Interactions between Chromophore-Labelled Ammonium Surfactants and Hydrophobically Modified Polyelectrolytes

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The interaction of poly(maleic acid-*co*-alkyl vinyl ether)s and poly(sulfonylethyl maleic acid monoamide-*co*-alkyl vinyl ether)s with and without (cyanobiphenylyl)oxy chromophores with *N*-[ω-(substituted azobenzoxy)alkyl]-*N*,*N*-dimethyl-*N*-hydroxyethylammonium bromide surfactants has been studied by UV spectroscopy. The azobenzene unit is functionalized at the 4′-position with a cyano or fluoro substituent and is connected to the surfactant headgroup via a decyl or dodecyl spacer. Upon addition of surfactants to poly(maleic acid-*co*-butyl vinyl ether) the absorption maxima (λ_{max}) of the azobenzene chromophores immediately show their maximum blue shift. This indicates cooperative binding of surfactant to this polymer, and the formation of micelle-like aggregates surrounded by polyelectrolyte is assumed. Upon addition of the surfactants to the other polyelectrolytes λ_{max} values of the azobenzoxy chromophores gradually shift to lower values indicating a lower cooperativity of surfactant binding. This is attributed to the formation of microdomains by the polyelectrolytes themselves. For these systems the formation of mixed micelles is assumed. The compactness of the microdomains of the maleic acid copolymers is influenced by the pH and binding with surfactants is also influenced by pH. The sulfonylethyl maleic acid monoamide copolymers show no pH dependence in binding above neutral pH. For these polyelectrolytes the cooperativity also becomes less with a longer spacer between backbone and chromophore. Upon elongation of the surfactant spacer or changing the end group from a cyano to the more hydrophobic fluoro substituent a lower λ_{max} is observed for the chromophores upon initial binding to the polyelectrolytes indicating more cooperative binding. When surfactants and polyelectrolytes are both labelled with chromophores, binding proceeds noncooperatively and the formation of mixed micelles is assumed.

Spectroscopic techniques like UV/Vis and fluorescence spectroscopy are often used to investigate the interactions between polymers and surfactants.[1−5] Spectral changes which occur upon the binding of surfactants to polymers, like shifts in absorption maxima, peak widths and peak asymmetry, result from a change in polarity of the micro-environment (solvatochromic shift) or from exciton formation.

Most polymers and surfactants do not possess internal probes to monitor spectroscopic changes, therefore external probes have to be added, like e.g. pyrene in fluorescence studies.[2] Another method which is often applied is the modification of polymers or surfactants by covalent bonding of small amounts of probe molecules. A disadvantage of both systems is that the presence of even a modest amount of probe molecules might disturb the interaction between polymers and surfactants.

In a previous paper we have described the use of UV spectroscopy to study the interaction between polymers and surfactants in which one or both components are labelled with a chromophore.[6] In these systems the chromophores form an intrinsic part of the polymer or surfactant and play a role in determining their physical behaviour.[7,8] Spectral changes observed upon interaction between these polymers and surfactants result from the aggregation or deaggregation of the chromophores.

It can be expected that changes in both the hydrophobicity and hydrophilicity of the polyelectrolytes and the surfactants will influence their interaction. In this paper a UV-spectroscopy study is presented on the interaction of poly(maleic acid-*co*-alkyl vinyl ether)s **Cn acid** and **I-n**, and the more hydrophilic poly(sulfonylethylmaleic acid monoamide-*co*-alkyl vinyl ether)s **Cn sulfonate** and **II-n** (Scheme 1) with ammonium surfactants that have a *N*,*N*-dimethyl-*N*-hydroxyethylammonium head group and fluoro- or cyanoazobenzene chromophoric units connected via a decyl or dodecyl spacer. The sulfonylethyl group containing polyelectrolytes **Cn sulfonate** and **II-n** are better water-soluble and form less compact microdomains.[9] The influence of this group and of the spacer length and end group of the surfactants on the cooperativity of the surfactant binding is investigated.

Results and Discussion

The polyelectrolytes and surfactants used in this paper are shown in Scheme 1. The synthesis and properties of the surfactants and polyelectrolytes have been described before.[7−9]

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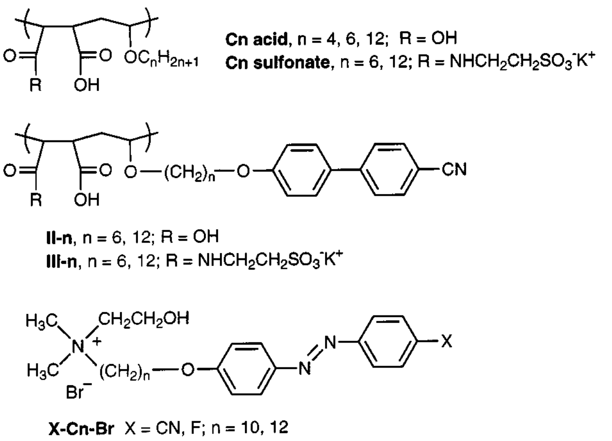

