Multichromophoric cyclodextrins as fluorescent sensors. Interaction of heptachromophoric β-cyclodextrins with surfactants

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A β-cyclodextrin derivative CD-NA bearing 7 negatively charged naphthoate chromophores is shown to strongly interact with cationic surfactants. In the absence of surfactant, the CD-NA emission spectrum is composed of two bands; one is assigned to the normal fluorescence and the other one to the fluorescence of intramolecular excimers. Interaction with a cationic surfactant leads to a drop in excimer emission. The ratio of the fluorescence intensities of the monomer and excimer bands is directly related to the concentration of the surfactant. In the case of electroactive surfactants such as cetylpyridinium chloride, the fluorescence quenching arising from photoinduced electron transfer can be additionally used for sensing. CD-NA can thus be used to detect cetyltrimethylammonium chloride (cetyl = hexadecyl) and cetylpyridinium chloride in an aqueous solution at concentrations as low as a few micromoles per litre and up to about 50 micromoles per litre. The interaction between CD-NA and cationic surfactants can be interpreted by a micellization process induced by CD-NA rather than by the formation of 1 : 1 inclusion complexes. The analogy with the interaction between cationic surfactants and polyelectrolytes bearing negative charges is outlined. It should be noted that addition of the anionic surfactant sodium dodecyl sulfate does not induce any photophysical effect.

Introduction

The design and technical accomplishment of sensors are major issues in supramolecular chemistry. At the molecular level, a basic sensing unit is generally made of two connected structural elements. The first one induces a specific interaction with a given substrate while the second one (transducer) converts the recognition event into a signal. In particular, optical transduction—mainly *via* fluorescence—has already been extensively investigated.[1–4] Optical sensors based on fluorescent probes can be designed according to two guiding principles: (i) the absorption and emission features of the fluorophore are directly affected by the close interaction with the substrate, and/or (ii) the modification of the photophysical properties results from the conformational changes of the sensor that are consecutive to the interaction with the substrate. In the present paper, we want to emphasize some advantages of using multichromophoric molecules for designing optical sensors along both principles.

Cyclodextrins have often been used as the recognition part of molecular sensors owing to their ability to include molecules in their cavities. Optical detection has been made possible by means of one or two absorbing or fluorescent molecules that are covalently linked to the cyclodextrin upper or lower rim.[5] In our previous work on the antenna effect in heptachromophoric β-cyclodextrins,[6,7] we showed that modified β-cyclodextrins such as CD-NA (Fig. 1) with seven appended naphthoate chromophores were much more efficient than the native β-cyclodextrin in binding DCM-OH, an elongated merocyanine. This observation suggested that the chromophores play an active role in the association process. The interaction with the substrate is likely to be accompanied by a modification of the naphthoate arrangement on the cyclodextrin primary rim. Due to the negative charge of each naphthoate chromophore, arrangements where charged head-groups are distant should

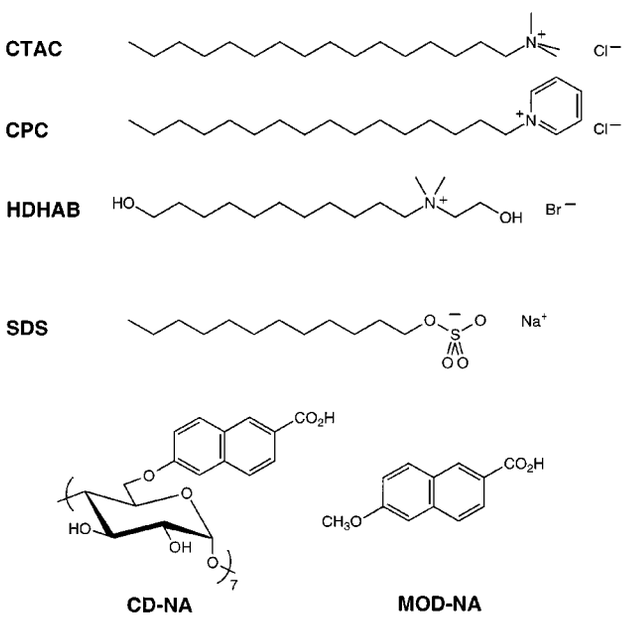
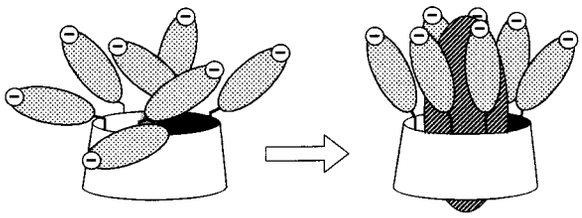


Fig. 1 Formulae of molecules that have been used in the present study. Cationic surfactants: cetyltrimethylammonium chloride (CTAC), cetylpyridinium chloride (CPC), *N*,*N*-dimethyl-*N*-(11-hydroxyundecyl)-*N*-(2-hydroxyethyl)ammonium bromide (HDHAB); anionic surfactant: sodium dodecyl sulfate (SDS), CD-NA and MOD-NA.

be favoured in the empty host (*e.g.* in head-to-tail relative chromophore orientation) whereas guest-induced naphthoate corollas should result from complexation (Scheme 1). In view of the small distance between the naphthalene rings, such a conformational change could considerably affect the absorption and emission properties, even in the absence of energy transfer to a substrate included into the cyclodextrin cavity.



