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ORIGINAL CONTRIBUTION

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The effect of poly(ethylene oxide) on the characteristics of Triton X-100/1-butanol/*n*-octane/water reverse micelles

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Abstract Nonionic poly(oxyethylene) surfactant with about ten ethylene oxide units and 1-butanol have been studied in reverse micelles with one nonpolar solvent(*n*-octane) at different water contents in the presence and in the absence of poly (ethylene oxide) (PEO) using two absorption probes, methyl orange and methyl blue *MB* and one spin probe, 5-doxylstearic acid. The study has focused attention on the effect of the addition of PEO on the phase behavior of the system, the state of water in the reverse micelles, and the locus of PEO solubilized in reverse micelles. In the presence of PEO, some PEO segments may penetrate into the interface close to the palisade layer of the reverse micelles and then replace some water molecules, which results in a less close arrangement between the chains of surfactants as well as between alcohol molecules.

Key words Reverse micelles · Triton X-100 · Water structure · Poly(ethylene oxide) · Solubilization

Introduction

In past 25 years, micelles have been the focus of extensive research worldwide due to their importance in a variety of technological applications. These applications include enhanced oil recovery, combustion, cosmetics, lubrication, enzymatic catalysis, organic and bioorganic reactions, chemical synthesis of nanoparticles, etc. [1–4]. More recently, high-molecular-weight additives, such as protein or synthetic polymers, have been dissolved or synthesized inside the water pool, which then serves as a microreactor for enzymatic or chemical reaction. However, the effects of high-molecular-weight additives on the phase behavior of reverse micelles and on the structure of water droplets have been studied only scarcely so far.

Surfactant self-assembly at high surfactant concentration shows a rich structure variation, governed by the spontaneous curvature of the surfactant aggregates and interaggregate interaction. The structures include micelles, liquid crystals, and microemlusions. The incorporation of polymer molecules into the bis(2-ethylhexyl) sulfosuccinate (AOT)–isooctane–water system has been studied in particular. It is expected that the addition of a polymer to the system will strongly affect the microstructure, stability, and dynamics. It is found that for a range of conditions, the structure of water-in-oil (w/o) nanometer-sized droplets is retained; however, by the association of the polymer segments with water cores of two different droplets, dimers of droplets may form [5]. At high polymer concentration, larger aggregates are formed. Several studies indicate that the solubilization of an absorbing water-polymer in the water core of a reverse micelle changes the flexibility of the interface [6, 7]. It has also been shown that the adsorption of poly(ethylene oxide) (PEO) at the interface of w/o micelles made of AOT/water/isooctane leads mainly to an increase in the elastic bending modulus, *K*, and to a lesser extent to a modification of spontaneous curvature [8]. This last finding suggests that the solvent properties of AOT solutions are unaffected as the polymer concentration is changed.

Surprisingly, so far the effect of a polymer additive on a micelle composed of a nonionic surfactant, an alcohol, oil, and water has been reported scarcely, although the micellar systems are very interesting in many respects. The present research lays emphasis on the effects of polymer additive on the water structure and the interfacial film in the w/o microemulsion droplets. We report here results concerning the effect of a high-molecular-weight additive, namely a synthetic polymer, on the phase behavior and the structure of w/o micelles. PEO was chosen as a typical polymer for water-soluble polymers, which can be dissolved in the water droplets of a w/o micelle under appropriate condition. All the w/o micelles studied were made using Triton X-100(TX-100) as a nonionic surfactant, 1-butanol as a cosurfactant, and *n*-octane as an oil phase. The ratio of TX-100 to 1-butanol was 2:3(weight) in all the micelle samples studied.

Experimental

Materials

Methanol, ethanol, and 1-butanol were A. R. grade, produced by Beijing Chemical Reagents Co. *n*-Octane(A. R.) was purchased from Shanghai Chemical Reagent factory. All the reagents were dried using a 4-Å molecular sieve before use. The surfactant (TX-100, $M_{w=}646.85$) was obtained from Roth & Hass PEO, with an average molecular weight of 20,000 and of a quality for gas chromatography, was from Merck. The spin probe 5-doxylstearic acid (5-DNS) was purchased from Sigma Chemical Co. The two dyes, methyl orange(MO) and methylene blue(MB), were indicator-grade products of Beijing Chemical Co. The water used in this work was deionized and distilled.