Scheme 1. Polyelectrolytes and surfactants used in this paper

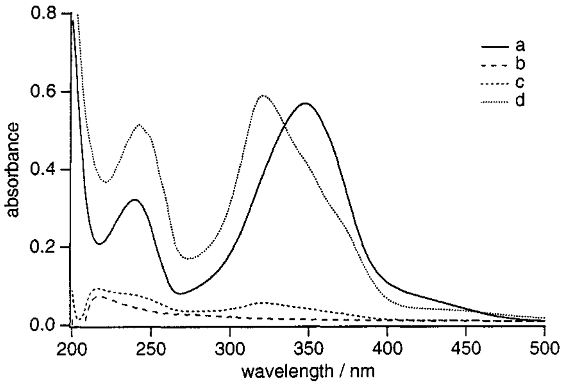

Figure 1. UV absorption spectra of **F-C12-Br** in pure water (a) and upon addition to **C4 acid** at pH = 7.8; ratio surfactant/repeating unit 0:1 (b), 0.1:1 (c) and 0.9:1 (d)

C4 Acid − X-Cn-Br

In Figure 1 the UV absorption spectrum of **F-C12-Br** in pure water is displayed. The concentration of the surfactant molecules used for the measurements is well below the critical aggregation concentration. For **F-C12-Br** an absorption maximum of 347 nm, associated with a π→π* transition, is observed for the monomeric species in aqueous solution.

Upon addition of **F-C12-Br** to an aqueous solution of **C4 acid** the absorption maximum is immediately shifted to 320 nm, a blue shift of 27 nm. According to the molecular exciton model proposed by Kasha,[10−12] the blue shift from the monomer band is indicative of linear chromophore aggregation with their transition moments parallel to each other and ordered perpendicular to the stacking direction (so-called H aggregates).[13] The wavelength shift depends, among others, on the mutual orientations and distance, and on the aggregation number of the chromophores. The observed blue shift of the fluoroazobenzoxy units results from the parallel aggregation of the fluoroazobenzoxy chromophores and is caused by π-π stacking interactions indicating the formation of ordered aggregates consisting of **F-C12-Br** molecules surrounded by the polyelectrolyte.

In Figure 2 the absorption maxima of the fluoroazobenzoxy chromophores of **F-C12-Br** at pH = 7.8 and 10.9 are displayed as a function of the ratio surfactant/**C4 acid** repeating units. One repeating unit contains two possible binding sites. The fact that the maximum blue shifts are already observed at a 0.1:1 ratio indicates cooperative binding of the surfactants to the polyelectrolyte. The surfactants bind close to each other to the polymer and the chromophores can have strong mutual π-π stacking interactions. This cooperativity suggests that the surfactants bind to the polyelectrolyte in the form of micelle-like aggregates. In a previous paper the cooperative binding of *N*-[ω-(4′-cyanobenz-4-oxy)decyl]-*N*,*N*,*N*-trimethylammonium bromide to **C4 acid** was already discussed.[6] Also the dodecyltrimethylammonium cation (DTA$^+$) is reported to bind cooperatively to **C4 acid** when this polymer has a charge density α ≥ 0.5.[14][15]

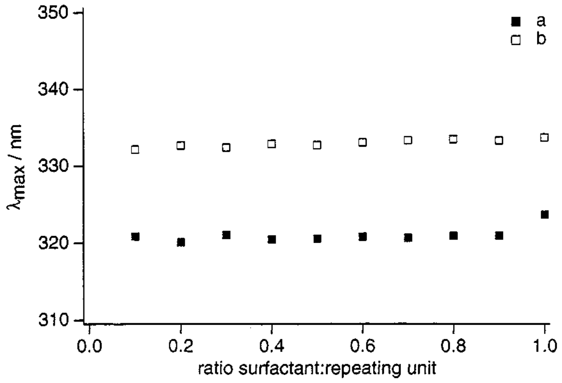

Figure 2. Change in absorption maximum of **F-C12-Br** upon addition to **C4 acid** at pH = 7.8 (a) and 10.9 (b)

Upon increasing the pH the charge density of the polyelectrolyte is increased resulting in a swelling of the polyelectrolyte due to increased electrostatic repulsion on the backbone. This affects the interaction with surfactants as can be seen from Figure 2. At higher pH **F-C12-Br** still binds cooperatively to the polyelectrolyte, but the blue shift has decreased with 10 nm as compared to the solution at pH = 7.8.

Besides the aggregation number and mutual orientation of the aggregated chromophores their distance is also a determining factor for the observed shift in λ_{max} and thus for the amount of π-π stacking interactions. The spectral shift (in wavenumber, Δν) for an aggregate consisting of *N* monomers with respect to the monomer absorption is given by[16]

$$\Delta\nu = \frac{2}{hc}\frac{N-1}{1}\frac{\mu^2}{r^3}\left(1-3\cos^2\alpha\right)$$

in which μ is the magnitude of the transition dipole moment, *r* is the centre-to-centre distance between the dipoles and α is the angle between the chromophore long axes and the chromophore centre-to-centre line. The decrease in blue shift upon increasing pH is mainly ascribed to the increased centre-to-centre distance *r* of the fluoroazobenzoxy chromophores which is forced onto the surfactants by the more extended polyelectrolyte.

In Table 1 the absorption maxima of **X-Cn-Br** in pure water and in the presence of **C4 acid** at various surfactant-to-repeating unit ratios are given. For all surfactants an immediate blue shift of the absorption maximum is observed when added to an aqueous solution of **C4 acid**. This implies that all surfactants bind cooperatively to **C4 acid** at both pH values studied. This agrees with reports in literature on cooperative binding of dodecyltrimethylammonium cations to this polyelectrolyte.[15,16] The alkyl spacer length of the surfactants hardly affects the amount of blue shift of the chromophores.

