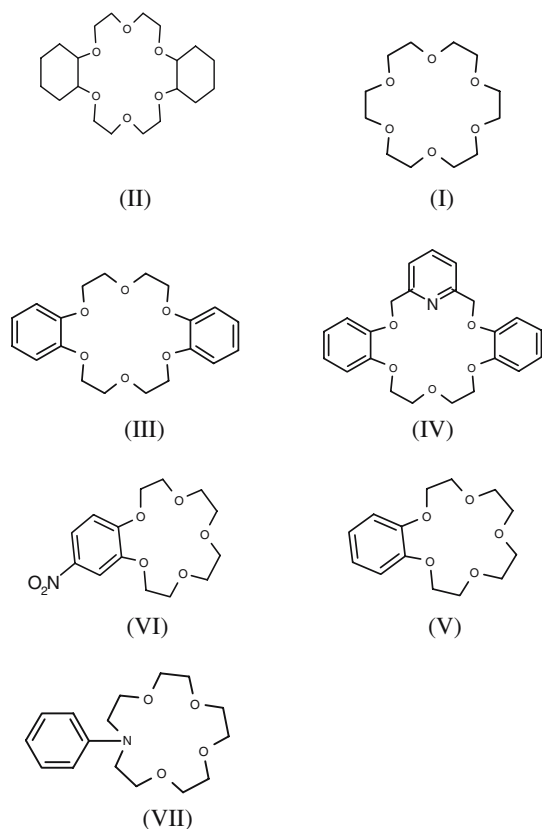


The total concentrations of  $Na^+$  and crown ether are written as:

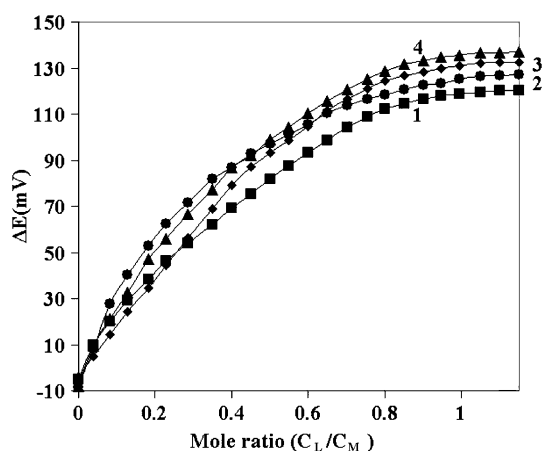
$$[Na^+]_{\text{tot}} = [Na^+] + [Na^+ - \text{crown}] \quad (2)$$

$$[\text{crown}]_{\text{tot}} = [\text{crown}] + [Na^+ - \text{crown}] \quad (3)$$

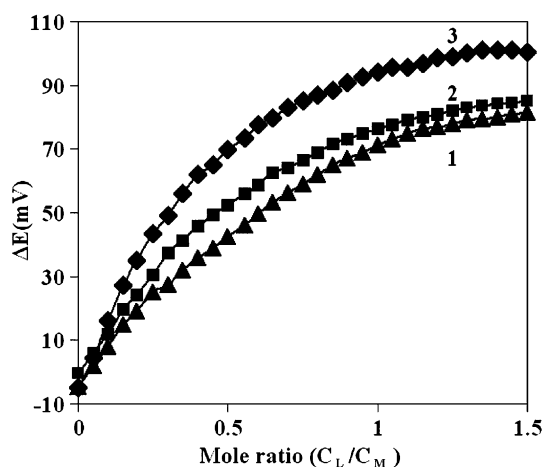
For evaluation of stability constants, the potentiometric titration of  $Na^+$  solution with a solution of the desired crown ether have been done at 25 °C as described in the procedure section [15–17]. The potentiometric profiles are shown in Figs. 1, 2. These plots show the 1:1 stoichiometry. The MINIQUAD program was used to support the stoichiometry and computation the formation constant  $K_{Na+}$  from the resulting potential-concentration data. The acceptance of final results at the desired significance level is based upon statistical parameters such as standard deviation, sum of square of residuals,  $\chi^2$  values (as a measure of the normality of residuals) and  $R$  factor [18, 19]. The resulting data are listed in Table 1.



**Scheme 1**



**Fig. 1** Potential difference versus mole ratio (L/M) plots for complexation of a  $2.50 \times 10^{-4}$  M  $\text{NaNO}_3$  solution with 0.02 M: (1) DBPY18C (2) DB18C6 (3) 18C6 (4) DCY18C6 in methanol at 25 °C and ionic strength 0.05 M TBAP



**Fig. 2** Potential difference versus mole ratio (L/M) plots for complexation of a  $2.50 \times 10^{-4}$  M  $\text{NaNO}_3$  solution with 0.02 M: (1) 4-nitrobenzo-15C5 (2) B15C5 (3) phenylaza-15C5 in methanol at 25 °C and ionic strength 0.05 M TBAP

The consideration of data given in Table 1, reveals a general trends for resulting stability constants,  $\text{DCY18C6} > \text{DB18C6} > \text{18C6} > \text{DBPY18C6} > \text{phenylaza-15C5} > \text{Benzo-15C5} > \text{4-nitrobenzo-15C5}$ . This trend is clearly in accordance with the size effect for fitting into 18-membered rings and 15-membered crowns [1–3, 20, 21].

