A small-angle neutron scattering study of sodium dodecyl sulfate-poly(propylene oxide) methacrylate mixed micelles

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Abstract

Mixed micelle of protonated or deuterated sodium dodecyl sulfate (SDS and SDSd25, respectively) and poly(propylene oxide) methacrylate (PPOMA) are studied by small-angle neutron scattering (SANS). In all the cases the scattering curves exhibit a peak whose position changes with the composition of the system. The main parameters which characterize mixed micelles, i.e., aggregation numbers of SDS and PPOMA, geometrical dimensions of the micelles and degree of ionisation are evaluated from the analysis of the SANS curves. The position $q_{\text{max}}$ of the correlation peak can be related to the average aggregation numbers of SDS–PPOMA and SDSd25–PPOMA mixed micelles. It is found that the aggregation number of SDS decreases upon increasing the weight ratio PPOMA/SDS (or SDSd25). The isotopic combination, which uses the “contrast effect” between the two micellar systems, has allowed us to determine the mixed micelle composition. Finally, the SANS curves were adjusted using the RMSA for the structure factor $S(q)$ of charged spherical particles and the form factor $P(q)$ of spherical core–shell particle. This analysis confirms the particular core–shell structure of the SDS–PPOMA mixed micelle, i.e., a SDS “core” micelle surrounded by the shell formed by PPOMA macromonomers. The structural parameters of mixed micelles obtained from the analysis of the SANS data are in good agreement with those determined previously by conductimetry and fluorescence studies.

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Keywords: Mixed micelle; Sodium dodecyl sulfate; Small-angle neutron scattering; RMSA method; Spherical core–shell structure

1. Introduction

The micellar system sodium dodecyl sulfate (SDS)–poly(propylene oxide) methacrylate (PPOMA) is used to prepare polyacrylamide based thermoassociative polymers, containing pendant groups of poly(propylene oxide) (PPO). Micellar copolymerization is well known to lead to copolymers characterized by a blocky distribution of pendant hydrophobic groups. The average number of hydrophobic monomers in a sequence is usually assumed to be equal to the number of hydrophobic monomers per micelle in the reaction mixture, and is calculated by assuming that the aggregation number of SDS, $N_{\text{ag,SDS}}$, is not affected by the presence of PPOMA macromonomers [1–4].

A systematic study of the SDS–PPOMA mixture in aqueous solution has been carried out by various classical techniques such as fluorescence, light scattering, conductimetry and $^1$H NMR [5]. The addition of PPOMA to SDS micellar solution induces a decrease of the number of SDS molecules per aggregate. $^1$H NMR and fluorescence quenching experiments have allowed us to propose a structural model for the SDS–PPOMA mixed micelle: (i) the hydrophobic core of micelle is primarily composed of the C12 chains of the SDS, (ii) the interface between the hydrophobic core and water is made up of the polar heads of the SDS as well as methacrylate functions of the PPOMA, and (iii) the PPO chains of the macromonomers are adsorbed preferentially at the surface, i.e., near the polar heads of the SDS, Fig. 1.

The small-angle neutron scattering (SANS) studies reported in the present paper aim to provide an unambiguous proof of this particular structural model of the mixed SDS–PPOMA ag-
ggregates. In the past decade, SANS has been extensively used to characterize the structure of SDS micelles, in pure water or in the presence of additives such as salts or other surfactants. While in pure water and for concentrations close to the critical micelle concentration (cmc), the micelles are generally considered as spherical, it has been shown that addition of salts induces an increase of the aggregation number of SDS and an elongation of the micelles which acquire the shape of prolate ellipsoids [6–12]. The structural model commonly used for fitting the scattering curves is a spherical (or ellipsoidal) core–shell particle with a core composed by a part of aliphatic chains of the surfactant and a shell made up by the remaining parts of the aliphatic chains, the polar heads, the counter-ions and some solvent molecules [13–17].

This paper presents a small-angle neutron scattering (SANS) study of SDS–PPOMA and totally deuterated SDS (SDSd25)–PPOMA mixed micellar systems. At first, we present a method to evaluate the aggregation numbers of the mixed micelle, based on the value of \( q_{\text{max}} \), the wave vector corresponding to the correlation peak position on the SANS curves. Secondly, in order to determine the composition of the mixed micelle, we use the isotopic substitution and compare two systems SDSd25–PPOMA and SDS–PPOMA in D\(_2\)O. Finally, we analyze the SANS curves obtained for the SDS–PPOMA and the SDSd25–PPOMA micellar systems in order to deduce information about an eventual structural organization and about the geometry of the mixed micelle.

2. Experimental

2.1. Materials

All solvents and reagents of the best reagent grade available were obtained from Aldrich (protonated SDS and PPOMA of molecular weight \( M_w = 437 \text{ g mol}^{-1} \) [5] and from Euriso-top (totally deuterated SDS, SDSd25, and heavy water, D\(_2\)O) and used without further purification.

