Tailorable Polyelectrolyte Complexes Using Cyclodextrin Polymers

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Association of a β-cyclodextrin polymer, a cationic surfactant, and an anionic polymer leads to ternary complexes involving both inclusion complexes and electrostatic interactions. Polyanions of different natures and architectures have been used: sodium polystyrene sulfonate (NaPSS), molecular weight 70 000, has a flexible and hydrophobic backbone whereas sodium dextran sulfate (NaDxS) (molecular weights 10 000 and 40 000) are hydrophilic and have branched structures. Phase diagrams have been established by mixing a β-cyclodextrin polymer (poly(β-CD)), a cationic surfactant (dodecyltrimethylammonium chloride, DTAC), and a polyanion (sodium salt polystyrene sulfonate, NaPSS) in water. For one of the soluble mixtures, the formation of poly(β-CD)/DTAC/NaPSS ternary complexes has been proved by using viscometry and small-angle neutron scattering. For fixed concentrations of both polymers, the structural properties of the ternary complexes have been studied as a function of the cationic surfactant concentration in the bulk solution. A change in the overall structure of the complexes has been observed, from diffuse aggregates at low N_{DTAC} to dense aggregates at higher concentration. The properties of the ternary complexes have been shown to depend on the polyanion nature and characteristics. Ternary complexes with NaPSS ($M_w = 70$ kg·mol^{-1}) are soluble to higher DTAC concentrations than those with NaDxS 1 ($M_w = 10$ kg·mol^{-1}), the latter being more soluble than those with NaDxS 2 ($M_w = 40$ kg·mol^{-1}). Neutron scattering experiments have shown that the inner structure of the aggregates are inhomogeneous (the elementary particles have a core−shell structure) at DTAC concentrations lower than a critical value (N_{DTAC}^{crit}) whatever the polyanion nature. At larger DTAC concentrations, compact and entangled inner structures are obtained with NaDxS 1 (of low molecular weight) when core−shell inner structures are obtained with NaDxS 2 and NaPSS (of higher molecular weight). Analysis at larger length scales allowed characterization of the overall structure of the aggregates. The flexible chains of NaPSS are able to maximize the electrostatic interactions by wrapping up the poly(β-CD)/DTAC elementary particles, whereas the more rigid NaDxS involves an aggregation mechanism between the same particles.

Introduction

By mixing two oppositely charged polyelectrolytes in aqueous solution, a spontaneous aggregation occurs via strong electrostatic interactions between both components. Stoichiometric polyelectrolyte complexes (PECs), being electroneutral, usually precipitate from the aqueous solution. This has been found to be useful in separation or purification processes (purification of proteins,[1] for instance). Nonstoichiometric PECs, i.e., with an excess of one of the constitutive charged components, are usually water-soluble. They have shown great potential in the design of composite structures such as microcapsules[2,3] and modified surfaces.[4] Nonstoichiometric PECs are applied for flocculating suspensions of dispersed solid particles such as cellulose,[5] clay,[6] and silica[7] (paper industry, water purification, or mineral processing applications). The strong structural changes occurring during the PEC formation from extended polymer chains to compact aggregates have also constituted the basis for application of PECs in the gene delivery domain. For

instance, Kabanov et al.[8,9] have shown that incorporation of DNA into soluble PECs with linear quaternized poly(4-vinylpyridines) imparts transmembrane properties to DNA and leads to a considerable increase in cell transformation efficiency. Pollard et al.[10] have demonstrated that complexation of DNA with poly(ethylenimine), of branched structure, promotes gene accessibility to the nucleus in mammalian cells.

Water-soluble tailorable PEC can be elaborated from the mixture in aqueous solution of three components: a branched polymer of β-cyclodextrin (poly(β-CD)), a cationic surfactant (dodecyltrimethylammonium chloride, DTAC), and a polyanion.[11] The driving forces for this ternary complex formation in aqueous solution are reversible inclusion complex interactions between the β-cyclodextrin cavities and DTAC on one hand, and electrostatic attractions between the cationic surfactant and the polyanion on the other hand. Inclusion complexes are specific interaction mechanisms between a cyclic host molecule or moiety and a guest one whose size fits the cavity interior. β-Cyclodextrin is a cyclic oligomer of seven α-D-glucose units, and it has a cone-shaped architecture with an internal cavity

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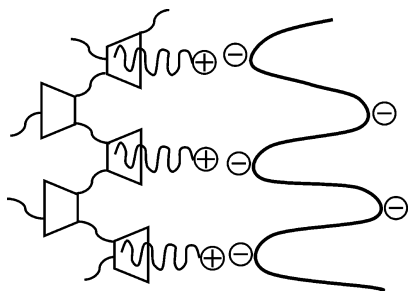*J. Phys. Chem. B, Vol. 108, No. 50, 2004* **19219**

Figure 1. Principle of ternary association between a β-cyclodextrin polymer (left), a cationic surfactant (middle), and a polyanion (right).

diameter of about 7 Å.[12] Because of the nonpolar character of this cavity, β-cyclodextrin shows a good affinity for alkyl groups possessing more than 10 carbons,[13] such as in DTAC. Figure 1 is a scheme of the ternary association. In comparison to the classical PECs based on electrostatic interactions alone, this new model of complex presents an enhanced versatility since the ratio of positive charges is easily controlled by adjusting the surfactant concentration in the mixture. Also, it presents an increased reversibility since the decomplexation of the ternary system can be obtained either by adding salt (screening of the electrostatic interactions) or by adding a competitor with a hydrophobic moiety (dissociation of the β-CD/DTAC inclusion complexes). A previous study[11] has shown for the first time the occurrence of the ternary complexes using sodium salt dextran sulfate (NaDxS) as the polyanion. It has also shown that the DTAC concentration (N_{DTAC}) played a major role in the structural properties of the complex. A structural transition from diffuse aggregates at low N_{DTAC} to compact aggregates at higher concentration occurred at a critical DTAC concentration (N_{DTAC}^{crit}). This structural transition of the ternary complexes has been related to a change of the DTAC distribution along the poly(β-CD) chains in the binary complexes poly(β-CD)/DTAC: from an inhomogeneous distribution at low surfactant concentration, the DTAC being distributed along a spherical outer shell of the poly(β-CD), to a more homogeneous distribution beyond N_{DTAC}^{crit}. Some of the questions remaining unanswered from the previous study are related to the nature of the three components of the complex. Does the occurrence of the ternary complex only depend on the combination of electrostatic and inclusion complex interactions between them, independently of their nature or structure? Moreover, how the structural properties of the complex depend on the nature and rigidity of the two chains present? Despite the numerous studies available for polyelectrolyte complexes that are similar systems, this last problem has not yet been really addressed.

The aim of the present paper is to discuss the influence of the nature of the polyanion on the formation and structural properties of the ternary complex. Sodium salt polystyrene sulfonate (NaPSS) and sodium dextran sulfate (NaDxS), of linear and branched structure, respectively, are polyanions of increasing rigidity. Moreover, NaPSS has a hydrophobic backbone whereas the NaDxS one is hydrophilic. The ternary associations involving NaPSS are studied by viscometry and small-angle neutron scattering (SANS). The use of deuterated NaPSS (dNaPSS) and surfactant (dDTAB) allows determination of the partial structure factor of the poly(β-CD) in the ternary complex. The solubility differences and the structural properties of both types of aggregates (involving NaPSS or NaDxS) are related to the conformations of the polymers. The influence of the polyanion chain length is also discussed with two samples of NaDxS: $M_w = 10$ kg·mol^{-1} (NaDxS 1) and $M_w = 40$ kg·mol^{-1} (NaDxS 2).

Experimental Section

Materials. The polymer of β-cyclodextrin (poly(β-CD)), synthesized by polycondensation with epichlorohydrin, has a branched architecture. Details of its synthesis[14] and structural characterization[11] are described elsewhere. The molecular weight of the sample used in this study has been measured by size exclusion chromatography coupled with a light scattering detector and is 160 kg·mol^{-1}. Its β-CD content, determined by NMR, is 59% weight/weight.

