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A Reversible Polyelectrolyte Involving a β-Cyclodextrin Polymer and a Cationic Surfactant

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ABSTRACT: A new model of polyelectrolyte has been elaborated by mixing in water a neutral polymer of β-cyclodextrin (poly(β-CD)) and a cationic dodecyltrimethylammonium chloride surfactant (DTAC). The driving forces for the poly(β-CD)/DTAC association in aqueous solution are reversible inclusion interactions between the CD cavities of the polymer and the alkyl group of DTAC. Viscometry, surface tension, and conductance measurements have first been used to prove the formation of such complexes. From these studies, it follows that both components form exclusively 1:1 inclusion complexes. Afterward, the association constant between poly(β-CD) and DTAC has been determined by considering 1:1 association from fluorescence, surface tension, and conductance data. It has been shown that both the architecture of poly(β-CD) and the electrostatic repulsions induced between the DTAC molecules are unfavorable to the association. The association constant is significantly stronger in the presence of salt, when the electrostatic repulsions are screened. Finally, the structural properties of the poly(β-CD)/DTAC complex have been studied by viscosimetry. A polyelectrolyte behavior has been observed when the stoichiometry of the poly(β-CD)/DTAC mixture in pure water reaches a critical value.

Introduction

Cyclodextrins (CDs) α-, β-, and γ- are the result of an enzymatic degradation of starch.[1] They are composed respectively of 6−8 (α-1,4)-linked α-D-glucopyranose units forming a rigid truncated cone-shaped structure (cf. Figure 1) with an internal cavity of size 5−8 Å. The narrow side of the truncated cone is bordered with the primary hydroxyl groups, whereas the secondary hydroxyl groups are at the wide side. No hydroxyl group is located inside the cavity, which confers a relative hydrophobic character on this region of the molecules. Consequently, CDs have the unique property of including various hydrophobic guest molecules or hydrophobic parts of molecules to form stable host−guest inclusion complexes through various interactions, such as hydrogen bonding, van der Waals, and hydrophobic interactions.

Native CDs can be modified through their hydroxyl groups for various purposes, for instance, to improve their low aqueous solubility or to improve their molecular binding abilities.[1−5] Polymers of CD are an example of CD derivatives that can present two different kinds of structure depending on the used synthesis ways. They can have linear structures where the CD units are located in dangling groups with respect to the main chain[6−8] or structures (generally branched) in which CDs are integrated in the skeleton.[9] In recent years, there has been increasing interest in using polymers of CD to create supramolecular assembling systems, partly because of the specific inclusion sites offered by the CD cavities and partly because of the reversible character of the inclusion interactions. Series of potential drug delivery systems have in this way been developed by forming inclusion complexes in water between a neutral polymer of CD and hydrophobic groups of a neutral[8,10−15] or ionic[16] amphiphilic polymer. The resulting assemblies display generally both thickening and specific inclusion properties (for an additional hydrophobic drug, for example). By using polymers of CDs and ionic surfactants, other types of supramolecular assembly have also been developed with various potential applications. Gel formation has, for instance, been observed in aqueous mixtures of a cationic polymer of CD and an anionic guest molecule.[17] In this system that can find a broad range of applications in drug delivery or separation operations in biotechnology, for example, the guest molecule included into CD cavities acts as a physical cross-linker between the poly(CD) chains by cooperative hydrophobic and ionic interactions. In our previous

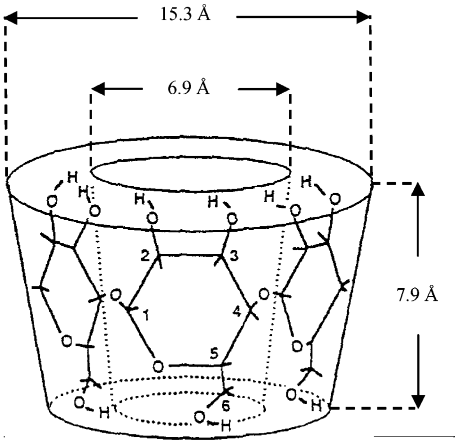

Figure 1. Truncated cone-shaped conformation of β-CD (7 D-glucopyranose units).

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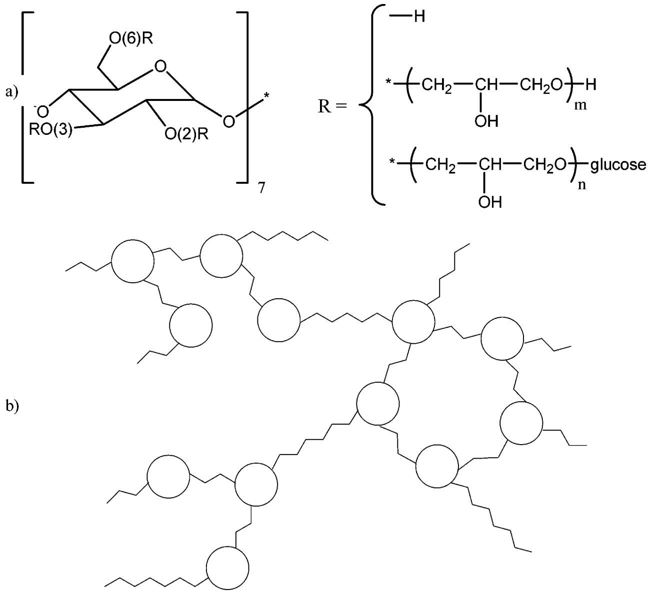


Figure 2. Structure of the poly(β-CD) copolymer.

paper,[18] we have also reported about the formation of multichain aggregates by mixing in water a neutral polymer of CD, a cationic surfactant, and an anionic polymer. The driving forces for this ternary complex formation are reversible inclusion interactions between the CD cavities and the surfactant and electrostatic attractions between the opposite charges of the cationic surfactant and the anionic polymer. Use of DNA as the anionic polymer in this system provides an original gene carrier in the framework of gene therapy. In this work, it has been revealed that the properties of the poly(CD)/surfactant/polyanion ternary complexes were strongly dependent on the structure of the poly(CD)/surfactant binary systems. To our knowledge, not many publications deal with the association between a polymer of CD and an ionic surfactant,[17,19] and there is no study where both the affinity between both components and the structural properties of the resulting aggregates are addressed in the same investigation.

The aim of this work is to characterize the aggregates formed in aqueous solution by inclusion interactions between a polymer of CD and a cationic surfactant. First, proofs of the poly(CD)/surfactant association will be provided by using several techniques including capillary viscometry, surface tension, and conductance measurements. Then, the affinity between both components will be estimated quantitatively before studying the structural properties of the aggregates as a function of the ionic strength and the stoichiometry of the mixtures.

Experimental Section

Materials. Monomers of β-cyclodextrin were supplied by Aldrich (France). The polymer of β-cyclodextrin (poly(β-CD)) has been synthesized by polycondensation with epichlorohydrin.[9] The sample has been purified by ultrafiltration of aqueous solutions on membranes of molecular weight cut off 30 000. The polymer has a branched architecture where β-CD molecules are modified by poly(2-hydroxypropyl)ether sequences of different lengths, possessing a free end or acting as a bridge between several CDs. Figure 2a depicts the chemical structure of this copolymer. The exact structure of the copolymer has not been determined precisely because of the polyfunctionality of the CDs; three positions O(2), O(3), and O(6) on the cavity are theoretically possible for the substitutions, but O(6) has been shown to be the most reactive.[9] This gives a functionality larger than 7 for a β-CD molecule. Moreover, epichlorohydrin has the same probability to react with hydroxyl groups of a CD as those of already-fixed epichlorohydrin. In the later case, epichlorohydrin polycondensation thus induces the formation of polytails and polybridges. The structure of the copolymer can become very compact and can be schematized as in Figure 2b. The sample used in this study is soluble in water. It has been characterized by size exclusion chromatography coupled with a light scattering detector; its weight-average molecular weight is M_w = 160 000, its polydispersity index M_w/M_n = 1.9, and its radius of gyration r_g = 55 Å. Its β-CD content, determined by ^{1}H NMR, is 59 wt %.

Hydroxypropyl β-CD (HP(β-CD)) is a monomer of β-CD that has been modified by 5−6 hydroxypropyl chains on average. It has been purchased from Aldrich (France).