2.2. Small-angle neutron scattering (SANS)

SANS experiments were performed on PAXY spectrometer at the Léon Brillouin Laboratory (LLB) (CEA, Saclay, France). The measurements were made using a wavelength of 10 Å and a sample–detector distance of 2 m. Scattering range was covered from 0.01 to 0.11 Å\(^{-1}\). The temperature was fixed at 25°C. The data were corrected for background scattering and detector response and converted to the scattering cross section or \( I(q) \) (in absolute units of cm\(^{-1}\)) using standard procedure [18].

2.3. Sample preparation

SDS and totally deuterated SDS (SDSd25) solutions were prepared in D\(_2\)O at a concentration of 0.05 mol L\(^{-1}\) and PPOMA added such as the weight ratios PPOMA/SDS (or SDSd25) were equal to 0, 0.25, 0.5, 0.75, and 1.

2.4. Effect of contrast on the SDS (and SDSd25)–PPOMA micellar systems

The values of the scattering length densities \( b \) and molecular volumes of the various compounds used in this study are reported in Table 2. One can observe that the \( b \) values of SDS are close to that of water and generally SANS studies of SDS have been performed in heavy water. For the same reason, close values of \( b \) for SDSd25 and D\(_2\)O, few SANS studies have been performed for deuterated SDS in D\(_2\)O. However, in our case, the comparison of the results obtained with deuterated SDS in D\(_2\)O and in heavy water enables us to determine localization of PPOMA in the micelles: at their surface as expected by the model of Fig. 1 or in their core, since in the latter case the main contribution to the scattering is that of PPOMA.

3. Results and discussion

3.1. Scattering spectra: general features

Fig. 2 presents SANS curves of the SDS–PPOMA mixtures in D\(_2\)O with various weight ratios \( R = \text{PPOMA}/\text{SDS} \), ranging from 0 to 1. The scattering length densities for SDS and PPOMA are very close, and far of D\(_2\)O (Table 2); both compounds contribute similarly to the scattered intensity. Whatever the ratio \( R \), a peak appears on the scattering curves \( I(q) \) at a wave vector \( q = q_{\text{max}} \). This peak can be considered as a correlation peak between the scattering particles, and \( q_{\text{max}} \) is inversely proportional to the average distance between the scattering particles, \( d_{\text{mic}} \):

\[
d_{\text{mic}} = k/q_{\text{max}}.
\]

When \( R \) increases from 0 to 1, \( q_{\text{max}} \) moves towards larger values and thus, the distance between the mixed micelles becomes smaller. For the same SDS concentration, i.e., 0.05 mol L\(^{-1}\), a decrease in the distance between the micelles corresponds to an increase in the concentration of the mixed micelles and consequently a decrease of the aggregation number. This confirms the trend observed by steady-state fluorescence quenching in our previous work [5].

Fig. 3 presents SANS curves of the SDSd25–PPOMA mixtures in D\(_2\)O with the same weight ratios \( R \). Let us recall that, under such conditions, SDSd25 micelle is matched by D\(_2\)O. For \( R \) values from 0.25 to 1, the scattering curves \( I(q) \) also exhibit
Fig. 2. SANS curves \( I(q) = f(q) \) for SDS–PPOMA mixed micelle in \( D_2O \) for various weight ratios \( R = \text{PPOMA}/\text{SDS} \). \( R = 0 \) (●), 0.25 (■), 0.5 (▲), 0.75 (□), and 1 (○). \( C_{\text{SDS}} = 0.05 \text{ mol L}^{-1} \). (—) theoretical fits of the SANS curves for \( R = 0–1 \).

Fig. 3. SANS curves \( I(q) = f(q) \) for SDSd25–PPOMA mixed micelle in \( D_2O \) for various weight ratios \( R = \text{PPOMA}/\text{SDSd25} \). \( R = 0 \) (●), 0.25 (■), 0.5 (▲), 0.75 (□), and 1 (○). \( C_{\text{SDSd25}} = 0.05 \text{ mol L}^{-1} \). (—) calculated scattered intensity for \( R = 0 \) and theoretical fits of the SANS curves for \( R = 0.25–1 \).

a peak as for the SDS–PPOMA micellar system. When \( R \) increases from 0.25 to 1, \( q_{\text{max}} \) also moves towards larger wave vector values as in the case of SDS–PPOMA in \( D_2O \) and, as expected, the same values of \( q_{\text{max}} \) are obtained for a given ratio \( R \).

The analysis of the SANS curves enables us to evaluate such structural parameters of the mixed micelles as: (i) the aggregation numbers of SDS, SDSd25, and PPOMA, \( N_{agSDS} \), \( N_{agSDSd25} \), and \( N_{agPPOMA} \), respectively, of the mixed micelle by using the position of the peak \( q_{\text{max}} \), (ii) the mixed micelle composition i.e., the SDS molar fraction \( f_{molSDS} \) in the mixed micelles using “contrast” effect by isotopic combination (SDS–PPOMA and SDSd25–PPOMA), (iii) geometrical parameters of the core–shell particles mimicking the micelles through the fit of the scattering curves.

