Scientific paper

Host-guest Interactions of Coumarin 6 with β-cyclodextrin in Polar Solvents

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Abstract

The complexation of coumarin 6 (3-(benzothiazol-2-yl)-7-diethylaminobenzopyran-2(2*H*)-one) in β-cyclodextrin media was studied by the fluorescence emission spectroscopy and NMR titrations in polar solvents. The excitation wavelength used to monitor the fluorescence was 445 nm. The emission spectra were recorded at 450–650 nm in water. The additions of β-cyclodextrin resulted in a substantial enhancement of the fluorescence emission of coumarin 6, especially at concentrations of 1×10^{-4} to 1×10^{-3} mol dm^{-3}. The shift of the fluorescence maximum towards higher frequencies was also observed. The formation of the inclusion complex of coumarin 6 with β-cyclodextrin is proposed. Furthermore, the effect of the hydrophobic cavity on spectral properties of the guest molecule is discussed. The inclusion phenomenon was further studied by liquid state NMR in dimethylsulfoxide. The measured ^{1}H NMR shifts showed that coumarin molecule provided a significant electron shielding of protons located inside the β-cyclodextrin cavity. The geometry of the host-guest complex is discussed and the possible location of the guest molecule inside the cavity is suggested.

Kewords: β-cyclodextrin, coumarin 6, fluorescent probe, NMR titration, inclusion complex

1. Introduction

Cyclodextrins represent a large and important family of cyclic oligosacharides.[1–10] The compounds consist of several glucopyranose units that form a characteristic, torus-like structure with an interior cavity of a specific volume. The cavity has a hydrophobic character and serves as a host for a number of organic compounds. β-Cyclodextrin consists of seven glucopyranose units connected by α(1 → 4) glycosidic bonds.[4] The inclusion of the molecule inside the cavity may increase its solubility in water and enhance its physico-chemical properties. Host-guest complexes have multiple industrial, biological and chemical applications.[11–15] Cyclodextrins are used, for example, as complexing agents,[12] stabilizers and mediators of chemical reactions[13,14] or as specific drug delivery systems.[15]

Cyclodextrins are also capable of controling the light absorption and emission of the guest molecules.[3] Fluorescent properties of the probe, located inside the cavity, may be shielded from solvation effects and this may provide a significant fluorescence enhancement. Coumarins are a family of fluorescent heterocyclic compounds derived from benzopyran-2(2*H*)-one.[16–21] They form inclusion complexes with cyclodextrins.[22–26] Depending on the substitution pattern of the coumarin molecule and the type of cyclodextrin employed, the complexes with guest-host stoichiometries 1:1, 2:1, 2:2 and 2:3 were identified in the solid state.[27,28] Scypinski and Drake[29] showed that different types of complexes may also result from a diffe-

rent orientation of the guest molecule inside the cavity. The two different complexes found, labeled as "normal" and "inverted", possess strikingly different spectroscopic features and may be used as specific fluorescent probes.[29] The cyclodextrin cavity forms a restricted space with a limited number of water molecules. The solvation dynamics, studied for coumarin 480 (7-diethylamino-4-methylbenzopyran-2(2*H*)-one) in pure water and inside the γ-cyclodextrin cavity, revealed that additional, long-term solvation processes observed in host-guest complexes are due to the slow motion of the probe molecule into and out of the cavity and by the reorientation of highly constrained water molecules.[30–35] The slower relaxation of guest molecules inside the cavity comparing to pure solvents is a significant mark of complexation.

Coumarin 6 (3-(benzothiazol-2-yl)-7-diethylaminobenzopyran-2(2*H*)-one contains two different functional groups appended at opposite sites of benzopyran-2(2*H*)-one (Figure 1). The bulky substituents make it interesting for the study of inclusion complexes. In a recent study authors investigated inclusion complexes between coumarin 6 and thiolated β-cyclodextrin, both adsorbed on a gold surface.[36] It was found by laser-induced thermal desorption and subsequent fluorescence detection of coumarins that at least half of the adsorbed molecules came from inside the cyclodextrin cavity.[36] To the best of our knowledge, the investigations of these complexes in aqueous media have not yet been reported. We have, therefore, decided to study the inclusion phenomenon between coumarin 6 and β-cyclodextrin in water. The formation of the inclusion complexes was followed by monitoring the fluoresence emission of coumarin molecules in cyclodextrin media. Additional insights into the host-guest interactions were obtained from the ^{1}H NMR spectroscopy.

