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Interaction between surfactants and colloidal latexes in nonpolar solvents studied using contrast-variation small-angle neutron scattering

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Abstract

The interaction between deuterium-labeled Aerosol OT surfactant (AOT-D₃₄) and sterically-stabilized poly(methyl methacrylate) (PMMA) latex particles dispersed in nonpolar solvents has been studied using contrast-variation small-angle neutron scattering (CV-SANS). The electrophoretic mobilities (μ) of the latexes have been measured by phase-analysis light scattering,

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indicating that μ is negative. Two analogues of the stabilizers for the particles have been studied as free polymers in the absence of PMMA latexes: poly(12-hydroxystearic acid) (PHSA) polyester and poly(methyl methacrylate)-*graft*-poly(12-hydroxystearic acid) (PMMA-*graft*-PHSA) stabilizer copolymer. The scattering of PHSA in dodecane and PMMA-*graft*-PHSA in toluene are consistent with extended polymer chains in good solvents. In dodecane, PMMA-*graft*-PHSA forms polymer micelles, and SANS is consistent with ellipsoidal aggregates formed of around 50 polymer chains. CV-SANS measurements were performed by measuring SANS from systems of PHSA, PMMA-*graft*-PHSA, and PMMA latexes with 10 and 100 mM surfactant solutions of AOT-D₃₄ in both polymer/particle and AOT contrast-matched solvent. No excess scattering above the polymer or surfactant was found for PHSA in dodecane or PMMA-*graft*-PHSA in dodecane and toluene. This indicates that AOT does not significantly interact with the free polymers. Excess scattering was observed for systems with AOT-D₃₄ and PMMA latexes dispersed in particle contrast-matched dodecane, consistent with the penetration of AOT into the PMMA latexes. This indicates that AOT does not interact preferentially with the stabilizing layers but, rather, is present throughout the colloids. Previous research (*Langmuir* **2010**, 26, 6967–6976) suggests that AOT surfactant is located in the latex PHSA-stabilizer layer, but all the results in this study are consistent with AOT poorly interacting with alkyl-stabilizer polymers.

Introduction

Charge in nonpolar solvents, although less prevalent than in water or polar solvents, can be stabilized by different charge control additives (CCAs) with many particle types.^{1,2} The formation of charged species is important in many nonaqueous systems, including petroleum safety and the electrophoretic displays used in electronic paper devices.^{3,4} A common system used to produce charged species in nonpolar solvents is by preparing dispersions of poly(methyl methacrylate) (PMMA) latexes with poly(12-hydroxystearic acid) (PHSA) brushes as steric stabilizers and the anionic surfactant, sodium dioctylsulfosuccinate (Aerosol OT or AOT), added as CCA.^{5–12} In addi-

tion to AOT, these particles can be charged with other CCAs, such as calcium octanoate,¹³ sodium acetate,¹⁴ or through the incorporation of ionizable monomers.^{15–17} These model PMMA colloids, originally developed by Antl *et al.*,¹⁸ have been well-studied in nonpolar solvents, due to the ability to produce highly monodisperse particles that can behave essentially as hard-spheres.¹⁹ Previous work has demonstrated that small-angle neutron scattering (SANS) is a powerful technique for providing insight into the structure of the polymer colloids, both alone and in combination with CCAs.^{13,20–27}

Despite the importance of charge stabilization in nonpolar solvents, there have been few studies into the structural origin of surfactant-induced charging. The only previous study proposed that AOT surfactant adsorbs as monomers in tightly-bound layers around the PMMA cores.¹¹ This study was limited by the use of only one particle type and one surfactant concentration achieving sufficient scattering intensity resolution. Given the number of previous studies of PMMA latexes using SANS and chemical characterization,^{13,20–28} it is known that latexes and analogues for the stabilizing polymers can be readily generated for precise characterization.

The benefit of using neutron scattering to study such complex systems, consisting of multiple components, is that hydrogen-deuterium isotopic substitution can enable scattering from individual components to be masked or highlighted. This approach, called contrast-variation SANS (CV-SANS), has been used in this study to determine how AOT interacts with PMMA latexes in dodecane. Two analogues of the PMMA latex surface have been prepared, the PHSA polyester forming the stabilizer brushes and the poly(methyl methacrylate)-*graft*-poly(12-hydroxystearic acid) (PMMA-*graft*-PHSA) copolymer added during the particle synthesis. These have been studied both as free polymers and in colloid-free binary polymer-AOT surfactant mixtures. These polymers were investigated as simple model systems to explore the interaction of AOT with the polymer stabilizer used for the latex. The structures of free and aggregated polymers (PHSA and PMMA-*graft*-PHSA) have been studied in an aliphatic solvent (dodecane) and an aromatic solvent (toluene). These solvents were chosen because dodecane is a good solvent for PHSA and not PMMA, whereas toluene is a good solvent for both PHSA and PMMA. Additionally, small

PMMA latexes have been prepared to directly probe the interaction between the surfactants and the colloids including the steric stabilizer. CV-SANS has been used with both polymers and particles to highlight scattering from either component, the polymer/particle or surfactant, by tuning the solvent scattering length density.