3.2. Evaluation of the aggregation numbers from the peak position

As follows from Eq. (1), it is possible to write that the micellar concentration \( C_{\text{mic}} \) (mol L\(^{-1}\)) is proportional to \( (q_{\text{max}})^3 \) \( (q_{\text{max}} \text{ being expressed in } \text{Å}^{-1}) \):

\[
C_{\text{mic}} = a \frac{10^{27}}{(2\pi/q_{\text{max}})^3 N_A},
\]

where \( N_A \) is the Avogadro number and \( a \) is the numerical factor which depends on the (average) position of neighbouring micelles with respect to each other. The aggregation numbers \( N_{ag} \) of the mixed micelles (the total aggregation number \( N_{ag\text{total}} \) and the numbers of SDS, \( N_{agSDS} \), SDSd25, \( N_{agSDSd25} \), and PPOMA, \( N_{agPPOMA} \), per micelle) can be evaluated as

\[
N_{ag\text{total}} = \frac{(C_{SDS} - \text{cmc}) + C_{PPOMA}}{C_{\text{mic}}},
\]

\[
N_{agSDS} = \frac{(C_{SDS} - \text{cmc})}{C_{\text{mic}}},
\]

\[
N_{agPPOMA} = \frac{C_{PPOMA}}{C_{\text{mic}}},
\]

where \( \text{cmc} \) is the critical micellar concentration, \( C_{PPOMA} \) and \( C_{SDS} \) are the PPOMA and the SDS concentrations, respectively. When deuterated SDS is considered, \( C_{SDSd25} \) and \( N_{agSDSd25} \) should
Table 1
Summary of the various parameters of the SDS–PPOMA mixed micelle determined in previous work: cmc and α, the critical micellar concentration and the ionisation degree (from conductivity measurements), N\textsubscript{ag total}, N\textsubscript{ag SDS}, and N\textsubscript{ag PPOMA}, the total, SDS and PPOMA aggregation numbers (from fluorescent measurement) \cite{5}. C\textsubscript{SDS} = 0.05 mol L\textsuperscript{-1}. R = PPOMA/SDS (weight ratio).

<table>
<thead>
<tr>
<th>R</th>
<th>cmc (mol L\textsuperscript{-1})</th>
<th>α</th>
<th>N\textsubscript{ag total}</th>
<th>N\textsubscript{ag SDS}</th>
<th>N\textsubscript{ag PPOMA}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0084</td>
<td>0.371</td>
<td>58</td>
<td>58</td>
<td>0</td>
</tr>
<tr>
<td>0.25</td>
<td>0.0070</td>
<td>0.485</td>
<td>47</td>
<td>39</td>
<td>8</td>
</tr>
<tr>
<td>0.5</td>
<td>0.0059</td>
<td>0.612</td>
<td>45</td>
<td>32</td>
<td>13</td>
</tr>
<tr>
<td>0.75</td>
<td>0.0055</td>
<td>0.616</td>
<td>39</td>
<td>24</td>
<td>15</td>
</tr>
<tr>
<td>1</td>
<td>0.0048</td>
<td>0.696</td>
<td>38</td>
<td>21</td>
<td>17</td>
</tr>
</tbody>
</table>

Table 2
Scattering length densities (b) and molecular volumes (V) for several compounds used in this work.

<table>
<thead>
<tr>
<th>Mixed micelle composition</th>
<th>b (10\textsuperscript{10} cm\textsuperscript{-2})</th>
<th>V (Å\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPOMA</td>
<td>0.343</td>
<td>720.9</td>
</tr>
<tr>
<td>SDS</td>
<td>0.39</td>
<td>435.4</td>
</tr>
<tr>
<td>SDSd25</td>
<td>6.73</td>
<td>435.4</td>
</tr>
<tr>
<td>D\textsubscript{2}O</td>
<td>6.41</td>
<td>30.2</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>-0.56</td>
<td></td>
</tr>
</tbody>
</table>

Fit of the SANS curves

<table>
<thead>
<tr>
<th>Fit of the SANS curves</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CD\textsubscript{3}O</td>
<td>9.78</td>
<td>54.3</td>
</tr>
<tr>
<td>CD\textsubscript{2}O</td>
<td>7.43</td>
<td>26.9</td>
</tr>
<tr>
<td>SO\textsubscript{4}\textsuperscript{-}</td>
<td>1.63</td>
<td>57.9</td>
</tr>
<tr>
<td>Na\textsuperscript{+}</td>
<td>9.31</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Table 3
C\textsubscript{mic}, N\textsubscript{ag} total, N\textsubscript{ag} SDS, N\textsubscript{ag} SDSd25, N\textsubscript{ag} PPOMA and N\textsubscript{ag} total (micellar concentration, SDS, SDSd25, PPOMA and total aggregation numbers respectively) calculated from q\textsubscript{max} (the wavelength of the correlation peak), assuming a simple cubic lattice, for the SDS–PPOMA and the SDSd25–PPOMA micellar systems for various weight ratios R = PPOMA/SDS (or SDSd25). C\textsubscript{SDS} = C\textsubscript{SDSd25} = 0.05 mol L\textsuperscript{-1} and N\textsubscript{ag} PPOMA, for both SDS–PPOMA and SDSd25–PPOMA micellar systems, are reported versus the ratio R assuming α = 1. Remarkably, for all the ratios R, the q\textsubscript{max} values for the two systems (deuterated and hydrogenated SDS) are in good agreement. This finding indicates that, in the first approximation, deuteration of SDS does not perturb significantly the structure of mixed micelles and the CMC. Moreover, as shown by the comparison of Tables 1 and 3 and by Fig. 4, the aggregation numbers determined from the values of q\textsubscript{max} are in good agreement with those measured by fluorescence. This result proves that incorporation of PPOMA in the SDS micelles leads to a decrease in the aggregation number of the surfactant.