Table 1. UV absorption maxima (in nm) of **X-Cn-Br** in pure water and in the presence of **C4 acid** at various surfactant to repeating unit ratios at pH = 7.8 and 10.9

		pH = 7.8		pH = 10.9	
Surfactant	H_2O	Ratio 0.1:1	Ratio 0.9:1	Ratio 0.1:1	Ratio 0.9:1
CN-C10-Br	361	339	338	346	349
CN-C12-Br	360	339	338	347	347
F-C10-Br	349	325	324	331	331
F-C12-Br	347	321	320	332	333

As was already clear from Figure 2, the conformation of the polyelectrolyte has a strong influence on the amount of aggregation of the surfactants. Upon increasing the pH the polyelectrolyte becomes more stretched resulting in a larger distance between the polyelectrolyte binding sites. The distance between the surfactant molecules bound to the polyelectrolyte at higher pH therefore also increases which results in a smaller blue shift of azobenzene chromophores of **CN-Cn-Br** and **F-Cn-Br** at pH = 10.9 as compared to pH = 7.8.

C6 Acid − X-Cn-Br

After the first addition of **F-C12-Br** to **C6 acid** at pH = 7.8 the absorption maximum of the fluoroazobenzene chromophores is observed at 332 nm, a blue shift of 15 nm as compared to the monomeric chromophores. Upon increasing the surfactant concentration the absorption maximum decreases even more, reaching 323 nm at a 0.9:1 surfactant to repeating unit ratio. The maximum blue shift of the fluoroazobenzoxy chromophores is reached at a higher surfactant to repeating unit ratio than was observed for **C4 acid** (Figure 2). This implies a less cooperative surfactant binding to **C6 acid**.

For **CN-Cn-Br** and **F-C10-Br** the binding to **C6 acid** is also less cooperative than their binding to **C4 acid**. As for **F-C12-Br** the decrease in cooperativity can be attributed to the increase in polyelectrolyte side chain length which causes the formation of microdomains by **C6 acid** itself.

For the surfactants with a dodecyl spacer a lower absorption maximum of the azobenzene chromophores is observed at a ratio of 0.1:1 than for the surfactants with a shorter decyl spacer. This implies a more cooperative binding for **X-C12-Br**. The increased hydrophobicity of **X-C12-Br** as compared to **X-C10-Br** results in stronger attraction between the surfactants. This results in the lower absorption maxima for their chromophores after the first addition of surfactant.

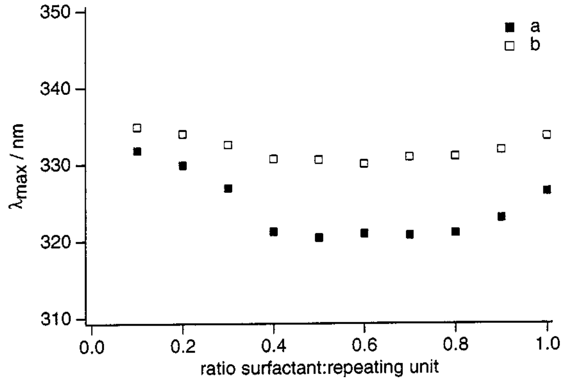

Figure 3. Change in absorption maximum of **F-C12-Br** upon addition to **C6 acid** at pH = 7.8 (a) and 10.9 (b)

From Figure 3 and Table 2 it can be seen that at pH = 10.9 the binding of **F-C12-Br** to **C6 acid** results in a higher λ_{max} at a 0.9:1 ratio than at pH 0 7.8.[17] Binding of **CN-Cn-Br** also gives higher λ_{max} values at pH = 10.9. At high pH the distance between the polyelectrolyte binding sites is increased due to deprotonation which forces the surfactant molecules to bind at a larger distance from each other. Therefore a higher λ_{max} is observed at pH = 10.9 as compared to pH = 7.8.

Table 2. UV absorption maxima (in nm) of **X-Cn-Br** in pure water and in the presence of **C6 acid** at various surfactant to repeating unit ratios at pH = 7.8 and 10.9

		pH = 7.8		pH = 10.9	
Surfactant	H_2O	Ratio 0.1:1	Ratio 0.9:1	Ratio 0.1:1	Ratio 0.9:1
CN-C10-Br	361	353	339	355	343
CN-C12-Br	360	344	338	347	345
F-C10-Br	349	340	326 [a]	336	330
F-C12-Br	347	332	323	335	332

[a] Ratio 0.7:1.

C12 Acid − X-Cn-Br

From literature it is known that **C12 acid** forms microdomains in aqueous solution between pH = 1 and 14.[18,19] The compactness of these microdomains depends on the charge density of the polyelectrolytes and thus on the pH of the solution. When **F-C10-Br** is added to **C12 acid** at pH = 7.8 a gradual decrease in λ_{max} of the fluoroazobenzoxy chromophores is observed. From Figure 4 it can be seen that the absorption maximum is shifted from 350 nm at a 0.1:1 ratio to 327 nm at a 0.9:1 surfactant to repeating unit ratio. This is seen more clearly in Figure 5 which displays λ_{max} as a function of the ratio of the surfactant to polyelectrolyte repeating unit.

The gradual decrease in λ_{max} implies a noncooperative binding of the surfactant molecules to the **C12 acid** microdomains. At pH = 7.8 $\Delta\lambda_{max}$ is larger than at pH = 10.8.

