^{1}H-NMR Studies of Nonionic Surfactant Adsorption onto Colloidal Particles

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SYNOPSIS

Proton Nuclear Magnetic Resonance (NMR) spectroscopy was used to study the adsorption of a hexadecyl-terminated poly(oxyethylene) surfactant (nominal molecular weight of 1120 g/mol) onto hydrophobic polystyrene latex particles. The adsorption process affects the NMR response of the surfactant; various surfactant populations are represented by different features in the NMR spectra. An analytical method that utilizes surfactant systems with and without polystyrene latex particles was employed to determine the capability of NMR to observe adsorbed surfactant close to the particle surface. At the initial stages of surfactant adsorption, the oxyethylene chain interacts with the particle surface in a pancake-like conformation. At higher surfactant concentrations, surfactant molecules are bound to the particle surface and also exist as micelles or are free in solution; approximately one-third of the bound, 20-unit oxyethylene chains are near the surface and are not detected by NMR. Using a theoretical monomer density profile, laser light-scattering measurements, and the NMR results, an effective NMR detection limit of 1 nm from the particle surface has been calculated. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Nonionic surfactants of the poly(oxyethylene) monoalkyl ether type and the adsorption of these surfactants at the solid/liquid interface are the subject of much experimental and theoretical research.[1-8] The adsorption of nonionic surfactants generally leads to an increase in colloidal stability of the particles.[9] The effectiveness of the surfactant is dependent on the ability of the surfactant to adsorb to a surface in a conformation that optimizes the desired effect. Much of the work conducted to date involves adsorption of these surfactants onto hydrophilic surfaces such as silica.[4,10]

Hansen and co-workers have used Nuclear Magnetic Resonance spectroscopy to study the adsorption phenomena of associative thickeners and nonionic surfactants onto hydrophobic polystyrene (PS) latex particles.[11,12] These studies concentrated on the effect that nonionic surfactants had on the performance of the associative thickeners. Cosgrove and co-workers have also used NMR to investigate poly(ethylene oxide) terminally attached at the PS/water interface in polymer systems and have concluded that NMR relaxation phenomena may be used to describe the adsorption process.[13-15]

This study reports NMR experiments concerning the adsorption of a poly(oxyethylene) surfactant ($C_{16}H_{33}$—(O—CH_2—CH_2—)$_{20}$—OH) onto PS latex particles. This surfactant is referred to as $C_{16}(EO)_{20}$ throughout this article. Ou-Yang and co-workers measured a strong binding energy between the hydrophobe and the particle surface with laser light scattering (LLS).[16] This energy is 7 to 10 k_bT, where k_b is Boltzmann's constant.

Cory and Rodgers proposed a three-stage model for the adsorption of nonionic surfactants onto both hydrophobic and hydrophilic surfaces.[17] Their model is used to aid in the explanation of the possible surfactant conformations on the PS latex particles.

Proton (^{1}H) NMR spectroscopy was used to observe adsorbed surfactant close to the PS particle

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surface. The relative motions of the individual molecules and functionalities determine the spectral features observed via NMR. The 109 nm diameter PS particles are large compared to molecular dimensions, and both rotate and translate extremely slowly in comparison to the NMR time scale, yielding resonances so broad that they are indistinguishable from the baseline.[18] If the hydrophobe or the oxyethylene chain adsorb to the surface or are sufficiently close to the surface, they rotate as one with the particle and similarly broaden away. Depending on the conformation of individual molecules, portions of the oxyethylene chain are free from interaction with the particle surface. In this case, portions of the oxyethylene chain have a high degree of motion; NMR detects the resonances from this part of the chain as a strong, narrow resonance. If a particular surfacant molecule does not adsorb onto the surface and is free in solution or in a small micelle, then NMR should detect all of the surfactant resonances from that molecule, including the hydrophobe resonances.