The *n*-dodecyltrimethylammonium chloride (DTAC) surfactant was supplied by Acros Organics, Noisy-le-Grand, France. Its critical micellar concentration (cmc) in water is about 2.0 $\times 10^{-2}$ mol L^{-1} at 25 °C.[20] It has been used without further purification.

All the solutions have been prepared with ultrapure water by weighting the solvent and the dried products. Thus, concentrations are expressed in g/g^{-1} of water.

Samples have been prepared at least 12 h before measurements.

Surface Tension Measurements. Surface tension measurements were carried out with a Nima ST 9000 tensiometer using filter paper sheets of 10.25 mm width and 0.25 mm thickness.

All measurements were made at room temperature around 25 °C.

Conductance Measurements. Conductance measurements were realized using a Tacussel CD 6N apparatus equipped with a measure cell consisting of two platinum electrodes. The constant of the conductance cell was estimated to be 2 cm^{-1}.

All the samples were kept in a thermostated bath at 25 °C before each measurement.

Viscometric Measurements. The viscosity of the solutions was measured with an Ubbelohde viscometer at 25 ± 0.1 °C in a thermostated bath.

Samples have been previously filtered using glasses of porosity 2 (diameter of pores between 40 and 100 μm). All the dilutions were directly performed by adding ultrapure water into the viscometer.

Fluorescence Measurements. A SLM Aminco 8100 spectrofluorimeter, equipped with a xenon lamp and a monochromator, has been used for fluorimetric measurements. A fluorescent probe 4-amino-*N*-tertiobutylphthalimide able to make inclusion complexes with CDs has been used as a competitor for DTAC.

Samples have been prepared in quartz cells of 1 cm sides. They have been maintained at 25 °C using a water-jacketed cell holder coupled with a thermocryostat Lauda RM6 circulating bath.

Results and Discussion

1. Evidence of the Poly(CD)/Surfactant Association. Surface Tension Measurements. Figure 3 compares the surface tension variations of a DTAC solution and an aqueous mixture of DTAC and poly(β-CD) ($N_{\beta\text{-CD}}$ = 14 $\times 10^{-3}$ M) as a function of the surfactant concentration. For DTAC concentrations lower than the cmc of the pure surfactant (i.e., $N_{\text{DTAC}} \leq 20 \times 10^{-3}$ M approximately), the surface tension values (γ) of the mixture involving poly(β-CD) are higher than those measured for the DTAC solution. This reveals a reduction of the DTAC surface activity in the presence of poly(β-CD) and, consequently, indicates an interaction between the hydrophobic chain of the surfactant molecules and the polymer. We notice that the

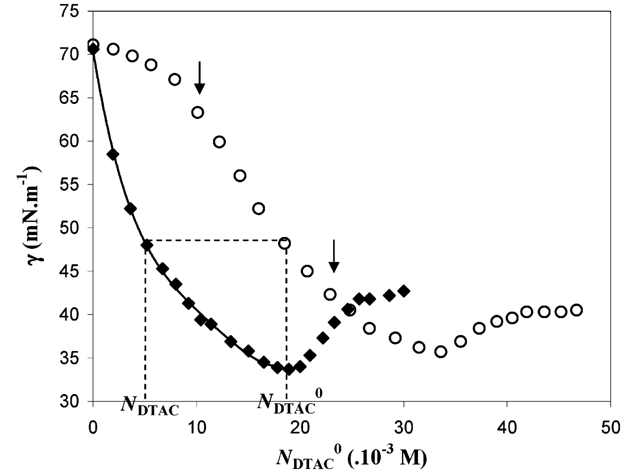


Figure 3. Variations of the surface tension of solutions of DTAC alone (◆) and in the presence of 14×10^{-3} M of cavities of poly(β-CD) (○), as a function of the total concentration in DTAC. The arrows delimit the concentration range for affinity constant determination.

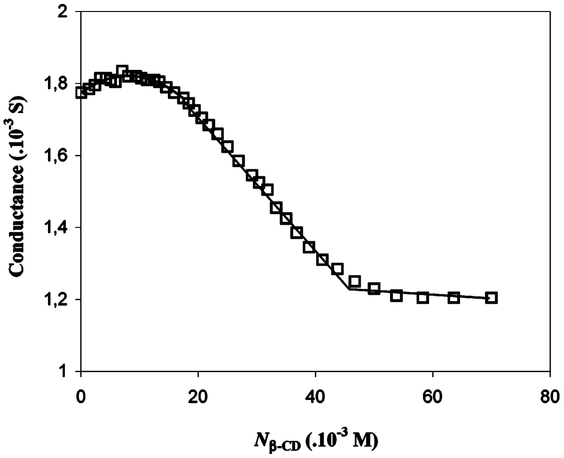


Figure 4. Influence of the concentration in β-CD cavities of poly(β-CD) on the conductance of a DTAC solution with $N_{\mathrm{DTAC}} = 40 \times 10^{-3}$ M.

γ values measured at low DTAC concentration for the poly(β-CD)/DTAC mixture are comparable to those of pure water ($\gamma_{\mathrm{water}} = 72$ mN m^{-1} at 25 °C[21]). This result shows that neither poly(β-CD) nor the poly(β-CD)/DTAC aggregates have surface activity. Thus, the γ values measured in the premicellar concentration range principally reflect the variations of the equilibrium concentration of the nonassociated DTAC.

In comparison with classical surface tension−concentration curves of surfactant solutions (cf. refs 22 and 23, for instance), curves in Figure 3 show a minimum in the micellar domain. This is ascribed to the presence of surface-active impurities[24] that may result from the manufacture process of DTAC. The interpretation of this minimum is as follows. For DTAC concentrations lower than the cmc, impurities are adsorbed among the DTAC molecules at the air/water interface. That makes the γ values lower than those measured in the case of pure DTAC. For DTAC concentrations larger than the cmc, impurities are progressively solubilized in the DTAC micelles, which induces a rise of the surface tension to the value observed in the case of pure DTAC. However, the presence of 2% of impurities (DTAC is 98% pure, according to the supplier) may affect only slightly the value of the cmc. Indeed, for the DTAC solution (without poly(β-CD)), the value of cmc given by the position of the minimum in γ values is 19×10^{-3} M, in accordance with the literature data (the cmc of pure DTAC is 20×10^{-3} M in water at 25 °C[20]).

Figure 3 also displays a marked increase of the apparent cmc (cmc*) of the system in the presence of poly(β-CD) ($N_{\beta\mathrm{-CD}} = 14 \times 10^{-3}$ M); cmc* is 34×10^{-3} M in this case. As asserted by many authors,[22,25−28] this result proves the formation of inclusion complexes between the DTAC molecules and the CD cavities present in solution. As the complexed surfactant monomers are not available anymore for forming micelles, these later are formed at a higher DTAC concentration when the interface is saturated and all the CD cavities are occupied. According to Junquera et al.,[29] the increase of the cmc value in the presence of CD is expressed as:

$$\mathrm{cmc}^* = \mathrm{cmc} + \frac{N_{\beta\mathrm{-CD}}}{R} \qquad (1)$$

where R is the $N_{\beta\mathrm{-CD}}/N_{\mathrm{surfactant}}$ stoichiometric ratio of the inclusion complexes. Given that a surfactant such as DTAC forms only 1:1 inclusion complexes with the native β-CD (because of sterical and dipolar interactions of the surfactant polar heads[30]), a value of R close to 1 is expected in the case of poly(β-CD). Actually, a value of 0.93 is obtained in the presence of 14×10^{-3} M of β-CD cavities, which indicates that neither the polymerization of the CD cavities nor the presence of the (hydroxypropyl)ether chains (second component of the poly(β-CD)) affect the process of interaction. In the premicellar domain, each of the DTAC molecules is included specifically in a nonoccupied β-CD cavity. Indeed, if the surfactant molecules were also interacting with the (hydroxypropyl)ether chains, the cmc* value would be observed at a DTAC concentration larger than 34×10^{-3} M $\approx$ cmc + $N_{\beta\mathrm{-CD}}$.

