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Polymeric Surfactant P84/Polyoxometalate α-PW₁₂O_{40³⁻}—A Model System to Investigate the Interplay Between Chaotropic and Hydrophobic Effects

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Abstract: Low charge density nanometric ions were recently shown to bind strongly to neutral hydrated matter in aqueous solution. This phenomenon, called (super-)chaotropic effect, arises from the partial dehydration of both, the nano-ion and the solute, leading to a high gain in enthalpy. Here, we investigate the chaotropic effect of the polyoxometalate α -PW₁₂O_{40³⁻} on the triblock copolymer P84: (EO)₁₉(EO)₁₉ with (EO)₁₉ the polyethoxylated and (PO)₄₃ the polypropoxylated chains. The combination of phase diagrams, spectroscopic (nuclear magnetic resonance) and scattering (small angle neutron/X-ray scattering) techniques reveals that (*i*) below the micellization temperature of P84, PW₁₂O_{40³⁻} exclusively binds to the propylene oxide moiety of P84 unimers and (*ii*) above the micellization temperature, PW₁₂O_{40³⁻} to the PPO chain over the PEO chains suggests that the binding is driven by the chaotropic effect and reinforced by the hydrophobic effect. At higher temperatures, the copolymer micellization leads to the displacement of PW₁₂O_{40³⁻} from the PPO chain to the PEO chains. This study deepens the understanding of the subtle interplay between the chaotropic effects in complex salt-organic matter solutions.

Keywords: chaotropic effect; hydrophobic effect; polyoxometalates; polymeric surfactants; small angle scattering, salt effects

1. Introduction

Polyoxometalates (POMs) show a continuously growing interest in chemistry due to their outstanding properties, e.g. their (photo-)catalytic activity[1–3], applications in medicine[4–6] and many more[7,8]. Currently, the solution behavior of POMs in aqueous medium has attracted much attention in the literature.[9,10] It was demonstrated that POMs with a low charge density, such as phosphotungstate (α -PW₁₂O₄₀³⁻, PW), see Error! Reference source not found.a, bind strongly and non-covalently to neutral hydrated surfaces of non-ionic micelles in aqueous solution.[11] This phenomenon – known as the (super-)chaotropic effect – has been described as a water-mediated effect: the hydration shells of both the POM and (surface) moieties are partially stripped off during binding. The superchaotropic effect is an enthalpy driven process which has been discussed as an extension of the well-known Hofmeister series observed for smaller classical chaotropic ions, such as I- or SCN-, on many physico-chemical and biological phenomena.[12,13] The association constants of superchaotropic POMs and other nanoions (NIs), e.g. ionic boron clusters, with neutral organic solutes/surfaces is typically around three orders of magnitude stronger than for common chaotropic ions. For this reason low charge density NIs were called "superchaotropes".[11,14–16]

A broad spectrum of non-ionic systems was probed regarding their binding with superchaotropic NIs, such as small aromatic molecules,[17] surfactant self-assemblies,[11,15,18,19] oligo- and polymers,[18,20,21] macrocyclic molecules [14,16,22–24] and short-chain amphiphiles.[25]



Figure 1. Molecular representation of (a) the α -Keggin-type anion phosphotungstate (PW₁₂O₄₀³, PW) and (b) the triblock copolymer P84, providing an ABA architecture (Pluronic®-type) with A: ethylene oxide and B: propylene oxide. A sketch of P84 is shown below the molecular structure.