Scheme 1

In particular, the probability of forming excimers (excited dimers) should be affected. The possibility of detecting and quantifying interaction by the sole observation of the CD-NA photophysical features together with the expected large association constants prompted us to evaluate multichromophoric cyclodextrins as fluorescent sensors.

We turned our attention to surfactants as guests to address the CD-NA sensing capability. Surfactants are indeed extensively used in domestic and industrial applications and their slow degradation poses a severe problem of environmental pollution. Moreover association of surfactants with the native α- or β-cyclodextrins has been the object of various investigations.[8–14] Among surfactants, our attention has been focused on cationic species whose large toxicity is linked to a slow biodegradation owing to their bactericidal nature. The extensively investigated cetylpyridinium chloride (CPC) and cetyltrimethylammonium chloride (CTAC) have thus been chosen as substrates for this investigation. The aim of the present paper is to propose a simple and reliable method based on analysis of CD-NA fluorescence emission for detecting low amounts of surfactants in aqueous solution.

Experimental

The synthesis of CD-NA was previously described[7] together with that of the reference compound MOD-NA (see formula in Fig. 1). Cetylpyridinium chloride was purchased from Prolabo, cetyltrimethylammonium chloride from Kodak and sodium dodecyl sulfate from Janssen-Chimica. They were used without further purification. *N*,*N*-Dimethyl-*N*-(11-hydroxyundecyl)-*N*-(2-hydroxyethyl)ammonium bromide (HDHAB) was kindly provided by Professor A. Laschewsky and its synthesis has already been reported.[15]

The Britton–Robinson buffers were prepared according to reference 16 (they were obtained by mixing solutions of NaOH, acetic acid, boric acid and phosphoric acid at appropriate concentrations; the desired ionic strength is obtained by addition of KCl). pH values greater than 8 were chosen in order to ensure complete ionisation of the carboxylic groups of the chromophores in CD-NA.[7] There is indeed no significant pH-dependence of the photophysical properties of CD-NA above pH = 8.

The UV–Vis absorption spectra were recorded on a Kontron Uvikon-940 spectrophotometer. Corrected fluorescence spectra were obtained with a SLM 8000c spectrofluorimeter. All measurements were performed at 25 °C.

Light scattering experiments were done at 20 °C. Incident irradiation at 514.5 nm was produced by a coherent argon laser. A Brookhaven multiautocorrelator was used to generate the full autocorrelation function of the scattered intensity. The time correlation function was analyzed by a method of cumulants.

Results

Addition of cationic surfactants to CD-NA

The naphthoate chromophores of CD-NA can form an excimer, as revealed by the characteristic long wavelength emission band. Since it was expected that inclusion of an elongated molecule would hinder excimer formation, the ratio of excimer and monomer fluorescence intensity was chosen for monitoring complexation. Since the CD-NA–surfactant interaction is expected to depend on ionic strength, experiments were carried out at ionic strengths of 0.005 and 0.1 M.

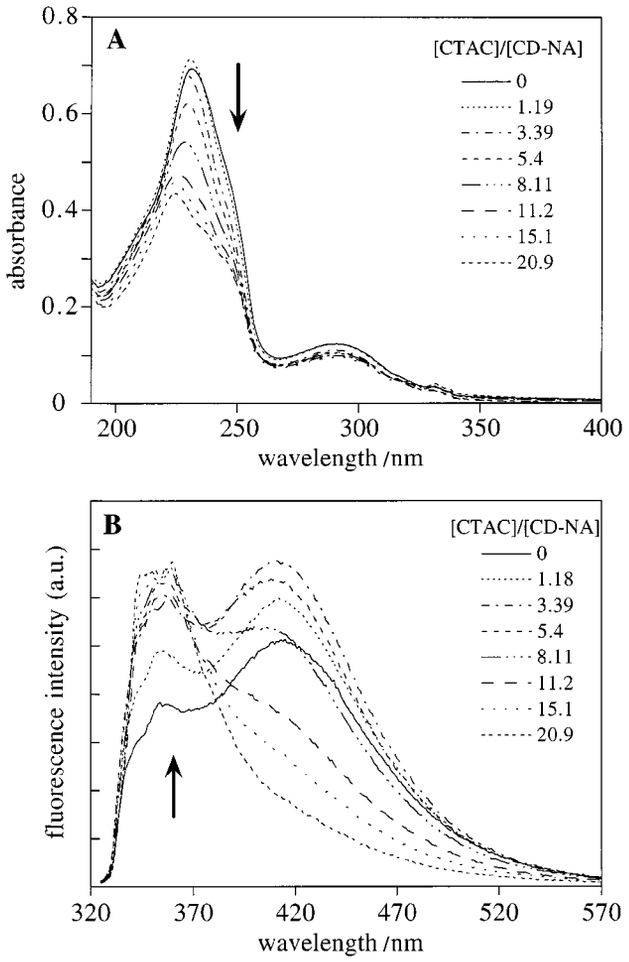


Fig. 2 Evolution of the absorption spectrum (A) and the fluorescence spectrum (λ_{exc}: 300 nm) (B) of CD-NA (3.08×10^{-6} M) on addition of CTAC in an aqueous buffer at pH 9 (ionic strength: 0.005 M). The fluorescence spectra are corrected for the instrumental response and for the changes in absorbance at the excitation wavelength.