Experimental

Characterization

Small-Angle Neutron Scattering

Neutron scattering measurements were performed at both at the ISIS Pulsed Neutron Source (STFC Rutherford Appleton Laboratory, Didcot, U.K.) and the Institut Laue-Langevin (Grenoble, France). The momentum transfer vector (Q) is defined in Equation 1, where θ is the scattered angle and λ is the incident neutron wavelength.

$$Q = \frac{4\pi \sin \frac{\theta}{2}}{\lambda} \quad (1)$$

Two instruments were used at ISIS. On Sans2d,²⁹ a simultaneous Q -range of 0.004–0.80 Å^{−1} was achieved utilizing an incident wavelength range of 1.75–16.5 Å and employing an instrument set up with source-sample and sample-detector distances of $L_1=L_2=4$ m and the 1 m² detector offset vertically 150 mm and sideways 269 mm. On LOQ,³⁰ data were recorded on a single two-dimensional detector to provide a simultaneous Q -range of 0.008–0.24 Å^{−1} utilizing neutrons with $2 \leq \lambda \leq 10$ Å. The beam diameter on both instruments was 8 mm. Each raw scattering data set was corrected for the detector efficiency, sample transmission and background scattering and converted to scattering cross-section data ($\partial\Sigma/\partial\Omega$ vs. Q) using the instrument-specific software, Mantid. These data were placed on an absolute scale (cm^{−1}) using the scattering from a standard sample (a solid blend of hydrogenous and perdeuterated polystyrene) in accordance with established procedures.³¹

Two instruments were used at the Institut Laue-Langevin. On D11, two sample-detector dis-

tances of 1.2 and 8 m were used with collimation distances of 4 and 8 m. This gave an accessible Q -range of 0.004–0.3 Å⁻¹ at $\lambda = 10$ Å. On D22, a sample-detector distance of 14 m was used with a collimation distance of 14 m. This gave an accessible Q -range of 0.002–0.02 Å⁻¹ at $\lambda = 10$ Å. The beam size was 7 mm $\times$ 10 mm; the data were placed on an absolute scale (cm⁻¹) by the measurement of a 1 mm thick sample of H₂O as a standard. The instrument setup determined the uncertainty in Q , which was used to account for instrumental pinhole smearing.

The dispersions were contained in either 2 mm or 1 mm path length Hellma quartz cells, depending on the amount of D-labeled solvent. For contrast matched samples, scattering in the matched solvent alone was measured to verify the contrast-match point. For samples where excess scattering was observed, it was subtracted from the total scattering curve.

Scattering length densities (ρ) have either been calculated from chemical structure and density or experimentally determined using SANS. This can be done by measuring the magnitude of $I(Q)$ at different ρ_{solvent} and determining where $I(Q = 0) = 0$ cm⁻¹.

Data have been fit to models as described in text using both SasView and Insanity small-angle scattering analysis software packages. The fit values for radii and lengths are considered to have a certainty of ± 1 Å arising from the instrumental resolution.

Gel Permeation Chromatography (GPC)

Polymer molar masses were determined using an Agilent 1100 GPC. Small masses of polymers (approximately 1 mg) were dissolved in chlorobenzene, and then injected onto the column, which was held at 50°C. The elution of polymers was observed using refractive index detection.

Electrophoretic mobility

Electrophoretic mobilities were measured using a Malvern Zetasizer Nano ZS with a universal dip cell electrode. The applied field strength used was 3.0×10^{-4} V m⁻¹. Five runs of 100 measurements were performed, and the average of these runs was used.

Materials

The polymers and surfactants used were synthesized as outlined in the sections below. Deuterium-labeled n-dodecane-D₂₆ (98% D₂₆) was obtained from Cambridge Isotope Laboratories (Tewksbury, MA, U.S.A.), and n-dodecane-H₂₆ ($\geq 99\%$) was obtained from Sigma-Aldrich (Gillingham, Dorset, U.K.). Deuterium-labeled toluene-D₈ (> 99.50 atom % D₈) was obtained from Apollo Scientific (Stockport, Cheshire, U.K.), and toluene-H₈ (puriss. p.a., ACS Reagent, $\geq 99.7\%$) was also obtained from Fluka (Gillingham, Dorset, U.K.). Deuterium-labeled solvents and toluene-H₈ were used as supplied. Dodecane-H₂₆ was purified over a basic alumina column to remove surface-active impurities.³²

Poly(12-hydroxystearic acid)

The polyester poly(12-hydroxystearic acid) (PHSA) was prepared through the condensation of the monomer, 12-hydroxystearic acid (12-HSA).^{18,28} 12-hydroxyoctadecanoic acid (99%) was obtained from Aldrich (Gillingham, Dorset, U.K.). 12-HSA (4.7721 g) was combined with toluene and *p*-toluenesulfonic acid monohydrate (0.0475, ACS Reagent, $\geq 98.5\%$, Sigma-Aldrich, Gillingham, Dorset, U.K.). The solution was refluxed at 160°C for 48 hours in a Dean-Stark apparatus to separate water from the toluene-water azeotrope.

PMMA-graft-PHSA stabilizer

The PMMA-*graft*-PHSA stabilizer graft copolymer consists of a methyl methacrylate backbone with PHSA brushes.¹⁸ The batch used (R8893/252) was a gift from Dr. Paul Bartlett (University of Bristol, U.K.).

PMMA particle synthesis

PMMA latex particles were prepared by a classic dispersion polymerization process.¹⁸ In a typical preparation methyl methacrylate (MMA) and methacrylic acid (MAA) monomers were weighed into a three-necked round bottom flask along with hexane, dodecane, azobisisobutyronitrile (AIBN)

initiator, the PMMA-*graft*-PHSA comb polymer stabilizer and 1-octanethiol. The round bottom flask was equipped with a condenser, septum and magnetic stirrer bar. The reaction mixture was purged with nitrogen for 15 minutes before being lowered into a stirred oil bath which had been preheated to 80°C. After 15 minutes the reaction mixture turned opalescent, indicating that nucleation had occurred. After 2 hours, diethanolamine and an amount of dodecane equal in mass to the amount of hexane used in the first part was added and the temperature was raised to 120°C. After 18 hours the flask was removed from the oil bath and the dispersion was filtered through glass wool in order to remove large aggregates. The flask was then rinsed with approximately 80ml of dry dodecane. The particle diameter was 95.5 nm as measured by DLS (Malvern Zetasizer Nano S) with a polydispersity index of 0.068.