In a previous contribution, our group has explicitly drawn a focus on the interaction of PW with polyethylene oxide (PEO) oligomers. We showed that PW in its acidic form, *i.e.* H₃PW₁₂O₄₀ (HPW), and PEO form nano-assemblies comprising one PW and approximately two PEO oligomers.[20] Such strong binding of POMs on PEO chains was also observed on PEO non-ionic surfactant micelles.[11] The binding of NIs to the PEO corona of these PEO surfactant micelles was monitored by the surfactant's cloud point (CP) evolution which was used as a powerful tool to rank the NIs according to their superchaotropicity.[15,19,23] Later, the interaction of HPW with polypropylene oxide (PPO) chain based was investigated. In the presence of dipropylene oxide *n*-propylether (C₃P₂), HPW forms nano- to mesoscopic self-assemblies in aqueous solution.[25]

As a conclusion, the interaction of HPW was intensively investigated with (*i*) polymers, (*ii*) non-ionic surfactant micelles, (*iii*) PEO-based and (*iv*) PPO-based compounds. A class of compounds, gathering all four features (*i-iv*), are triblock copolymers with an ABA architecture (A: PEO and B: PPO). ABA triblock copolymers are present as unimers (unaggregated form) at low temperature and as micellar aggregates at elevated temperatures (above their critical micellization temperature (CMT)) in aqueous solution.[26–29] Such well-known polymeric surfactants (Pluronic® or Polaxamer®) are used in a broad field of applications, as they solubilize oily compounds,[26,30] are used as drug delivery systems[31,32] or templates in the synthesis of mesoporous materials.[33,34]

Here, we investigate the superchaotropic effect of HPW on the Pluronic® surfactant P84, (EO)₁₉(PO)₄₃(EO)₁₉, see **Error! Reference source not found.**b. We monitored the CP of P84 as a function of HPW concentration to investigate the HPW-P84 association in water. At low temperatures (P84 unimers), ¹H-nuclear magnetic resonance (¹H-NMR) was used to probe the local environment of the PPO and PEO blocks. Above the CMT (P84 micelles), scattering techniques, *i.e.* small angle X-ray and neutron scattering (SAXS and SANS, respectively), were used to investigate shape/charge of the micellar assemblies. The obtained experimental results are discussed in the context of the two water mediated

driving forces[16]: the chaotropic effect (interaction of POM and P84) and the hydrophobic effect (micellization of P84).

2. Materials and Methods

2.1. Materials

Phosphotungstic acid hydrate (H₃PW₁₂O₄₀ · *x*H₂O, HPW, M = 2898 g/mol, 99.995% purity) was purchased from Sigma Aldrich. Concentration calculations were done with $x_{HPW} = 7$. P84 (M = 4200 g/mol) was received as a gift from BASF and used as obtained. Milli-Q water was used with a conductivity lower than 10.5 µS/cm and a total organic carbon content of 400 ppb.

2.2. Cloud point (CP) measurements/phase diagrams

For phase diagrams, 3 g of binary/ternary mixtures were prepared into screwable tubes from borosilicate glass and the samples were heated in a thermostat (Thermomix_1460, B.Braun Melsungen AG) in special tube holders. The thermostat was heated with a rate of 1 °C min⁻¹. The expected precision of the measurements is \pm 1 °C.

2.3. ¹H-nuclear magnetic resonance (¹H-NMR)

Solution ¹H-NMR spectra were recorded with an Avance300 (Bruker) spectrometer using tetramethyl silane as an internal standard. Chemical shifts (δ) are provided in parts per million (ppm) and coupling constants (J) are reported in Hertz (Hz). D₂O was used instead of H₂O.

2.4. Small angle X-ray scattering (SAXS)

SAXS measurements, using Mo radiation ($\lambda_{Mo} = 0.071$ nm), were performed on a bench built by XENOCS. The scattered beam was recorded using a large online scanner detector (diameter: 345 mm, from MAR Research). A large *q*-range (0.2 to 40 nm⁻¹) was covered with an off-center detection. The collimation was applied using a 12: \propto multilayer Xenocs mirror (for Mo radiation) coupled to two sets of scatter less FORVIS slits providing a 0.8 × 0.8 mm X-ray beam at the sample position. Pre analysis of data was performed using FIT2D software. 1 and 2 mm quartz capillaries were used as sample containers for the solutions. The samples were thermostated at given temperatures. Usual corrections for background (empty cell and detector noise) subtractions and intensity normalization using a high density polyethylene film as a standard were applied. Experimental resolution was $\Delta Q/Q = 0.05$. Silver behenate in a sealed capillary was used as the scattering vector calibration standard.

