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Spectroscopic Study of the Complexation of Benzo-15-crown-5 and Dibenzo-30-crown-10 with Sodium and Potassium Ions in Binary Acetonitrile–Water Mixture

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Abstract

The interaction between Na^+ and K^+ ions and benzo-15-crown-5 and dibenzo-30-crown-10 in CH_3CN-H_2O mixtures has been studied spectrophotometrically, at 25 °C and at ionic strength of 0.015. The formation constants for 1:1 complexes at different weight percentages of acetonitrile in water were determined. In all solvent mixtures used, the stabilities of the complexes vary in the order DB30C10–K^+ > B15C5–K^+ > B15C5–Na^+. A linear relationship is observed between log K_f of the three complexes and the mole fraction of acetonitrile. The solvent dependence of the stability constants is most notable with B15C5–K^+ and the least with DB30C10–K^+ complex.

Introduction

Since the initial observation of Pedersen [1] that certain macrocyclic crown ethers selectively bind some cations, extensive work has been done on the ability of these ligands to complex univalent and bivalent metal ions [2]. Among a variety of factors which affect the selectivity and stability of crown ether complexes, solvent plays an important role [2, 3].

Since the complexation takes place by the replacement of all or part of the inner solvation shell of the cation by the crown ether donor atoms, there is a competition between the macrocycle and solvent molecules for the cations. As a result, variations in the nature of the solvent produce significant changes in the binding properties of the macrocyclic ligands, so that the selectivity and stability of the complexes can be greatly altered.

In this paper we report a study of Na^+ and K^+ complexes with two crown ethers with different sizes of cavity, namely benzo-15-crown-5 (B15C5) and dibenzo-30-crown-10 (DB30C10). These studies were carried out in acetonitrile (AN)–water (W) mixed solutions in order to determine the effect of the solvent properties on the selectivity and stability of the resulting complexes.

Experimental

Dibenzo-30-crown-10 and benzo-15-crown-5 were synthesized by a slight modification of Pedersen's method [1]. The resulting crown ethers were recrystallized from reagent grade n-heptane and vacuum dried. Acetonitrile was purified and dried using the previously reported method [4]. Doubly distilled deionized water was used for the mixed solvent preparation. Sodium iodide (Merck) and potassium iodide (Merck) were of reagent grade quality, and were dried at 110 °C for several hours. Triethylammonium chloride was synthesized from reagent grade triethylammine and hydrochloric acid, recrystallized from water and dried.

The formation constants of 1:1 complexes

$$K_f = \frac{[ML^+]}{[M^+][L]}$$

were determined by the measurement of absorbance changes resulting from the complex formation between Na^+ and K^+ ions and the ligands, using a Model 34 Beckman Spectrophotometer. The concentration of the ligands was kept constant at 1.0×10^{-5} M and the concentration of the salts was varied up to 100 times the original ligand's concentration. In all cases, the ionic strength was maintained at 0.015 with triethylammonium chloride. The measurements were carried out at 25 ± 1 °C.

K_f was determined from a linear plot of $1/(\epsilon_a - \epsilon_L)$ *vs.* $1/[M^+]$ [5], since

$$\frac{1}{\epsilon_a - \epsilon_L} = \frac{1}{\epsilon_{ML^+} - \epsilon_L} + \frac{1}{K_f[M^+]} \qquad (1)$$

where $\epsilon_a = A/[L]_{tot}$, A is the absorbance of each solution, $[L]_{tot}$ is the initial concentration of the ligand, ϵ_L or ϵ_{ML^+} are molar absorptivities of the ligand and the complex, respectively, and $[M^+]$ is the equilibrium concentration of metal ion, calcu-

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lated by an iteration procedure. The wavelengths 240 nm and 250 nm were used for benzo-15-crown-5 and dibenzo-30-crown-10, respectively.

Results and Discussion

The UV spectra of solutions, with constant concentration of the ligands and varying concentration of the salts, were obtained at 25 °C and ionic strength of 0.015. The spectra of B15C5–NaI solutions in pure acetonitrile are shown in Fig. 1. In each case, plots of $1/(\epsilon_a - \epsilon_L)$ *vs.* $1/[M^+]$ gave a straight line, in accordance with eqn. (1) (Fig. 2), and the formation constants of the complexes were calculated using intercepts and slopes of the resulting lines. K_f values of the 1:1 complexes between Na^+ and K^+ ions and B15C5 and DB30C10 at different weight percentages of acetonitrile in $CH_3CN–H_2O$ mixed solvents are listed in Table I.

