

# The Cation Binding of Benzo Crown Ethers in Acetonitrile Using Fluorescence Spectroscopy

AYTEN GÖÇMEN and ÇAKIL ERK\*

*Department of Chemistry, Technical University of Istanbul, Maslak 80626, Istanbul, Turkey.*

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**Abstract.** The effects of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Li}^+$  cations on the fluorescence spectra of benzo[15]crown-5, benzo[18]crown-6 and dibenzo[18]crown-6 were investigated in acetonitrile. The alkali cation role observed was usually the complexation-enhanced quenching fluorescence effect (CEQF) in acetonitrile due to the increased fluorescence quenching rate of the complexed fluoroionophore. The association constants for 1:1 stoichiometry  $\ln K_a$  have been obtained using the relationship  $1/K_a[L_0] = (1 - P)^2/P$ . It was shown that the preferential interaction rule of compatibility of cationic radii and macrocyclic ring size is in excellent agreement with the association constants obtained by fluorescence spectroscopy. The order of  $\ln K_a$  found for benzo[15]crown-5 complexation was  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$  and  $\text{K}^+ > \text{Na}^+ > \text{Li}^+$  for benzo[18]crown-6 in acetonitrile.

**Key words.** Benzocrown ethers, cation complexation, fluorescence spectroscopy.

## 1. Introduction

Spectroscopic methods capable of detecting molecular motions within the frequency range of  $10^{-3}$ – $10^{-12}$  s in nonviscous liquids allow the study of intramolecular effects and particularly the role of inclusion or complexation.

The effect of cations on the fluorescence spectra of benzo-15-crown-5 was first reported by Morita *et al.* [1] whilst the naphtho-crown ethers were studied by Sousa *et al.* [2]. Fluorescence spectroscopy was used recently in our laboratory on coumarin-crown ether derivatives with alkali and alkaline earth cations giving good quantitative results in dry acetonitrile solutions [3, 4]. The strong effect of cation binding on the coumarin-crown spectra was revealed.

The present work deals with investigation of the complexing effects of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Li}^+$  cations on the fluorescence spectra of benzo[15]crown-5, benzo[18]crown-6 and dibenzo[18]crown-6 in acetonitrile. The role of counterions like  $\text{SCN}^-$  and  $\text{ClO}_4^-$  was also examined over a large intensity and concentration range. The alkali cation role on the benzocrowns was mostly observed as the complexation-enhanced quenching fluorescence effect (CEQF) in acetonitrile due to an increased quenching rate of the fluorescence decay [3–6]. Most probably, the molecular dynamics of

\* Author for correspondence.

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the macrocyclic ring is altered in the case of strong metal complex formation in solution.

Accordingly, the association constants of the given equilibrium, Equation (1), were estimated from fluorescence spectra of complex solutions. The 1 : 1 stoichiometry association constants were calculated with Equation (2) where  $P$  is the mole fraction of complexed ligand  $P' = P/(1 - (m - 1)P)$ , and  $L_0$  is the initial concentration of the macrocyclic ligand which is the same as the cation concentration [3, 7, 8].



$$1/K_a[L_0] = (1 - P')^2/P' \quad (2)$$

$$1/K_a[L_0]^{n+m-1} = (1 - nP')^n(1 - mP')^m/P' \quad (3)$$

The association constants in acetonitrile were found to be in the order of  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$  for benzo[15]crown-5 but the order for benzo[18]crown-6 is  $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ , as expected. The cation radius is the governing factor regarding the ion-dipole interaction depending on the average macrocyclic hole size with the optimized molecular geometry [9]. However, some other physical effects are involved in addition to the size complementarity but they only limit the concentration range which is not so important for analytical procedures [6].

## 2. Experimental

The chemicals were from Fluka AG unless otherwise cited. Dibenzo[18]crown-6 was synthesized according to Pedersen and twice purified on alumina with  $\text{CHCl}_3$ . Thiocyanate salts were dried prior to use. In order to estimate the association constants the solutions were prepared in acetonitrile with various identical initial cation-ligand concentrations,  $[A_0] = [L_0]$ . The  $(1 - P)^2/P$  values were found experimentally, where  $P$  is the mole fraction of the complex then plotted versus the inverse of the initial macrocyclic ligand concentrations,  $1/[L_0]$  and the inverse of the slope gave the association constants,  $\ln K_a$ , within a  $\pm 0.2$  precision and  $\Delta G$  within  $\pm 200 \text{ J M}^{-1}$  (Table I) [8].

