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Ionic pseudopolyrotaxanes bearing a chromophore in the side chain – A spectroscopic study in water

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ABSTRACT

The formation of pseudopolyrotaxanes based on a polyelectrolyte, a surfactant and α-cyclodextrin (α-**CD**) in aqueous solution is investigated. The polyelectrolyte and the surfactant form an ionic complex the side chains of which interact with each other. These interactions are strongly influenced by the formation of inclusion complexes with α-**CD**. It is shown by ^{1}H NMR and UV–vis spectroscopy that threading of the α-**CD** rings onto the side chains causes a shielding effect which increases the mobility of the side chains. The structure of the pseudopolyrotaxanes is concluded from ROESY spectra and their stoichiometry is determined by Job plots based on shift effects observed in the ^{1}H NMR spectra.

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1. Introduction

According to the definition, supramolecular self-assembly is the spontaneous association of molecules by non-covalent bonds into stable structures with definite composition [1,2]. Polyrotaxanes are supramolecular structures consisting of macrocyclic low molecular weight compounds threaded on a polymer main or side chain, where dissociation of the rings from the chain is significantly sterically hindered by bulky moieties so called stoppers [3] usually attached to the ends of the chain. The term pseudopolyrotaxane describes polyrotaxanes without stoppers [4]. Because of the lacking stoppers, the macrocyclic component of the pseudopolyrotaxanes are able to dissociate in solution reversibly from polymers. Polyrotaxanes and pseudopolyrotaxanes, assembled by the template approach, are of increasing relevance, as they give rise to new polymeric materials with interesting properties in a straightforward and modular way from known building blocks [5–7]. The detailed nomenclature of polyrotaxanes is referred to in a recent publication [8].

Examples of supramolecular self-assembly are host–guest inclusion complexes made of cyclodextrins (**CD**) and guest molecules. **CD**s are cyclic oligomers of D-(+)-glucopyranose units bound through an α-1,4-glucoside bonding forming a cone-shaped structure with an internal hydrophobic cavity of about 5–8 Å while external hydroxyl groups give the whole molecule a hydrophilic character. **CD**s of 6, 7, and 8 glucopyranose units are known as α-, β-, and γ-**CD**s, respectively. The special form of **CD**s allows inclusion of hydrophobic compounds matching size and shape of the **CD**s' cavities resulting in increased solubility in water. This has attracted much interest in utilizing such complexes in biomimetic applications, as for example as enzyme models [9–11]. Before the 90 s, there were only a few papers on interactions of **CD**s with polymer side chains in aqueous media, but, since the end of the last century, an increasing number of research groups have focused their attention on the interaction of **CD**s with polymer side chains [12–14].

The recent years have brought considerable interest in studying amphiphilic polymers obtained by hydrophobic modification of water-soluble polymers. Such polymers are highly relevant for probable applications in biological systems, as water-borne paints and coatings, cosmetics, drug delivery systems, and for water treatments [15–17]. Intra- and intermolecular hydrophobic self association of such amphiphilic polymers is observed in water depending on the macromolecular architecture [18]. When the hydrophobic moieties of the amphiphilic polymers are shielded by **CD**s, intermolecular hydrophobic association is suppressed preventing formation of polymer micelles. This distinctly reduces the solution viscosity of the system [19–26]. On the other hand, if intramolecular hydrophobic association is predominant in an amphiphilic polymer, the formation of inclusion complexes after addition of **CD**s may alter the polymer

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conformation from a compact to an extended one [27,28]. It was also shown that the lower critical solution temperature of thermally responsive polymers was sensitive to complexation with **CD**s [29–32]. Another interesting approach was published by Harada et al. [33]. The authors functionalized single walled carbon nanotubes with β-**CD** which formed hydrogels by inclusion complex formation with an acrylic acid based amphiphilic polymer.

Complexation between a polymer and an amphiphilic surfactant via ionic interactions is another type of supramolecular self-assembling [34,35]. In such complexes, the low molecular weight surfactant molecules are usually attached along the polymer chain via ionic interactions. Driven by attractive and repulsive interactions, polymer–surfactant complexes often self-organize in bulk into ordered structures resulting in completely different properties compared to the individual components.

Several studies dealt with inclusion complexes based on surfactants and **CD**s [36,37]. Such associates may also interact with polymers in a similar manner as described above for pure amphiphilic surfactants. One example is the formation of non-covalent side chain polymers based on poly(4-vinylpyridine) and various inclusion complexes of dodecyl benzenesulfonic acid and **CD**s of different size [38]. The complexation resulted in an increase of the chain rigidity. Müller et al. described an ionic polymer–surfactant complex with a chain conformation switchable by inclusion complex formation with α- and β-**CD** [39].

Recently, Tenkovtsev et al. [40] introduced a new ternary system based on poly(2-acrylamido-2-methylpropanesulfonic acid) (**1**), N,N-dimethyl-N′-(4-nitro-phenyl)-decane-1,10-diamine (**2**), and α-**CD** which is supposed to form the ionic pseudopolyrotaxane (**4**). The authors discussed briefly complex formation in DMSO which however was strongly influenced by interactions with the solvent. The effects found by ^{1}H NMR spectroscopic investigations were marginal and neither allowed concluding on the structure nor on the stoichiometry of the complex.

The present publication concerns a detailed spectroscopic study of the same ternary system in water. Here, the ^{1}H NMR effects are much more pronounced. With the help of NMR techniques such as ROESY, the formation of pseudopolyrotaxanes could be evidenced unambiguously. Concentration dependent UV/vis measurements based on the UV/vis absorption of the 4-nitroaniline moiety complete the results and support the conclusions made from the NMR spectroscopic findings.

