

Quantifying the micellar structure formed from hydrocarbon-fluorocarbon surfactants

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ABSTRACT

Many technological formulations contain mixtures of surfactants, each contributing some distinct property. Characteristics of each surfactant are often modulated in the mixture, based on the interactions between the various components present. Here, the mixing of the hydrocarbon surfactant cetyltrimethyl ammonium bromide (C₁₆TAB) and the fluorocarbon surfactant, Zonyl-FSN-100 with average chemical structure of C₈F₁₇C₂H₄(OC₂H₄)₉OH, is quantified, in particular, the size and shape of the micelles and their critical micelle concentration (CMC). The CMC data suggest there are specific interactions between the two components which are strongly antagonistic. Small-angle neutron scattering (SANS) has been used to quantify the size and shape of the micelle, and these data indicate that the single component FSN-100 forms disc-like micelles with a small aggregation number (~65) and the C₁₆TAB forms globular, charged micelles with a larger aggregation number (135). The aggregation number of the mixed micelle ~~formed by in the mixed case~~ is substantially

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greater than either of the pure species. Overall, a detailed study of CTAB, FSN-100 and their mixture systems will be presented in this paper.

HIGHLIGHTS

- Unusual micellisation process occurs in the system CTAB/ FSN-100 mixture solutions
- FSN-100 forms disc-like micelles with aggregation number of 65.
- CTAB forms globular, charged micelles with a larger aggregation number than FSN-100.

Keywords: Critical micelle concentration (CMC); Micelle shape and size; Mixed micelles.

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4. Introduction

1.

Surfactant solutions have been a subject of many investigations [1-7]. Surfactants self-assemble in aqueous solutions to form a wide variety of aggregated structures and many techniques have been developed to study these structures, most based on determining the shape/size of the micelles formed, and their critical micelle concentration. The latter gives an idea of the strength and nature of the interaction between the surfactants in the solution. Here, surface tension, fluorescence, small-angle neutron scattering (SANS), pulsed-gradient spin-echo NMR (PGSE-NMR) spectroscopy and electron paramagnetic resonance spectroscopy (EPR) have been employed to provide a detailed insight into one interesting system, a mixture of a charged, hydrocarbon surfactant and a non-charged, fluorocarbon surfactant.

Hydrocarbon surfactant micelle systems have been extensively studied [3-6], however there are far fewer studies on fluorinated and partially fluorinated surfactant micelles, even though the latter material possess many unique features, especially increased surface activity and hydrophobicity [7-10]. The miscibility of fluorocarbon and hydrocarbon surfactants often presents a challenge to formulation. In this study, we are concerned with the aggregation of C₁₆TAB as the model hydrocarbon surfactant and FSN-100 as a model fluorocarbon surfactant; C₁₆TAB has been well-characterised [3, 11], whereas FSN-100 has been less well studied, but interestingly, it exhibits two CMC values in aqueous solution, indicating a rather more complex micellisation process [8, 10].

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2. Materials and methods

2.

2.1. Materials

Cetyltrimethyl ammonium bromide (C₁₆TAB) and Zonyl FSN-100 fluorosurfactant, 16-doxyl stearic acid methyl ester (16-DSE) spin-probe and pyrene fluorescent probe were purchased from Sigma-Aldrich and used as received. The solvent was D₂O in the SANS and PGSE-NMR, and deionized water in the surface tension, fluorescence and EPR measurements. Acetone (Aldrich) and ethanol (Aldrich) were used as solvents for the stock pyrene and 16-DSE solutions.

2.2. Surface tension

Surface tension measurements were carried out at room temperature and using LAUDA Drop Volume Tensiometer (TVT1). In this instrument, the volume of a drop that detaches from a capillary is determined. By increasing the volume of the drop, its weight increases until it reaches a critical value at which it cannot be counterbalanced by the surface tension. The force balance at the drop results in the following relation for the surface tension, equation (1).

$$\sigma = Vg\Delta\rho F / 2\pi r_{cap} \quad (1)$$

where σ = interfacial tension, V = drop volume, g = acceleration constant, $\Delta\rho$ = difference of the densities of both adjacent phases, F = correlation factor, and r_{cap} = radius of the capillary.

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2.3. Fluorescence

All solutions have been prepared from stock solutions of distilled water with 0.01 ml of acetone containing pyrene stock solution at concentration of 2×10^{-6} M. Photophysical data were obtained on a JobinYvon–Horiba Fluorolog spectrometer fitted with a JY TBX photodetection module. All spectra were recorded using an excitation wavelength of 340 nm. All samples have been measured at room temperature. CMCs were determined by the breakpoints in the concentration dependent ratio of the third to first vibronic peak, known as the I_3/I_1 ratio.