Experimental procedure

A large number of samples over the pseudoternary diagram were prepared by weighing the appropriate amount of substance such as TX-100-into a 10-ml graded tube, and then 1-butanol, *n*-octane, and water were added to the tube in proportion. The mixture was shaken and then equilibrated at 25 °C for 24 h. All the diagrams were expressed in weight. A lamellar liquid–crystalline phase was identified by examination of the texture with a polarizing optical microscope. In the following c_p represents the polymer concentration (percentage weight per volume) in water, and W_o corresponds to the molar ratio of water to surfactant

$$W_o = [H_2O]/TX\text{-}100] \ .$$

For the samples studied by UV-vis spectroscopy, to quantitatively introduce the probe (MO or MB) into the reverse micelles, a 2.5×10^{-3} M methanolic solution of MO or MB was prepared, an appropriate amount was transferred into a graded tube, and the methanol was evaporated by drying at 45 °C. Upon addition of the blend (surfactant, 1-butanol, oil, and water) to the solid residue followed by shaking, the MB or MO was solubilized to the reverse micelles, giving the desired concentration of the dye. In all samples, the concentration of MO or MB was 1.3×10^{-5} M. For the sample containing MB, a remarkable color change from green-blue(in water) to pink occurred in reverse micelles with appropriate composition. The color change equilibrium was reached within a few minutes to several hours, depending on the compositions of the micelles. Visible absorption spectra were recorded on a HP 8452A diode array spectrophotometer with a pair of quartz cells of 1-cm path length placed in thermostated holder at 25 °C ± 0.5.

The spin probe was added to the samples by the following procedure. The required amount of nitroxide in absolute ethanol was evaporated in a volumetric flask, and the sample was then added to give a concentration of the spin probe of 2.4×10^{-5} M. Precautions were taken to keep the electron spin resonance (ESR) tubes tightly closed to prevent evaporation. The ESR spectra were recorded at 25 °C on a ESP-200D(Bruker) spectrometer with 100-kHz field modulation using the X-band frequency.

Dynamic light scattering measurements were made using the apparatus installed at the Beijing University, China. The laser was a 200-mW Ar^+ (514.5 nm) Spectra Physics 2000 Model. The autocorrelator was a multi- τ model ALV-5000/E. Data were processed using second and third cumulant fits. All measurements were made at an angle of 90°. Hydrodynamic radii (R) were determined using the Stokes–Einstein relationship:

$$R = kT/6\pi\eta D \ ,$$

Where η is the viscosity of the continuous phase and D is the translational diffusion coefficient.

Results and discussion

Phase behavior

The pseudoternary diagram for the system of TX-100/1-butanol/*n*-octane/water is presented in Fig. 1, where the region of the w/o micelle (M phase) and the liquid-crystalline phases (L phase) are shown. In the absence of PEO, the M phase is bound by a solid line which represents the maximum of water solubilization in the reverse micelles at 25 °C. For example, the dotted line in Fig. 1 corresponds to the dilution line of water at a ratio of 2:3 for TX-100:1-butanol, where at the limit of the maximum water solubilization in the micelles, the W_o ratio is 52.2. The L region (liquid–crystalline phase) can also be seen in the diagram. In the presence of PEO it is found that phase-separation occurs when the W_o values

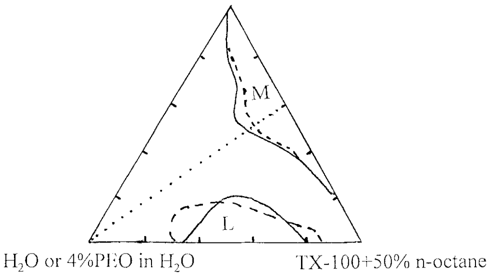

Fig. 1 The partial phase diagram at 25 °C of the pseudoternary system Triton X-100 (*TX-100*)/1-butanol/*n*-octane/water. *M* represents the isotropic water-in-oil micelles; *L* is the lamella liquid–crystalline phase. The *solid line* shows that pure water is used, and the *dashed line* indicates that 4% poly (ethylene oxide) (*PEO*) in aqueous solution is used. The *dotted line* indicates the "dry" micelles diluted by water or by 4% PEO in aqueous solution