2. Experimental

2.1. Materials

11-Aminoundecanoic acid, 1-fluoro-4-nitrobenzene, and 2-arylamido-2-methylpropanesulfonic acid were purchased from Aldrich. α-**CD** was purchased from Acros. All chemicals were used without further purification. Poly(2-acrylamido-2-methylpropanesulfonic acid) (**1**) ($M_\eta = 6.4\ 10^5$ g/mol) was synthesized by radical polymerization in water (initiator $Na_2S_2O_8$–Na_2SO_3–$FeSO_4$) according the known procedure [41].

2.1.1. N,N-dimethyl-N′-(4-nitro-phenyl)-decane-1,10-diamine (*2*)

Compound **2** was synthesized as described earlier [40]. Yield: 5.1 g (79%). Mp.: 98–99 °C.^{1}H NMR (DMSO d_6) δ (ppm): 7.98 (d, 2H, H_m), 7.24 (t, 1H, NH), 6.62 (d, 2H, H_o), 3.13 (q, 2H, H_l), 2.16 (t, 2H, H_b), 2.10 (s, 3H, H_a), 1.55 (quintet, 2H, H_k), 1.4–1.2 (14H, H_c–H_i). ^{13}C NMR (DMSO d_6) δ (ppm): 154.61 (C_{ipso}), 135.41 (C_{para}), 126.22 (C_m), 110.6 (C_o), 59.11 (C_b), 45.11 (C_a), 42.35 (C_l), 28.96, 28.93 (2C), 28.73, 26.84 (C_d–C_h), 28.28 (C_k), 26.99 (C_c), 26.47 (C_i).

2.1.2. Polymer–surfactant complex *3*

The ionic complex **3** was prepared by mixing methanolic solutions of 0.41 g of polymer **1** (2 mmol of sulfonic groups in 15 mL) and 0.16 g of compound **2** (0.5 mmol in 15 mL) with following heating under reflux for 6 h. After evaporation of the solvent under reduced pressure and subsequent drying under vacuum (0.1 mm Hg), the complex **3** (**1**:**2** = 4:1 mol/mol) was obtained.

2.1.3. Inclusion complexes *4* and *5*

An appropriate amount of the ionic complex **3** was mixed with a saturated aqueous solution of α-**CD** at room temperature. Then, the mixture was heated at 70 °C with stirring for 2 h and left overnight at room temperature. A feed ratio of 1:4 (ionic complex: α-**CD**, w/w) was used. The crystalline precipitate was isolated by centrifugation and dried in vacuum.

An inclusion complex of **2** and α-**CD** (in the following referred to as **5**) was prepared in a similar way.

2.2. Measurements

The ^{1}H NMR spectra were recorded on a Bruker DRX 500 NMR spectrometer operating at 500.13 MHz for ^{1}H. D_2O was used as solvent and lock, and a capillary tube containing a solution of sodium 3-(trimethylsilyl)-3,3,2,2-tetradeuteropropionate in D_2O was taken as a standard (δ (^{13}C) = 0 ppm; δ (^{1}H) = 0 ppm). The measurements were carried out at 303 K. The gradient-selected (gs) rotating frame Overhauser effect spectroscopy (ROESY) spectra were obtained using a series of 180° pulses with 180 μs duration as spin-lock with a total duration of 498 ms. Signal assignments were obtained by evaluation of 1D and 2D NMR spectra. The Job plots were obtained from 5×10^{-3} M stock solutions of α-**CD**, **2**, and **3** (referring to the surfactant content in the 4:1 complex).

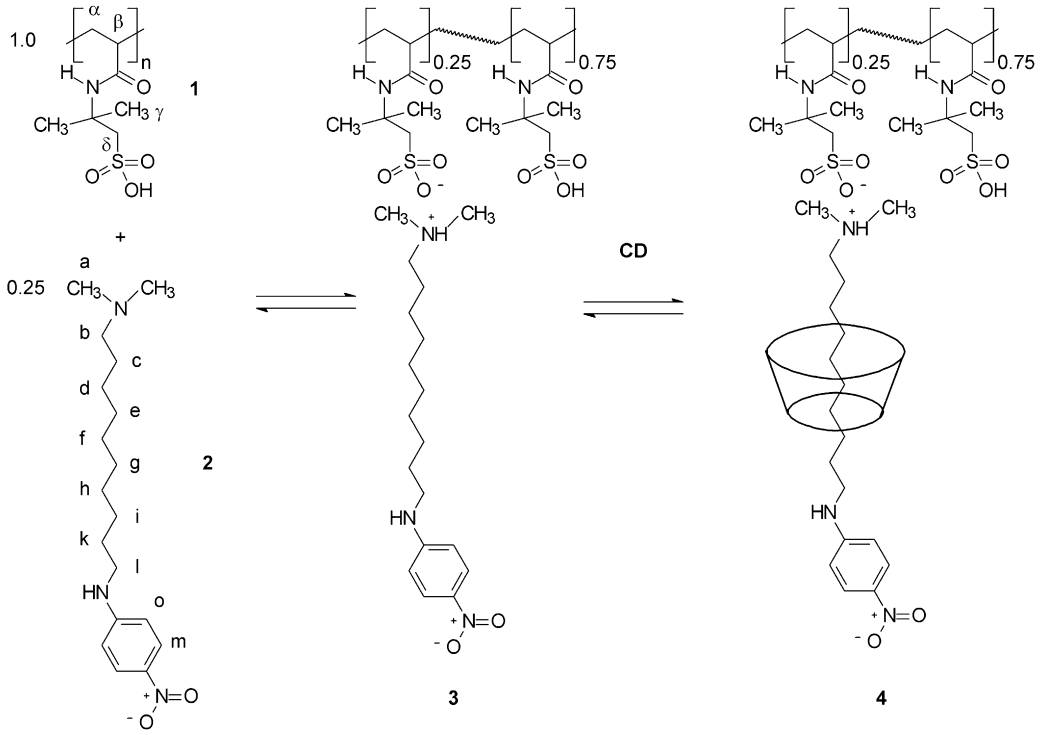
UV–vis analysis was carried out at room temperature using a Lambda 800 UV–vis spectrophotometer (Perkin–Elmer, Germany). The slit width was 1 nm. Titrations of the hydrochloride of **2** with HCl and **1** (starting volume 2.5 ml) were carried out at room temperature (22 ± 2 °C) in a sealed cuvette (quartz glass Suprasil, thickness $d = 10$ mm, HELLMA, Germany) by stepwise addition (gas-tight micro liter syringe, through the serum cap) of appropriate amounts of concentrated solutions of HCl and **1**, respectively. During titration, compound **2** was diluted by approximately 30%. The dilution effect on the spectra was corrected by applying an appropriate factor.