The underlying assumptions for interpreting the NMR data are: (1) The surfactant molecules do not exchange on and off the particle surface, or the exchange is extremely slow with respect to the NMR time scale for exchange. (2) Only monolayer coverage exists. (3) An insignificant number of adsorption sites are blocked by impurities, solvent molecules, etc.; and (4) The critical micelle concentration of the surfactant does not interfere with the amount of the oxyethylene chain detected by NMR.

Quantitative determination of the amount of the oxyethylene chain not detected by NMR upon adsorption is achieved by the use of a simple analytical method. This method requires measurements on two sets of samples: (1) examine the surfactant/D_2O system as a function of surfactant concentration with no PS latex particles present; and (2) examine the surfactant/PS/D_2O system as a function of the surfactant concentration with a constant PS latex concentration.

A straightforward comparison of the two data sets yields information without requiring extensive calculations or transformations. This analytical technique yields a value for the amount of the oxyethylene chains that are close to the particle surface. These data are interpreted in terms of the molecular conformations of the surfactant molecules upon adsorption to the latex substrate.

The effective NMR detection limit is found by combining the NMR data with laser light-scattering results for the hydrodynamic radius. The EO chain could be in several possible conformations such as an *all-trans* stretched conformation or a collapsed conformation. If some of the chains are on the particle surface, they are not detectable by NMR. Milner and co-workers have proposed a theory for the monomer density profile for connected monomers on colloidal particles.[19] The NMR and laser light-scattering measurements yield the actual distance from the particle surface at which the EO chains are detected by NMR, assuming a given monomer density profile.

Milner and co-workers used a self-consistent field method to demonstrate the equilibrium brush profile as a function of monomer density and the height from the particle surface. This monomer density profile is a parabola.[19] The monomer density function is defined under eq. (1):

$$\Phi(z) = (B/w)[(h^*)^2 - z^2] \qquad (1)$$

where B is a monomer molecular weight dependent term, w is an excluded volume term that is set to 1, h^* is the length of the monomer chain, and z is the distance from the particle surface of interest.[19] B is defined in eq. (2):

$$B = \pi^2/(8N^2) \qquad (2)$$

where N is the molecular weight of the monomer.

EXPERIMENTAL SECTION

Nonionic Surfactant and Polystyrene Latex

The poly(oxyethylene) surfactant was furnished by Union Carbide and has the general structure of:

$$C_{16}H_{33}-(O-CH_2-CH_2)_x-OH$$

where x is approximately 20. The nominal molecular weight of this surfactant is 1120 g/mol. A polydispersity index of 1.06 was determined by gel permeation chromatography.[20] The donated sample was used without further purification. The hydrodyanmic radius of the poly(oxyethylene) chain of 3 nm was determined by laser light scattering after adsorption onto PS particles.[16]

The monodisperse polystyrene (PS) latex was supplied by the Dow Chemical Company. The latex was cleaned by ion exchange chromatography. Transmission Electron Microscopy was used to measure a particle diameter of 109 nm.[18] The specific surface area is 55.5 m^2/g.[18] Due to large water (solvent) signals in the proton NMR spectra, a serum

replacement technique that involves continual dialysis was used to replace approximately 98% of the H_2O with D_2O (99.9%, Cambridge Isotope Laboratories). The PS/D_2O latex dispersion contained 2.18% solids as determined by gravimetric analysis.

Sample Preparation

The first set of samples was made with the surfactant and D_2O only; no PS particles were present. Surfactant samples in 99.9% D_2O were prepared by pipeting a known amount of surfactant from a 0.5002% stock solution of surfactant in D_2O into a 2 dram glass vial and then diluting with D_2O to obtain the desired concentration. Aluminum foil was placed inside the lid for leakage prevention, the lid was replaced, and the sample was tumbled for a minimum of 24 h at room temperature before the NMR experiments were performed. Both the surfactant and D_2O were added by weight (±0.0001 g); the desired sample size in all cases was 4.5 g. All components were added using a polyethylene pipet in order to maximize the transfer into the glass vial.