2.5. Small angle neutron scattering (SANS)

All measurements were performed on beamline D33 at the Institut Laue-Langevin (ILL) in Grenoble. The applied measurement mode was a monochromatic mode ($\lambda_{neutron} = 0.6$ nm). Detection was done at 2 and 5 m. Quartz cuvettes from Helma with thicknesses of 1 mm or 2 mm were used as sample containers. The samples were thermostated at given temperatures. The acquisition times were set to 15 minutes taking into consideration sample thickness and composition, *i.e.* the scattering. Water was used as a calibrant in order to obtain absolute intensities. The spectra were treated and normalized using the available software on site. Note, that the presented SANS spectra are subtracted by the signal of D₂O but do contain incoherent scattering. The apparatus was controlled by the NOMAD software and the data treatment was done with the GRASP software on site.[35]

2.6. Light scattering

Samples were measured using a Zetasizer Nano ZS from Malvern Instruments. The samples were illuminated with a 632.8 nm laser and detection was done in backscattering position at an angle of 173°. 1 cm quartz glass cuvettes with a plastic cap served as sample containers. Once set into the measurement chamber the samples were equilibrated for 300 s at the set temperature before the acquisition started. Count rates were collected in

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triplicates for each sample where one measurement consisted of 10 runs of 10 seconds each, which would then be automatically averaged.

3. Results and Discussion

3.1. P84: phase diagram and aggregation

We investigated first the binary phase diagram of P84 and water at $c(P84) \le 10$ wt%, see Fig. 2a. This phase diagram shows three different regions, *i.e.* a transparent (black star), a blueish (red star) and a turbid phase (green star), see pictures in Fig. 2a. For c(P84) > 1 wt%, the phase transitions appear at rather constant temperatures: 60 ± 4 °C (transparent to blueish) and 74 ± 3 °C (blueish to turbid), respectively. Here, the blueish to turbid phase transition temperature is attributed to the CP.[29,36] For c(P84) < 1 wt%, the two phase transitions are shifted to much higher temperatures by decreasing P84 concentration. In the following, a concentration of P84 of 2.5 wt% (6 mmol L⁻¹) was chosen to ensure (i) low concentration that is required for a more convenient fitting and interpretation of the scattering experiments.

The count rate of a 2.5 wt% P84 solution was measured as a function of temperature (along red line in Fig. 2a), see Fig. 2b. The count rate evolution can be divided in three different temperature regimes, called (I), (II) and (III) hereafter. In regime (I) (20-28 °C) the count rate is low (around 300 kcps) as expected for the scattering of unaggregated P84 unimers. In regime (II) (28-54°C) the count rate increases strongly upon heating. This increase in the scattered light intensity can be attributed to the formation of spherical micelles above 28°C, which corresponds to the CMT as expected from previous works.[37] Above the CMT, the micellar core is formed by the partially dehydrated PPO chains and



Figure 2. (a) The binary phase diagram of water and P84 up to c(P84) = 10 wt% shows the presence of a transparent, a blueish and a turbid phase, which is related to the CP of P84. (b) Count rate of 2.5 wt% P84 as a function of temperature, see red line in a), indicating the presence of three types of aggregation of P84((I) - (III)). (c) Schematic representation of the P84 transition with increasing temperature. At room temperature (I) unimers are present which self-assemble to spherical micelles in (II) and to rod-like micelles in (III). In the following emphasis is put on unimers and spherical micelles.

the micellar corona contains the well-hydrated PEO chains.[37,38] At higher temperatures in regime (III), above 55 °C, a drastic increase in the count rate is observed. This high increase in the scattered intensity is attributed to the formation of rod-like micelles, see Fig. 2c. Indeed, this is in agreement with previous works where a transition from spherical to rod-like micelles was reported at 55°C.[38] Reasonably, the blueish phase obtained in Fig. 2a, is likely to arise from elongating rod-like micelles (Tyndall scattering typically in the (sub-)µm regime). In the present study the focus was made on unimers and spherical micelles.Therefore we investigated P84 (2.5 wt%) at 20 °C (unimers) and 50°C (spherical micelles).

