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Influence of colloid suspensions of humic acids upon the alkaline fading of carbocations

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The influence of humic substances (HSs) upon the alkaline hydrolysis of crystal violet (CV) and malachite green (MG) has been studied. Important inhibition of hydrolysis reaction has been reported. This inhibition has been explained in terms of association of reactants to the humic substances. Kinetic results have been modelized using the micellar pseudophase model. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: colloid suspensions; humic; crystal violet; malachite green; basic hydrolysis

INTRODUCTION

Humic substances (HSs) make up a large portion of the organic matter found in natural environments with a typical concentration ranging from 0.1 to 200 mg L^{-1} dissolved organic carbon.[1] HSs are anionic polyelectrolyte that represents 65–75% of the total organic matter in soils. Average molecular weight ranges from 2 to 400 kDa, depending on the determination method.[2] An empirical formula for the basic structure of HA has been proposed[3]: $C_{72}H_{43-95}O_{30}N_4 \cdot (0\text{–}38)\ H_2O$. They are characterized spectrosocopicaly by a strong band of aliphatic absorption (C—H) between 2980 and 2920 cm^{-1} and other two bands at 1720 and 1650 cm^{-1} due to the presence of carbonyl and carboxyl groups. HSs specific surface is around 900 $m^2\,g^{-1}$ and their negative surface charge presents a large dependence with pH (surface charge increases on increasing pH). This surface charge is mainly due to the deprotonation of carboxyl and phenol groups (both of them represent the 85–90% of surface charge of humic aggregates).[1] The presence of amino groups may justify the presence of positive charges in the humic surfaces but as compared with the negative charges due to carboxyl and phenol groups, it is negligible. Full ionized the capacity of cationic interchange (CIC) is 0.3–0.6 $mol_{(+)}\,kg^{-1}$.

HSs can complex many environmental pollutants.[4,5] In particular, they are able to complex heavy metals[6,7] (due to presence of —COOH and —OH groups in their molecules), and persistent organic xenobiotics[8,9] (due to presence of hydrophobic structures in their molecules), but also strongly interact with mineral surfaces.[10] The interaction of HSs with xenobiotics may modify the uptake and toxicity of these compounds by living organisms, and affect the fate of pollutants in the environment. If traditionally HSs have been considered as inert, then nowadays many aspects of their reactivity change understanding about their role in the environmental processes and rather they are considered as reactive carriers, influencing fluxes of substances. In the same time just the reactivity of HS has been comparatively little analysed, although HSs contain many groups and structures which in similar macromolecules are responsible for their catalytic activity.[11,12] This question is of particular importance, as far as commonly as the main factor responsible for removal of organic xenobiotics (pesticides, PCBs, PAHs and many other substances) are regarded micro-organisms, neglecting the role of HSs. Amongst properties of HS possibly influencing their catalytic activity can be mentioned in their ability to form micelles.[13–16] There are few studies in which catalytic activity of HSs has been compared.[11,12,17–19] In the same time the study of the catalytic activity of HSs may be very important, considering their possible role in the fate in biogeochemical cycling of elements and high concentrations of HSs in natural environments. Velocity of different reactions could be influenced by the presence of HSs. Reactions of interest would be related to hydroxyl ion attack, much studied to evaluate different aspects of micellar catalysis.[20–23]

The alkaline fading of stable triarylmethyl carbocations (Scheme 1) is a reaction with a long chemical tradition. The rate for the process – in spite of being a cation-anion combination – is slow enough for a conventional kinetic study, and in fact, the reaction has become a popular one for undergraduate laboratories.[24,25] Reaction also takes place with nucleophiles other than OH^-, a fact that has been used for the construction of the familiar Ritchie N^+ nucleophilicity scale.[26–32] In spite of the many studies made of the mechanism of these reactions, some mechanistic essential details are still confused and the reaction has become one of the main challenges to the reactivity-selectivity principle.[33–44]

