Temperature-Dependent Adsorption of Pluronic F127 Block Copolymers onto Carbon Black Particles Dispersed in Aqueous Media

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The adsorption properties of Pluronic F127 poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) PEO−PPO−PEO block copolymer onto carbon black (CB) particles dispersed in water have been investigated. The CB particles have fractal structure according to small-angle neutron scattering (SANS) measurements. The Langmuir isotherm could describe the adsorption behavior of Pluronic F127 onto CB particles below the block copolymer critical micellization concentration (CMC). Temperature plays an important role in determining the thickness and structure of the adsorbed layer. Below the temperature where micelles start forming (CMT), the added Pluronic F127 block copolymer molecules contribute to an increase of the adsorbed layer thickness (determined by dynamic light scattering) by forming a monolayer. Above the CMT, SANS experiments, performed under contrast matching conditions where either the block copolymer or the CB particles were rendered "invisible", confirmed that the adsorbed layer had structure and dimensions similar to these of Pluronic F127 block copolymer micelles that form in aqueous solution in the absence of CB. One of the aims of this work is to provide information on how to control the adsorbed layer thickness and structure (and correspondingly, colloidal stability) by tuning variables such as temperature, block copolymer concentration, and/or solvent quality.

Introduction

Pigments and other particles are widely used in the ink and coatings industry.[1] Amphiphilic molecules (low molecular weight surfactants and higher molecular weight block or graft copolymers) are often added in these systems to function as dispersants, wetting agents, emulsifiers, or antifoaming/defoaming agents.[2] The colloidal stability of the dispersed particles depends largely on the adsorbed amount and the hydrodynamic thickness of the adsorbed surfactant or polymer layer.[3,4] Considering the conformation of macromolecules adsorbed at a surface, de Gennes[5] and Scheutjens and Fleer[6,7] showed theoretically that the interaction between polymer-coated particles is affected by the thickness of the adsorbed polymer layer.

Carbon black (CB) nanoparticles are used in ink formulations where surfactants and amphiphilic polymers are also present. Block copolymers are expected to adsorb onto CB particles by their hydrophobic parts and extend their hydrophilic parts into the aqueous medium, providing steric stabilization.[8–10] CB particles typically contain 90−99% elemental carbon with oxygen and hydrogen as the other major constituents. This composition renders CB particles strongly hydrophobic and prone to aggregation when dispersed in water. When CB is treated with oxidizing solution, surface oxides with acidic functional groups are formed that render the carbon surface polar in character[11] and the CB particles become easier to disperse in aqueous media.

Several studies[12–14] addressed the adsorption of low molecular weight ionic surfactants onto CB in aqueous solution. Langmuir-type adsorption isotherms were found in such systems with a plateau region reached in the vicinity of the CMC value.[13–15]

Small-angle neutron scattering (SANS)[16] can provide information on the coverage of the surfactants.

Pluronic PEO−PPO−PEO (PEO: poly(ethylene oxide), PPO: poly(propylene oxide)) block copolymers are known to adsorb onto hydrophobic particles such as polystyrene latex. The layer thickness was strongly dependent on the hydrophilic PEO block size but less dependent on the hydrophobic PPO block size.[17] However, the adsorbed amount depended on the relative PPO and PEO block sizes. The adsorption isotherms of several Pluronic block copolymers onto CB particles have been reported in the literature.[18] The adsorption plateau region occurs at a concentration that is much smaller than the CMC of Pluronic P103, P104, P105, and F108 and the plateau was higher when EO chains are shorter.[18] The CMC and CMT values of Pluronic block copolymers have been expressed as a function of the copolymer molecular weight, PPO/PEO composition, temperature, or concentration.[19–21] Pluronic P105 has been found by SANS to form Gaussian coils at low temperatures and concentrations, but to associate into spherical micelles with a hydrophobic core composed of PPO blocks surrounded by a solvated corona consisting of PEO blocks and solvents at elevated temperature. The addition to water of polar organic solvents alters its solvent quality and can thus affect the PEO−PPO−PEO block copolymer micelle formation and structure.[22–26]

The study presented here addresses the amount and structure of Pluronic F127 adsorbed on carbon black nanoparticles dispersed in water. The amount of Pluronic F127 adsorbed on CB was determined by dialysis, and the adsorption data were fitted by the Freundlich and Langmuir isotherms. The structure of the adsorbed layer was probed by SANS, whereas the adsorbed layer thickness was determined by dynamic light scattering at various temperatures, block copolymer concentrations, or solvent type conditions. One of the aims of this work

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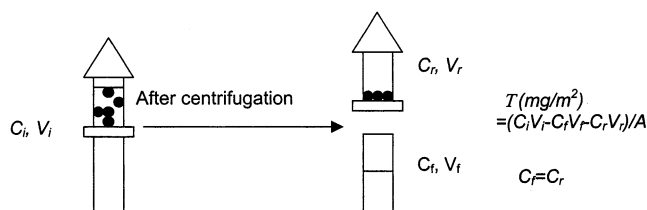
Figure 1. Schematic of the method for the determination of the adsorbed amount of Pluronic F127 on CB particles.

is to provide information on how to control the adsorbed layer thickness and its structure by tuning these variables.

Experimental Section

Materials. An aqueous dispersion of carbon black (15%) was supplied by Xerox Corp. The nominal diameter of the CB particles was reported in the range 100−120 nm, but we provide further evidence in this work on the CB particle size and structure. The surface (top 2−10 nm) chemical composition of the CB particles was determined using ESCA (electron spectroscopy for chemical analysis).[27] The atomic percent concentration at the surface was 87% C and 10% O; 93% of the C was unoxidized and 6% was in the form $O-C=O$. This indicates that the surface of the CB particles is oxidized in small portion with $COO-$ groups.[27] The pK_a of the carbon black aqueous dispersion is 3.8. We worked at a pH of 7; under these conditions the carboxylic acid groups on the surface of the particles are ionized. Pluronic F127 poly(ethylene oxide)−poly-(propylene oxide)−poly(ethylene oxide) block copolymer with MW = 12600 and 70% PEO content was supplied by BASF Co. The formula of this copolymer is $EO_{100}PO_{65}EO_{100}$. The solutions was prepared by dissolving the block copolymer in Milli-Q water (18 MΩ. cm). D_2O (used in SANS) was obtained by Cambridge Isotope Laboratories Inc. (Andover, MA). Ethanol, glycerol, and formamide were obtained from Acros Co. Ethyl acetate, cobalt nitrate, ammonium thiocyanate, and acetone were purchased from Sigma-Aldrich Co.

Adsorption Isotherm. 15% CB aqueous suspension was mixed with aqueous Pluronic F127 solution (the block copolymer concentrations ranged from 0.1 to 1%) so that the final concentration of CB particles equaled 1.5%. The prepared slurries were rotated end-over-end for 24 h. The suspensions were placed in Millipore Centricon Centrifugal filter tubes (MW cutoff: 100 000) and centrifuged at 3500*g* for 1 h. The slurries were then separated into retentate (with CB particles) and clear filtrate (see schematic in Figure 1). The Pluronic F127 concentration of the filtrate solution was determined by the calibration curve shown in Figure 2 that has been obtained by following a colorimetric method as described in ref 27.

