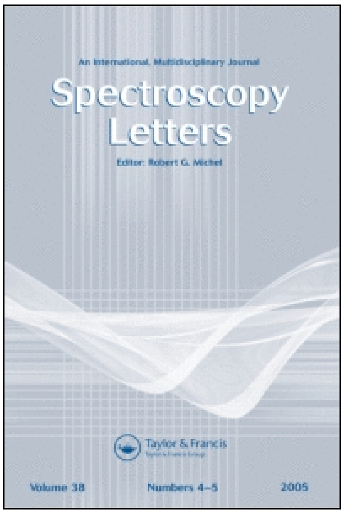

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Spectroscopic Study of Some Alkali and Alkaline Earth Complexes with Benzo Crown Ethers in Ethanol Solution

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SPECTROSCOPIC STUDY OF SOME ALKALI AND ALKALINE EARTH COMPLEXES WITH BENZO CROWN ETHERS IN ETHANOL SOLUTION

Key Words: Alkali; Alkaline earth; Benzo crowns; Complexes; Ethanol; UV-spectrophotometry.

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ABSTRACT

The interaction between Na^+, K^+, Mg^{2+} and Ca^{2+} ions and benzo crown ethers B15C5, DB18C6, DB21C7, DB24C8 and DB30C10 in ethanol solution has been studied spectrophotometrically at 25 °C. The formation constants for 1:1 complexes were determined by computer fitting of the resulting UV-absorbance-mole ratio data. In the case of all crown ethers used, K^+ ion was found to form the most stable complexes. The observed selectivities of different benzo crowns for the cations used are discussed in terms of the cavity-cation size ratio, number of the donating oxygens participating in the cation binding, conformations of the free and complexed ligands and ionic solvation.

INTRODUCTION

Since the first synthesis of macrocyclic polyethers (crown ethers) by Pedersen,[1] the studies of these ligands and their metal ion complexes became a very popular field of research,[2,3] mainly

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due to their similarities in many respects to the naturally occuring molecules such as ionophorous antibiotics.[4] An ipmportant part of crown ether chemistry deals with their alkali and alkaline earth complexes.[5,6] These cations are widely distributed in living organisms[7] and play vital roles in a wide varity of biological activities (e.g. trnsmission of nerve impulses, muscle contruction, etc.).[8] Many of these biological activities, however, are based on the selective complexation and transport of a given cation.[9,10] Stability constants and thermodynamic data for the reaction of alkali and, in less extent, of alkaline earth ions with macrocyclic ligands in aqueous and nonaqueous solvents have been reported.[5,6] On the other hand, such data are quite sparse in ethanol solution.

It was of interest to us to study the thermodynamics[11-14] and kinetics[15-17] of the complexation of macrocyclic ligands with alkali and alkaline earth cations in nonaqueous solvents. We have previously used the ultraviolet absorption band of benzo-15-crown-5 and dibenzo-30-crown-10 as a sensitive probe to study their complexation reactions with Na^+ and K^+ ions in acetonitrile-water mixtures.[18] In this paper we report a study of Na^+, K^+, Mg^{2+} and Ca^{2+} complexes with benzo-15-crown-5 (B15C5), dibenzo-18-crown-6 (DB18C6), dibenzo-21-crown-7 (DB21C7), dibenzo-24-crown-8 (DB24C8) and dibenzo-30-crown-10 (DB30C10) in ethanol solution at 25 °C by a previously reported UV-spectroscopic technique.[18,19]

EXPERIMENTAL

Perchlorate salts of sodium, potassium, magnesium and calcium (all from Merck) were of the highest purity available and used without further purification except for vacuum drying over P_2O_5. Crown ethers B15C5, DB18C6 (both from Merck), DB21C7, DB24C8 and DB30C10 (all from Parish) were purified and dried as described elsewhere.[11,20] Spectroscopic grade ethanol (Merck) was used as received.

