

SOLVENT EFFECT ON COMPLEXATION OF CS⁺ AND K⁺ CATIONS BY CALIX[4]-BIS-CROWN-6

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Abstract

The complexive abilities of 1,3-alternate calix[4]-bis-crown-6 (L) towards alkali metal ions (K⁺ and Cs⁺) in different mixtures of methanol with water have been evaluated by UV/Vis spectroscopy. The results reveal that the ligand is capable to complex potassium and cesium ions with a 1:1 metal to ligand ratio. Although the stability constants of the complexes changes but the selectivity presented by L (Cs > K) in all studied mixed solvents doesn't differ from those observed in pure methanol.

Keywords: calix[4]crown, solvent effect, alkali cations, selectivity.

Introduction

Calixarene-based molecules ⁽¹⁻⁴⁾ have received intense attention in the last few years. One of the most important features of these compounds is their diversity. Calixarenes find applications as selective binders and carriers, as analytical sensors, as catalysts and as model structures for biomimetic studies.

Recently, a series of calix[4]-bis-crowns (crown-5, crown-6 and crown-7) have been synthesized and their application in the transport of ¹³⁷Cs ions from nitric acid media through a supported liquid membrane was investigated ⁽⁵⁾. Molecules with crown-6 moieties present to be much more efficient and selective ligands for cesium. Binding properties of some calix[4]-bis-crowns-6 towards alkali ions in acetonitrile and methanol have been reported using the extraction experiments of the alkali picrates and the measurements of complex stability constants by UV/Vis spectroscopy ⁽⁶⁾. These calixcrowns show a preference toward cesium ions as the results obtained in the transport experiments ⁽⁵⁾.

In this paper we describe the complexive properties of 1,3-alternate calix[4]-bis-crown-6 (Figure 1) towards potassium and cesium ions in different mixtures of methanol with water. The results will be compared with those reported previously in acetonitrile, methanol and the acetonitrile/water mixture solvents ^(6,7).

Experimental

Materials: 1,3-Alternate calix[4]-bis-crown-6 were synthesized according to a procedure reported previously ⁽⁵⁾. Methanol was used without further purification. The metallic salts were KCl (Merck, p.a.) and CsCl (Merck, p.a.). The supporting electrolyte used, Me₄NCl (Fluka, purum), was dried under vacuum for 24 hr at room temperature.

Stability constant measurements: The stability constants of the complexes were determined by UV/Vis spectrophotometry ⁽⁸⁾ as the stepwise addition of an alkali cation solution in methanol/water (95/5, 90/10, 85/15) to the calixarene solution in the same solvent. In all solutions, the ionic strength was maintained at 0.01 M by use of Me₄NCl. Upon addition of metal the UV/Vis spectrum of the ligand undergoes small changes in the 240-290 nm. The changes were sufficient to allow a multiwavelength treatment of the data by the Specfit program.

Results and Discussion

Assuming a 1:1 stoichiometry for the complexes formed between alkali ions ($M^+ = K^+$ and Cs^+) and the ligand (L), the equation describing the complexation equilibrium of the cations is as follow:

$$M^+ + L \rightleftharpoons ML^+ \quad \beta = \frac{[ML^+]}{[M^+][L]}$$

The corresponding stability constant β is then defined as:

The spectra of the solution of L (3×10^{-4} M) containing increasing amounts of metal ion have been recorded between 240-290 nm. The addition of metal ion induces

a decrease of the absorption bands of the ligand in all cases. Figure 2 shows as an example the change in the spectrum of the ligand upon addition of CsCl. The treatment of the data based on the formation of 1 : 1 complexes using the Specfit program allows to measure the stability constants of the complex formed (Figure. 3). Table 1 contains the measured stability constants together with those obtained for the same ligand in pure methanol.

The results show a significant larger solvent effect in the case of cesium in methanol/water (95/5, 90/10) mixtures and also the selectivity of BC6 for Cs^+/K^+ increase in these mixture solvents comparing to the pure methanol. (Table 1, Figure 4)

The results for Cesium can be interpreted by a better size fitting of the ion and positive entropy changes because of dehydration of cation.

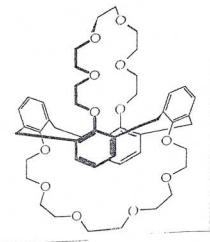


Figure 1: Structure of 1,3-Alternate calix[4]-bis-crown-6 (BC6)

Table 1. Logarithm of stability constants ($\log \beta$) in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (90/10) for the Complexation of potassium and cesium ions by BC6.

Cation	CH_3OH^a	$\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (95/5)	$\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (90/10)	$\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (85/15)
K^+	4.0 ± 0.1	4.4 ± 0.2	4.6 ± 0.1	4.2 ± 0.3
Cs^+	4.8 ± 0.3	4.8 ± 0.3	5.8 ± 0.3	5.9 ± 0.4

a) Data are taken from reference 8.

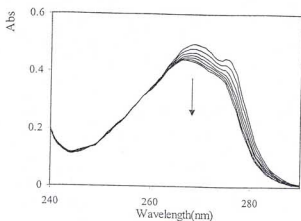


Fig. 2. Change in UV absorption spectrum of BC6 (upper curve) upon addition of CsCl in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (90/10). (after correction for dilution effects)

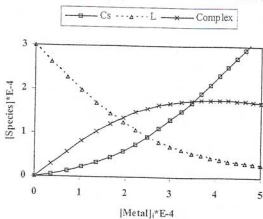


Fig. 3. Concentrations of different species of a 3×10^{-4} M solution of BC6 in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (90/10) upon addition of CsCl at 25°C ($I = 0.01\text{M}$, Me_4NCl)

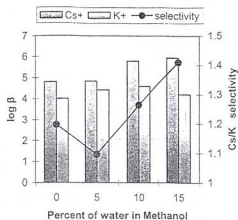


Fig. 4. Concentrations of different species of a 3×10^{-4} M solution of BC6 in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (90/10) upon addition of CsCl at 25°C ($I = 0.01\text{M}$, Me_4NCl)

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