are low, which results from the fact that PEO may be practically insoluble in microemulsion droplets with a radius (R) comparable to the radius of gyration of the polymer (R_G), while it is solublilized in droplets with a radius R (which is controlled by the ratio W_o) larger than R_G. (R_G of isolated PEO macromolecules ($M = 20{,}000$) is about 30 Å [6], According to our light-scattering data, R is 47 and 57 Å at $W_o = 10.7$ and 26.2, respectively. So it is expected that the polymer is not soluble at very low water contents; however, when the water content increases it has been found that when the polymer size is equal to or smaller than the apparent droplet diameter(R), then the polymer can be solubilized in the w/o microemulsion [9]. On the other hand, it can also be seen that the area of the M region decreases slightly, but the L phase seems to solubilize more water compared with the system in the absence of PEO. The reason why the L phase can solubilize more water is that hydrophilic PEO will be solubilized between layers formed by surfactant polar groups in the L phase and this may result in the space of the surfactant layers increasing due to the larger volume of the PEO molecules than that of the water molecules; therefore, more water can be solubilized. However, this assumption needs to be proved through further experiments.

In our experiments, the dotted line in the w/o micelle region in Fig. 1 indicates our choice for preparing w/o micellar samples.

Absorption spectra of MO and MB in reverse micelles without PEO

Firstly, we monitor the dependence of MO and MB absorption on the solvent medium. In neutral aqueous solution, MO and MB exhibit an absorbance maximum (λ_{max}) at 462 and 664 nm, respectively, in agreement with the literature values [10, 11]. A wide variation in λ_{max} is observed for MO for different solvent media as shown in Table 1. Values of 414 and 418 nm in less polar solvents to a redshifted value of 462 nm in water (higher polarity) are observed. From these results, it is clear that MO can be used to monitor the microenvironment of w/o micellar systems. In fact, Zhu and Schelly [12] have successfully studied the micropolarity of reverse micelles from the absorption spectra of MO.

Table 1 λ_{max} of absorption of methyl orange (*MO*) and methyl blue (*MB*) in different solvents

Solvents	λ_{max} (nm) of absorption probes	
	MO	MB
1-Butanol	414	654
Ethanol	418	656
Methanol	420	656
Water	464	664

Table 1 also shows the absorbance of MB in different solvents. It is found that the λ_{max} of MB does not show an obvious polarity dependence, particularly for different alcohols. This is consistent with the literature. In fact, due to a strong and definition interaction between the nonionic surfactant (TX-100) and the cationic dye (MB), as evidenced by the markable color change that occurs under appropriate conditions, MB has been confirmed as an ideal probe to investigate the state of water in the polar core of reverse micelles [13].

It has been shown that MO dissolves at the interface between the water phase and the organic phase and may preferentially penetrate the interfacial layer with its conjugated azo group embedded between the EO chains of TX-100 [14]. The peak at about 416 nm can be assigned to absorbance of MO molecular monomer at the interface. MB molecules in the MB–surfactant complexes with TX-100 EO chains are considered to be located at the interface near the water phase, while the uncomplexed MB (free MB) may be saturated with water and located at the core of the water pool. MB absorbances of complexed MB and of uncomplexed MB were observed at λ_{max} of 520 and 652 nm, respectively.

According to Jain et al. [15], there are at least three different distinct solubilizate environments available, viz., in an interfacial environment, in the bound water layer, and in the water pool in reverse micelles. The interfacial water (trapped water) can be considered as those water molecules that are located at the interface and are not bound to any other molecular group but are trapped between polar head groups of surfactant molecules at the interface. These water molecules should behave either as monomers or dimers and are considered to have penetrated the interfacial layer. For AOT reverse microemulsions, the bound water is composed of water molecules bonded to negatively charged polar head groups of AOT though sodium ions; however for the revese micelles of poly(oxyethlene nonylphenyl) (ethers nonionic surfactant) in cyclohexane, the bound water molecules interact directly with the EO chains of the surfactant by hydrogen bonding [16].

The adsorption spectra of MO in reverse micelles with different W_o are shown in Fig. 2. At W_o values below 0.54, λ_{max} remains unchanged, but a further increase in W_o leads to a redshift of λ_{max}. When W_o reaches 5.27, λ_{max} increases to 418 nm and then remains constant. This means that the micropolarity monitored by MO is enhanced when more water is added to the w/o micelle. The characteristics are very similar to that of the TX-100/hexanol/cyclohexane system studied by Qi et al. [13]. With increasing water content, there are three states of water in the w/o microemulsion: bound water, trapped water, and bulklike water [13].