The *n*-dodecyltrimethylammonium chloride (DTAC) was supplied by Acros Organics, Noisy-le-Grand, France. In this study, it has always been used under its critical micellar concentration which is about 2.0×10^{-2} mol·L^{-1} at 25 °C. A deuterated *n*-dodecyltrimethylammonium bromide (dDTAB) has been used in SANS measurements. Its synthesis has been described previously.[11]

The polyanion sodium salt polystyrene sulfonate (NaPSS) was supplied by Alfa Aesar, Karlsruhe, Germany. The sulfur content in NaPSS (determined by elemental analysis) is about 10%, which corresponds to a rate of sulfonation of about 80%. The NaPSS weight-average molecular weight is 70 kg·mol^{-1}. A deuterated polystyrene sulfonate (dNaPSS) with a molecular weight of 37 kg·mol^{-1}, kindly supplied by F. Cousin (LLB, Saclay, France), has been used in SANS measurements.

Two samples of sodium salt dextran sulfate (NaDxS) have been used in this study. A low molecular weight sample, NaDxS 1, was supplied by Sigma, Saint Quentin Fallavier, France. Its weight-average molecular weight is 10 kg·mol^{-1}. ICN Biomedicals, Aurora, OH, supplied a larger molecular weight sample, NaDxS 2, with a weight-average molecular weight of 40 kg·mol^{-1}. The sulfur content in NaDxS 1 and NaDxS 2 is about 17%, which corresponds to an average of two sulfate groups per glucose unit. In each sample, 5% approximately of the glucose units are branched and three glucose units on average are involved in a branching. For the NaDxS 1 chain which is composed of about 27 units, that corresponds to only one branching. Thus, the structure of this polymer can be considered as almost linear. On the other hand, for the NaDxS 2 chain which is composed of about 110 glucose units, that corresponds to an average of six branching. However, according to the suppliers, the ratio of branched units is slightly higher than 5% for NaDxS samples of increasing chain length. Thus, the mean number of branching for NaDxS 2 is most probably higher than 6.

Determination of Phase Diagrams. Ternary aqueous samples with an anionic group concentration in the range $(1-45) \times 10^{-3}$ mol·L^{-1}, a DTAC concentration of about $(2-12) \times 10^{-3}$ mol·L^{-1}, and a β-CD concentration in the range $(1-18) \times 10^{-3}$ mol·L^{-1} were thoroughly mixed and equilibrated for 48 h in a thermostated bath at 25 ± 0.5 °C before being observed. We checked that no evolution took place for at least 1 week after this period. Ultrapure water was used as solvent in all the experiments.

Viscometric Measurements. The viscosity measurements were performed with an Ubbelohde viscometer at 25 ± 0.5 °C in a thermostated bath. All the dilutions were directly performed into the viscometer by adding ultrapure water.

SANS Measurements. The SANS experiments were carried out with the PACE spectrometer at the Laboratoire Léon Brillouin (LLB), Saclay, France. The experimental q range was $3 \times 10^{-3} < q$ (Å^{-1}) $< 10^{-1}$, and all the samples were prepared in D$_2$O to maximize the contrast between the β-CD polymer ($\rho_{poly(\beta-CD)} = 2.29 \times 10^{10}$ cm^{-2}) and the solvent ($\rho_{D_2O} = 6.41 \times 10^{10}$ cm^{-2}). The scattering length densities of the hydroge-
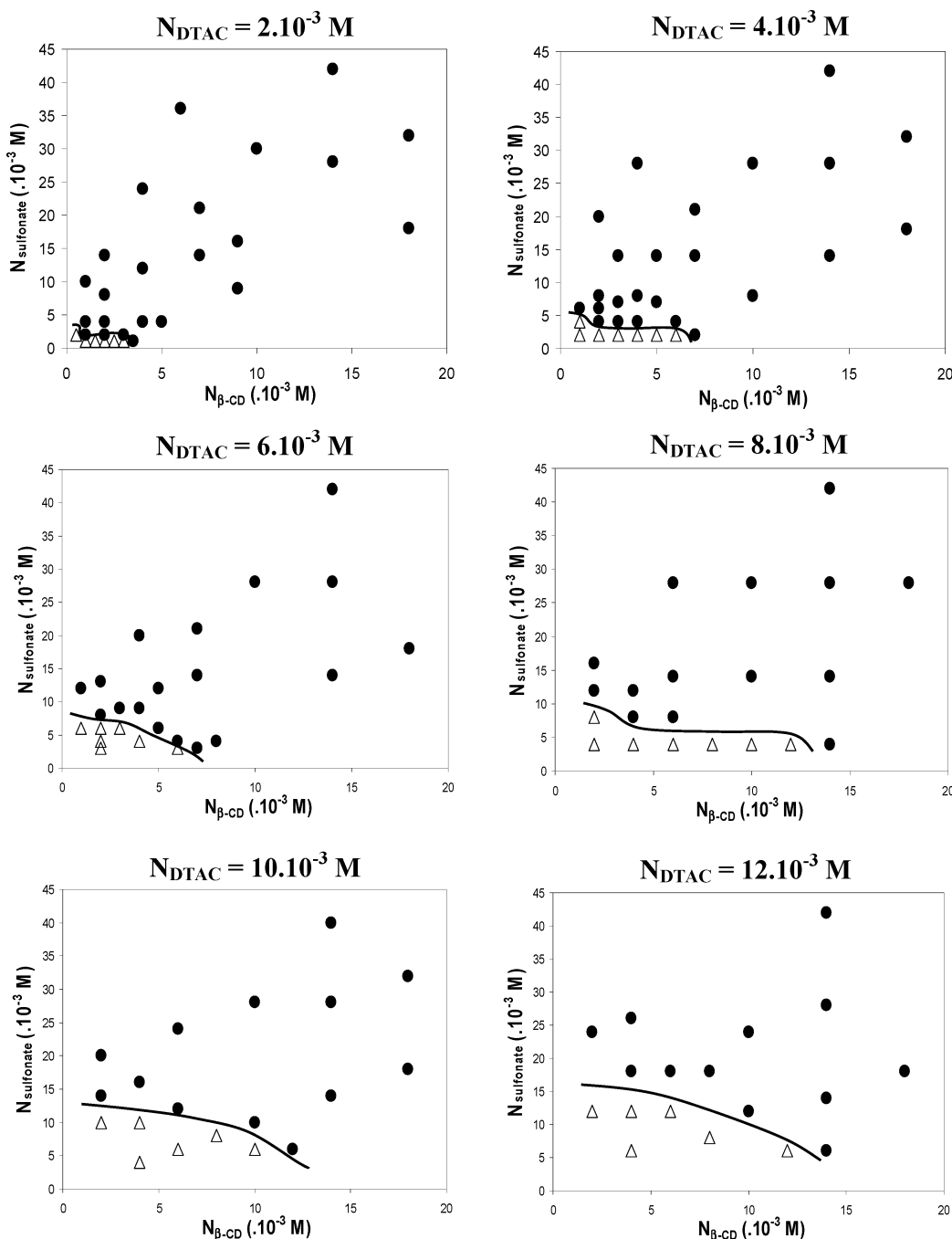
Figure 2. Phase diagrams for poly(β-CD)/DTAC/NaPSS ternary mixtures in water. Filled symbols ($\bullet$) refer to clear one-phase solutions, and open symbols ($\triangle$) refer to several-phase dispersions. The lines (solubility limits) are a guide for the eyes.

nated cationic surfactant, dextran sulfate, and polystyrene sulfonate are -0.43×10^{10}, $+1.75 \times 10^{10}$, and $+2.49 \times 10^{10}$ cm^{-2}, respectively (without the counterions). The deuterated surfactant and polystyrene sulfonate ones are 6.95×10^{10} and 6.48×10^{10} cm^{-2}, respectively, close to the scattering length density of the solvent.

Results and Discussion

Phase Diagrams. Different phase diagrams obtained by varying the poly(β-CD), DTAC, and NaPSS concentrations in ternary aqueous mixtures are presented in Figure 2. For increasing molar concentrations of DTAC, we observe a spreading of the several-phase domains toward high molar concentrations of both β-CD cavities and sulfonate groups of NaPSS. It may be due to the formation of poly(β-CD)/DTAC/

NaPSS ternary complexes of increasing hydrophobicity or dehydration: the higher the DTAC concentration, the more numerous the connections created between poly(β-CD) and NaPSS, impeding the polymeric chains from swelling in solution (i.e., to be hydrated) and leading to a precipitate. We note that the mixtures are soluble when the sulfonate groups are in excess compared to the surfactant, which has similarly been observed with binary aqueous mixtures of NaPSS and DTAC.[15] Conversely, mixtures with an excess of β-CD cavities compared to the DTAC are monophasic in all the sulfonate concentration range.

