The Effects of Alkali Cation Complexation on the Fluorescence Properties of Crown Ethers

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The effects of alkali metal complexation on the fluorescence properties of two crown ethers (a podand and a coronand) were investigated. Metal ion binding leads to changes in fluorescence intensity along with slight shifts in the emission maxima. This is attributed to a rigidization of the fluorophore and an interaction of the metal ion with non-bonding electrons of the crown ethers. The effects on the spectra are more pronounced in fluorescence than in absorption.

Fluorescence titration with metal ions provides a simple and sensitive means for the determination of complexation constants, which were found to be highly dependent upon the water content of the methanol solution. Halide counterions, in particular iodide, act as dynamic fluorescence quenchers with *Stern-Volmer* constants that are different for the sodium and potassium complexes, respectively.

(Keywords: Complexation; Crown ether; Fluorescence; Solvent effects)

Die Effekte der Komplexierung von Alkalimetallionen auf die Fluoreszenzeigenschaften von Kronenethern

Die Effekte der Komplexierung von Alkalimetallionen auf die Fluoreszenzeigenschaften zweier Kronenether (eines Podanden und eines Coronanden) wurden untersucht. Die Bindung des Metallions führt zu Veränderungen in der Fluoreszenzintensität und zu Verschiebungen in den Emissionsmaxima. Dies wird einer gesteigerten Starrheit des Fluorophors und einer Wechselwirkung des Metallions mit nichtbindenden Elektronen des Kronenethers zugeschrieben. Die Auswirkungen auf die Spektren sind in der Fluoreszenz ausgeprägter als in der Absorption.

Fluoreszenztitrationen mit Metallionen bieten eine einfache und empfindliche Möglichkeit zur Bestimmung von Komplexkonstanten, welche stark vom Wassergehalt der methanolischen Lösung abhängig befunden werden. Halogenidgegenionen, insbesonders Iodid, wirken als dynamische Fluoreszenzlöscher und weisen *Stern-Volmer*-Konstanten auf, welche für die Natrium- bzw. Kalium-Komplexe verschieden sind.

Introduction

Since the original work of *Pedersen*[1] the chemical and physicochemical properties of crown ethers have received considerable attention due to their ability to complex alkali and related metal ions. However, only little is known about the fluorescence properties of crown ethers, although fluorescence techniques are known to provide a sensitive means to probe perturbations of both conformation and dynamics of large molecules.

The first study on the fluorescence of a crown ether was presented by *Sousa* and *Larson*[2], who reported the fluorescence quenching as well as the enhancement of naphthalene derived crown ethers following the addition of various alkali metal ions in ethanol at 77 K. Later, *Shizuka* et al.[3] found that the fluorescence intensity of dibenzo-18-crown-6 is enhanced by alkali cations, which was interpreted in terms of a decrease in the internal quenching rate of the molecule.

In the case of lanthanide ion complexes with benzo-15-crown-5 energy transfer from the ligand to the central metal atom was observed[4], and very recently it was found that the fluorescence of a diphenyl maleinimid-type fluorophore in a podand-like ionophore is quenched after complexation[5]. In alternative approaches fluorescent tags such as coumarins[6] or aminonaphthalenesulfonates[7] were covalently linked to crown ethers, thus allowing their investigation by fluorescence techniques.

Here we report the fluorescence properties of two commercially available crown ethers, namely dibenzo-18-crown-6 (dibenzo-1,4,7,14,17,20-hexaoxa[7,7]orthocyclophane, "*DBC*") and 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (*Kryptofix 5**, "*K 5*") in organic and aqueous phases.

Experimental

Dibenzo-18-crown-6 and *Kryptofix* were obtained from Merck (Darmstadt, West Germany). *DBC* was recrystallized from isopropanol to give soft white needles of m.p. 161–163 °C. *K 5* (99% purity) was used without further purification. Both ethers did not contain TLC visible impurities. The agreement between the excitation and absorption spectra was sufficiently good in each experiment.

Methanol (fluorescence grade, Merck), Triton B (benzyltrimethyl-ammonium hydroxide, 40% solution in methanol, from Fluka, Switzerland), the alkali and earth alkali salts and phosphoric acid were used as obtained, since their contribution to the fluorescence of the crown ethers was negligible. Water was first distilled from potassium permanganate plus sulfuric acid and then twice from Pyrex glass.

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* *Kryptofix* is a tradename of Merck.

Absorption spectra were run on a Perkin-Elmer Lambda 5 spectrophotometer in 1 cm cells. The fluorescence spectra are uncorrected and were obtained with an Aminco SPF 500 spectrofluorimeter (Amer. Instr. Co., MD) with undegassed solutions in 1×1 cm quartz cells at room temperature.

