# Critical Micelle Density for the Self-Assembly of Block Copolymer Surfactants in Supercritical Carbon Dioxide

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# Critical Micelle Density for the Self-Assembly of Block Copolymer Surfactants in Supercritical Carbon Dioxide

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The parameters which influence the self-assembly of molecules in solution include the temperature and solvent quality, and this study illustrates the use of these variables to regulate the degree of association of block copolymer amphiphiles in highly compressible supercritical carbon dioxide. Small-angle neutron scattering (SANS) has been used to examine the association behavior of a block copolymer containing a $CO_2$-phobic moiety, poly(vinyl acetate), and a $CO_2$-philic block, poly(1,1-dihydroperfluoro-octylacrylate). By adjustment of the density of the medium through pressure and temperature profiling, the self-assembly can be reversibly controlled from unimers to core–shell spherical micelles and this establishes a critical micelle density (CMD), a phenomenon distinctive of highly compressible fluids, such as supercritical $CO_2$. Mathematical modeling of the data in terms of core–shell micelle structures permits a detailed description of the structure and the degree of swelling (penetration) of the solvent into the different regions of the aggregates throughout this transition.

## Introduction

Above its critical point (temperature > 31 °C; pressure > 73 bar), carbon dioxide forms a supercritical fluid (SCF) that promises to be an environmentally responsible replacement for organic solvents and water in many commercial applications.[1–4] It is nontoxic, nonflammable, and inexpensive, and its high compressibility allows the density to be controlled via pressure and temperature profiling to tune the solvent quality of the medium. Despite these inherent advantages, it has a significant drawback in that few substances exhibit appreciable solubility[2,5] at readily accessible temperatures (<100 °C) and pressures (<350 bar). To overcome the poor dissolving power of $CO_2$, molecularly engineered surfactants containing both $CO_2$-phobic and $CO_2$-philic segments have recently been developed.[3,4,6–12]

Such surfactants have been used in a wide range of applications including the stabilization of polymer colloids during dispersion polymerizations,[1,6,13–15] in the formation[16,17] and swelling[4,6] of micelles with $CO_2$-insoluble substances transferred from solid surfaces, as well as for liquid–liquid extractions via the phase transfer of water-soluble substances from water into a surfactant-rich liquid $CO_2$ phase.[3] Emulsification of both hydrophilic and lipophilic $CO_2$-insoluble materials has previously been achieved in supercritical as well as liquid $CO_2$,[3,4,12,16] though in these examples, the entrained materials were bound to the surfactant system, limiting their potential utility.

Molecular shape, hydrogen bonding, dipole–dipole interactions, electrostatics, temperature, and solvent

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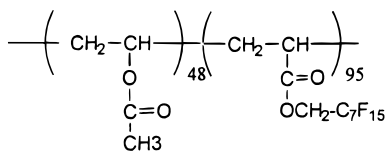
**Figure 1.** Structure of PFOA-*b*-PVAc.

quality play important roles in controlling the degree and the nature of association of amphiphilic molecules in solution.[18-22] The ability to design appropriate surfactant molecules for $CO_2$ depends on knowing the density dependence of the solubility characteristics of the various segments, and manipulating the chemical composition or molecular weight so that a given molecular segment becomes soluble or goes through a cloudpoint curve at the desired density.[15,23] One can then combine segments having different solubility characteristics to achieve the desired transition point for a specific application. We have therefore attempted to synthesize surfactants, which will permit the solubilization process to be reversed, so that at intermediate densities $CO_2$ acts as a solvent for only one block, and when the density is increased to the point where both blocks are soluble, the micelles are able to disassociate into unimers. This leads to the precipitation and hence separation of the previously emulsified $CO_2$-insoluble substances and opens the door to their use in separation, extraction, and recycling applications.

