INFLUENCE OF METAL ION COMPLEXATION ON THE ACID DISSOCIATION OF 4'-CARBOXYBENZO-24-CROWN-8 IN AN ETHANOL-WATER MIXTURE☆

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ABSTRACT: *A spectrophotometric method was used to determine the acidity constant of 4'-carboxybenzo-24-crown-8 in 52% (w/w) ethanol-water mixture. The acid dissociation constant, K_a , was found to increase in the presence of Na^+, K^+, Rb^+, Cs^+ and Tl^+ ions. The formation constants of the resulting 1:1 complexes between the carboxycrown and the metal ions used were evaluated from the observed changes of K_a value with varying concentration of cations and found to vary in the order $Rb^+ > Cs^+ > Tl^+ > K^+ > Na^+$.*

KEY WORDS: *4'-Carboxybenzo-24-crown-8, K_a , Ethanol-water mixture, Alkali and Tl^+ ions, Complexation, Spectrophotometry.*

INTRODUCTION

It is well known that the substituents incorporated into flexible macrocyclic rings may alter both the stability and selectivity of their complexes with metal ions [1,2]. Addition of two benzo rings to 18-crown-6 diminished the stability of its complexes with alkali [3,4] and alkaline earth cations considerably [5]. This behavior is attributed to some combination of the electron-withdrawing effect of benzo groups, which weakens the electron-donating ability of the ether oxygens of the ring and the reduced flexibility of the ligand, which prevents the macrocyclic wrapping itself around the cation. On the other hand, while the stability constant of Ba^{2+}-18-crown-6 in methanol is ten times larger than that of K^+-18-crown-6 [6], dibenzo-18-crown-6 displays an opposite preference, binding K^+ ion stronger than Ba^{2+} ion in methanol by about the same extent [7]. Moreover, the substitution of electron-withdrawing and elec-

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tron-donating groups on the benzo rings of the ben-zocrowns can alter the stability of their metal ion complexes [8].

We have recently reported the synthesis and alkali metal complexation of 4'- carboxybenzo-24-crown-8 and 4'-amidobenzo-24-crown-8 in some aprotic non-aqueous solvents [9]. In all cases, the former crown ether was found to form a less stable alkali complex. This is because the substitution of a carboxy-group with a higher electrophilic character than an amido-group in 4'-position of the crown ether's benzo ring will result in lowering basicity of the donating oxygens of the macrocyclic ring.

In the present work we noticed that, in alcohol-water mixtures, the acid dissociation constant of 4'-carboxybenzo-24-crown-8 increases in the presence of Na^+, K^+, Rb^+, Cs^+ and Tl^+ ions, from which the equilibrium constants for cation binding can then be deduced. Thus, in this paper we wish to report the results of the investigation of the influences of these cations on the acid dissociation constant of the carboxycrown ether in 52% (w/w) ethanol-water mixture at 25 °C using a spectrophotometric method.

EXPERIMENTAL

Analytical grade chloride salts of lithium, sodium, potassium, rubidium, cesium and thallium (all from *Merck*) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5 . Absolute ethanol (*Merck*) and doubly distilled deionized water were used to prepare the solvent mixture by weight. The crown ether 4'-carboxybenzo-24-corwn-8 (COOH-B24C8, I) was synthesized and purified as described before [9]. All other chemicals used (from either *Merck* or *Fluka*) were of the reagent grade and used as received.

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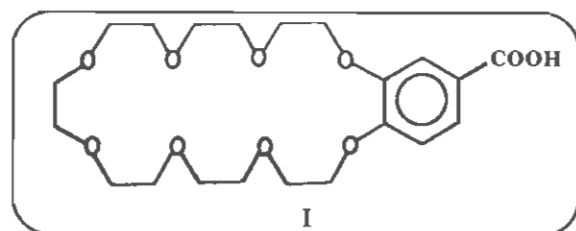
The *pH* measurements were made with a Corning Ion Analyzer 250 using a combined glass electrode. All absorbance measurements at 25±1 °C were

carried out on a Shimadzu UV-256 FW spectro-photometer.

RESULTS AND DISCUSSION

We have recently reported the synthesis of COOH-B24C8 and the stability of its 1:1 complexes with alkali metal ions in nitromethane, acetonitrile and dimethylformamide solutions [9]. In other preli-minary experiments carried out in ethanol-water mixtures we noticed that the acidity of COOH-B24C8 is increased by the presence of alkali ions (other than Li^+) and Tl^+ ion.