Results and Discussion

Dibenzo-18-crown-6 (DBC)

We confirm the observation[3] that complexation of *DBC* with either Na^+ or K^+ leads to fluorescence enhancement and vibrational resolution of the absorption spectrum even at room temperature. Possibly because of a more sensitive instrumentation our fluorescence spectra could be acquired at high spectral resolution (bandpasses between 0.5 and 2.0 nm). The excitation spectra exhibit a vibrational resolution that closely matches the respective absorption spectra after complexation.

Fig. 1 shows a plot of fluorescence intensity of *DBC* versus concentration of Na^+ in 1% and 50% aqueous methanol. A complexation constant of $2{-}4 \cdot 10^4\,M^{-1}$ may be extracted from the curve for the 99% methanol solution. Unfortunately, the value cannot be calculated more accurately, since *DBC* was used as a $10^{-4}\,M$ solution. Titrations at lower
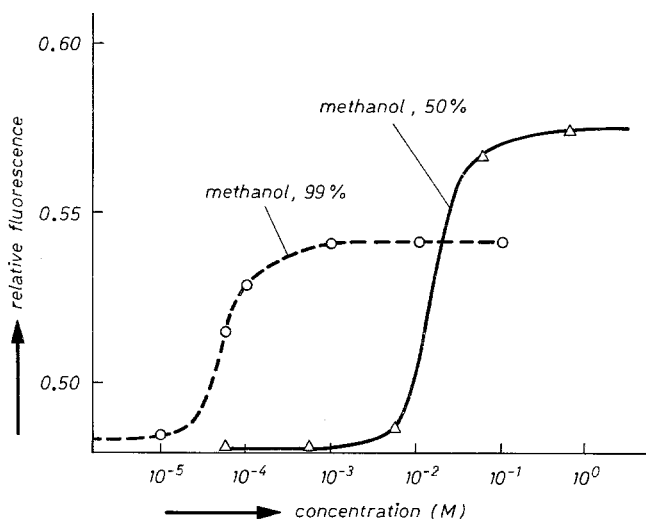

Fig. 1. Plot of fluorescence intensity of dibenzo-18-crown-6 (0.1 mM) versus concentration of sodium acetate in methanol containing 1% and 50% water, respectively, at 23 °C. Excitation wavelength 280 nm, emission taken at 312 nm

concentrations (e.g. $10\,\mu M$) did not give more precise data due to a higher signal-to-noise ratio. The respective constant for 50% aqueous methanol is $50\,M^{-1}$. The enormous difference in the two values reflects the different hydratation energies of the ions in the two solvent systems.

In methanol containing 1% water maximal fluorescence is already found at slight molar excess of sodium ion, indicating strong binding of the "naked" ion. Complexation must occur in a time much smaller than 0.5 s (the time constant of our instrument), since there are no changes in intensity with time to be observed after mixing the crown ether and the halide solution. Titration curves similar to those of Na^+ are obtained with K^+ (not shown).

When titrations are performed with alkali acetates, the fluorescence intensities remain constant at high salt concentrations. If, however, alkali halides are used, fluorescence drops at high salt concentrations. Fig. 2 shows plots of fluorescence intensity versus concentrations of alkali halides.

The decrease in intensity is interpreted in terms of dynamic fluorescence quenching of the DBC fluorophore, since there are almost no changes evident in the absorption spectra at halide concentration of $10^{-3}\,M$ or higher. Small contributions of static fluorescence quenching can, however, not be excluded.
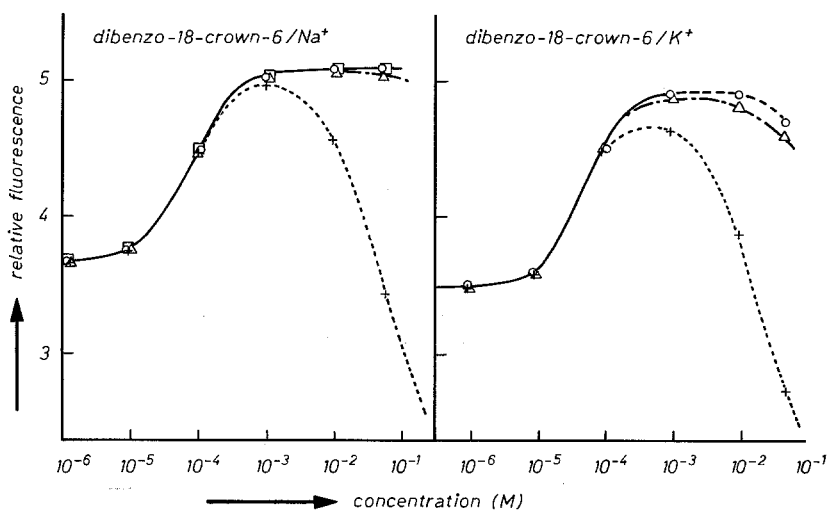

Fig. 2. Plot of fluorescence intensity of dibenzo-18-crown-6 (0.1 mM) in 99% methanol versus concentrations of sodium salts (left) and potassium salts (right). (———————): acetate, (— — — — —): chlorides, (— · — · —): bromides, (· · · ·): iodides. In case of the Na^+ complexes, the curves for the acetate and the chloride are identical

It is interesting to note that the DBC/Na^+ complex is quenched by iodide only, whereas the DBC/K^+ complex is quenched by chloride, bromide and iodide with increasing efficiency. The fluorescence of the DBC/KBr complex is weaker than that of the respective KCl complex, and the onset of quenching is at lower concentrations for the latter.