Conductance Measurements. The conductance variations of an aqueous mixture involving DTAC in a quantity higher than the cmc of the pure surfactant are depicted in Figure 4 as a function of the concentration in β-CD cavities of poly(β-CD). The shape of the curve is quite similar to those generally obtained for an aqueous mixtures of ionic surfactants and monomers of CD;[31] as the concentration in CD cavities rises, the conductance of the mixture increases (slightly in this case), passes through a maximum, and decreases following two straight lines (existence of a break in the slope). Such a behavior denotes the formation of inclusion complexes between the surfactant molecules and the CD cavities. The initial increase of conductance at low N_{CD} is ascribed to the progressive destruction of the micelles by inclusion of the surfactant chains into the CD cavities (the CD/surfactant interactions are stronger than the surfactant/surfactant interactions[32]). The destruction of the micelles is accompanied by a release of surfactant monomers and a release of counterions initially linked to the surface of the micelles, leading to an increase of the conductance values. This initial increase of conductance is nevertheless small in Figure 4, probably because the counterions located around the bulky poly(β-CD)/DTAC aggregates have a weak overall mobility (in comparison with those that would be located around complexes involving monomers of CD and distributed more homogeneously in the medium). At the maximum of the conductance, micelles are supposed to have completely disappeared and an excess of CD cavities reduces the quantity of free DTAC by formation

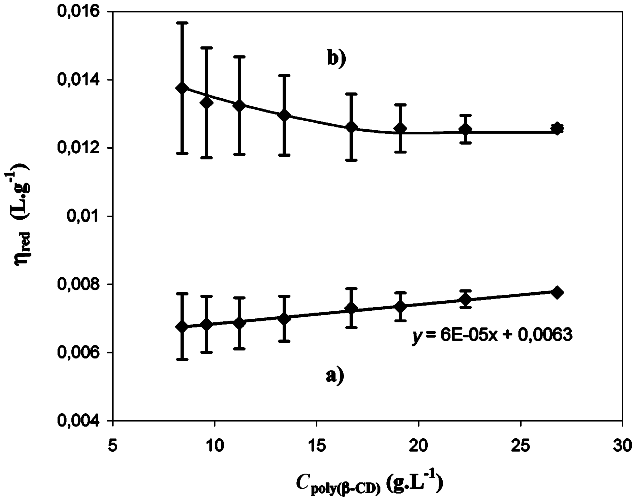


Figure 5. Influence of the polymer concentration on the reduced viscosity of a pure poly(β-CD) solution (a) and a poly(β-CD)/DTAC mixture involving 14 × 10^{-3} M of β-CD cavities and 6 × 10^{-3} M of DTAC before dilution (b).

of inclusion complexes, leading to a decrease of the conductance values. When most of the surfactant molecules are included in the CD cavities, a plateau of conductance is observed and its value is ascribed only to the charged inclusion complexes and to the counterions Cl^-. In Figure 4, it can be noticed that the value of conductance at the plateau (at high $N_{\beta-CD}$) is weaker than the one measured in the absence of polymer (at $N_{\beta-CD} = 0$), i.e., in the presence of micelles of DTAC. This gives an additional proof of the formation of poly(β-CD)/DTAC complexes because the free DTAC concentration, which gives the main contribution to the conductance (including the counterions), should be greatly reduced between these two limits. Indeed, micelles as well as poly(β-CD)/DTAC complexes, including their counterion clouds, are expected to be less mobile than free surfactants and free counterions. Information about the poly(β-CD)/DTAC association process can finally be obtained from the value of the $N_{\beta-CD}/N_{DTAC}$ ratio at the break in the decrease of conductance (beginning of the plateau). Data of Figure 4 allowed the determination of this ratio: $N_{\beta-CD}/N_{DTAC} = 1.1$. This shows that the poly(β-CD)/DTAC complexes are mainly formed with a 1:1 stoichiometry, i.e., with one molecule of DTAC per β-CD cavity.

Viscometric Measurements. The reduced viscosity (η_{red}) of a poly(β-CD) solution is presented in Figure 5 (curve a) as a function of its concentration. By extrapolating the values to the zero concentration according to the Huggins equation: $\eta_{red} = [\eta] + A[\eta]^2C + \cdots$, we obtain the intrinsic viscosity of the branched polymer:

$$[\eta]_{poly(\beta-CD)} = (6.3 \pm 0.5) \times 10^{-3}\ \mathrm{L\ g^{-1}}$$

The intrinsic viscosity of a linear poly(ethylene oxide) (POE) determined in the same conditions (same solvent, same temperature, and same molecular weight) is almost 10 times larger ($[\eta]_{POE} = 62.4 \times 10^{-3}$ L g^{-1}). This comparison shows that the structure of poly(β-CD) is more compact than that of a linear and flexible polymer.

On the same figure (curve b) are reported the reduced viscosities of a poly(β-CD)/DTAC mixture with a 14:6 stoichiometry (14 β-CD cavities for 6 DTAC molecules). It appears that the addition of DTAC to the poly(β-CD) solution affects dramatically the viscometric properties of this later. While the pure poly(β-CD) solution shows a behavior typical of a neutral polymer (i.e., a decrease of η_{red} with dilution), the poly(β-CD)/DTAC mixture displays a behavior typical of a polyelectrolyte in solution; the reduced viscosity of the mixture rises as the polymer concentration decreases. Such a behavior proves that cationic DTAC molecules are included in the β-CD cavities of the polymer. Complexed surfactant molecules tend to repel each other by electrostatic interactions, which results in stretching of the polymer chain.

By extrapolation to zero concentration according to the Fuoss equation: $\eta_{red}^{-1} = [\eta]^{-1} + B[\eta]^{-1}C^{1/2} + \cdots$, the intrinsic viscosity of the polycation resulting from the poly(β-CD)/DTAC association ($N_{\beta-CD}/N_{DTAC} = 14:6$) can be obtained:

$$[\eta]_{poly(\beta-CD)/DTAC} = (15.3 \pm 0.5) \times 10^{-3}\ \mathrm{L\ g^{-1}}$$

This last result emphasizes the swelling undergone by the poly(β-CD) chain decorated with the complexed DTAC molecules. The molecular weight increase of the complex compared to bare poly(β-CD) being less than 10%, the large intrinsic viscosity increase observed can be attributed to the swelling of the chain. The hydrodynamic volume of the resulting polycation chain is 2.5 higher than the one of the corresponding poly(β-CD) chain (without DTAC).

So, evidence of the formation of inclusion complexes between the polymer of β-CD and the DTAC surfactant has been provided. In the presence of the polymer, reduction of both surface activity and micellization properties of DTAC has been noticed. A decrease of the conductance of DTAC has also been reported. Moreover, viscometric measurements have highlighted the formation of a polycation by mixing poly(β-CD) and DTAC in a ratio $N_{\beta-CD}/N_{DTAC} = 14:6$; an increase of reduced viscosity with dilution has been observed.

Information on the structure of the aggregates has also been obtained. Surface tension, conductance, and viscometric results suggest that DTAC and β-CD cavities mainly form 1:1 inclusion complexes (one DTAC molecule per β-CD cavity).

2. Determination of the Association Constant of the Poly(CD)/DTAC Complex. According to the literature,[33] the association constant between CD cavities and surfactant molecules can strongly depend on the used experimental method, especially if the considered surfactant has the ability to form multiple associations with the CDs (formation of 1:1, 2:1, and 1:2 complexes, for instance). So, it seems interesting to compare the values of $K_{1:1}$ obtained by means of several techniques: the fluorimetric method, which allows measuring directly the concentrations in free and complexed DTAC in solutions containing known amounts of poly(β-CD), and the conductance and surface tension methods, which are sensitive to the variations of physicochemical properties of DTAC solutions induced by the addition of poly(β-CD).

