Self-Assembly at High Pressures: SANS Study of the Effect of Pressure on Microstructure of C₈E₅ Micelles in Water

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We present the results of a high-pressure small-angle neutron scattering study of the effect of pressure on surfactant microstructure. The study was carried out on a solution of 1 wt % C₈E₅ in D₂O at 29.4 °C and pressures up to 310 MPa. The C₈E₅ micelles that form under these conditions are noninteracting. We find that applying pressure leads to a pronounced decrease in the micelle radius of gyration and the forward scattering intensity over the pressure range from ambient to 150 MPa. The partial molecular volume of the surfactant and the extent of hydration of the surfactant head groups in the micelle were also determined using the method of solvent contrast variation. Both quantities decrease with the application of pressure up to 150 MPa. Core–shell model fits to the scattering spectra over the entire q-range indicate that the shell radius decreases, while the hydrophobic core radius increases slightly with pressure. The pressure dependence of the shell radius is notably similar to that observed for the radius of gyration. Collectively, these observations lead to the conclusion that the effect of pressure on C₈E₅ micelization is to induce the dehydration of surfactant head groups and the collapse of the hydrophilic micelle shell at pressures between ambient and 150 MPa.

Introduction

Nonionic surfactants of the type C₈E₅ (n-alkyl polyoxyethylene ether) form a variety of microstructures in water, ranging from simple micelles at low surfactant concentrations to complex mesophases, such as hexagonal or lamellar phases, at high concentrations.¹² The formation of these microstructures has been studied as a function of temperature, the hydrophobic–lipophbic balance of the amphiphile, and the addition of alkanes, salts, or ionic cosurfactants. However, the effect of pressure on microstructure has not been studied as extensively. Our motivation for exploring this pressure dependence is to assess the use of pressure as an independent thermodynamic variable to control surfactant self-assembly. An advantage of applying pressure to stabilize certain microstructures would be to effectively uncouple self-assembly from other thermodynamic variables in processes where the microstructure is used as a template, for example, in the fabrication of nanostructured materials.

In general, small-angle neutron scattering (SANS) is particularly well-suited for accurate measurements of surfactant microstructures because the range of length scales probed includes both the particle size and the interparticle spacing. The effect of pressure on microstructure observed in SANS measurements³⁻⁶ is a manifestation of the geometric packing constraints that govern microstructure formation and stability.⁷ For example, recent high-pressure SANS experiments to measure microstructure in a solution of pentaethylene glycol mono-n-dodecyl ether (C₁₂E₅) in D₂O revealed a pressure-induced transition from a network of branched, threadlike micelles to hexagonally ordered bundles of cylindrical micelles.⁸ The instability of this network at elevated pressures was predicted from an analysis of the geometric packing constraints on the branch points, which showed that these branch points, and hence the network, become unstable with the application of pressure. The hydrophobic micelle core also freezes at elevated pressures, which leads to the formation of ordered bundles of cylindrical micelles. The significance of this finding is to show that pressure can be used to direct self-assembly to obtain certain microstructures in aqueous solutions that are virtually impossible to obtain by changing temperature.

Here, we report the results of high-pressure SANS experiments to study the effect of pressure on microstructure in a solution of 1.0 wt % pentaethylene glycol monoctyl ether (C₈E₅) surfactant micelles in water at 29.4 °C and pressures up to 310 MPa. At this temperature and surfactant concentration, a single-phase micellar solution forms at ambient pressure, well below the lower critical solution temperature (LCST) for liquid–liquid equilibrium,⁹ and far removed from the critical micelle concentration (cmc) of C₈E₅ in D₂O at much lower surfactant concentrations.¹⁰ The C₈E₅ micelles are roughly spherical, monodisperse, and noninteracting at these conditions.¹¹,¹² Applying pressure shifts the LCST to higher temperatures,¹³ and raises the cmc to a maximum of 0.33 wt % C₈E₅ at ~150 MPa. The cmc decreases with pressure above 150 MPa.¹⁰

Experimental Section

Scattering experiments were performed on the NG-7 30 m SANS instrument at the NIST Center for Neutron
Research in Gaithersburg, MD. Neutrons of wavelength \(\lambda = 6\,\text{Å}\) with a distribution of \(\Delta\lambda/\lambda = 15\%\) were incident on samples held in a custom-built high-pressure SANS cell. The intensity of elastically scattered neutrons, \(I(q)\), was measured as a function of the magnitude of the scattering vector, \(q = (4\pi/\lambda)\sin(\theta/2)\), over the range \(0.02 \leq q/\text{Å}^{-1} \leq 0.30\). Sample scattering was corrected for background and empty cell scattering, and the sensitivity of individual detector pixels was normalized. Corrected data sets were circularly averaged and placed on an absolute scale using standard samples and software supplied by NIST.\(^{14}\) Instrumental smearing was simulated\(^{15}\) for the instrument configurations used, eliminating smeared data points from the combined data set.