The *Stern-Volmer* overall quenching constants K of the DBC/Na^+ complex were calculated to be below $0.2\,M^{-1}$ for chloride and bromide, and $10\,M^{-1}$ for iodide (taking the intensity of the DBC/Na-acetate or DBC/NaCl complex as the unquenched intensity F_0). The respective values for the DBC/K^+ complex are 0.8 ± 0.1, 1.2, and $12\,M^{-1}$, respectively.

Kryptofix 5 (K5)

The pH-dependent absorption and fluorescence properties of $K5$ have not been described so far. Owing to its 8-alkoxyquinoline chromophore the absorption, excitation and emission spectra are at distinctly longer wavelengths than those of DBC. As may be expected, they closely resemble the spectra of 8-methoxyquinoline[8]. The absorption and emission spectra of $K5$ are shown in Fig. 3. Phosphoric acid rather than other mineral acids was used in order to avoid fluorescence quenching by the counterion, and *Triton B* was used as a strong base possessing a non-complexing cation.

The longest-wave absorption peaks are at 312.1 nm ($\varepsilon\ 5500\,M^{-1}\,cm^{-1}$) for the uncharged species, and 353.9 nm ($\varepsilon\ 3340\,M^{-1}\,cm^{-1}$) for the protonated species. The fluorescence emission maximum of the cation (495 nm) is at an unusually long wavelength, when compared with the maximum of the uncharged molecule (409 nm). In addition, its *Stokes* shift of more than $8000\,cm^{-1}$ is rather high.

The fluorescence maxima of $K5$ are solvent dependent and shift from 395 nm in chloroform to 405 nm in methanol. The fluorescence intensity is around 8% higher in water than in methanol. The ratio of the fluorescence intensities of the protonated and unprotonated forms is 3 : 1, the protolytic equilibrium is governed by a pK_a value of 5.0 ± 0.1 (spectrophotometrically at 22 °C at ionic strength below 0.05).

Fluorescence titration of $K5$ with alkali and earth alkali cation indicates complex formation in organic solvents and, much weaker, in mixed organic-aqueous solvents. There is no evidence from fluorescence data that $K5$ binds alkali cations at acidities below its pK_a value.

There are two effects of complex formation upon the fluorescence to be discerned, namely (a) changes in intensity, and (b) spectral shifts. Fig. 4 shows the emission spectra in methanol before and after complexation
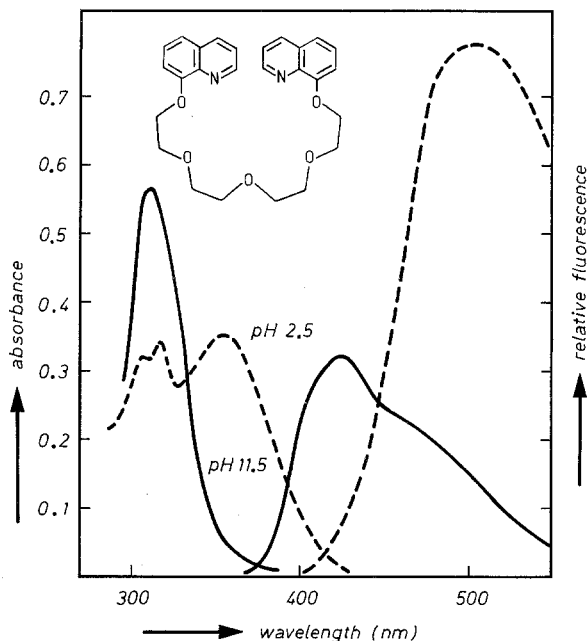
Fig. 3. Absorption and fluorescence emission spectra of *Kryptofix 5* (0.1 m*M*) in
10 m*M* aqueous phosphoric acid of *pH* 2.5 (— — — —) and in 10 m*M* aqueous
Triton B of *pH* 11.5 (————)

with different cations. Na^+ produces the most pronounced effect in
giving a 55% increase in intensity, accompanied by a +4 nm
bathochromic shift of the maximum.