3. Results and discussion

3.1. Preparation of pseudopolyrotaxanes

For the preparation of ionic pseudopolyrotaxanes with chromophores in the side chain (see Scheme 1), poly(2-acrylamido-2-methylpropanesulfonic acid) (**1**) was chosen as matrix polymer since it forms stable complexes with tertiary amines [42]. Additionally, **1** does not absorb light in the region from 270 to 700 nm making it possible to investigate the properties of the ionically bound chromophore (**2**) by optical methods. As chromophoric group, the 4-nitroaniline moiety was chosen since it shows an intensive absorption at 350–450 nm and exhibits luminescence and nonlinear optical effects in the solid state. The decamethylene spacer in **2** was selected because of its high binding constants with α-**CD** [43]. The composition of the ionic complexes was adapted according to our previous investigations, concerning ionic bindings between a basic polymer and low molecular weight chromophores [44,45].

As shown in Scheme 1, the pseudopolyrotaxane (**4**) was prepared in two steps. In the first step, an ionic complex between



Scheme 1. Preparation of pseudopolyrotaxane **4**.

polymer **1** and the amphiphilic chromophore **2** was formed. To improve distribution of the chromophore in the polymeric complex **3,** mixing of the components was performed in methanol under reflux.

The inclusion complex **4** was prepared by dissolving the ionic complex **3** in a saturated aqueous solution of α-**CD** followed by heating at 70 °C. The pristine transparent reaction mixture became gradually turbid because of the formation of the crystalline inclusion complex. Although the complex formation was assumed to be fast, it was necessary to keep the solution at room temperature at least for 12 h since the crystallization rate of **4** in water was low. For comparison purposes, the inclusion complex of **2** and α-**CD** (compound **5**) was prepared as well.

3.2. NMR analysis

Both the polymer–surfactant complex **3** and the precipitated inclusion complexes **4** and **5** were characterized by ^{1}H NMR measurements in D_2O. Fig. 1a depicts the spectrum of a 5×10^{-3} M solution of **3**. Not only the signals of the polymer backbone are broadened but also the signals of the ionically bonded surfactant indicating restricted mobility in the polymer complex. Since twenty-fold dilution has no significant effect on chemical shifts and line widths, micelle formation can be excluded as reason of line-broadening. However, poor solvation of the hydrophobic aliphatic chains may induce cluster formation of neighboring surfactant molecules.

The dimethylamine signal of **2** in complex **3** (2.91 ppm) correlates well with the respective signal of a strongly acidified aqueous solution of **2**. This shows that the dimethylamine group of **2** is completely protonated in the polymer–surfactant complex. By contrast, the ^{1}H chemical shifts of the aromatic protons in *ortho* and *meta* position to the secondary amino group (6.54 and 7.89 ppm, resp.) rather suggest that the secondary amino group of **2** remains unprotonated in the complex. The respective signals of a completely protonated surfactant **2** appear at ~7.7 and ~8.45 ppm, respectively. These results clearly show that the complex formation proceeds by ionic interactions between the sulfonate groups of the polymer and the protonated tertiary amino group of the surfactant as indicated in Scheme 1. The calculated molar ratio of repeating units of **1** to surfactant molecules **2** is in satisfying agreement with the 4:1 ratio from synthesis regarding that the broad signals hamper the accurate signal integration.

The sparingly soluble inclusion complexes **4** and **5** were dissolved by addition of methylsulfonic acid. The molar ratio is not affected by this procedure, but, as a side effect the interactions between the surfactant and the polymer were reduced resulting in significant signal narrowing (Fig. 1b) and so in more accurate signal

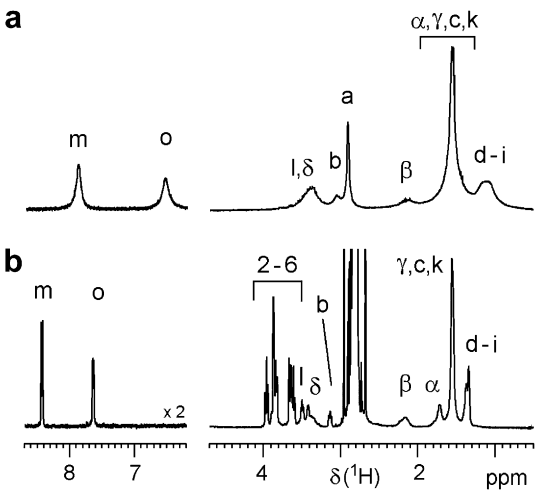


Fig. 1. ^{1}H NMR spectra of the surfactant–polymer complex **3** ([**3**] = 5×10^{-3} M in D_2O) (a) and of the precipitated pseudopolyrotaxane **4** (dissolved in D_2O by acidification with methylsulfonic acid) (b).