Deuterium-labeled AOT

Deuterium-labeled AOT (AOT-D₃₄) was synthesized as previously reported¹¹ using deuterated 2-ethyl-1-hexanol-D₁₇. The purity was of AOT-D₃₄ confirmed using elemental analysis (Calc. for C₂₀H₃D₃₄NaO₇S: C, 50.2%; H, 7.7%; S, 6.7%; Na, 4.8%. Found: C, 50.4%; H, 7.6%; S, 6.6%; Na, 4.5%).

SANS samples

Samples were prepared for SANS in small volumes (0.75–1 mL) due to the requirement to use deuterium-labeled solvents and surfactant. The solvents were prepared at calculated H/D ratios to give appropriate scattering length densities.

PHSA, PMMA-*graft*-PHSA, and PMMA latexes were used as stock dispersions in dodecane-H₂₆ with a concentration by mass of ~ 10%. AOT-D₃₄ was dried under vacuum for 12 hours at 70°C before use. Surfactant solutions were prepared by combining the desired mass of AOT-D₃₄ with both D and H forms of dodecane or toluene until dissolved. An aliquot of the appropriate polymer or particle stock was then added to this surfactant solution. Samples were left to equilibrate 24–48 hours before SANS analysis.

For mixtures of pure PHSA and AOT-D₃₄, the polymer and surfactant were dissolved in hexane. The solvent was then allowed to evaporate at ambient temperature under vacuum to prepare a homogenous dispersion of surfactant in polymer at constant mass.

Results and Discussion

SANS measurements have been performed on analogues for the PMMA latex surface, shown in Figure 1, as well as on PMMA latexes. The surface of the latex consists of PHSA brushes, and the PHSA polyester itself has been studied in dodecane, a good solvent for the polymer. The PHSA brushes are incorporated into the particle through the graft copolymer PMMA-*graft*-PHSA, which consists of PHSA modified with a methacrylate endgroup and a backbone of MMA and glycidyl methacrylate (GMA). This copolymer has been studied in two solvents: toluene, which is a good solvent for both the grafts and the backbone, and dodecane, which is a good solvent for PHSA but not for PMMA.

The measured electrophoretic mobilities (μ) for the PMMA latexes are found to be $(-1.5 \pm 0.2) \times 10^{-10} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ for 10 mM AOT and $(-2.36 \pm 0.06) \times 10^{-10} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ for 100 mM AOT. Both concentrations are above the inverse micelle critical micelle concentration measured for AOT in alkane solvents.³³ The negative electrophoretic mobility agrees with previous measurements on this system.^{5,6,8,11} The electrophoretic mobility of AOT inverse micelles in aliphatic solvents can be estimated to be $\mu = 3.8 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$.³⁴ This is an order of magnitude greater than is measured for the PMMA latexes and shows that the mobility of the larger PMMA particles is being measured. The magnitude of μ is less than for previous measurements also made using phase-analysis light scattering, and this is likely due to the large difference in particle radius, 48 nm in this study compared to 780 nm in Hsu *et al.*⁵ It is not possible to eliminate the existence of a small number of charges on the surface of the PMMA latexes,^{6,9,35-37} but the potential small number of charges would be below the detection limit of the phase-analysis light scattering technique and is much lower than the charge present with AOT present. The electrophoretic mobility

Figure 1: The structure of the stabilizer graft copolymer, PMMA-*graft*-PHSA. The brush polyester consists of a PHSA polyester with a methacrylate linker. The backbone of the graft polymer consists primarily of methyl methacrylate with some glycidyl methacrylate. Reprinted with permission from Elsesser and Hollingsworth.²⁸ Copyright 2010 American Chemical Society.

measurements have been performed under the exact conditions used for CV-SANS measurements ($\phi = 0.02$ in dodecane). There is a small, statistically-significant difference in the magnitude of μ between the different AOT concentrations, but this difference is less than observed for the same concentration difference in previous studies.⁵

By performing SANS measurements of stabilizer polymers and PMMA latexes, it is possible to determine the degree of interaction of surfactant and polymer at concentrations where the particles are known to be charged. Using analogues of the stabilizer layer on the particle surface (PHSA and PMMA-*graft*-PHSA) simplifies the analysis, and using the latexes at the same conditions as the electrophoretic mobility measurements means that no assumptions have to be made about the effect of colloid volume fraction, size, or surfactant concentration.

The interactions between the AOT surfactant and the polymers or latexes were probed using CV-SANS. Two contrasts were measured: surfactant contrast-matched solvent, which highlights polymer-only scattering, and polymer contrast-matched solvent, which highlights surfactant-

only scattering. Contrast has been obtained using mixtures of deuterium-labeled solvents (either dodecane-D₂₆ or toluene-D₈) and AOT-D₃₄. By measuring these two contrasts, it is possible to determine whether the addition of the surfactant causes any difference to the structure of the polymer, as well as the structure of aggregated and adsorbed surfactant.