The sodium cation has a more proper size (2.04 Å) for fitting into 18-crown-6 ring (2.68–2.86 Å) and less for 15-crown-5 (1.72–1.82 Å) [7], the variation seen among the  $\text{Na}^+$  complexes in each series is mainly due to different substitution groups on 18-crown-6 and 15-crown-5 rings. In the series of 18-crowns-6, the effect of introducing dicyclohexyl-, and dibenzo- groups into 18-crown-6 ring have been described before [22, 23]. The presence of cyclohexyl-group allow pumping electrons into the ligand

**Table 1** Logarithm of stability constants ( $\text{Log } K_f \pm \sigma^*$ ) for resulting complexes of a series 18-crown-6 and derivatives of 15-crown-5 with sodium ion methanol at 25 °C, and ionic strength 0.05 M TBAP

Crown	$\text{Log } K \pm \sigma^a$	Sum. of sq	$\text{Log } K \pm \sigma^*$
DCY18C6	$4.61 \pm 0.02$	$9.3 \times 10^{-8}$	$4.33 \pm 0.03^b$ $4.70^c$
18C6	$4.48 \pm 0.01$	$8.5 \times 10^{-8}$	$4.25 \pm 0.04^b$ $4.32^c$
DB18C6	$4.27 \pm 0.03$	$9.4 \times 10^{-8}$	$4.15 \pm 0.0^b$
DBPY18C6	$4.12 \pm 0.02$	$8.8 \times 10^{-8}$	$3.96 \pm 0.01^b$
PhAza15C5	$3.83 \pm 0.02$	$8.5 \times 10^{-8}$	–
B15C5	$3.27 \pm 0.01$	$9.6 \times 10^{-8}$	$3.05^c$
NB15C5	$2.73 \pm 0.02$	$8.7 \times 10^{-8}$	–

\* Standard deviation. The sum of squares of residuals,  $\chi^2$  and  $R$  values associated with formation constants were in the range of  $0.4 \times 10^{-8}$ – $2.30 \times 10^{-8}$ , 2.2–56.7 and 0.01–0.04, respectively

<sup>a</sup> This work, <sup>b</sup> [13], <sup>c</sup> [4]

ring and increase the basicity of the oxygen atoms, while the flexibility of the ligand remains almost the same as 18C6. The commercial DCY18C6 is a mixture of two isomers and this may cause the unexpected results. The effect of substitution of two benzo-groups on the 18C6 ring remarkably lowers the stability of its complexes. It should be noted that by introducing two electrons withdrawing groups reduce the donicity of the oxygen atoms in the ring and they decrease the cation-crown interaction [22, 23]. We also considered the effect of pyridino-group on the DB18C6 ring [11–13]. According to our previous reports the stability of  $\text{Na}^+$ –DBPY18C6 complex was weaker than other used 18-crown-6 [13]. In DBPY18C6, the presence of three aromatic moieties reduces the affinity of the donor atoms towards hard metal ions such as sodium ion. The presence of a pyridyl-group increases the rigidity of the macrocylce, and on other hand, pyridino nitrogen in 18-membered ring remarkably increases the softness of this ligand. So, the weak interaction could be partially due to the weak interaction of the pyridino nitrogen of this ligand as a soft base with  $\text{Na}^+$  ion as a hard acid [13, 24]. The comparison of 15-crowns-5 series, with series of 18-crowns-6 is quite expected [22]. Although, according to ‘ion-in-the-hole’ model [4], the size of sodium ion is proper for both two series of crown ethers, but in case of 18-crowns-6 series, the flexibility of rings of donor atoms and its side groups permits the perfect interaction of them with sodium ion.

Among the used 15-crown-5, the stability of complex of phenylaza-15-crown-5 with sodium ion is unique and not comparable with others. In this case, although, the tendency of nitrogen interaction as soft base toward the sodium ion which is a hard acid should be low, but the presence of phenyl group attached to this nitrogen

increases the charge density around it. Since the  $\text{Na}^+$  do not fit in the cavity of this crown ether, it is possible that the  $\pi$  system of phenyl ring interacts with vacant 3p orbital of sodium cation and increases the stability constant of this crown in comparison with Aza15-crown-5 [25, 26].

The trend of stability constants of B15C5 and 4-nitrobenzo-15C5 which decreased in the latter is quite expected. This is due to the presence of a withdrawing group of nitro in benzo ring attached to 15-crown-5, which decreases the electron density of 15-membered ring. Moreover, it should be noted that the thermodynamic stability constants are not just a measure of the absolute strength of the complexes, but a measure of the relative strength as compared to the ionic solvation. Contributions of the solvent-complex and even solvent-ligand interactions on the stability of the resulting complexes should be considered [27].

In order to comparing the results of this work with data from the literatures, the stability constants of the complexation of these crown ethers with sodium ion are listed in Table 1. We selected the data from literatures which has been done with  $\text{Na}^+$ -ISE, and our pervious study [4, 5, 13]. The comparison of the results of this study with our previous paper and reported in the literature which have been done by potentiometric method using  $\text{Ag}^+/\text{Ag}$  electrode is perfectly in agreement [13]. Low variation are seen which may be due reproducibility of different experimental conditions [28]. There are not any report about phenylaza-15C5 and 4-nitrobenzo-15C5 in the literature for comparison [4, 5, 7]. So the obtained results in particular stability constants of complexes of dibenzopyridino-18-crown-6, phenylaza-15C5 and 4-nitrobenzo-15C5 with  $\text{Na}^+$  are precise, novel and interesting.

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