The second set of samples contained PS particles and surfactant in D_2O. The PS latex concentration employed corresponded to a surfactant concentration of 200 ppm (by weight) at the onset of the hydrodynamic radius plateau determined by laser light scattering (100% surface coverage). Surfactant/particle samples were then prepared at surface coverage values from 25% to 500% based on the constant amount of PS particles.[16,21] All components were again added by weight. A known amount of the surfactant was pipeted from the 0.5002% stock solution into a 2 dram glass vial using a polyethylene pipet. The PS latex dispersion (0.8000 ± 0.0001 g) was added to each sample. D_2O (99.9%) was introduced to obtain the final surfactant concentration. All samples were tumbled for a minimum of 24 h at room temperature before further analysis.

^{1}H-NMR Measurements

All solution-state ^{1}H-NMR experiments were performed on a Bruker AM-500 500 MHz spectrometer. A 10 mm carbon/hydrogen probe was utilized. The temperature was held constant at 303 K; each sample was spun at 15 Hz. A 10 μs pulse width (38°) was used. A 16-bit analog-to-digital converter was employed. The number of acquisitions utilized was either 64 or 128, depending on the surfactant concentration and the observed signal-to-noise ratio. The number of data points used throughout the NMR experiments was 16,384; the acquisition time for each scan was approximately 1 s. The dwell time was 62 μs, and a 10-s relaxation delay was used. Each free induction decay was muliplied by a decreasing exponential function equivalent to 2 Hz before Fourier transformation. The residual solvent resonance was saturated with a low level irradiation field during the 10-s relaxation delay prior to excitation and data acquisition. Longer relaxation delays (60 s) did not alter the integration values obtained.

An external standard was prepared by sealing a 20 mg/mL mixture of tetrakis(trimethylsilyl)-silane (TKS, Aldrich) in deuterated benzene (99.9%, Cambridge Isotope Laboratories) in a glass capillary tube. This external standard was placed directly in the middle of the 10 mm NMR tube with the sample; the same standard was used for each sample and measurement. The integrated value of the resonance from this standard (0.27 ppm) was set at 100 intensity units. The residual water peak was used as the chemical shift reference and was set at 4.70 ppm. Typical experimental error for the integration values was approximatetly 5%, as determined by replicate measurements.

RESULTS AND DISCUSSION

Adsorption Affects NMR Lineshape

Figure 1 presents the ^{1}H-NMR spectra of the surfactant with and without PS latex particles. The sample used for spectrum A contained surfactant at a concentration of approximately 250 ppm and also contained PS particles. The surface coverage value for spectrum A was calculated to be 126.3%. The sample yielding spectrum B contained only the $C_{16}(EO)_{20}$ in D_2O at a concentration of 251.2 ppm. The surfactant-only spectrum has three distinct families of resonances. These peaks represent the external standard at 0.27 ppm, the C16 hydrophobe from 0.8–1.6 ppm and 3.45 ppm, and the EO chain at 3.7 ppm. The small peak at 3.45 ppm arises from the —CH_2— group of the C16 hydrophobe bonded to the first oxygen atom of the oxyethylene chain. The presaturated residual HDO resonance at 4.7 ppm (not shown) is smaller than the EO peak at 3.7 ppm. The small resonance at 7.2 ppm from the residual protons of the external standard in the capillary tube is not shown.

The overall appearance of the spectrum changes due to adsorption phenomena on PS particles. Of particular interest is the lineshape of the peak for the EO chain. The 126.3% surface coverage spectrum is used as an example. The resonances in this