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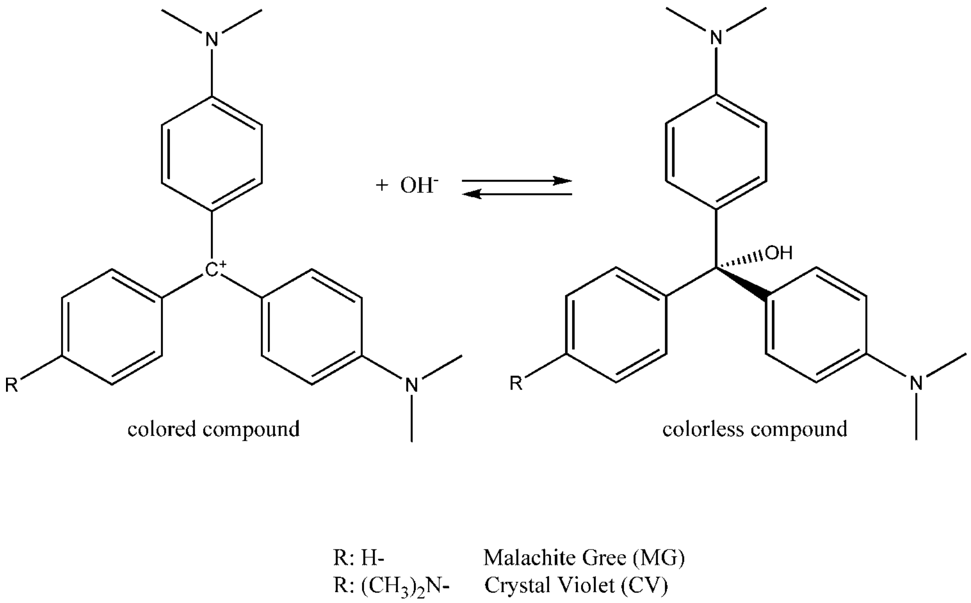


Scheme 1.

The reaction has also become a useful one for studying chemical reactivity colloids and other micro-organized media. One of the first studies on micellar catalysis and inhibition referred to the alkaline fading of crystal violet (CV),[45] and these reactions have been used later very often for studies in normal micelles,[46–49] micelles in the presence of additives,[50–53] reverse micelles or microemulsions[54–61] and clusters.[62] The reaction is typically a 'well-behaved' one and has become an interesting source of information on the role of the different factors that affect overall reactivity in micelles of HSs (i.e. compartmentalization of the reagents, characteristics of the humic aggregate as reaction medium). The aim of the present work was to study the catalytic activity of HSs in mentioned reactions and its rationalization in the bases of the pseudophase model for micellar catalysis.

EXPERIMENTAL

Reactives

All reagents were Merck or Sigma-Aldrich products of the maximum commercially available purity, and none required further purification. All aqueous solutions were prepared by weight using double-distilled degasified water.

Humic substances isolation and characterization

HSs used in this study were isolated from soil.[63] The composition of the HSs used was determined by CNH elemental analysis using a Fisons EA-1108 elemental analyser (518 g kg^{-1} C, 40 g kg^{-1} N and 40 g kg^{-1} H). Its ash content was 61 g kg^{-1}. HSs functional group distribution has been determined by the Schinitzer methods.[64] The functional group distribution was: total acidity 5.99 mol kg^{-1}, COOH groups 3.30 mol kg^{-1} and total OH groups 2.91 mol kg^{-1}.[65,66]

Kinetic measurements and data analysis

Reaction kinetics was recorded at 25.0 ± 0.1 °C in a Kontron Uvikon 923 spectrophotometer equipped with thermostated cell carriers ($T = 25\,°C$). The disappearance of the absorbance at 590 nm (CV) and 610 nm (MG) due to dye consumption was followed. The initial concentration of dye (8.0×10^{-6} M for VC and 1.5×10^{-5} M for MG) was always much lower than that of the other reagents. The kinetic data always fitted the first-order integrated rate equation satisfactorily ($r > 0.999$; Eqn (1)); in what follows, k_{obs} denotes the pseudo first-order constant:

$$\ln(A_t - A_\infty) = \ln(A_i - A_\infty) - k_{\text{obs}}t \qquad (1)$$

where A_i, A_t and A_∞ are the absorbance at $t = 0$, at a given time, and at $t = \infty$, respectively.