integrals. The molar ratio α-**CD**/**2** of the pseudopolyrotaxane **4** and the pseudorotaxane **5**, respectively, was calculated from the total integral value of the α-**CD** protons H_2–H_6 (3.6–4.0 ppm, 36H) and the sum of the integrals of both aromatic proton signals of the chromophore (~7.6 and ~8.4 ppm, depending on the amount of methylsulfonic acid added, 4H). The molar ratios were found to be slightly larger than equimolar (1.23 and 1.14, resp.). To prove these results, Job plots were recorded for the formation of the inclusion complexes of **2** and **3** with α-**CD** respectively. For this, the concentrations of **2** (free or complexed in **3**) and α-**CD** were altered systematically while the total concentrations [**2**] + [α-**CD**] and [**2** in **3**] + [α-**CD**], respectively, were kept constant at 5 mM. Depending on the molar fraction $X = [\mathbf{2}]/([\mathbf{2}] + [\alpha\text{-}\mathbf{CD}])$, chemical shift changes $\Delta\delta$ of the H_m and the H_c signals of the surfactant related to the position of these signals for the free surfactant ($X = 1$) were observed. These changes were multiplied with the corresponding molar fraction of **2** and plotted against the molar fraction of **2** (free or complexed in **3**) as shown in Fig. 2.

For surfactant **2**, the evaluation of the signal of the aliphatic proton H_c gives clear evidence for a 1:1 complex (open triangles). However, for the aromatic proton H_m, the plot shows a maximum complex concentration at a molar fraction close to 0.4 (filled triangles). This is in excellent agreement with the maximum at 0.6 (not shown) considering the chemical shift changes of α-**CD** in dependence on the α-**CD** molar fraction. A similar plot with a maximum at about 0.4 was obtained for the proton H_m of the polymer–surfactant complex **3** (filled circles). The values for the polymeric complex scatter a little more since the chemical shift changes determined from the broadened signal in the polymer complex are less accurate. The maxima at a molar ratio of about 0.4 exclude the formation of pure 1:1 complexes. It was reported that in the case of similar pseudopolyrotaxanes based on poly(4-vinylpyridine), 4-dodecyl benzenesulfonic acid, and α-**CD** each side chain carried about three macrocyclic wheels [38]. Therefore, it is reasonable to assume that also in our example **2** (free or complexed in **3**) does not only form 1:1 complexes with α-**CD** but also higher pseudorotaxanes with two and possibly three α-**CD**s on one alkyl chain. Thus, the molar ratios of 1.23 and 1.14 determined for the precipitated inclusion complexes **4** and **5,** respectively, result from mixtures of equimolar and higher pseudorotaxane complexes.

In a next step ^{1}H NMR effects caused by addition of α-**CD** to solutions of **2** and **3** in D_2O were studied. Here, the complexation of **2** with α-**CD** served as a model to understand the behavior of **2** in the ionic complex **3**. Fig. 3a shows the spectrum of **2** acidified with four equivalents of methylsulfonic acid. After addition of 5.2 equivalents of α-**CD** (Fig. 3b) chemical shift changes both in the aromatic and the aliphatic proton region are observed, but, not all signals are involved in the same extent. The curves in Fig. 3c demonstrate different influences of complexation on the signal positions of the aromatic proton H_m and the aliphatic proton H_c, respectively, suggesting that complexation processes with different binding constants are involved. For the aliphatic proton H_c, a stable state is already reached after addition of about an equimolar amount of α-**CD** whereas in the case of the aromatic proton H_m the chemical shift changes even occur after addition of a fivefold excess of α-**CD**. This behavior is in accordance with the aforementioned assumption that also higher pseudorotaxanes with two and possibly three α-**CD**s on the surfactant molecule are formed. The formation of an equimolar complex as depicted in Scheme 1 is well supported by the aliphatic proton's chemical shift change which shows that the macrocyclic wheel should be located on the aliphatic chain. This corresponds with the finding of the Job plot that a 1:1 complex is formed for the aliphatic chain. The binding constant is large and nearly complete complex formation is reached with a slight excess of α-**CD**. To thread a further α-**CD** onto the surfactant needs high excess of α-**CD** as indicated by the chemical shift change for the aromatic end group proton. Such higher loading on the aromatic end of the surfactant does not influence the

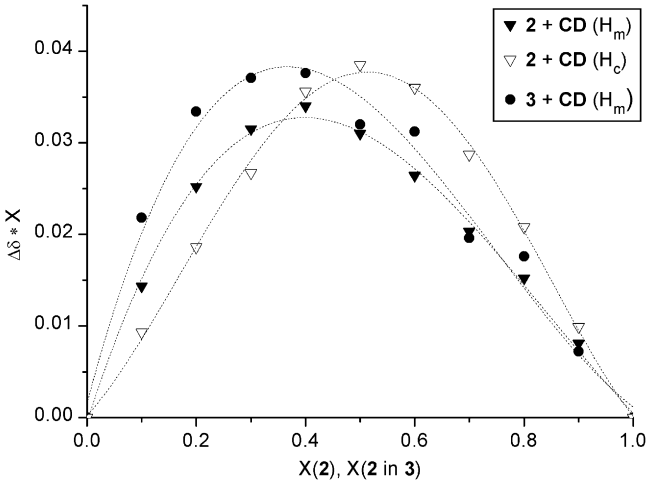


Fig. 2. Job plots for the complex formation between **2** (pure or complexed in **3**) and α-**CD**: (a) based on proton H_m of the pure surfactant **2**, (b) based on proton H_c of the pure surfactant **2**, and (c) based on proton H_m of surfactant **2** complexed in **3**. Measurements were carried out in D_2O at 303 K.