Fluorescence emission and excitation spectra were obtained with a Perkin Elmer Luminescence spectrometer model LS-50 in dry  $\text{CH}_3\text{CN}$  within the concentration range of  $10^{-2}$ – $10^{-7}$  M in 10 mm quartz cells. The emission spectra of free and complexed benzo[15]crown-5 were measured at  $\lambda_{\text{max}} = 308$  nm (excitation  $\lambda_{\text{max}} = 288$  nm). Benzo[18]crown-6 emissions were measured at  $\lambda_{\text{max}} = 306$  nm (excitation  $\lambda_{\text{max}} = 286$  nm). The electronic noise was removed from the spectra prior to peak maxima being measured and then plotted with a HP XY plotter. No quinine bisulfate was used to compare the quantum efficiencies [6].

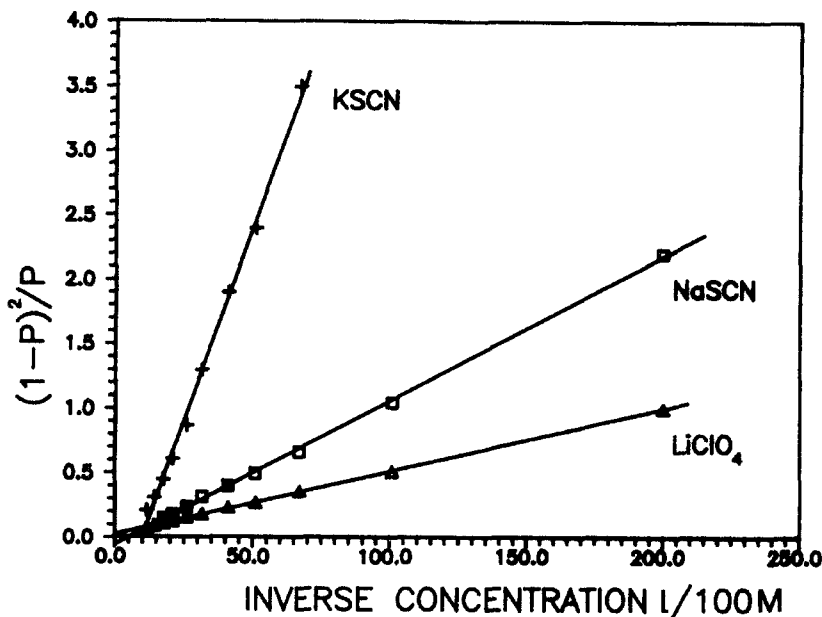


Figure 1. The plot of inverse concentration of salts versus  $(1 - P)^2/P$  in the presence of equimolar benzo[15]crown-5 in  $\text{CH}_3\text{CN}$ . Equation (2) was used with the data obtained from fluorescence emission spectra at  $\lambda_{\text{max}} = 308$  nm.

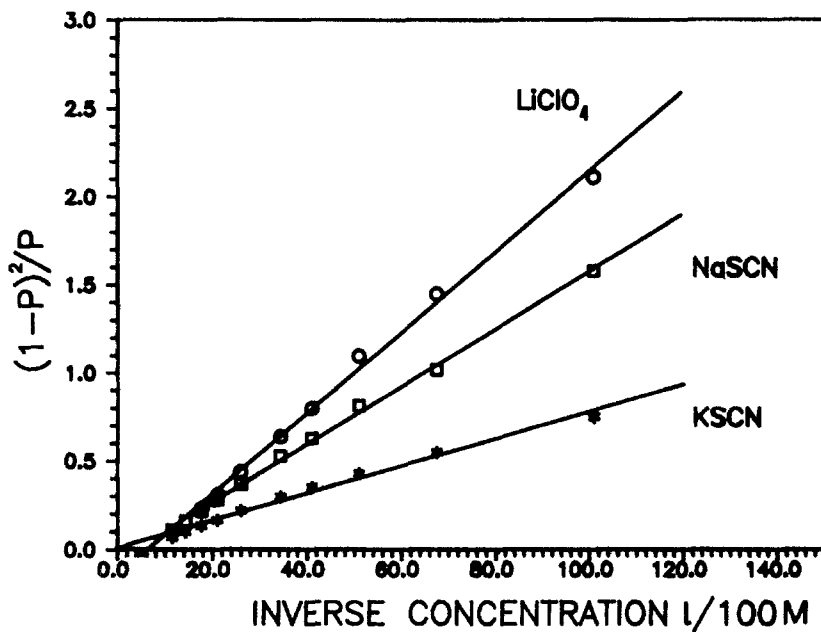


Figure 2. The plot of inverse concentration of salts versus  $(1 - P)^2/P$  in the presence of equimolar benzo[18]crown-6 in  $\text{CH}_3\text{CN}$ . Equation (2) was used with the data obtained from fluorescence emission spectra at  $\lambda_{\text{max}} = 306$  nm.