3.2. P84: Cloud point evolution upon addition of HPW



Figure 3. Phase diagram of 2.5 wt% P84 as a function of c(HPW) showing a tremendous CP increase (dark squares) and a strong increase in the temperature of appearance of the blueish phase (blue circles).

The CP evolution of a non-ionic surfactant upon the addition of POMs was established as a simple but efficient tool to classify the adsorption of NIs on micelles.[15] Hence, the CP and occurrence of the blueish phase at 2.5 wt% P84 is recorded as a function of c(HPW), see Fig. 3. In absence of HPW the blueish phase occurs at 62 °C and the CP at 72.5 °C. The blueish phase shifts to higher temperatures upon increasing HPW concentration (87 °C for 1 mmol kg⁻¹ HPW), while the temperature of the transparent-to-blueish transition increases and then levels off upon HPW addition. The CP increase is tremendous, as it increases from 72.5 °C up to 100 °C in a very narrow range of concentration (from 0 to 0.05 mmol kg⁻¹ HPW). Such a strong CP increase at low HPW concentration indicates a strong association constant, that can be estimated (KA ~ 20.0 mM⁻¹, see the fitting results, red curve in Fig. 3) from a Langmuir fit according to a previous procedure.[15] The association of HPW with P84 is then around one order of magnitude stronger than with previously investigated systems (using CP measurement to estimate the association constant): poly-N-isopropylamide (PNiPAM10000, KA ~ 2.1 mM-1)[21], polyethoxylated micelles $(C_8E_4, K_A \sim 1.4 \text{ mM}^{-1})[15]$. This stronger association constant obtained with P84 is likely to be due to stronger binding to the more hydrophobic (but still hydrated) PPO chains.

Note, that above 6 mmol kg⁻¹ HPW the system phase demixes (precipitation) which is likely to arise from the strong HPW-P84 binding. The ternary phase diagram water-P84-HPW at room temperature is given in Fig. S1.

3.3. Association of HPW with P84 unimers

To access detailed information on the interaction of HPW with P84, unimeric P84 (20 °C, 2.5 wt%) is investigated by ¹H-NMR in the presence of HPW. First, we checked that P84 remains in the unimeric form in the presence of HPW by SANS (Fig.S2) and SAXS (Fig.S3-4), see the corresponding discussion in section S2.

¹H NMR spectrum for P84 2.5 wt% in D₂O is given in Fig. 4b. P84 exhibits several NMR-active protons: (*i*) CH₂ protons of the PEO moieties (red ellipse), (*ii*) the quaternary proton (yellow circle) in PPO, (*iii*) CH₂ protons (green ellipse) in PPO and (*iv*) protons in the methyl group (blue ellipse) in PPO, see Fig. 4a. These protons were assigned using Shoolery's rules, see Fig. 4b bottom spectrum.[39]

- (*i*) The CH₂ protons of PEO produce a sharp singlet at 3.55 ppm.
- (*ii*) The quaternary proton of PPO produces a multiplet at around 3.49 ppm as it couples with all the neighboring CH₂/CH₃ protons in PPO via a ³J coupling.
- (*iii*) The CH₂ protons of PPO are detected at around 3.41 ppm as a doublet that is overlayed by the multiplet of the PPO quaternary proton (*ii*).

(iv) The CH₃ protons of PPO produce a doublet at 1.01 ppm.