Whilst there is no clear-cut evidence for formation of 2:1 (ligand to metal ion) complexes between Na^+ and B15C5 in acetonitrile or in solvents of larger donicities [6], evidence for existence of 2:1 sandwich complexes between K^+ ion and this ligand has been reported [7]. Thus, the condition was arranged so that the possibility for the formation of these relatively weak [6, 8] sandwich complexes remained as low as possible (*i.e.*, working at high metal ion/ligand mole ratios). Since identification of three different types of complexes, with the respective stoichiometries Na_2L, Na_3L_2 and NaL, between Na^+ ion and DB30C10 in acetonitrile solutions was previously reported [9] calculation of the formation constant of the 1:1 complex seems to be somewhat confusing; therefore in our study this case was not included.

TABLE I. Formation Constants of Na^+ nd K^+ Ion Complexes of B15C5 and DB30C10 in Various $CH_3CN–H_2O$ Binary Mixtures at Ionic Strength of 0.015 and at 25 °C

Solvent composition (wt.% CH_3CN in H_2O[a])	log K_f		
	B15C5–NaI	B15C5–KI	DB30C10–KI
20	0.76 ± 0.05	0.81 ± 0.06	2.42 ± 0.09
40	1.18 ± 0.07	1.34 ± 0.08	2.71 ± 0.11
60	1.68 ± 0.11	2.00 ± 0.10	3.23 ± 0.12
80	2.45 ± 0.09	2.88 ± 0.11	3.88 ± 0.10
100	3.65 ± 0.07	4.27 ± 0.15	4.90 ± 0.13

[a] These solutions have the following X_{AN}: 20% (0.10), 40% (0.23); 60% (0.40); 80% (0.64); 100% (1.00).

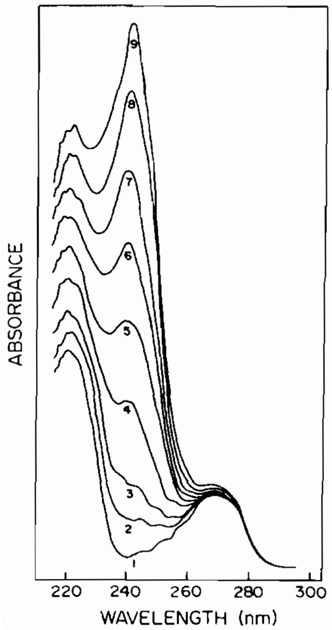

Fig. 1. UV spectra of mixtures of B15C5 (1.0×10^{-5} M) and NaI in pure acetonitrile. The respective NaI concentrations are: (1) 0.0; (2) 1.0×10^{-5} M; (3) 2.0×10^{-5} M; (4) 4.0×10^{-5} M; (5) 6.0×10^{-5} M; (6) 8.0×10^{-5} M; (7) 1.0×10^{-4} M; (8) 1.2×10^{-4} M; (9) 1.5×10^{-4} M.

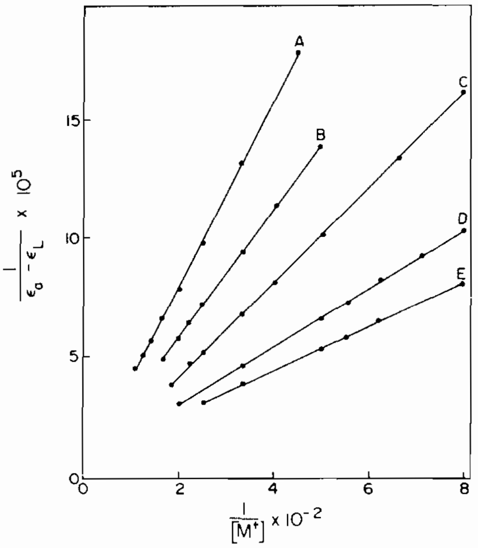

Fig. 2. Linear plots of $1/(\epsilon_a - \epsilon_L)$ *vs.* $1/[M^+]$ in different binary acetonitrile–water mixtures. Respective wt.% of CH_3CN in H_2O are: (a) 20; (b) 40; (c) 60; (d) 80; (e) 100.

The data shown in Table I clearly illustrate the important influence of the nature of the solvent in the complexation reactions. In all cases, the stability of the complexes increases rapidly with decreasing weight percent of water in mixed solvents. It has been shown that the donor (or solvating) ability of the solvent, as expressed by the Gutmann donicity scale [10], plays a fundamental role in the complexation reactions [2, 3]. Water is a solvent of high solvating ability, *i.e.*, DN = 33(18), which can strongly compete with the ligands for cations. Thus, it can be expected that the addition of water to acetonitrile, which is a low donicity solvent (DN = 14.1), will decrease the extent of interaction between the ligand donor atoms and the cations.