The custom-built high-pressure SANS cell consists of a stainless steel outer cell, rated to 4 kbar, and an inner cell containing the surfactant solution. The design of this high-pressure cell is described in detail elsewhere.\(^{16,17}\) A unique feature of the cell design is to isolate the sample from the pressurizing fluid and the metal walls of the outer cell by enclosing it in the inner cell. This inner cell consists of a flexible Teflon sleeve that fits tightly around the two sapphire windows of the outer cell such that the sample path length (i.e., the distance between the windows) is 1.00 mm at atmospheric pressure. The change in path length due to deformation of the high-pressure cell at elevated pressures was accounted for based on an independent calibration of this deformation.\(^{16}\)

Temperature was controlled using a constant-temperature bath provided by NIST (±0.01 °C sensitivity) that circulated ethylene glycol through the aluminum jacket that held the high-pressure cell. Temperature was measured with an Omega E-type thermocouple and meter (±0.5 °C accuracy). The stability of temperature readings during an experiment was ±0.1 °C. Pressure was generated manually using a pressure generator and measured at the cell using a Viatran Model 345 transducer (0–60,000 psi, <±60 psi nonlinearity) and meter (±1 psi sensitivity).\(^{16}\)

C\(_8\)E\(_5\) (>97% purity) was purchased from Bachem Bioscience and used without further purification. D\(_2\)O (99.9% purity) was purchased from Aldrich Chemicals. The surfactant was apportioned into 2.5-mL aliquots in a glovebox and then stored at 15 °C until used.

Aqueous solutions of 1 wt % C\(_8\)E\(_5\) were prepared by dissolving 1 g E\(_5\) in 100 mL of D\(_2\)O at 29.4 °C and pressures of 4, 69, 138, and 310 MPa. The spectra at the three higher pressures have been offset by factors indicated on the figure.

SANS measurements of the C\(_8\)E\(_5\) micelle radius in D\(_2\)O at the same conditions: 23.5 ± 0.15 Å and 25.5 ± 0.10 Å.\(^{18}\) The latter value was determined by fitting \(I(q)\) over the entire q-range using a model for noninteracting, monodisperse hard spheres. A slightly smaller radius of \(\sim 22\,\text{Å}\) was observed in a molecular dynamics (MD) simulation of the C\(_8\)E\(_5\) micelle in water.\(^{19}\) The application of pressure up to \(\sim 150\,\text{MPa}\) reduces \(R_g\), which then increases slightly with pressure at higher pressures up to 310 MPa. Values for \(R_g\) derived from the SANS spectra using the pair distance distribution function\(^{20}\) (not shown) show a similar pressure dependence up to \(\sim 150\,\text{MPa}\), but are constant at higher pressures. These values are also shifted down by \(\sim 1\,\text{Å}\) across the entire range of pressures compared to those obtained from the Guinier analysis. The pair distance distribution functions also vanish at values greater than the length of a fully extended surfactant molecule, indicating that the micelles have on average a slightly nonspherical shape. A globular, but slightly ellipsoidal shape was noted in the MD simulation of the C\(_8\)E\(_5\) micelle in water.\(^{19}\)

\[ I(q) = I(0) \exp(-\frac{1}{3}R_g^2q^2) \tag{1} \]

where \(R_g\) is the radius of gyration of the micelle and \(I(0)\) is the scattering intensity at \(q = 0\). These results are shown in Figure 2. In each case, a linear plot of \(\ln I(q)\) vs \(q^2\) was obtained for \(q \leq 0.01\,\text{Å}^{-1}\); \(R_g\) and \(I(0)\) calculated from the slope and \(q = 0\) intercept, respectively, are shown in Figure 3.