¹H-NMR was measured for 2.5 wt% P84 in the presence of HPW, for $c(HPW) \le 5.5$ mmol kg⁻¹, see Fig. 4b and Fig. S5. A broadening of all peaks is observed by increasing HPW concentration. This peak broadening results from a decreased diffusion of the P84 molecules in solution, i.e. due to the formation of [HPW-P84] assemblies, as previously observed by investigating the superchaotropic effect of HPW on PEO oligomers[20] and γ -cyclodextrin.[23]

Fig. 4c shows the shift of chemical shifts, $\Delta\delta$, of signals stemming from P84 as a function of c(HPW). The CH₂ protons of PEO moieties (singlet) is unaffected upon addition of HPW. On the contrary, the peak positions of CH₂ and CH₃ protons of the PPO moieties are strongly down-field shifted, *i.e.* shifted to higher chemical shifts (ppm): $\Delta\delta$ of 0.035 ppm



Figure 4. (a) Molecular representation of P84 with ¹H-NMR active protons marked in colored ellipses with following scheme: CH₂ protons of the PEO moieties in red and the CH₃ protons of the methyl group (blue), CH₂ protons (green) and the quaternary proton (yellow) in the PPO moiety. (b) Evolution of the ¹H-NMR spectrum of 2.5 wt% P84 upon an increasing concentration of HPW (0, 2.75 and 5 mmol kg⁻¹ from bottom to top). Spectra measured at 20 °C. The color code corresponds to the colors in (a) and therefore indicates the signals stemming from these specific protons. (c) Shift of the chemical shift, *i.e.* $\Delta\delta$, of protons in P84 as a function of c(HPW) indicating a strong interaction of HPW exclusively with the PPO part of P84.

and 0.05 ppm respectively for CH₂ and CH₃ protons upon addition of 5.5. mmol kg⁻¹ HPW. Note, that $\Delta\delta$ cannot be determined for the quaternary proton in PPO due to a strong peak broadening, see Fig. S5.

As a conclusion, HPW binds to P84 unimers which is due to its polymeric nature, while monomeric species (*e.g.* only one PO repetition unit) are not expected to associate with a chaotropic anion[40] such as PW. Here, the HPW binds selectively to the PPO moiety over to the PEO moieties of P84 unimers. PPO is more hydrophobic than PEO and therefore less or weaker hydrated. Therefore, the stronger and selective adsorption of HPW to PPO results from a combination of the chaotropic and hydrophobic effects.

3.4. Association of HPW with P84 micelles

Figure 5a&b show the SANS and SAXS spectra respectively of 2.5 wt% P84 in water (green rectangles) at 50°C, *i.e.* above the CMT. The SANS spectrum of 2.5 wt% P84 in D₂O (green symbols in Fig. 5a) shows the typical shape obtained for isotropic scattering objects which can be attributed to P84 micelles. To access more information on the micelles, a core (PPO-part)-shell (PEO-part) sphere model was used to fit the experimental data (red line in Fig. 5a). The influence of micelle-micelle interactions was considered by using a hard-sphere structure factor *S*(*q*), see details in section S4.2 and Table S3.



Figure 5. (a) SANS and **(b)** SAXS spectra of 2.5 wt% P84 in water (D₂O or H₂O respectively) and in the presence of 2 mmol kg⁻¹ HPW at 50 °C including fits. **(c)** Scattering length density profiles of a P84 micelle in aqueous solution showing that the major contrast giving moiety is PPO in SANS and PEO in SAXS in absence of POM. In presence of HPW, the scattering length density in SAXS is dominated by the PW anions, which are located mostly in the PEO corona. The sketch represents the size shrinkage of P84 micelles and the penetration of PW anions in the micellar PEO corona and partially the micellar PPO core. In the sketch, one P84 represents the whole micelle.