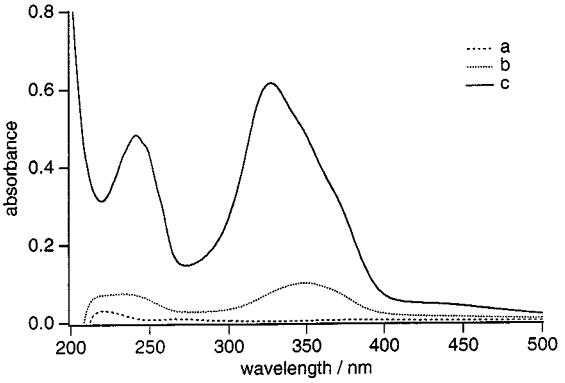

Figure 4. UV absorption spectra of **F-C10-Br** upon addition to **C12 acid** at pH = 7.8; ratio surfactant/repeating unit 0:1 (a), 0.1:1 (b) and 0.9:1 (c)

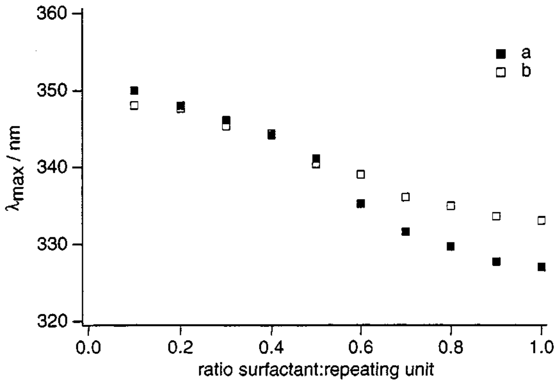

Figure 5. Change in absorption maximum of **F-C10-Br** upon addition to **C12 acid** at pH = 7.8 (a) and 10.8 (b)

This was also observed for surfactant binding to **C4 acid** and **C6 acid** and can be attributed to the smaller distance between the binding sites on the polyelectrolyte backbone at lower pH. **F-C12-Br** and **CN-Cn-Br** show the same decrease in λ_{max} upon addition to **C12 acid** upon increasing the pH.

From Table 3 it can be concluded that **X-Cn-Br** binds noncooperatively to **C12 acid**. The addition of **F-C12-Br** to **C12 acid** results in an absorption maximum of 335 nm at a 0.1:1 ratio. This is a blue shift of 12 nm as compared to the monomeric surfactant. The blue shift is clearly less than the blue shift observed for **F-C12-Br** in the presence of **C4 acid** and **C6 acid** at a 0.1:1 ratio. This indicates that the surfactant molecules bind less closely to each other in the presence of **C12 acid** at pH = 7.8 as compared to **C4 acid** and **C6 acid**. However, at this pH **F-C12-Br** shows a larger blue shift upon binding to **C12 acid** than **F-C10-Br**, **CN-C10-Br** and **CN-C12-Br**. This may be attributed to the more hydrophobic nature of **F-C12-Br** as compared to **F-C10-Br** and **CN-Cn-Br**.

An increase in alkyl spacer length of the surfactant results in more cooperative surfactant binding to **C12 acid**, as is clear from the lower absorption maxima for **X-C12-Br** than for **X-C10-Br** after the first addition of surfactant. This was also observed for surfactant binding to **C6 acid**.

Table 3. UV absorption maxima (in nm) of **X-Cn-Br** in pure water and in the presence of **C12 acid** at various surfactant to repeating unit ratios at pH = 7.8 and 10.9

		pH = 7.8		pH = 10.9	
Surfactant	H_2O	Ratio 0.1:1	Ratio 0.9:1	Ratio 0.1:1	Ratio 0.9:1
CN-C10-Br	361	366	337	363	347
CN-C12-Br	360	356	337	358	347
F-C10-Br	349	350	327	348	333
F-C12-Br	347	335	328	346	332

The small red shift of the absorption maximum at the 0.1:1 ratio of **CN-C10-Br**/**C12 acid** at both pH values results from the dissolution of the surfactant tails into the microdomains formed by the alkyl groups of the polyelectrolyte. These microdomains provide an apolar environment for the surfactant tails. The absorption maximum of these chromophores is shifted to higher wavelength upon decreasing the polarity of the solvent. In a 1,4-dioxane or THF solution, which are less polar than water, the absorption maximum of e.g. **CN-C10-Br** is found at 364 nm.

C6 Sulfonate – X-Cn-Br

The binding of **F-C10-Br** to **C6 sulfonate** is presented in Figure 6. The absorption maximum of **F-C10-Br** in pure water is 349 nm. As can be seen in Figure 6 the absorption maximum of this surfactant is already blue shifted at a 0.1:1 surfactant to repeating unit ratio resulting from aggregation of the fluoroazobenzoxy chromophores. A further decrease of the absorption maximum with increasing surfactant concentration is observed.