SANS of stabilizer polymers (PHSA and PMMA-*graft*-PHSA)

Free polymer without AOT

Before determining the interaction of the stabilizer polymers with AOT, the conformation of the free polymer was studied. The molar mass of PHSA has been measured in dodecane, and the molar mass of PMMA-*graft*-PHSA has been measured in both dodecane and toluene. PHSA is found to have a molar mass of $5.02 \times 10^3 \text{ g mol}^{-1}$ in dodecane, which compares favorably to the molar mass of $4.76 \times 10^3 \text{ g mol}^{-1}$ in chlorobenzene measured using GPC. This indicates that PHSA does not aggregate in dodecane and that the solvent is, therefore, “good” for the polymer. PMMA-*graft*-PHSA is found to have a molar mass of $3.92 \times 10^4 \text{ g mol}^{-1}$ in toluene, which also compares favorably to the molar mass of $4.22 \times 10^4 \text{ g mol}^{-1}$ in chlorobenzene measured using GPC. The SANS-determined effective molar mass of PMMA-*graft*-PHSA in dodecane is $2.00 \times 10^6 \text{ g mol}^{-1}$, which is much greater than the value in toluene or chlorobenzene. This indicates that PMMA-*graft*-PHSA forms polymer micelles in dodecane, which is a poor solvent for the MMA backbone but a good solvent for the PHSA brushes. A value for n_{agg} was calculated to be 51 using Equation 2.

$$n_{agg} = \frac{M_{s,micelle}}{M_{s,monomer}} \quad (2)$$

These results regarding the aggregation of PMMA-*graft*-PHSA agree with those previously performed by Papworth and Ottewill in octane and toluene.²⁶

The monomeric polymer scattering was fit to the Guinier-Debye model,³⁸ and the contrast, volume fraction, and the density were fixed, as they are coupled variables. The contrast and volume fraction are known from sample preparation, and the density of the 12-HSA monomer (944 kg

m^{-3}) was used for all polymers. The scattering profile then depends on the radius of gyration (R_g) and $\overline{M}_n$ of the polymer. The fit parameters agree well with the values determined from GPC and the Debye extrapolation. For PHSA in dodecane, the fit R_g is effectively identical to that determined from the Guinier approximation in the low- Q scattering limit, and the fitted $\overline{M}_n$ is within 10% of that measured by SANS using the Debye extrapolation or by GPC. For PMMA-*graft*-PHSA in toluene, the larger molar mass and radius of gyration agree with the fact that PHSA is polymerized into a graft copolymer. The R_g and $\overline{M}_n$ deviate from the Guinier and GPC values, but this poorer fit is due to dispersity of the polymer, which is not accounted for in the Guinier-Debye model fitting.

As PMMA-*graft*-PHSA is aggregated in dodecane, the structure is different than in toluene. The scattering curve can be fit to an ellipsoidal form factor depending the polar radius (r_p) and the equatorial radius (r_e).³⁹ The polymer micelles are prolate ellipsoids, and the fit parameters are shown in Table 1. The ellipsoids have a 2:1 polar-to-equatorial radius ratio (r_p/r_e), and the best fit is obtained with Schulz dispersity (σ)⁴⁰ in both the polar and equatorial axes. This can be explained due to the nature of the scattering aggregates. As they are formed of brush copolymer chains, the boundary of the ellipsoids may well be dynamic, poorly defined, and solvated.

Table 1: SANS data fitting parameters for stabilizer polymers

Guinier-Debye model			
Polymer	Solvent	$\overline{M}_n / (\text{g mol}^{-1})$	$R_g / \text{\AA}$
PHSA	Dodecane	4.52×10^3	26
PMMA- <i>graft</i> -PHSA	Toluene	1.93×10^4	69
Ellipsoid model			
Polymer	Solvent	$r_p / \text{\AA}$	$r_e / \text{\AA}$
PMMA- <i>graft</i> -PHSA	Dodecane	139 ($\sigma = 0.31$)	67 ($\sigma = 0.13$)

Poly(12-hydroxystearic acid) with AOT

The simplest model for the PMMA particle stabilizer surface is the free PHSA polyester. The CV-SANS on these model systems are shown in Figure 2 along with the SANS of free PHSA with no added surfactant. The SANS profile for the PHSA-highlighted and the two AOT-highlighted systems are clearly different. Although the size of the PHSA chains and the AOT micelles are similar,

the scattering measured in the two solvent contrasts clearly originates from different structures, as can be seen by the different slopes in the high- Q Porod region ($Q > 0.03 \text{ \AA}^{-1}$). The scattering arising from the PHSA highlighted system with 10 mM AOT can be fit to the Guinier-Debye model, with an R_g of $26 \text{ \AA}$ and an $\overline{M}_n$ of $4.78 \times 10^3 \text{ g mol}^{-1}$, similar to the values in dodecane alone (Table 1). This indicates that the addition of surfactant does not modify the conformation of the polymer in solution. From the AOT-highlighted systems, it is possible to determine if surfactant incorporates into the polymer coils. The AOT contrast scattering curves have been fit to a spherical form factor, and as can be seen in Figure 2, there does not appear to be any excess scattering over the AOT inverse micelles. The inverse micelles at both surfactant concentrations were fit to a spherical radius of $17 \text{ \AA}$, which is consistent with previous values for AOT in aliphatic solvents.⁴¹

Figure 2: CV-SANS profiles for PHSA and AOT in dodecane. The PHSA-highlighted scattering curves, both with and without surfactant, can be fit to the Guinier-Debye model with the same R_g of $26 \text{ \AA}$. The AOT-highlighted scattering can be fit to a spherical model with a radius of $17 \text{ \AA}$. This indicates that the two do not interact in dodecane.