The amount of Pluronic F127 block copolymer adsorbed on CB was calculated from the difference between the total amount of the block copolymers initially added (C_iV_i) and that present in the filtrate (C_fV_f) and retentate (C_rV_r) following adsorption (the retentate is assumed to have the same Pluronic F127 concentration as the filtrate). The adsorbed amount was calculated as follows:

$$m_2^s = (C_iV_i\text{-}C_fV_f\text{-}C_rV_r)/A \ (\text{g/mL} \times \text{mL/m}^2) \qquad (1)$$

where m_2^s is the adsorbed block copolymer amount per unit area, C_i, C_f, and C_r are the initial, filtrate, and retentate block copolymer concentration ($C_f = C_r$), respectively, V_i, V_f, and V_r are the initial, filtrate and retentate volume, respectively, and A is the surface area of the carbon black particles.
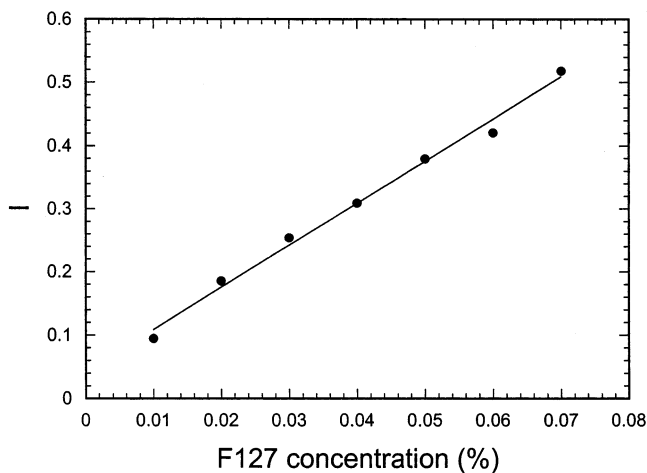
Figure 2. Calibration curve for the colorimetric determination of Pluronic F127 PEO−PPO−PEO block copolymer concentration in water in the concentration range 0.01% to 0.1%.

Dynamic Light Scattering. We used DLS to determine the size of the Pluronic F127 micelles (1% block copolymer in water at 30 °C) and of the CB particles. Because the CB aqueous dispersion scattered light strongly, we diluted it to a concentration ($3.75 \times 10^{-4}\%$) at which the scattered light could be quantified. The block copolymer concentration that we used to study the adsorbed layer thickness was 0.01% (at this concentration, the temperature where micelles start forming (CMT) can be extrapolated to 38 °C as shown in Figure 4a) and 1% (with CMT = 24 °C).[19]

The measurements were carried out with a Brookhaven BI-200SM goniometer equipped with a Lexel model 95 argon ion laser as a light source. The detection angle was 90° and the wavelength of the laser light was 514 nm. The measurements span temperatures from 20 to 60 °C. The scattered intensity is recorded by means of a multichannel digital correlator and converted to the correlation function. The electric field correlation function $|g^{(1)}(\tau)|$ was analyzed by the exponential sampling method, yielding information on the distribution function of Γ from

$$|g^{(1)}(\tau)| = \int G(\Gamma) \exp(-\Gamma \tau) \, d\Gamma$$

$$\bar{\Gamma} = \int \Gamma G(\Gamma) \, d\Gamma \qquad (2)$$

$G(\Gamma)$ can be used to determine an average (translational) diffusion coefficient $D_{app} = \Gamma/q^2$ where $q = (4\pi n/\lambda)\sin(\theta/2)$ is the magnitude of the scattering wave vector. The apparent hydrodynamic radius R_h was related to D_{app} via the Stokes−Einstein equation:

$$D_{app} = kT/6\pi\eta R_h \qquad (3)$$

where k is the Boltzmann constant, T is the absolute temperature, and η is the solvent viscosity.

To better visualize and quantify the measured micelle and particle diameter distribution data, and given that the Gaussian (bell-shaped) curve can describe well the micelle size distribution,[28] the size distribution data obtained from DLS were fitted by Gaussians.[29]

Small-Angle Neutron Scattering. SANS measurements were performed at the National Institute of Standards and Technology (NIST) Center for Neutron Research, beam guide NG3. The neutron wavelength used was $\lambda = 0.6$ nm, the sample-to-detector distance was 260.0 and 1300.0 cm, and the resolution ($\Delta q/q$)

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(a)

(b)
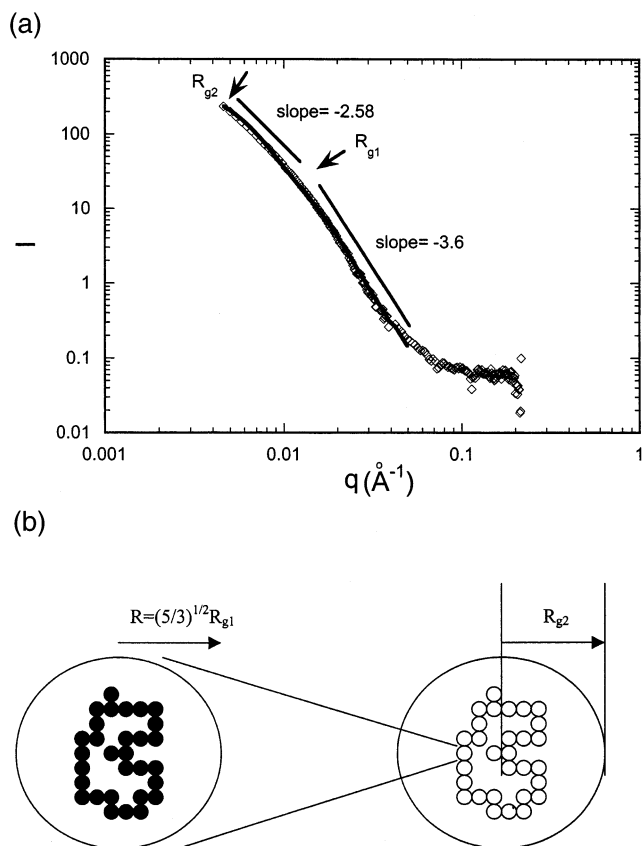
Figure 3. (a) SANS intensity of 0.3% CB particles dispersed in 84% H$_2$O and 16% D$_2$O (no Pluronic F127 is present) at 25 °C. Two structure levels are observed: the higher q range originates from primary particles and the lower q range from CB clusters. The data were fitted by the unified approach (see text for details); the R_{g1} and R_{g2} are the limits for the mass fractal. (b) A schematic of the fractal structure of CB particles.

was about 0.15. The angular distribution of the scattered neutrons was recorded in a two-dimensional detector; the radial average was subsequently obtained and used for data analysis. The samples were placed in 1 mm path length stopper "banjo" quartz cells. Adequate time was allotted for thermal and kinetic equilibration. Scattering intensities from the samples were corrected for detector background, empty cell scattering, and sample transmission. The resulting corrected intensities were normalized to absolute cross section units.

Experiments of 0.3% CB in water with and without 1% Pluronic F127 were performed at 50 °C. Two contrasts were used to study the structure of CB and of adsorbed Pluronic F127. If we match the scattering length density (SLD) of the aqueous solvent using an appropriate mixture of D$_2$O and H$_2$O, then we can detect the CB structure; on the other hand, if we match the SLD of the aqueous solvent with that of the CB, we can detect the structure of Pluronic F127. The scattering length densities of CB and Pluronic F127 are 6.5×10^{10} cm^{-2} and 0.48×10^{10} cm^{-2}, respectively. We could eliminate the scattering contribution from CB at 100% D$_2$O (SLD = 6.33×10^{10} cm^{-2}) and the scattering contributions of Pluronic F127 block copolymers at 84% H$_2$O + 16% D$_2$O solvent.