We have previously used small-angle neutron scattering (SANS) to characterize the formation of micelles in supercritical $CO_2$ and the solubilization of $CO_2$-insoluble material.[3,4,16,17] For example, a block copolymer containing a $CO_2$-phobic moiety, polystyrene, and a $CO_2$-philic block, poly(1,1-dihydroperfluorooctylacrylate) (PFOA) was shown to be capable of solubilizing polystyrene (PS) oligomer (molecular weight, ∼500) in $CO_2$ at a pressure of ∼340 bar in the temperature range 40-65 °C. In this paper we describe the application of SANS to examine the association behavior of a block copolymer containing a $CO_2$-phobic moiety, poly(vinyl acetate) (PVAc, 4.4k Da; polydispersity index, 1.55) and a similar $CO_2$-philic block (PFOA, 43.1k Da; polydispersity index, ∼2). The structure of this molecule is shown in Figure 1.

## Experimental Section

PFOA-*b*-PVAc samples were synthesized according to procedures established in the literature.[24] PFOA has been shown[15,25,26] to be highly soluble in supercritical $CO_2$ at solvent densities greater than 0.772 g cm$^{-3}$ and to be an effective $CO_2$-philic moiety in the design of $CO_2$-targeted surfactants.[4,27,28] Conversely, PVAc is insoluble at similar conditions yet becomes solvated at higher temperatures and pressures (approaching 515 bar). It was previously shown[4,16] that there was virtually no $CO_2$ penetration

into the core of a PS−PFOA block copolymer micelle. However, as indicated above, PVAc is much less "$CO_2$-phobic" than PS, which permits significant swelling of the PVAc core, and mathematical modeling of the SANS data allows this "invasion" to be quantified as a function of concentration, $CO_2$ pressure, and temperature.

Experiments were conducted with concentrations from 2% < $C$ < 8% (w/v), temperatures of 40 and 65 °C, and pressures in the range of 165-344 bar on the W. C. Koehler 30m SANS facility at Oak Ridge National Laboratory.[29] The wavelength was $\lambda = 4.75$ Å ($\Delta\lambda/\lambda \sim 5\%$) and the data were corrected for instrumental backgrounds and detector efficiency on a cell-by-cell basis, prior to radial averaging to give a range of momentum transfer $0.006 < Q = 4\pi\lambda^{-1} \sin\theta < 0.06$ Å$^{-1}$, where $2\theta$ is the angle of scatter. The net intensities were converted to an absolute ($\pm3\%$) differential cross section [$d\Sigma(Q)/d\Omega$] per unit sample volume (in units of cm$^{-1}$) by comparison with precalibrated secondary standards.[30] The experiments were conducted in a cell similar to those that have been used extensively for polymer synthesis,[6] and because of the high penetrating power of the neutron beam, it passed through two 1-cm thick sapphire windows (transmission, ≈93%) with virtually no parasitic scattering. The cross section of the "blank" cell filled with $CO_2$ (∼0.04 cm$^{-1}$) formed only a minor correction to the data.[17]

## Results and Discussion

A collection of unimers, uncorrelated in space and in time, may be modeled as a set of independent random coils (RC) and the coherent cross section is given by[31]

$$[d\Sigma(Q)/d\Omega]_{RC} = 2N_p(V_p\Delta\rho)^2\ [(QR_g)^2 + \exp[(QR_g)^2] - 1]/(QR_g)^4$$

$$= N_p(V_p\Delta\rho)^2\ P_{RC}(Q) \qquad (1)$$

where $N_p$ is the number density of polymer chains of volume $V_p$, $\rho$ is the scattering length density (SLD), $\Delta\rho$ is the SLD contrast with $CO_2$, $P_{RC}(Q)$ is the random coil[31] form factor [$P(0) = 1$], and $R_g$ is the radius of gyration. In principle, the scattering from individual chains should be modeled via a block copolymer form factor. However, the PFOA block length and contrast are much higher than those for PVAc, so its contribution to the scattering is over an order of magnitude greater and, to a good approximation, the scattering can be modeled as a single-species coil with $R_g \sim 45$ Å. When the $CO_2$ pressure is decreased, changes in solvation induce space−time correlations between the unimers and consequently generate stable composition fluctuations. These are similar to the structures which, in aqueous media, are called micelles and have been extensively characterized via SANS,[32,33] which gives their "time-averaged" structure and integrates over the dynamic unimer−micelle exchange.