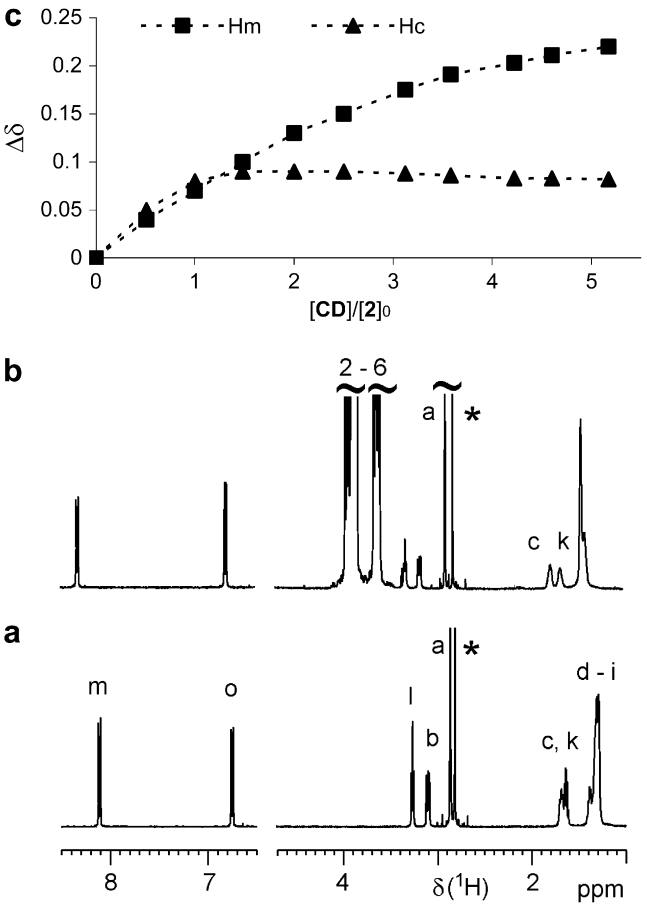
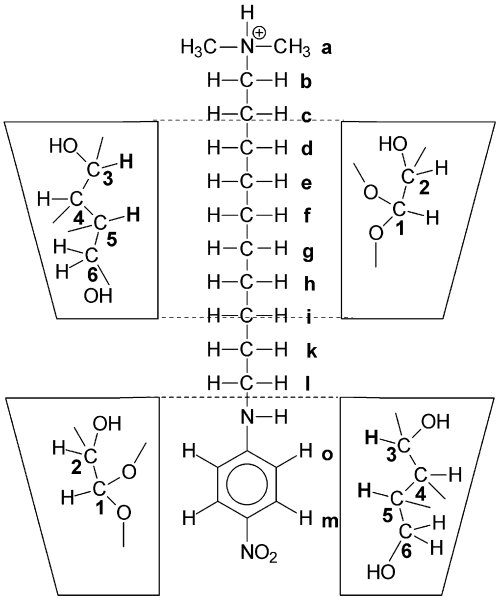


Fig. 3. ^{1}H NMR spectra of a D_2O solution containing 5×10^{-3} M **2** and 2×10^{-2} M methylsulfonic acid (a) and after addition of 2.6×10^{-2} M α-**CD** (b). (c) gives the chemical shift changes for the signals of H_m ($\delta_0 = 8.11$ ppm) and H_c ($\delta_0 = 1.69$ ppm) after addition of different amounts of α-**CD**.

chemical shift of H_c explaining the different complex compositions determined from the H_m and H_c signals of **2** in the Job plot (Fig. 2).

A rough structure of the α-**CD** complex can be estimated from ROESY cross-peaks between signals of the surfactant and α-**CD** [46]. Fig. 4 depicts the significant region of the ROESY spectrum of the higher loaded inclusion complex **5** corresponding to Fig. 3b. The circle contains the observed transient ROEs of the aliphatic protons. In contrast to the methylene group protons H_c to H_k, the terminal methylene groups (H_b and H_l) and the methyl groups (H_a) do not show an ROE. Obviously, one α-**CD** ring shuttles between the charged dimethylalkylammonium end group and the secondary arylalkylamino group forming a stable 1:1 complex. The repulsive effect of bulky cationic groups on α-**CD** is well documented [47–49]. Threading α-**CD** rings should occur mainly from the aromatic end. Since H_3 shows an ROE only to H_c and H_5 to H_k, the orientation of the wider rim of α-**CD** should be towards the dimethylalkyl ammonium end group (Scheme 2). This finding is in accordance with detailed studies of Funasaki et al. [47] on complexes of short-chain and long-chain surfactants with α-**CD**s. The aromatic protons also show ROEs to a α-**CD** ring (box in Fig. 4) indicating a second α-**CD** ring on the surfactant. It is obvious that a α-**CD** ring threaded on a terminal group can easier be released than a α-**CD** ring located on the backbone of the surfactant which is in accordance with the two different binding constants deduced from Fig. 3c. With H_m showing ROEs to H_3 and H_5 and H_o showing an ROE only to H_3, the orientation of the second α-**CD** ring should be as depicted in Scheme 2. The head-to-tail arrangement of neighboring α-**CD** macrocycles is surprising because polyrotaxanes with several cyclodextrins threaded onto a chain where often described with head-to-head/tail-to-tail arrangement [48,50]. However, the head-to-tail arrangement is also found in crystalline inclusion complexes [51]. Possibly, a reported stabilizing contact between same rims of neighboring α-**CD** rings is hampered by the secondary arylalkylamino group and, thus, the direction of threading of the second α-**CD** ring on the surfactant is not determined by the orientation of the first one. Furthermore, for nitrophenols and derivatives, it is found that the nitro group is inserted first and oriented towards the narrow side of the cavity [46].