A Perkin-Elmer Lambada 5 UV-Visible Spectrophotometer was used for recording the spectra and the absorbance measurements. A Julabo-

U3 thermostirer was used to maintain the temperature of the cell at 25.0 ± 0.5 °C.

The formation constants of 1:1 complexes between sodium, potassium, magnesium and calcium ions and the benzo crowns used were determined by the absorbance measurements, at the maximum absorption wavelength of the ligands (202 nm), of solutions in which varying concentration of metal ion (6.0×10^{-5}-3.0×10^{-3} M) was added to a fixed concentration of crown ether (2.0×10^{-5} M) in ethanol. Attainment of equilibrium was checked by the observation of no change in the spectra after several hours.

When a metal ion, M, reacts with a benzo crown ether, L, to form a 1:1 complex, the formation constant is given as

$$K_f = \frac{[ML]}{[M][L]} \qquad (1)$$

The mass balance equations and the observed absorbance, A_{obs}, are given by

$$C_M = [M] + [ML] \qquad (2)$$

$$C_L = [L] + [ML] \qquad (3)$$

$$A_{obs} = \varepsilon_L[L] + \varepsilon_{ML}[ML] = A_o/C_L[L] + \varepsilon_{ML}[ML] \qquad (4)$$

where C and ε values are the analytical concentration and molar absorptivities of the species indicated, respectively, and A_o is the absorbance of the ligand in the absence of metal ion. The mass balance equations can be solved in order to obtain an equation for the free ligand concentration, [L], as

$$K_f[L]^2 + (1 + K_f(C_M - C_L))[L] - C_L = 0 \qquad (5)$$

For the evaluation of the formation constant from absorbance-mole ratio data, a non-linear least-squares curve fitting program KINFIT was used.[21] The program is based on the iterative adjustment of the calculated values of the absorbances to the observed values by using either the Wentworth matrix technique[22] or the Powell procedure.[23] The adjustable parameters are K_f and ε_{ML}.

The free ligand concentration was calculated from equation (5) by means of a Newton-Raphson procedure. Once the value of [L] had been obtained, the concentration of all other species involved were

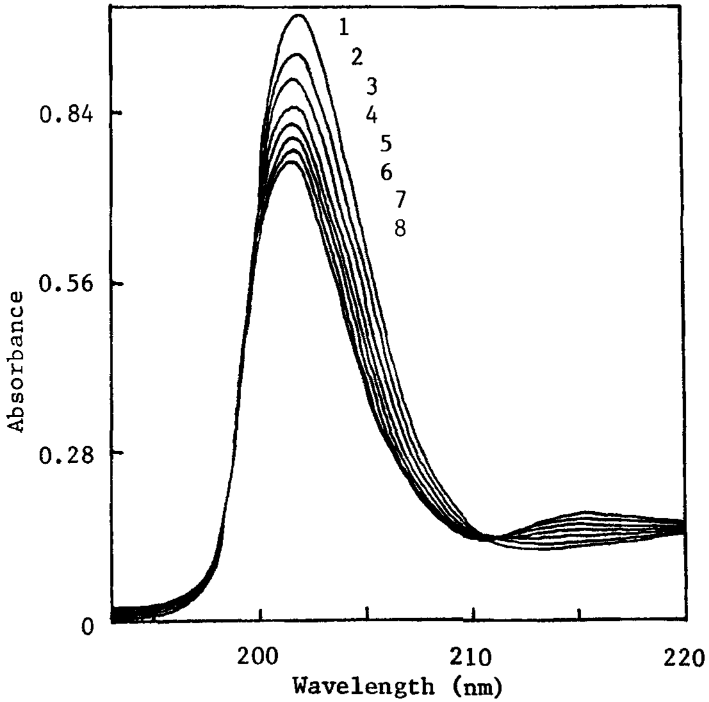

FIG. 1. UV-absorption spectra of DB24C8 (2.0 x 10^{-5}M) in the presence of varving concentration of Na^+ ion: 1, 0.0; 2, 1.5 x 10^{-4}M; 3, 3.0 x 10^{-4}M; 4, 4.5 x 10^{-4}M; 5, 7.6 x 10^{-4}M; 6, 1.1 x 10^{-3}M; 7, 1.5 x 10^{-3}M: 8, 2.3 x 10^{-3}M.