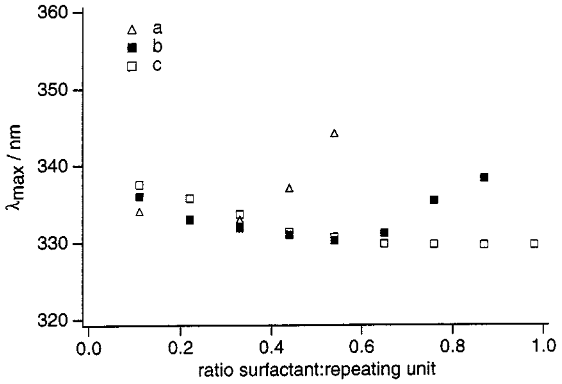

Figure 6. Change in absorption maximum of **F-C10-Br** upon addition to **C6 sulfonate** at pH = 4.3 (a), 8.1 (b) and 10.8 (c)

The pH of the solution hardly affects the cooperativity of the binding but the pH does affect the solubility of the formed polyelectrolyte–surfactant complex. The increase in

λ_{max} which can be seen in Figure 6 at pH = 4.3 and a surfactant to repeating unit ratio beyond 0.4:1, results from precipitation of the formed complex. The charge density on the polyelectrolyte backbone is reduced at lower pH, resulting in a reduced hydrophilicity of the formed complex at similar ratios, and a decrease of its water solubility.

For the surfactants **F-C12-Br**, **CN-C10-Br**, and **CN-C12-Br** precipitation above pH = 7 is less serious. From Table 4 it can be seen that the λ_{max} values obtained at pH = 7.8 and 10.9 are very similar at both ratios. This means that the polymers have a similar conformation at these pH values. From the values in Table 4 it can also be deduced that the surfactants with a C_{12} spacer bind more cooperatively than those with a C_{10} spacer, because the λ_{max} values at a 0.1:1 binding ratio are lower for the compounds with a C10 spacer. This is in line with the results obtained for the previously discussed **Cn acid** polyelectrolytes. Also the surfactants with a fluoroazobenzoxy chromophore bind more cooperatively than the compounds with a cyanoazobenzoxy chromophore, because for these compounds most of the change in λ_{max} has already taken place at a binding ratio of 0.1:1. For the most apolar surfactant **F-C12-Br** essentially cooperative binding to **C6 sulfonate** is found.

Table 4. UV absorption maxima (in nm) of **X-Cn-Br** in pure water and in the presence of **C6 sulfonate** at various surfactant to repeating unit ratios at pH = 7.8 and 10.9

		pH = 7.8		pH = 10.9	
Surfactant	H_2O	Ratio 0.1:1	Ratio 0.9:1	Ratio 0.1:1	Ratio 0.9:1
CN-C10-Br	361	352	338	346	341
CN-C12-Br	360	348	344	345	342
F-C10-Br	349	336	331 [a]	338	330
F-C12-Br	347	334	336	335	333

[a] Ratio 0.7:1.

The binding of the surfactant molecules to **C6 sulfonate** is less cooperative than binding to **C4 acid**, but more cooperative than to **C12 acid**, which forms microdomains at all pH values studied. Due to the presence of the sulfonic acid groups polymer **C6 sulfonate** is more water soluble than **C6 acid**. The sulfonic acid group also affects the polyelectrolyte conformation and the microdomains of **C6 sulfonate** are therefore expected to be more open than those of **C6 acid**. In contrast to **C6 acid**, the degree of deprotonation of **C6 sulfonate** above neutral pH does not change much, therefore essentially the same results are obtained for surfactant binding at pH values of 7.8 and 10.9.

C12 Sulfonate − X-Cn-Br

From Figure 7 it is clearly seen that **CN-C10-Br** binds noncooperatively to **C12 sulfonate** at all pH values studied. At a 0.1:1 surfactant to repeating unit ratio the absorption maximum of the cyanoazobenzoxy groups is 362 nm. Upon increasing the surfactant concentration the absorption maximum shifts to lower values indicating the gradual aggregation of the chromophores.

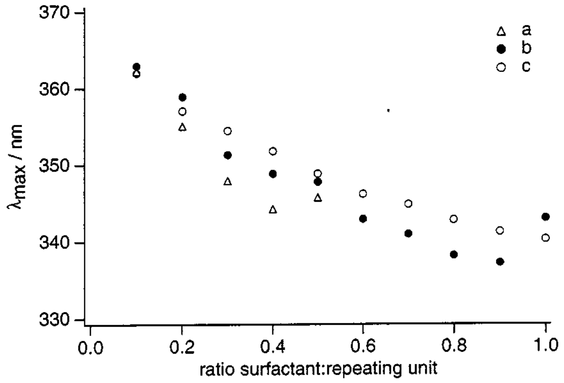

Figure 7. Change in absorption maximum of **CN-C10-Br** upon addition to **C12 sulfonate** at pH = 3.9 (a), 7.8 (b) and 11.1 (c)

An increase in spacer length from 10 to 12 methylene units of the surfactant results in a significant increase in cooperativity of binding, which is clear from a lower absorption maximum of **X-C12-Br** after the first addition of surfactant (see Table 5). When the data for binding of **F-C12-Br** and **CN-C12-Br** to **C12 sulfonate** are compared it is also seen that the fluoroazobenzoxy substituted surfactants bind more cooperatively than the cyanoazobenzoxy substituted surfactant. From the experiments with the sulfonate containing polyelectrolytes we see that above neutral pH the binding is not influenced by the pH. This seems logical since the polyelectrolytes contain enough charges above neutral pH to be in an extended open conformation.