RESULTS AND DISCUSSION

Basic hydrolysis of CV and MG in water

Although the hydrolysis of CV and MG in homogeneous media has been thoroughly studied[67] we examine the basic hydrolysis of both carbocations to ensure good consistency in the evaluations of the experimental results. Figure 1 shows the influence of [NaOH] upon the pseudo first order rate constant of both reactions. The rate constant (k_w) for the basic hydrolysis of CV in aqueous medium is $k_w = (12.3 \pm 0.2)$ M^{-1} min^{-1}, and the corresponding one value for basic hydrolysis of MG is $k_w = (181 \pm 6)$ M^{-1} min^{-1}. They are in good concordance with the literature.

Association of dyes to humic substances

UV spectra of CV and malachite green (MG) have been carried out in the presence and in the absence of humic aggregates. CV and MG UV spectra are strongly influenced by the medium.[68–73]

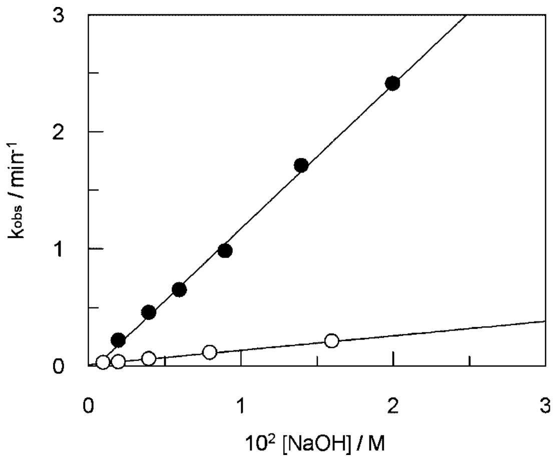


Figure 1. Influence of [NaOH] upon the pseudo first order rate constant of basic hydrolysis of CV (○) and MG (●) in water. $T = 25\,°C$

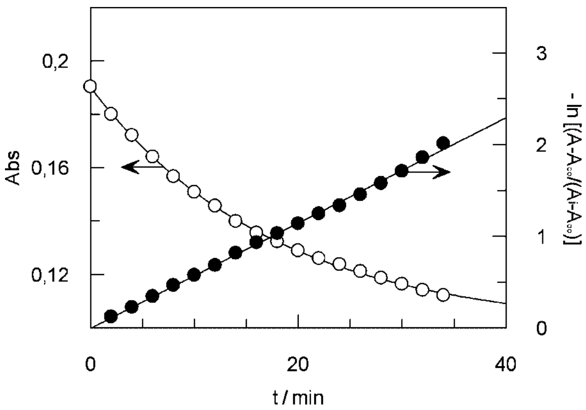


Figure 3. Pseudo-first order kinetics for alkaline fading of CV in the presence of HSs. [HSs] = 24 mg L^{-1}, [NaOH] = 0.01 M. (○) Exponential fit (●) linearized fit (Eqn (1)) [$\lambda = 580$ nm]

Figure 2 shows the changes in the UV spectra of CV in the presence of HSs. The increase in HSs concentration implies a decrease in the absorbance value at $\lambda = 580$ nm. Also changes in the spectrum shoulder ($\lambda = \sim 545$) have been observed. The addition of HSs results in changes of Maximum/Shoulder ratio. It is well known that CV and MG spectrums have high sensibility to the nature of the solvent and the chemical environment of the molecule, hence, large solvatochromic effects were reported in the literature[68–73] as well as the formation of ionic pairs between the CV and different substrates.[74–77] In particular this result was observed previously in the literature due to the sorption of CV to other colloid aggregates.[78–81] Similar results (data not shown) were found for MG. In both cases the association of dyes to the HSs has been proved.

Basic hydrolysis of dyes in the presence of HSs

The influence of humic aggregates on the alkaline fading of VC and MG has been studied. The concentration of HSs has been varied between 0 and 24 mg L^{-1}. To minimize the possible consumption of NaOH by HS, for each concentration of HSs the influence of NaOH concentration on the basic hydrolysis of both carbocations was investigated. Figure 3 shows a typical Absorbance versus time trace for this reaction. Solid line represents the satisfactory fit of Eqn (1) to experimental results. The NaOH concentrations were 0.01, 0.02, 0.03 M for the basic hydrolysis of CV and 0.001 M, 0.002 M and 0.003 M for the basic hydrolysis of MG. These concentrations of NaOH imply that all humic acid would be as sodium humate.