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2.4. Small-Angle Neutron Scattering

The SANS measurements were performed as detailed previously [12] on the fixed-geometry, time-of-flight LOQ diffractometer (ISIS Spallation Neutron Source, Oxfordshire, UK). All measurements were carried out at 25°C. Experimental measuring times were between 40 and 80 minutes. All scattering data were normalised for the sample transmission and incident wavelength distribution, corrected for instrumental and sample backgrounds using an empty quartz cell, and for the linearity and efficiency of the detector response. The data were put onto an absolute scale using a well-characterised partially-deuterated polystyrene-blend standard sample.

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2.4.1. SANS Data fitting and analysis

The intensity of scattered radiation, $I(Q)$, as a function of the wave-vector, Q , is given by;

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$$I_{\text{surf} \tan t}(Q) = n \left[S(Q) \langle |F(Q)|^2 \rangle + \langle |F(Q)|^2 \rangle - \langle |F(Q)|^2 \rangle \right] + B_{\text{inc}} \quad (2)$$

Where in the case of a core-shell morphology, $F(Q) = V_1(\rho_1 - \rho_2)F_0(QR_1) + V_2(\rho_2 - \rho_0)F_0(QR_2)$. The first term represents the scattering from the core (subscript 1) and the second, the polar shell (subscript 2).

$V_i = \frac{4}{3}\pi R_i^3$ and $F_0(QR) = \frac{3j_1(QR)}{QR}$ (j_1 is the first-order spherical Bessel function). $S(Q)$

represents the spatial arrangement of the micelles in solution and n the micelle number density. ρ_i is the neutron scattering length density of the micellar core (subscript 1), the polar shell (subscript 2) and the solvent (subscript 0). These constants are combined into a single fittable parameter used to “scale” the model intensity to the absolute value. Post-fitting, this scalar is recalculated using the parameters describing the micelle morphology/composition and the molar concentration of micelles to validate the fit. The calculated and observed values should lie within ~10%.

The model of the micelle adopted here is that of a charged particle with an elliptical core-shell morphology. In the model the average volume per headgroup average tail volume and their average scattering length densities are input as constants, calculated assuming the composition of the micelle is the same as the solution composition. For C₁₆TAB, $\rho_{C16TAB\ head} = 2.4 \times 10^{-6} \text{ \AA}^{-2}$ and volume 412 \AA^3 . For the FSN-100, $\rho_{FSN\ head} = 0.6 \times 10^{-6} \text{ \AA}^{-2}$ and volume 2000 \AA^3 . The bromide ion dissociation in the C₁₆TAB case does however, significantly affect the charge on the micelle and hence the structure factor $S(Q)$, a point we return to later in the discussion. The average core scattering length density is also similarly calculated, with $\rho_{C16TAB\ tail} = -0.4 \times 10^{-6} \text{ \AA}^{-2}$ and volume 460 \AA^3 whereas $\rho_{FSN\ tail} = 2.0 \times 10^{-6} \text{ \AA}^{-2}$ and volume 295 \AA^3 .

The structure factor $S(Q)$ was calculated using the Hayter and Penfold model [13] for spheres of a given micellar concentration, charge and ionic strength, incorporating refinements for low volume fractions and a penetrating ionic background. Various approaches to parameterising the structure factor were adopted based on known or measured estimates of the micelle size and surfactant concentration to calculate the hard sphere volume fraction, charge and Debye length. We have shown that this method of calculating the structure factor, which assumes spherical particles, remains valid for dilute, isotropic samples of micelles with small degrees of Ellipticity, as is the case here [14].

The fitting of SANS data is insensitive to the headgroup region, the shell comprising the various headgroups and associated water. The prevailing shell scattering length density is calculated from the average headgroup scattering length density and their hydration, given

$\bar{\rho} = \phi_{water} \rho_{water} + (1 - \phi_{water}) \bar{\rho}_{headgroups}$. Since $\phi_{water} = \frac{V_{water}}{V_{shell}}$, the parameters V_{water} and V_{shell}

are strongly coupled and not amenable to fitting. We adopt the approach of fixing ϕ_{water} at the EPR determined value that *inter alia*, defines the shell volume (thickness). The scattering length density of the hydrated shell region is then (re-)calculated within the analysis software, based on ϕ_{water} . Hence, constraining this value eliminates the trial-and-error aspects required in previous work to find the overall “best fit” value of ϕ_{water} due to local minima in the least-squares fits [13].