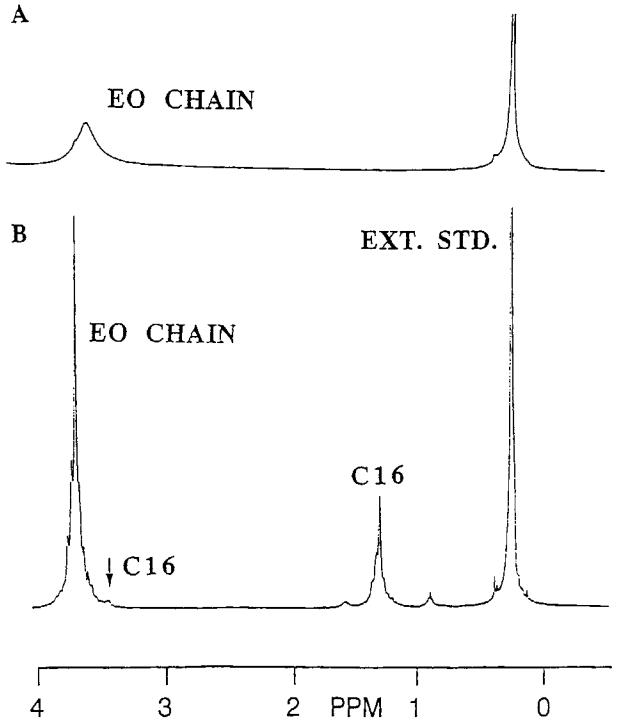

Figure 1 Spectrum A is a 500 MHz ^{1}H-NMR spectrum of $C_{16}(EO)_{20}$ on 109 nm PS latex particles at a calculated surface coverage of 126.3% (surfactant concentration of approximately 250 ppm). The C16 hydrophobe resonances (0.8–1.6 ppm, 3.45 ppm) are not observed at this surface coverage value. Spectrum B is a 500 MHz ^{1}H-NMR spectrum of $C_{16}(EO)_{20}$ in D_2O at a concentration of 251.2 ppm in surfactant. No PS latex particles are present and all resonances of the surfactant molecule are detected.

spectrum represent the external standard at 0.27 ppm, the portion of the EO chain (—O—CH_2—CH_2—) very close to the surface at 3.6 ppm, and the unbound EO chains in solution and in micelles at 3.7 ppm. The EO chain resonance at 3.6 ppm is assigned to the portion of the EO chain that is close to the particle surface. This peak is broad due to restricted chain motion. The narrow peak at 3.7 ppm (a very weak shoulder) is attributed to oxyethylene chains that are not adsorbed to the particle surface. These EO units have more motion yielding a narrow linewidth. However, the C16 hydrophobe is not detected in the top spectrum of Figure 1 due to the strong adsorption of the hydrophobe onto the PS particle surface. The PS particles were not detected because of the size and motion constraints previously stated. The peak at 3.7 ppm became more prominent as the total surfactant concentation increased. At very high surface coverage values the EO chain peak appeared to shift entirely to 3.7 ppm, but with a linewidth that was larger than the linewidth of the EO chain peak for a surfactant/D_2O-only sample. The observed linewidth is a superposition of resonances from unbound surfactant molecules and those molecules interacting strongly with the PS particles.

Analysis of the Surfactant/D_2O System

Figure 2 presents the integrated values of EO resonances as a function of surfactant concentration. Integration of the ^{1}H-NMR signals of the EO chains and the hydophobe peaks yields the average number of repeating EO monomers in the surfactant, which corresponds to the number-average molecular weight (M_n). In all cases, the peak area of the weak feature at 3.45 ppm from the C16 hydrophobe was included in the integral for the peak area of the EO chains resonance and, therefore, excluded from the sum of the peak areas for the hydrophobe. In all samples where the C16 hydrophobe resonance at 3.45 ppm was observed, a correction was made to attain more accurate integration values for the EO chains and C16 hydrophobe resonances. This correction was made by using the ratio of the number of protons in the peak at 3.45 ppm (2) to the number of remaining protons in the C16 hydrophobe (31). This ratio (2/31) was then multiplied by the integration