Based on our previous experiences on the spectro-photometric determination of the acidity constants of some anthraquinone and anthrone derivatives in alco-hol-water mixtures [10,11] as well as the well known sensitivity and reliability of the method, we studied the acid dissociation of COOH-B24C8 at 25 °C in 52% (w/w) ethanol-water mixture by absorbance measure-ments at 264 nm in buffer solutions made up from solutions of acetic acid and LiOH. The spectra of the dissociated (COO^--B24C8) and undissociated (COOH-B24C8) carboxycrowns were obtained in the presence of 0.01 M LiOH and 0.01 M HCl, respec-tively. In all cases the ionic strength of solutions was adjusted to 0.1 M using tetramethylammonium chlo-ride. The detailed procedure for the spectrophoto-metric determination of the acidity constants is given elsewhere [10,11]. It should be noted that no evi-dence for the measurable binding of tetramethyl-ammonium chloride and lithium chloride to the carboxycrown ether in the solvent system used was observed, even at 0.1 M concentration, as noticed before [1,7].
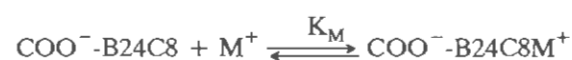
The calculated acidity constants of COOH-B24C8 in the absence and presence of varying concentration of Na^+, K^+, Rb^+, Cs^+ and Tl^+ ions in the solvent mixture used are summarized in Table 1. As it is obvious, the values of K_a in the presence of metal ions used are larger than the value with Li^+ and Me_4N^+. Such an enhanced acidity results from the stabilization of the carboxylate crown anion via complexation of a cation in an adjacent site (i.e., the cavity of the crown ether). As the concentration of cation increases, a greater fraction of the macrocycle with be complexed which, in turn, results in an

enhanced acidity of the carboxy crown ether. It is interesting to note that, at a constant concentration of the metal ions used, the increase in K_a value of the ligand is strongly depend on the nature of metal ion and vary in the order $Na^+ < K^+ < Tl^+ < Cs^+ < Rb^+$. This trend most probably reflects the stability order of the resulting complexes with the ligand.

Based on the above observation and considering the fact that the metal ions used form predominantly complexes of 1:1 stoichiometry with different 24-crown-8 derivatives [1,2,9,12], it seems reasonable to assume that equilibria (1) and (2) prevail in solution at *pH* values near the pK_a value of the protonated carboxycrown ether.

$$COO^- \text{-B24C8} + H^+ \xrightleftharpoons{K_H} COOH\text{-B24C8}$$
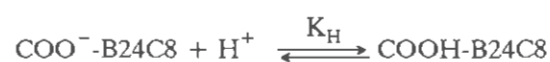
$$K_H = \frac{[COOH\text{-B24C8}]}{[COO^-\text{-B24C8}][H^+]} = \frac{1}{K_a} \qquad (1)$$

$$COO^-\text{-B24C8} + M^+ \xrightleftharpoons{K_M} COO^-\text{-B24C8M}^+$$

$$K_M = \frac{[COO^-\text{-B24C8M}^+]}{[COO^-\text{-B24C8}][M^+]} \qquad (2)$$

Consequently, the apparent protonation constant, K'_H, can be expressed as

$$K'_H = \frac{[COOH\text{-B24C8}]}{[H^+]([COO^-\text{-B24C8}]+[COO^-\text{-B24C8M}^+])} = \frac{K_H}{1 + K'_H[M^+]} \qquad (3)$$

Equation (3) can be then rearranged as

$$\frac{K_H}{K'_H} = 1 + K_M[M^+] \qquad (4)$$

According to equation (4), a plot of the ratio K_H/K'_H against $[M^+]$ should yield a straight line with the intercept equal to unity and the slope equal to K_M The resulting linear plots in the presence of various concentrations of all cations used are shown in Fig. 1 and the calculated K_M values are also included in Table 1.

The data given in Table 1 indicate that the stability of 1:1 complexes of COOH-B24C8 with the metal ions used, vary in the order $Rb^+ > Cs^+ > Tl^+ >$

Table 1: Acidity constants, K_a , of COOH-B24C8 in the presence of varying concentration of different metal ions and the corresponding formation constants, K_M , in 52% (w/w) ethanol-water at 25 °C