The possibility of forming micelles in SCFs, similar to those formed in aqueous media, has been extensively debated and was first explored by small-angle X-ray scattering (SAXS) by Fulton and co-workers[9] on $H_2O$-swollen PFOA−poly(ethylene oxide) (PFOA-*g*-PEO) graft copolymers in $CO_2$. The data were modeled in terms of polydisperse, concentric spherical shells[9] and subsequent SANS experiments,[17] using absolute units, allowed a more stringent test of the model. The polydispersity was described via a Schutz[16,17,32] distribution of particle sizes and the results confirmed the overall conclusions of the

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SAXS experiments, despite the widely different contrast factors for SAXS and SANS. This methodology has been extensively used to model SANS from micelles in aqueous media,[32,33] including data from poly(propylene oxide)−PEO triblock copolymers in the micelle−unimer transition region.[34] Using a three-parameter model, it was possible to quantify the dimensions and the penetration of water into the core as a function of temperature.[34] A similar approach[4,16] was used to confirm the existence of micelles formed by PS−PFOA block copolymers in supercritical $CO_2$, for which the polydisperse spherical "core−shell" model gave excellent fits to the SANS data. When the pressure was lowered, it was found that the aggregation increased, and this was the first indication[4] of a critical micelle density (CMD), analogous to the critical micelle concentration (CMC). In this work, we continue to use a Schultz distribution to describe the polydispersity of the aggregated particles, though we have generalized the model to allow for solvent penetration into the core. We have modeled the aggregate−aggregate interactions via a structure factor, $[S(Q)^{PY}]$, calculated via the Percus−Yevick approximation.[35] In a few cases, we have also observed critical fluctuations (e.g., near phase boundaries), which were described by the Ornstein−Zernike[36] formula $S(Q)^{OZ} \sim [1 + Q^2 a^2]^{-1}$, where a is the concentration fluctuation correlation length. For runs where this term was finite, the correlation length was sufficiently high ($>10^3$ Å) that this component decayed rapidly with $Q$, and in the observable range ($Q \geq 0.006$ Å$^{-1}$) it was an order of magnitude less than the aggregate scattering, which is maximized in this region of the phase diagram. Thus, under conditions of decoupling between position and orientation of the particles,[32] the total coherent cross section of a mixture of random coil chains and core−shell aggregates is

$$[d\Sigma(Q)/d\Omega]_{tot} = N_p(V_p\Delta\rho)^2 P_{RC}(Q) + N_{agg}(V_{agg}\Delta\rho)^2 P_{agg}(Q)[S(Q)^{PY} + S(Q)^{OZ}] + \Delta(Q) \quad (2)$$

where $N_{agg}$ is the number of chains per aggregate. $\Delta(Q)$ is the difference between the "average squared" and the "square of the average" scattering amplitude and is zero for spherical, monodisperse particles.[32] For the spherical micelles observed in this work, it is roughly independent of $Q$, and a function of the same parameters used to calculate $P_{agg}(Q)$, the aggregate form factor. Thus, the inclusion of the $\Delta(Q)$ term does not introduce an additional fitting parameter.

To minimize interparticle interactions in eq 2, it is desirable to work below the overlap concentration, $C^*$, above which the micelles interpenetrate. $C^*$ may be estimated[37] via $C^* = 3N_{agg}MW/(4\pi R_g^3 A_0)$, where $A_0$ is Avogadro's number and MW is the molecular weight of an individual molecule. This identity, which is based on the plausible idea that overlap occurs when the space pervaded by the micelle equals the average volume per particle, leads to an estimate of $C^* \sim 0.17$ g/m$^3$ and other formulas[38,39] for $C^*$ give even higher estimates. Thus, in this work, $C < C^*$ and the micelles should scatter as single particles modulated by the structure function, $S(Q)$.