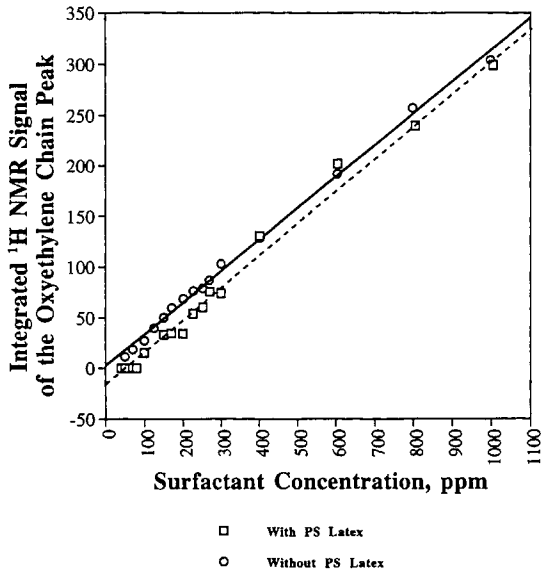

Figure 2 A plot of the integrated ^{1}H-NMR signal of the EO chain peak as a function of the surfactant concentration. The line through the "o"s is the linear regression line of the data points with no PS latex particles present. The dashed line is the linear regression line of the data points greater than 100 ppm in surfactant concentration with PS latex particles present. The points below 100 ppm have an integrated NMR signal value of zero.

value for the sum of the C16 resonances in the 0.8 to 1.6 ppm range. The value obtained was then added to the C16 hydrophobe peak area and subtracted from the peak area of the EO chains resonance to obtain the "corrected" integration values. The average M_n value calculated from surfactant/D_2O-only samples is 1210 g/mol. The reference line is linear ($r^2 = 0.997$) over the selected concentration range, indicating micelle formation does not affect the amount of EO chain detected by ^{1}H-NMR. A similar observation was made for the C16 hydrophobe. The critical micelle concentration of this surfactant is approximately 5 ppm.[22]

Analysis of the Surfactant/PS Particle System

Figure 3 presents ^{1}H-NMR spectra of the surfactant/particle system with surfactant concentrations of 226.4 ppm (110.9% surface coverage) for the top spectrum (A) and of 1004 ppm (506.9% surface coverage) for the bottom spectrum (B). At higher surface coverage values, all of the surfactant resonances were detected. In these cases some of the surfactant molecules form micelles or are free in solution and have more motion than those surfactant molecules that are bound. As the surfactant concentration increased, the EO chain peak shifted to 3.7 ppm and sharpened.

Table I presents the surfactant concentrations and calculated surface coverage values with the corrected integrated ^{1}H-NMR signals of EO chains and the sum of the integration values for the hydrophobe resonances. The EO chain is detected from samples with surface coverage values greater than 50% based on the LLS hydrodynamic radius plateau onset. At lower surface coverage values a significant number of adsorption sites are empty on the PS particle surface, so virtually no surfactant molecules are free in solution. The EO chain does have a weak attraction to the particle surface due to van der Waals interactions. When a significant area is available on the particle surface, the EO chain can lay close to the particle surface in a pancake conformation. When the EO chain interacts with the particle surface, it rotates with the particle and is not detected. As the surface coverage values rise due to an increase in the surfactant concentration, the EO chain is displaced by the C16 hydrophobe, which has a much stronger attraction to the PS particle surface due to hydrophobic interactions. Once all of the adsorption sites are occupied and a monolayer of surfactant is formed on the particle surface, any additional surfactant molecules are free in solution or in micelles and do not interact with the surface. These stages