2.5. PGSE-NMR spectroscopy

Pulsed-Gradient Spin-Echo (PGSE-) NMR measurements were performed on a Bruker AMX400 NMR spectrometer operating at 400 MHz (^1H) using a stimulated echo sequence. All the experiments were run at 25°C using the standard heating/cooling system of the spectrometer to an accuracy of $\pm 0.3^\circ\text{C}$. All solutions were prepared from stock solutions using D_2O , and 0.6 mL were transferred to 5 mm o.d. NMR tubes (Willmad NMR tubes from Sigma-Aldrich).

The self-diffusion coefficient, D_s , was deduced by fitting the attenuation of the integral for a chosen peak to eqn.3,

$$A(\delta, G, \Delta) = A_0 \exp(-k D_s) \quad (3)$$

where A is the signal intensity in the presence and absence (0) of the field gradients, and $k = -\gamma^2 G^2 \delta^2 (\Delta - \frac{\delta}{3})$.

where γ is the magnetogyric ratio, Δ the diffusion time, δ the gradient pulse length, and σ the ramp time, and G is the gradient field strength [15].

Association and complexation processes can both be extracted from an analysis of the self-diffusion coefficients D_s . In case of micellization studies, the attenuation function observed in the ^1H NMR spectra corresponded to the methylene resonance associated to $-(\text{CH}_2)_x-$ of the inner part of the hydrocarbon chains related to the broad peak between $\delta = 1.11 - 1.20$ ppm

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and thus, reflects the time-average population-weighted average mobility of the monomeric and micellized surfactant. In case of complexation, the attenuation function was recorded from the peak corresponding to the methylene in the spacer (singlet at $d= 5.36$ ppm) and again, reflected the time-average population-weighted average mobility of monomeric and micellised surfactant.

2.6. EPR spectroscopy

To prepare samples for EPR, 16-DSE ($2 \times 10^{-4} \text{M}$) was first dissolved in ethanol and then 0.02ml of the solution transferred into a separate glass vial. After allowing for ethanol evaporation, 1.0 ml of the sample was added to the vial and mixed for at least 1h to give a final spin-probe concentration at $2 \times 10^{-6} \text{M}$ and to ensure that the probe has been incorporated into the micelle solutions.

Experimental details for the EPR measurements are also identical to those described previously [14] and only brief details are repeated here. These non-degassed samples were sealed with a gas-oxygen torch into melting point capillaries, which were housed within a quartz EPR tube for the measurements. The temperature was controlled to $\pm 0.2 \text{K}$ by a Bruker Variable Temperature Unit BVT 2000. Five spectra were taken at X-band on a Bruker ESP-300 spectrometer.

2.6.1. EPR lineshape fitting and analysis

The lineshapes were fitted to a Voigt approximation to separate the Gaussian and Lorentzian components of the spectral lines and to locate the resonance fields of the three EPR lines arising from the nitroxide radical to a precision of a few mG. Rotational correlation times are computed from the overall linewidth of the centre line and the peak-to-peak heights of the three lines and corrected for inhomogeneous broadening using the procedure outlined by Bales [12, 14].

The separation $A+$ of the low and centre lines ($M_i=+1$ and $M_i=0$) is directly related to the polarity index H (25°C), defined as the molar ratio of OH groups in a given volume relative to water (eqn.4). H (25°C) therefore corresponds to the volume fraction of water in the polar shell, ϕ_{water} , and may be used to constrain the SANS fitting.

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$$H(25^{\circ}\text{C}) = (A+ - 14.21) / 1.52 \dots\dots\dots (4)$$

3. Results and discussion

3.

3.1. Critical micelle concentration (CMC) determinations

Surface tension measurements have been carried out for a range of solution compositions expressed as a function of C₁₆TAB (solution) mole fraction. The two limits correspond to the single component species, for which our CMC values (C₁₆TAB= 0.8x10⁻⁴ M, FSN-100= 6.8x10⁻⁵ M) are in excellent agreement with literature ones [6,8], (supplemental Fig-Figure 1). FSN-100 shows two break points (6.8x10⁻⁵ M, 1.0x10⁻³ M) again as observed previously [8], these have previously been ascribed to pre-association and micellization processes.