SANS Data Analysis: Micelles. The absolute SANS intensity can be expressed as a product of $P(q)$ which is related to the form factor and the structure factor $S(q)$:[22−24]

$$I(q) = NP(q)S(q) \quad (4)$$

where N is the number density of the scattered particles, in our

(a)

(b)
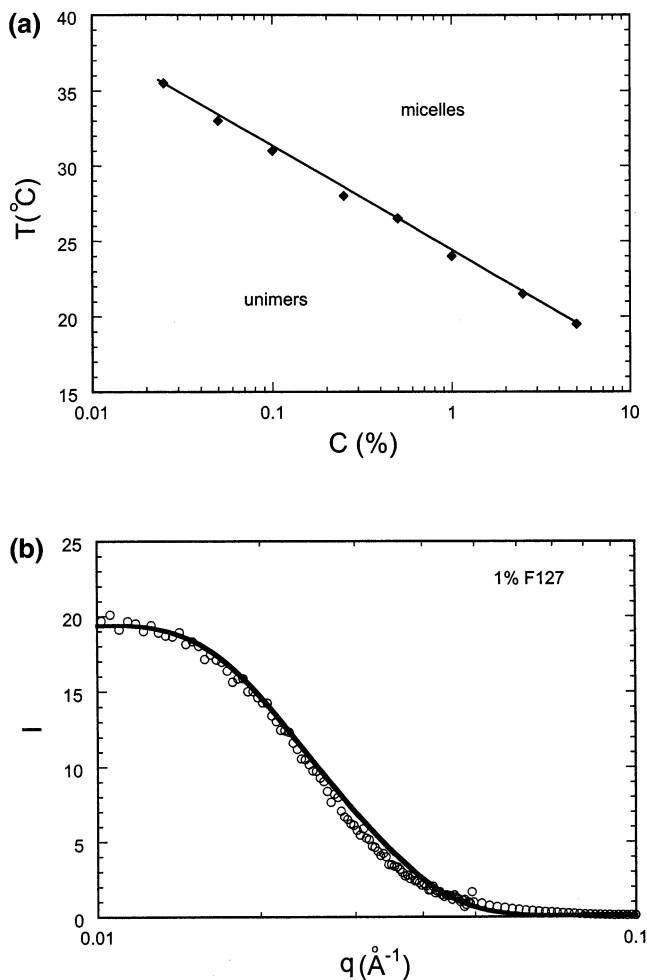
Figure 4. (a) Micelle formation boundary of Pluronic F127 in water as a function of temperature and block copolymer concentration (C). Unimers are present in the solution at temperatures and concentrations below the line, whereas micelles form above. (b) Fit of core−corona form factor and hard sphere interaction structure factor to SANS data from 1% Pluronic F127 in 100% D2O.

case micelles, which depends on the block copolymer concentration and the association number of micelles. The form factor $P(q)$, which takes into account the intramicelle structure, depends on the shape of the colloidal particle. A core−corona form factor has been proposed to describe the scattering generated from the contrast between the micelle core and corona,[22−24] which have different solvent contents (the core is usually "dry" or has small amounts of solvent, whereas the corona is highly solvated), and the scattering due to the contrast between the micelle corona and the solvent phase:

$$P(q) = \{(4\pi R_{core}^3/3)(\rho_{core} - \rho_{corona})[3J_1(qR_{core})/(qR_{core})] +$$
$$(4\pi R_{micelle}^3/3)(\rho_{corona} - \rho_{solvent})[3J_1(qR_{micelle})/(qR_{micelle})]\} \quad (5)$$

where R_{core} and $R_{micelle}$ are the radii of the micelle core and whole micelle (core + corona), respectively; ρ_{core}, ρ_{corona}, and $\rho_{solvent}$ are the scattering length densities (SLD) of the core, corona, and solvent (assuming a homogeneous solvent distribution in each of the domains), respectively. $J_1(y)$ is the first-order spherical Bessel function:

$$J_1(y) = [\sin(y) - y\cos(y)]/y^2 \quad (6)$$

In fitting the core−corona model into the scattering data, we view the micelle particles as consisting of a hydrophobic core

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composed of PPO segments (with little or no solvent present) and a relatively hydrated corona consisting of solvated PEO chains. The SLD of the core, ρ_{core}, and of the corona, ρ_{corona}, are a function of the average (over the core radius) volume fraction of PPO in the core (α_{core}) and of the average volume fraction of PEO in the corona (α_{corona}), respectively:

$$\rho_{core} = \alpha_{core}\rho_{PPO} + (1 - \alpha_{core})\rho_{solvent}$$

$$\rho_{corona} = \alpha_{corona}\rho_{PEO} + (1 - \alpha_{corona})\rho_{solvent} \qquad (7)$$

where ρ_{PPO} (= 0.325×10^{10} cm^{-2}) and ρ_{PEO} (= 0.547×10^{10} cm^{-2}) are the SLD of PPO and PEO, respectively, and $\rho_{solvent}$ is the SLD of the water ($\rho_{D_2O} = 6.33 \times 10^{10}$ cm^{-2}).[30] The volume fraction of PPO in the core (α_{core}) and the volume fraction of PEO in the corona (α_{corona}) can be expressed in terms of the core and micelle radii (R_{core} and $R_{micelle}$) and the micelle association number, N_{assoc}, i.e., the number of block copolymer molecules which (on the average) participate in one micelle:

$$\alpha_{core} = 3N_{assoc}V_{PPO}/(4\pi R_{core}^3) \qquad (8)$$

$$\alpha_{corona} = 3N_{assoc}V_{PEO}/[4\pi (R_{micelle}^3 - R_{core}^3)] \qquad (9)$$

where V_{PPO} is the volume of the PPO block (= 6283 Å^3) and V_{PEO} is the volume of the PEO blocks (= 14667 Å^3) of one Pluronic F127 molecule.

In addition to the form factor described above, the structure factor must be accounted for in order to describe intermicellar interactions. Interactions between the micelles are manifested in the correlation peak that appears in the low q range of the neutron scattering patterns generated from the 1 wt % Pluronic F127 block copolymer solutions. To describe such intermicellar interactions, we utilized the structure factor, $S(q)$, applicable for hard spheres.[23]

SANS Data Analysis: CB Particles. The structure of CB solids can be defined at three levels: primary particles (typically 10 to 100 nm in size) are fused together into aggregates (50 to 500 nm in size) which are then packed into agglomerates (5 μm or larger in size). Electron microscopy has been used to characterize the morphology of CB in terms of bulkiness, anisotropy, or shape factor, and more recently in terms of fractal dimension.[31-34] Small-angle scattering has been used to obtain surface fractal values for CB, various carbonaceous materials, and fumed silica,[35-37] and also the specific surface area (area/mass) of fractals.[38-39]

Under a mass-fractal model, the fractal dimension d_f describes the geometry of many random objects and scaling laws in small-angle scattering. The fractal dimension d_f is defined by

$$M(R) \propto R^{d_f} \qquad (10)$$

where M is the mass of material contained in a sphere of radius R centered at an arbitrary point on the object. The fractal dimension can be obtained experimentally from SANS measurements, and is determined from the negative slope of log-(scattering intensity) vs log(scattering vector q) in a power-law regime.

We used the unified equation developed by Beaucage et al.[38,40] to describe the limits to mass-fractal scaling at the aggregate radius of gyration R_{g2} and the primary particle radius of gyration R_{g1}. The unified equation under mass-fractal constraints is further constrained by assuming spherical primary particles. The unified approach breaks a complex scattering pattern into structural levels, each of which contains a Guinier

regime reflecting the R_g, and particle contrast followed by a power-law regime which describes the type of structures to which the Guinier regime pertains. Each structural level is described, in the unified approach, by four generic parameters, a constant G, radius of gyration R_g, power-law prefactor B, and power law slope P. The scattering intensity in our data was fitted by

$$I(q) = G_1 \exp(-q^2R_{g1}^2/3) + B_1(1/q_1^*)^p +$$
$$G_2 \exp(-q^2R_{g2}^2/3) + B_2 \exp(-q^2R_{g1}^2/3)(1/q_2^*)^{d_f} \quad (11)$$

where subscript 1 denotes the low q region (surface fractal and primary particles) and subscript 2 denotes the intermediate-q region (mass-fractal region and composite). The radius of gyration, R_{g2}, for a mass fractal with mass-fractal dimension d_f, and degree of aggregation, z, is given by

$$R_{g2} = \{b^2z^{2/d_f}/[(1 + 2/d_f)(2 + 2/d_f)]\}^{1/2} \qquad (12)$$

where b is the primary particle diameter, and $b = 2R$. Assuming CB has spherical primary particles, then $R = (5/3)^{1/2}R_{g1}$. The power-law prefactor B_2 for mass-fractal aggregates is given by

$$B_2 = (G_2d_f/R_{g2}^{d_f})\Gamma(d_f/2) \qquad (13)$$

where Γ is the gamma function. A mass fractal with spherical primary particles is described by four parameters under this model: z, R_{g1}, d_f, and G_1.