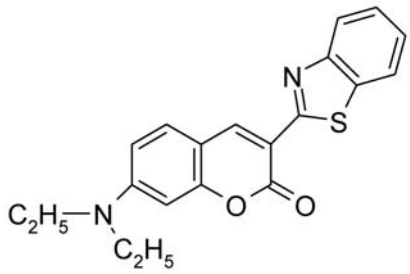

Figure 1: Chemical structure of coumarin 6.

2. Experimental Part

2. 1. Materials

β-Cyclodextrin was purchased from Cyclolab (Budapest, Hungary) and coumarin 6 (3-(benzothiazol-2-yl)-7-diethylaminobenzopyran-2(2*H*)-one) was purchased from Fluka. Both chemicals were of spectroscopic purity and were used without any further purification.

2. 2. Methods

For the fluorescence emission study, a saturated solution of coumarin 6 in distilled water was prepared. The emission spectra were recorded for the saturated aqueous solutions of coumarin 6 first and then for the mixed solutions of coumarin 6 with β-cyclodextrin. The solubility of coumarin 6 in water was negligible. The concentrations of β-cyclodextrin in the solutions with coumarin 6 were 0, 1×10^{-5}, 5×10^{-5}, 1×10^{-4}, 5×10^{-4} and 1×10^{-3} mol dm^{-3} respectively. The spectra were recorded on a Fluorolog spectrometer (Horiba, Japan) working with transparent quartz cells at room temperature. The excitation wavelength was 445 nm (xenon lamp). The emission spectra were recorded at 450–650 nm.

For ^{1}H NMR analysis the stock solutions of coumarin 6 and β-cyclodextrin in deuterated dimethylsulfoxide were prepared and mixed together in the molar ratios of 1:7 to 1:1 (guest:host). The titration analysis was carried out in dimethylsulfoxide instead of water due to the negligible solubility of coumarin 6 in water. The stock solution concentrations were 3.35×10^{-3} mol dm^{-3} for β-cyclodextrin and 3.99×10^{-3} mol dm^{-3} for coumarin 6. The NMR spectra were recorded at 300 K with a Bruker Avance DPX spectrometer at 200.13 MHz for ^{1}H nuclei. Chemical shifts were referenced to the signal of tetrametylsilan (TMS).

3. Results and Discussion

3. 1. Fluorescence Enhancement of Coumarin 6

The effect of β-cyclodextrin on the fluorescence behaviour of coumarin 6 is illustrated in Figure 2 where the individual emission spectra are presented. The fluorescence intensity of the fluorophore in water was negligible, mainly due to the low solubility. However, the addition of β-cyclodextrin in a suitable concentration resulted in a significant, more than 7-fold emission enhancement. The addition of the complexing agent had an effect on both the intensity and the position of the fluorescence maximum. It was observed that the addition of β-cyclodextrin caused shift of the fluorescence maximum towards smaller wavelengths (blue shift). It is suggested that β-cyclodextrin enhances the fluorescence emission since it increases the solubility of coumarin in water by the formation of an inclusion complex. The fluorophore of coumarin 6 inside the cyclodextrin cavity is relatively free of negative solvation and may provide a significant fluorescence upon excitation. The β-cyclodextrin contributes to the stabilization of the guest molecule.