Association Constant from Fluorescence Measurements. The determination of $K_{poly(\beta-CD)/DTAC}$ by means of a steady-state fluorescence method requires the use of a fluorescent probe that associates with β-CD cavities. By competition between the probe and the surfactant molecules for association with the CD cavities, one determines the association constant of the surfactant. The synthesis of the probe 4-amino-*N*-tertiobutylphthalimide and the description of the competitive complexation method have been detailed in a previous paper.[34] Assuming that the probe and the DTAC molecules form 1:1 inclusion complexes with the β-CD cavities, the two following equilibriums can be written:

$$\text{probe} + \beta\text{-CD} \rightleftharpoons \beta\text{-CD/probe} \tag{2}$$

$$\text{DTAC} + \beta\text{-CD} \rightleftharpoons \beta\text{-CD/DTAC} \tag{3}$$

The complexation constant of equilibrium (2) is K_{probe}:

$$K_{\text{probe}} = \frac{N_{\text{compl1}}}{N_{\text{probe}}^{\text{free}} \times N_{\beta-\text{CD}}^{\text{free}}} \tag{4}$$

where N_{compl1}, $N_{\text{probe}}^{\text{free}}$, and $N_{\beta-\text{CD}}^{\text{free}}$ are the molar equilibrium concentrations in β-CD/probe complexes, free probe, and free β-CD cavities, respectively. Note that in writing equilibriums (2) and (3), it has been implicitly assumed that the different CDs of a poly(β-CD) chain behave independently upon complexation with the probe or with DTAC molecules. As the probe concentration is much lower than the CD concentration, this assumption is generally valid for (2). This assumption will be discussed later for (3). On the basis of the fact that the fluorescence quantum yield of the complexed probe is much larger than the one of the free probe, the fluorescence intensity measurements allow determination of $N_{\beta-\text{CD}}^{\text{free}}$ using the following relationship:

$$N_{\beta-\text{CD}}^{\text{free}} = \frac{1}{K_{\text{probe}}} \times \frac{N_{\text{compl1}}}{N_{\text{probe}}^{\text{free}}} = \frac{1}{K_{\text{probe}}} \times \frac{I_f - I_0}{I_\infty - I_f} \tag{5}$$

where I_f, I_0, and I_∞ are the fluorescence intensities of the studied sample, of a sample containing only a free probe, and of a sample where all the probe molecules are complexed, respectively. K_{probe} is first determined from measurements on samples containing only poly(β-CD) and probe:

$$K_{\text{probe}} = 5250 \pm 60\ \text{M}^{-1}$$

In the presence of DTAC, equilibrium (3) leads to the $K_{\beta-\text{CD/DTAC}}$ complexation constant:

$$K_{\beta-\text{CD/DTAC}} = \frac{N_{\text{compl2}}}{N_{\text{DTAC}}^{\text{free}} \times N_{\beta-\text{CD}}^{\text{free}}} \tag{6}$$

N_{compl2} is the molar concentration in β-CD/DTAC complexes at equilibrium. On the other hand, N_{compl2} represents the equilibrium concentration in β-CD cavities bound to DTAC ($N_{\text{compl2}} = N_{\beta-\text{CD}}^{\text{bound}}$). Mass conservation of the β-CD cavities can be written as follows:

$$N_{\beta-\text{CD}}^{\text{bound}} = N_{\beta-\text{CD}}^{0} - N_{\beta-\text{CD}}^{\text{free}} - N_{\text{compl1}} \tag{7}$$

where $N_{\beta-\text{CD}}^{0}$ is the total concentration in β-CD cavities. $N_{\beta-\text{CD}}^{\text{bound}}$ is thus directly determined from fluorescence intensity measurements, as is $N_{\beta-\text{CD}}^{\text{free}}$. Equation 6 becomes:

$$\frac{N_{\beta-\text{CD}}^{\text{bound}}}{N_{\beta-\text{CD}}^{\text{free}}} = K_{\beta-\text{CD/DTAC}}(N_{\text{DTAC}}^{0} - N_{\beta-\text{CD}}^{\text{bound}}) \tag{8}$$

Thus, by plotting the ratio $N_{\beta-\text{CD}}^{\text{bound}}/N_{\beta-\text{CD}}^{\text{free}}$ as a function of ($N_{\text{DTAC}}^{0} - N_{\beta-\text{CD}}^{\text{bound}}$), a straight line with a slope equal to $K_{\beta-\text{CD/DTAC}}$ is expected.

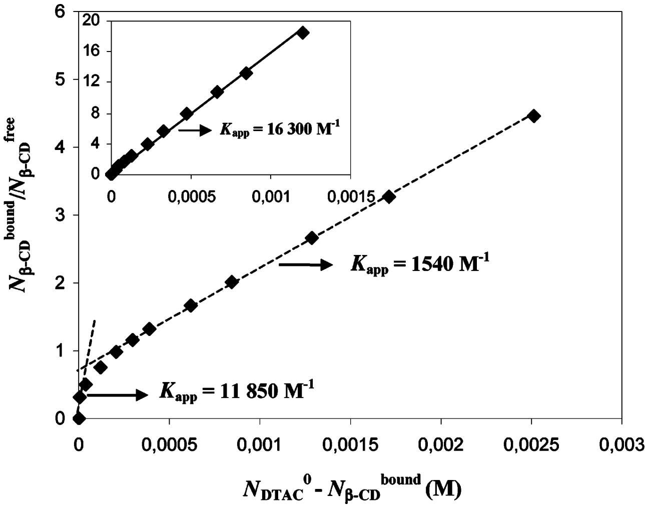


Figure 6. Variations of the ratio $N_{\beta-\text{CD}}^{\text{bound}}/N_{\beta-\text{CD}}^{\text{free}}$ measured for a poly(β-CD)/probe/DTAC mixture ($N_{\beta-\text{CD}}^{0} = 5 \times 10^{-4}$ M, $N_{\text{probe}}^{0} = 6.5 \times 10^{-5}$ M) as a function of the concentration in free DTAC ($N_{\text{DTAC}}^{\text{free}} = N_{\text{DTAC}}^{0} - N_{\beta-\text{CD}}^{\text{bound}}$). The insert plot shows the fluorimetric results obtained for a corresponding native β-CD/probe/DTAC mixture ($N_{\beta-\text{CD}}^{0} = 5 \times 10^{-4}$ M, $N_{\text{probe}}^{0} = 6.5 \times 10^{-5}$ M).

Figure 6 shows the results obtained for a mixture involving 5×10^{-4} M of cavities of poly(β-CD). The behavior is not linear, but two limiting straight lines can be deduced at low and large N_{DTAC}:

$$K_{\text{poly}(\beta-\text{CD})/\text{DTAC}} = 11\,900 \pm 1200\ \text{M}^{-1} \qquad (\text{for } N_{\text{DTAC}}^{0} < 2 \times 10^{-4}\ \text{M})$$

and

$$K_{\text{poly}(\beta-\text{CD})/\text{DTAC}} = 1500 \pm 50\ \text{M}^{-1} \qquad (\text{for } N_{\text{DTAC}}^{0} > 5 \times 10^{-4}\ \text{M})$$

The same competitive complexation measurements have been performed using native β-CD as described in ref 34. The complexation constant of the probe was $K_{\text{probe}} = 3100\ \text{M}^{-1}$, lower than the constant determined with poly(β-CD) by a factor of less than 2. The plot $N_{\beta-\text{CD}}^{\text{bound}}/N_{\beta-\text{CD}}^{\text{free}}$ as a function of ($N_{\text{DTAC}}^{0} - N_{\beta-\text{CD}}^{\text{bound}}$) shown in the inset in Figure 6 follows a straight line on a large range of $N_{\text{DTAC}}^{0} - N_{\beta-\text{CD}}^{\text{bound}}$ values ($0-1.5 \times 10^{-3}$ M). The complexation constant in this case is $K_{\beta-\text{CD/DTAC}} = 16\,300 \pm 500\ \text{M}^{-1}$.

It can be noticed that, at a very low free DTAC concentration (i.e., for $N_{\text{DTAC}}^{0} < 2 \times 10^{-4}$ M), the apparent association constant of the poly(β-CD)/DTAC complex is of the same order of magnitude as the one obtained with native β-CD. On the other hand, at a higher free DTAC concentration ($N_{\text{DTAC}}^{0} > 5 \times 10^{-4}$ M), $K_{\text{poly}(\beta-\text{CD})/\text{DTAC}}$ is about 10 times lower. This behavior can be ascribed to the nonindependency of the different β-CD cavities belonging to a same chain, in disagreement with the implicit assumption of eq 6. Linking charged surfactants to a poly(β-CD) chain brings repulsive electrostatic interactions along the polymer, and the strength of the resulting electrostatic potential is correlated to the ionization degree of the chain. The electrostatic potential of the chain is low when the ionization degree is low. Thus, electrostatic repulsions do not reduce the affinity of surfactants for the β-CD cavities, and the apparent complexation constant determined at low N^0_{DTAC} should be close to the one determined for β-CD monomers as it has been observed. As the ionization degree of the chain becomes larger, its increased electrostatic potential disfavors the association of new surfactants on the chain. Indeed, a DTAC ion trying to link to a free β-CD cavity neighbored by several already charged cavities experiences a strong electrostatic repulsion that can greatly reduce its affinity for the free cavity. In fact, the problem of $K_{\beta-\mathrm{CD/DTAC}}$ determination can be paralleled to the well-known problem of potentiometric titration of polyelectrolytes.[35] In the later case, the electrostatic field of the charged chain considerably increases the ionization energy of a given group on the chain and reduces its apparent acidity constant compared to the one of a simple electrolyte. As for polyelectrolytes, it can be claimed that the $K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}$ determined here are only apparent complexation constants as their values are dependent on the ionization degree of the chain; $K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}$ decreases by a factor 10 between the two limiting cases of low and large ionization degrees.