calculated from the mass balance equations (2) and (3), by using the estimated value of the formation constant at the current iteration step of the program. Refinement of the parameters is continued untill the sum-of-squares of the residuals between calculated and observed values of the absorbance for all experimental points is minimized. The output of the program KINFIT comprises refined paramrters, the sum-of-squares and the standard deviation of the data.

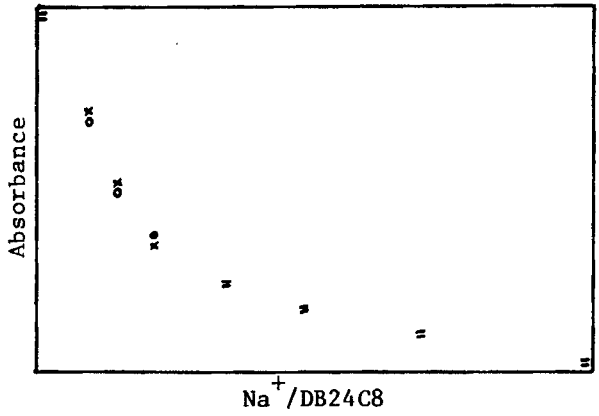

FIG. 2. Computer fit of the absorbance-mole ratio data for complexation of Na^+ ion with DB24C8 in ethanol: (x) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

RESULTS AND DISCUSSION

The formation constants of different metal ion-benzo crown complexes were determined by recording the UV-spectra of a series of solutions of fixed ligand concentration and varying amounts of the metal ions in ethanol. A sample spectra are shown in Figure 1. As it is seen, increasing the cation concentration results in a decrease in the benzocrown absorbance at 220 nm and appearance of a broad band at about 216 nm, indicating the formation of a new benzo crown species. In all cases studied, the resulting absorbance-mole ratio data showed the best computer fitting to the 1:1 metal ion-macrocycle stoichiometry. A sample computer fit of the data is shown in Figure 2. Moreover, the existence of a well defined isosbestic point in the absorbanse spectra of benzo crown upon the titratuon with metal ions is further evidence for a simple 1:1 equilibrium. All calculated K_f values are summarized in Table 1.

TABLE 1

Stability Constants of Na^+, K^+, Mg^{2+} and Ca^{2+} complexes with Different Benzo Crown Ethers in Ethanol Solution at 25 °C

Ligand[a]	log K_f			
Cation[b]	Na^+ (2.04)	K^+ (2.76)	Mg^{2+} (1.44)	Ca^{2+} (2.00)
B15C5 (1.7-2.2)	3.19±0.07	3.52±0.05	2.57±0.07	2.90±0.02
DB18C6 (2.6-3.2)	4.12±0.04	5.71±0.19	3.74±0.06	2.94±0.06
DB21C7 (3.4-4.3)	2.16±0.15	4.93±0.08	3.32±0.02	3.07±0.10
DB24C8 (>4.0)	3.41±0.04	3.99±0.03	3.51±0.09	3.94±0.11
DB30C10 (>4.0)	3.20±0.06	4.63±0.10	1.71±0.03	3.04±0.16

[a] Cavity size, Å, in parentheses, ref. 24.

[b] Ionic size, Å, in parentheses, ref. 32.