Table I. The 1 : 1 association constants obtained using fluorescence data in acetonitrile at 25 °C.

		KSCN		NaSCN		LiClO <sub>4</sub>	
		$\ln K_a$	$\Delta G$ (J M <sup>-1</sup> )	$\ln K_a$	$\Delta G$ (J M <sup>-1</sup> )	$\ln K_a$	$\Delta G$ (J M <sup>-1</sup> )
I	Bz[15]cr5	7.50	9350	9.13	11378	9.89	12318
II	Bz[18]cr6	9.64	12014	8.79	10950	8.38	10490
III	DB[18]cr6	9.04	11264	9.15	11399	—	—

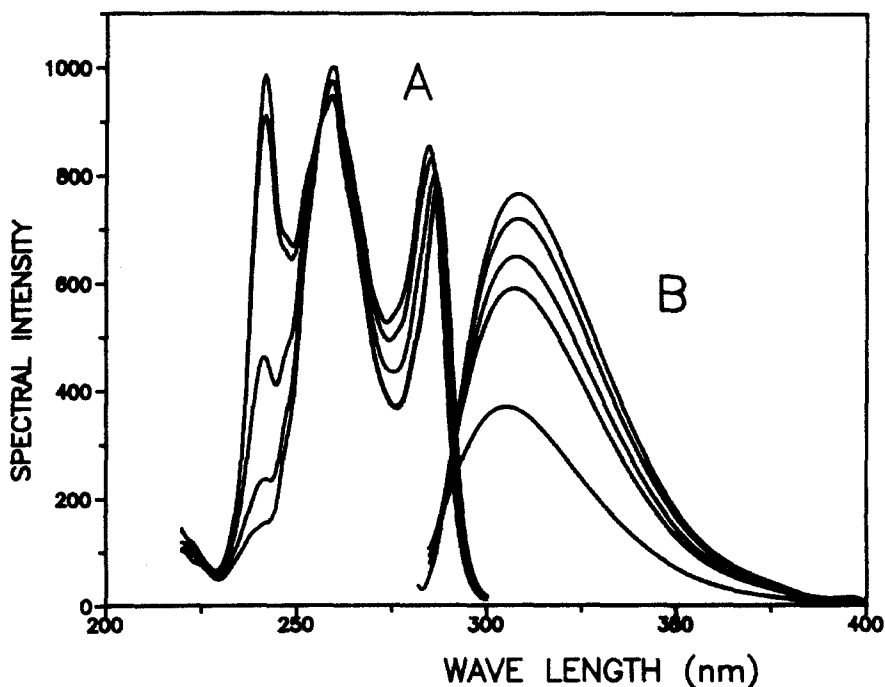


Figure 3. (A) The fluorescence excitation spectra (emission  $\lambda_{\max} = 308$  nm), (B) emission spectra (excitation  $\lambda_{\max} = 288$  nm) of benzo-15-crown-5 in the presence of various concentrations of NaSCN in acetonitrile.

### 3. Results and Discussion

Fluorometric methods used for the analytical determinations of ions and the complexation induced fluorescence changes attributed to relative energy changes were reviewed recently [5].

During an electronic dipole transition to a lower state with the same spin multiplicity fluorescence quenching may occur if any chemical change involved opens