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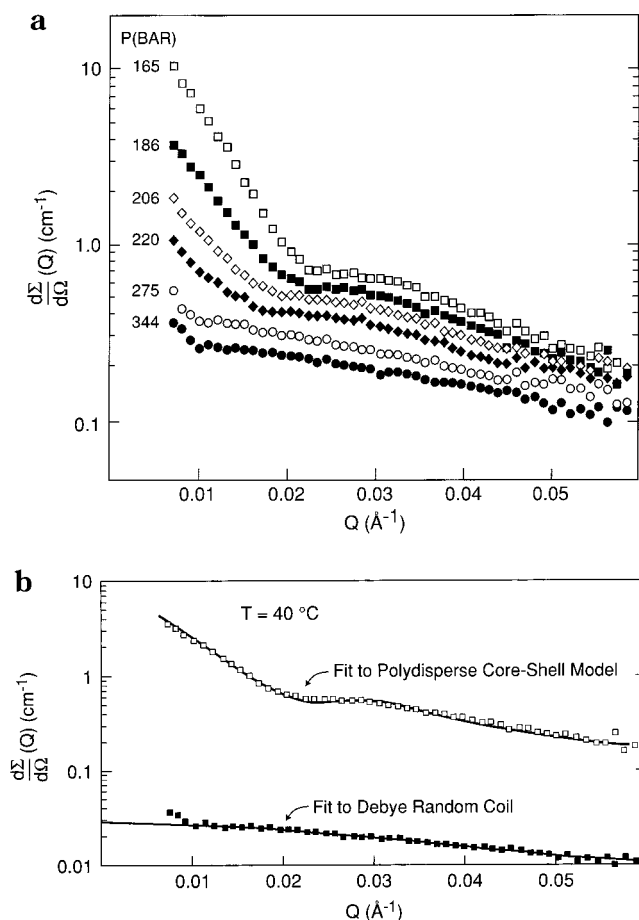


**Figure 2.** (a) Pressure scan through critical micelle density for 8% PVA$_c$−PFOA in $CO_2$. (b) Fit to polydisperse core−shell and Debye random coil models for 8% W/V PVA$_c$−PFOA micelles ($P = 186$ bar) and unimers ($P = 344$ bar).

A similar estimate of $C^*$ ($\sim$10%) was quoted by Buhler and co-workers,[40] who used static and dynamic light scattering (LS) techniques to study pressure-induced micellization transition in diblock PVAc−fluoropolymers with $R_g \sim 150$ Å. PVAc-*b*-PFOA diblock copolymers in $CO_2$ have also been studied via LS by Zhou and Chu.[41] In addition to pressure-induced micellization, small amounts of anomalous large aggregates were observed around the critical phase separation pressure ($\sim$225 bar), though the size of these assemblies ($\sim$5000 Å) is beyond the resolution range of SANS. Little difference was reported in the results from solutions with concentrations of 5.7 and 9.6% (w/v), indicating that both were below the overlap concentration, and the aggregation numbers and $R_g$'s were similar to those observed via SANS (see below).

Figure 2 shows the scattering curves for 8 w/v% PFOA-*b*-PVAc in $CO_2$ at 40 °C, as a function of pressure (165 < $P$ < 344 bar) along with fitted curves (Figure 2b) for both the unimer (344 bar, $CO_2$ density = 0.940 g cm$^{-3}$) and the micellar states (185 bar, $CO_2$ density = 0.837 g cm$^{-3}$). As the pressure is lowered from 344 to 165 bar, the shapes and absolute magnitudes of the scattering curves change dramatically from curves characteristic of unimers [d$\Sigma$(0)/d$\Omega \sim 0.4$ cm$^{-1}$], to those indicative of micellar aggregates [d$\Sigma$(0)/d$\Omega \sim$ 10−20 cm$^{-1}$]. As the pressure is reduced, the shape of the scattering curves clearly indicate the presence of aggregates via the peak at $Q \simeq 0.03$ Å$^{-1}$.

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This is the first maximum in the intramolecular (core–shell) form factor [$P(Q)$], and the upturn as $Q \rightarrow 0$ in Figure 2a reflects the product of $P(Q)$ and the intermolecular structure factor [$S(Q) \simeq S(Q)^{PY}$]. Near the phase boundary (e.g., at 40 °C and 187 bar) concentration fluctuations make an additional contribution to the total $S(Q)$, which can be described by $S(Q)^{OZ}$.