Fig. 2 shows the changes in the absorption and emission spectra of CD-NA (concentration: 3.08×10^{-6} M; ionic strength: 0.005 M) on addition of cetyltrimethylammonium chloride (CTAC) up to a concentration of 6.4×10^{-5} M, which is much less than the typical critical micellar concentration of CTAC in water (1.3 mM at 25 °C[17]). The absorption band corresponding to the $S_0 \rightarrow S_2$ transition (peaking at about 230 nm) appears to be more sensitive than the $S_0 \rightarrow S_1$ transition (peaking at about 290 nm) to the interaction with CTAC (Fig. 2A) owing to the higher oscillator strength of the former transition. After normalization, the absorbances at 230 nm and at 300 nm continuously drop with increasing surfactant concentration; however, at higher ionic strengths (0.1 M), the absorbance at 300 nm increases for [CTAC]/[CD-NA] greater than 7 (Fig. 3A). This peculiar behaviour will be discussed later on. The fluorescence spectrum (Fig. 2B) exhibits two maxima at 353 and 410 nm; the first one corresponds to monomer emission and the second one to excimer emission. The evolution of the fluorescence spectrum on addition of CTAC is quite complex (Fig. 3B). The decrease in the ratio of the fluorescence intensities at 410 and 353 nm (Fig. 3C) reveals a gradual decrease of the probability of excimer formation on addition of CTAC. It is interesting to note that, at low ionic strength, the variation is found to be almost linear up to a ratio [CTAC]/[CD-NA] of about 15.

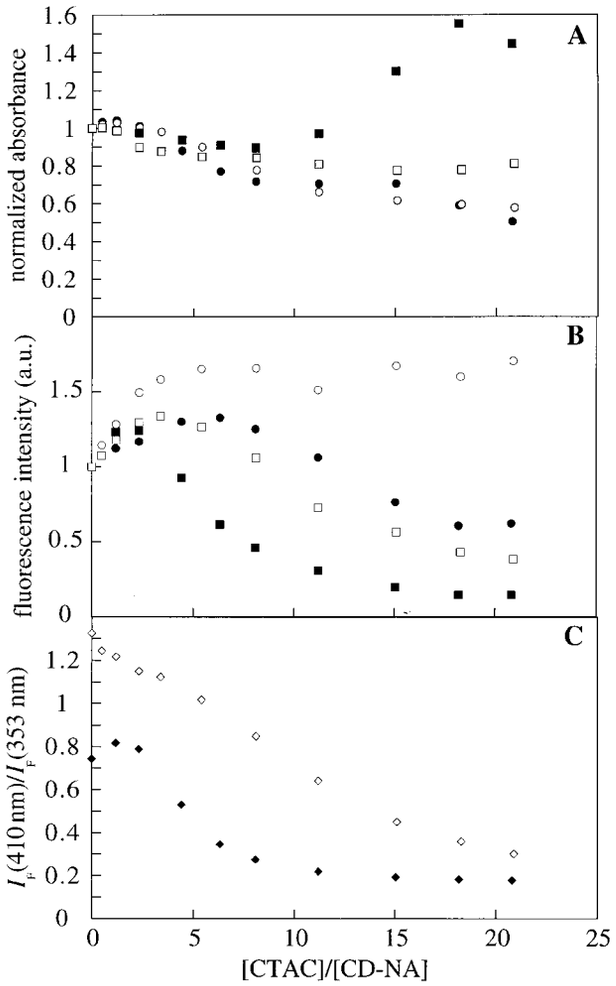


Fig. 3 (A) Evolution of the absorption spectrum at 230 nm (circles) and at 300 nm (squares) as a function of the ratio [CTAC]/[CD-NA]; (B) Evolution of the fluorescence intensities at 410 nm (excimer: squares) and at 353 nm (monomer: circles) (λ_{exc}: 300 nm); (C) Evolution of the ratio of the fluorescence intensities at 410 nm and at 353 nm (diamonds) on addition of CTAC to CD-NA. Empty markers: pH = 9, ionic strength: 0.005 M, [CD-NA] = 3.08×10^{-6} M. Filled markers: pH = 10, ionic strength: 0.1 M, [CD-NA] = 2.9×10^{-6} M.