In comparison to the phase diagrams established in the previous work by using NaDxS 1 ($M_w = 10$ kg·mol^{-1}, Figure 3a), the domain of solubility of the ternary systems with NaPSS ($M_w = 70$ kg·mol^{-1}) is extended toward lower β-CD and anionic

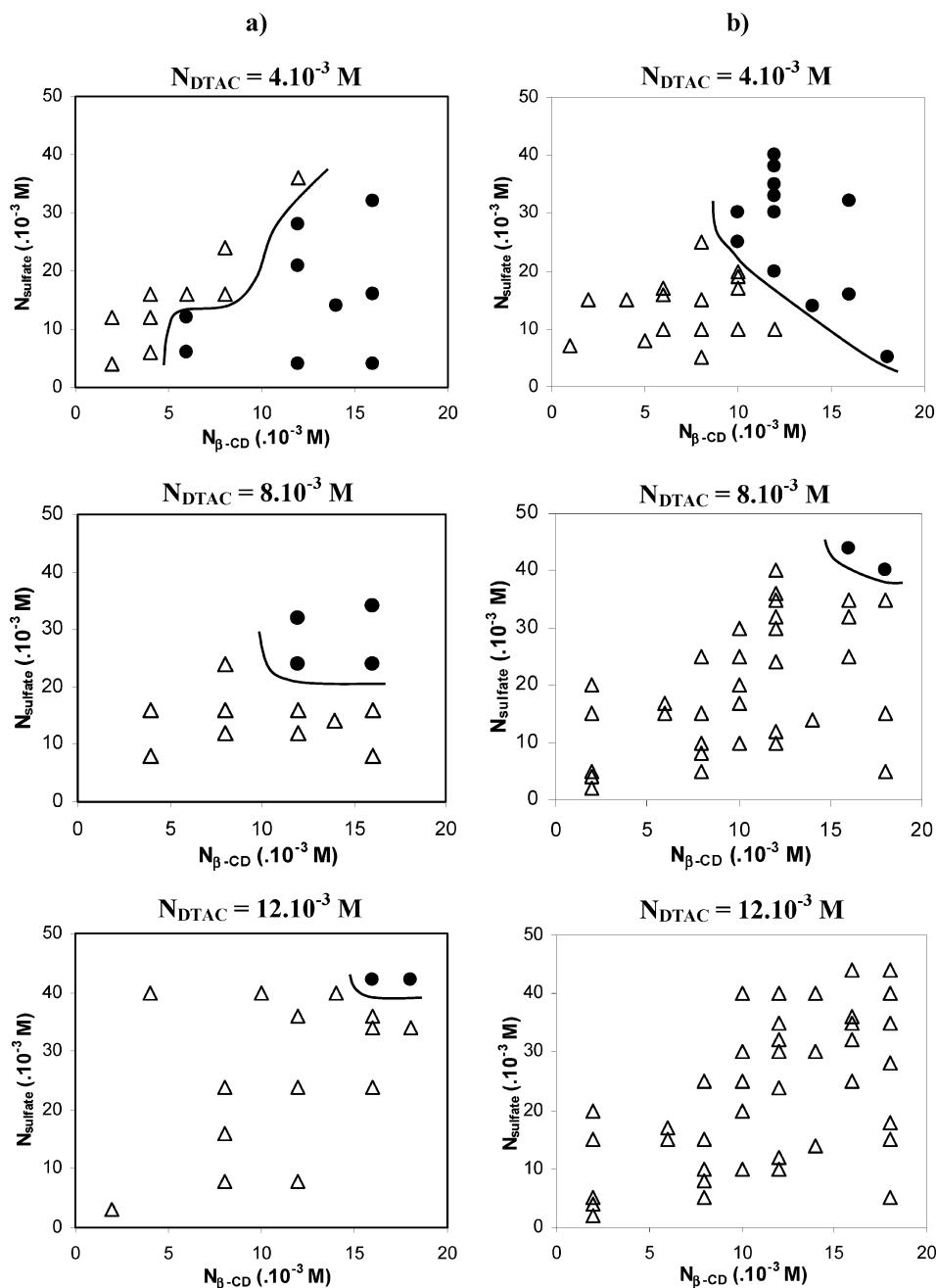Polyelectrolyte Complexes by Cyclodextrin Polymers

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Figure 3. Phase diagrams for poly(β-CD)/DTAC/NaDxS aqueous mixtures with different NaDxS molecular weights: (a) $M_w = 10$ kg·mol^{-1}; (b) $M_w = 40$ kg·mol^{-1}. Filled symbols ($\bullet$) refer to clear one-phase solutions, and open symbols ($\triangle$) refer to several-phase dispersions. The lines (solubility limits) are a guide for the eyes.

TABLE 1: Lower DTAC Concentrations at Which the Poly(β-CD)/DTAC/Polyanion Ternary Complexes Precipitate from Solutions, for $N_{\beta-CD} = N_{\text{anionic group}} = 14 \times 10^{-3}$ mol·L^{-1}

polyanion	NaPSS ($M_w = 70$ kg·mol^{-1})	NaDxS 1 ($M_w = 10$ kg·mol^{-1})	NaDxS 2 ($M_w = 40$ kg·mol^{-1})
N_{DTAC} (10^{-3} mol·L^{-1})	14	7	6

group concentrations at a given DTAC concentration. The solubility differences between the NaPSS and NaDxS 1 systems could be ascribed to the large difference of the polyanion chain lengths: the average polymerization index, N, is 340 for NaPSS and 27 for NaDxS 1. However, an opposite solubility trend is seen between the two NaDxS samples: the phase diagrams using NaDxS 2, of higher chain length ($M_w = 40$ kg·mol^{-1}, $N = 110$), show in Figure 3b a reduction of the solubility domains of the mixtures compared to the system with NaDxS 1. Thus, the NaDxS systems are less soluble for increased NaDxS chain lengths and for increased degrees of branching of the polyanions.

These solubility differences are illustrated in Table 1, which presents the lower DTAC concentrations at which the systems phase separate for fixed poly(β-CD) and polyanion concentrations ($N_{\beta-CD} = N_{\text{negative charges}} = 14 \times 10^{-3}$ mol·L^{-1}).

Viscometric Results. Viscometry has first been chosen to prove the formation of ternary complexes for a particular soluble mixture in water, containing before dilution with pure water poly(β-CD) with 14×10^{-3} mol·L^{-1} β-CD cavities, NaPSS with 14×10^{-3} mol·L^{-1} sulfonate groups, and 6×10^{-3} mol·L^{-1} surfactant. The reduced viscosities of different mixtures (two- and three-component solutions) with these maximal

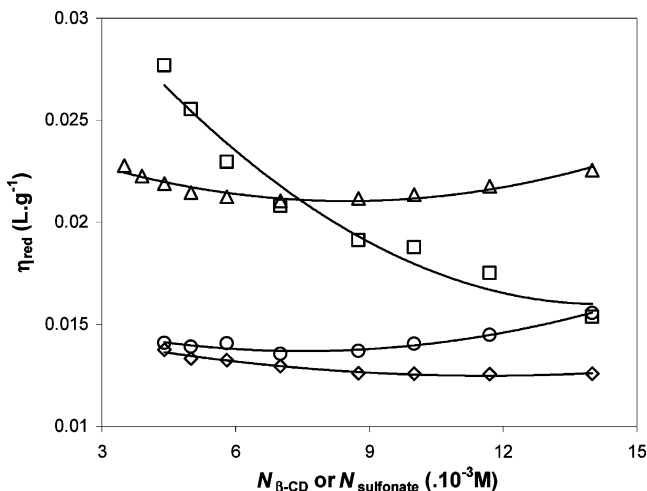**Figure 4.** Reduced viscosity vs $N_{\beta-CD}$ or $N_{sulfonate}$ plots of poly(β-CD)/DTAC ($\diamond$), poly(β-CD)/NaPSS ($\triangle$), NaPSS/DTAC ($\square$), and poly-(β-CD)/DTAC/NaPSS ($\bigcirc$) mixtures in water, where maximal concentrations of both β-CD cavities and sulfonate groups are 14×10^{-3} mol·L^{-1} and the maximal concentration of surfactant is 6×10^{-3} mol·L^{-1}.

concentration values are shown in Figure 4 as a function of the β-CD concentration (or the sulfonate group concentration for the NaPSS/DTAC binary solution).