In the simplest case, a host-guest complex with a 1:1 geometry can be expected. The formation of the inclusion complex can, in principle, be expressed by the

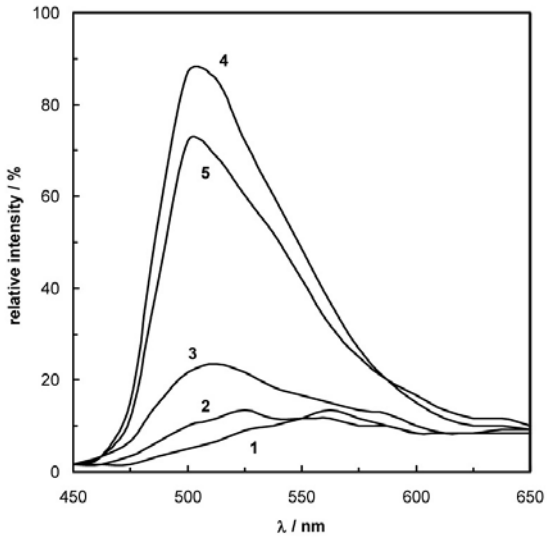

Figure 2: Fluorescence emission spectra of aqueous coumarin 6 in mixtures with β-cyclodextrin: c(β-cyclodextrin) = 0 mol dm^{-3} (**1**), 1 × 10^{-5} mol dm^{-3} (**2**), 1 × 10^{-4} mol dm^{-3} (**3**), 5 × 10^{-4} mol dm^{-3} (**4**), 1 × 10^{-3} mol dm^{-3} (**5**).

following equation:

$$H + G = HG \quad (1)$$

where H denotes the host (cyclodextrin), G is the guest (coumarin) and HG denotes the host-guest complex. The equilibrium constant of reaction (1) is given by the following equation:[37]

$$K = \frac{[HG]}{[H][G]} \quad (2)$$

where [H] is the equilibrium concentration of cyclodextrin, [G] is the equilibrium concentration of coumarin and [HG] is the equilibrium concentration of host-guest complexes. The complex stability constant, K, is an important property characterizing the stability of the respective inclusion complex.[37]

The effect of β-cyclodextrin on the fluorescence maxima intensity is shown in Figure 3. The concentration dependence has a sharp maximum near 5 × 10^{-4} mol dm^{-3}. The most significant fluorescence enhancement was observed when the complex agent was added in a relatively narrow concentration range. Concentrations less than 1 × 10^{-4} mol dm^{-3} did not have any significant effect on the light emission intensity since the number of host molecules was relatively small. However, higher concentrations of the host also resulted in decreased fluorescence intensity. The fluorescence intensity is proportional to the number of coumarin molecules bound in the inclusion complexes with β-cyclodextrin, i.e., proportional to the number of host-guest complexes. However, it was suggested that cyclodextrin molecules may form aggregates at high concentrations.[24] The aggregation decreases the amount of host molecules available and the fluorescence intensity of coumarin 6 may, as a consequence, decrease. Another explanation might be that the amount of guest molecules became too small for the number of hosts. The formation of host-guest complexes is governed by equation (2). Since the concentration of guests was small, the number of host-guest complexes had to decrease to keep the value of K constant. This might have led to the observed decrease of the fluorescence intensity.

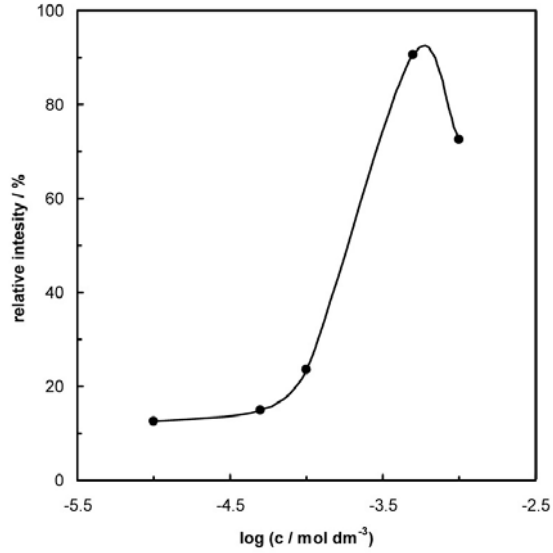

Figure 3: The effect of β-cyclodextrin on the fluorescence maximum intensity of coumarin 6 in water. The curve is provided to be a guide for the eye.