From Table 1, it is obvious that the stabilities of the resulting 1:1 complexes between each crown ether and different metal ions vary in the order:

B15C5: $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$
DB18C6: $K^+ > Na^+ > Mg^{2+} > Ca^{2+}$
DB21C7: $K^+ > Mg^{2+} > Ca^{2+} > Na^+$
DB24C8: $K^+ > Ca^{2+} > Mg^{2+} > Na^+$
DB30C10: $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$

There are at least four factors which can make significant contributions to the stability of the cation complexes with macrocyclic ligands: (1) the cavity size-cation diameter ratio, (2) the number of donating oxygen atoms participating in cation binding, (3) conformations of the free and complexed crown ethers and (4) the ionic solvation of the charged species involved.

As can be seen, among different cations studied, potassium ion forms the most stable complexes with all benzo crowns used. Although the size of Na^+ ion is such that it can fit inside the B15C5 cavity,

K^+ ion with larger size and less suitable fit condition[24] forms a more stable complex with this ligand. Similar results have been reported previously.[24,25] This behavior probably reflects the fact that the K^+ ion has a lower charge density than Na^+ and, therefore, it is rather weakly solvated by the solvent molecules. Thus, competition between the ligand and solvent molecules for Na^+ ion is stronger than that for the K^+ ion which, in turns, causes the weakening of the B15C5-Na^+ complex. The ionic solvation of Mg^{2+} and Ca^{2+} ions is even stronger[26,27] and, consequently, weakening of their complexes, compared with K^+ and even Na^+ ions, is not surprising.

Similarly. in the case of DB18C6, the resulting complexes with strongly solvated bivalent ions are less stable than those with the monovalent cations. It is interesting to note that, because of the much more suitable fitting condition of K^+ ion for DB18C6 cavity compared with that for B15C5 ring, the stability constant of DB18C6-K^+ complex is more than two orders of magnitude larger than that of B15C5-K^+.

The data given in Table 1 show that DB21C7 forms a less suitable potassium complex than DB18C6, most probably due to the poor fitting condition between the cation size and the larger cavity of the macrocycle. In addition, Mg^{2+}, Ca^{2+} and Na^+ are too loose for the cavity of DB21C7, resulting in much weaker complexes than DB21C7-K^+.

Among the large crown ethers used (i.e. DB24C8 and DB30C10), DB30C10 despite its too large cavitysize forms a fairly stable complex with K^+ ion. This is a rather flexible ligand that can easily wrap itself around a metal ion of proper size such as K^+ ion so that all ten oxygen atoms of the polyether ring participate in bond formation with the cation, resulting in a stable three-dimensional "wrap around" complex. Evidences for the formation of such "wrap around" structure for DB30C10-K^+ both in crystaline state[28] and in solution[29,30] have been reported previously. In the case of Na^+ and Ca^{2+} ions, where the cavity size is much larger than the cation, the ligand can still form a three-dimensional structure, but in this case the oxygen atoms of the ligand will have to be in close proximity so that the repulsive forces will weaken the complex. Accordingly, Mg^{2+} ion with the smallest size among the cations used forms the least stable DB30C10 complex in the series.

On the other hand, DB24C8 with lower flexibility and less donating atoms than DB30C10 forms a less stable complex with K^+ ion. In this case, the cation is too large for the formation of a complete three-dimensional structure; consequently, a weaker complex results. It is interesting to note that, in the case of other cations studied, the resulting DB24C8 complexes are more stable than the corresponding complexes with DB30C10, probably due to the more suitable sizes of these cations for the formation of a "wrap around" complex with this ligand. Beside the previously reported evidences for the existence of a "wrap aroun" DB24C8-Na^+ complex in solution,[20] recently Buchanan and coworkers[31] have reported a three-dimensional structure for dicyclohexano-24-crown-8-Na^+ complex in which the macrocycle ring adopts a conformation that allows all eight crown ether oxygens to be coordinated to the sodium ion.

The data given in Table 1 revealed that magnesium ion despite its smaller size forms a more stable complex than calcium ion with DB21C7 and DB18C6. This could be a result of some twisted structure of the crown ethers around Mg^{2+} ion which provide more donating oxygen atoms of the rings for the interaction with central cation.

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