The surface area was also determined for the mass-fractal scaling regime of the small-angle scattering pattern. To calculate the surface area, the volume of the substructural unit (V_{pp}) needs to be determined from the Porod invariant, Q, and Guinier prefactor, G_1:

$$Q = \int_0^\infty I(q)'q^2 \, dq = 2\pi^2 G_1/V_{PP} \qquad (14)$$

where $I(q)'$ is given by the last two terms of eq 11. For spherical primary particles, the surface area of per primary aggregate S_{pp} can be estimated by

$$S_{pp} = K_{sph}R_{g2}^{d_f}R^{2-d_f} \qquad (15)$$

where $K_{sph} = 4\pi \, 2^{-d_f}(1 + 2/d_f)^{d_f/2}(2 + 2/d_f)^{d_f/2}$. The specific area S can be obtained by taking the density ρ of the carbon black to be 2 g/cm^3:[11]

$$S = S_{pp}/\rho z V_{pp} \qquad (16)$$

Results and Discussion

Structure and Specific Surface Area of CB Particles. The CB particles that we used in our study have been found by both SANS and TEM (transmission electron microscopy) to possess fractal structures.[27] To determine the adsorbed amount per surface area used in the adsorption isotherm, the surface area of CB particles should first be estimated. From SANS data, we can estimate the surface area of the particles by eq 16. Figure 3 shows a typical SANS profile for CB particles (0.3%) suspended in water with no block copolymer added. The scattering patterns exhibit 2 power-law regimes: At high q, a power-law of -3.6 is observed for the surface of the primary particle. At low q, a weak slope of -2.58 corresponds to a mass-fractal regime. Gerspacher et al. found that the surface fractal dimension was nearly constant at a value ~ 2.4 for 15 different grades of CB.[36]

We can obtain eight parameters from fitting the scattering curve with eqs 11–14, i.e., G_1, B_1, P_1, R_{g1}, G_2, B_2, R_{g2}, and d_f. The lower and upper limits of the mass fractal are characterized by R_{g1} and R_{g2}. The determination of degree of aggregation is somehow difficult, i.e., G_2 and R_{g2} are obscured due to the lack of the information in the lower q region. We assume that R_{g2} is located at the limit of q (0.004 Å^{-1}). Six clearly distinguishable parameters, the high-q power law prefactor B_1, P_1, R_{g1}, G_1, d_f, and low-q power law prefactor B_2, can be estimated, from which the four parameters of the model, G_1, d_f, R_{g1} and z, can be obtained by fitting. The R_{g1} and R_{g2} values are 118.5 and 349 Å, respectively. The radius of a spherical primary particle is $R = (5/3)^{0.5}R_{g1} = 153$ Å. If we assume that the aggregates form spherical particles then their radius is $R' = (5/3)^{0.5}R_{g2} = 450$ Å, which is very close to the radius obtained for the same particles by DLS (where diameter $\sim$ 100 nm). In the remainder, when we mention carbon black particles we refer to the "aggregates" of diameter $\sim$ 100 nm. This size is more relevant to the adsorption of the macromolecules of interest here.

The surface area was estimated by eq 15 to be 283 m^2/g with $z = 11$ and $Q = 6.84 \times 10^{-5}$ cm^{-1} Å^{-3} (most CB particles have specific surface area in the order of 100–900 m^2/g[11]). The volume of the primary particle that is obtained from the high Q invariant by eq 14 (5.2×10^7 Å^3) and by using the radius of spherical primary particle ($\frac{4}{3}\pi R^3 = 1.5 \times 10^8$ Å^3) shows some discrepancies. The reason lies in the fact that the particles deviate from spheres and in the uncertainty of R_{g2}. Another way to estimate the surface area is to assume the diameter of the CB articles to be 100 nm (as obtained by DLS) and the density of the particle to be 2 g/cm^3. Thus, we obtain the specific surface area of CB to be 30 m^2/g. In this study, we use 283 m^2/g as the specific area in extracting data for the adsorption isotherm. Note, however, that this surface area may not be available in its entirety for the adsorption of the block copolymer if the block copolymer is hindered from accessing the inner surface of the fractal. In the later case, the surface area accessible to the block copolymer will most likely be closer to the 30 m^2/g value estimated for a compact sphere than the 283 m^2/g value estimated for fractals. This is probably the case for the adsorption of block copolymer micelles (as discussed below) of size comparable to that of the primary particles.

Micelle Formation and Structure of Pluronic F127. A systematic study of the CMC, CMT, micellization thermodynamics, and lyotropic liquid crystalline structure for Pluronic F127 PEO–PPO–PEO block copolymers can be found in the literature.[26,41–45] The effects of aqueous solution temperature and Pluronic F127 concentration on the micelle formation can be realized through Figure 4a. At concentrations and temperatures below the solid line (obtained from interpolation of CMC vs temperature data), Pluronic F127 molecules are present in the solution as unimers, but they associate to form micelles above the line. The CMT of 1% Pluronic F127 block copolymer is at 24 °C, and the CMT of 0.01% is extrapolated from Figure 4a to 38 °C. We examined 1% Pluronic F127 by SANS at 50 °C, which brings the system well above the CMT. The core–corona model with hard sphere structure factor, that has been used to analyze the micelle structure of Pluronic P105,[22–24] was also used to extract such information on Pluronic F127 block copolymers. The micelle core, micelle radii, hard sphere radii (R_{core}, $R_{micelle}$, and R_{HS}) and the micelle association number (N_{assoc}) values were obtained by fitting eq 2 to the scattering patterns. Figure 4b shows the fit of the model into the SANS pattern. The micelle has a core radius of 38 Å, overall (core + corona) radius of 92 Å, N_{assoc} of 39, and R_{HS} of 160 Å.
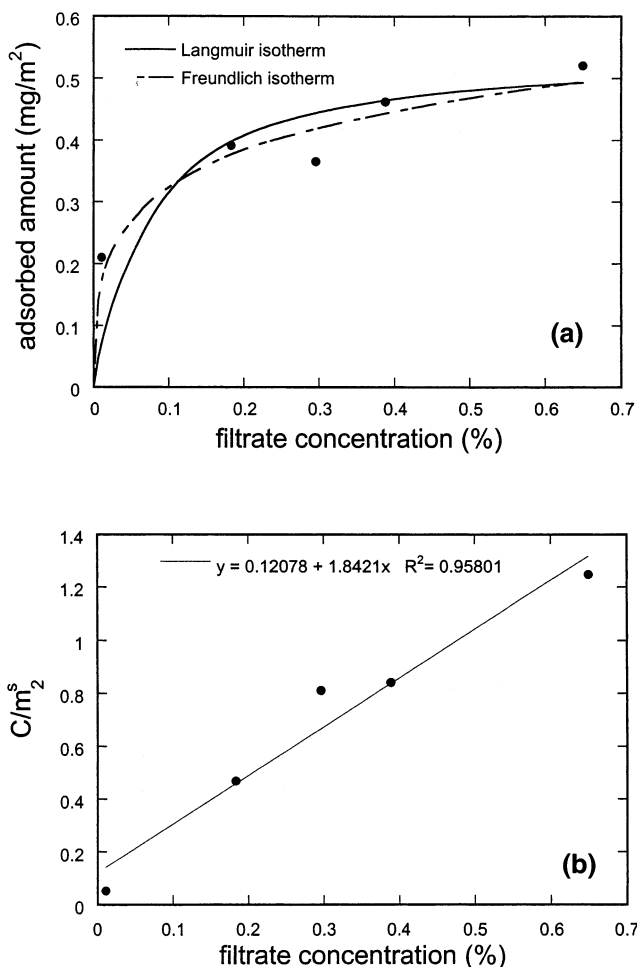
Figure 5. (a) Two adsorption isotherm equations, Langmuir and Freundlich, are used to fit the adsorption data of Pluronic F127 onto 1.5% CB at 24 °C. Both isotherms give a good fit for the concentration range considered. (b) Langmuir isotherm parameter determination: the C_f/m_2^s vs C_f plot gives a straight line. The parameters obtained from the fit are listed in Table 1.