The effect of β-cyclodextrin on the fluorescence maximum position is given in Figure 4. The addition of host molecules led to an increase in the light emission frequency. The emission frequency reflects the energy difference between the ground and excited states of the molecule. Since the energy difference increased, it can be suggested that either the ground state of the molecule was stabilized or the excited state was destabilized due to the intermolecular interactions inside the cavity. The fluorescence maxima frequencies of coumarin 6 were measured in a number of solvents with different polarity and are available in a reference by Raikar et al.[38] It was found that the frequency of emission increases with decreasing polar character of the solvent. Raikar et al. experimentally found from the solvatochromic Stokes shifts in two series of solvents that the molecule of coumarin 6 had higher dipole moment in the excited state than in the ground state.[38] This observation demonstrates that the ground state is less polar than the excited state. The ground state can thus be stabilized by hydrophobic interactions inside the cyclodextrin cavity. The authors assigned the fluorescence emission to the π^*-π electron transition.[38]

The frequency increase, observed in Figure 4, reaches a plateau at concentrations of 5×10^{-4} mol dm^{-3}. A further concentration increase did not provide any further frequency increase and it may be concluded that the complexation capacity of β-cyclodextrin was saturated by the amount of guest molecules available in the solution. The effect of β-cyclodextrin on the fluorescence frequency of coumarin 6 may have multiple implications for the use of this molecule as a fluorescent dye.

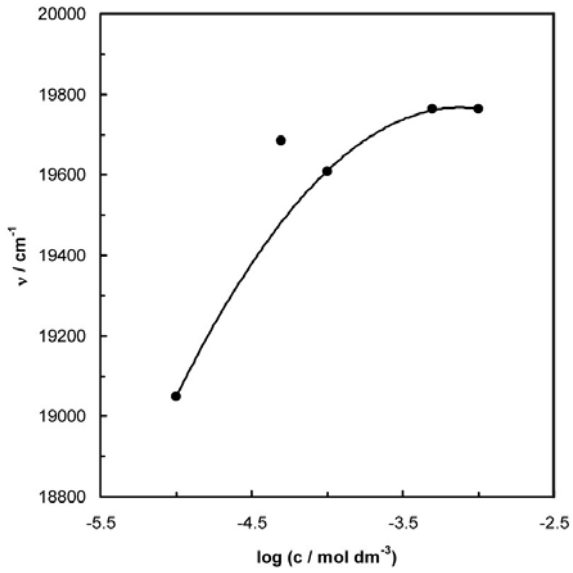

Figure 4: The effect of β-cyclodextrin on the position of the fluorescence maximum of coumarin 6 in water. ν denotes the wavenumber (1/λ) of the fluorescence emission. The curve is provided to be a guide to the eye.

3. 2. NMR Titrations

Cyclodextrins possess a number of protons that are located inside and outside of the cavity. The schematic overview of the location of protons was provided by Schneider et al.[39] According to the scheme, protons H-3 and H-5 are located inside the cavity, while other protons are located outside the cavity.[39] ^{1}H NMR spectroscopy is a powerful tool which provides independent information about the chemical environment of protons. Therefore, the inclusion complex coumarin 6-β-cyclodextrin has also been investigated by ^{1}H NMR spectroscopy. This study was pursued in order to reveal the influence of the guest on the chemical shifts of protons located inside and outside of the cavity. This information is important in order to claim the existence of host-guest complexes. We monitored the positions of individual chemical shifts with respect to the concentration of coumarin 6. This technique is called NMR titration.[39] The coumarin solution was added in small portions to the solution of β-cyclodextrin. The final concentration of the titration corresponded approximately to the host: guest molar ratio of 1 : 1. The titration was followed in deuterated dimethylsulfoxide (DMSO-d_6), due to the low solubility of coumarin 6 in water. Dimethylsulfoxide has polar character (relative permittivity 48.9, dipole moment 13.0×10^{-30} C m),[40] and it was expected that coumarin 6 would preferably occupy the hydrophobic cavity of the host. The measurements in DMSO-d_6 have a further advantage as the hydroxyl protons are detectable, which is impossible in water due to the fast proton exchange with the solvent.