The fluorescence intensity of the $K5/Na^+$ complex is rather
sensitive towards the water content of the methanol solution. It is
highest in pure solvent, only 95% of the maximal intensity in the
presence of 1% water, and only 70% in the presence of 10% water. This
reflects dramatically the decrease in the complexation constants in
going to aqueous solutions due to high hydratation energies. In fact, we
were unable to detect any alkali cation complexation of $K5$ by
fluorimetry in pure water at neutral *pH*.

Potassium ion gives an approximately 10% increase in intensity,
along with a shortwave shift of the maximum to 400 nm. The changes in
fluorescence intensity are therefore more significant at analytical
wavelengths between 370 and 390 nm, being e.g. +38% at 380 nm.

We interpret the increase in fluorescence intensity as a consequence
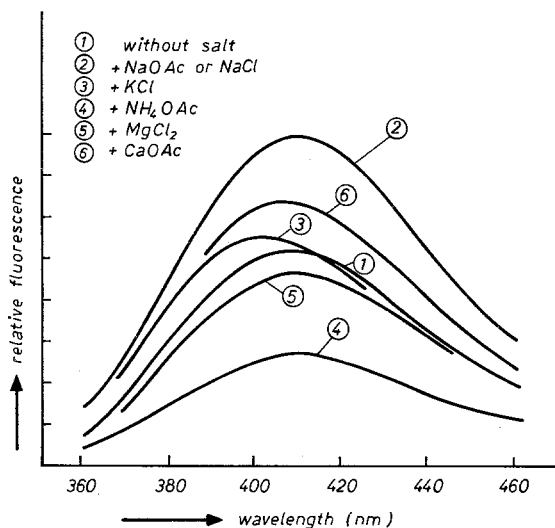of the rigidification of the molecule due to strong complexation. The

Fig. 4. Effect of the addition of 0.1 M alkali ions upon the fluorescence emission spectra of *Kryptofix 5* (0.1 mM) in pure methanol. Excitation wavelength 322 nm, 23 °C
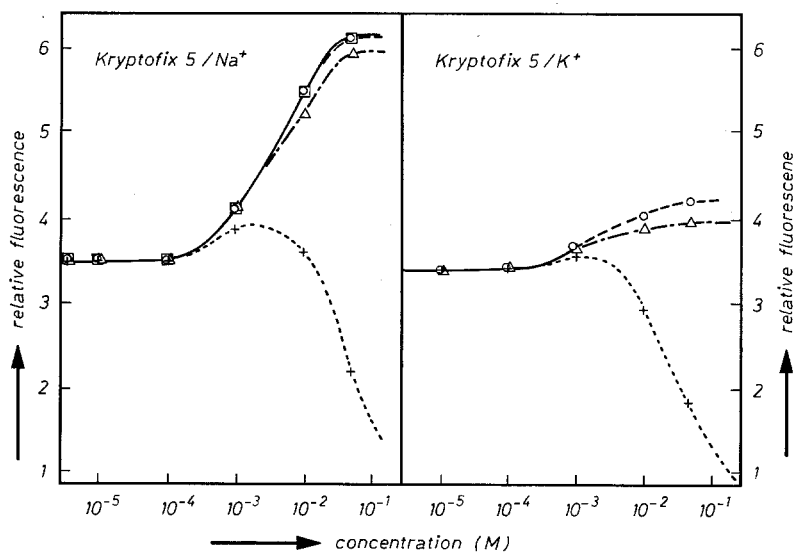

Fig. 5. Changes in fluorescence intensity of *Kryptofix 5* (0.1 mM) in 99% methanol during titration with sodium salts (left) and potassium salts (right). (————): acetate, (—————): chlorides, (—·—·—): bromides, (····): iodides. Excitation at 322 nm, emission taken at 405 nm, 23 °C

hypsochromic shift of the emission maximum of the K^+ complex indicates a strong interaction of the central metal atom with the nitrogen atom of the heterocyclic fluorophore.

Fig. 5 shows plots of fluorescence intensity of *K5* versus concentrations of various alkali halides. Unlike with *DBC*, there is no quenching of *K5* by chloride evident in concentrations up to 50 mM. Bromide and, in particular, iodide act as dynamic quenchers, since there are no changes in the absorption spectra to be observed. Deviations from the linearity of *Stern-Volmer* plots at higher halide concentrations point, however, to certain contributions of static quenching at iodide concentrations above 20 mM.

Again, the quenching of the K^+ complex is different from the quenching of the Na^+ complex. The following quenching constants have been estimated: $K5/Na^+$-bromide $1\,M^{-1}$, $K5/K^+$-bromide $4\,M^{-1}$, $K5/K^+$-iodide $33\,M^{-1}$.

Stability constants of $200\,M^{-1}$ have been found by fluorescence titration for both the Na^+ and the K^+ complex in methanol containing 1% water. These relatively high values are in agreement with findings that open chain polyethers have stability constants much smaller than coronands and kryptands[9].

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