The CMC vs $\alpha_{\text{C}_{16}\text{TAB}}$ behaviour in figure (1) shows a number of distinct features, in particular, significant regions where the CMC is greater than would be predicted by an ideal mixing approach. Therefore, there are specific interactions between the two molecules, and these are strongly antagonistic. What is surprising in this system is the presence of a region of apparent ideality around $0.5 > \alpha_{\text{C}_{16}\text{TAB}} > 0.7$. Such increases in CMC, crucially to a concentration of one of the species to a value greater than its single component CMC, emphasises a loss of surfactant activity and the presence of a substantially different micellization process. Clearly, further analysis of the micelle composition and size/shape is warranted.

Surface tension detects changes in the surface composition, which generally reflects the prevailing solution structure. To provide a contrasting measure of the CMC, pyrene solubilisation has also been used. The two curves show remarkable similarity (figure 2), indicating that there is indeed some unusual micellization process occurring in this system.

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3.42. Electron Paramagnetic Resonance spectroscopy (EPR) measurements

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The hyperfine coupling constant from the EPR measurements are plotted versus C₁₆TAB mole fraction in figure (4). It is obvious that there is a greater degree of water (52%) associated with the FSN-100 headgroup, presumably because of the larger headgroup providing a greater volume for water penetration. The C₁₆TAB is a larger, spherical structure and the predicted value for ϕ_{H₂O} at 50mM would be calculated from equation (5) is 0.30, in fair agreement with the experimental value (0.32) (table 1). Calculation of the estimate for FSN-100 is less precise due to the uncertainty in the headgroup structure, but again the calculated value (0.53) is in good agreement with the experimental one (0.52).

$$\phi_{H_2O} = \frac{V_{shell} - V_{headgroups}}{V_{shell}} = \frac{\left(\frac{4}{3}\pi(R + \sigma)^3 X - \frac{4}{3}\pi R^3 X\right) - N_{agg} \cdot V_{CTAB}}{\left(\frac{4}{3}\pi(R + \sigma)^3 X - \frac{4}{3}\pi R^3 X\right)} \dots\dots\dots (5)$$

<u>C₁₆TAB/M</u>	<u>FSN-100/M</u>	Exp. ϕ _{H₂O} ^{shell} <u>50mM/(± 0.2)</u>	Exp. ϕ _{H₂O} ^{shell} <u>(20mM/ (± 0.2)</u>
<u>0</u>	<u>1</u>	<u>0.52</u>	<u>0.52</u>
<u>0.15</u>	<u>0.85</u>	<u>0.50</u>	<u>0.50</u>
<u>0.2</u>	<u>0.8</u>	<u>0.50</u>	<u>0.50</u>
<u>0.33</u>	<u>0.67</u>	<u>0.48</u>	=
<u>0.4</u>	<u>0.6</u>	<u>0.47</u>	=

<u>0.5</u>	<u>0.5</u>	<u>0.46</u>	<u>0.47</u>
<u>0.6</u>	<u>0.4</u>	<u>0.45</u>	=
<u>0.8</u>	<u>0.2</u>	<u>0.37</u>	=
<u>0.9</u>	<u>0.1</u>	<u>0.37</u>	<u>0.40</u>
<u>1</u>	<u>0</u>	<u>0.32</u>	<u>0.35</u>

Table 1. Experimental values for volume fraction of water in the polar shell (ϕ_{H_2O}) using EPR, in the single surfactant solutions and mixtures at two different total surfactant concentration.

The headgroup region of the cationic micelle is densely populated with the spherical, cationic headgroups and accordingly, the spin-probe will experience a relatively viscous environment (figure 5). By contrast the non-ionic micelle headgroup region will be populated by fairly large, oligomeric sterically hindering headgroups and accordingly, the spin-probe will also experience a viscous environment. These features are not that sensitive to the aggregation number.

For each cationic molecule ($C_{16}TAB$) that is removed from the mixed headgroup region, by the mixing of the cationic and non-ionic headgroups, there will be a change in amount of water equivalent to the difference in the respective headgroup volumes, consistent with the change in aggregation number. This is seen as the largely linear dependence of hydration (figure 4) as a function of CTAB mole fraction. Interestingly, the spin-probe experiences a more mobile, a less viscous environment (figure 5), between the two single surfactant extremes, as evidenced by the minimum in the rotational correlation time, a minimum in the viscosity.

—Finally, the EPR experiment provides an additional characterisation of the micelle via the rotational correlation time (τ_c) which is a measure of the dynamics with the micelle and the micelle tumbling itself (fig-figure 5).