Table 5. UV absorption maxima (in nm) of **X-Cn-Br** in pure water and in the presence of **C12 sulfonate** at various surfactant to repeating unit ratios at pH = 7.8 and 10.9

		pH = 7.8		pH = 10.9	
Surfactant	H_2O	Ratio 0.1:1	Ratio 0.9:1	Ratio 0.1:1	Ratio 0.9:1
CN-C10-Br	361	362	337	361	341
CN-C12-Br	360	352	340	352	343
F-C10-Br	349	346	333	346	333
F-C12-Br	347	336	338	336	333

When the data of Tables 4 and 5 are compared it is seen that **C12 sulfonate** induces stronger noncooperative binding of the surfactants than **C6 sulfonate**. This agrees well with what can be expected. When the λ_{max} values of the surfactants at a 0.9:1 ratio are compared for the different polymers at different pH values it is seen that the values for the **Cn sulfonates** at pH = 7.8 and 10.9 and the **Cn acids** at pH = 10.9 are very similar: about 332 nm for the fluoro group containing surfactants and 345 nm for the cyano group containing surfactants, indicating that the final aggregates are very similar. The **Cn acids** at pH = 7.8 give much lower values at a 0.9:1 ratio of the surfactants: about 325 nm and 337 nm for the fluoro and cyano surfactants, respectively. This indicates a better ordering of the chromophores in the aggregates due to the more compact conformation of these polymers at pH = 7.8.

I-6 – X-Cn-Br

In previous papers the formation of microdomains by polyelectrolytes **I-n** and **II-n** was discussed.[7,9] By determining the λ_{max} of their pendant chromophores it was shown that both series of polymers form compact microdomains in aqueous solution at low pH values. Upon increasing the pH the microdomains become more open as reflected by the partial loss of chromophore aggregation. In the previous section it was shown that the compactness of the microdomains plays an important role in the interaction with surfactants.

The use of different chromophores on a polyelectrolyte and surfactant can provide valuable information on the interactions between these components. The monomerically dispersed (cyanobiphenylyl)oxy chromophores have their absorption maximum at 292 nm in water. The absorption maximum of the (cyanobiphenylyl)oxy chromophores of **I-6** at pH = 7.6 is 280 nm. The blue shift of the absorption maximum shows that this polyelectrolyte forms microdomains at this pH. From Figure 8 the gradual loss of π-π stacking interactions between the (cyanobiphenylyl)oxy chromophores upon titration with **CN-C12-Br** can be seen.[20] Simultaneously, the cyanoazobenzoxy chromophores seem to aggregate as can be seen from the blue shift of the absorption maximum of these chromophores.

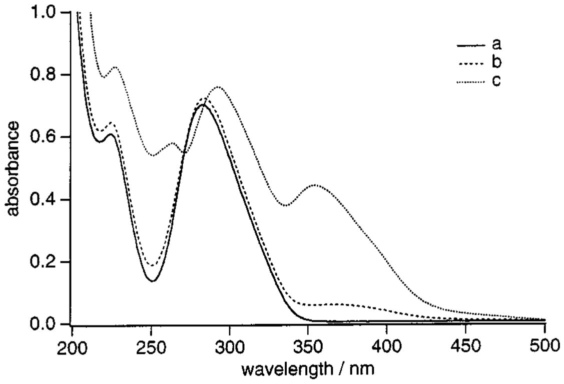

Figure 8. UV absorption spectra of **I-6** upon addition of **CN-C12-Br** at pH = 7.6; ratio surfactant/repeating unit 0:1 (a), 0.1:1 (b) and 1:1 (c)

Figures 9 and 10 display the shifts in absorption maxima more clearly. The aggregation between the (cyanobiphenylyl)oxy units of the polyelectrolyte is largely lost upon interaction with **CN-C12-Br**. The surfactant molecules penetrate between the polyelectrolyte side chains disrupting the π-π stacking interactions. The cyanoazobenzoxy chromophores of the surfactant initially show a red shift as compared to the absorption maximum of the monomeric compound. This solvatochromic shift is due to the burial of individual surfactant molecules in the apolar polyelectrolyte microdomains.

In binding of surfactants to polyelectrolyte microdomains, a delicate balance exists between the solvation of individual surfactant molecules in the apolar microdomains and binding of surfactant molecules in close proximity of each other (cooperative binding). The first factor will cause an increase in λ_{max}, whereas the second will increase the interactions between the surfactant chromophores and cause a decrease in λ_{max}. Together these two effects determine the overall absorption maximum of these chromophores.

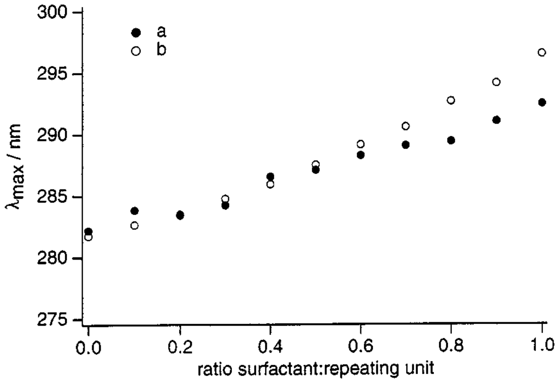

Figure 9. Change in absorption maximum of the (cyanobiphenylyl)oxy chromophores of **I-6** upon titration with **CN-C12-Br** at pH = 7.6 (a) and 10.6 (b)