The observed ^{1}H NMR chemical shifts show a very good agreement with previously published data (Table 1). The individual chemical shifts of H-2 and H-4 protons were not observed due to the overlap of the crystal water at 3.30–3.40 ppm. Namely, the crystals of β-cyclodextrin contain approximately 12 water molecules per formula unit.[4]

The chemical shifts of H-3, H-5 and H-6 protons showed a significant variation with coumarin concentration. The concentration dependence is given in Figure 5. The chemical shifts of H-3 and H-5 protons gradually decreased with increasing guest concentration. This reflects a significant electron shielding induced by coumarin 6. Since H-3 and H-5 protons are located inside the cyclodextrin cavity, the coumarin molecule must have also been located inside the cavity. The most interesting behavior was observed in the case of H-6 protons. The chemical shift for H-6 first decreased and then increased back to the initial value. This behavior suggests that H-6 protons also partially experienced the electron shielding from the guest molecule. Since H-6 protons are located outside the cavity but close to the torus opening, the shielding might have been due to the guest molecule parts located at the cavity end. The electron shielding of H-6 protons diminished probably due to the adjustment and re-orientation of the molecule inside the cavity at high concentrations. The chemical shifts of H-1, OH-2, OH-3 and OH-6 protons did not show any significant variation with coumarin concentration. This reflects that the chemical environment of

Table 1: ^{1}H chemical shifts of β-cyclodextrin in DMSO-d_6 at 300 K. The data were referenced to the signal of TMS. The comparison with the previously published data is provided.

	H-2	H-4	H-5	H-3	H-6	OH-6	H-1	OH-3	OH-2
Observed	–[a]	–[a]	3.54	3.59	3.64	4.44	4.83	5.66	5.70
Ref. 39	3.29	3.40	3.59	3.64	3.64	4.46	4.82	5.68	5.75

[a] Chemical shifts of H-2 and H-4 protons could not be observed due to the overlapping signal of the crystal water of β-cyclodextrin.

these protons was not significantly altered during the NMR titration. These protons are located outside the cyclodextrin cavity and they did not experience any electron effect of the guest molecule.

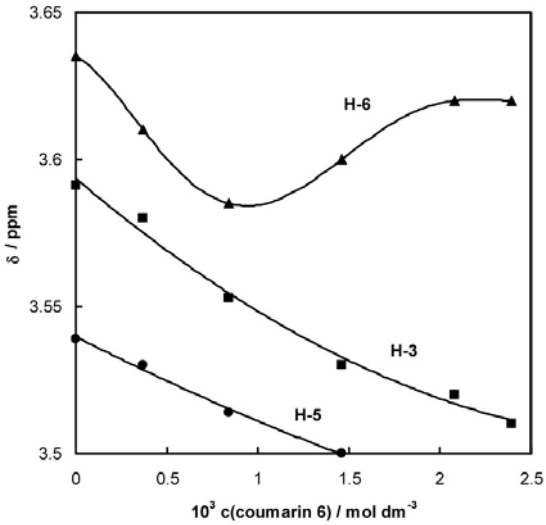

Figure 5: The effect of coumarin 6 on the chemical shifts of β-cyclodextrin protons located inside the cavity (H-3, H-5). The H-6 protons are located at the smaller opening of the β-cyclodextrin cavity. The experiments were performed in DMSO-d_6 at 300 K.

The coumarin moiety provided shielding of the protons located inside the β-cyclodextrin cavity. Similar observations were reported for H-3 and H-5 protons of other host-guest complexes too. The decrease in the chemical shifts of β-cyclodextrin induced by substituted 4-hydroxy-7-metoxycoumarins was from –0.06 to –0.11 ppm.[41] These values are comparable to the shielding effects observed in the present case. Considering the structural differences between 4-hydroxycoumarins and comarin 6, it is suggested that the electron effect of the bulky substituents on the cyclodextrin protons was not very large. It was preferably the bezopyranone part of coumarin 6 which was located inside the cavity and interacted with inner protons. The substituents were probably directed towards the torus openings and were located mostly outside. Some of the possible orientations of the molecule inside β-cyclodextrin are given in Figure 6. The results in literature suggest that the lactone group of the coumarin could be oriented towards the larger opening of the cyclodextrin.[41,42] The structure b in Figure 6 could therefore be favourable. However, based on the present NMR titration data, it is not possible to unambiguously conclude on the final geometry of the inclusion complex. High resolution data on the intermolecular nuclear Overhauser effect (NOE) could be helpful as it would provide information about through-space interactions that would shed further light onto the geometry of the host-guest complex.[39] The NOE data were not be obtained in the present work due to the low resolution of the NMR spectrometer (200 MHz).