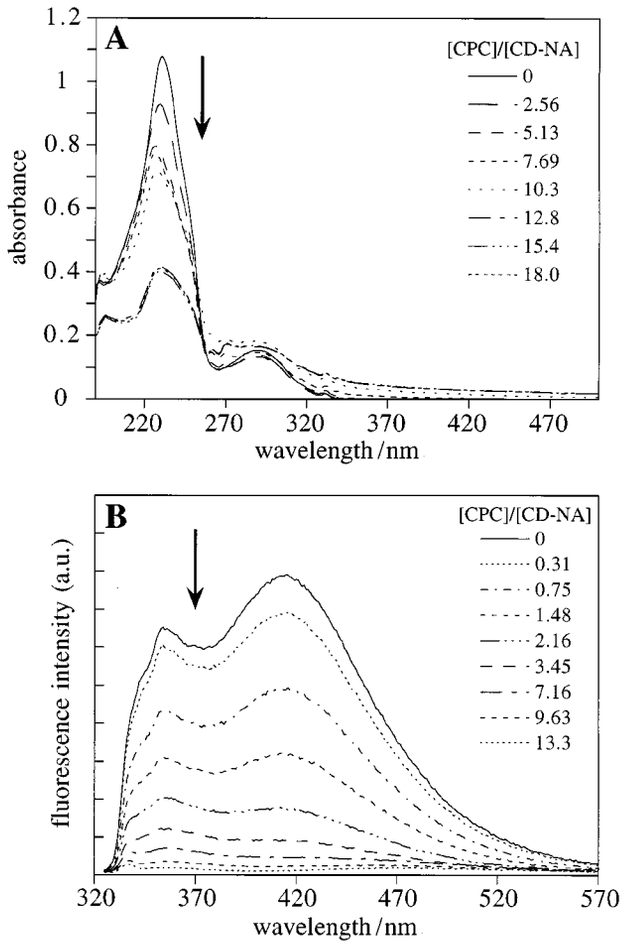


Fig. 4 Evolution of the absorption spectrum (A) and the fluorescence spectrum (λ_{exc}: 300 nm) (B) of CD-NA (4.23×10^{-6} M) on addition of CPC in an aqueous buffer at pH 9 (ionic strength: 0.005 M). The fluorescence spectra are corrected for the instrumental response and for the changes in absorbance at the excitation wavelength.

Investigation of the effect of cetylpyridinium chloride (CPC) on the absorption spectrum of CD-NA (concentration: 4.23×10^{-6} M; ionic strength: 0.005 M) requires special care because CPC absorbs UV light up to 280 nm. Disturbance of the absorption spectrum of CD-NA can be avoided by subtracting the contribution of CPC; this can be achieved by introducing the same amount of CPC into the reference cuvette (containing the same volume) as in the sample cuvette. The changes in the absorption spectrum of CD-NA are then similar to those observed with CTAC up to a ratio [CPC]/[CD-NA] of about 7 (Fig. 4A). The concentration of CPC is then 5.6×10^{-5} M which is much less than the critical micellar concentration in water at room temperature (8.2×10^{-4} M).[18] In contrast to the CTAC series of experiments, a long tail of the absorption band gradually appears as the surfactant concentrations increases, especially at concentration greater than 3×10^{-5} M (Fig. 5A). This means that the incident light is gradually more and more scattered by the solution owing to the formation of aggregates. The existence of aggregates was confirmed by light scattering experiments. The dramatic evolution of the fluorescence spectrum on addition of CPC (Fig. 4B) clearly shows a very efficient quenching of fluorescence which is very likely to be due to photoinduced electron transfer, in accordance with previous studies showing the electron transfer from pyrene and perylene excited singlet states to CPC.[19] The Stern–Volmer plots turned out to be far from linear as a result of the variety of quenching rates due to differences in accessibility of the naphthoate chromophores to the quencher molecules.

In conjunction with this quenching effect, the ratio of excimer emission to monomer emission decreases. The fluorescence intensities at 410 nm and at 353 nm are shown in Fig. 5B and the ratio of them in Fig. 5C.

The results obtained with CTAC and CPC show that the nature of the CD-NA–surfactant interactions is quite complex. Therefore, an investigation of the effects of the same surfactants on the reference compound MOD-NA is a prerequisite before any attempt at interpretation.

Addition of cationic surfactants to MOD-NA

The effects of addition of CTAC to the reference chromophore MOD-NA were investigated under the same conditions (pH and ionic strength) and in the same range of relative concentrations of chromophore and surfactant (the concentration range is thus about seven times smaller for MOD-NA than for CD-NA). The absorption spectrum (Fig. 6A and 7A) is significantly affected in the presence of CTAC, but much less than in the case of CD-NA (Fig. 2A). After correction for the changes in absorbance at the excitation wavelength, the fluorescence spectrum is only slightly affected (Fig. 6B and 7B) and the ratio of fluorescence intensities at 410 and 353 nm remains essentially constant.