Several particle shapes were used to calculate $P(Q)$, and as observed previously,[4,16,17] the best fits were given by a spherical core–shell model,

$$P_{agg}(Q) = \frac{4\pi}{3}[R_1^3(\rho_1 - \rho_2)F_0(QR_1) + R_2^3(\rho_2 - \rho_s)F_0(QR_2)]$$

$$F_0(x) = \frac{3}{x^3}(\sin x - x \cos x) \tag{3}$$

where $R_1$ and $R_2$ are the core and shell radii. The polydispersity was best described via a Schultz distribution[33] of particle sizes,

$$f(R) = \frac{(Z+1)^{Z+1} X^Z \exp[-(Z+1)X]}{\bar{R}\Gamma(Z+1)}$$

$$Z = [1 - (\sigma/\bar{R})^2]/(\sigma/\bar{R})^2$$

$$X = R/\bar{R} \tag{4}$$

where $\sigma^2$ is the variance of the distribution, $Z$ is the breadth parameter, and $\rho_1$, $\rho_2$ are the core/shell SLDs. The mole fraction of the copolymer present as nonaggregated random coils (unimers) was obtained by minimizing the standard deviation of the fits with respect to this variable and a relatively constant value of 1.2 w/v% was found at all the pressures and temperatures for which aggregation occurred. The solubility of both PFOA and PVAc becomes better with increasing solvent density, leading to a decrease in the aggregation number. Thus, the $R_g$ of PFOA will increase with increasing density as discussed by DeSimone and co-workers.[42] However, as shown below, the process of aggregate-to-unimer transition mainly occurs through swelling of the micellar core with $CO_2$.

Table 1 shows the results from fitting of SANS data for pressure profiles at temperatures of $T = 65$ and 40 °C for concentrations in the range 2% $< C <$ 8% (w/v). The main fitting parameters are the core/shell volumes and the corresponding scattering length densities. The volumes depend on the same parameters that determine the SLDs (i.e., the aggregation number, the amount of $CO_2$ that swells the various regions of the micelle (i.e., the core/shell solvation), and the (known) segment/$CO_2$ volumes]. Thus, had the micelles been monodisperse, three independent parameters (aggregation number and core/shell solvation) would have been sufficient to model the data, though for these particular micelles, it was necessary to add a fourth variable ($Z$) to describe the polydispersity. As pointed out previously,[32,34] $R_1$ and $R_2$ are not independent parameters, as they can be calculated (e.g., $R_1 \simeq$ 72 Å, $R_2 \simeq$ 120 Å, and $R_g \simeq$ 100 Å for $C = 6$% w/v, $P = 164$ bar, and $T = 40$ °C) from the core and shell solvation and $N_{agg}$. Furthermore, the fits must reproduce the absolute cross section (in cm$^{-1}$) and this further constrains the fitting parameters. The fact that the aggregation numbers and micelle dimensions from independently calibrated SAXS and SANS data, with quite different contrast factors,

**Table 1. Results from Modeling of SANS Data from PVAc-*b*-PFOA Block Copolymer Surfactants in Supercritical CO₂**

*(a) 40 °C Results*

| C (w/v) | P (bar) | density[b] (g cm⁻³) | $R_g$ (±5 Å) | shell solvation (±3) | core invasion (±0.2) | $N_{agg}$ (±3) | Schultz index, Z (±4) |
|---|---|---|---|---|---|---|---|
| 2 | 274 | 0.905 | 56 | N/A[f] | N/A[f] | N/A[f] | N/A[f] |
| 2 | 187 | 0.837 | 52 | N/A[f] | N/A[f] | N/A[f] | N/A[f] |
| 4 | 185 | 0.837 | 102 | 18 | | 26 | 15 |
| 4 | 267 | 0.899 | 52 | N/A[f] | N/A[f] | N/A[f] | N/A[f] |
| 6 | 164 | 0.808 | 99 | 18 | 1.0[c] | 36 | 15 |
| 6 | 185 | 0.837 | 98 | 18 | 2.2 | 26 | 14.5 |
| 6 | 205 | 0.852 | 107 | 25 | 3.0 | 29 | 22 |
| 6 | 219 | 0.865 | 117 | 33 | 4.2 | 29 | 18 |
| 6 | 274 | 0.900 | TR[e] | TR[e] | TR[e] | TR[e] | TR[e] |
| 6 | 342 | 0.940 | 43 | N/A[f] | N/A[f] | N/A[f] | N/A[f] |
| 8 | 165 | 0.808 | 90 | 12 | 1.0[d] | 27 | 13 |
| 8 | 186 | 0.837 | 97 | 17 | 1.2 | 27 | 15 |
| 8 | 197 | 0.845 | 104 | 22 | 1.3 | 29 | 19 |
| 8 | 206 | 0.852 | 108 | 27 | 1.4 | 29 | 22 |
| 8 | 220 | 0.870 | 118 | 34 | 1.8 | 34 | 28 |
| 8 | 240 | 0.880 | 130 | 36 | 2.6 | 36 | 31 |
| 8 | 275 | 0.905 | 43 | N/A[f] | N/A[f] | N/A[f] | N/A[f] |
| 8 | 344 | 0.940 | 41 | N/A[f] | N/A[f] | N/A[f] | N/A[f] |