The Job plot results point out that **2** complexed in **3** show a similar complexation behavior with α-**CD** as the free **2**. Thus, the H_m signal of the surfactant in the surfactant–polymer complex shows a similar low-field shift with increasing α-**CD** concentration (Fig. 5). However, the significant decrease of the line width of the signals of the complex is a clear prove that complexation with α-**CD** is accompanied with increasing mobility within the former polymer–surfactant complex. Without doubt, the threaded α-**CD** wheels result in a widening of the polymer coil of **3**. Cluster formation of the hydrophobic aliphatic chains is suppressed and the overall mobility within the pseudopolyrotaxane **4** is increased resulting in signal narrowing. It is obvious that the chemical shift effects observed cannot only be attributed to complexation. At least for the aliphatic protons, changes in the surrounding are assumed to have an influence. ROESY spectra cross-peaks between the inner aliphatic protons H_d–H_i and the protons H_3 and H_5 of α-**CD** prove that in the case of the pseudopolyrotaxane **4** the α-**CD** ring is also threaded to the side chain but a detailed study as for **5** was not possible because of the poor signal-to-noise ratio in the regions of interest.



Scheme 2. Proposed structure of a pseudorotaxane formed from surfactant **2** and two α-**CD** macrocyles based on observed ROEs (comp. Fig. 3).

3.3. UV–Vis analysis

The chromophoric group in surfactant **2** opens the possibility to use UV–vis spectroscopy to detect optical effects caused by proton exchange mediated complexation. In order to get general information about the influence of protonic acids on the absorption behavior of **2**, UV–vis spectra of **2** were recorded in water in

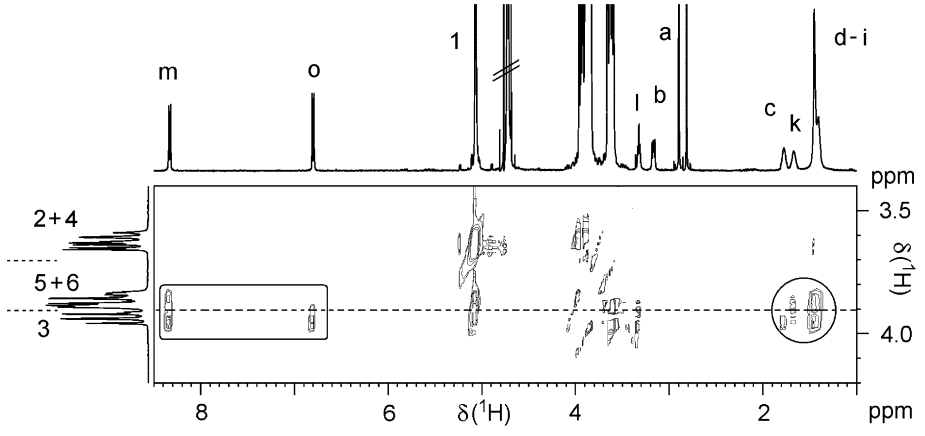


Fig. 4. Partial ROESY spectrum (positive levels only) of a D_2O solution containing 5×10^{-3} M **2**, 2×10^{-2} M methylsulfonic acid, and 2.6×10^{-2} M α-**CD**. (For signal assignment see 3).

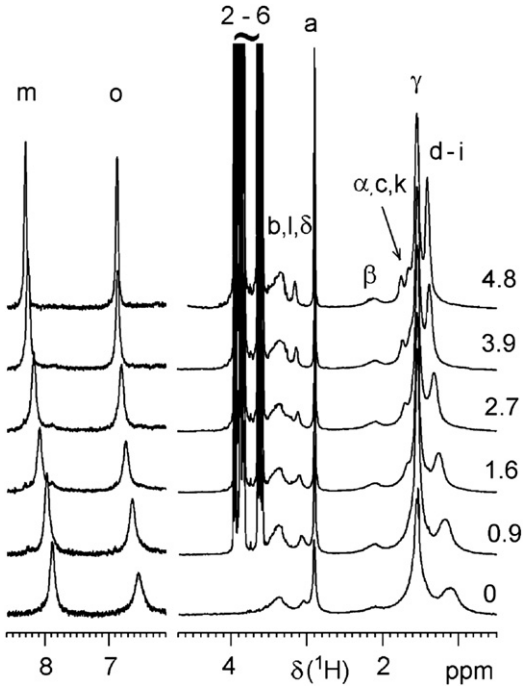


Fig. 5. ^{1}H NMR spectra obtained from a 5×10^{-3} M solution of **3** in D_2O after addition of different aliquotes of α-**CD**.

dependence on the amount of hydrochloric acid added. Since the solubility of **2** in water is very weak, all UV–vis measurements were started from the mono hydrochloride of **2**. Fig. 6 shows that the UV–vis spectrum of **2** is barely influenced by the amount of hydrochloric acid. Only at a very big excess of HCl (1000 fold), the main absorption band at 412 nm starts to diminish and a new band at 250 nm appears. It is assumed that the protonation of the secondary amino group is the reason for that. Because of the vicinity of this group to the aromatic group, protonation at this position influences the absorption significantly. At low concentrations protonation of the secondary amino group is negligible. Since the complex formation with the polymer **1** was investigated at low acid concentrations and the acidity of sulfonic acid groups is distinctly lower than that of HCl, it is reasonable to assume that the secondary amino group remains also unprotonated in presence of polymer **1**. This is confirmed by the results of the NMR

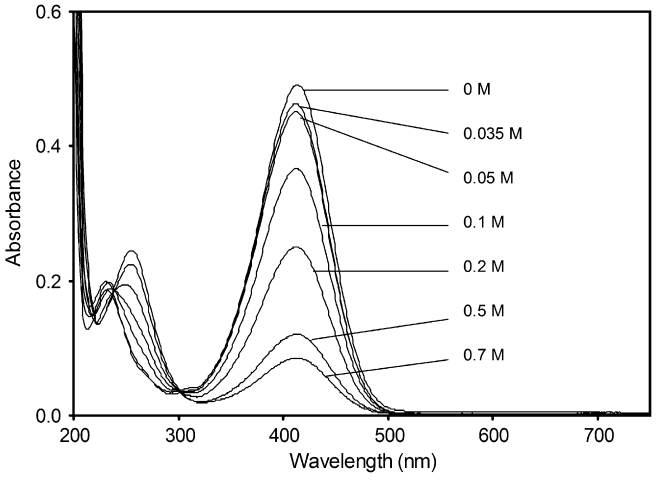


Fig. 6. UV–vis spectra of the mono hydrochloride of **2** (3×10^{-5} M in H_2O) in dependence on the concentration of HCl (0–0.7 M).