The fit could well reproduce the experimental data and revealed a micellar radius of 6.5 nm, with a core radius is 4.1 nm (PPO part) and a shell thickness (PEO corona) of 2.4 nm, an aggregation number of around 60. These values are in well agreement with literature.[29][41]

In Fig. 5b the SAXS spectrum of 2.5 wt% P84 in H₂O (green rectangles) is shown. The SAXS spectrum differs a lot from the SANS spectrum because of the different scattering length density (q) profiles of the micelles in SAXS and SANS, see the orange (SAXS) and green (SANS) curves in Fig.5c. SAXS is mostly sensitive to the (higher electron density) PEO-corona whereas SANS is mostly sensitive to the micellar dehydrated PPO-core.[26] A fit was applied to the SAXS spectrum, which perfectly reproduces the experimental spectrum (details see section S4.2 and Table S4). The fitting results are in good agreement with literature.[29]

SANS and SAXS spectra were collected in the presence of HPW (2 mmol kg⁻¹) for 2.5 wt% P84 (blue circles). HPW is "invisible" in SANS, as its scattering length density is close to the one of D₂O, whereas it shows a large contrast with H₂O and P84 in SAXS, see Table S1. The SANS spectrum of 2.5 wt% P84 - 2 mmol kg-1 HPW shows a similar shape as the spectrum of 2.5 wt% P84 for q > 0.4 nm⁻¹. At q = 0.26 nm⁻¹ a pronounced correlation peak occurs in the presence of HPW. The correlation peak and the low scattered intensity in the low q (< 0.26 nm⁻¹) reflect strong repulsive micelle-micelle interactions (S(q)). The arising of these repulsive interactions upon addition of HPW is attributed to electrostatic repulsions resulting from the adsorption of the negatively charged PWs on the micelles. To access more information, the experimental SANS spectrum was fitted by using a coreshell sphere model with a Hayter-MSA S(q) that takes into account for electrostatic repulsions.[42,43] The fit reproduces perfectly well the experimental data. The result of the fit revealed a micellar radius of 5.5 nm with a micellar core (PPO) radius of 3.6 nm and a shell thickness (PEO) of 1.9 nm (details see section S4.2 and Table S5). Therefore, SANS suggests that upon the addition of HPW, the radius of P84 micelles shrinks from 6.5 nm to 5.5 nm. This effect is reasonable, as especially PEO is known to "wrap around" PW upon their binding.[11,20] The charge of the micelles obtained from the fitting is 47. From the micelle charge, the number of PW anions per micelle was estimated at around 16, i.e. 47/3, if full dissociation of HPW is considered.

The SAXS spectrum of 2.5 wt% P84 - 2 mmol kg⁻¹ HPW (blue circles in Fig. 5b) differs greatly from the SAXS spectrum of 2.5 wt% P84 (green squares in Fig. 5b): (i) the overall scattered intensity is strongly increased (by a factor of ten), (ii) a correlation peak occurs at 0.31 nm^{-1} , (*iii*) an oscillation appears at 1.12 nm^{-1} and (*iv*) the scattered intensity decreases at q < 0.31 nm⁻¹. The overall intensity increase is attributed to the adsorption of the high electron density (ρ^{SAXS}) HPW. The location of the correlation peak and the pronounced oscillation can only be explained by a tremendous change of the scattering length density profile of P84 micelles. The decreased scattered intensity in the low *q*-regime results from the adsorption of PW anions on the charged micelles, that induces strong electrostatic repulsions between the micelles, as observed in the SANS spectrum (Fig.5a blue circles). Therefore, a core-shell model with a Hayter-MSA S(q) was used to fit the experimental data. The fit gives a micellar core radius is 2.3 nm, composed of PPO, and a shell thickness 2.9 nm, composed partly of the PPO chains and of the PEO chains with adsorbed HPW (see section S4.2 and Table S6). HPW is mostly located in the well-hydrated PEO chains and only partly in the dehydrated PPO micellar core close the PEO-PPO region (as in the sketch in the lower part of Fig. 5c.). These results were precisely confirmed by evaluating the effect of each parameter in the fit, see section S4.2, Fig. S6 and Table S7.