*(b) 65 °C Results*

| C (w/v) | P (bar) | density[b] (g cm⁻³) | $R_g$ (±5 Å) | shell solvation (±3) | core invasion (±0.2) | $N_{agg}$ (±3) | Schultz index, Z (±4) |
|---|---|---|---|---|---|---|---|
| 4 | 373 | 0.864 | 54 | N/A[f] | N/A[f] | N/A[f] | N/A[f] |
| 4 | 397 | 0.877 | 53 | N/A[f] | N/A[f] | N/A[f] | N/A[f] |
| 6 | 295 | 0.812 | 117 | 10 | | 26 | 19 |
| 8 | 274 | 0.792 | 98 | 22 | 1.0 | 21 | 17 |
| 8 | 308 | 0.823 | 118 | 27 | 1.0 | 26 | 22 |
| 8 | 366 | 0.860 | 46 | N/A[f] | N/A[f] | N/A[f] | N/A[f] |

[a] 40 °C results. [b] 65 °C results. [c] Normalized value based on lowest available aggregated system where the number of $CO_2$ molecules per PVAc segment is 13:1. [d] Normalized value based on lowest available aggregated system where the number of $CO_2$ molecules per PVAc segment is 20:1. [e] TR denotes transition region. [f] N/A denotes states where molecules exist predominantly as unimers, and the core–shell model is inapplicable.

are virtually identical[16] gives a cross check on the reliability of this methodology.

For a given concentration, the invasion of $CO_2$ into the core of the micelle has been normalized on the basis of the lowest available pressure data set to show swelling of the aggregate core with $CO_2$, affecting the transition toward solvation and dissociation. For $CO_2$ densities lower than 0.79 g cm$^{-3}$, the system turns translucent and approaches phase separation. While the aggregation number ($N_{agg}$) remains fairly constant over the pressure range that aggregates exist, the core solvation increases by a factor $\sim 3-4$. It was not obvious a priori that the PVAc swelling could increase as dramatically as indicated via SANS. However, the VAc monomer is very soluble in $CO_2$, and a PVAc of high molecular weight (MW) has been shown to be soluble at $\sim 500$ bar by McHugh.[1] Similarly, low- to intermediate-MW PVAc solubility curves are a very strong function of MW and the cloudpoint curves shift dramatically[43] for small changes in MW, so PVAc does have regions of solubility in $CO_2$.

Dissociation of the aggregated structures occurs at a sharp transition point over a range of approximately 0.05 g cm$^{-3}$ in density. Near this transition, SANS data cannot

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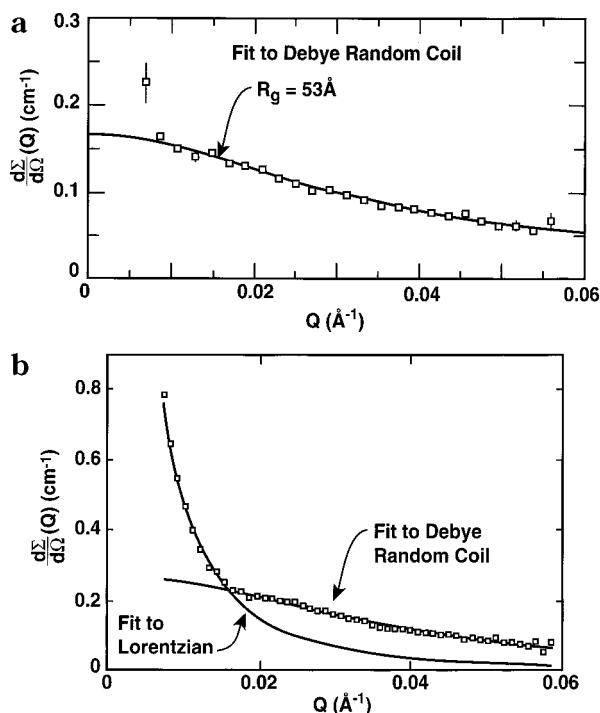
**a**