The two single component micelles have a similar microviscosity and there is a pronounced minimum in τ_c across the entire mole fraction range, consistent with a decrease in local viscosity experienced by the probe.

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It is customary to separate the dynamics of the spin probe within the micelle $\tau_{Relative}$ to that of the micelle itself $\tau_{micelle}$ in order to comment on the microviscosity of the headgroup region. We use the SANS estimate of the size to obtain $\tau_{micelle}$ to arrive at $\tau_{Relative}$, which is over-plotted in figure 5, for selected data points [17]. Clearly, as expected, the Tau correction has little impact on the appearance. There is still a pronounced minimum in microviscosity as a function of C₁₆TAB mole fraction.

The microviscosity does not show any obvious dependence of N_{agg} as curvature, being largely defined by the numbers, and bulkiness of the headgroups, modulated by the prevailing degree of hydration. There is a clearly an opposite influence of the smaller TAB headgroup and the bulky, but hydrated ethylene oxide headgroup of the FSN-100.

3.23. Small- angle ~~neutron~~ Neutron scattering Scattering (SANS) studies

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One mechanism by which apparent antagonistic micellization may occur is the coexistence of multiple types of micelles. Therefore, SANS was carried out to quantify the size/shape of the micelles as a function of solution composition.

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SANS measurements were performed on a single component C₁₆TAB and FSN-100 as well as selected C₁₆TAB/FSN-100 mixtures at specific C₁₆TAB mole fractions, in order to detect micelle shape and size corresponding to the features in the CMC plot. Figure 3 shows the SANS data for the single components and four mixtures. The scattering curves are a composite of the form factor describing the size and the shape, and the structure factor describing the electrostatic interaction between micelles.

The scattering from ionic surfactant micelles possess an oscillatory structure factor which will lead to reduction in intensity at low Q and “bumps” at higher Q. These features are not expected in the scattering from a non-ionic micelle, at least at moderate concentrations. This simple interpretation occurs for many of the gross features in the data, in particular, the most striking difference in the curve from FSN-100 compared with all other mixtures. Expressed differently, once C₁₆TAB is added to the solution, the micelles show less variance in structure. As predicted, the scattering intensity decreases at low Q as the C₁₆TAB mole fraction increases, with shoulders around Q=0.06 Å becoming more pronounced.

In order to constrain various parameters in the analysis of the scattering data, EPR was used to quantify the hydration of the micelle headgroup region.

The EPR technique introduces a very small amount of nitroxide free radical as a spin probe (in this case, 16-DSE) into the micelle and by measuring the hyperfine coupling constant, the micelle structure can be estimated. The data in this experiment were also recorded at two different total surfactant concentrations (20mM and 50mM) to assess whether the micelle structure undergoes a significant change with total concentration.

The hyperfine coupling constant from the two different measurements are plotted versus C₁₆TAB mole fraction in figure (4). It is obvious that there is a greater degree of water (52%) associated with the FSN-100 headgroup, presumably because of the larger headgroup providing a greater volume for water penetration. The C₁₆TAB is a larger, spherical structure and the predicted value for ϕ_{H₂O} at 50mM would be calculated from equation (5) is 0.30, in fair agreement with the experimental value (0.32) (table 1). Calculation of the estimate for FSN-100 is less precise due to the uncertainty in the headgroup structure, but again the calculated value (0.53) is in good agreement with the experimental one (0.52).

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C ₁₆ TAB/M	FSN-100/M	Exp. ϕ _{H₂O} ^{shell} 50mM/(± 0.2)	Exp. ϕ _{H₂O} ^{shell} (20mM/(± 0.2)
0	1	0.52	0.52

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0.15	0.85	0.50	0.50
0.2	0.8	0.50	0.50
0.33	0.67	0.48	-
0.4	0.6	0.47	-
0.5	0.5	0.46	0.47
0.6	0.4	0.45	-
0.8	0.2	0.37	-
0.9	0.1	0.37	0.40
1	0	0.32	0.35

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Considering the fit for the single component surfactant solutions, the data have been fitted to a model describing the micelle morphology as globular, with a varying degree of ionic character. In both cases, constants have been applied to the analysis; specifically, using the known chemical structure, concentration molar volumes, dimensions and scattering length densities, in constraining with the known concentrations and the experimental values of the degree of hydration from EPR (table 1). The fitting parameters that are allowed to freely float are the Ellipticity, the charge and the incoherent background.