It is seen from Figure 4 that the reduced viscosity of both poly(β-CD)/DTAC and NaPSS/DTAC two-component solutions increases with dilution, which is typical of polyelectrolyte behavior. Thus, addition of DTAC to the neutral poly(β-CD) results in the formation of a polycation, as a consequence of the inclusion complex interactions between the alkyl chains of the DTAC molecules and the β-CD cavities. A complexation constant $K \approx 20\,000$ L·mol^{-1} DTAC with β-CD monomers is reported in the literature.[13] When poly(β-CD) is used instead of β-CD monomer, the affinity of the polymer for the surfactant depends on the charge ratio of the chain. At low $N_{DTAC}/N_{\beta-CD}$ ratio, the affinity is comparable to the one determined with β-CD monomer, whereas the affinity decreases by a factor of about 10 when the $N_{DTAC}/N_{\beta-CD}$ ratio is greater than 0.5. The positive charges already present on the poly(β-CD)−DTAC chain exert electrostatic repulsions toward free DTAC in solution and consequently reduce their affinity to the chain. However, the apparent complexation constant determined at $N_{DTAC}/N_{\beta-CD}$ close to 1, $K = 1500$ L·mol^{-1}, is large enough to ensure that more than 95% of the surfactant molecules are complexed in the CD cavities, under the conditions of the experiments described in this paper ($N_{\beta-CD}$ varying in the range 3×10^{-3}−14×10^{-3} mol·L^{-1}).[11]

Addition of DTAC to NaPSS in the 6/14 stoichiometry does not lead to a charge neutralization of the NaPSS chains. Indeed, these latter, associated with DTAC, still behave like polyelectrolyte chains although in a more compact conformation than in the free case: the reduced viscosities are 3−4 times less than those for free NaPSS. In the previous work,[11] the mixture of DTAC and NaDxS (of hydrophilic backbone) in the same 6/14 stoichiometry led to a precipitate without poly(β-CD). It was due to a cooperative effect resulting from the mutual action of electrostatic binding of DTAC on the NaDxS chains and hydrophobic interactions between the alkyl chains of the bound DTAC molecules, respectively.[15] Large micelles of DTAB (dodecyltrimethylammonium bromide) with aggregation numbers of ca. 107 were formed by interaction with NaDxS[16] (the aggregation numbers were found to be independent of the type of counterion[17]). NaPSS has been found to interact more strongly

with the surfactant than NaDxS; however, the association is less cooperative, as illustrated by a lower value of the aggregation number (38 for DTAB).[18] Moreover, the NaPSS/DTAC aqueous mixtures are monophasic as long as NaPSS is in excess. Both lower rigidity and increased hydrophobicity of the NaPSS backbone are at the origin of these behavior differences. Units of the NaPSS (benzene rings) should be incorporated at the micelle surface and, thus, induce a close contact between the charges of the surfactant and the polyelectrolyte ones, reducing the electrostatic internal energy.[19] The sharp viscosity decrease upon addition of the surfactant on NaPSS has also been observed by Abuin and Scaiano,[20] using DTAB instead of DTAC. It was attributed to a coiling of the chain that accompanies the cooperative binding of the surfactant.

For the poly(β-CD)/NaPSS binary solution, we notice in Figure 4 that polyelectrolyte behavior can only be observed at high dilution. Furthermore, it can be shown that the viscosity values are always higher than those predicted by eq 1 for a mixture of noninteracting neutral and charged polymers:[21]

$$(\eta_{red})_{mixture} = w_A\left(\frac{[\eta]_A}{1 + B_A C_A^{1/2}}\right) + w_B([\eta]_B + b_B C_B) \quad (1)$$

where B_A and b_B are the viscometric interaction parameters of the charged polymer A and the neutral one B, respectively, w_A and w_B are their weight percentages in the mixture, $[\eta]_A$ and $[\eta]_B$ are their intrinsic viscosities, and C_A and C_B are their concentrations in grams per liter. Measurements of the reduced viscosity of the neutral poly(β-CD) and charged NaPSS separately in water (not shown), and their respective plots fitted through the Huggins equation (for neutral polymer solutions)

$$\eta_{red} = [\eta]_{poly(\beta-CD)} + b_B C_{poly(\beta-CD)} \quad (2)$$

and the Füoss equation (for polyelectrolyte solutions)

$$\eta_{red}{}^{-1} = [\eta]_{NaPSS}{}^{-1} + B_A[\eta]_{NaPSS}{}^{-1} C_{NaPSS}{}^{1/2} \quad (3)$$

respectively, have led to the calculations of the viscometric parameters: $[\eta]_{poly(\beta-CD)} = 6.3 \times 10^{-3}$ L·g^{-1}, $b_B = 6.0 \times 10^{-5}$ (L·g^{-1})^2, and $[\eta]_{NaPSS} = 325.6 \times 10^{-3}$ L·g^{-1}, $B_A = 218.3 \times 10^{-2}$ (L·g^{-1})$^{1/2}$. The weight percentages of polymers in the mixture are $w_{poly(\beta-CD)} = 0.86$ and $w_{NaPSS} = 0.14$, respectively. The fact that the experimental values do not follow the theoretical behavior of the mixture (well out of the error bars) indicates the existence of an interaction between the poly(β-CD) and NaPSS which reduces the stretching of the charged chains. This interaction has been clearly shown by quartz crystal microbalance measurements.[22] Indeed, styrene groups are known to have a small affinity for the β-CD cavities.[23] Inclusion complexes between the residual nonsulfonated groups of NaPSS and poly(β-CD) could be at the origin of the interaction between both polymers.

When DTAC is added to the poly(β-CD)/NaPSS/water mixture, a significant decrease of the viscosity values is observed in Figure 4, meaning a compaction of the chains (screening of the electrostatic interactions). This suggests the formation of a ternary complex, first by NaPSS/DTAC interactions which lead to a compaction of the NaPSS chains, and second by interactions between the poly(β-CD) and NaPSS/DTAC complex which reduce extensively the polyelectrolyte behavior of the latter. We notice that the weak increase of viscosity observed at high dilution for the three-component solution could be ascribed to a charge effect, assuming that the aggregates bear an overall nonzero charge. One should note that pure NaPSS/DTAC
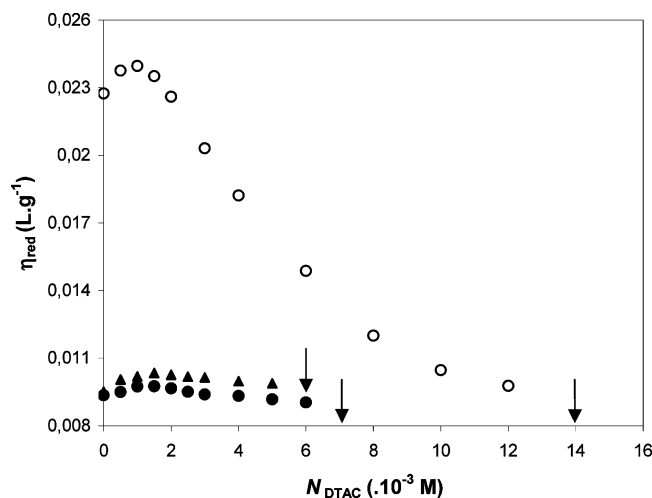
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Figure 5. Influence of molar concentration of DTAC on reduced viscosity of poly(β-CD)/DTAC/NaPSS ($\bigcirc$) and poly(β-CD)/DTAC/NaDxS (NaDxS 1, $\bullet$; NaDxS 2, $\blacktriangle$) ternary mixtures in water, where molar concentrations of both β-CD cavities and anionic groups (sulfonate and sulfate) are 14×10^{-3} mol·L^{-1}. The arrows indicate the DTAC concentrations at which the systems phase separate.