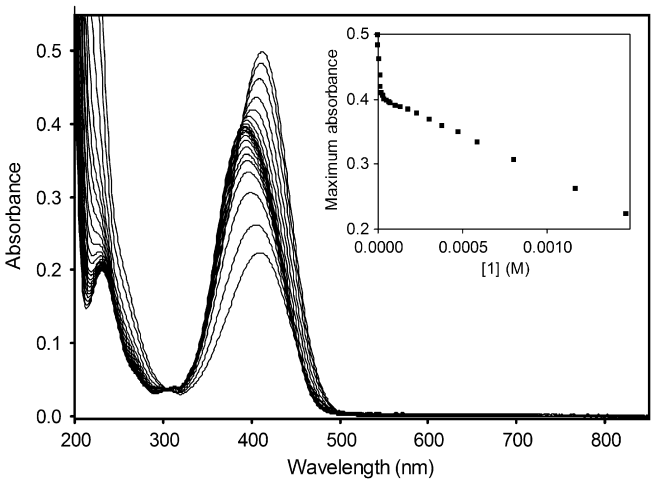


Fig. 7. UV–vis spectra of the mono hydrochloride of **2** ($[\mathbf{2}] = 3 \times 10^{-5}$ M in H_2O) in dependence on the concentration of **1** ($[\mathbf{1}] = 3.4 \times 10^{-6}$–$1.5 \times 10^{-3}$, related to the number of sulfonic acid groups).

spectroscopic measurements which show that for the complexation between **1** and **2** the interaction with the second amino group does not play an important role.

A much more distinct spectral alteration is observed when polymer **1**, which acts as a strong polymeric protonic acid, is added to an aqueous solution of the hydrochloride of **2**. The UV–vis spectra of **2** in dependence on the amount of **1** are shown in Fig. 7.

At the beginning, with increasing concentration of **1**, a steady hypsochromic shift of the absorption band of **2** at 412 nm is observed which turns into a bathochromic shift at higher concentrations. This is clarified through Fig. 8 which presents the position of the absorption maximum in dependence on the acid concentration. The minimum of the curve is reached at approximately equimolar ratio between **2** and the acidic groups of **1**. This is strong evidence that a 1:1 complex is formed. After reaching the minimum, the band position and also the intensity keeps constant over a broad concentration range. Only at higher acid concentration, the signal position turns gradually back to its initial value and the band intensity diminishes.

To interpret the results, one has to take into account that only the tertiary amino group of **2** is protonated in the aqueous solution of the hydrochloride of **2**. The addition of polymer **1** results into the

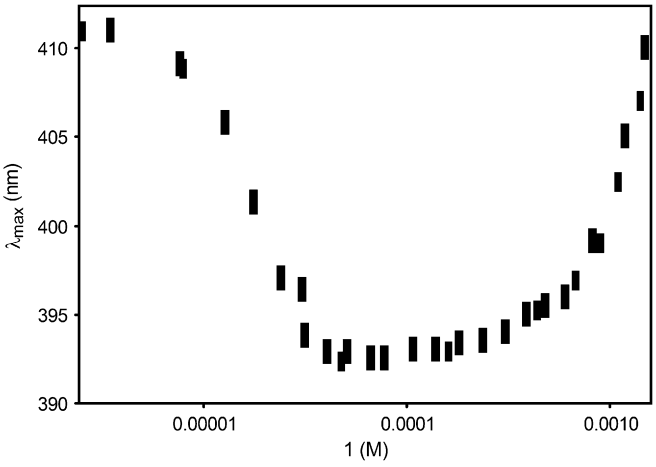


Fig. 8. UV–vis peak maximum of the mono hydrochloride of **2** ($[\mathbf{2}] = 3 \times 10^{-5}$ M in H_2O) in dependence on the concentration of **1** ($[\mathbf{1}] = 3.4 \times 10^{-6}$–$1.5 \times 10^{-3}$ M, related to the number of sulfonic acid groups).

formation of an ionic polymer–surfactant complex in the course of which the chloride anion is replaced by the sulfonate group. The driving force for this anion exchange is an increase in entropy. This process, however, does not change the structure (protonation) of **2**. From that point of view, it is not immediately obvious where the spectral alterations come from. Protonation of the secondary amino group seems to be unlikely since it occurs only at very high concentrations as mentioned above.