For CPC, the changes in the MOD-NA absorption spectrum (studied using the same subtracting procedure as for CD-NA) are similar to those observed with CTAC. No significant evolution of the fluorescence spectrum was observed after correction for the changes in absorbance, although some

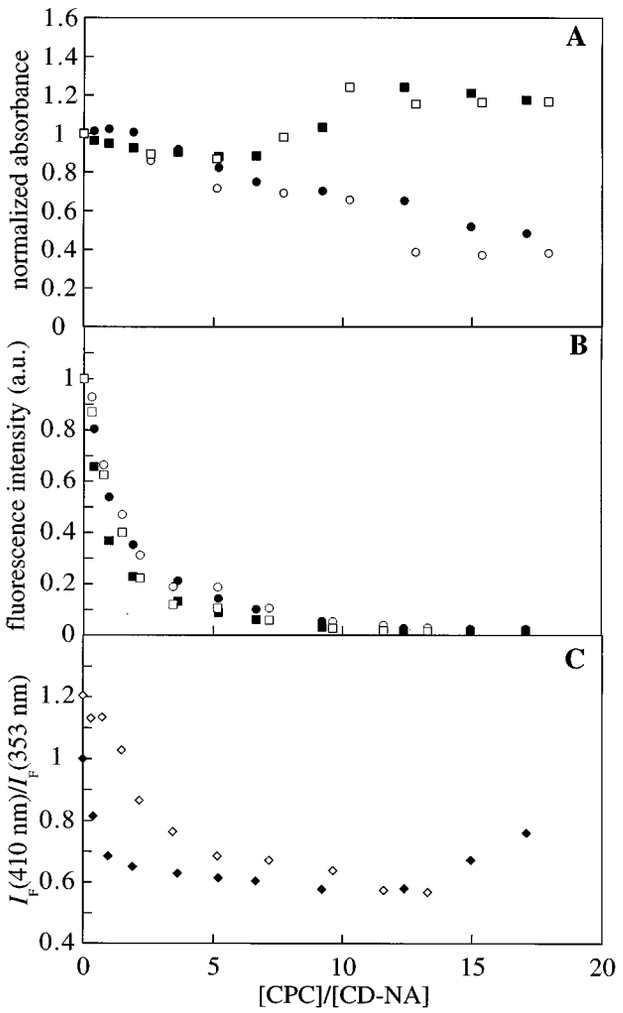


Fig. 5 (A) Evolution of the absorption spectrum at 230 nm (circles) and at 300 nm (squares) as a function of the ratio [CPC]/[CD-NA]; (B) Evolution of the fluorescence intensities at 410 nm (excimer: squares) and at 353 nm (monomer: circles) (λ_{exc}: 300 nm) (4.23×10^{-6} M); (C) Evolution of the ratio of the fluorescence intensities at 410 nm and at 353 nm (diamonds) on addition of CPC to CD-NA. Empty markers: pH = 9, ionic strength: 0.005 M, [CD-NA] = 4.23×10^{-6} M. Filled markers: pH = 10, ionic strength: 0.1 M, [CD-NA] = 2.95×10^{-6} M.

decrease of the fluorescence intensity was expected from the quenching due to photoinduced electron transfer. The possible concomitant increase in quantum yield due to environmental effects (as observed with CTAC at low ionic strength) may compensate for this decrease.

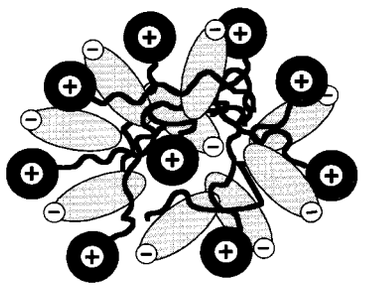
These observations suggest that i) an interaction occurs between MOD-NA and the positively charged surfactant molecules at concentrations as low as 10 μM for both CTAC and CPC; ii) the corresponding interaction is not associated with a major change of the MOD-NA photophysical properties apart from a small hypochromic effect.

Discussion

Before discussing the interaction between cationic surfactants and CD-NA, attention should first be paid to the reference chromophore MOD-NA.

MOD-NA–surfactant interaction

In view of their respective structures in basic aqueous solutions, the interaction between MOD-NA and the surfactant molecules can be tentatively accounted for by assuming the formation of mixed micelles involving the positively charged surfactants and the oppositely charged naphthalenic MOD-NA counter-ions (Scheme 2). Such observations have already been made in