At 4 MPa, \(R_g = 19.77 \pm 0.03\,\text{Å}\), which corresponds to a micelle radius of 25.5 Å for a spherical micelle with uniform scattering properties. This micelle radius is in good agreement with values obtained from independent MD simulations of the C\(_8\)E\(_5\) micelle in water.\(^{19}\)
The effect of pressure on $I(0)$ (Figure 3) is notably similar to that obtained for $R_g$ and can be attributed to the pressure dependence of the cmc, the micelle aggregation number, $N_{agg}$, and the partial molecular volume of the surfactant, $V_s$:

$$I(0) = \frac{(c - \text{cmc})}{N_{agg}} [N_{agg}(b_s - V_{s\rho}^0)]^2$$

(2a)

$$= (c - \text{cmc})N_{agg}[b_s - V_{s\rho}^0]^2$$

(2b)

where $(c - \text{cmc})$ is the surfactant concentration in excess of the cmc and $(c - \text{cmc})/N_{agg}$ is the concentration of micelles (scattering particles) in solution. The contrast in scattering for a single micelle relative to the solvent is given by $N_{agg}$ times the difference in scattering lengths of a surfactant molecule, $b_s$, and a solvent molecule that would occupy the same volume; that is, the product of $V_s$ and the scattering length density of the solvent, $\rho_s$. The pressure dependence of the cmc has been measured for C$_8$E$_5$ in D$_2$O at 30 °C by $^1$H NMR chemical shifts and, thus, can be accounted for by defining the forward scattering intensity relative to the surfactant concentration in excess of the cmc,

$$I'(0) = \frac{I(0)}{(c - \text{cmc})} = N_{agg}[b_s - V_{s\rho}^0]^2$$

(3)

which gives the effect of pressure on $I'(0)$ in terms of the pressure dependence of $N_{agg}$ and $V_s$. These quantities and their pressure dependence can, in principle, be evaluated using the method of solvent contrast variation.

The method of solvent contrast variation involves systematically adjusting the scattering length density of the solvent by preparing solvent mixtures of D$_2$O and H$_2$O. Thus,

$$\rho_i = x_\text{D}_2\text{O}\rho_\text{D}_2\text{O} + (1 - x)\rho_\text{H}_2\text{O}$$

(4)

where $x$ is the fraction of D$_2$O in the solvent and $\rho_i$ is the scattering length density of component $i$. The scattering length densities of D$_2$O and H$_2$O are at opposite extremes of the range of scattering length densities of most molecules. Thus, an advantage of the method is that solvent mixtures of D$_2$O and H$_2$O can be prepared to match the scattering contrast of almost any molecule of interest. It follows from eqs 3 and 4 that $V_s$ and $N_{agg}$ can be obtained from the slope and $\rho_i = 0$ intercept of a plot of $\sqrt{I'(0)}$ vs $x$. These plots are shown in Figure 4 for four representative pressures; $V_s$ at each pressure, obtained from the slope, is given in Table 1. At 4 MPa, $V_s = 596$ Å$^3$/molecule, in good agreement with $V_s = 575$ Å$^3$/molecule, calculated assuming additive specific volumes for the surfactant head and tail groups.

The plots at the three higher pressures essentially superimpose, such that $V_s \approx 350$–370 Å$^3$/molecule, independent of pressure.

A determination of $N_{agg}$ requires the $\rho_i = 0$ intercept, which is typically located by interpolating measurements made at D$_2$O:H$_2$O compositions well above and below the solvent composition corresponding to $\rho_i = 0$, the so-called match point. However, the match point for C$_8$E$_5$ in D$_2$O:H$_2$O mixtures at ambient pressure is located at $x \approx 0.09$, which precludes such an interpolation. An accurate extrapolation could be contemplated, but would require measurements at a much larger number of D$_2$O compositions well above the match point. Since this approach is not feasible for the full range of pressures of interest, an accurate determination of $N_{agg}$ and its pressure dependence using the method of solvent contrast variation was not pursued for this surfactant solution.

As noted above, however, the pressure dependence of $I'(0)$ is similar to that obtained for $R_g$, which can also
be defined in terms of \(N_{agg}\) and \(v_s\),

\[
c_1R_g^3 = N_{agg}v_s + N_{DO}v_{DO} \quad (5a)
\]

\[
= N_{agg}(v_s + \alpha v_{DO}) \quad (5b)
\]

where \(c_1\) is a geometric constant, \(N_{DO}\) is the number of water molecules in the micelle, \(v_{DO}\) is the partial molecular volume of water, and \(\alpha = N_{DO}/N_{agg}\) is the number of water molecules per surfactant molecule in the micelle. Combining eqs 3 and 5b to eliminate \(N_{agg}\) gives

\[
\frac{c_1R_g^3}{l'(0)} = \frac{v_s + \alpha v_{DO}}{(b_s - v_{DO})^2} \quad (6)
\]

which provides a relationship for determining the extent of hydration of the \(C_8E_5\) surfactant in the micelles through the parameter, \(\alpha\). The calculation of \(\alpha\) is based on two assumptions: the micelles are spherical with uniform scattering properties, which defines \(c_1 = (4\pi/3)(5/3)^{3/2}\), and the molecular volume for pure liquid \(D_2O\) is a reasonable approximation for \(v_{DO}\). The values of \(\alpha\) calculated using eq 6 are given in Table 1. At 4 MPa, \(\alpha \approx 1.5\), which corresponds to 3 water molecules per surfactant \(EO\) group if, as expected, water hydrates the hydrophilic micelle shell, but does not penetrate the hydrophobic core. The phenomenon is reminiscent of the pressure-induced dehydration of the surfactant head groups and a collapse of the hydrophilic micelle shell.