Figures 4 and 5 show the influence of NaOH concentration for different HSs concentrations for CV and MG fading, respectively. From the slope of these linear fits the apparent bimolecular rate constant ($k_{2,app}$) for our reactions is obtained.

The presence of HSs inhibits the basic hydrolysis of both carbocations. Figures 6 and 7 show the influence of HSs upon the apparent bimolecular rate constant for our reactions ($k_{2,app}$). The presence of HSs implies an inhibition of 4.5 times in the CV fading and 24 times in the MG hydrolysis. This inhibition is due to the association of carbocations to the HSs substances and it can be explained in terms of pseudophase model.

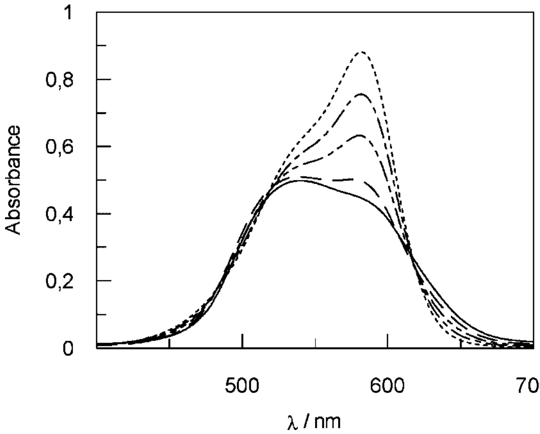


Figure 2. UV spectrum of CV in the presence of humic substances. Dot line $C_{HSs} = 0$ mg L^{-1}, dash-dot line $C_{HSs} = 1.0$ mg L^{-1}, dash-dot-dot line $C_{HSs} = 2.0$ mg L^{-1}, dash line $C_{HSs} = 4.0$ mg L^{-1}, solid line $C_{HSs} = 8.0$ mg L^{-1}. [CV] = 8.5×10^{-6} M

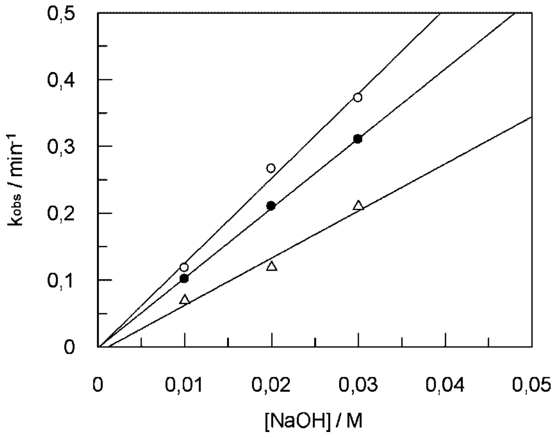


Figure 4. Influence of [NaOH] upon pseudo-first order rate constant for alkaline fading of CV in the presence of HSs. (○) [HSs] = 2mg L^{-1}. (●) [HSs] = 4 mg L^{-1}. (Δ) [HSs] = 8 mg L^{-1}

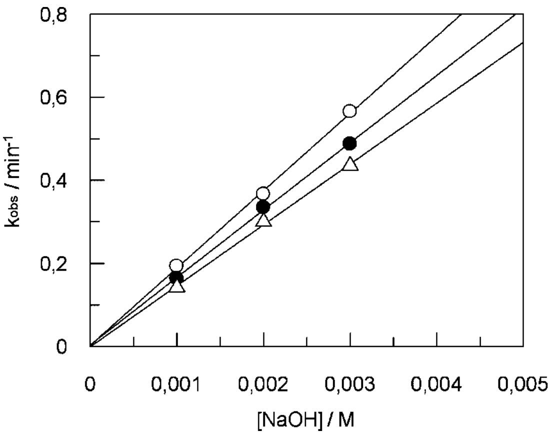


Figure 5. Influence of [NaOH] upon pseudo-first order rate constant for alkaline fading of MG in the presence of HSs. (○) [HSs] = 2 mg L^{-1}. (●) [HSs] = 4 mg L^{-1}. (Δ) [HSs] = 8 mg L^{-1}