Additionally, the scattering arising from AOT- D_{34} dispersed in pure PHSA has been measured, as shown in Figure 3. This form of PHSA is a liquid (melt) at room temperature, and no solvent has been added. Two concentrations of AOT were chosen, 0.54 and 5.6 weight %. While PHSA is not a typical “solvent”, it is nonetheless worth considering the structure of AOT when embedded in the pure polymer. The pure PHSA polymer does not show any structure over the length-scale commensurate with AOT inverse micelles, although it does show longer-range correlations at $Q <$

$0.05 \text{ \AA}^{-1}$. The high Q -scattering is different for the three systems, due to the difference incoherent scattering between H and D, and so a small constant background has been added to the AOT-D₃₄ containing curves to match the PHSA curve in the high- Q limit. At 0.54 weight % AOT, the profile is very similar to that of pure polymer, and there is no difference between the polymer scattering at $Q > 0.03 \text{ \AA}^{-1}$. At 5.6 weight % AOT, however, there is significant excess scattering above the polymer background. This excess scattering (in the region $Q > 0.03 \text{ \AA}^{-1}$) can be fit to a spherical form factor, with a r of $15 \text{ \AA}$ and a ϕ of 0.025. This correlates with the size of AOT inverse micelles in organic solvents⁴¹ and the concentration of surfactant. However, it should not be assumed that this phase separation in PHSA is identical to the formation of inverse micelles in dodecane, as the two solvents are not equivalent.

Figure 3: SANS profiles for AOT-D₃₄ in pure PHSA. The scattering for PHSA alone is flat with the only deviations occurring at $Q < 0.03 \text{ \AA}^{-1}$. AOT does not appear to be structured in the low concentration mixture, but it does show excess scattering at the higher concentration. This can be fit to a spherical form factor with an r of $15 \text{ \AA}$, consistent with small phase-separated regions of surfactant. The inset shows the scattering curves from the high- Q region only to accentuate that there is no detectable difference between the scattering from pure PHSA and the 0.54% AOT-D₃₄ containing system over a narrower intensity range.

PMMA-*graft*-PHSA with AOT

The stabilizer copolymer, PMMA-*graft*-PHSA, was also studied as another, more realistic model system. PMMA-*graft*-PHSA is present in toluene as free molecules; whereas in dodecane, it

aggregates into ellipsoidal polymer micelles.

CV-SANS results in toluene are shown in Figure 4 along with the SANS from free PMMA-*graft*-PHSA without surfactant. The scattering curve for the PMMA-*graft*-PHSA-highlighted sample with 10 mM AOT appears similar to that measured in the absence of surfactant. Both these PMMA-*graft*-PHSA-highlighted curves have been fit to the Guinier-Debye model, and the fit R_g is 60 Å and $\overline{M}_n$ is 1.89×10^4 g mol⁻¹. These values are very similar to those obtained for the polymer alone (Table 1). This indicates that the addition of AOT does not significantly modify the conformation of this graft polymer. The scattering from the AOT-highlighted sample is also shown in Figure 4. The scattering curves do not show excess scattering in the Q -range expected for the polymer alone and can be well fit to a spherical form factor with an r of 17 Å, consistent with the size of AOT inverse micelles. This suggests that the AOT does not penetrate into the PSHA-*g*-PMMA chains in toluene.

Figure 4: CV-SANS profiles for polymer and surfactant contrasts for mixtures of AOT and PMMA-*graft*-PHSA in toluene. Both scattering curves from the PMMA-*graft*-PHSA-highlighted system with and without surfactant have been fit to the Guinier-Debye model. The R_g of the PMMA-*graft*-PHSA-highlighted system with AOT is 60 Å. The scattering arising from the AOT-highlighted system has been fit to a sphere model with an r of 17 Å. This is consistent with there being little interaction between the two components.

As both PHSA in dodecane and PMMA-*graft*-PHSA in toluene can be considered as free polymer chains extended in “good” solvents, it is perhaps not surprising that there is no interaction between the added surfactant and the polymer chains. As determined from its molar mass and

SANS in dodecane, shown in Table 1, PMMA-*graft*-PHSA aggregates into ellipsoidal polymer micelles.

As these polymer micelles present larger volume objects, it might be expected that AOT will be more likely to adsorb onto the polymer aggregate surfaces, but this is not found to be the case. CV-SANS results for PMMA-*graft*-PHSA and AOT-D₃₄ in dodecane are shown in Figure 5 along with SANS of the PHSA-*graft*-PMMA polymer micelles without surfactant. The scattering from the PMMA-*graft*-PHSA-highlighted samples both with and without surfactant can be fit to an ellipsoidal form factor. The dimensions of the PMMA-*graft*-PHSA polymer micelles with 10 mM AOT are found to be $r_p = 120 \text{ \AA}$ ($\sigma = 0.41$) and $r_e = 70$ ($\sigma = 0.12$), very similar to the those for the polymer micelles alone (Table 1). The fit to the ellipsoid model for AOT-containing systems results in a smaller r_p and a greater σ_p , but these differences are not so significant to attribute a structural change to the presence of AOT. The AOT-highlighted scattering curves do not exhibit significant excess scattering above that expected for inverse micelles; the change in scattering arising from any possible partitioning into the polymer micelles should be readily detected given the larger aggregate volume. The AOT-highlighted scattering curves can be fit to a spherical form factor, with a r of 17–18 $\text{\AA}$, as would be expected for AOT inverse micelles in an aliphatic solvent.⁴¹ This indicates that AOT does not interact with PMMA-*graft*-PHSA polymer micelles in dodecane and that the two can be considered to exist as separate populations.