**b**



**Figure 3.** (a) $d\Sigma/d\Omega(Q)$ vs $Q$ for 2% (w/v) PVAc[4.4k]-$b$-PFOA[43.1k] block copolymer in $CO_2$ at 40 °C/4000 psi (275 bar). (b) $d\Sigma/d\Omega(Q)$ vs $Q$ for 2% (w/v) PVAc[4.4k]-$b$-PFOA[43.1k] block copolymer in $CO_2$ at 40 °C/2700 psi (185 bar).

be fitted by either the core–shell or Debye coil models. The onset of dissociation generally occurs at a solvent density of 0.87 g cm$^{-3}$ for the 40 °C data and slightly higher for 65 °C. The disparity with temperature is based on increases in the solubility of oligomeric PVAc with temperature, which is supported by literature precedent of low–moderate vapor pressure, low-MW species which tend to be very soluble[5,44] in $CO_2$.

Experiments conducted over a range of concentrations realize a phenomenon similar to the critical micelle concentration (CMC) for traditional surfactant systems. At 2 w/v% we are unable to detect core–shell aggregate formation, as indicated in Figure 3a, which shows typical scattering curves, including an analysis in terms of unimers, fitted via a Debye coil function at $P = 275$ bar and 40 °C. Near the phase boundary (e.g., at $P = 185$ bar), it is necessary to include a contribution from critical

fluctuations, fitted via an Ornstein–Zernike (Lorentzian) term, in addition to the unimer (Debye coil) scattering. To illustrate these contributions, we chose a region of the phase diagram where these contributions are strongest (and the scattering from micelles is virtually nonexistent).

As the concentration increases from $C = 2\%$ to 4% w/v ($T = 40$ °C; 186 bar), micellar structures emerge as the predominant species over the low-density régime. Zhou and Chu[41] measured CMCs of 2.2–3.3% at $T = 65$ °C in a pressure range of 275–379 bar for a 10/43$k$ PVAc–PFOA copolymer and established an empirical correlation that would extrapolate to a CMC of 1.5% (w/v) at 186 bar. Thus, the appearance of micelles in the concentration range 2–4% (w/v) is reasonably consistent with the LS data,[41] as are the aggregation numbers (Table 1). For example, at 275 bar and 65 °C Zhou and Chu[41] measured $N_{agg} = 18$, whereas the equivalent numbers for SANS are (21–26) $\pm$ 3 in the range 274–295 bar. While exact comparison is not possible, both the lower MW of the PVAc block and temperature would be expected to lead to somewhat higher values of CMC and $N_{agg}$ in this work. However, it is puzzling that, for the 8% sample, $N_{agg}$ increases (from 27 to 36) before the aggregates break into unimers, though the trend appears to be greater than the statistical error ($\pm 3$) and is accompanied by an increase in $R_g$ (from $\sim$ 90 to 130 Å).