Obviously, the absorption behavior of **2** is distinctly influenced by its surrounding. In the highly diluted state of the pure hydrochloride, the chromophore is mainly surrounded by water molecules. Self association and micelle formation is unlikely since the typical concentrations for UV–vis measurements are to low. After adding polymer **1**, the surrounding of **2** changes drastically. Complex formation between both components results in a very strong increase in the local chromophore concentration within the polymeric coil. The strong proximity of the chromophores, maybe in clusters as argued in the NMR part, enables dipole–dipole interactions which might be the reason for the spectral alterations observed. At low polymer concentrations, coexistence of the free and the complexed chromophore is the reason for the steady hypsochromic shift of the chromophore's absorption band until the equimolar ratio between **2** and the acid groups of **1** is reached. Further increase in polymer concentration does not change the absorption behavior much. Only at a very high excess of the polymer, a further effect can be seen (see Fig. 8). This can be explained by the progressive dilution of the chromophore in the polymer coil which reduces dipole–dipole interactions. At the same time the local acid concentration becomes higher which eventually may result in the protonation of the secondary amino group of **2** as already discussed above for HCl as protonation agent. The results presented so far confirm ionic complex formation between polymer **1** and surfactant **2**.

UV–vis measurements on the ternary mixture of **1**, **2**, and α-**CD** should give evidence for the formation of pseudopolyrotaxane **4**. Fig. 9 shows the influence of the α-**CD** concentration on the absorption behavior of a 1:1 mixture of **1** and **2** in water. With increasing α-**CD** concentration, a bathochromic shift and an increase in the intensity of the absorption band is observed. Evidently, these alterations follow the opposite trend as observed in Fig. 7. Therefore, it is very likely that the addition of α-**CD** interrupts the dipole–dipole interactions of the chromophores as discussed above. Consequently, the absorption of the chromophore is equal to that of the free hydrochloride at high dilution in water. To what an extent the formation of the pseudopolyrotaxane **4** is responsible for these observations is not completely clear. One has to take into account that the alterations observed only appear at a very high excess of α-**CD**, but, the formation of pseudopolyrotaxane **4** might already be possible at lower concentrations. As known from the NMR spectroscopic investigations, interactions of **3** and α-**CD** result first in the formation of 1:1 complexes and at higher α-**CD** concentrations also in the formation of higher complexes. In complexes with at least two α-**CD** rings the aromatic groups are shielded. Although the UV–vis measurements are carried out at significantly lower concentrations, this shielding effect seems also to be responsible for the effects shown in Fig. 9.

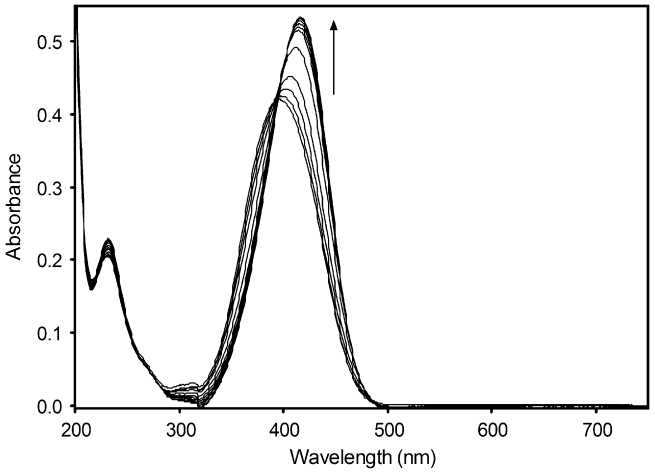


Fig. 9. UV–vis spectra of a 1:1 mixture of the mono hydrochloride of **2** and **1** ($[\mathbf{1}] = [\mathbf{2}] = 3 \times 10^{-5}$ M in H_2O) in dependence on the concentration of α-**CD** [α-**CD**] = 2.7×10^{-4}–1.1×10^{-2}, related to the number of sulfonic acid groups.

4. Conclusions

As shown by ^{1}H NMR spectroscopic investigations in water, ionic interactions between polymer **1** and surfactant **2** result in the formation of the ionic complex **3**. Complete protonation of the dimethylamine group of **2** indicate that complexation mainly occurs at this group. Protonation of the secondary amino group is only observed at a very high excess of acid. Distinctly broadened surfactant signals point at a confined mobility of **2** in the complex. These observations are supported by UV–vis measurements in aqueous solution. The absorption spectrum of **2** in the absence of **1** has proved to be almost independent from the addition of acids. Obviously, protonation of the dimethylamine group does not influence the spectral behavior of **2** much since its distance from the chromophoric group is too big. Only at very high acid concentrations, spectral alterations are observed owing to the protonation of the secondary amino group. By contrast, a small amount of the polymeric acid **1** influences the absorption behavior of **2** distinctly. Due to the incorporation of **2** into the polymer coil of **1**, the local concentration of the surfactant increases resulting in stronger dipole–dipole interactions which influence the absorption behavior of **2**.

The ^{1}H NMR spectroscopic measurements unambiguously evidence the formation of the inclusion complex **4** if α-**CD** is added to a solution of **3**. The complex stoichiometry has proved to deviate slightly from that of a 1:1 complex. An excess of α-**CD** even promotes the formation of complexes with two α-**CD** rings, one situated at the aliphatic chain and the other at the aromatic part of the surfactant. These rings exert a shielding effect which reduces the dipole–dipole interactions of the side chains. This is reflected in narrower NMR signals but also in an altered UV–vis absorption behavior. The UV–vis spectrum of **3** in the presence of α-**CD** resembles that of **2** in a highly diluted state were interactions between the side chains are shielded.

Although the concentration ranges of the NMR and UV–vis spectroscopic investigations differ about two magnitudes, complementary results are obtained by these methods. This is due to the fact that both the ionic interactions and inclusion complex formation occur mainly within the polymer coils so that the environmental influences on the chromophores become more or less independent on the overall concentration. Both methods indicate the formation of a polymer–surfactant complex, the ionically bound side chains of which interact with each other. Addition of α-**CD** results in the formation of pseudopolyrotaxanes with shielded interactions between the side chains.

Our results clearly show that with the combination two different kinds of interaction namely ionic interactions between the polymer and the surfactant and threading of the α-**CD** rings onto the surfactant defined pseudopolyrotaxanes are available.

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