It should be mentioned that the interpretation of the scattering peak position in terms of the average distance between the micelles and in terms of the aggregation numbers is the object of some controversies in literature.

In a crystallographic way, one can attribute the peak observed in SANS curves at q = q\textsubscript{max}, to the scattering from reticular planes of cubic lattices, by assuming that the mixed micelles adopt a regular space organization on a cubic lattice due to the electrostatic repulsions. Several types of cubic lattices could be considered, for example a simple cubic sc, a body-centered cubic bcc, or a face-centered cubic fcc structure, and q\textsubscript{max} corresponds to scattering from (100), (110), and (111) planes, respectively. Generally, in order to distinguish the sc, bcc, and fcc lattices from each other, the positions of seven successive peaks must be known. The lattice constant of the lattice \textalpha\textsubscript{i} is related to the distance between the planes \textalpha\textsubscript{hkl} through the equations

\begin{align}
\textalpha\textsubscript{sc} &= d\textsubscript{100}, \\
\textalpha\textsubscript{bcc} &= 2d\textsubscript{110}, \\
\textalpha\textsubscript{fcc} &= 3d\textsubscript{111}.
\end{align}

Considering that (\textalpha\textsubscript{i})\textsuperscript{3} is the volume of the cubic lattice, \textalpha\textsubscript{hkl} = 2π/q\textsubscript{max}, and that there are 1, 2 and 4 micelles per cube for the sc, bcc, and fcc, respectively, the pre-factor \textalpha\textsubscript{i} in Eq. (2) depends on the nature of the cubic lattice and is equal to 1, \textalpha\textsuperscript{2}/2, and 4 \cdot (3\textsuperscript{3}/2) for sc, bcc, and fcc, respectively.
Although in dilute micelle solution there is no long-range crystalline order, strong Coulomb interactions result in strong correlation in positioning of individual micelles, that is reflected by the pronounced peak in the scattering curves. Therefore it is tempting to assume cubic structure for the average position of the micelles and for the solvent, respectively. Here $N_{\text{ag SDS neutron}}$ obtained by either $a = 1$ (sc lattice), 0.707 (bcc lattice), or 0.770 (fcc lattice) are compared to $N_{\text{ag SDS (fluor)}}$ obtained from fluorescence. It clearly appears that the assumption of simple cubic lattice leads to a much better agreement with the fluorescence data while the body-centered cubic and the face-centered cubic structures give overestimated values of the aggregation number of SDS.

Similarly, Iijima et al. have shown that the aggregation number values for a cesium perfluorooctanoic acid micelle, determined fitting SANS curves, can not be correlated to a micelle distribution in a fcc lattice, described by Boden et al. for the same system [19,20]. However, Durand had employed this method to evaluate the number of poly(N-isopropylacrylamide) pendant chain forming physical reticulation between poly(sodium acrylate) main chains, assuming a simple cubic lattice organization between the reticulation points [21].

### 3.3. Evaluation of mixed micelle composition

For the solution of spherical monodisperse micelles the scattered intensity can be written as

$$I(q) = (b_p - b_S)NV P(q)S(q),$$

where $b_p$ and $b_S$ are the scattering length densities for the micelle and for the solvent, respectively. $N$ is the number of micelles per unit volume, $V$ is the volume of one micelle, $P(q)$ is the micelle form factor and $S(q)$ the structure factor arising from the inter-micellar interactions in the solution [13,25,26].

Penfold et al. have proposed a method to determine the composition of SDS–hexaethylene glycol mono- n-dodecylether (C12E6) mixed micelles in presence of NaCl, using the isotopic substitution between C12E6 and totally deuterated C12E6 [22–24]. From the Penfold’s method, we can write that the volume and mole fractions of SDS in mixed micelle respectively, calculated from aggregation number values determined by fluorescence (Table 1) for various weight ratios $R = \text{PPOMA/SDS}$ or SDS for the SDS–PPOMA mixed micelle, $C_{\text{PPOMA}} = C_{\text{SDS}} = 0.05 \text{ mol L}^{-1}$.

$$f_{\text{vol SDS}} + f_{\text{mol SDS}} = 1$$

Using different methods, Penfold et al. determined the composition of SDS–C12E6 mixed micelles in presence of NaCl, using the isotopic substitution between C12E6 and totally deuterated C12E6 [22–24]. From the Penfold’s method, we can write that the volume and mole fractions of SDS in mixed micelle respectively, calculated from aggregation number values determined by fluorescence (Table 1) for various weight ratios $R = \text{PPOMA/SDS}$ or SDS for the SDS–PPOMA mixed micelle, $C_{\text{PPOMA}} = C_{\text{SDS}} = 0.05 \text{ mol L}^{-1}$.