Association Constant from Surface Tension Measurements. The determination of $K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}$ from surface tension measurements makes reference here to the numerical method developed by Lu et al.[23] for complexation with β-CD monomers. The use of this technique requires that neither poly(β-CD) nor poly(β-CD)/DTAC complexes have surface activity that has been shown in the previous section (see comments for Figure 3).

According to Lu et al., when the surface tension (γ) variations of a CD/surfactant solution can be ascribed only to the change in the free surfactant concentration ($N_{\mathrm{s}}^{\mathrm{free}}$), this later can be calculated from the relationships between γ and the concentration in surfactant in the absence of CD (N_{s}). As indicated in Figure 3, which depicts the surfactant concentration dependencies of γ for a DTAC solution and a poly(β-CD)/DTAC mixture, each total surfactant concentration in the presence of poly(β-CD) (N^0_{DTAC}) corresponds to a γ value that corresponds itself to a N_{DTAC} value (surfactant concentration in the absence of poly(β-CD)). Thus, N_{DTAC} represents the free surfactant concentration in the poly(β-CD)/DTAC mixture, whose total concentration in DTAC is N^0_{DTAC} ($N_{\mathrm{DTAC}} = N^{\mathrm{free}}_{\mathrm{DTAC}}$ in the presence of poly(β-CD)). It has to be noticed that, in this work, the γ values of the DTAC solutions have been measured, taking the presence of surface-active impurities into account. To ascribe the γ variations of the poly(β-CD)/DTAC mixture only to the change in the free DTAC concentration (as required to determine $K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}$ with Lu's method), it is necessary that the surface activity of the impurity is not changed in the presence of the polymer (its contribution to the γ value measured in the absence and in the presence of the polymer must be identical). The similar shapes of the two surface tension curves of Figure 3 (with and without poly(β-CD)) allow justification of this assumption.

In the premicellar region, the equations relative to the formation of 1: 1 inclusion complexes between the DTAC molecules and the β-CD cavities of poly(β-CD) are:

$$K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}} = \frac{N_{\mathrm{compl}}}{N_{\mathrm{DTAC}} \times N_{\beta-\mathrm{CD}}} \tag{9}$$

$$N^0_{\beta-\mathrm{CD}} = N_{\beta-\mathrm{CD}} + N_{\mathrm{compl}} \tag{10}$$

$$N^0_{\mathrm{DTAC}} = N_{\mathrm{DTAC}} + N_{\mathrm{compl}} \tag{11}$$

where $N_{\beta-\mathrm{CD}}$, N_{DTAC}, and N_{compl} are the equilibrium concentrations in free β-CD cavities, free DTAC, and β-CD/DTAC inclusion complexes, respectively, and $N^0_{\beta-\mathrm{CD}}$ and N^0_{DTAC}, the total concentrations in β-CD and DTAC, respectively. Equation 9 can be written as:

$$N^0_{\mathrm{DTAC}} - N_{\mathrm{DTAC}} = -\frac{1}{K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}}\left(\frac{N^0_{\mathrm{DTAC}}}{N_{\mathrm{DTAC}}} - 1\right) + N^0_{\beta-\mathrm{CD}} \tag{12}$$

Thus, by plotting ($N^0_{\mathrm{DTAC}} - N_{\mathrm{DTAC}}$) as a function of ($N^0_{\mathrm{DTAC}}/N_{\mathrm{DTAC}} - 1$) (values deduced from surface tension measurements), it is possible to determine the association constant $K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}$ of the inclusion complexes (inverse of the slope).

Figure 7 presents the results obtained by using the Lu's method with the experimental values delimited by the arrows in Figure 3 (the surface tension variations generated by the change in the free DTAC concentration are more significant in this domain). The apparent association constant of the poly(β-CD)/DTAC complexes is then extracted from the slope of the straight line:

$$K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}} = 1800 \pm 300\ \mathrm{M}^{-1}$$

This apparent complexation constant has been determined in a high ionization regime of the chain; the N^0_{DTAC} range is 10−23 mM, while $N^0_{\beta-\mathrm{CD}}$ is 14 mM. It correlates well, within the error bar, with the value determined by fluorescence at the largest DTAC concentration.

Association Constant from Conductance Measurements. Let f be the fraction of DTAC bound to the β-CDs, i.e.,

$$f = \frac{N_{\mathrm{compl}}}{N^0_{\mathrm{DTAC}}} \tag{13}$$

Λ_0 and Λ are the equivalent conductivities (in S cm^2 mol^{-1}) of a dilute solution of DTAC in the absence and in the presence of β-CDs, respectively. According to Satake et al.,[36] the equivalent conductivity of the medium is linearly related to the conductivities of the free and bound surfactant when N^0_{DTAC} is lower than the cmc:

$$\Lambda_0 - \Lambda = f(\lambda_0 - \lambda) \tag{14}$$

where λ_0 and λ are the equivalent ionic conductivities of DTAC and β-CD/DTAC complexes, respectively. The fraction of bound DTAC can be calculated using the following expression of the association constant (9−11):

$$K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}} = \frac{f}{(1-f)(N^0_{\beta-\mathrm{CD}} - fN^0_{\mathrm{DTAC}})} \tag{15}$$

Replacing f in eq 14 leads to the final expression relating the conductance to the total concentrations N^0_{DTAC} and

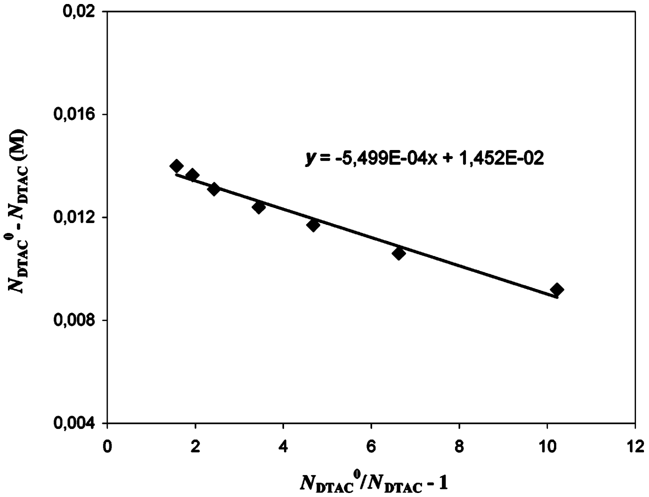


Figure 7. Relationship between ($N^0_{\mathrm{DTAC}} - N_{\mathrm{DTAC}}$) and ($N^0_{\mathrm{DTAC}}/N_{\mathrm{DTAC}} - 1$) for solutions of DTAC alone and mixed with poly(β-CD) ($N^0_{\beta\text{-CD}} = 14 \times 10^{-3}$ M).

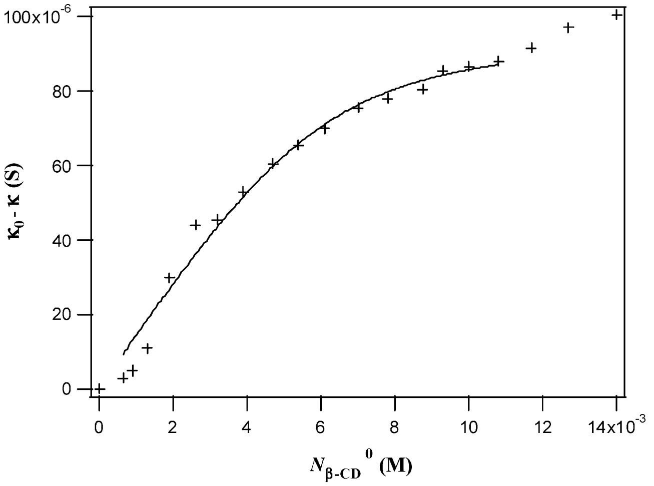


Figure 8. Variations of ($\kappa_0 - \kappa$) as a function of the concentration in β-CD cavities for a poly(β-CD)/DTAC mixture ($N^0_{\mathrm{DTAC}} = 6 \times 10^{-3}$ M). The continuous line represents the fit of the experimental data to the theoretical eq 15.