Observations

The structure of the free stabilizer polymers PHSA and PMMA-*graft*-PHSA (schematically shown in Figure 1) will not be identical to the structure of bound PHSA brushes on the surface of PMMA latexes. Despite this, the two polymers can serve as useful analogues of the stabilizer layer surface of PMMA latexes. If AOT is to adsorb onto the surface of PMMA latexes, an affinity between the surfactant and the stabilizer polymers should be observed. The CV-SANS measurements performed to examine interactions between AOT and the stabilizer polymers suggest that this is not the case.

Figure 5: CV-SANS profiles for polymer and surfactant contrasts for mixtures of AOT and PMMA-*graft*-PHSA in dodecane. The polymer-highlighted scattering can be fit to an ellipsoid model with $r_p = 120 \text{ \AA}$ and $r_e = 70 \text{ \AA}$, consistent with undisturbed polymer micelles. The AOT-highlighted scattering can be fit to a sphere model with $r = 17\text{--}18 \text{ \AA}$, consistent with spherical inverse micelles. This indicates that the two solutes do not interact in dodecane.

The same measurements have been performed on several combinations of stabilizer polymer and solvent, for both good and poor solvents for the polymer (Figures 2, 4, and 5). In all cases, the scattering curves do not suggest any partitioning of surfactant into the polymers. The structure of the stabilizer does not depend on the presence of the polymer, and likewise, the structure of surfactant inverse micelles are not modified by the presence of the polymer.

Given that the ratio of number of inverse micelles to polymer chains varies between 0.1 and 14 for PHSA in dodecane and PMMA-*graft*-PHSA in toluene, it might be possible for the free polymers that inverse micelles and polymer chains interact but that surfactants are still randomly dispersed, as observable by SANS. For PMMA-*graft*-PHSA in dodecane, this is not the case, as the ratio of inverse micelles to polymer micelles is 58 for 10 mM AOT and 697 for 100 mM AOT. If whole surfactant inverse micelles were to penetrate into the polymer micelle, a sufficient number would be localized for a structure factor to be observed in the SANS; this is not the case.

SANS of PMMA latexes

PMMA latexes without AOT

The scattering from sterically-stabilized PMMA latexes was measured in dodecane at different H/D-ratios. By measuring the scattering curves at different solvent contrasts, it has been possible to determine the average contrast match point ($\rho = 1.07 \times 10^{-6} \text{ \AA}^{-2}$). The data were fit to a core-shell sphere model,⁴² including instrumental pinhole smearing.

The shell comprises of PHSA brushes, and the thickness (r_s) was fixed to 100 $\text{\AA}$ with no dispersity. This value has been used previously to fit SANS data measured for similar particles.²¹ (Values between 60 and 100 $\text{\AA}$ have been used in other studies,^{11,20,21} but here the choice of r_s had little impact on the quality of the fit.) The core SLD (ρ_c) was fixed to the value for PMMA latexes, and the shell SLD (ρ_s) was allowed to vary between of $-6 \times 10^{-8} \text{ \AA}^{-2}$ (the calculated value used by Cebula *et al.*²⁰) and the value for the solvent. The fit value for ρ_s was nearly identical to the known value of ρ_{solvent} . It appears that the PHSA stabilizing shell is highly solvated; therefore, the core scattering dominates. The best-fit values for the particle core radius (r_c) vary between 335 and 352 $\text{\AA}$ with dispersities (σ_c) between 0.18 and 0.20. This core-shell model is justified, as the size of the fit particle is consistent with the value measured using dynamic light scattering and because the fit value of ϕ is similar to that for the prepared dispersions ($\phi = 0.02$).

PMMA latexes with AOT

CV-SANS measurements were performed using the PMMA latexes, which are found to be charged in dodecane. The AOT contrast only was studied, and the results are shown in Figure 6. The high- Q portion ($Q > 0.02 \text{ \AA}^{-1}$) are reminiscent of the SANS from an equilibrium population of AOT inverse micelles. As can be seen from the scattering curves, there is clearly additional scattering above the inverse micelle baseline in the region $Q < 0.01 \text{ \AA}^{-1}$. This suggests that a high contrast material (the AOT-D₃₄ surfactant) is located in a region comparable in size to the PMMA latexes. As PMMA latexes are charged in dodecane and AOT is determined to be present with the volume

of the particles, it is clear that the interaction between particles and surfactants plays an important role in the electrophoretic properties of the particles.

Figure 6: CV-SANS profiles for surfactant contrasts for systems of AOT and PMMA latexes in dodecane. The high- Q data are fit to a spherical form factor, the scattering arising from an equilibrium population of free AOT inverse micelles. The excess scattering measured at $Q < 0.03 \text{ \AA}^{-1}$ indicates that AOT is present in an environment other than inverse micelles, and the curves correlate to the spatial region occupied by PMMA latexes.