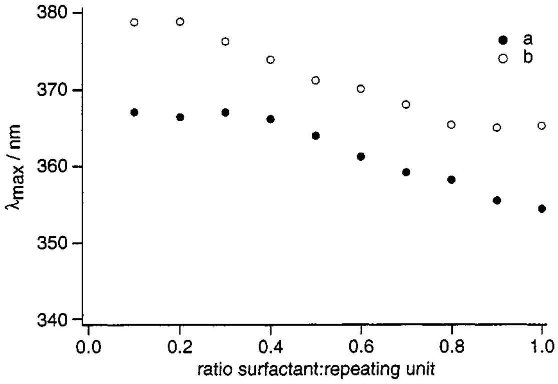

Figure 10. Change in absorption maximum of the cyanoazobenzoxy chromophores of **CN-C12-Br** upon addition to **I-6** at pH = 7.6 (a) and 10.6 (b)

In Table 6 the absorption maxima of the (cyanobiphenylyl)oxy chromophores of **I-6** and the azobenzene chromophores of **X-Cn-Br** are displayed at various surfactant to repeating unit ratios and two pH values.

I-12 – X-Cn-Br

In Table 7 the UV absorption maxima of the (cyanobiphenylyl)oxy units of **I-12** and the azobenzene chromophores of **X-Cn-Br** are presented. For these systems a gradual shift in absorption maximum for both the (cyanobiphenylyl)oxy and azobenzene units is found, indicative for noncooperative binding.

Table 6. UV absorption maxima (in nm) of the (cyanobiphenyl)oxy chromophores of **I-6** (CB) and the azobenzene chromophores of **X-Cn-Br** (AB) at various surfactant to polymer repeating unit ratios and at various pH values

		CB		AB	
Surfactant	pH	Ratio 0.1:1	Ratio 1:1	Ratio 0.1:1	Ratio 1:1
CN-C10-Br	7.8	282	289	373	356
	10.7	283	296	379	360
CN-C12-Br	7.6	283	292	367	354
	10.6	283	296	379	365
F-C10-Br	7.8	282	284	355	350
	10.7	282	293	356	351
F-C12-Br	7.6	284	287	351	348
	10.3	284	293	355	353

Table 7. UV absorption maxima (in nm) of the (cyanobiphenylyl)oxy chromophores of **I-12** (CB) and the azobenzene chromophores of **X-Cn-Br** (AB) at various surfactant to polymer repeating unit ratios and at various pH values

		CB		AB	
Surfactant	pH	Ratio 0.1:1	Ratio 1:1	Ratio 0.1:1	Ratio 1:1
CN-C10-Br	7.5	278	283	368	353
	10.7	281	290	373	364
CN-C12-Br	7.7	281	287	361	351
	10.7	281	291	372	362
F-C10-Br	7.5	278	287	352	347
	10.7	281	292	355	350
F-C12-Br	7.7	282	287		
	10.4	281	289	352	348

For both systems with chromophores in both polyelectrolyte and surfactant an increase in the absorption maximum of the (cyanobiphenylyl)oxy chromophores is observed. Simultaneously, the absorption maximum of the azobenzene chromophores is seen to decrease. All azobenzene surfactants show a red shift of their absorption maxima at a 0.1:1 surfactant to polyelectrolyte repeating unit ratio. This solvatochromic shift is larger at higher pH due to the more open microdomain structure which makes them more penetrable. The solvatochromic shifts are also larger for polymers **I-6** than for **I-12**, probably for the same reasons.

At a 1:1 ratio it is seen that aggregation of the cyanobiphenylyloxy chromophores is almost completely lost and that only some aggregation of the azobenzoxy chromophores has occured. This seems to indicate the formation of mixed micelle-like aggregates with a small degree of clustering of the chromophores. At high pH the aggregation of the chromophores is decreased. This is seen in both the λ_{max} values of the cyanobiphenylyloxy and the azobenzoxy chromophores, which are both higher at high pH. This is in agreement with a more open microdomain structure of the polyelectrolytes at high pH.

For both **I-6** and **I-12** the alkyl spacer length and the end group of the surfactants have only a small influence on the interaction between polyelectrolyte and surfactant.

Although polyelectrolytes **II-n** have a more open conformation than **I-n** at equal pH values the effect of surfactants is similar.[9] As for **I-n** a small, gradual increase in λ_{max} of the (cyanobiphenylyl)oxy chromophores is observed which indicates noncooperative interaction between the polyelectrolyte microdomains and surfactant molecules. The surfactants are initially solvated within the microdomains formed by the polyelectrolytes **II-n** resulting in a small red shift of the azobenzoxy absorption maxima (not shown). Increasing the surfactant concentration results in a decrease of the absorption maxima of these surfactants due to chromophore aggregation. Based on the observed changes in the absorption spectra the formation of mixed micelles is also proposed for the **II-n**−**X-Cn-Br** systems.

Conclusions

The interactions between chromophore-labelled surfactants and oppositely charged polyelectrolytes can be probed with UV/VIS spectroscopy.

The short-chained polyelectrolyte **C4 acid**, which is in its extended conformation at pH > 3 and does not form microdomains at the pH values used, shows cooperative binding with the azobenzene labelled surfactants. The surfactant molecules form micelle-like aggregates which are surrounded by the polyelectrolyte chains.

Upon increasing the polymer side chain length from 4 to 6 to 12 methylene units the surfactant binding becomes increasingly less cooperative. This is due to the formation of microdomains by **C6 acid** and **C12 acid**. In these cases the formation of mixed micelles is assumed upon binding of surfactants.