N^0_{CD} and to the association constant:

$$\kappa_0 - \kappa = \frac{\lambda_0 - \lambda}{2kK_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}}[K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}(N^0_{\mathrm{DTAC}} + N^0_{\beta-\mathrm{CD}}) + 1 - \{(K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}(N^0_{\mathrm{DTAC}} + N^0_{\beta-\mathrm{CD}}) + 1)^2 - 4(K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}})^2 N^0_{\mathrm{DTAC}} N^0_{\beta-\mathrm{CD}}\}^{1/2}] \quad (16)$$

with κ_0 and κ, the conductance (in S) of the DTAC solution in the absence and in the presence of β-CDs, and k, the characteristic constant of the conductance cell. Thus, the values of $K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}$ and ($\lambda_0 - \lambda$) can be calculated from the plots of ($\kappa_0 - \kappa$) vs $N^0_{\beta-\mathrm{CD}}$ using eq 16.

Figure 8 presents the dependency of ($\kappa_0 - \kappa$) on $N^0_{\beta-\mathrm{CD}}$ for a poly(β-CD)/DTAC mixture with a constant DTAC concentration. The augmentation of ($\kappa_0 - \kappa$) observed as $N^0_{\beta-\mathrm{CD}}$ increases (i.e., a diminution of κ) is ascribed to the progressive formation of bulky poly(β-CD)/DTAC inclusion complexes with reduced mobility compared to that of free DTAC. A fit of these experimental data to eq 16 leads to the conductometric parameters of the poly(β-CD)/DTAC aqueous system:

$$\lambda_0 - \lambda = 33.0 \pm 0.7 \text{ S cm}^2 \text{ mol}^{-1}$$

$$K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}} = 1400 \pm 200 \text{ M}^{-1}$$

It can be noticed that the difference obtained between the equivalent ionic conductivities of DTAC and poly(β-CD)/DTAC complex ($\lambda_0 - \lambda$) is higher than the one determined by Satake et al. for the native β-CD/DTAB system:[37] $\lambda_0 - \lambda = 12.5$ S cm^2 mol^{-1}. (The influence of the nature of the counterion, Cl$^-$ or Br$^-$, on the β-CD/ionic surfactant association is not very explicit in the literature. Nevertheless, we can assume that its influence is minor because only the hydrophobic tail of the surfactant is supposed to be included in the CD cavities). This result backs up the hypothesis of the formation of inclusion complexes less mobile with the polymer than with the monomers of β-CD.

As is shown in Figure 8, the fit of the experimental data using eq 16 has been adjusted only in the intermediate $N^0_{\beta-\mathrm{CD}}$ range: 2×10^{-3}–10×10^{-3} M, N^0_{DTAC} being fixed at 6×10^{-3} M. The assumption used in eq 15 is that the equivalent ionic conductivity of the poly(β-CD)/DTAC complex is a constant. However, the total charge and the hydrodynamic radius of this complex may vary as the ratio $N^0_{\beta-\mathrm{CD}}/N^0_{\mathrm{DTAC}}$ is changed. In fact, λ can be assumed to be constant in a range of concentration where the chain is highly charged. At $N^0_{\beta-\mathrm{CD}}$ larger than 10^{-2} M, the chains should not be totally ionized and their ionization degree should decrease as $N^0_{\beta-\mathrm{CD}}$ increases. Consequently, λ should decrease with increasing $N^0_{\beta-\mathrm{CD}}$, explaining the positive drift of the experimental data from the fit in this domain. At low $N^0_{\beta-\mathrm{CD}}$, the highly charged poly(β-CD)/DTAC should be in equilibrium with a non-negligible amount of free DTAC, which contributes to the ionic strength of the medium and consequently reduces the swelling of the chain. λ is thus increased compared to its value in the intermediate range, and this explains the observed negative drift of the experimental data from the fit.

Thus, the apparent complexation constant has been determined in the high ionization regime and its value is in good agreement with the two values determined by the fluorescence and surface tension methods in the same regime.

Table 1 summarizes the results of the quantitative studies of the poly(β-CD)/DTAC association, enumerating the N^0_{DTAC} and $N^0_{\beta-\mathrm{CD}}$ concentration ranges of the experiments. Except for a low $N^0_{\mathrm{DTAC}}/N^0_{\beta-\mathrm{CD}}$ ratio, the values of $K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}$ determined from three different experimental methods are equivalent ($K \sim 1600$ M^{-1}). This finding suggests strongly that cavities of poly(β-CD) and DTAC molecules form exclusively 1:1 inclusion complexes, the existence of multiple equilibriums leading generally to a dispersion in the $K_{1:1}$ values using different experimental methods. The determined complexation constants are apparent values that depend on the ionization degree of the chain, this parameter being controlled by the $N^0_{\mathrm{DTAC}}/N^0_{\beta-\mathrm{CD}}$ ratio. At a low $N^0_{\mathrm{DTAC}}/N^0_{\beta-\mathrm{CD}}$ ratio, $K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}$ is of the same order of magnitude as the equilibrium constant of complexes with DTAC and native β-CD ($K_{\beta-\mathrm{CD}/\mathrm{DTAC}} \sim 16\,000$ M^{-1}), showing that repulsive electrostatic interactions due to the charge of the chain have negligible effect on the cavity/DTAC affinity in this range. Conversely, at a large $N^0_{\mathrm{DTAC}}/N^0_{\beta-\mathrm{CD}}$ ratio, the electrostatic interactions

Table 1. Values of $K_{1:1}$ for the Poly(β-CD)/DTAC Aqueous System as a Function of the Used Experimental Method and the Investigated Domains of β-CD and DTAC concentrations

	fluorescence		surface tension	conductance
concentrations	$N^0_{\mathrm{DTAC}} < 0.2$ mM $N^0_{\beta-\mathrm{CD}} = 0.5$ mM	$N^0_{\mathrm{DTAC}} > 0.5$ mM $N^0_{\beta-\mathrm{CD}} = 0.5$ mM	$10 < N^0_{\mathrm{DTAC}}$ (mM) < 23 $N^0_{\beta-\mathrm{CD}} = 14$ mM	$N^0_{\mathrm{DTAC}} = 6$ mM $2 < N^0_{\beta-\mathrm{CD}}$ (mM) < 11
$K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}$	11900 (± 1200)	1500 (± 50)	1800 (± 300)	1400 (± 200)

Table 2. Influence of Salt on the cmc of DTAC Alone in Solution (cmc$_{\mathrm{DTAC}}$) and the cmc* of the Poly(β-CD)/DTAC Mixed System ($N_{\beta-\mathrm{CD}} = 14 \times 10^{-3}$ M) Determined by Surface Tension Measurements[a]

N_{NaCl} (M)	0	0.015	0.15	0.5
cmc$_{\mathrm{DTAC}}$ (*10^{-3} M)	19	13	6	2.5
cmc* (*10^{-3} M)	34	29	21	18
κ^{-1} (Å)	55.5	22.7	7.8	4.3

[a] The Debye lengths (κ^{-1}) have been calculated in the following conditions: $N_{\beta-\mathrm{CD}} = 14 \times 10^{-3}$ M, $N_{\mathrm{DTAC}} = 6 \times 10^{-3}$ M and variable NaCl concentrations.

of the charges along the chain play a major role and reduce the apparent complexation constant by a factor of ~10.

Thus, DTAC concentration has a relative effect on the strength of the poly(β-CD)/DTAC association. Given the ionic nature of the surfactant, N_{DTAC} should be above all a key parameter for the structural properties of the formed aggregates as the ionic strength of the medium (intrachain Coulomb repulsions more or less intense). That is the point of the next part.

3. Ionic Strength and DTAC Concentration Influences. cmc* as a Function of Ionic Strength. The apparent critical micellar concentrations of DTAC solutions containing a given amount of poly(β-CD) have been determined using surface tension measurements (as in Figure 3). The results, at ionic strength ranging from 0.015 to 0.5 M, are reported in Table 2. The cmc of the pure surfactant at the same ionic strengths have also been reported in this table for comparison. It is obvious that eq 1, cmc* = cmc + $N^0_{\beta-\mathrm{CD}}/R$, with R a number close to 1, is verified at all ionic strengths.