At all three higher pressures, \(\alpha\) decreases to \(-1\). This pronounced decrease in \(\alpha\) and the concomitant decreases in \(v_s\) and \(R_g\) with increasing pressure, suggest a pressure-induced dehydration of the surfactant head groups and a collapse of the hydrophilic micelle shell. The radius of a perfect hard sphere approximates \(R_g\) if \(\alpha = 0\), and in the context of the core–shell model, the micelles consist of a spherical hydrophobic core having a uniform scattering length density, \(\rho_c\), surrounded by a spherical hydrophilic shell with a different, but likewise uniform scattering length density, \(\rho_{sh}\). The scattered intensity given by the core–shell model is

\[
I(q) = \frac{3J_1(qR_c)}{qR_c} + (1 - x)\frac{3J_1(qR_{sh})}{qR_{sh}}^2 \quad (7)
\]

where \(R_c\) and \(R_{sh}\) are the core and shell radii, respectively, \(J_1\) is the first-order Bessel function, and

\[
x = \frac{R_c^3(\rho_c - \rho_{sh})}{R_c^3(\rho_c - \rho_{sh}) + R_{sh}^3(\rho_{sh} - \rho_0)} \quad (8)
\]

is the contribution to \(I(q)\) due to scattering from the micelle core in excess of that from a micelle with a uniform scattering length density corresponding to \(\rho_{sh}\). Using \(I(0)\) from the Guinier analysis, the scattering spectra were fit to eq 7 with \(R_c\), \(R_{sh}\), and \(x\) as adjustable parameters. Excellent fits were obtained at all conditions as illustrated in Figure 5 for spectra at two representative pressures. The parameters obtained from the fits are given in Table 2. As expected, attempted fits of the spectra assuming spherical micelles with a uniform scattering length density produced much different and less accurate descriptions, especially at high \(q\). Radii of gyration calculated using these fitted parameters were also found to be within 1.5% of those values obtained directly from the Guinier analysis.

![Figure 5. Core–shell model fits (eq 7) to the measured scattering intensities as a function of the magnitude of the scattering wave vector for a solution of 1 wt% \(C_8E_5\) in \(D_2O\) at 29.4°C and pressures of 69 and 310 MPa. The spectrum at 310 MPa has been offset by a factor of 4 as indicated on the figure.](image3)

### Table 2. Parameters from the Core–Shell Model Fits (eq 7) of the Measured Scattering Intensities as a Function of the Magnitude of the Scattering Wave Vector for a Solution of 1% by Weight \(C_8E_5\) in \(D_2O\) at 29.4°C

<table>
<thead>
<tr>
<th>(P) (MPa)</th>
<th>(R_c) (Å)</th>
<th>(R_{sh}) (Å)</th>
<th>(x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>69</td>
<td>10.80</td>
<td>30.66</td>
<td>0.414</td>
</tr>
<tr>
<td>138</td>
<td>10.90</td>
<td>30.00</td>
<td>0.409</td>
</tr>
<tr>
<td>220</td>
<td>10.98</td>
<td>29.86</td>
<td>0.407</td>
</tr>
<tr>
<td>296</td>
<td>11.19</td>
<td>29.89</td>
<td>0.407</td>
</tr>
<tr>
<td>310</td>
<td>11.20</td>
<td>29.88</td>
<td>0.401</td>
</tr>
</tbody>
</table>

*See Figure 5. The estimated uncertainties in these parameters are \(\pm 0.018\) Å for \(R_c\), \(\pm 0.026\) Å for \(R_{sh}\), and \(\pm 0.003\) for \(x\).
high q will be more sensitive to the value of $R_c$. Thus, accurate descriptions of both $R_g$ and $I(q)$ indicate that the values obtained for $R_c$ and $R_{sh}$ are reasonable. The range of values obtained for $R_c$ (10.8–11.2 Å) is also reasonable based on a predicted maximum chain length for the C₈ hydrocarbon tail group of 11.6 Å, and the observation that the C₈ hydrocarbon chains in the C₈E₅ micelle adopt liquid n-octane-like, extended conformation at ambient pressure.