Deprotonation of the **Cn-acid** polymers at high pH results in a more extended conformation of the backbone and after binding of surfactants a smaller shift in absorption maximum is observed than at neutral pH. This pH dependence is not found for the **Cn sulfonates**, where the situation after binding of the surfactants is similar at neutral and high pH and similar to the situation for **Cn acids** at high pH. Binding of surfactants to the **Cn sulfonates** occurs with a varying degree of cooperation. It was found that a higher degree of cooperation was obtained for the more apolar surfactants i.e. with a longer spacer and a fluoro end group instead of a cyano end group. A higher cooperativity is favoured for polyelectrolytes with a shorter spacer, depending on their ability to form apolar microdomains by themselves.

Polymers **I-n** and **II-n** also form microdomains in aqueous solution. The binding of azobenzoxy-labelled surfactants to these polymers is strongly noncooperative and mixed micelles are formed in which the surfactants and/or the polyelectrolyte side chains can show some aggregation.

Experimental Section

General: UV spectra were recorded with a Perkin-Elmer Lambda 18 UV/VIS spectrophotometer, which was thermostatted at 25 ± 0.1°C. Aqueous solutions of **Cn acid** and **I-n** were prepared by addition of a solution of 5.0 mg of dry polymer in 2 mL of THF to water at pH = 12 (final volume of 10 mL). Subsequently, the THF was removed by stirring under a nitrogen flow. Solutions of **Cn sulfonate** and **II-n** were prepared by dissolving 5.0 mg of dry polymer in 10 mL of water at pH = 12. For the UV experiments the polymer concentration was $5 \cdot 10^{-5}$ M in repeating units L^{-1} ($\varepsilon \approx$ 13000 L mol^{-1} cm^{-1}). Aliquots of a surfactant stock solution were added to obtain surfactant-to-polyelectrolyte repeating unit ratios in the range 0:1−1:1. In some cases, the addition of surfactant was stopped as soon as a drastic increase in light scattering, indicative of precipitation of the formed complex, was observed.

Synthesis: The synthesis of the polymers and the *N*-[ω-(substituted azobenzoxy)alkyl]-*N*,*N*-dimethyl-*N*-hydroxyethylammonium bromides, **X-Cn-Br**, has been described before.[7−9]

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[1] E. D. Goddard, *Colloids Surf.* **1986**, *19*, 301−329.

[2] F. M. Winnik, S. T. A. Regismond, *Colloids Surf. A: Physicochem. Eng. Aspects* **1996**, *118*, 1−39.

[3] K. Hayakawa, S. Shinohara, S. Sasawaki, I. Satake, J. C. T. Kwak, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2179−2185.

[4] J. Kido, M. Hiyoshi, C. Endo, K. Nagai, *J. Colloid Interface Sci.* **1991**, *142*, 326−330.

[5] D. M. Bloor, Y. Li, E. Wyn-Jones, *Langmuir* **1995**, *11*, 3778−3781.

[6] A. C. Nieuwkerk, A. T. M. Marcelis, E. J. R. Sudhölter, *Langmuir* **1997**, *13*, 3325−3330.

[7] A. C. Nieuwkerk, A. T. M. Marcelis, E. J. R. Sudhölter, *Macromolecules* **1995**, *28*, 4986−4990.

[8] A. C. Nieuwkerk, A. Koudijs, A. T. M. Marcelis, E. J. R. Sudhölter, *Liebigs Ann.* **1997**, 1719−1724.

[9] A. C. Nieuwkerk, E. J. M. van Kan, A. Koudijs, A. T. M. Marcelis, E. J. R. Sudhölter, *Langmuir* **1998**, *14*, 5702−5711.

[10] E. G. McRae, M. Kasha, *J. Chem. Phys.* **1958**, *28*, 721−722.

[11] M. Kasha, H. R. Rawls, M. Ashraf El-Bayoumi, *Pure Appl. Chem.* **1965**, *11*, 371−392.

[12] E. G. McRae, M. Kasha, *Physical Processes in Radiation Biology*, Academic Press, New York, **1964**, p. 23.

[13] J. M. Kroon, R. B. M. Koehorst, M. van Dijk, G. M. Sanders, E.R. J. Sudhölter, *J. Mater. Chem.* **1997**, *7*, 615−624.

[14] O. Anthony, R. Zana, *Langmuir* **1996**, *12*, 1967−1975.

[15] M. Benrraou, R. Zana, R. Varoqui, E. Pefferkorn, *J. Phys. Chem.* **1992**, *96*, 1468−1475.

[16] M. Shimomura, S. Aiba, N. Tajima, N. Inoue, K. Okuyama, *Langmuir* **1995**, *11*, 969−976.

[17] **F-C10-Br** precipitated already at a surfactant-to-repeating unit ratio of 0.7:1 at pH = 7.8 and the absorption maximum at this pH can thus not be directly compared to the value found at pH = 10.9. However, **F-C10-Br** shows the same trend as the other surfactants upon increasing the pH.

[18] W. Binana-Limbelé, R. Zana, *Macromolecules* **1990**, *23*, 2731−2739.

[19] Y. Morishima, T. Kobayashi, S. Nozakura, *Polymer J.* **1989**, *21*, 267−274.

[20] UV studies of an ammonium surfactant carrying both a cyanoazobenzoxy and a (cyanobiphenylyl)oxy chromophore showed no influence of the two chromophores on their respective monomeric spectra: M. D. Everaars, personal communication.

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