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methods using the isotopic combination and the fluorescence technique, we find that the mixed micelles have a molar composition of 0.64 and 0.62 of SDS, respectively.

This method of the determination of the mixed micelle composition gives results in agreement with those previously found [5]. On the other hand, this method does not give us any information on the localization of PPOMA inside mixed micelle. In order to definitively confirm the model of mixed micelles presented in Fig. 1, we have performed fitting of the SANS curves (Figs. 2 and 3), using the form factor, \( P(q) \), of core–shell particles and the structure factor, \( S(q) \), of charged hard spheres. Moreover, the fit of the SANS curves constitutes an alternative way for evaluating such micellar parameters as the aggregation numbers and the ionisation degree.

3.4. Structural model of mixed micelle and fit of the SANS curves

For fitting the SANS curves, we assume that at any solution composition mixed micelles have spherical core–shell shape and are monodisperse. The structure factor \( S(q) \) corresponds to an organization of the scattering objects in solution, i.e., to the interaction between the scattering particles. Therefore, it is the same for solutions of pure SDS and SDSd25 micelles and for solutions of mixed SDS–PPOMA or SDSd25–PPOMA micelles. The interaction between charged micelles can be described by the potential of neutral hard sphere of radius \( r \), complemented by a screening Coulomb interaction potential \( V(x) \) given by:

\[
V(x) = \frac{C_B e^2}{x} \exp[-\kappa(x - 2r)],
\]

\((8)\)

for \( x > 2r \), the distance between the particle centers. \( C_B = e^2/\kappa \), where \( \kappa \) is the solvent permittivity, \( e \) is the elementary charge, \( z \) is the charge number per particle, and \( \kappa \) is the inverse of Debye–Hückel screening length. The structure factor for solutions of charged hard spheres has been calculated by a Mean-Spherical Approximation (MSA) by Hayter et al. [27]. Nevertheless, this structure factor is valid only for sufficiently large volume fractions of scattering objects (\( \eta > 0.2 \)). For smaller volume fraction, Hansen et al. have improved the method and proposed the Rescaled MSA (RMSA) which introduces a rescaled hard core radius \( r_{res} \) larger than the real radius \( r \) [28].

The form factor \( P(q) \) depends on the shape of the scattering particles and we consider micelles as spherical core–shell particles, described by Pedersen et al. and various authors [11–17,26]. Then, for SDS–PPOMA and SDSd25–PPOMA mixed micelles, \( P(q) \) can be written:

\[
P(q) = \left[ [(b_1 - b_2)V_1 f(qr_1) + (b_2 - b_1)V_2 f(qr_2)]^2 \right]
\]

\((9)\)

with

\[
f(x) = \frac{3\sin x - x \cos x}{x^3}.
\]

\((10)\)

The hydrophobic core of radius \( r_1 \) has a scattering length density \( b_1 \) and a volume \( V_1 \). The shell, extended between \( r_1 \) and \( r_2 \), has the scattering length density \( b_2 \). \( V_2 \) is the volume of the whole micelle (core + shell) and \( b_3 \) is the scattering length density of the solvent. The various scattering length densities \( b_1 \), \( b_2 \) and \( b_3 \) are calculated according to the compositions of the core, the shell and the solvent. For SDS–PPOMA or SDSd25–PPOMA mixed micelles:

- the core of radius \( r_1 \) is made up of CH3 or CD3 and of a fraction of the (CH2)11 or (CD2)11 surfactant chains. The number of methylene groups in the core, \( n_c \), is calculated from \( N_{ag}SDS_{d25} \), \( r_1 \), \( V_{CD2} \), or \( V_{CD3} \), and \( V_{CH3} \), the volumes of CD3 or CH3 and CD2 or CH2, respectively, as follows:

\[
n_C = \frac{(4\pi r_1^3/3) - N_{ag}SDS_{d25}V_{CD3}}{N_{ag}SDS_{d25}V_{CD2}}.
\]

\((11)\)

- the shell of internal and external radius \( r_1 \) and \( r_2 \) is composed of: (i) the remaining fraction of the methylene groups of volume \((1 - n_c)b\) of SDSd25 \( V_{CD2} \), (ii) the sulfate groups, of volume \( N_{ag}SDS_{d25}V_{SO4}^{-} \), (iii) the sodium ions, of volume \((1 - \alpha)N_{ag}SDS_{d25}V_{Na}^{+} \), where \( \alpha \) is the degree of ionisation of surfactants in the mixed micelle, (iv) the D2O solvating sulfate groups and sodium ions, of volume \( w_i V_{D2O} \), where \( w_i \) is the hydration number of the compounds \( i \), and (v) the PPOMA macromonomer, of volume \( N_{ag}PPOMA V_{PPOMA}W_{SO4}^{-} \) and \( w_{Na}^{+} \) were taken at 5 and 6 according to literature data [11].