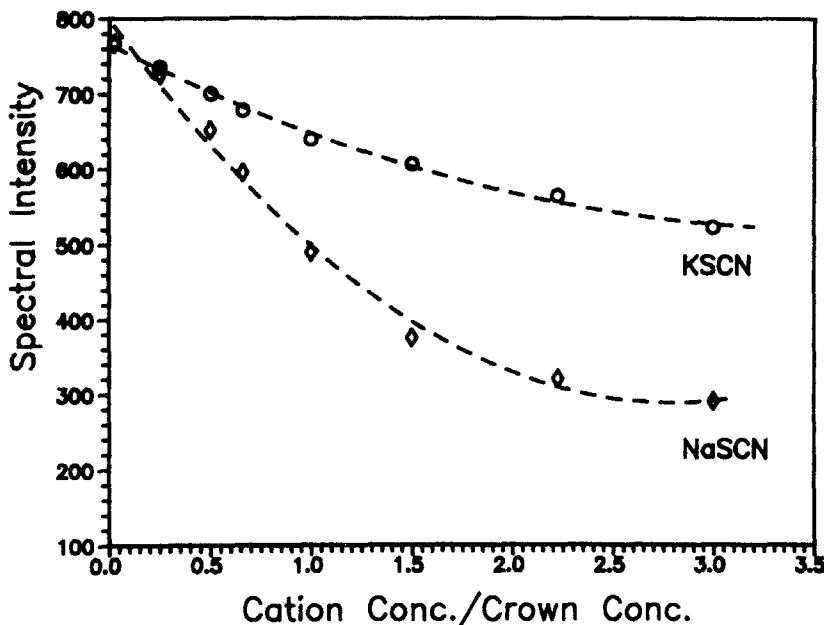


Figure 4. The titration with emission spectra of benzo[15]crown-5 ( $0.998 \times 10^{-3} \text{ ML}^{-1}$ ) with NaSCN and KSCN measured at  $\lambda_{\text{max}} = 308 \text{ nm}$  in acetonitrile. Dotted lines are the 2nd order polynomial regressions.

a new decay channel causing a decrease in the intensity. However, the rate of alteration of decay depends on the complex kinetics of controlled processes [6].

The emissions of crown ether fluorophores with  $\pi$ -systems are altered upon complexation. This has been also reported with some cryptates designed with similar chromophores [10]. The effect of cations on the fluorescence spectra of benzo[15]crown-5 studied by Morita in methanol indicated a fluorescence enhancement (CEF) with complexation [1]. The naphtho-crown ethers studied by Sousa have shown both effects of CEF and complexation enhancing quenched fluorescence (CEQF) [2]. The fluorescence spectra of coumarin-crown ether derivatives studied recently in our laboratory with alkali and alkaline earth cations have shown interesting results [3, 4]. The qualitative treatments have been successfully carried out in coumarin-crown studies giving good quantitative results in dry acetonitrile [7]. However, the effects of CEF and CEQF were observed and we have reported the strong cation binding effect by this way.

In the present work,  $\text{Na}^+$  was found to be more effective on the fluorescence altered spectra of a rigid five oxygen member benzo[15]crown-5 compared to  $\text{K}^+$  due to the contribution of the rotational diffusion or molecular motion rate which decreases in the  $S_1$  state in a complex (Figure 1).  $\text{Li}^+$  seems most effective for such a macrocyclic, which is not surprising in nonhydroxylic media. Popov has reported similar results using  $^7\text{Li}$  NMR and calorimetry [11].

For the benzo[18]crown-6/salt systems KSCN is favored for a six oxygen macrocycle and  $\text{Li}^+$  has the smallest role (Figure 2). On the other hand, the quantum yields are rather large in salt/dibenzo[18]crown-6 complexes due to doubling of  $\pi$ -systems but the selectivity is relatively poor since the 2s oxygen electrons are more delocalized. However, it is interesting to note that  $\text{Li}^+$  with the smallest cation radius exhibited almost no role with dibenzo[18]crown-6 in  $\text{CH}_3\text{CN}$  [9, 12].

The interesting part of this work is the determination of the complexation of benzocrowns at a constant cation concentration in  $\text{CH}_3\text{CN}$ . The alkali cation concentrations were changed experimentally in the presence of constant ligand concentration and the decrease in the emission intensities compared to the free macrocyclic spectra were recorded (Figures 3 and 4). The data did not, however, indicate any fixed stoichiometries. This could be explained in terms of ion pair theory as discussed by Popov in regard to the several steps of complexation [11]. Such titration experiments have been performed for similar structures with different analytical methods to estimate the complex formation stoichiometries [9, 11]. The complex formation was, however, evidenced strongly in acetonitrile but poorly in water. However, we conclude that such studies are satisfactory for the investigations of molecular recognition. Recent reports have indicated that fluorescence spectroscopy can be used to study the complexation of various macrocycles with fluorophore groups although they have complex physical mechanisms [6, 12].

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