Adsorption Isotherm. Figure 5a shows the adsorption isotherm of Pluronic F127 block copolymers onto different concentrations of CB particles at 24 °C. We fitted the Freundlich and Langmuir isotherm models to the experimental data. The Langmuir adsorption isotherm is theoretically derived, and assumes one-to-one binding between the adsorbate and the binding site on the adsorbent. The Freundlich adsorption isotherm is empirical. The actual adsorption phenomenon, however, is complex and neither equation covers a wide range of adsorbate concentrations. The Freundlich equation can be described as

$$m_2^s = aC_f^{1/n} \qquad (17)$$

where m_2^s is adsorbed amount per unit surface area (mg/m^2). The constant a gives a measure of the adsorbent capacity, and $1/n$ gives a measure of the intensity of adsorption.

The Langmuir isotherm is given by the following equation:

$$m_2^s = \frac{m^s b C_f}{1 + bC_f} \qquad (18)$$

Figure 5a shows the fit of Freundlich and Langmuir isotherms to the experimental data of 1.5% CB with Pluronic F127 concentration in the range 0.1%–1%, which is below the CMC

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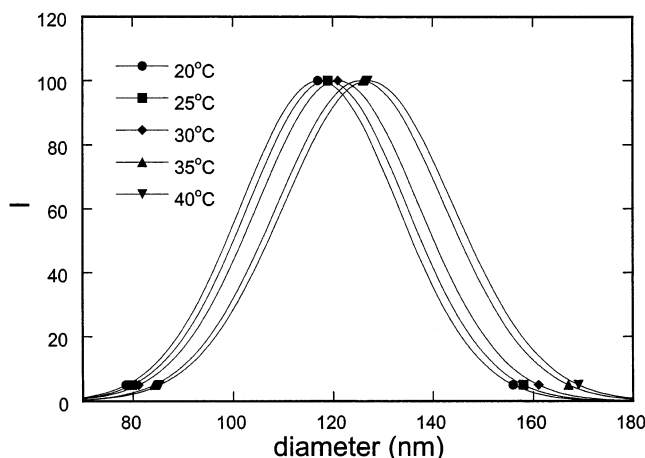
Figure 6. Size distribution (obtained by DLS at various temperatures) of CB particles dispersed in water in the presence of 0.01% Pluronic F127.

TABLE 1: Freundlich Isotherm Parameters, Langmuir Isotherm Parameters, and Surface Area Occupied by One Pluronic F127 Block Copolymer Molecule When Adsorbed on CB Particles

| | | Freundlich isotherm | | Langmuir isotherm | | |
| | block | | | m^s | | σ |
particle	copolymer	a	n	(mg/m^2)	b	(nm^2)
1.5% CB	F127	0.542	4.715	0.543	15.25	38.6

of the block copolymer in water ($\sim$1% at 24 °C). Both the Langmuir and Freundlich isotherms provide adequate fits to the experimental data (with a correlation coefficient = 0.95). The Langmuir isotherm assumes monolayer adsorption; the Pluronic F127 block copolymers thus appear to exhibit monolayer adsorption behavior in the concentration range studied. The structure of the adsorbed layer under these conditions will be explored later in this paper. The Langmuir isotherm parameters can be determined graphically by the following equation (obtained from rearrangement of eq 18), at conditions where monolayer adsorption applies:

$$\frac{C_f}{m_2^s} = \frac{1}{m^s b} + \frac{C_f}{m^s} \tag{19}$$

A plot of C_f/m_2^s versus C_f should give a straight line of slope $1/m^s$ and intercept $1/m^s b$. m^s, the maximum adsorbed amount per unit surface area, is a measure of the adsorption capacity of the CB particles, while b (also called binding constant) is a measure of the intensity of the adsorption. The Langmuir isotherm parameters for 1.5% CB are determined in Figure 5b. The maximum adsorbed amount, equilibrium constants, surface area σ^0 occupied by one block copolymer molecule calculated from Figure 5b, and the Freundlich isotherm equation constants a and n are listed in Table 1. The surface area σ^0 for one Pluronic F127 molecule is 38.7 nm^2. Pluronic F108 PEO–PPO–PEO block copolymer (of molecular weight and PEO wt % comparable to that of Pluronic F127) has been found to have σ^0 equal to 26 nm^2 on CB particles.[18]

The plateau of adsorption isotherm of 1.5% CB particles is 0.543 mg/m^2. If we use the surface area estimated by using the particle diameter we obtained from DLS, the plateau will be nine times higher than these values, and the surface area per molecule will be 4.3 nm^2.

Adsorbed Layer Thickness Determined by DLS. In addition to SANS that gives R_{g2} which corresponds to the aggregate
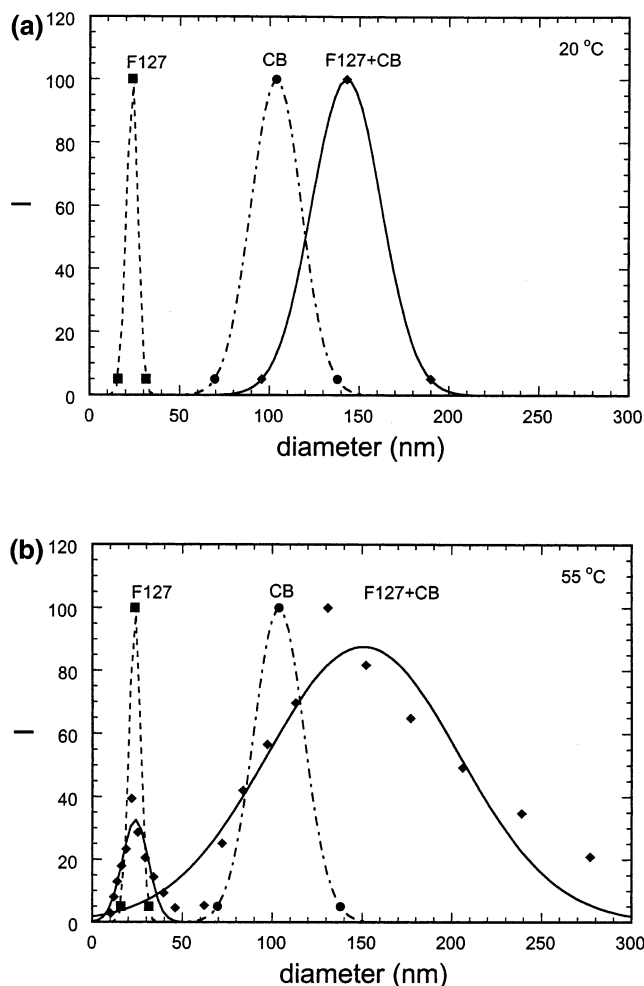
Figure 7. (—) Size distribution data (obtained by dynamic light scattering) from 3.75×10^{-4}% CB aqueous dispersion in the presence of 1% Pluronic F127. (– · –) fits the size distribution of the CB particles in water in the absence of block copolymer. (– – –) fits the size distribution of the block copolymer in aqueous solution in the absence of CB particles. At (a) 20 °C (below CMT), one size distribution was observed (—). At (b) 55 °C (above CMT), two size distributions appear. The lower size peak coming from the CB dispersion containing Pluronic F127 agrees well with the peak from the aqueous block copolymer solution (– – –), which corresponds to the micelle diameter. The mean hydrodynamic diameter (146 nm) of the higher peak in the case of CB + block copolymer dispersion is larger than that of CB ($\sim$100 nm) in the absence of block copolymer (– · –).

size as discussed above (349 Å), DLS can provide information on the aggregate size. The CB particles at 3.75×10^{-4}% have a hydrodynamic diameter of about 104 nm in plain water.[27] Figure 6 shows the size distribution exchibited by a CB dispersion with 0.01% Pluronic F127 at various temperatures in the range 24 to 40 °C (below or close to the CMT). Water becomes a worse solvent for Pluronic F127 and the PEO–PPO–PEO block copolymer is dehydrated at elevated temperatures. As the temperature increases from 20 to 40 °C, the diameter of 0.01% Pluronic F127-coated carbon black particles increases from 117 to 127 nm.