- the solvent D2O is composed by the SDSd25 or SDS at the concentration equal to cmc and by a fraction of the sodium ions, at the concentration \((C_{SDSd25} - \text{cmc})/\alpha + \text{cmc} \).

The micelle number density \( N \) (in units of \( \text{cm}^{-3} \)) is given by

\[
N = \frac{(C_{SDSd25} - \text{cmc})N_A \times 10^{-3}}{N_{ag}SDS_{d25}} = \frac{C_{PPOMA}N_{A} \times 10^{-3}}{N_{ag}PPOMA}
\]

\((12)\)

where all the concentrations are expressed in \( \text{mol L}^{-1} \). In this expression, when hydrogogenated SDS is considered, \( C_{SDS} \) is replaced by \( C_{SDS} \).

A schematic representation of the spherical core–shell model of the mixed micelles is given in Fig. 6a. The fits were performed for the SANS curves presented in Figs. 2 and 3. A Fortran program for parameter fitting, based on a traditional optimization method called simulated annealing, with a 0.95 tolerance was used. Several parameters have been optimized: \( r_1 \) the radius of the core, \( r_2 \) the external radius of the shell, \( N_{ag}SDS_{d25} \) and \( N_{ag}PPOMA \) the SDS and PPOMA aggregation numbers, respectively, and \( \alpha \) the ionisation degree of the surfactant in the mixed micelles. The cmc values used for the fits are those previously determined by conductimetry in Ref. [5] (Table 1).
Fig. 6. (a) Core–shell model of SDSd25–PPOMA mixed micelle. (b) Relative radial scattering length density profiles, calculated from the fit of the SANS curves, for the SDSd25–PPOMA mixed micelle with various weight ratios $R = \text{PPOMA/SDSd25}$. $b_1$, $b_2$, and $b_s$ are the scattering length densities of the core, the shell, and the solvent respectively; $r_1$ and $r_2$ are the radius of the core and of the external shell, respectively.

Table 5
Values of the optimized parameters: the core radius $r_1$, the external radius of the shell $r_2$, the SDSd25 and PPOMA aggregation numbers $N_{ag \text{SDSd25}}$ and $N_{ag \text{PPOMA}}$, respectively, the ionisation degree $\alpha$, for the SDSd25–PPOMA mixed micelle for various weight ratios $R = \text{PPOMA/SDSd25}$. $C_{\text{SDSd25}} = 0.05 \text{ mol L}^{-1}$.

<table>
<thead>
<tr>
<th>$R$</th>
<th>$r_1$ ($\text{Å}$)</th>
<th>$r_2$ ($\text{Å}$)</th>
<th>$\Delta r$ ($\text{Å}$)</th>
<th>$N_{ag \text{SDSd25}}$</th>
<th>$N_{ag \text{PPOMA}}$</th>
<th>$\alpha$</th>
</tr>
</thead>
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<tr>
<td>0</td>
<td>16.9</td>
<td>21.1</td>
<td>4.2</td>
<td>58</td>
<td>0</td>
<td>0.371</td>
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<td>19.3</td>
<td>5.6</td>
<td>35</td>
<td>8</td>
<td>0.401</td>
</tr>
<tr>
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<td>15</td>
<td>0.492</td>
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<tr>
<td>0.75</td>
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<td>17.4</td>
<td>5.9</td>
<td>20</td>
<td>15</td>
<td>0.671</td>
</tr>
<tr>
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<td>17.4</td>
<td>6.1</td>
<td>19</td>
<td>17</td>
<td>0.725</td>
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3.4.1. Results of the fits for the SDSd25–PPOMA/D$_2$O system

Fig. 3 shows the fits of the experimental curves $I(q)$, for the SDSd25–PPOMA system, as obtained by optimization of the previous described parameters. The values of the optimized parameters are reported in Table 5.

For the pure SDSd25 micelles in D$_2$O, we have not optimized the parameters because the scattered intensity $I(q)$ is very low. However, we have used $N_{ag \text{SDSd25}}$, $N_{ag \text{PPOMA}}$ and $\alpha$, determined by fluorescence (Table 1) to calculate (i) $r_1$ considering that all the deuterated chains of SDSd25 form the core ($n_c = 11$) and (ii) $r_2$ from the whole volume of all other compounds forming the mixed micelle (deuterated chains, sulfate groups, sodium ions and D$_2$O). With this set of parameters, the scattering curve exhibits a peak, but in the whole range of $q$, the calculated scattered intensity is very small and lies inside the uncertainties of the SANS measurements. This curve, calculated from the model described previously, is reported in Fig. 3.