Figure 6. SANS from poly(β-CD)/DTAC/D$_2$O ($\diamond$), poly(β-CD)/NaPSS/D$_2$O ($\triangle$), NaPSS/DTAC/D$_2$O ($\square$), and poly(β-CD)/DTAC/NaPSS/D$_2$O ($\bigcirc$) mixtures ($N_{\beta-CD} = N_{\text{sulfonate}} = 14 \times 10^{-3}$ mol·L^{-1}, $N_{\text{DTAC}} = 6 \times 10^{-3}$ mol·L^{-1}).

complexes involve both electrostatic interactions between the polymer and surfactant charges and hydrophobic interactions responsible for the formation of micellar aggregates along the polymer chains. This leads to a cooperative binding between NaPSS and DTAC which occurs at DTAC concentrations much lower than the critical micelle concentration. A ternary complex of poly(β-CD)/DTAC/NaPSS should imply the dissociation of some hydrophobic microdomains of DTAC to make inclusion between the alkyl tails and the CD cavities. The question is whether the NaPSS/DTAC binary complexes are more or less stable than the poly(β-CD)/DTAC/NaPSS ternary ones. Conductimetry experiments conducted with DTAB and β-CD monomers prove that the inclusion of the alkyl tails into the CD cavities are favored compared to the hydrophobic autoassociation of the alkyl tails, as shown by the reported critical micelle concentration increases which are comparable to the β-CD molar concentration.[24] This gives an argument in favor of a stability of the ternary complexes involving both electrostatic and inclusion complex interactions larger than the stability of the NaPSS/DTAC binary complexes (electrostatic and hydrophobic interactions). The formation of poly(β-CD)/DTAC/NaPSS ternary complexes is strongly supported by the large viscosity reduction upon addition of poly(β-CD) to NaPSS/DTAC and, as will be shown in the following section, by the large increase of the neutron scattering intensities.

We present in Figure 5 the influence of the molar concentration of surfactant on the reduced viscosity of poly(β-CD)/DTAC/NaPSS three-component solutions ($N_{\beta-CD} = N_{\text{sulfonate}} = 14 \times 10^{-3}$ mol·L^{-1}). A behavior comparable to those of ternary systems involving NaDxS can be observed.[11] For N_{DTAC} less than 10^{-3} mol·L^{-1}, the reduced viscosity increases with the amount of surfactant, suggesting the formation of diffuse aggregates. For N_{DTAC} greater than 10^{-3} mol·L^{-1}, the viscosity values decrease as the DTAC concentration increases, indicating the formation of denser and denser aggregates up to their precipitation.

Though ternary solutions involving NaDxS and NaPSS present comparable viscosity behavior toward the amount of incorporated DTAC, two main differences can be observed. First, compaction of chains by addition of DTAC appears more pronounced for the NaPSS systems that show the greatest variations of viscosity values. Then, systems with NaPSS are
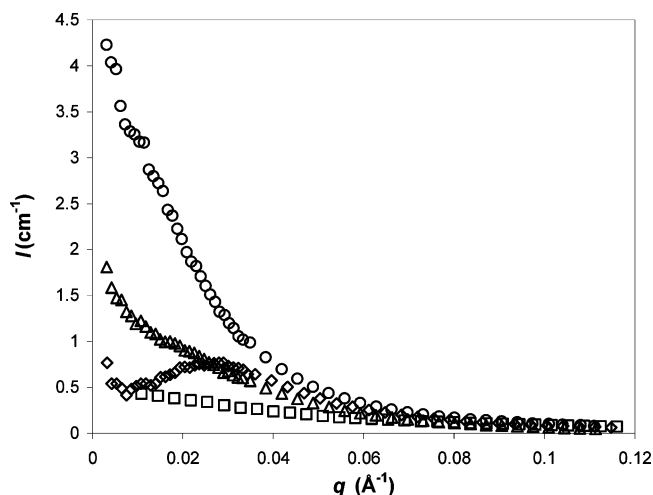
soluble to higher DTAC concentrations than those with NaDxS. Indeed, clear solutions with NaPSS ($N_{\text{sulfonate}} = 14 \times 10^{-3}$ mol·L^{-1}) are obtained until $N_{\text{DTAC}} = 14 \times 10^{-3}$ mol·L^{-1}, where a precipitate is observed, while ternary complexes involving NaDxS ($N_{\text{sulfate}} = 14 \times 10^{-3}$ mol·L^{-1}) start to be insoluble at $N_{\text{DTAC}} = 7 \times 10^{-3}$ mol·L^{-1} (for NaDxS 1). These compaction and solubility differences can be related to the different charge densities or the different rigidities of the polyanions. NaPSS presents an average of 0.8 negative charge per monomer unit (2.5 Å), while NaDxS has about 2 negative charges per glucose unit (5 Å). Thus, for a given DTAC/anionic group molar ratio, complexation may involve 2 times more monomer units in the NaPSS case than in the NaDxS one. This higher solicitation of the NaPSS chains could explain the higher compaction effect they undergo. Also, the NaDxS chains, being more constrained (branched structure), can be less prone to sharp conformational changes.

SANS Results. The scattering intensities from two- and three-component solutions with 14×10^{-3} mol·L^{-1} β-CD cavities and sulfonate groups and 6×10^{-3} mol·L^{-1} cationic surfactant are shown in Figure 6.

For the poly(β-CD)/DTAC/D$_2$O system, a marked peak in the scattering is observed at $q^* = 2.5 \times 10^{-2}$ Å^{-1}, which is typical of polyelectrolyte behavior. This confirms the viscometric results: a polycation is formed by inclusion complex interactions between the surfactant molecules and the β-CD cavities of the polymer.

The NaPSS/DTAC/D$_2$O mixture presents low values of scattering intensity. This can be ascribed to the low weight concentrations of both components, $N_{\text{DTAC}} = 6 \times 10^{-3}$ mol·L^{-1} and $N_{\text{sulfonate}} = 14 \times 10^{-3}$ mol·L^{-1}, corresponding to $C_{\text{DTAC}} = 1.6$ g·L^{-1} and $C_{\text{NaPSS}} = 4.5$ g·L^{-1}, respectively (when $N_{\beta-CD} = 14 \times 10^{-3}$ mol·L^{-1} corresponds to $C_{\text{poly}(\beta-CD)} = 26.8$ g·L^{-1}). Nevertheless, NaPSS is at a high enough concentration to contribute to the signal of the poly(β-CD)/NaPSS/D$_2$O mixture in a weak correlation peak; the hump observed around $q^* = 2 \times 10^{-2}$ Å^{-1} can indeed be eliminated by adding salt (not shown).

When the three compounds are mixed together in D$_2$O, a significant increase in the scattering intensity values is observed compared to the poly(β-CD)/DTAC/D$_2$O, NaPSS/DTAC/D$_2$O, and poly(β-CD)/NaPSS/D$_2$O mixtures, indicating the formation of large aggregates. We notice that a hump can be observed
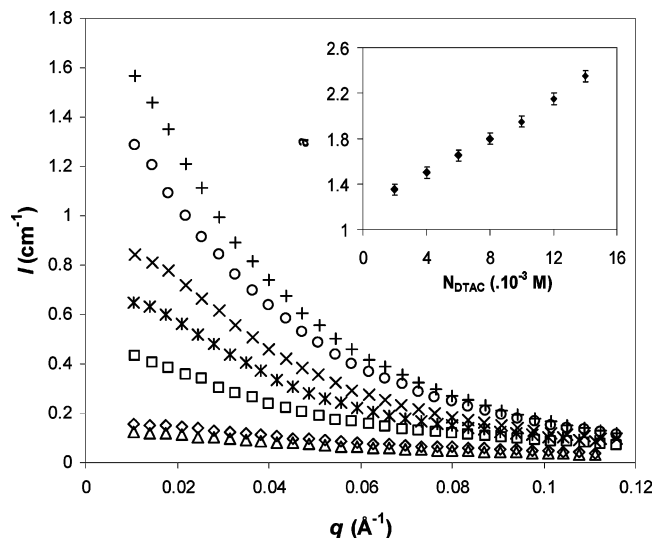
Figure 7. Influence of molar concentration of DTAC cationic surfactant on SANS from NaPSS/DTAC/D$_2$O mixtures, where the molar concentration of sulfonate groups is 14×10^{-3} mol·L^{-1}. The DTAC concentrations are ($\triangle$) 2×10^{-3}, ($\diamond$) 4×10^{-3}, ($\square$) 6×10^{-3}, (*) 8×10^{-3}, ($\times$) 10×10^{-3}, ($\bigcirc$) 12×10^{-3}, and (+) 14×10^{-3} M. Insert: a exponents determined from the q^{-a} variation of the intensity at large q as a function of the DTAC concentration.