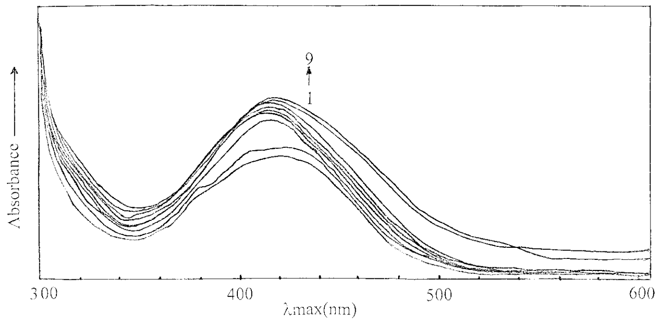

Fig. 2 Absorption spectra of methyl orange (*MO*) in reverse micelles as a function of water content, W_o, (from *bottom* to *top*) 'dry micelles' 0.54, 1.05, 2.05, 2.63, 3.69, 5.27, 7.91, and 10.54: the corresponding λ_{max} values are 412, 412, 413, 414, 416, 418, 419, 420, and 420 nm, respectively

Table 2 Spectral data of MB–surfactant interaction in reverse micelles at 25 °C. MB concentration: 1.3×10^{-5} mol/l

W_o	λ_{max} (nm)	
	Complexed	Uncomplexed
"Dry micelles"	514	630 (weak)
2.05	514	640
2.63	514	646
5.27	Weak	656
7.91	Very weak	658
10.54	Very weak	660
18.50	No	660

Table 2 lists the effect of successive additions of water on the adsorption spectra of MB in the reverse micelle and reveals that λ_{max} of MB in dry reverse micelles is 514 nm, and this band can be ascribed to the complex formation between MB and TX-100. As the water content is increased to $W_o = 5.27$, λ_{max} remains unchanged, the absorbance at λ_{max} decreases markedly, and a new absorbance band with an absorbance maximum at about 646 nm that can be ascribed to the uncomplexed MB in the solvent appears. The addition of more water leads to the disappearance of the band at 514 nm and to an increase in the intensity of the band at about 646 nm. This implies that that in dry micelles, the strong interaction between MB and TX-100 results in the formation of a 1:1 complex. With the increase in water content, the water is first bound to the complex as well as to the EO groups of the polar chain of the surfactant. The addition of more water results in a decrease in the intensity of the characteristic band of the bound MB in the complex and a corresponding increase in the intensity of the band in the higher-wavelength region (free MB). λ_{max} (the band of higher wavelength) gradually increases with the addition of water ($W_o = 2.05$–2.63) and corresponds to the presence of another state of water. The water can be assigned as those water molecules that are located at the interface and that are not directly bound to the EO groups (trapped water). When W_o exceeds 5.25, λ_{max} (the higher wavelength) remains unchanged. This indicates the formation of bulklike water, and the water pool is formed, the addition of more water leads to a larger pool but leaves the microenvironment of MB and, thus, λ_{max} of free MB relatively unchanged.

At high enough W_o values, λ_{max} of MO or MB in the reverse micelle is lower than that in pure water. This means that although the large water pool is formed, the polarity of the bulklike water in the micelle is significantly lower than that of pure water.

Absorption spectra of MO and MB in reverse micelles with PEO

Although the dye–surfactant interaction has been used to study the microstructure of reverse micelles, rather surprisingly, the microstructure in reverse micelles in the presence of PEO has rarely been investigated by absorption probes. In order to explain the effect of PEO on the structure of the reverse micelles, we used MO and MB as absorption probes and interpreted the spectral changes due to the addition of PEO to the reverse micelles.

The effect of the addition of 4% PEO aqueous solution on the adsorption spectra of MO in the TX-100 reverse micelles is shown in Fig. 3. It is found that increasing W_o leads to an increase in λ_{max}, which is very similar to the reverse micelles without PEO; however at the same W_o values, the λ_{max} of MO in reverse micelles with PEO is lower than that in reverse micelles without PEO (compared with Fig. 2). Because MO molecules are located at the interfacial layer, a decrease in the λ_{max} of MO in the presence of PEO must be attributed to the fact that some PEO segments must be located at the