M^{+a}	Metal ion concentration(M)	$10^6 K_a$	$\log K_M$
—	—	0.86	
Na^+(1.02)	2.5×10^{-3}	1.00	
	5.0×10^{-3}	1.01	
	1.0×10^{-2}	1.02	
	2.0×10^{-2}	1.04	0.33 ± 0.08
K^+(1.38)	2.5×10^{-3}	1.06	
	5.0×10^{-3}	1.33	
	1.0×10^{-2}	1.43	
	2.0×10^{-2}	2.22	1.87 ± 0.06
Rb^+(1.52)	2.5×10^{-3}	1.32	
	5.0×10^{-3}	2.05	
	1.0×10^{-2}	2.56	
	2.0×10^{-2}	5.20	2.41 ± 0.03
Cs^+(1.67)	2.5×10^{-3}	1.17	
	5.0×10^{-3}	1.87	
	1.0×10^{-2}	2.09	
	2.0×10^{-2}	3.12	2.08 ± 0.07
Tl^+(1.50)	2.5×10^{-3}	1.21	
	5.0×10^{-3}	1.27	
	1.0×10^{-2}	1.60	
	2.0×10^{-2}	2.73	2.02 ± 0.05

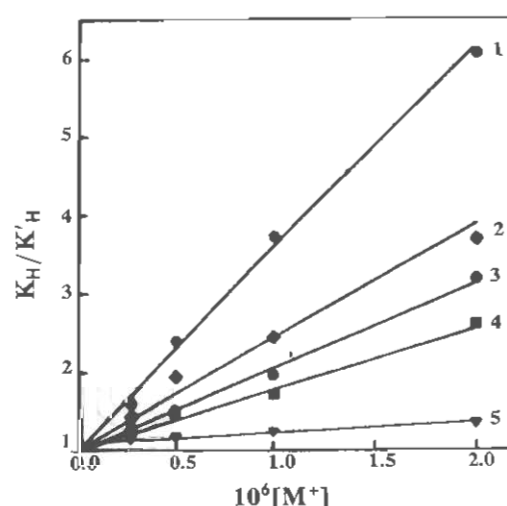*a : Values in parentheses are the ionic radii in $\mathring{A}$, Ref. 16.*

Fig. 1: Linear plots of K_H/K'_H vs. $[M^+]$ for different COOH-B24C8. M^+ systems in 52% (w/w) ethanol-water mixture: (1) Rb^+, (2) Cs^+, (3) Tl^+, (4) K^+, (5) Na^+.

$K^+ > Na^+$, similar to the trend observed for the extent of shift in K_a value of the ligand with the metal ions. It is well known that, among several factors affecting the metal ion-macrocycle binding [1,2,7], the relative size of the metal ion and the cavity of crown ether plays an important role. For example, for both alkali and alkaline earth cations the maximum stability for their complexes with 18-crown-6 occurs when the metal ion to ligand cavity ratio is approximately unity, as is the case of K^+ and Ba^{2+} ions [5-7]. However, such an "ion-in-the-hole" model will have limited usefulness in predicting relative binding strength of metal ions with larger crown ethers (i.e., larger than 18-crown-6), due to the increased number of ring atoms which results in enhanced flexibility of the macrocycle. Such a large flexibility of large crown ethers like COOH-B24C8 in solution would not only makes it difficult to define their cavity size, but also makes the molecule capable of twisting and wrapping itself around the cations to form a three-dimensional cavity with all oxygen atoms coordinated to the cation [12-15].

The results obtained in this study show that Rb^+ ion has probably the best fitting condition inside the twisted structure of COOH-B24C8, while larger and smaller size cations fail to reach such a proper structural situation. It is interesting to note that, although the ionic size of Tl^+ is about the same as Rb^+ ion [16], it forms a less stable complex with the ligand. This is most probably due to the softer acid character of Tl^+ ion, as compared with Rb^+, which results in its weaker interactions with the donating ether oxygens of the macrocyclic ring as hard bases [17].

However, it should be noted that the thermodynamic stability constant is not just a measure of absolute strength, as understood from the cation-macrocycle ion-dipole interactions, but a measure of the relative strength as compared to the ionic solvation. Thus it is only for the weakly solvated larger cations such as Rb^+ and Cs^+ ions that the cation size can be considered primarily responsible for the complexing characteristics. While, in the case of smaller cations such as Na^+ and, especially, Li^+ ions, the cation is so strongly solvated that considerably more energy must be expended in the desolvation step that for the larger cations. Depending on the solvent properties, the energy required for desolvation of metal ion may vary and, in some cases, may be too high to be compensated by the cation-macrocycle complexation step. This effect seems to be operating for Li^+ complexes which generally do not like to form in aqueous solution or in alcohol-water mixtures [1,7], but which are stable in solvents of low donating ability such as nitromethane [9].

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