Scheme 2

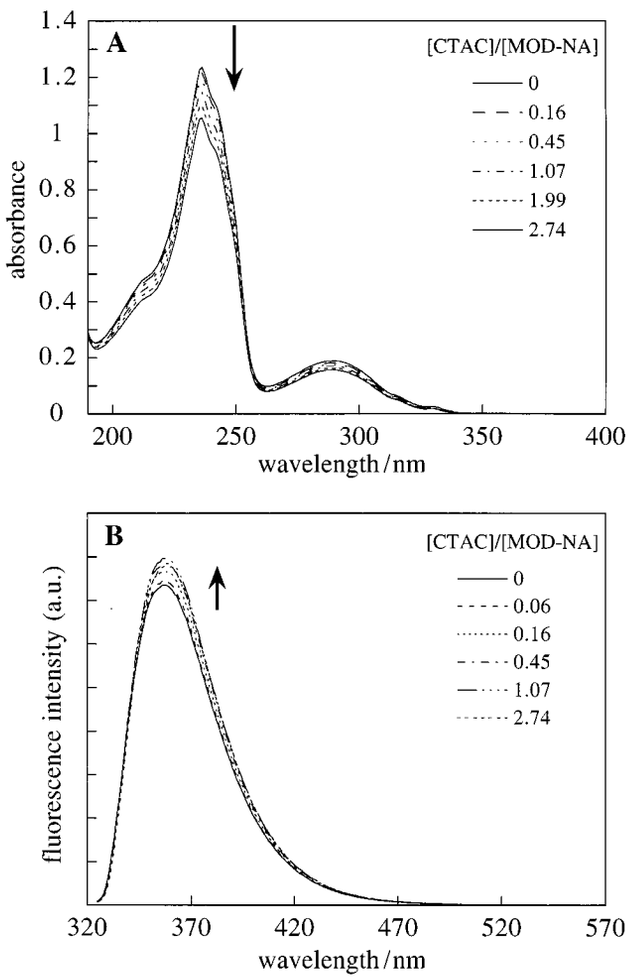


Fig. 6 Evolution of the absorption spectrum (A) and the fluorescence spectrum (λ_{exc}: 300 nm) (B) of MOD-NA (2.34×10^{-5} M) on addition of CTAC in an aqueous buffer at pH 9 (ionic strength: 0.005 M). The fluorescence spectra are corrected for the instrumental response and for the changes in absorbance at the excitation wavelength.

other series[20] and were explained by the attractive hydrophobic and electrostatic terms between interacting species. In the present system, the formation of small aggregates was confirmed by light scattering experiments for both MOD-NA–CTAC and MOD-NA–CPC experiments. Accordingly, the hypochromic effect observed upon addition of surfactants to MOD-NA could result from the regime of weak coupling between several MOD-NA molecules contained in the same aggregate (Scheme 2).[21] Along this line, the larger hypochromic effect upon addition of CPC may be accounted for by the additional hetero-coupling of the naphthalene and pyridinium chromophores.

The observed effect of ionic strength on the evolution of absorption and fluorescence spectra is consistent with a micellization process. The observed delay in the micellization process that manifests itself by a slower evolution at 0.1 M than at 0.005 M (Fig. 7A and 7B) is in line with the smaller capability of inducing micelle formation at larger ionic strength due to

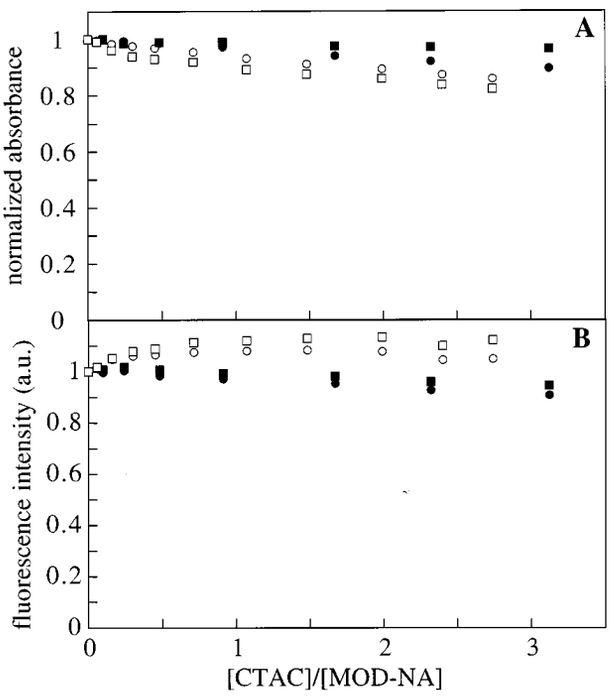


Fig. 7 (A) Evolution of the absorption spectrum at 230 nm (circles) and at 300 nm (squares) as a function of the ratio [CTAC]/[MOD-NA]; (B) Evolution of the fluorescence intensities at 410 nm (excimer: squares) and at 353 nm (monomer: circles) (λ_{exc}: 300 nm) on addition of CTAC to MOD-NA. Empty markers: pH = 9, ionic strength: 0.005 M, [MOD-NA] = 2.34×10^{-5} M. Filled markers: pH = 10, ionic strength: 0.1 M, [MOD-NA] = 1.4×10^{-5} M.

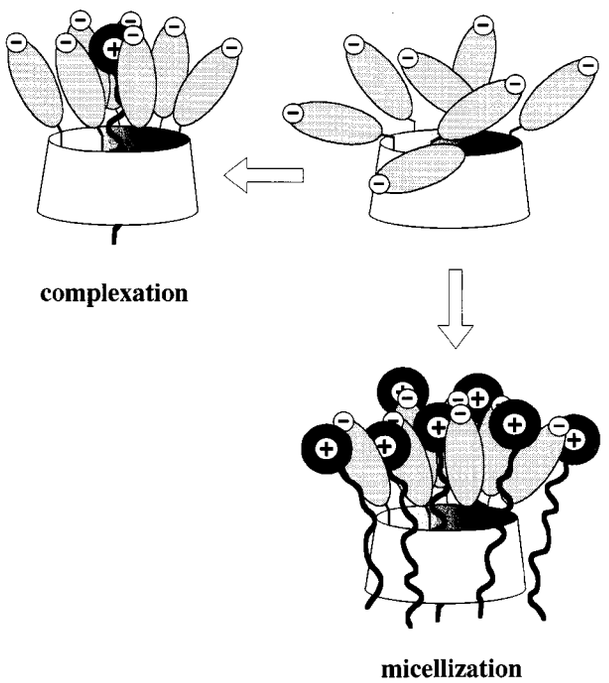
the screening of the electrostatic interaction between MOD-NA and the surfactant molecules.