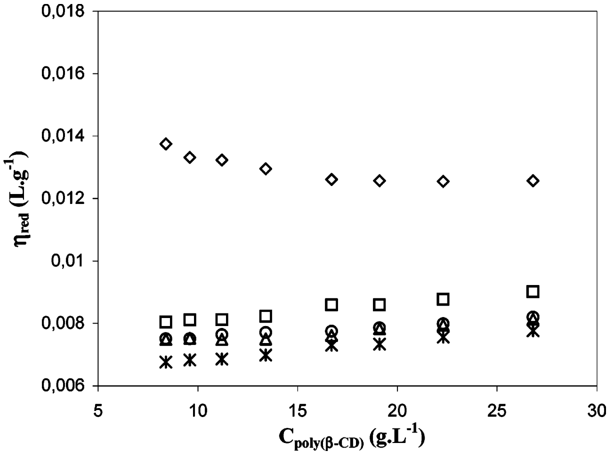


Figure 9. Reduced viscosity of a poly(β-CD)/DTAC mixture ($N_{\beta-\mathrm{CD}}/N_{\mathrm{DTAC}} = 14/6$ mM before dilution) as a function of the poly(β-CD) concentration at different NaCl concentrations: (◇) $N_{\mathrm{NaCl}} = 0$ M; (□) $N_{\mathrm{NaCl}} = 0.015$ M; (△) $N_{\mathrm{NaCl}} = 0.15$ M; (○) $N_{\mathrm{NaCl}} = 0.5$ M. Symbols (*) represent the reduced viscosity values of poly(β-CD) alone in solution ($N_{\mathrm{NaCl}} = 0$ M).

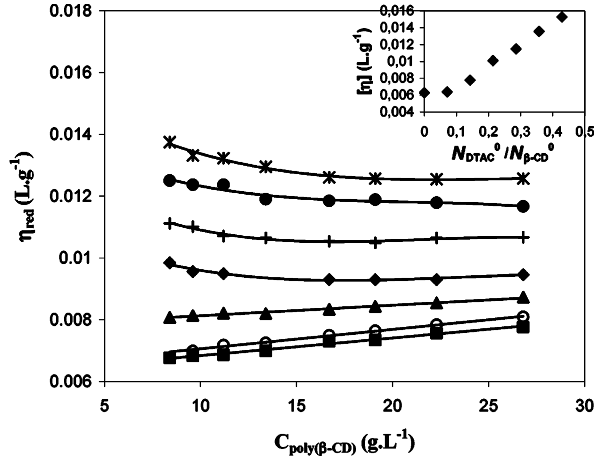


Figure 10. Influence of dilution on the reduced viscosity of poly(β-CD)/DTAC aqueous mixtures involving (before dilution) 14×10^{-3} M of β-CD cavities and variable DTAC concentrations: * $N^0_{\mathrm{DTAC}} = 6$ mM, ● $N^0_{\mathrm{DTAC}} = 5$ mM, + $N^0_{\mathrm{DTAC}} = 4$ mM, ◆ $N^0_{\mathrm{DTAC}} = 3$ mM, ▲ $N^0_{\mathrm{DTAC}} = 2$ mM, ■ $N^0_{\mathrm{DTAC}} = 1$ mM, $N^0_{\mathrm{DTAC}} = 0$ mM. The insert plot shows the influence of the stoichiometry of the mixtures on the intrinsic viscosity of the systems.

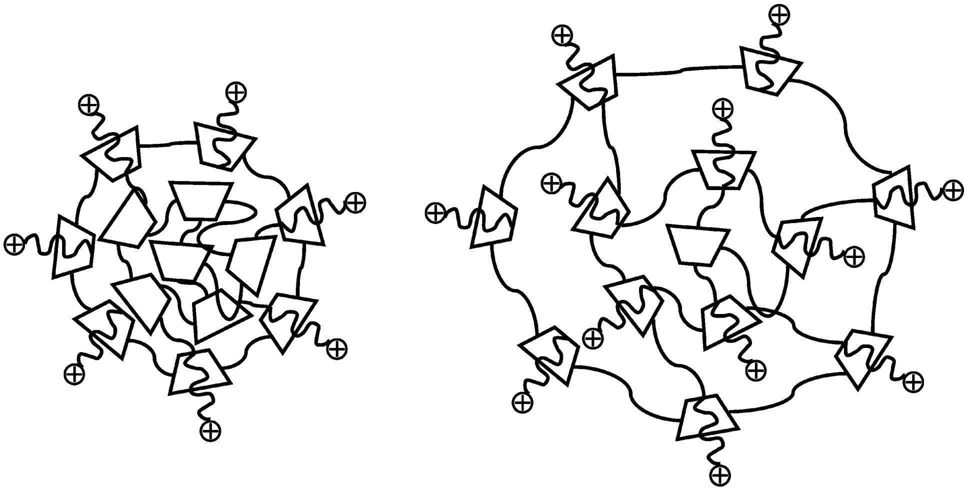
Affinity Constants. The three methods used in this paper for complexation constant measurements require a DTAC concentration range where the solution is free from micellar structures. This condition could prevent determinations as the cmc decreases strongly with the ionic strength. However, the cmc* are shifted to larger values because of the complexation with β-CD cavities as shown above. Measurements were thus possible in the same $N^0_{\beta-\mathrm{CD}}$ and N^0_{DTAC} range as the one used in the previous section. Conductivity experiments have not been performed at ionic strengths larger than 10^{-2} M because the signal was not sensitive to $N^0_{\beta-\mathrm{CD}}$ variations. The apparent complexation constants limited to the high ionization regime, determined by fluorescence and surface tension measurements, have been reported in Table 3. At 0.5 M NaCl, both methods are in relatively good agreement. $K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}$ increases markedly with the ionic strength. This is due to a progressive screening of the electrostatic interactions and thus to a weakening of the electrostatic repulsions opposing to the inclusion of DTAC into β-CD cavities. However, the value of $K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}$ estimated for $N_{\mathrm{NaCl}} = 0.5$ M (cf. Table 3) is still lower than the one determined in the same conditions for complexes with native β-CD ($K_{\beta-\mathrm{CD}/\mathrm{DTAC}} = 17\,100 \pm 700$ M^{-1} for $N_{\mathrm{NaCl}} = 0.5$ M). $K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}$ is rather of the same order of magnitude as the association constant of complexes with hydroxypropyl(β-cyclodextrin) (HP(β-CD)), a monomer of β-CD modified by 5−6 hydroxypropyl chains on average and which has a comparable structure as β-CD in the polymer ($K_{\mathrm{HP}(\beta-\mathrm{CD})/\mathrm{DTAC}} = 9600 \pm 200$ M^{-1} for $N_{\mathrm{NaCl}} = 0.5$ M). This finding shows that the electrostatic interactions are completely screened at 0.5 M NaCl, as the apparent complexation constant becomes comparable to the one of the corresponding nonpolymerized β-CD.

Viscometric Measurements. Figure 9 shows the influence of ionic strength on the reduced viscosity of a mixture involving poly(β-CD) and DTAC in a stoichio-

Table 3. Influence of Salt on the Apparent Values of $K_{\mathrm{Poly}(\beta-\mathrm{Cd})/\mathrm{DTAC}}$ Determined by Fluorescence and Surface Tension Measurements[a]

	$K_{1:1}$ (M^{-1})	
N_{NaCl} (M)	**fluorescence** ($N^0_{\mathrm{DTAC}} > 0.5$ mM, $N^0_{\beta-\mathrm{CD}} = 0.5$ mM)	**surface tension** ($9 < N^0_{\mathrm{DTAC}}$ (mM) < 23, $N^0_{\beta-\mathrm{CD}} = 14$ mM)
0	1500 ± 50	1800 ± 300
0.015		2500 ± 400
0.15		5300 ± 400
0.5	9000 ± 600	7700 ± 200
0.5	HP(β-CD)[b]: 9600 ± 200	
0.5	β-CD: 17100 ± 700	

[a] $K_{\mathrm{HP}(\beta-\mathrm{CD})/\mathrm{DTAC}}$ and $K_{\beta-\mathrm{CD}/\mathrm{DTAC}}$ in the presence of 0.5 M NaCl are also reported. [b] HP(β-CD) is hydroxypropyl β-CD.



a) b)

Figure 11. Schematic structure of the poly(β-CD)/DTAC complexes as a function of the stoichiometry: (a) $N_{\mathrm{DTAC}}/N_{\beta-\mathrm{CD}} < 0.14$, the charges are distributed on a "spherical" corona; (b) $N_{\mathrm{DTAC}}/N_{\beta-\mathrm{CD}} \geq 0.14$, the charges are distributed homogeneously along the poly(β-CD) chain.

metric ratio $N_{\beta-\mathrm{CD}}/N_{\mathrm{DTAC}} = 14{:}6$. As it can be seen, the addition of salt to the mixture results in a strong decrease of the reduced viscosities and in the disappearance of the polyelectrolyte behavior; the viscosities decrease with dilution in the presence of salt. This behavior, typical of neutral chains, could result from dissociation of inclusion complexes, but it is known that the association between CD cavities and ionic surfactants is reinforced in the presence of salt.[28] Measurements of the association constant for the poly(β-CD)/DTAC system at different NaCl concentrations lead to the same conclusion: $K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}$ increases with the ionic strength (cf. Table 3). Moreover, as shown in Figure 9, the reduced viscosities observed at high ionic strength for the mixture are still higher than the one measured for free poly(β-CD) (without DTAC), which also implies that both components are still associated.