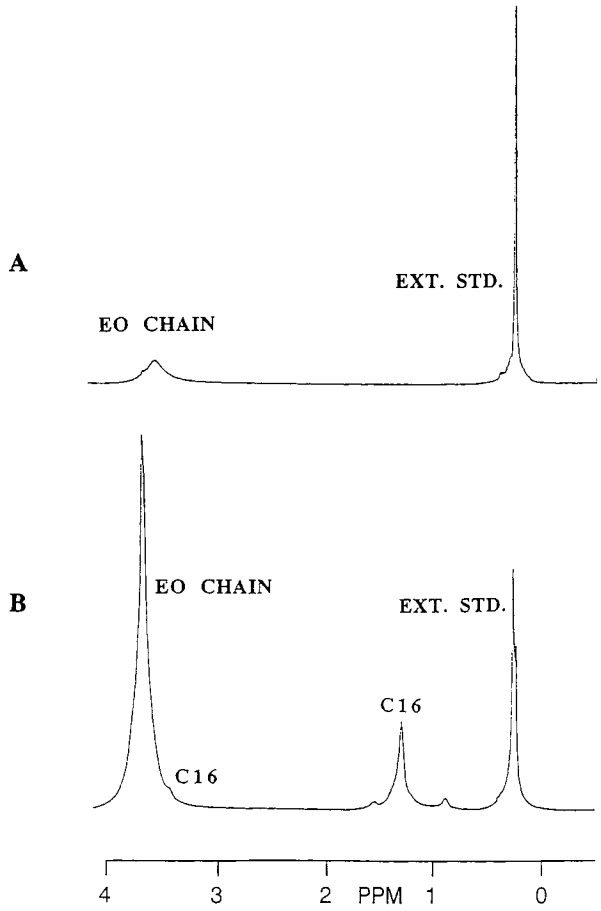

Figure 3 Spectrum A is a 500 MHz ^{1}H-NMR spectrum of $C_{16}(EO)_{20}$ on 109 nm PS latex particles at a calculated surface coverage of 110.9% (surfactant concentration of 226.4 ppm). The C16 hydrophobe resonances are not detected in spectrum A. Spectrum B is a 500 MHz ^{1}H-NMR spectrum of $C_{16}(EO)_{20}$ on 109 nm PS latex particles at a calculated surface coverage of 506.9% (surfactant concentration of 1004 ppm). In both cases, the PS particle concentrations are approximately the same.

of adsorption are in agreement with those postulated by Cory and Rodgers.[17]

The hydrophobe is not detected until surface coverage values greater than 200% are reached. The hydrodynamic radius plateau onset obtained using laser light scattering may not be the appropriate reference for full surface coverage. In the LLS experiments, the actual number of adsorbed surfactant molecules is not directly known. The hydrodynamic radius could reach its limiting value while adsorption sites on the particle surface are still vacant. In contrast, NMR directly measures the adsorption of the C16 hydrophobe onto the latex substrate. The results of the NMR experiments indicate that surfactant molecules added after saturation of the PS sur-

Table I Proton NMR Integration Values for Surfactant Samples with PS Latex

Surfactant Conc., ppm	Surface Coverage, %	^{1}H Signal of EO Chain	^{1}H Signal of C16
40.0	19.8	0	0
50.0	25.0	0	0
69.9	35.0	0	0
79.7	39.2	0	0
99.9	49.9	15.05	0
150.0	78.9	33.52	0
169.4	84.3	35.12	0
199.6	101.0	34.55	0
225.6	110.9	53.98	0
251.9	126.3	60.52	0
270.2	130.9	75.57	0
300.0	150.8	74.06	0
400.8	200.0	130.67	5.89
604.5	304.3	202.29	32.62
805.1	400.9	239.92	54.46
1004.1	506.9	298.79	73.19

face as determined by the hydrodynamic radius of LLS do not remain in solution, but the C16 hydrophobes bind to vacant sites on the particle surface. Only at surface coverage values greater than 200% (by the hydrodynamic radius of LLS) are the hydrophobe resonances detected by NMR, indicating these molecules are, indeed, free from interactions with the particle surface.

Determination of the Effective NMR Detection Limit

Quantitative analysis of the two sets of data yields the amount of the EO chain in close proximity with the particle surface. Figure 2 presents a plot of the integrated ^{1}H-NMR signal of the EO chain peak with and without PS particles as a function of the surfactant concentration. The linear regression line through the data points for samples with the PS particles is only for the data points that are greater than 100 ppm in surfactant concentration. Within experimental error, the slopes of the two lines are identical. From these observations, the portion of the EO chain not observed by ^{1}H-NMR is one-third of the total EO chains bound to the PS particles.