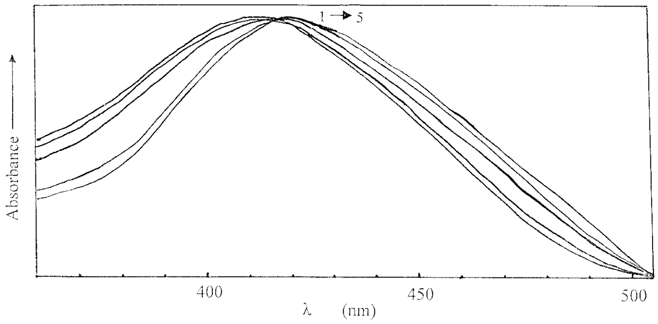

Fig. 3 Absorption spectra of MO in TX-100 reverse micelles as a function of water content (containing 4% PEO). W_o (*left* to *right*) 2.05, 2.63, 5.27, 10.54, 18.50; the corresponding λ_{max} values are 412, 412, 414, 416, and 416 nm, respectively

interface between the water phase and the organic phase, penetrating the interfacial layer. These PEO segments may take the place of some water, which decreases the micropolarity sensed by the absorption probe.

It can be also seen from Fig. 4 that in the reverse micelles, only the absorption band of MB at high wavelength is observed and that this band is redshifted from 636 to 656 nm when the water content is increased from 2.07 to 18.50. In the presence of PEO, at the same W_o value as for the systems without PEO (Table 2), the λ_{max} of MB decreases significantly. Because the high wavelength of MB corresponds to the absorbance of free MB in solvent, this implies that some PEO segments are located in the water core of water droplets.

Tables 3 and 4 list the spectral data of MB and MO in the presence of PEO when W_o remains constant but the PEO concentration in aqueous solution is increased (TX-100:1-butanol = 2:3). The λ_{max} of both MO and MB decrease with increasing PEO concentration. It is concluded that the higher the PEO concentration is, the smaller the polarity at the interfacial layer or in the core of the water pool becomes, which may result from the fact that more water molecules are replaced by PEO segments.

In order to confirm further this result, the ESR spectra were measured. The addition of the spin probe (5-DNS) to the system yields spectra whose patterns are characteristic of an isotropic spectrum (Fig. 5). The rotational correlation time, τ_c was calculated according to the formula [17]

$$\tau_c = 6.51 \times 10^{-10} \Delta H(0)[(h_0/h_{-1})^{1/2} + (h_0/h_{+1})^{1/2} - 2] \ ,$$

where $\Delta H(0)$ is the central line width in gauss and h_{-1}, h_0 and h_{+1} are the peak heights of the $M = -1$, 0, and +1 lines, respectively.

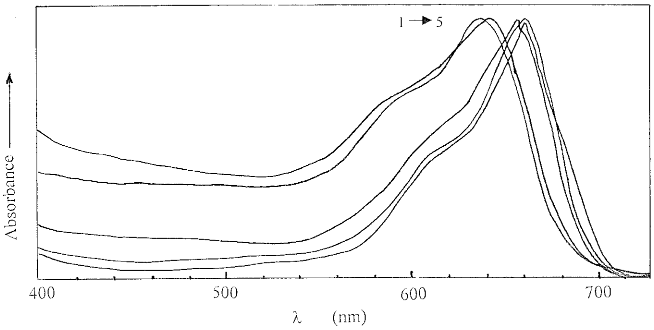

Fig. 4 Absorption spectra of methyl blue in TX-100 reverse micelles as a function of water content (containing 4% PEO). W_o (*left* to *right*) 2.05, 2.63, 5.27, 10.54, 18.50; the corresponding λ_{max} values are 636, 640, 654, 656, and 656 nm, respectively

Table 3 Dependence of λ_{max} of absorption of MO in the reverse micelles on poly (lethylene oxide)/(*PEO*) concentration (c_p, 90 w/v) in aqueous solution at 25 °C. MO concentration: 1.3×10^{-5} mol/l

c_p	λ_{max} (nm)			
	W_o:	2.05	7.91	18.54
0		414	416	420
0.5		414	416	420
1.0		412	414	420
2.5		411	412	418
4.0		410	–	–

The hyperfine coupling constant, A_N, can give information on the micropolarity of the micro-environment sensed by the nitroxide probe. A more polar environment produces a larger value of A_N due to a greater electron density at nitrogen.