The CMT of 1% Pluronic F127 in water is 24 °C;[19] the block copolymer molecules are present in the solution as unimers below this temperature but form micelles above it. Figure 7 shows the size distribution of CB particles dispersed in water in the presence of 1% Pluronic F127 block copolymer at 20 °C (below CMT) and at 55 °C (well above CMT). To better compare the block copolymer-coated CB particle size distribu-

(a)

(b)
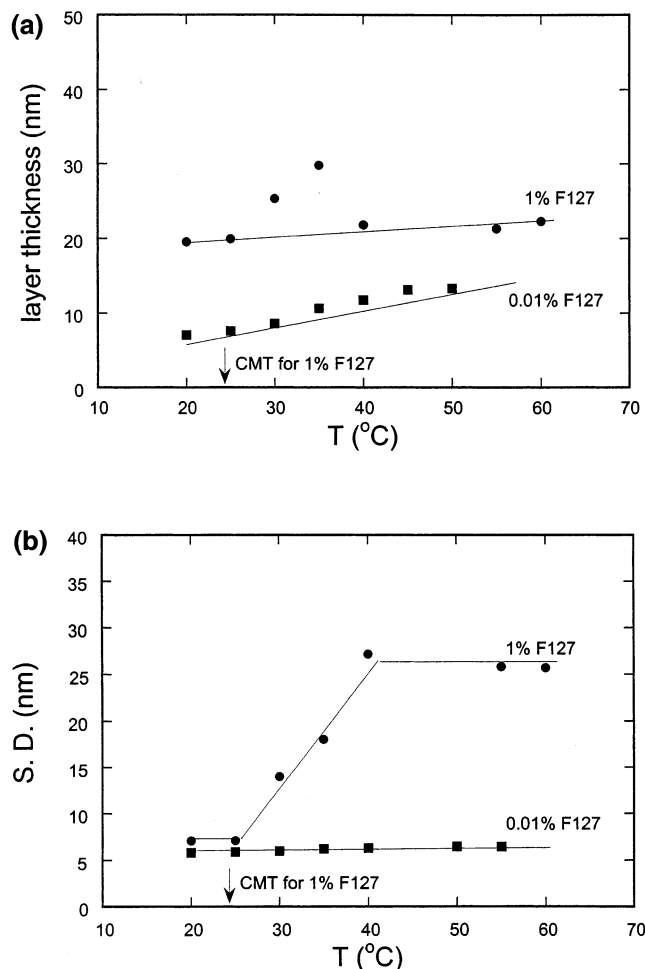
Figure 8. (a) The adsorbed layer thickness of CB particles dispersed in water in the presence of 0.01% and 1% Pluronic F127 in the temperature range from 20 to 60 °C. The adsorbed layer thickness increases from 7 to 13 nm at 0.01% block copolymer as the temperature increases from 20 to 60 °C. The adsorbed layer thickness at 1% block copolymer has similar values below and well above the CMT (24 °C as indicated by the arrow), but goes through an intermediate region. (b) The standard deviation of the size distribution of CB particles dispersed in water in the presence of 0.01% and 1% Pluronic F127 in the temperature range from 20 to 60 °C. The standard deviation almost remains constant for 0.01% Pluronic F127 throughout the temperature range examined. The standard deviation for 1% Pluronic F127 has a low value below CMT, but increases significantly as the temperature increases, and reaches a plateau above 40 °C.

tion to that of plain CB particles and to that of block copolymer solution when no CB particles were present, we present in the same plot distributions from three different systems: that of CB particles with adsorbed Pluronic F127 block copolymer layers (solid lines), that of Pluronic F127 block copolymer aqueous solution (dashed lines), and that of plain CB particles (dashed−dot lines) dispersed in water. Note that the concentration conditions in these experiments are such that the micelle concentration (1%) is much higher than the particle concentration (3.75×10^{-4}%). At 20 °C, one size distribution from the block copolymer-coated CB is centered at around 142.5 nm and the adsorbed layer thickness is ∼20 nm (Figure 7a). However, at 55 °C, where Pluronic F127 molecules form stable micelles, two size distributions appear from the CB plus Pluronic F127 dispersion (Figure 7b). The lower peak, centered at 22 nm, corresponds to the diameter of Pluronic F127 micelles. The higher peak of the Pluronic F127 block copolymer-coated CB particle size distribution shifts to a higher value (146 nm) than

(a)

(b)
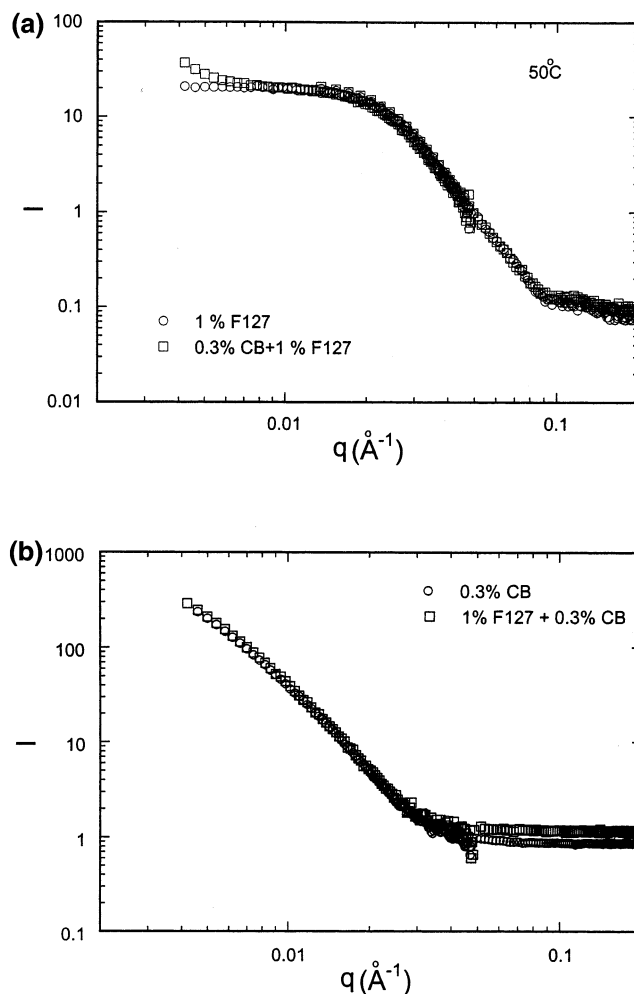
Figure 9. (a) SANS patterns originating from Pluronic F127 block copolymer solution in 100% D_2O in the absence and in the presence of CB particles (50 °C). The circle symbols indicate the scattering from 1% block copolymer in the absence of CB and the square symbols indicate the scattering from 1% block copolymer in the presence of CB (0.3%). The two curves coincide with each other, indicating that the presence of CB does not affect the Pluronic F127 block copolymer self-assembled structure. Note that at 100% D_2O contrast the CB particles scatter very little. (b) SANS patterns from 0.3% CB particles dispersed in 16% D_2O + 84% H_2O in the absence (○) and in the presence (□) of 1% Pluronic F127. The CB particles exhibit the same scattering profile in the presence and in the absence of block copolymers, indicating that the addition of Pluronic F127 does not affect the structure of the CB particles.

that resulting from the CB particles in the absence of block copolymer (∼104 nm). We choose the mean diameter of the higher distribution of the solid curves in Figure 7 as the diameter of the CB particles with adsorbed block copolymer layer.