From table (2), describing the fit for the single components and the mixtures parameters, reflect what is also evident from the data, namely that the mixtures are strongly characterised by the ionic C₁₆TAB component. The aggregation numbers have been calculated via equation (6), the ratio of the core volume divided by a simple weighted value of the effective tail volume, this assumes that the micelle composition is identical to the solution one. In addition, the aggregation number of FSN-100 micelles is a little smaller than the literature value [10], whereas C₁₆TAB micelle aggregation number is in a good agreement with the literature one [16].

$$N_{agg} = \frac{V_{core}}{V_{tail}} = \frac{\frac{4}{3} \pi R_{core}^3 X}{\alpha_{CTAB} V_{CTAB}^{tail} + (1 - \alpha)_{CTAB} V_{FSN-100}^{tail}} \dots \dots \dots (6)$$

where, N_{agg}. Is the aggregation number, X is the Ellipticity, R_{Core} is the core radius, V_{tail} is the surfactant tail volume, V_{Core} is the surfactant core volume.

C ₁₆ TAB mole fraction	R _{Core} /Å	Shell thickness (±5)/ Å	Ellipticity, X	V _{s(dry)} /V _{Core}	N _{agg} (±10)
0	13.3	24	1.5	0.8	65
0.2	27.8	12	1.1	0.9	310
0.4	27.8	11	1.0	0.9	250

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0.6	26.2	10	1.0	0.9	190
0.8	21.6	10	1.1	1.0	140
1.0	25.8	8.0	0.85	0.9	135

Table 2. Parameters describing the fits of SANS data from C₁₆TAB, FSN-100, and their mixtures as a function of C₁₆TAB mole fraction using a model that describes the micelle as a globular elliptical with some ionic character.

The model assumes a single micelle type and the success of this approach in describing the data suggests that either a single micelle type is indeed present or any coexisting population of micelles are not substantially different. As a complimentary approach, PGSE-NMR was employed to provide more information about micelle structures.

3.3.4. PGSE- NMR spectroscopy studies

In this experiment, the measured diffusion coefficient is a weighted value of the non-micellised and micellised components. One would expect that if a coexisting micelle population were present, coupled with varying levels of non-micellised surfactant, the diffusion coefficient of the C₁₆TAB and FSN-100 would be quite different. Clearly, they are not (supplemental [fig-figure 2](#)), again, consistent with the SANS conclusion that these two surfactants mix, further, the diffusion coefficient values are mutually comparable consistent with the relative volumes of the respective micelles, also suggest that the solution composition is the same as the micellar one.

3.4. Electron paramagnetic resonance spectroscopy (EPR) measurements

Finally, the EPR experiment provides an additional characterization of the micelle via the rotational correlation time (τ_c) which is a measure of the dynamics with the micelle and the micelle tumbling itself (fig.5).

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~~The two single component micelles have a similar microviscosity and there is a pronounced minimum in τ_e across the entire mole fraction range, coincident with a decrease in local viscosity experienced by the probe.~~

~~It is customary to separate the dynamics of the spin probe within the micelle τ_{relative} to that of the micelle itself τ_{micelle} in order to comment on the microviscosity of the headgroup region. We use the SANS estimate of the size to obtain τ_{micelle} to arrive at τ_{relative} , which is over plotted in figure 5, for selected data points [17]. Clearly, as expected, the Tau correction has little impact on the appearance. There is still a pronounced minimum in microviscosity as a function of C₁₆TAB mole fraction.~~

~~The microviscosity does not show any obvious dependence of N_{agg} on curvature, being largely defined by the numbers, and bulkiness of the headgroups, modulated by the prevailing degree of hydration. There is a clearly an opposite influence of the smaller TAB headgroup and the bulky, but hydrated ethylene oxide headgroup of the FSN-100.~~

4. Conclusions

Mixed micelles of cationic C₁₆TAB and non-ionic FSN-100 surfactants have been studied by various techniques. The data show that the two surfactants mix nonideally with CMCs higher than predicted for ideal mixtures whilst some concentrations show a degree of ideality. This behaviour confirms that there is a substantially different micellization process across a range of compositions. It is clear that from SANS data the mixed micelles are strongly characterised by the C₁₆TAB component, and micelles have less variable in structure when different amount of C₁₆TAB was added to the solution. With increasing C₁₆TAB mole fraction, there is a reduction in the amount of water present in the headgroup region. Furthermore, combining resulted data from several techniques has been used to conduct a full picture of the micellar system of CTAB, FSN-100 and the mixtures.

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