Figure 8. Influence of molar concentration of DTAC cationic surfactant on SANS from poly(β-CD)/DTAC/NaPSS/D$_2$O mixtures, where molar concentrations of both β-CD cavities and sulfonate groups are 14×10^{-3} mol·L^{-1}. The DTAC concentrations are ($\triangle$) 0.5×10^{-3}, ($\times$) 2×10^{-3}, ($\bigcirc$) 6×10^{-3}, ($\diamond$) 10×10^{-3}, and ($\square$) 14×10^{-3} M. Insert: a_{app} exponents determined from the $q^{-a_{\text{app}}}$ variation of the intensity at large q as a function of the DTAC concentration. Filled symbols ($\blacklozenge$) refer to measurements with hydrogenated DTAC and NaPSS, and open symbols ($\bigcirc$) refer to measurements with dDTAB and dNaPSS.

around $q^* = 10^{-2}$ Å^{-1}, which could be the contribution of a charge effect to the overall signal. Indeed, this hump disappears by increasing the salt concentration (not shown). Therefore, the combination of SANS and viscometry shows the formation of aggregates of large size, with a dense overall structure and probably a charge activity, by mixing poly(β-CD), DTAC, and NaPSS in aqueous solution in a 14/6/14 molar ratio.

The influence of the DTAC concentration on the scattering intensity from soluble NaPSS/DTAC binary mixtures in D$_2$O ($N_{\text{sulfonate}} = 14 \times 10^{-3}$ M) is shown in Figure 7. As the DTAC concentration increases, the intensity values increase partly because the charge of the complexes is progressively reduced (complexation by opposite charges between NaPSS and DTAC), and partly because the DTAC micelles linked to the polymer contribute to the scattering. The intensities at high q values can be represented by a power law $I(q) \sim q^{-a}$, where a characterizes the compactness of the scatterers: the more compact the scattering bodies, the higher the a value.[25] The insert of Figure 7 presents the a coefficients measured at high q values for the NaPSS/DTAC binary complexes. We note that the scattering intensities observed for pure NaPSS were too low to precisely measure a. It is seen from Figure 7 that the a values at low DTAC concentration are close to 1, as can be expected from the diffusion of rods. Then the a coefficient increases almost linearly up to 2.4 at $N_{\text{DTAC}} = 14 \times 10^{-3}$ M. It should be noted that this variation cannot be attributed solely to the presence of dense micellar structures because their radius, assuming an aggregation number of 38 and a spherical structure, should be on the order of 6 Å (the length scales investigated at high q values are 30−60 Å). These results are in agreement with the usual picture of the compaction of the NaPSS chains as the DTAC concentration is increased, due to a coiling around an increasing number of DTAC micelles.

The addition of increasing amounts of DTAC to poly(β-CD)/DTAC/NaPSS ternary mixtures in D$_2$O ($N_{\beta-\text{CD}} = N_{\text{sulfonate}} = 14 \times 10^{-3}$ M) produces high intensity increases, as shown in Figure 8. The scattered intensities are much higher than those observed for each of the poly(β-CD)/DTAC[11] and NaPSS/DTAC binary complexes. Thus, the results cannot be attributed
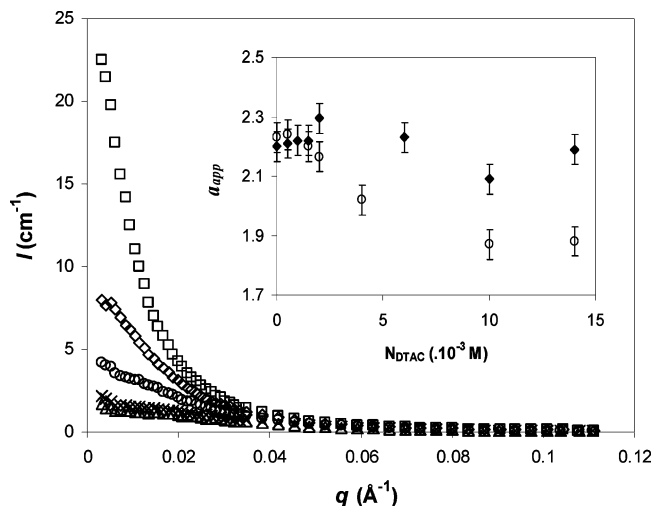
to the scattering from a mixture of binary aggregates but involve the formation of ternary complexes in the whole range of DTAC concentrations studied. The a exponents characterizing the high q power laws of these ternary mixtures in D$_2$O have been reported as a function of the DTAC concentration in the insert of Figure 8. When the different components of the mixtures are homogeneously distributed in the aggregates, the a exponent is a measure of their fractal dimension. By contrast, aggregates with an inhomogeneous distribution (core−shell structures, for instance) display an apparent power law that results from a combination of those due to the scattering from each microdomain. It is seen from Figure 8 that the apparent exponent, a_{app}, does not vary with N_{DTAC} and keeps a value comparable to the one of pure poly(β-CD): $\sim$2.2 (the a exponent of pure poly(β-CD) is 2.25 ± 0.05).[11]

To get some insight into the aggregate internal structures, the structure factor of the poly(β-CD) in the ternary complexes has been determined by using contrast matching conditions: deuterated dodecyltrimethylammonium (dDTAB) and NaPSS (dNaPSS) have been added to the poly(β-CD) in D$_2$O. Figure 9 shows, for instance, a comparison between the pure poly(β-CD) structure factor and the two ternary system (hydrogenated and deuterated) scattered intensities for $N_{\text{surfactant}} = 6 \times 10^{-3}$ M ($N_{\beta-\text{CD}} = N_{\text{sulfonate}} = 14 \times 10^{-3}$ M). In the deuterated case, lower intensities comparable to those measured for the pure solution of poly(β-CD) are obtained, suggesting that the ternary complexes involve only one poly(β-CD) chain at these surfactant and poly(β-CD) concentrations. The a exponents, deduced from the power law at high q, are reported in Figure 8 as a function of the dDTAB concentration. As observed for the poly(β-CD)/dDTAB binary complexes,[11] there is a critical surfactant concentration ($N_{\text{dDTAB}} \sim 2 \times 10^{-3}$ M) corresponding to a change in compactness of the poly(β-CD) chains. At low N_{dDTAB}, a is constant and close to 2.25, the value measured for pure poly-(β-CD). For N_{dDTAB} greater than 2×10^{-3} M, a decreases to values close to 1.9. This suggests that the poly(β-CD) chains are less and less compact as the surfactant concentration is increased. This behavior is not easy to understand from a simple picture of the association mechanism where the poly(β-CD) and
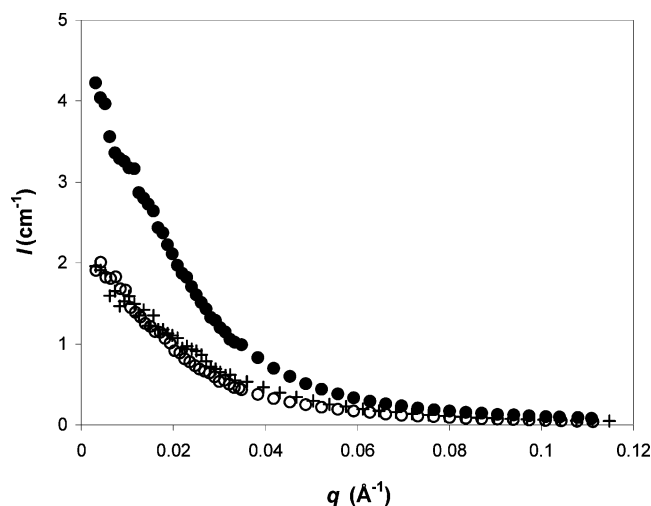
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Figure 9. SANS from poly(β-CD)/cationic surfactant/NaPSS/D$_2$O mixtures ($N_{\beta-CD} = N_{sulfonate} = 14 \times 10^{-3}$ mol·L^{-1}, $N_{surfactant} = 6 \times 10^{-3}$ mol·L^{-1}), with hydrogenated (●) and deuterated (○) surfactant and NaPSS. Symbols (+) refer to SANS from the poly(β-CD)/D$_2$O mixture ($N_{\beta-CD} = 14 \times 10^{-3}$ mol·L^{-1}).
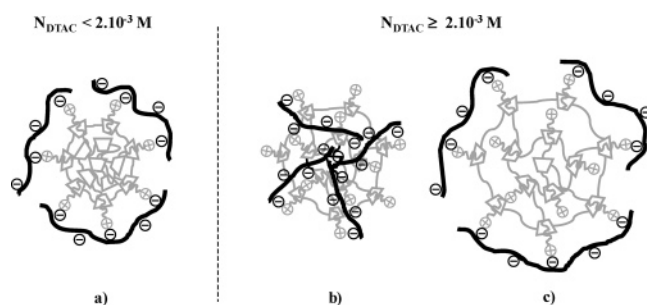

Figure 10. Scheme of internal structure of poly(β-CD)/surfactant/polyanion ternary complexes ($N_{\beta-CD} = N_{anionic\ group} = 14 \times 10^{-3}$ mol·L^{-1}), depending on DTAC concentration and polyanionic component: (a) $N_{DTAC} < 2 \times 10^{-3}$ mol·L^{-1}, whatever the polyanion; (b) $N_{DTAC} \geq 2 \times 10^{-3}$ mol·L^{-1}, with NaDxS 1; (c) $N_{DTAC} \geq 2 \times 10^{-3}$ mol·L^{-1}, with NaDxS 2 and NaPSS.