The MOD-NA induced micellization process was further supported by the result of an experiment using the surfactant HDHAB (Fig. 1) whose molecular structure is close to CTAC except for a shorter alkyl chain and the presence of terminal hydroxy groups. A similar contribution of the electrostatic term for MOD-NA–surfactant interaction is thus expected whereas a marked increase of the critical micellar concentration of the corresponding surfactant † suggests that the hydrophobic driving force for association is much lower. Under the same conditions as for CTAC and CPC, no significant change in either absorption or emission spectra of MOD-NA was observed on addition of HDHAB.

CD-NA–surfactant binding

The interactions between CD-NA and the cationic surfactants can now be discussed. The absence of drastic changes in the photophysical properties of the naphthalene chromophore—only a small hypochromic effect upon addition of surfactant—suggested *a posteriori* that the evolution of the absorption and emission spectra of CD-NA is governed by conformational changes at the level of the CD-NA crown of grafted chromophores. In fact the steep drop of the absorption band corresponding to the $S_0 \rightarrow S_2$ transition could be reasonably explained by a change of coupling regime between the elementary naphthalene chromophores on the CD-NA rim.[22] Additionally, the decrease of the excimer/monomer emission ratio could reveal a related modification of the static and/or dynamic distribution of the naphthalene chromophores.‡

With the MOD-NA–induced micellization of the surfactant molecules in mind, we attempted to address the behavior of the surfactants towards CD-NA. Indeed the conformational changes at the level of the circular arrangement of naphthalene chromophores could be satisfactorily explained by complexation of the surfactant tail within the CD-NA cavity and/or by CD-NA–induced micellization (Scheme 3). These two



Scheme 3

processes will be successively examined in the light of observations previously reported in the literature.

Let us consider first the complexation process: it has previously been shown that native β-cyclodextrin can form 1:1 inclusion complexes with decyltrimethylammonium bromide[10] and cetyltrimethylammonium bromide.[14] The presence of charges on the cyclodextrin rim has a strong influence on the ability to include a guest. Kano and coworkers[23] have recently shown that the association constant of a methylbenzoate anion with a β-cyclodextrin bearing 7 NH_3^+ groups is 60 times larger than with the native β-cyclodextrin.

In addition to this complexation process, micellization deserves special attention because of the analogy that can be made with the association of oppositely charged polyelectrolytes and surfactants:[24] it has been shown that such an association takes place according to an exchange process where the electrostatic forces of interaction are reinforced by a cooperative process involving aggregation of the alkyl chains of the bound surfactant molecules.

The relative contributions of the complexation and micellization processes can be addressed by examining the effect of addition of HDHAB and the influence of the ionic strength under the same conditions as in experiments with CTAC and

† The critical micellar concentration of HDHAB was not determined but can be crudely estimated in the following way. First the critical micellar concentration in water at room temperature of the corresponding methacrylate derivative $HO–(CH_2)_{11}–N^+(Me)_2–CH_2–CH_2–OOC–C(CH_3)=CH_2$ is about 13–25 mM according to the method for determining the cmc (S. M. Hamid and D. C. Sherrington, *Polymer*, 1987, **28**, 325). Additionally, the same authors report on the significant effect on cmc of the OH group terminating the long alkyl chain. A comparision between the simple C_{10} and C_{12} alkyl homologues (without a terminal OH group) and the corresponding hydroxy terminated surfactants suggests that the presence of OH increases the cmc by a factor of 2–3. Since the cmc of $C_{12}H_{25}–N^+(CH_3)_2–CH_2–CH_2–OH$, Br^- is equal to 6 mM in water at room temperature (D. Cochin, A. Laschewsky and F. Nallet, *Macromolecules*, 1997, **30**, 2278), one can thus extrapolate a cmc in the 10–20 mM range for HDHAB.

‡ No major change in the lifetime of the first singlet excited state is expected so as to be responsible for the change of the excimer/monomer emission ratio.

CPC. First, in view of the rather close structure between HDHAB and CTAC or CPC (head-group charge, presence of a large alkyl tail), the interaction according to the complexation model within the CD-NA cavity should be similar for HDHAB and the other investigated positively charged surfactants. In contrast, due to the much larger value of the critical micellar concentration for HDHAB, the association involving the formation of a micelle at a few tens of micromoles should be strongly disfavoured with respect to CTAC and CPC. In fact, no interaction was experimentally observed between CD-NA and HDHAB, which is in favour of a major contribution of the micellization process.