The effective NMR detection limit was obtained by combining the NMR results with the hydrodynamic radius determined by light scattering and a model density profile of the EO chains. Two-thirds of the bound EO chain resonances were observed by NMR. The EO chain could be in several possible conformations. Limiting cases include a fully stretched *all-trans* conformation or a collapsed structure in which some of the EO chains are on the particle surface and, thus, not detectable by NMR. Milner and co-workers have proposed a theory of a monomer density profile for monomers on colloidal particles.[19]

Using the molecular modeling software, SPARTAN™, and trigonometric calculations, the length of the *all-trans* conformation of $(EO)_{20}$ was determined to be 6 nm.[23] Figure 4(A) presents the density profile when the 6 nm length of the *all-trans* conformation was used as the hydrodynamic radius. This profile is a zeroth-order approximation to the

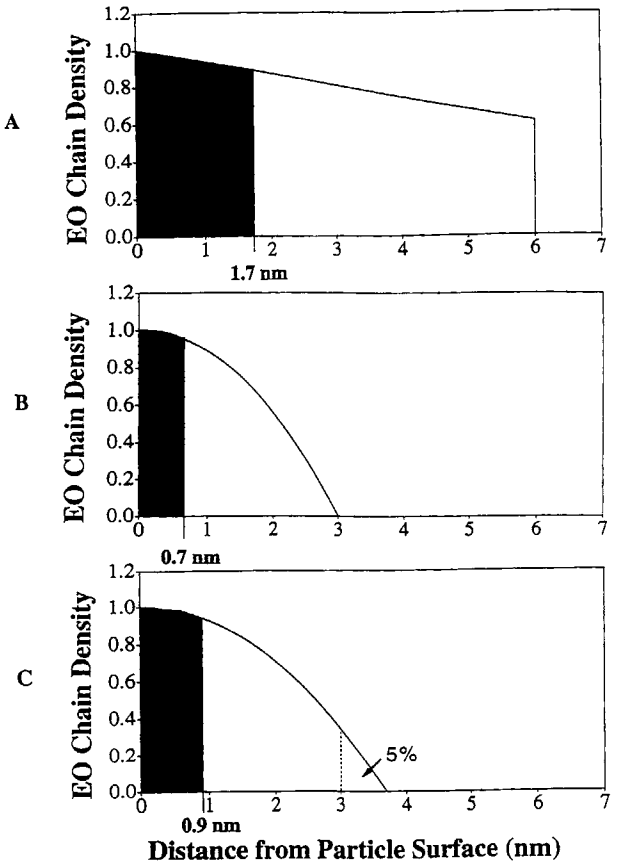

Figure 4 Plot A is the zeroth-order EO chain density profile when the 6 nm length of the *all-trans* conformation was used as the hydrodynamic radius. Plot B is the EO chain density profile when the hydrodynamic radius of the EO chain (3 nm) contains all of the EO chain density assuming a parabolic profile. Plot C is the EO chain density profile when the hydrodynamic radius contains 95% of the total EO chain density for a similar situation. The shaded areas in the profiles represent one-third of the total area of the respective profile, and the distances from the particle surface that yield one-third of each area are also presented.

monomer density profile. All monomer density profiles were normalized to unit area for comparison purposes. The diameter of the spherical latex particles was taken into account for this profile while the EO chains were assumed to remain in an *all-trans* conformation. The integrated area up to a distance of 1.7 nm from the particle surface yields one-third of the total area of the density profile. On average, NMR detects the EO chain resonances above 1.7 nm from the particle surface for this particular profile. However, this profile is not realistic because the hydrodynamic radius of the EO chain is proportional to the square root of the molecular weight of the surfactant molecule;[16] a parabolic profile is more reasonable.