NaPSS are increasing their interconnections as the number of DTAC molecules is increased, implying an intimate mix between them and a compaction of the structures. On the contrary, the swelling observed for the poly(β-CD) chains in the ternary mixture is comparable to the one obtained for the poly(β-CD) chains in the poly(β-CD)/dDTAB complexes in the same dDTAB concentration range.[11] In the latter case, the swelling was attributed to the homogeneous distribution of the surfactant charges along the polymer chains. Similarly, the only way to explain the swelling of the poly(β-CD) in the poly(β-CD)/surfactant/NaPSS ternary system is to assume the presence of nonneutralized surfactant charges inside the poly(β-CD) branched structure. This leads to a new picture of the inner structure of the aggregates which should be of the core–shell type: a core constituted of poly(β-CD) and surfactant; a shell constituted of NaPSS interacting with the surface of the core via anionic site/cationic surfactant/CD cavity ternary complexation (Figure 10c). Indeed, it is reasonable to assume that the dNaPSS chains are too large to penetrate deeply into the branched structure of the poly(β-CD) chains: the radius of gyration of dNaPSS in θ solvent (high salt concentration) is on the order of 35 Å, about 2/3 the radius of gyration of pure poly-(β-CD) (55 Å).

The range of investigation of the DTAC concentration is reduced in the case of the poly(β-CD)/DTAC/NaDxS 2 ternary mixtures in D$_2$O ($N_{\beta-CD} = N_{sulfate} = 14 \times 10^{-3}$ mol·L^{-1}), due to the
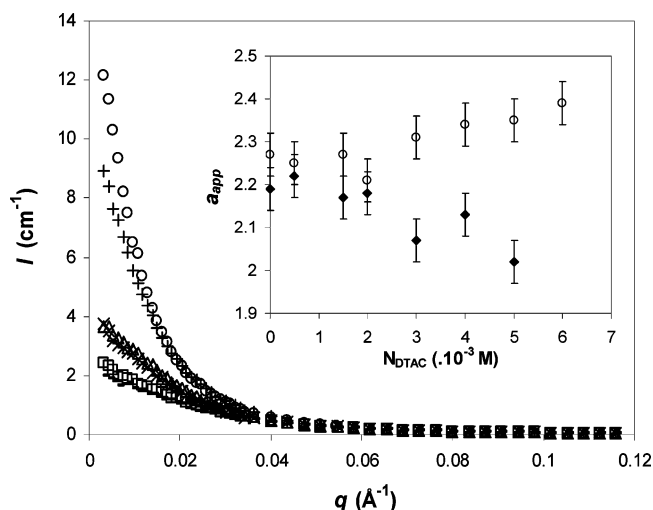

Figure 11. Influence of molar concentration of DTAC cationic surfactant on SANS from poly(β-CD)/DTAC/NaDxS2/D$_2$O mixtures, where molar concentrations of both β-CD cavities and sulfate groups are 14×10^{-3} mol·L^{-1}. The DTAC concentrations are (−) 0, (□) 0.5 $\times 10^{-3}$, (×) 1.5×10^{-3}, (△) 2×10^{-3}, (+) 4×10^{-3}, and (○) 5×10^{-3} M. Insert: a_{app} exponents determined from the $q^{-a_{app}}$ variation of the intensity at large q as a function of the DTAC concentration. Open symbols refer to measurements with NaDxS 1, and filled symbols refer to measurements with NaDxS 2.

low precipitation limit ($N_{DTAC} = 6 \times 10^{-3}$ M). The corresponding scattered intensities shown in Figure 11 increase upon addition of increasing amounts of DTAC, similar to the behavior observed with the NaDxS 1 ternary systems[11] or the NaPSS ones (Figure 9). The apparent a_{app} exponents deduced from the high q behavior are presented in the insert of Figure 11. As observed for the dNaPSS systems, a_{app} is almost constant below $N_{DTAC} = 2 \times 10^{-3}$ M, equal to 2.2, i.e., close to the a exponent of pure poly(β-CD). Then a_{app} decreases to values close to 2 at higher DTAC concentrations. The a_{app} values obtained in the previous work with NaDxS 1 are also reported in Figure 11. In this case, a_{app} is also constant below $N_{DTAC} = 2 \times 10^{-3}$ M, close to 2.25, but an opposite trend is observed at higher DTAC concentrations: a_{app} increases to 2.4. This behavior has been related to the DTAC charge distribution in the CD cavities. At low DTAC concentration, the surfactant molecules are only located on the outer corona of the quite dense poly(β-CD) structure and the NaDxS 1 chains interact with the poly(β-CD) only via this corona. The resulting core–shell structure (Figure 10a) does not involve any compaction of the core, or of the shell. At N_{DTAC} greater than 2×10^{-3} M, the surfactant molecules are distributed homogeneously along the poly(β-CD) chains. The increase of a_{app} results from an intimate mix of the three components and a compaction of the structures (Figure 10b). This compaction implies that the NaDxS 1 chains can penetrate into the poly(β-CD) branched structure: the estimated radius of gyration of NaDxS 1 in θ solvent is close to 20 Å, lower than the poly(β-CD) radius of gyration (55 Å). In the case of NaDxS 2 (of larger molecular weight), the lower and decreasing a_{app} values observed for N_{DTAC} greater than 2×10^{-3} M indicate a swelling of the inner structure of the aggregates. That suggests that these have still a core–shell structure in this N_{DTAC} range, as discussed for the NaPSS systems. Indeed, the NaDxS 2 chains can be too large to penetrate into the core of poly(β-CD) since the estimated radius of gyration of NaDxS 2 in θ solvent is close to 40 Å.

In summary, association of dextran sulfate or polystyrene sulfonate to poly(β-CD)/DTAC complexes gives aggregates with a core–shell internal structure at DTAC concentrations less than
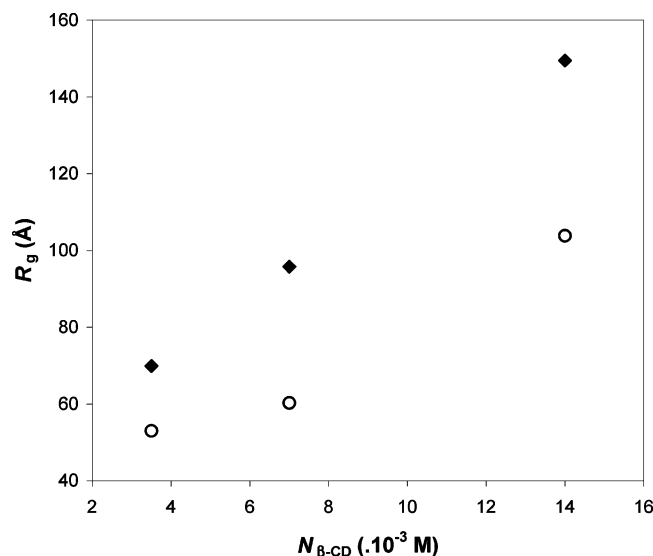
Figure 12. Influence of dilution on apparent R_g estimated for poly-(β-CD)/DTAC/NaDxS ternary systems in D$_2$O, with $N_{\beta-CD} = N_{sulfate}$ $= 14 \times 10^{-3}$ mol·L^{-1} and $N_{DTAC} = 6 \times 10^{-3}$ mol·L^{-1} as maximal concentrations. Open symbols refer to measurements with NaDxS 1, and filled symbols refer to measurements with NaDxS 2.

Figure 13. Scheme of different mechanisms of charge neutralization during the process of poly(β-CD)/cationic surfactant/polyanion ternary association: (a) with a rigid polyanion such as NaDxS 1 or NaDxS 2; (b) with a flexible polyanion such as NaPSS.