The effect of ionic strength will now be examined. In contrast to the experiment performed at an ionic strength of 0.005 M, the absorption spectra at 0.1 M exhibit a noticeable increase in absorbance at 300 nm at surfactant/CD-NA ratios exceeding 7 for both CTAC and CPC. Light scattering experiments showed that this increase in absorbance is due to the presence of large aggregates under such conditions. This is compatible with the formation of large objects such as elongated micelles, while it is difficult to invoke a complexation process. From this point of view, two points are worth mentioning: i) in agreement with its lower critical micellar concentration, CPC is more easily aggregated by CD-NA than CTAC; ii) the light scattering manifested at 0.1 M ionic strength upon addition of CTAC could reveal the smaller area of the CTAC head-group under such conditions that leads to the formation of more elongated micellar structures than during the experiments performed at 0.005 M ionic strength.

All these observations support an association of CD-NA and cationic surfactants *via* a micellization process as pictured in Scheme 3. In the presence of micromolar CD-NA concentrations, the surfactant critical micellar concentration is shown to drop by a factor of 20–30 for positively charged species. This inducing power is sufficient to promote the micellization of CTAC and CPC, whereas it is not large enough to overcome the large critical micellar concentration of HDHAB that consequently does not interact with CD-NA in the investigated range of concentrations.

It is worth noting that CD-NA compares well to polyelectrolytes in the presence of oppositely charged surfactants, qualitatively as well as quantitatively. The following features relevant to polyelectrolytes[24] are equally valid for CD-NA: (i) the critical micellar concentration of a surfactant is much lower in the presence of an oppositely charged polyion; (ii) addition of salt substantially reduces the affinity of binding because of the electrical shielding of charges; (iii) the turbidity of solutions of polyions and oppositely charged surfactants sharply increases in the range of molar equivalence (*e.g.* polyvinyl sulfate–cetyltrimethylammonium bromide mixtures); (iv) alkylpyridinium surfactants are bound more strongly to negatively charged polymers than alkyltrimethylammonium.

CD-NA–SDS interaction

It is now of interest to examine the effect of an anionic surfactant like SDS (sodium dodecyl sulfate). No significant changes in absorption and emission spectra when SDS was added to CD-NA were observed. This result is in line with the large intrinsic value of the critical micellar concentration (8.1 mM in water at 25 °C) that is expected to disfavour the CD-NA–SDS interaction at rather low surfactant concentrations, as in the case of HDHAB. Additionally, the presence of CD-NA would not strongly induce a micellization at low surfactant concentrations since the charges of CD-NA and SDS species are of the same sign. Similarly, the association between polyelectrolytes and surfactants of the same charge has been shown to be feeble or absent.[24] The charge–charge repulsion dominates over the attractive hydrophobic interaction involving the surfactant tail.

The absence of photophysical effects on the addition of SDS does not necessarily mean that there is no interaction at all with CD-NA. Inclusion of the surfactant tail in the cavity through the secondary rim bearing no charge is indeed to be considered since several studies have shown that native β-cyclodextrin can form 1:1 inclusion complexes with SDS.[12,13] However, it has been shown that the presence of charged groups significantly decrease the hydrophobic nature of the cyclodextrin cavity.[23]

CD-NA as a fluorescent sensor of cationic surfactants

Regarding the sensing capability of CD-NA towards cationic surfactants, the stability of the aggregates of CD-NA with CTAC and CPC is to be considered. Information can be drawn from the variations of several spectroscopic parameters: the absorbance at 230 nm, the monomer emission and the ratio I_F(410 nm)/I_F(353 nm). Given the total CD-NA and surfactant concentrations, the concentration ratio [surfactant]/[CD-NA] at which the spectroscopic parameters are decreased by a factor of 2 (at an ionic strength of 0.005 M) are: 2.5×10^{-5} M (CTAC) and 5×10^{-6} M (CPC) (these numerical values would be equal to the apparent dissociation constants if the stoichiometries of the complexes were 1:1). Such low values make the CD-NA assay a sensitive method for detecting very low amounts of surfactant molecules in residual water: the ranges are 3×10^{-6} to 5×10^{-5} M with CTAC and 10^{-6} to 1.5×10^{-5} M with CPC. It should be noted that complexation can be monitored by the ratio I_F(excimer)/I_F(monomer). Ratiometric measurements at two emission wavelengths are thus possible which is a distinct advantage for practical applications; in fact the ratio is directly related to the surfactant concentration, so that no external calibration is necessary.

Conclusion

In contrast to anionic surfactants, addition of cationic surfactants induces strong changes in the emissive properties of the heptachromophoric β-cyclodextrin CD-NA. The association of cationic surfactants with CD-NA can be understood in terms of formation of mixed micelles as in the case of oppositely charged polyelectrolytes and surfactants.

The changes in emissive properties, and in particular the ratio of the fluorescence intensities corresponding to excimer and monomer emissions of the appended chromophores, provide a new tool for the detection of surfactants in aqueous solutions with an outstanding sensitivity (concentrations ranging from a few μM to tens of μM).

Acknowledgements

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