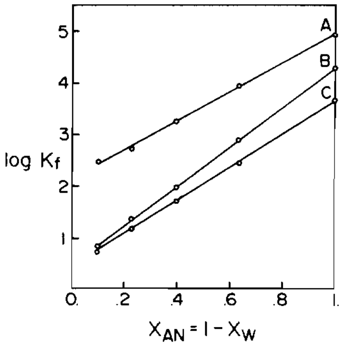

Fig. 3. Variation of the stabilities of B15C5 and DB30C10 complexes with X_{AN} of the binary mixtures. (a) DB30C10–K$^+$; (b) B15C5–K$^+$; (c) B15C5–Na$^+$.

It is interesting to note that there is actually a linear relation between the log K_f and the mole fraction of acetonitrile (X_{AN}) in the mixed solvents (Fig. 3). The same trend is also observed for the data obtained in the study of B15C5–Na$^+$ complexes in methanol–water mixed solvents by a calorimetric technique [7] It seems reasonable to assume that the preferential hydration of the sodium and potassium ions is mainly responsible for this monotonic dependence of the stability constants upon solvent composition. The same conclusion has been reached for C222–K$^+$ complexes in acetonitrile–water mixtures [11].

In all the solvent mixtures used in this study, the stabilities of the complexes decrease in the order DB30C10–K$^+$ > B15C5–K$^+$ > B15C5–Na$^+$. Dibenzo-30-crown-10 is a rather flexible ligand that can wrap itself around a metal ion of proper size (e.g., K$^+$ ion) so that all ten oxygen atoms of the polyether ring participate in bonding with the cation, resulting in a three-dimensional 'wrap around' stable complex [12]. Although the size of the sodium ion is such that it can fit inside the B15C5 cavity [13], the potassium ion, with larger size and less suitable fit condition, forms a more stable complex with this ligand. Similar results have been previously reported [7, 13]. This behavior probably reflects the fact that the K$^+$ ion has a lower charge density than the Na$^+$ ion, and, therefore, it is rather weakly solvated by the solvent molecules. Thus, competition between the ligand and solvent molecules for the Na$^+$ ion is stronger than that for the K$^+$ ion, which, in turn, causes the weakening of the B15C5–Na$^+$ complex.

From Fig 3, it is obvious that the variation of the stability of the complexes with acetonitrile mole fraction (X_{AN}) in the mixed solvents is most notable for B15C5–K$^+$ and is least for DB30C10–K$^+$. In the case of the K$^+$ ion complexes with two ligand molecules, the effect of solvent–cation interaction on the complexation reaction is actually the same. Thus, the difference in the variation of stability of their complexes with X_{AN} must arise from inequal contributions of the solvent–ligand and solvent–complex interactions on the complexation reactions. Recent studies have shown that in some solvents there are rather strong interactions between macrocyclic ligands and solvent molecules [14, 15], in which the extent of interaction depends on the structure of the ligand, as well as on the nature of the solvent. It is clear that such interactions can modify the complexing abilities of the macrocyclic ligands in solution. Dibenzo-30-crown-10 molecule contains ten oxygen atoms, which act as donor atoms capable of interacting with solvent molecules, twice that of benzo-15-crown-5 cycle. It has also a more flexible structure which gives the molecule the opportunity to alter its conformation in solution easily. Thus, we may expect different interactions of solvent molecules with these ligands.

Benzo-15-crown-5 has a cavity size that is too small for the potassium ion [13]. Therefore, the cation can only partially penetrate inside the cavity of the ligand and, consequently, the complexed cation remains largely exposed to the solvent molecules On the other hand, Bush and Truter [12] have shown that dibenzo-30-crown-10 can alter its conformation so as to enable all ten oxygen atoms to coordinate the potassium ion. The result is a 'wrap around' structure, even in solution as postulated by Live and Chan [16], in which K$^+$ ion is completely trapped into the cavity of the twisted ligand. Clearly, in this situation, the complexed cation is virtually isolated from the solvent. The net result of the two interactions (*i.e.* solvent–ligand and solvent–complex) is that the effect of the nature of the solvent on the stability of the potassium ion complex is more pronounced in B15C5–K$^+$ than in the DB30C10–K$^+$ complex.

Comparing B15C5–Na$^+$ and B15C5–K$^+$ complexes, it is clear that in acetonitrile–water mixtures the selectivity of B15C5 for the K$^+$ ion (over the Na$^+$ ion) increases with increasing mole fraction of acetonitrile, X_{AN} (Fig. 3). Considering the same solvent–ligand interaction and the negligible difference in solvent–complex interactions, this may result from a larger decrease in the solvation of Na$^+$ ion compared with the K$^+$ ion, as reported by Evans and coworkers [17].

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