2×10^{-3} M. At larger DTAC concentrations, the inner structure of the aggregates is largely influenced by the molecular weight and architecture of the anionic polymer, depending on its ability to penetrate into the branched structure of the poly(β-CD). Compact entangled structures are obtained for NaDxS 1 (M_w $= 10$ kg·mol^{-1}), while core–shell structures could be at the origin of the behavior observed for NaPSS ($M_w = 70$ kg·mol^{-1}) and NaDxS 2 ($M_w = 40$ kg·mol^{-1}).

Thus, analysis of the high q behavior of the scattering allows the understanding of the inner aggregate organization. Conversely, the low q behavior can be used to determine the molecular weight and the apparent radius of gyration of noninteracting aggregates. The apparent radius of gyration of the formed aggregates can be estimated by using the Guinier equation at small q values:

$$\ln I(q) = \ln I_0 - q^2 R_g^2/3 \tag{4}$$

Figures 8 and 9 show that poly(β-CD)/DTAC/NaPSS systems are interacting via repulsive interactions, as characterized by the hump present on the I versus q curves. The overall charges of these aggregates are probably nonzero; thus the Guinier analysis cannot be applied to these systems. On the contrary, the intensity decreases monotonically as a function of q for the poly(β-CD)/DTAC/NaDxS systems, which apparently behave as neutral particles. The apparent R_g values estimated for the poly(β-CD)/DTAC/NaDxS 2 ternary complexes at the 14/5/14 stoichiometry are reported in Figure 12 as a function of the poly(β-CD) concentration. The influence of the dilution on the apparent R_g of the ternary complexes involving NaDxS 1 at the 14/6/14 stoichiometry is presented in the same figure for comparison. It appears that the aggregates involving NaDxS 2 show a behavior comparable to that of the poly(β-CD)/DTAC/ NaDxS 1 complexes: their apparent sizes decrease with dilution. The low q intensities (I_0) have also been determined using eq 4. I_0/C_{total}, where C_{total} is the total concentration (in grams per liter), should vary proportionally to the apparent molecular weight of the aggregates (M_w)$_{app}$. In both cases (NaDxS 1 and NaDxS 2 systems), I_0/C_{total} decreases by factors greater than 2 for dilutions of 4. Thus, the apparent molecular weight of the
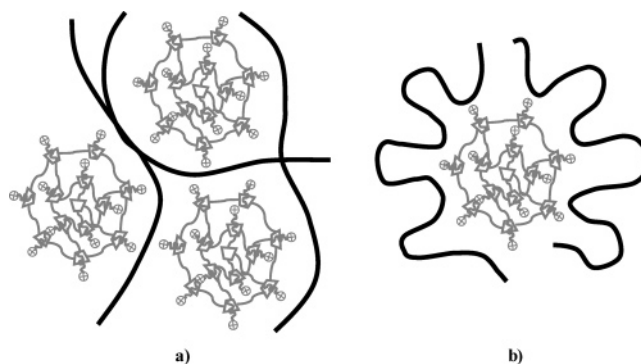
aggregates decreases with dilution, correlatively with the decrease of their apparent R_g. The dilution could either dissociate the complexes or decrease the number of components in the aggregates, keeping the same stoichiometry between them. Even for the lower concentration ($N_{\beta-CD} = 3.5 \times 10^{-3}$ M), the scattered intensity at low q is more than 2 times greater than the one of pure poly(β-CD) (not shown), suggesting that aggregates are formed in the whole studied concentration range. Thus, the apparent sizes of the NaDxS systems decrease with dilution as a consequence of the reduction of the quantity of poly(β-CD) chains in the mixture. This suggests that both systems (with NaDxS 1 and NaDxS 2) have comparable molecular arrangements at the studied stoichiometries (higher solubilization limits): both contain more than one poly(β-CD) chain. Conversely, the poly(β-CD)/DTAC/NaPSS complexes at the same 14/6/14 stoichiometry as the NaDxS 1 system obviously contain only one poly(β-CD) chain per aggregate, as shown in Figure 9 from the comparison of the poly(β-CD) scattered intensities in the complex (with dNaPSS and dDTAB) and in pure poly(β-CD) solution. These different behaviors of the NaPSS and NaDxS aggregates can be related to the flexibility differences between the anionic polymers. According to Dautzenberg et al.,[26,27] the level of aggregation of the classical polyelectrolyte complexes (based principally on electrostatic interactions between a polyanion and a polycation) results from a competition between two different processes of charge neutralization: by an appropriate conformational adaptation between two chains of opposite charges, or by incorporation of several charged macromolecules into the complexes. For ternary complexes involving a cationic poly(β-CD) of branched structure, it is obvious that the charge compensation by conformational changes is not made easier in the presence of the rigid and branched NaDxS. A proposed mechanism of association, adapted from the ones used to describe the classical polyelectrolyte complexes,[26,27] is schematized in Figure 13a. The ternary association should lead to high levels of aggregation in this case. The finding from neutron scattering experiments that there is more than one poly(β-CD) per poly(β-CD)/DTAC/NaDxS aggregates is in favor of this mechanism. Conversely, the mechanism of charge neutralization by conformational changes seems to be more favorable in the presence of the linear and flexible NaPSS. As suggested by the SANS results, lower levels of aggregation are expected in this case (Figure 13b).

Conclusion

The occurrence of soluble ternary complexes obtained by mixing a neutral polymer of β-cyclodextrin, a cationic surfactant,

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and an anionic polymer in aqueous medium has been proved for two different polyanions: a polystyrene sulfonate (NaPSS) and dextran sulfate (NaDxS) samples. Thus, the formation of ternary complexes does not depend on the chemical nature of the used polyanion. Moreover, the use of NaPSS and NaDxS leads to comparable macroscopic behaviors of the complexes as the DTAC amount connecting the poly(β-CD) and polyanion chains in the aggregates is increased. Indeed, both types of complexes (with NaPSS or NaDxS) show a structural transition from diffuse to dense aggregates when the DTAC concentration in the mixtures increases. However, the NaPSS aggregates experience much larger compaction than the NaDxS aggregates. Similarly, the solubility properties of the ternary complexes depend strongly on the nature of the polyanion. The poly(β-CD)/DTAC/NaPSS complexes are soluble until the ratio DTAC/sulfonate groups = 1/1 is reached, when the complexes with NaDxS, of slightly higher charge density than NaPSS, start to precipitate for the stoichiometry of 1 positive charge (DTAC) per 2 sulfate groups. The solubility properties of the complexes are also strongly dependent on the chain architecture of the polyanion. For instance, for a given β-CD/DTAC/sulfate group stoichiometry, the use of a NaDxS of higher molecular weight and degree of branching leads to less soluble ternary complexes.

On the other hand, the use of polyanions of different chain lengths leads to aggregates of different internal structures, depending on their ability to penetrate into the branched architecture of the poly(β-CD). At DTAC concentrations less than a critical value, N_{DTAC}^{crit}, which corresponds to a change from a spherical to a more homogeneous DTAC distribution along the poly(β-CD) chain, the association of NaDxS or NaPSS to poly(β-CD)/DTAC complexes gives aggregates with a core–shell inner structure. At larger DTAC concentrations, compact entangled structures are obtained with NaDxS 1 (M_w = 10 kg·mol^{-1}) and core–shell structures are obtained with NaDxS 2 (M_w = 40 kg·mol^{-1}) and NaPSS (M_w = 70 kg·mol^{-1}). Also, the use of polyanions of different stiffness leads to different molecular arrangements in the aggregates. For the ternary stoichiometry studied in this work (14/6/14), complexes involving NaDxS contain several poly(β-CD) chains when the NaPSS ones involve only one poly(β-CD) chain. Because of the high flexibility of the NaPSS, we can assume that it is more able to wrap up one poly(β-CD) chain when NaDxS, of higher rigidity and branched structure, is less prone to undergo such conformational changes and leads to an aggregation mechanism involving several poly(β-CD) chains.

Incorporation of DNA in such a model of ternary complexes should provide an original gene carrier with interesting properties compared to the actual vectors of gene. Indeed, the DNA compaction can be controlled by a simple adjusting of the ratio of the cationic surfactant vs the negative charges of DNA. Moreover, the dissociation of the DNA complexes can be improved considering the reversible characteristic of the inclusion complex interactions between the surfactant and the β-CD cavities. Future work will focus on DNA ternary complexes. Their structural properties and their stability will be studied as a function of the ionic strength and in the presence of a competitor able to form inclusion complexes with the β-CD cavities.

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