In order to determine the structure of the AOT present within the PMMA latexes, the scattering from inverse micelles alone, which dominates at high- Q , has been subtracted. This approach has been previously applied to binary mixtures of surfactant aggregates and core-shell models to successfully determine the structure of surfactant.^{11,43} The scattering from inverse micelles was fit to a spherical form factor, and the best fit curves are shown in Figure 6 with the best fit parameters shown in Table 2. The scattering length densities for solvent and AOT are fixed to the calculated values, and the volume fraction (ϕ) and spherical radius (r) were allowed to vary. As can be seen in Table 2, the fit ϕ correlates well to the value calculated from the prepared dispersion, and the fit r correlates well to the value expected for AOT inverse micelles in aliphatic solvent.⁴¹

Table 2: SANS data fitting for AOT inverse micelles in PMMA latex contrast-matched dodecane

$[\text{AOT-D}_{34}] / (\text{mM})$	ϕ AOT (calculated)	ϕ AOT (fit)	$r / \text{\AA}$
10	0.004	0.003	19
100	0.042	0.030	17

The analysis of previous SANS measurements of the structure of the adsorbed AOT-D₃₄ with

PMMA latexes assumed that the surfactant was adsorbed in the stabilizer layer.¹¹ This approach has been applied to analyze the data presented here. By using the fit PMMA latex dimensions to constrain the data fitting (ϕ PMMA = 0.02; core radius, $r_c = 340$ Å), the CV-SANS data for AOT-D₃₄ with PMMA latexes has been fit to a core-shell model, where the core contrast is fixed to that of the solvent and the shell thickness and contrast (r_s and ρ_s) were allowed to vary. These calculations are shown in Figure 7a, along with a schematic of the fit structure in Figure 7b and the scattering length density profile in Figure 7c. As is clear from Figure 7, this assumed structure does not agree well with the data.

Figure 7: (a) Calculations of CV-SANS profiles for surfactant contrasts in systems of AOT and PMMA latexes in dodecane. These curves are calculations of a core-shell spherical form factor, constrained to the particle dimensions as described in the text. The core contrast (ρ_c) is fixed to that of the solvent to impose shell-only scattering, and the best-fit shell thickness is 17 Å. It is clear that this model does not accurately describe the measured data. (b) Schematic of data fitting. (c) SLD profile of data fitting.

The regions at low- Q arising from Porod scattering from the particle do not align, and the

interference peak arising from the thin layer of adsorbed AOT-D₃₄ (shell radius, $r_s = 17 \text{ \AA}$) is not observed in the data. In the previous analysis,¹¹ r_s was fixed at $17 \text{ \AA}$ (the thickness of an AOT monomer). If this is applied to the new data presented here, the fit Porod scattering agrees better to the experimental data, but the fit value of r_c decreases to $240 \text{ \AA}$, an unrealistic value given the determined size of the particles. Also, the interference peak arising from a shell layer of surfactant remains.

Another possibility is that the surfactant molecules adsorb onto the PMMA latex as localized inverse micelles rather than forming a halo of surfactant. While the free volume between stabilizer chains would suggest that such an arrangement is not possible, such a form factor has recently been used to describe CV-SANS data measured for the adsorption of nonionic surfactant micelles on silica nanoparticles in water.⁴⁴ The scattering from AOT-D₃₄ with PMMA latexes in PMMA-matched solvent has been fit using a “raspberry” model, which is appropriate for Pickering emulsions or nanocomposite raspberry particles.⁴⁵ As in Figure 7, the core dimensions were fixed, and parameters describing the inverse micelles were allowed to vary (r ; ϕ ; and χ , the fraction of interfacial area covered). The size and volume fraction of inverse micelles is similar to that when only the high- Q scattering is fit to a spherical form factor (Table 2). The best fit value of χ is 0.086 for 10 mM AOT-D₃₄ and is 0.592 for 100 mM AOT-D₃₄. This form factor describes the low- Q region better than the core-shell model in Figure 7, but due to the localized regions of surfactant, there is an interference peak in the mid- Q range which is not found in the experimental data.

Therefore, it is apparent that a raspberry form factor does not accurately describe the data presented here, and a different model must be used. As excess low- Q scattering is observed above the AOT-D₃₄ inverse micelle baseline (Figure 6), there is likely deuterated material within the volume of the PMMA latexes. If the assumption that the surfactant adsorbs onto the particle is relaxed, there is more flexibility in how the particles can be modeled.

A core-shell model was again used,⁴² and the core and shell radii (r_c and r_s) as well as the volume fraction were still fixed to the best-fit values for the particles alone ($r_c = 340 \text{ \AA}$ with $\sigma = 0.19$; $r_s = 100 \text{ \AA}$; $\phi = 0.02$). The only difference between this new approach and that previously

used is that the core and shell scattering length densities (ρ_c and ρ_s) were allowed to vary. This provides the possibility that deuterium-labeled material can be located in the PMMA latex core, rather than stipulating that it be located in the stabilizer shell. This best fit to the data is shown in Figure 8a, along with a schematic of the fit structure in Figure 8b and a scattering length density profile in Figure 8c. The scattering length density difference between core and solvent ($\rho_c - \rho_{solvent}$) is found to be $0.08 \times 10^{-6} \text{ \AA}^{-2}$ for 10 mM AOT and $0.50 \times 10^{-6} \text{ \AA}^{-2}$ for 100 mM AOT.

A small flat background is added to improve the fit at high- Q as displayed on a logarithmic scale. This is necessary due to small differences between the theoretical and experimental curves at higher- Q where the inverse micelle scattering dominates. However, this background is less than 1.5% of the $Q = 0$ scattering intensity.

This relaxation of the assumption that AOT is only located in a halo or shell gives a much improved fit to the data. By using the dimensions of the PMMA latexes obtained from data fitting in non-contrast matched solvents, it is possible to account for the SANS arising from AOT-D₃₄ by only varying the contrast of the core. The core contrast (ρ_c), differs from that of the solvent, and the scattering curve can be described by increased contrast in the particle core. This suggests that AOT-D₃₄ penetrates into the latexes.