A second basis for the NMR detection limit calculations is to use the measured hydrodynamic radius as the total length of the EO chain. Using eq. (1) and integrating over the total length (h^*, 3 nm) of the EO chain in this conformation, the area of the profile is calculated and then normalized to 1. Because one-third of the bound EO chain resonances were not observed by NMR, a calculation was performed to determine the distance from the particle surface, which yielded one-third of the total area. Figure 4(B) presents the density profile when the hydrodynamic radius of the oxyethylene chain was used as h^*. For this model, on average, NMR detects the resonances for any portion of the EO chains above 0.7 nm from the particle surface.

The third calculation method is not straightforward. The hydrodynamic radius was used as the length of reference. Using eq. (1) and the hydrodynamic radius, the total distance (h^*), which yielded the hydrodynamic radius (z) as a certain percentage of the overall density of the oxyethylene chain, was calculated. Utilizing the calculated h^*, the distance from the particle surface that yielded one-third of the total area of the profile for the hydrodynamic radius containing 95% of the EO chain density was determined to be 0.9 nm. Figure 4(C) presents an example of the profile from this protocol with 95% of the EO chain density contained within the hydrodynamic radius of 3 nm for $C_{16}(EO)_{20}$. Table II presents the total surfactant height from the surface (h^*) and the NMR detection limit as a function of the hydrodynamic radius location.

The effective NMR detection limit is less than or equal to 1 nm. This conclusion is based on the hydrodynamic radius containing most of the bound EO chains. The hydrodynamic radius depends on the square root of the EO chain length.[16] The *all-trans* model requires the EO chain length be directly proportional to the EO chain length, so it is not a viable conformation. This puts a lower limit of 70% on the percentage of EO chain density within the hydrodynamic radius, as listed in Table II.

Table II Results of Calculations for NMR Detection Limit When the Hydrodynamic Radius Contains a Certain Percentage of the Total EO Chain Density

Amount of EO Chain Density within Hydrodynamic Radius	Total Length of EO Chain (nm)	Distance at One-Third of the Area of the Profile (nm)
95	3.7	0.9
90	4.1	1.0
85	4.5	1.0
80	4.9	1.1
75	5.4	1.2
70	5.9[a]	1.4

[a] This is essentially the *all-trans* configuration, so the model breaks down at or before this value.

CONCLUSIONS

Proton NMR spectroscopy, laser light scattering, and a theory of the monomer density profile for connected monomers on colloidal particles were utilized to determine the NMR detection limit of less than 1 nm for $C_{16}(EO)_{20}$ adsorbed onto polystyrene colloidal particles. The mobilities of the groups within molecules are the main driving force for the detection of the respective resonances. The change in the NMR lineshape of the EO chain peak at various surface coverage values on the latex substrate confirmed the presence of two distinct populations of the EO chains. One peak was assigned to the free surfactant molecules in solution or in micelles, and the other to the adsorbed but detectable portion of the EO chain. At low surface coverage values (i.e., less than 50%), the adsorbed EO chains were not detected by NMR. These EO chains interact with the particle surface in a pancake conformation at low total surfactant concentration. As full surface saturation was approached, two-thirds of the bound EO chains were detected by NMR.

The C16 hydrophobe was not detected until a very high surface coverage of 200% based on the laser light-scattering hydrodynamic radius plateau was reached. The LLS hydrodynamic radius onsets are not appropriate for the use in the interpretation of the NMR results. The absolute number of adsorbed

surfactant molecules is not directly known from the light-scattering experiments. As the light-scattering hydrodynamic radius plateaus, adsorption sites on the substrate are still unoccupied; thus, surface coverage values obtained from the hydrodynamic radius are not correct. In contrast, NMR directly measures the adsorption of the C16 hydrophobe on the particle surface. The NMR experiments indicate surfactant molecules added after the LLS hydrodynamic radius plateau onset do not remain free in solution, but the hydrophobes bind to vacant sites on the PS particle surface. Only at surface coverage values greater than 200% (by light scattering) are the hydrophobe resonances detected by NMR, indicating these molecules are, indeed, in micelles or free in solution.

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