4. Conclusions

The complexation of β-cyclodextrin with coumarin 6 was monitored in aqueous media. The addition of β-cyclodextrin provided a substantial fluorescence intensity enhancement of the probe. It is suggested that this is due to the formation of the host-guest complexes which provide a stabilization of the coumarin molecule and increase its solubility in water. The effect of β-cyclodextrin was most pronounced at concentrations near 5×10^{-4} mol dm^{-3}. The addition of β-cyclodextrin resulted in a fluorescence maximum shift towards higher frequencies. β-Cyclodextrin provided a significant stabilization of the ground state of the guest molecule due to the hydrophobic intermolecular interactions inside the cavity.

The inclusion complex of coumarin 6 with β-cyclodextrin was further followed by NMR titrations in DMSO-d_6. Coumarin 6 had a substantial shielding effect on H-3 and H-5 protons located inside the cavity. However, the effect on the protons located outside of the torus was not observed. This confirms that coumarin molecule was, at least partially, located inside the cavity. The comparison of the present data with the previously published studies suggests that the benzopyranone part of the molecule was located inside the cavity and the bulky substituents were located outside the torus.

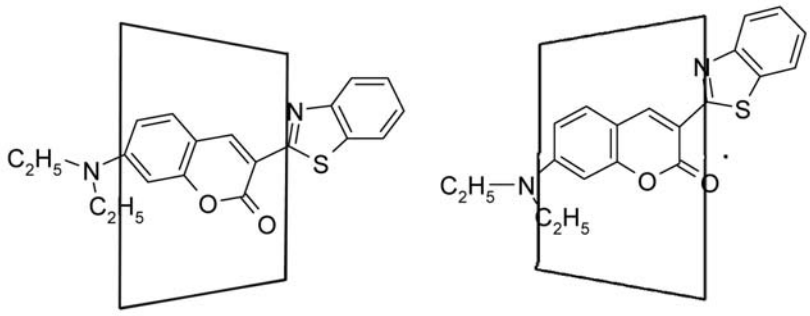

Figure 6: Possible orientations of the coumarin 6 molecule inside the β-cyclodextrin cavity.

5. Acknowledgements

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Povzetek

S fluorescenčno emisijo in metodo NMR titracije smo študirali kompleksacijo kumarina 6 (3-(benzotiazol-2-il)-7-dietilaminobenzopiran-2(2*H*)-ona) z β-ciklodekstrinom v polarnih topilih. Vzbujevalna valovna dolžina pri fluorescenci je bila 445 nm, emisijski spektri pa so bili snemani v vodi pri 450–650 nm. Dodatki β-ciklodekstrina so povzročili znatno povečanje fluorescenčne emisije kumarina 6, še posebej pri koncentracijah med 1×10^{-4} in 1×10^{-3} mol dm^{-3}. Opažen je bil tudi premik fluorescenčnega maksimuma proti višjim frekvencam, kar razlagamo z nastankom inkluzijskega kompleksa med kumarinom 6 in β-ciklodekstrinom. Študirali smo tudi vpliv hidrofobnega žepa cikoldekstrinov na spektralne lastnosti gostujoče molekule. Nadalje smo pojav inkluzijskih kompleksov študirali z NMR spektroskopijo v dimetilsulfoksidu kot topilu. Izmerjeni ^{1}H NMR kemijski premiki kažejo na znatno senčenje vodikovih jeder, ki so locirani znotraj β-ciklodekstrinskega žepa. V prispevku obravnavamo geometrijo tovrstnih kompleksov in možno lego gostujoče molecule v žepu.