Consequently, only a screening of electrostatic repulsions induced by the presence of salt can explain the decrease of viscosity and the disappearance of the polyelectrolyte behavior observed in Figure 9. In other words, the influence of salt results in reduction of the Debye length, κ^{-1}:

$$\kappa^{-1} = \frac{1}{(8\pi l_{\mathrm{B}} N_{\mathrm{a}} I)^{1/2}} \tag{17}$$

where $l_{\mathrm{B}} = 7.135$ Å is the Bjerrum length in water at 25 °C, N_{a} is the Avogadro number and I, the ionic strength. Note that in the presence of $N^0_{\beta-\mathrm{CD}} = 14 \times 10^{-3}$ M of β-CD cavities and $N^0_{\mathrm{DTAC}} = 6 \times 10^{-3}$ M of DTAC, all the surfactant molecules can be considered as included in the cavities of the polymer whatever the salinity. Indeed, as indicated in Table 2, the apparent critical micellar concentration of the mixed system, cmc*, is far from being reached at the chosen β-CD, DTAC, and NaCl concentrations. The Cl^- counterions of DTAC are assumed to be free, as the minimum spacing between charged groups on the poly(β-CD)/DTAC complex is larger than 15 Å (the minimum distance between two complexed DTAC molecules, $d_{\min}$, corresponds to the total width of a β-CD cavity, i.e., 15.3 Å). In these conditions, the ionic strength I can be approximated as the half sum of concentrations in Na^+ and Cl^- ions of salt, added to the concentration in Cl^- counterions of DTAC:

$$I = \frac{1}{2}(2N_{\mathrm{NaCl}} + N_{\mathrm{DTAC}}) \tag{18}$$

The values of κ^{-1} determined with eqs 17 and 18 for the different considered NaCl concentrations are reported in Table 2. It has to be noticed that, for $N_{\mathrm{NaCl}} \geq 0.15$ M, the value of κ^{-1} is lower than that of $d_{\min}$. Thus, repulsive interactions should be completely screened beyond 0.15 M in NaCl. This explains the superposition of the corresponding viscosity curves in Figure 9.

Figure 10 presents the influence of the DTAC concentration on the reduced viscosity of poly(β-CD)/DTAC aqueous mixtures involving the same amount of polymer, measured as a function of the poly(β-CD) concentration. It appears that poly(β-CD)/DTAC systems behave like polyelectrolytes when the stoichiometry

$N^0_{\mathrm{DTAC}}/N^0_{\beta-\mathrm{CD}}$ of the mixtures is higher than 0.14 (= 2/14). Below this value, the reduced viscosity of the mixtures decreases with dilution, which is typical of neutral polymer in solution. Above $N^0_{\mathrm{DTAC}}/N^0_{\beta-\mathrm{CD}} = 0.14$, the reduced viscosities increase with dilution, proving the existence of repulsive Coulomb interactions along the polymer chains.

In a previous paper,[18] the poly(β-CD)/ DTAC aggregates have been studied by small-angle neutron scattering. It has been shown that the charge distribution is not homogeneous in the aggregates at low DTAC concentration; the surfactant molecules are complexed at the periphery of the branched architecture of poly(β-CD), defining an outside corona as illustrated in Figure 11a. In these conditions, repulsive interactions between DTAC molecules do not affect the internal structure of the polymer; no swelling of the chain can be observed. For a $N^0_{\mathrm{DTAC}}/N^0_{\beta-\mathrm{CD}}$ ratio larger than a critical value, the charge distribution becomes more homogeneous along the poly(β-CD) chain (Figure 11b). A swelling of the chain can thus be observed as a consequence of incipient electrostatic repulsions inside the polymer structure. Note that this change from inhomogeneous to homogeneous charge distribution in the complexes has been observed for a $N^0_{\mathrm{DTAC}}/N^0_{\beta-\mathrm{CD}}$ ratio equal to 0.11. This is in agreement with the viscometric results: the intrinsic viscosity of the system starts to increase for a $N^0_{\mathrm{DTAC}}/N^0_{\beta-\mathrm{CD}}$ ratio higher than 0.1 (cf. inset in Figure 10).

Conclusion

The mixture of poly(β-CD) and DTAC in aqueous solution results in the formation of soluble complexes involving inclusion interactions between the β-CD cavities and the alkyl chains of the DTAC molecules. As in the case of β-CD monomers,[29] the poly(β-CD)/DTAC inclusion complexes are formed with a stoichiometry of 1:1 (one DTAC molecule per β-CD cavity). Thus, the fact that the β-CD cavities are linked together with (hydroxypropyl)ether chains does not affect their mode of association with the cationic surfactant.

The affinity of DTAC for the cavities of poly(β-CD) ($K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}$) has been shown to depend on the $N^0_{\mathrm{DTAC}}/N^0_{\beta-\mathrm{CD}}$ ratio and thus on the ionization degree of the complex. The poly(β-CD) chains decorated with DTAC behave like polyelectrolytes whose electrostatic potential opposes an increase of their ionization degree. The strength of these electrostatic repulsions being dependent on the ionization degree of the complex, the determined association constants are apparent values that are similarly defined as the apparent acidity constants determined by titration of polyacids. A fluorescence method allowed determination of $K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}$ at low and large $N^0_{\mathrm{DTAC}}/N^0_{\beta-\mathrm{CD}}$ ratios. $K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}$ decreases from a value close to the one of β-CD monomers at low ratio to a value ~10 times lower than that at large ionization ($K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}} \sim 1600$ M^{-1}). The affinity constant in the high ionization regime has also been determined by two other methods: surface tension and conductimetry. The good agreement found between the three determinations confirms the validity of our assumptions. Moreover, it has been shown that electrostatic repulsions in the poly(β-CD)/DTAC complex are reduced in the presence of salt. The association is then correlatively favored and, at high salt concentration, $K_{\mathrm{poly}(\beta-\mathrm{CD})/\mathrm{DTAC}}$ becomes comparable to the complexation constant of nonpolymerized β-CD cavities of (hydroxypropyl(β-CD), whose chemical structure is comparable to that in poly(β-CD)).

The resulting poly(β-CD)/DTAC complex shows different structural properties depending on the DTAC concentration. Viscometric results highlight the existence of a critical $N^0_{\mathrm{DTAC}}/N^0_{\beta-\mathrm{CD}}$ ratio below which poly(β-CD) decorated with DTAC behaves like the corresponding free chain (i.e., neutral). On the other hand, above this critical ratio, the complex adopts a swollen conformation and behaves like a polyelectrolyte. This behavior has been ascribed to a change in the distribution of the charges along the chain. Below the critical $N^0_{\mathrm{DTAC}}/N^0_{\beta-\mathrm{CD}}$ ratio, the DTAC molecules are distributed at the periphery of the branched architecture of poly(β-CD), which has no consequence on the polymer swelling. Above the critical ratio, the charge distribution becomes more homogeneous inside the branched structure of poly(β-CD), leading to a swelling of the chain (by repulsive Coulomb interactions).

Thus, it appears that the structural properties of the poly(β-CD)/DTAC complex are governed by an intricate interplay between the level of surfactant addition and the architecture of the polymer of CD. Also, one of the questions that remain unanswered about this system concerns the structures formed with a linear polymer of CD. This will be the topic of a future work.

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