Observations

These two sets of CV-SANS measurements (with PHSA/PMMA-*graft*-PMMA and with PMMA latexes) provide a consistent set of observations describing the interaction of AOT-D₃₄ and PMMA latex stabilizers. This is not necessarily a causal relationship; that surfactant does not interact with free stabilizer polymers does not mean that it would not interact with bound stabilizer brushes. The two interpretations are consistent, though, indicating that AOT does strongly associate with the stabilizer PHSA in either free or bound forms.

The CV-SANS measurements performed on PMMA latexes in this study provide additional insight into the possible mechanism for charging of particles in nonpolar solvents. It is clear from the excess scattering present at low- Q in the particle contrast-matched solvent, shown in Figure

(a)

(b)

(c)

Figure 8: (a) Data fitting to CV-SANS profiles for surfactant contrasts for dispersions of AOT and PMMA latexes in dodecane. The best fits are obtained using a core-shell spherical form factor, corresponding to the observed scattering arising from increased contrast in the particle core, which is consistent with the penetration of AOT throughout the PMMA latex. A small flat background is added to improve plotting on a logarithmic scale at high- Q . (b) Schematic of data fitting. (c) SLD profile of data fitting.

6, that surfactant partitions into the particles. Unlike solid nanoparticles, such as carbon black or TiO_2 , PMMA latexes are soft and dynamic with a degree of porosity. Fluorescence energy transfer studies of similar PMMA latexes show that the interior of the colloids are composed of microdomains rather than glassy polymer, which demonstrates the possibility of small molecules, such as AOT, entering the PMMA latexes.^{46–48} From the CV-SANS measurements presented here it seems that the activity of AOT as a charge control additive with PMMA latexes in nonpolar solvents depends on the penetration of the surfactant molecules throughout the particles, rather than as adsorbed species on the surfaces or entrapped in stabilizing layers.

Conclusions

Contrast-variation small-angle neutron scattering (CV-SANS) has been used to study the interaction of AOT surfactant with PMMA latexes and non-surface bonded free polymeric analogues for the stabilizer surface of the latexes. The multi-component structure of these latexes enables analogues of the surfaces to be readily generated. Two analogues of the PHSA brush polymer on the PMMA latex surface were studied: the PHSA polyester itself and the PMMA-*graft*-PHSA stabilizer copolymer, which is introduced into the polymerization to generate the colloids.¹⁸

AOT does not disrupt the structure of PHSA in toluene (where the polymer exists as monomers in a “good” solvent) or of PMMA-*graft*-PHSA in toluene (also monomers in a “good” solvent) or dodecane (where it aggregates into polymer micelles). Additionally, in polymer contrast-matched hydrocarbon solvent, the scattering arising from AOT is consistent with the presence of inverse micelles alone.

The situation is different when CV-SANS measurements are performed on dispersions of AOT and PMMA latexes in contrast-matched solvent. At low- Q , significant excess scattering is observed above the scattering baseline seen for free AOT inverse micelles. Unlike the previous report which treats this layer as an AOT shell in the stabilizer layer around the PMMA core,¹¹ the data in the current study are not consistent with this model. Instead, the excess scattering arising from the

AOT-D₃₄ present in the latex is best described by the penetration of deuterated material throughout the colloids. The greater neutron contrast arising from the higher surfactant concentrations used in this new study improves confidence in the data fitting.

Of the models commonly used to explain the origin of charging of particles in nonpolar solvents, the preferential adsorption of charged species seems most appropriate for PMMA latexes, given the importance of surfactant-particle complexation.^{1,2} Schematically, this is often described as the competition of oppositely charged micelles for the particle surfaces.⁸ For non-polymeric surfaces, such as carbon black or TiO₂, it has also been proposed that inverse hemi-micelles adsorb, rather than complete inverse micelles.^{49,50} This expectation that AOT micelles are the charge-carrying species presumably arises from the many studies showing that there is a measurable conductivity for surfactant solutions of AOT in nonpolar solvents, with inverse micelles as charge carriers.^{1,9,11,51,52} However, the theoretical models describing preferential adsorption only require that ionizable sites are present on the particle surface and, therefore, do not specify the nature or location of the charged species.^{53,54}

Despite AOT penetration into these types of colloids not being previously observed, this result is consistent with ability to charge PMMA latexes stabilized with other brush copolymers. The most common steric stabilizer used to prepare monodisperse PMMA latexes is indeed the PMMA-*graft*-PHSA brush used in the synthesis by Antl *et al.*,¹⁸ but this is not the only polymer that has been used. For example, there are reports with butyl or lauryl methacrylate copolymers⁵⁵ and poly(dimethylsiloxane),³⁷ and these particles can be charged by AOT as well. The ability to use AOT to produce charged particles, therefore, does not seem to depend on the chemical identity of the stabilizer, and the PMMA core is the common constituent between all of these charged particles. Given that AOT is a salt, it appears that it has sufficient affinity for the polar methyl methacrylate groups. There is little difference between the polarities of the PHSA brushes and the aliphatic solvent, which is why PHSA is an effective stabilizer; therefore, it seems unlikely that AOT would show a high affinity for the stabilizer alone. This is supported by the CV-SANS results in this study which show no interaction between the surfactant and any PHSA-containing surface

species. These results shed new insight on the phenomenon of charge stabilization of polymeric colloids in nonpolar solvents and are expected to contribute to design and optimization of charge control additives for these technologically relevant systems.

Supporting Information Available

Additional information about materials characterization and SANS data analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Data sharing statement

Data from this study is commercially confidential and, therefore, cannot be made fully accessible. Some data may be available from the corresponding author subject to agreement about the use of the data.

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