The data at the highest $CO_2$ pressures are consistent with the scattering of individual molecules, as illustrated in Figure 2b which shows the fits to the random coil model (eq 1) for $P = 344$ bar. The radius of gyration ($R_g$), the rms distance of scattering elements from the center of gravity, is a measure of the volume pervaded by a single polymer chain and was in the range $48 \mp 5$ Å over the temperatures and concentrations studied. The ($Q = 0$) cross section, which reflects the state of aggregation ($d\Sigma(0)/d\Omega = 0.27$ $\pm$ 0.05 cm$^{-1}$ at 344 bar), may be compared to a calculated value of $d\Sigma(0)/d\Omega = 0.29$ cm$^{-1}$ for unimers. Although a Debye coil (as opposed to a block copolymer) form factor is used to extrapolate the scattering to $Q = 0$, the calculated $d\Sigma/d\Omega(0)$ includes both components and alternative extrapolation methods (e.g., linear regression via Zimm plots[45]) give the same forward scattering ($d\Sigma(0)/d\Omega = 0.26$ $\pm$ 0.05 cm$^{-1}$) within the experimental errors. The SANS contrast factors depend on the $CO_2$ density and at $T = 40$ °C, $P = 241$ bar, and $C = 8\%$ (w/v), the fitted and calculated values of $d\Sigma/d\Omega(0)$ are 0.45 and 0.42 cm$^{-1}$, respectively. The average molecular weight of the unimers, estimated
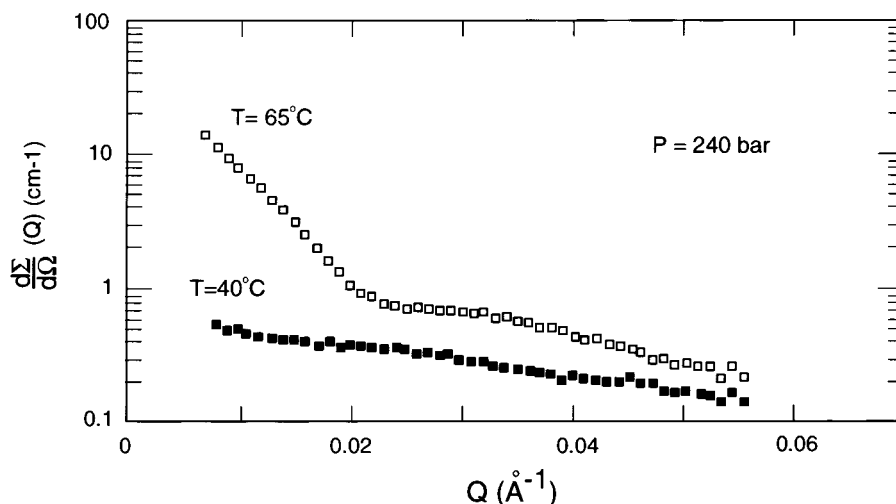


**Figure 4.** Sans cross section for 8% (W/V) 4.4$^k$-$b$-43.1$^k$ PVAc–PFOA copolymers in supercritical $CO_2$. By changing the temperature from 65 to 40 °C the molecular aggregates (micelles) are dispersed into individual molecules (unimers).

from the experimental $d\Sigma/d\Omega(0)$ is MW $\simeq 47\,500$ g mol$^{-1}$, which is in good agreement with that derived from synthetic methods.[24] Thus, values for $d\Sigma(0)/d\Omega$ are consistent over the range of concentration where unimers predominate, confirming the assumption of single, non-interacting coils.

In addition to pressure, changes in temperature can dramatically alter the solubility as illustrated in Figure 4, which shows that the SANS cross section changes by over an order of magnitude, thus reflecting the break up of micellar aggregates into individual molecules as the temperature is increased from 40 to 65 °C at $P = 240$ bar. When the data are plotted versus density for both temperatures, it may be seen that the transition region occurs at a slightly lower pressure for the higher temperature, but the effects of density are overwhelming. Thus, it is the density that appears to be the controlling variable, rather than temperature or pressure.

The self-assembly of molecules in condensed phases is a ubiquitous phenomenon found in many biological structures as well as in systems of interest to colloid and surface science. Supercritical $CO_2$ affects unique perturbations over associative block copolymer systems, as the solvent strength is easily tunable with density and the system may be driven from an aggregated to a dispersed state simply by changing the pressure or temperature to control the solubility.

The CMD represents a novel phenomenon, into which neutron scattering provides detailed structural insight. While it is analogous in some respects to other transitions (e.g., changing the solvent properties by adding a cosolvent), we believe that the beauty of the CMD is that it is reversible with exquisite control and it is possible to design precisely where this transition will occur.[4] The ability to create and disperse micelles, coupled with the fact that $CO_2$-phobic materials can be solubilized within the aggregates,[4,16] makes the CMD an effect that may be of technological importance in the development of environmentally benign processes.

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