The SAXS/SANS fitting results are well summarized in Fig. 5c that shows the ρ profiles in 1D along the micelle (*i.e.* from its center to the surrounding water) in SANS (green and red curves) and SAXS (blue and orange curves) of P84 micelles in presence (green and blue curves) and absence (red and orange curves) of HPW. *r* is the distance from the center of the micelle to the surrounding (heavy) water. In SANS for P84 micelles in D₂O (green line in Fig. 5c), ρ of the PPO micellar core and of the PEO corona were fitted ($\rho_{PPO}^{SANS} = 1.40 \cdot 10^{10}$ cm⁻² and $\rho_{PEO}^{SANS} = 5.55 \cdot 10^{10}$ cm⁻²) and the values were found to be well in agreement with the literature.[26] ρ_{D2O}^{SANS} for the solvent was fixed to 6.40 $\cdot 10^{10}$ cm⁻². Upon addition of HPW, the ρ profiles inform clearly on the micelle shrinkage (from green

to red curve in Fig. 5c). In SAXS for P84 micelles in H₂O (orange line in Fig. 5c) the major contrast is produced between the PEO ($\rho_{PEO}^{SAXS} = 9.75 \cdot 10^{10} \text{ cm}^{-2}$) and PPO/H₂O ($\rho_{PPO}^{SAXS} = 9.47 \cdot 10^{10} \text{ cm}^{-2} \approx \rho_{H_2O}^{SAXS} = 9.40 \cdot 10^{10} \text{ cm}^{-2}$). Upon the addition of HPW, the ρ^{SAXS} profile drastically changes (from orange to blue curve in Fig. 5c). A strong increase in ρ up to 18.70 $\cdot 10^{10} \text{ cm}^{-2}$ is obtained for $2.3 \le r \le 5.1$ nm, which can only be attributed to the presence of PW.

We conclude by combining SAXS and SANS results that the (*i*) addition of HPW to P84 micelles leads to a size decrease of P84 micelles and (*ii*) HPW mostly adsorbs on the PEO micelle corona, see sketch in Fig. 5c.

4. Conclusions

In the first part, we investigated the different aggregation states of the polymeric P84 (ABA block copolymer) surfactant in aqueous solution. At 2.5 wt%, unimers of P84 are present at 20 °C. By increasing temperature above the CMT (28°C) spherical micelles are observed at 50 °C. The micelles undergo a sphere-to-rod transition at >55 °C. The tremendous CP increase of 2.5 wt% P84 in presence of micromolar concentrations of HPW confirmed strong association between HPW and P84 with an adsorption constant of K_A ~ 20.0 mM⁻¹. Interestingly, such a high K_A was never observed for the binding of HPW with other polymers (PNiPAM) or micelles (CsE4).

It was shown by ¹H-NMR experiments, that HPW selectively binds to the PPO moiety of P84 unimers (below the CMT at 20 °C). This effect was attributed to a combination of the chaotropic and hydrophobic efffects due to the higher hydrophobicity of PPO over PEO.

Via the combination of SANS/SAXS and modelisation spherical micelles of P84 with a radius of 6.5 nm (4.1 nm PPO core and 2.4 nm PEO corona) were observed in absence of HPW above the CMT at 50 °C. Upon the addition of HPW the micelle shrinks in size down to a radius of 5.5 nm. HPW were found to be mostly located in the micellar PEO corona and only partially located in the PPO micellar core (close the PEO-PPO region). Therefore, upon heating above the CMT, the micellization of P84 - driven by the hydrophobic effect – leads to a displacement of HPW from PPO to PEO.

This study shines light on the subtle balance of two effects: the chaotropic effect (binding of HPW to P84) and the hydrophobic effect (micellization of P84 and binding of HPW to P84). The chaotropic effect and the hydrophobic effects act here as two interplaying driving forces. We propose, that the balance of the chaotropic effect and the hydrophobic effect plays a decisive role in assembly of hierarchical systems and requires high attention for future rational bottom-up syntheses based on self-assembly.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Figure S1: title; Table S1: title; Video S1: title.

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