If the SDSd25 micelle is considered as an uniform sphere and if one takes into account the small difference between the scattering length densities for SDSd25 and D$_2$O i.e. $\Delta b = 0.32 \times 10^{10}$ cm$^{-2}$, one can conclude that in the first approximation SDSd25 is matched by D$_2$O. In Fig. 6b the relative radial scattering length density profiles, $\Delta b$ for the spherical core–shell model are presented. Remarkably the difference between scattering length densities of the core and of the shell, i.e., $\Delta b_{\text{C-S}} = b_2 - b_1 = 2.21 \times 10^{10}$ cm$^{-2}$ on one hand and $\Delta b$ between those for the shell and the solvent, i.e., $\Delta b_{\text{S-S}} = b_s - b_2 = 0.82 \times 10^{10}$ cm$^{-2}$ on the other hand are relatively small. Even if $\Delta b$ values were larger than these ones, they would be not sufficient to obtain significant scattered intensity $I(q)$ (Fig. 3). For the ratios $R > 0$, the difference between the scattering length densities of SDSd25 and PPOMA enables us to obtain sufficiently high scattered intensity values that makes possible to fit the scattering spectra by optimizing parameters of the spherical core–shell model. For example, for $R = 0.25$, $\Delta b_{\text{C-S}}$ and $\Delta b_{\text{S-S}}$ are only about $3.96 \times 10^{10}$ and $2.51 \times 10^{10}$ cm$^{-2}$. For $R = 1$, $\Delta b_{\text{C-S}}$ and $\Delta b_{\text{S-S}}$ are about $5.71 \times 10^{10}$ and $4.29 \times 10^{10}$ cm$^{-2}$.

The SANS measurements of the SDSd25–PPOMA micellar system and the fit of the results confirm that when $R$ increases,
The results of the fit indicate that the external radius of the core–shell particles \( r_2 \) decreases from 19.3 to 17.4 Å, when \( R \) increases from 0.25 to 1. The radius of the whole micelle decreases for about 2 Å. The same variation is obtained for the core radius \( r_1 \) which decreases from 13.7 to 11.3 Å. Hence, the width of the shell \( \Delta r \) remains practically constant and equal to approximately 6 Å, even if the number of PPOMA in the shell changes from 8 to 17. We can also remark that \( n_C \), the number of CD\(_2\) groups composing the core, increases from 8.8 to 9.9, when \( R \) increases from 0.5 to 1, i.e., for \( R = 0.5 \), about 2 CD\(_2\) groups belong to the shell instead of 1 for \( R = 1 \). This means that addition of more PPOMA tends to exclude methylene groups from the shell, which could partly explain that no difference is observed for \( \Delta r \).

Altogether, the variations of the micellar radii obtained from the fitting of the SANS curves are very weak (a few Å) and it is delicate to give real conclusions on eventual radius evolution. The variations obtained for the aggregation numbers and the ionisation degree of the mixed micelle are more significant.

### 3.4.2. Results of the fits for the SDS–PPOMA/D\(_2\)O system

Fig. 2 shows the fits of the experimental curves \( I(q) \) whereas the values of the optimized parameters are reported in Table 6.

As for the SDSd25–PPOMA micellar system, a good agreement is obtained between the aggregation numbers, \( N_{ag\text{SDS}} \) and \( N_{ag\text{PPOMA}} \), determined by SANS and by fluorescence (Table 1). Table 5 shows that the ionisation degree \( \alpha \) increases while the cmc decreases when \( R \) increases, in accordance with the results obtained by fluorescence. However, similarly to the SDSd25–PPOMA micellar system, the values of \( \alpha \) determined from the fit of the SANS curves are systematically lower than those obtained by fluorescence.

### Table 6

<table>
<thead>
<tr>
<th>( R )</th>
<th>( r_1 ) (Å)</th>
<th>( r_2 ) (Å)</th>
<th>( \Delta r ) (Å)</th>
<th>( N_{ag\text{SDS}} )</th>
<th>( N_{ag\text{PPOMA}} )</th>
<th>( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>16.5</td>
<td>21.1</td>
<td>4.6</td>
<td>58</td>
<td>0</td>
<td>0.287</td>
</tr>
<tr>
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<td>6.7</td>
<td>22</td>
<td>17</td>
<td>0.703</td>
</tr>
</tbody>
</table>

Fig. 7. Structure factor \( S(q) \) versus \( q \) for various weight ratios \( R = \text{PPOMA/SDS} \) (or SDSd25) for SDS–PPOMA mixed micelle: \( R = 0.5 \) (○), and for the SDSd25–PPOMA mixed micelle: \( R = 0.5 \) (○) and 1 (●). \( C_{\text{SDSd25}} = C_{\text{SDS}} = 0.05 \text{ mol L}^{-1} \).
We find from our fit, that the outer radius of the SDS–PPOMA micelles, \( r_2 \), decreases from 21.1 to 18.2 Å, when \( R \) increases from 0 to 1. Hence, the dimensions of the SDS–PPOMA micelles are apparently slightly higher than those found for the SDSd25–PPOMA micelles. A similar variation is obtained for the core radius \( r_1 \) which decreases from 16.5 to 11.5 Å. The width of the shell \( \Delta r \) slightly increases from 4.6 to 6.7 Å. We can also remark that the number \( n_C \) of CH\(_2\) groups composing the core, decreases from 10.1 to 8.7, when \( R \) increases from 0 to 1, i.e., for \( R = 0 \), about 1 CH\(_2\) group belongs to the shell instead of 2 for \( R = 1 \).