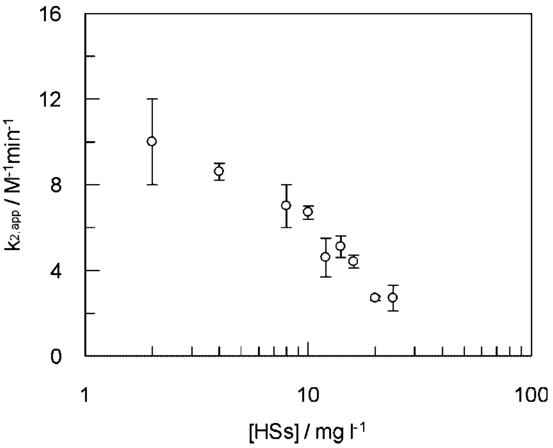


Figure 6. Influence of [HSs] upon apparent bimolecular rate constant for alkaline fading of CV

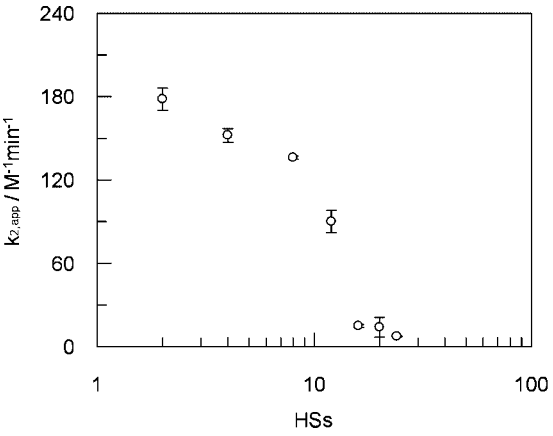


Figure 7. Influence of [HSs] upon apparent bimolecular rate constant for alkaline fading of MG

Pseudophase model

Over the last years, our research group had carried out an exhaustive study of reactivity in microheterogeneous media, and the pseudophase model had been used for a satisfactory quantitative interpretation of a large amount of kinetic results in different microheterogenoeus aggregates (as micelles,[82–84] microemulsions[85–94] or vesicles[95,96]). In HSs dispersions the loci of reaction may be inside the HSs aggregate, in the aggregate surface (at Stern Layer) or at the bulk solvent. The nature of the HSs aggregate, like the interior of a micelle, formed by the hydrophobic portion of the HSs, is not fully understood. But, taking into account the knowledge of micelles, the centre of the HSs aggregate would be similar to liquid hydrocarbon and that water can penetrate the aggregate, so that part of the hydrocarbon chains of HSs from the hydrophilic groups would be exposed to the water. A carbocation adsorbed in the very inner part of a micelle would be inert to hydroxide ion because the anionic nucleophile is certainly absent in the hydrocarbon core.

The HSs surface is another possible site of carbocation adsorption. The ionic portions of the HSs form highly charged surfaces which attract small counterions from the solution in order to relieve electrostatic repulsion. Thermal motion, which tends to produce uniform distribution of the ions, disturbs the ionic array resulting in the well-known electrical double layer. Basic hydrolysis of carbocation can be sensitive to ionic strength changes, so that the high concentration of ions at the double layer would itself greatly affect the reaction. However, adsorption of a dye at the surface of an anionic could result in considerable rate enhancement because some ionic groups of HSs surface can act as nucleophiles and promote himself the fading of the dye. On the other hand, long-range electrostatic effects originating from the charged HSs interface could well be a major factor affecting hydrolysis rates inside this region resulting in an inhibitory effect. Moreover, electrostatic considerations, taking into account the negative surface charge of HSs, can justify the absence of HO^- from the vicinity of HSs aggregate.[97–101] Whereas, in the case that HO^- can approximate to HSs aggregate, we must take into consideration the fact that HSs is a very compact unit, then most of the interior water will be highly structured and in these conditions is well known that basic hydrolysis would be markedly impeded.

A third possibility is that the carbocations are not adsorbed by the HSs aggregates and exist in the free water.