The difference in particle radius with and without the presence of Pluronic F127 block copolymer represents the thickness of the adsorbed layer. Figure 8 shows the adsorbed layer thickness and the standard deviation of the CB particle size distribution in the presence of 0.01% and 1% Pluronic F127 at various temperatures. The arrow in Figure 8 indicates the CMT of 1% Pluronic F127. As seen in Figure 8a, the adsorbed layer thickness increases from 7.1 to 13.3 nm as the temperature of 0.01% block copolymer solution increases from 20 to 50 °C. At 1% Pluronic F127, the adsorbed layer thickness is about 19.6 nm below CMT (24 °C). Above 40 °C the micelles are well formed and the adsorbed layer thickness becomes ∼22 nm. Between 25 and 40 °C, the adsorbed layer thickness encounters

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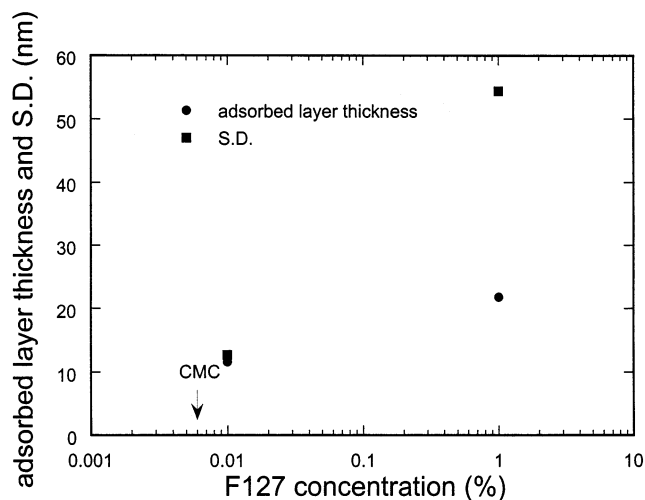
Figure 10. Concentration effect on the adsorbed layer thickness and on the standard deviation of the particle size distribution (obtained by DLS) at 40 °C. The arrow indicates the CMC of Pluronic F127.

an intermediate region where micelles are not so well formed as those at above 40 °C[19] and the adsorbed layer thickness obtained deviates from those in the lower and higher temperature range (with values in the range 20−30 nm). The standard deviation of the CB particle diameter distribution in the presence of 0.01% Pluronic F127 is ∼6 nm throughout the whole temperature range (Figure 8b). However, in the presence of 1% Pluronic F127 the standard deviation of the CB particle diameter is ∼7 nm when the block copolymer molecules are present as unimers and ∼26 nm when well-defined micelles form. The standard deviation increases during the intermediate adsorbed layer region.

At 0.01% Pluronic F127, the block copolymer may not pack so tightly on the surface of the particles, therefore the conformation of the polymer chains is not so extended and the adsorbed layer has smaller thickness in the studied temperature range. At higher temperature for 1% Pluronic F127, where stable micelles form, the standard deviation increases, and the observed sizes higher than 200 nm may result from aggregation of the CB particles due to "bridging effect" of the block copolymer. At 1% Pluronic F127 below the CMT, no micelle peak has been observed and the block copolymers only contribute to the increase on the CB particle size, implying that the block copolymer molecules prefer to adsorb onto the CB surfaces. At the same time, the adsorbed layer thickness is larger than that in the presence of 0.01% Pluronic F127 because the higher block copolymer concentration may lead to multilayer formation. But the standard deviation is still close to that of 0.01% F127, which is much smaller than that above CMT, indicating that the interactions between the Pluronic F127 molecules are not as complex as at the conditions where micelles form. The CMT can be regarded as an onset point where complex interactions occur as seen in Figure 8b.
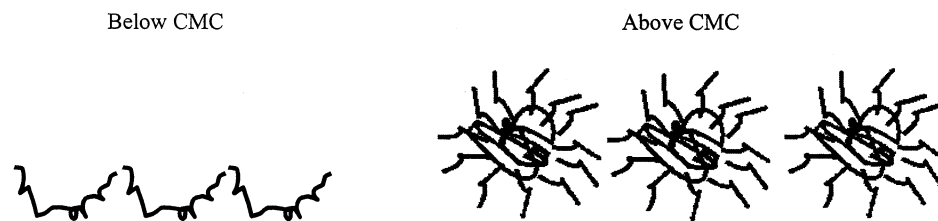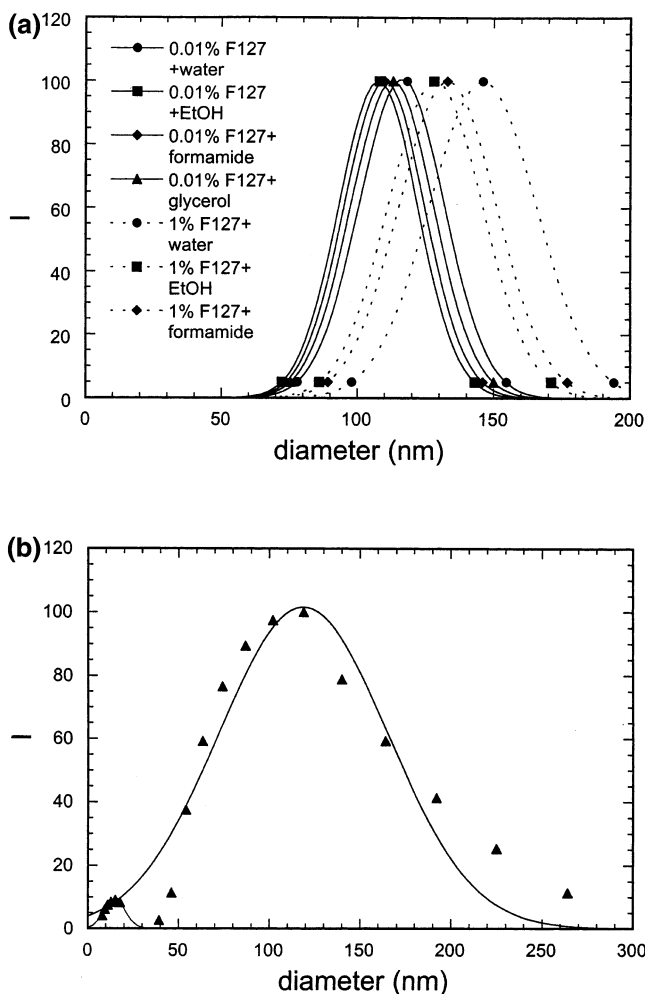
Structure of Adsorbed Layer Determined by SANS. Figure 9a shows the SANS pattern originating from 1% Pluronic F127 block copolymer in water (100% D$_2$O) with and without 0.3% CB particles at 50 °C. We first matched the SLD of the solvent with the SLD of the CB particles and therefore the structure of CB was rendered "invisible", i.e., we could only detect the structure of the block copolymers. The circle marks indicate the scattering from block copolymers in aqueous solution, while the square marks indicate the scattering from block copolymer in an aqueous CB dispersion. It appears that the two curves coincide with each other. This suggests that the adsorbed Pluronic F127 has the same structure as the Pluronic F127 in solution, i.e., that of micelles (above CMT). Note that the block copolymer concentration in solution is not so high as to mask the CB particles at this concentration (as seen in Figure 5a, at 0.7% of the filtrate concentration, the Pluronic F127 molecules still follow monolayer adsorption). As discussed above, the adsorbed layer thickness measured by dynamic light scattering is ∼23 nm after mixing Pluronic F127 block copolymers with CB particles in plain water above 40 °C, which is close to the micelle diameter as seen in Figure 7b. Therefore the Pluronic F127 layer surrounding the CB particles should be in the form of micelles.

Figure 9b shows the SANS pattern originating from 0.3% CB dispersed in 16% D$_2$O + 84% H$_2$O with and without the presence of 1% Pluronic F127. CB particles in the presence of block copolymer give the same scattering pattern as that in the absence of block copolymer, indicating that the addition of Pluronic F127 does not affect the structure of the CB particles.