If substitution of protonated SDS by deuterated one does not change the micellar parameters (e.g., dimensions and aggregation numbers) of mixed micelles, the structure factors \( S(q) \) of the micellar solution should be independent of the isotopic substitution for any value of \( R \). However, the \( S(q) \) functions derived from the fits of the SANS curves are different for the SDS–PPOMA and SDSd25–PPOMA systems as shown in Fig. 7 and this difference is more pronounced for \( R = 1 \) than for \( R = 0.5 \). In literature, when protonated SDS is studied in D\(_2\)O by SANS, the values of aggregation number deduced from the fits of the scattering curves are always greater than those obtained by fluorescence or light scattering in water. For example, the average value of \( N_{ag} \) found by several authors using fluorescence for SDS in water is around 60 [1,2,5] while, from SANS experiments performed with SDS in D\(_2\)O, Pilsl et al. have found \( N_{ag} = 83 \) by considering an ellipsoidal form for the micelles [9], and Cabane et al. have published \( N_{ag} = 74 \) with a spherical core–shell model [29]. Moreover, for totally deuterated SDS (SDSd25) in H\(_2\)O, Cabane et al. have found \( N_{ag} = 86 \) [29] using SANS. These differences are probably due to the fact that the use of the isotopic substitution (H by D) for improving the “contrast” between surfactant and solvent, change the micellar parameters. For tetramethyl-dimethylamine oxide-SDS mixed micelle studied in D\(_2\)O, Pilsl et al. have shown, similarly to our present study, that the structure factor \( S(q) \), representing the intermicellar interaction, is not the same when SDS is protonated or deuterated [9]. Nevertheless, we have shown that the positions of the scattering peaks are similar when SDS or SDSd25 is used, in our ternary system SDS (or SDSd25)–PPOMA–D\(_2\)O.

### 4. Conclusions

The presented analysis of the SANS spectra has enabled us to get a valuable insight into the structure of mixed micelles such as those present in solution of SDS or SDSd25 and PPOMA.

Three methods: (i) the evaluation of the aggregation numbers from \( q_{max} \), the wave vector of the correlation peak present on SANS curves, (ii) the determination of the mixed micelle composition, i.e., the molar fraction of SDS, from an isotopic combination (SDSd25–PPOMA and SDS–PPOMA), and (iii) the fit of the SANS curves using the core–shell model have been employed. As a result we have found that the aggregation numbers vary quantitatively in the same way: \( N_{ag} \) decreases from 58 to about 20 whereas \( N_{ag} \) increases from 0 to 17 when the weight ratio \( R = \) PPOMA/SDS increases from 0 to 1. We have only obtained a qualitative variation of the ionisation degree \( \alpha \) of the mixed micelle which increases for the same variation of \( R \).

Moreover, the SANS has also allowed us to perform a structural analysis of these mixed micelles, by seeking their shape via \( P(q) \) and the mutual interactions via \( S(q) \). The spherical core–shell structure, previously assumed by \(^1\)H NMR (Fig. 1), and a charged hard sphere model for the interaction have been used to fit SANS curves \( I(q) \). The core is composed by a part of the aliphatic chains of SDS. The shell is composed by the remaining fraction of the aliphatic chains, the sulfate polar head and Na\(^+\) ions, and PPOMA macromonomers. When \( R \) increases, we observe a decrease in the radius of the core \( r_1 \) and that of the whole micelle \( r_2 \).

The study of the isotopic substitution (H by D) for the SDS micelles in D\(_2\)O gives an important insight into the behaviour of the system and helps to rationalize why different micellar parameters were reported in literature for SDS–D\(_2\)O, SDSd25–H\(_2\)O and SDSd25–D\(_2\)O. A study of SDS–SDSd25 mixtures in D\(_2\)O for example, or variation of the solvent scattering length density with H\(_2\)O–D\(_2\)O mixtures could provide more insight into the behaviour of these systems. In the latter case the scattering length density of the solvent can be varied in the systematic way.

Finally, the knowledge of the micellar parameters of the system SDS–PPOMA which can be used as polymerization medium for preparing acrylamide based associating polymers with PPO chains as pendant groups can be used to predict the copolymer architecture. Hence clear relationships can be established between the characteristics of the polymerization medium and the rheological properties of the obtained polymer samples. Nevertheless, up to now, there is a lack of information about interaction between acrylamide and SDS and about the partition coefficient of acrylamide between water and micelles. A systematic study of the effects of acrylamide concentration with salt and temperature of SDS–PPOMA mixed micelles by combination of SANS with fluorescence, conductimetry and light scattering techniques is in progress. This will enable us to control the composition and microstructure of the synthesized copolymers by tuning the copolymerization conditions.

### Acknowledgment

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### References