We note, however, that the values of x in Table 2 imply a much higher $\rho_{sh}$ than expected, based on the scattering length densities of the C₈E₅ head group and D₂O with the extent of C₈E₅ head group hydration calculated using the values of $x$ in Table 1. Convergence to these high values was notably robust, even with initial values of $x \sim 0$. A similar observation was made in a SANS study of micelles formed by poly(ethylene-co-propylene)–PEO block copolymers in water and was attributed to a much higher density of waters hydrating the PEO chains of the micelles. The extent of hydration of the surfactant head groups in the C₈E₅ micelle calculated using the values of x in Table 2 is, however, about 1 order of magnitude too high to be physically realistic. An alternative interpretation is that the unusually high values of x reflect limitations in the core–shell model that can be attributed to the assumption of spherical symmetry. As noted above, the pair distance distribution functions that were calculated from the scattering spectra and the MD simulation of the C₈E₅ micelle in water both indicate a globular, but not perfectly spherical micelle. A core–shell model that accounts for nonspherical shapes will have additional fitting parameters and, as such, would require additional information in the form of either independent experimental data or molecular simulations to validate them, which is beyond the scope of the current study. Therefore, in the context of the core–shell model that was used here, we accept the parameter x as simply a fitting parameter without a physical interpretation.

The fitted values for $R_c$ and $R_{sh}$ are plotted as a function of pressure in Figure 6. The pressure dependence of $R_{sh}$ tracks almost quantitatively with that of $R_g$, while $R_c$ increases slightly with increasing pressure. The decrease in $R_{sh}$ with increasing pressure is also much more abrupt than the increase in $R_c$, which is nearly linear with pressure. These observations provide further support for a pressure-induced collapse of the micelle shell. It should also be noted that the increase in $R_c$ with increasing pressure is counter-intuitive. On the basis of the compressibility of pure liquid n-octane at 29.4 °C, we would expect the hydrophobic micelle core to compress slightly under pressure. Expansion of the core could be a manifestation of the intercalation of surfactant EO groups into the interfacial region as the shell collapses. This hypothesis is supported by the MD simulation of the C₈E₅ micelle in water where it was found that the surfactant head groups adopt on average partially coiled, nonlinear chain conformations in contrast to the C₈ hydrocarbon chains, which adopt on average liquid n-octane-like, extended conformations. Thus, the folding back and penetration of these relatively long and flexible head groups into the interfacial region of the micelle as the shell dehydrates with increasing pressure appears to be feasible. A resolution of the molecular origins of this observation is, however, beyond the scope of the primitive core–shell model that was used to fit our scattering spectra. Using the structural details obtained from MD simulations of individual C₈E₅ micelles in water at elevated pressures as a basis for analyzing these spectra would provide a molecularly unambiguous description of $I'(0)$. This molecularly detailed approach to modeling SANS spectra is currently in progress.

**Conclusions**

Our study of the effect of pressure on C₈E₅ micellization in D₂O has shown that the application of pressure induces the dehydration of the surfactant head groups, which leads to the collapse of the hydrophilic micelle shell. This conclusion is based on several findings. We found that increasing pressure leads to a pronounced decrease in the micelle radius of gyration. A similar pressure dependence was observed for the scattering intensity at $q = 0$. Using the method of solvent contrast variation, we determined the partial molecular volume of the surfactant and the extent of hydration of the surfactant head groups and found that these quantities decrease with the application of pressure. The pressure dependence in both cases is similar to that observed for...
the radius of gyration. From core–shell model fits to I(q) over the entire q-range, we determined that the micelle shell collapses, while the core expands slightly with increasing pressure. Moreover, the pressure dependence of the shell radius is notably similar to that for the radius of gyration. The pronounced decrease in the shell radius is in contrast to the nearly linear increase in the core radius with increasing pressure. The expansion of the micelle hydrophobic core was unexpected, and the molecular origins of this observation have yet to be resolved.

Finally, this dilute aqueous solution of nonionic C₆E₅ micelles was selected as a model system for this study for two reasons: interparticle interactions could be neglected and, more importantly, the surfactant microstructure at ambient pressure is well-known and simple. Our results establish that the microstructure for this surfactant system is sensitive to pressure; significant changes in core–shell structure of the micelle can be brought about with the application of pressures on the order of 150 MPa. Recent studies of the effects of pressure on incrementally more complex systems—for example, C₁₂E₅ in water—reveal changes in microstructure that are unique to pressure. We believe that further studies of surfactant self-assembly at high pressure are likely to lead to more discoveries of pressure effects that give rise to structures and structural transitions that have not been anticipated and that may have interesting practical applications.

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