Table 4 Dependence of λ_{max} of absorption of MB in the reverse micelles on PEO concentration at 25 °C. MB concentration: 1.3×10^{-5} mol/l

c_p	λ_{max} (nm)			
	W_o:	2.05	7.91	18.54
0		640	658	660
0.5		638	656	660
2.5		638	654	656
4.0		636	–	–

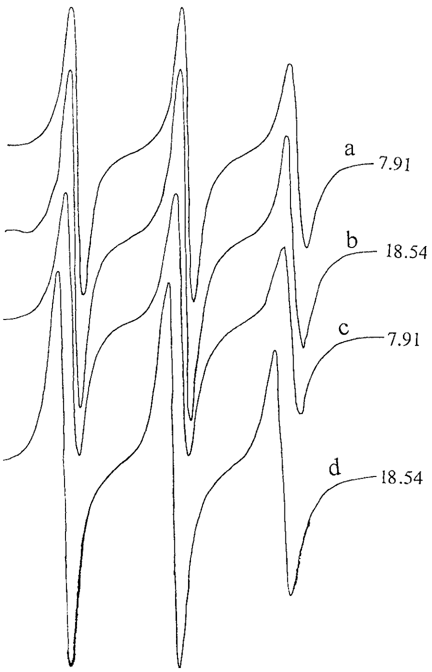

Fig. 5 Electron spin resonance spectra of the spin probe 5-doxylstearic acid in the TX-100 reverse micelles as a function of water content. The value of W_o given on the *right* of each spectrum is that in the absence (*a*, *b*) and in the presence (*c*, *d*) of 4% PEO in aqueous solution, respectively

Table 5 Electron spin resonance parameters of the spin probe 5-doxylstearic acid in the reverse micelles

c_p	τ_c ($\times 10^{-10}$ s)			A_N(G)	
	W_o:	7.91	18.54	7.91	18.54
0		4.18	3.91	14.89	14.95
4.0		3.82	2.90	14.72	14.77

Taking into account the solubility of the nitroxide in the reverse micelles, the nitroxide NO group is far from the water/surfactant interface and is buried in the poly(oxyethylene) part of the shell, near the palisade layer [18]. Figure 6 shows the spectra of 5-DNS in the reverse micelle in the absence and in the presence of PEO. The isotropic spectra observed probably result from a fast exchange of the spin probe between the oil phase(octane) and the micelle shell [19]. The A_N and τ_c values obtained from Fig. 6 are listed in Table 4. It is found that in the absence of PEO, with increasing W_o values, the A_N values increase slightly and the τ_c values decrease. This means that upon increasing the water content, the interfacial layer becomes more polar and less viscous. The probe sensing a much higher polarity than the other one corresponds to a more homogeneous hydration of the poly(oxyethylene) chains of surfactants by the solubilized water; therefore, with increasing water content, penetration of water molecules into the polyl (oryethlene) region occurs. On the other hand, in the presence of PEO, with increasing W_o values, the A_N values and the τ_c values display similar behavior to those in the absence of PEO; however, at the same W_o values, both the A_N values and the τ_c values of 5-DNS in the reverse micelles with PEO are lower than those without PEO. This implies that some PEO segments have penetrated into the locus of the spin probe and might be close to the palisade layer. Some water molecules (bound and trapped water) may be replaced by PEO segments, and then the chains of the surfactants become less close and form a more "open" structure, which results in the faster rotation of the spin probe, so the τ_c values decrease. This suggestion is consistent with the results when using MB and MO as absorption probes.

Conclusion

The addition of PEO to the TX-100/1-butanol/octane/water system has an influence on the phase behavior of the system. When PEO is added, the region of the w/o micelle becomes smaller; on the other hand, the liquid–crystalline region seems to become larger. Therefore, the addition of PEO may result in a stronger hydrophobicity in w/o micelles, and the increase in the amount of solubilized water in the liquid–crystalline region due to the presence of PEO may result from penetration of PEO segments into the surfactant layers in lamellar liquid crystals.

In the systems investigated (w/o micelles), both UV-vis and ESR spectroscopy have provided evidence for the presence of different types of water: bound water, trapped water, and bulklike water. At high water content, bulklike water is formed, and this type of water is different from pure water. The polarity of the water pool is significantly smaller than that of pure water.

In the reverse micelles with PEO, some PEO segments may penetrate into the interface close to the palisade layer of the micelles, which makes the chains of surfactants less close and less viscous, and a more "open" structure is formed.

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