From Figure 10 we can see that the apparent diameter of CB increases as Pluronic F127 is adsorbed on the particles. The adsorbed layer thickness is 11.8 nm at 0.01% block copolymer at 40 °C. We speculate that the structure of the adsorbed layer at this concentration is close to monolayer (Figure 5a). As the Pluronic F127 concentration increases to 1%, the adsorbed layer takes the form of micelles. This suggests that the PPO segments on the block copolymers have stronger affinity to each other than to the surface of the CB particles. Therefore, below CMC (or CMT), the PPO prefers CB surfaces to water; but above the CMC (or CMT) Pluronic F127 prefers to associate with other Pluronic F127 molecules. The decrease in the affinity of Pluronic F127 to the CB particles may be due to the lowering in the surface hydrophobicity, resulting from polar groups COO$^-$ on the CB surface (the surface composition of CB particles is discussed in a separate publication[27]). Figure 11 shows a schematic presentation of the adsorbed Pluronic F127 layer structure on CB particles below CMC (monolayer) and above CMC or CMT (micelles). It is notable that the same picture has emerged for the adsorption of poly(dimethylsiloxane)−polyether graft copolymers on the same CB particles that we consider here.[27]

Solvent Effects on Adsorbed Layer Thickness. In the case of PEO−PPO−PEO block copolymers where water is typically

Figure 11. Schematic of the block copolymer adsorbed structure below and above the CMC. At concentrations below the CMC, Pluronic F127 assumes monolayer adsorption. Above the CMC, the adsorbed layer thickness measured by DLS, as well as the structure determined by SANS, suggest that the adsorbed layer is in the form of micelles.

Figure 12. Solvent effects on Pluronic F127 adsorption on CB. When polar organic solvents such as ethanol or formamide are present, the adsorbed layer thickness is smaller than that in water (a). In the case of glycerol (b) micelles form at 1% F127, as seen by the peak centered around 20 nm.

used as a solvent (being selective for PEO), the addition to water of solutes[46,47] or polar organic solvents,[22–24,48,49] such as glycerol, ethanol, and formamide, provides extra degrees of freedom in tailoring the solution properties for specific applications.[21,25] However, the published information on the effects of solvents on the association behavior of polymeric amphiphiles (e.g., water-soluble block or graft copolymers) present in colloidal dispersions is rather limited.[50] We became therefore interested in how the added polar organic solvents influence the interactions between these amphiphiles and CB particles. From a comparison of the solvent effects with the temperature effects on the structure of micelles formed by PEO–PPO–PEO block copolymers, it has been observed that the addition to water of formamide or ethanol causes a micelle structure change similar to that caused by a reduction in temperature.[24] Correspondingly, the micelle core radii and the micelle association numbers decrease. On the contrary, the addition of glycerol into water leads to a micelle structure change comparable to that caused by an increase of temperature: upon addition of glycerol, the solvent conditions in the micelle corona become worse and the micelle association number increases, trends which are also observed in plain water solvent with an increase of the temperature.[24]

Figure 12 shows the size distribution of CB particles dispersed in water containing 0.01% or 1% Pluronic F127, obtained when

polar organic solvents (ethanol, formamide, or glycerol) are added into the aqueous solution. As the block copolymer concentration increases from 0.01% to 1%, the diameter of CB particles with adsorbed block copolymer increases from 118 to 146 nm in water, from 108 to 128 nm in water/ethanol, and from 110 to 133 nm in water/formamide mixtures at 24 °C. In the presence of 0.01% Pluronic F127, the diameter of CB particles with adsorbed layer is 113 nm in water/glycerol mixture, but micelles form at 1% Pluronic F127 as seen in Figure 12(b). At 0.01% Pluronic F127, the molecules adsorbed as monolayer on the CB particles while at 1% Pluronic F127 the adsorbed layer is in the form of multilayer. It has been observed that the size of Pluronic P105 micelles follows the trend: ethanol < formamide < water < glycerol.[24] Since the adsorbed layer structure resembles the structure of micelles at 1% Pluronic F127, the adsorbed layer thickness should have trends similar to those of micelles, i.e., ethanol < formamide < water, which agrees well with the data presented in Figure 12.

Conclusions

The dispersion stabilization of organic pigments in aqueous media is of great importance for the preparation of water-borne inks and coatings of good quality. CB, used as the pigment of black ink, is dispersed in aqueous medium by Pluronic F127 poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) block copolymer in this study. To understand the dispersion behavior, we first investigate the CB particle size and structure in the absence of added block copolymer and the Pluronic F127 solution structure in the absence of CB. We then determine the adsorption isotherm and adsorbed layer thickness and structure of the pluronic F127 block copolymer onto CB particles. Block copolymer concentration, temperature, and polar organic solvents are the variables considered in the study of the adsorbed layer. Such studies on the interactions between CB particles and amphiphilic polymers provide fundamental information as well as practical data for use in designing dispersion formulations.

The size and shape of the CB particles were characterized by DLS and SANS. The primary CB particles (20–40 nm diameter) aggregate to form clusters. The diameter obtained by DLS is estimated to be 100 nm and corresponds to the cluster size. From fitting SANS data with a unified approach we can estimate the primary particle radius (153 Å) and specific surface area (283 m^2/g). The surface of the CB particles is partly oxidized and presents to the solution ionized COO^- groups. The CMT of 1% Pluronic F127 block copolymer in water is 24 °C. Micelles with core radius of 38.5 Å and micelle radius of 88 Å form above this temperature.

The adsorption isotherm for the Pluronic F127 block copolymer onto CB particles has been determined by a dialysis method, and a colorimetric method was developed to determine the Pluronic F127 concentration in water. The adsorption isotherm reaches a pseudoplateau region below the CMC at the studied concentrations. The Langmuir and Freundlich isotherm fits the adsorption behavior in this low filtrate concentration of Pluronic F127 block copolymers onto CB particles, suggesting monolayer formation in lower filtrate concentration.

Dynamic light scattering provided information of the adsorbed layer thickness of Pluronic F127 block copolymer onto CB particles above and below CMT. At low block copolymer concentration with CB particles, the particle radius obtained by DLS increases by about 7 nm, corresponding to monolayer adsorption in all studied temperatures. At higher block copoly-

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mer concentration, the CB aqueous dispersion exhibits one size distribution below CMT; well above CMT, where well-defined micelles form, two size distributions were observed. One peak originates from the micelles and the other peak corresponds to CB particles with adsorbed layers, indicating that the block copolymers still prefer to adsorb onto CB particles and lead to the increase in the particle diameter. The adsorbed layer thickness is ~23 nm, which is the same the micelle diameter obtained by DLS, 23 nm.

Two contrasts were used in SANS experiments carried out at CB suspensions containing Pluronic F127 block copolymer at 50 °C. By matching the SLD of the solvent with that of CB, we can determine the structure of the Pluronic F127 block copolymers; by matching the SLD of the solvent with that of Pluronic F127, we can determine the structure of CB particles. SANS results suggest that the micelle structure is not altered by the addition of CB particles, and CB retains its structure following the addition of Pluronic F127 block copolymers. The SANS data, together with DLS data which show adsorbed layer thickness very close to the micelle diameter, strongly suggest that the adsorbed layer has a structure in the form of spherical micelles. This may result from the oxidized surface on the CB particles that lead to lower affinity of the PPO blocks of Pluronic F127 onto the particles.

Polar organic solvents present in the aqueous solution, such as ethanol or formamide, reduce the micelle diameter of PEO−PPO−PEO block copolymers. Because the adsorbed layer has the structure of micelles, the adsorbed layer thickness will decrease from 22 to 12 nm or 15 nm as ethanol or formamide added in the solution at 24 °C for 1% Pluronic F127. Though these added solvents cause similar effects on the micelle structure as a decrease in the temperature, i.e., reduction of the micelle size, the adsorbed layer thickness is influenced more strongly by the added solvents than by an increase in temperature.

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