To decide the possible mechanism, we now direct our attention to Figures 6 and 7 which show that HSs inhibit hydrolysis of VC and MG. The remarkable rate inhibitions may be explained by carbocation adsorption into the hydrocarbon centre of the aggregate where presumably there is no anionic nucleophile (HO^-) (*vide supra*). Alternatively, adsorption could occur within the outer aqueous areas of the aggregate where the hydroxide ion concentration might be greatly reduced because of electrostatic factors originating at the HSs surface. The former reason can be neglected taking into account the fact that both CV and MG are ionic substrates. Hence, it would be more reasonable to assume that both of them would not be located in the core of the aggregate. The location of VC and MG in the Stern layer is the most rationale location for our carbocations. The large inhibition observed (Fig. 8) would probe also that the reaction occurs in the bulk water. There are not any other reaction pathways for the alkaline fading of carbocations by the attack of the nucleophilic groups of HSs surface.

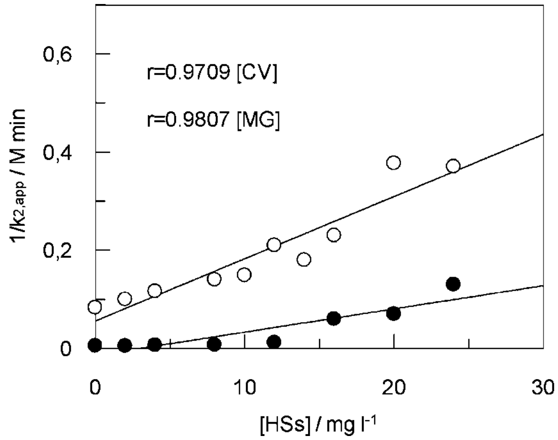


Figure 8. Fit of experimental data to Eqn (3). (○) CV and (●) MG. $T = 25\,°C$

Taking into account all these considerations, we can propose the following reaction (Scheme 2):

This model yields the following equation (Eqn (2)):

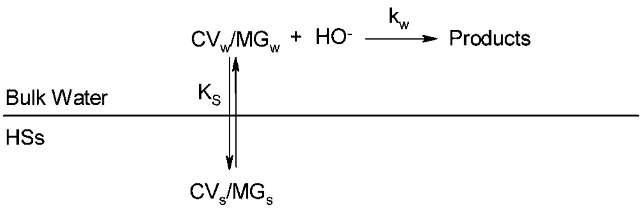
$$k_{2,\mathrm{app}} = \frac{k_\mathrm{w}}{1 + K_\mathrm{s}[\mathrm{HSs}]} \qquad (2)$$

This equation can be easily linearized as

$$\frac{1}{k_{2,\mathrm{app}}} = \frac{1}{k_\mathrm{w}} + \frac{K_\mathrm{s}}{k_\mathrm{w}}[\mathrm{HSs}] \qquad (3)$$

where k_w is the bimolecular rate constant in bulk water, K_s is the binding constant of the substrate to the HSs $\{K_\mathrm{s} = [\mathrm{CV}]_\mathrm{s}/([\mathrm{CV}]_\mathrm{w}[\mathrm{HSs}])$ and $K_\mathrm{s} = [\mathrm{MG}]_\mathrm{s}/([\mathrm{MG}]_\mathrm{w}[\mathrm{HSs}])$ for CV and MG, respectively$\}$. The values of k_w used were the corresponding one in bulk water (*vide supra*). The quality of the fit of the experimental data (Fig. 8) to Eqn (3) was satisfactory. The values of r for the linear fit were 0.9709 and 0.9807 for CV and MG, respectively.

The binding constant of carbocations to the HSs was for CV and MG, respectively $K_\mathrm{s} = (0.13 \pm 0.01)\ \mathrm{mg}^{-1}\,\mathrm{L}$ and $K_\mathrm{s} = (0.65 \pm 0.05)\ \mathrm{mg}^{-1}\,\mathrm{L}$. The higher inhibition of HSs upon the basic hydrolysis of MG that CV reaction is due to the higher value of K_s for this reaction. This value of K_s for MG is related to the lower polarity of this carbocation that CV (CV has got dimethylamino groups in para position in the three benzenic rings while MG has go only dimethylamino groups in two benzenic rings – refer to Scheme 1). For this reason the MG can penetrate deeply in the HSs.



Scheme 2.

CONCLUSIONS

The kinetic effect of the presence of HSs can be modelized using the pseudophase model. The HSs are colloid dispersions in water and their influence upon chemical reactivity can be rationalized considering that HSs are micelle-like colloids. The observed behaviour is similar to the observed one in traditional micelles.[102,103]

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