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Published in:
Langmuir

DOI:
10.1021/acs.langmuir.7b02257

Publication date:
2017

Document Version
Peer reviewed version

Citation for published version (APA):
Charging poly(methyl methacrylate) latexes in nonpolar solvents: Effect of particle concentration

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Abstract
The electrophoresis of a well-established model system of charged colloids in nonpolar solvents has been studied as a function of particle volume fraction at constant surfactant concentration. Dispersions of poly(12-hydroxystearic acid)-stabilized poly(methyl methacrylate) (PMMA) latexes in dodecane were prepared with added Aerosol OT surfactant as the charging agent. The electrophoretic mobility ($\mu$) of the PMMA latexes is found to decrease with particle concentration. The particles are charged by a small molecule charging agent (AOT) at finite concentration, and this makes the origin of this decrease in $\mu$ unclear. There are two suggested explanations. The decrease could either be due to the reservoir of available surfactant being exhausted at high particle concentrations or the interactions between the charged particles at high particle number concentrations. Contrast-variation small-angle neutron scattering measurements of PMMA latexes and deuterated AOT-$d_{34}$ surfactant in latex core contrast-matched solvent were used to study the former, and electrokinetic modeling were used to study the latter. As the same amount of AOT-$d_{34}$ is found to be incorporated with the latexes at all volume fractions, the solvodynamic and electrical interactions between particles are determined to be the explanation for the decrease in mobility. These measurements show that, for small latexes, there are interactions between the charged particles at all accessible particle volume fractions and that it is necessary to account for this to accurately determine the electrokinetic $\zeta$ potential.

Introduction

Stabilizing charged species in nonpolar, hydrocarbon solvents is well-known to be a challenging problem; however, charged species have a wide range of uses in many industries.\textsuperscript{1–4} It is difficult to stabilize charged species in nonpolar solvents, such as dodecane, due to the low relative permittivity, or dielectric constant, of the fluid ($\epsilon_r = 2.0120$) compared to that of a polar solvent such as water ($\epsilon_r = 80.100$). (Both $\epsilon_r$ values are at 20°C.\textsuperscript{5}) This can be well understood by considering the Bjerrum length ($\lambda_B$) of the medium (Equation 1), the sepa-
ration between two point charges where the Coulombic interaction is equal to the thermal energy \((k_B T)\), which depends on the elementary charge \((e)\), the vacuum permittivity \((\epsilon_0)\), \(\epsilon_r\), and \(k_B T\).

\[
\lambda_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T}
\]  

(1)

In water, \(\lambda_B\) is \(\sim 1\) nm, which is why ions can be easily stabilized in the solvent. In hydrocarbon solvents, \(\lambda_B\) is \(\sim 30\) nm, which means that dissociation fractions are low for moderately sized ions\(^6\)–\(^{11}\) or that large macroions must be used to attain high dissociation fractions.\(^{12}\)

Poly(methyl methacrylate) (PMMA) latexes with poly(12-hydroxystearic acid) (PHSA) graft copolymer stabilizer layers, developed in collaboration between the University of Bristol and ICI in the 1980s,\(^{13}\) have long been established as a model system for studying interactions in nonpolar solvents. Since it was reported in 2005 that these latexes could be charged by sodium dioctylsulfosuccinate (Aerosol OT or AOT) surfactant,\(^{14}\) these particles have been increasingly used as models for studying the nature of charged colloids in nonpolar solvents.\(^8,\)\(^{10,11,15–25}\) From all the studies in the literature on these particles, the impact of systematically varying many system parameters (such as particle size, surfactant concentration, surfactant polarity, and surfactant counterion) and the impact on the charge of the particle has been studied.\(^{26}\) However, particle volume fraction is one of the variables that can impact the electrophoresis of charged particles that has surprisingly not been reported for PMMA latexes charged by AOT. (There is a recent report in the literature of the impact of adding AOT to dispersions of PMMA latexes in a density and refractive index matched solvent mixture and the impact that it has on the structure of the colloidal crystal structure.\(^{25}\))

This variable has been studied for other methods of charging PHSA-stabilized PMMA, by either the incorporation of a polymerizable ionic monomer\(^{27}\) or by dispersing the particles in an autoionizable solvent.\(^{28}\) The effect of varying volume fraction has been studied for AOT charging of other types of polymer particles,\(^{29,30}\) although only simple analysis of the electrophoresis data was performed. For AOT-charged PMMA latexes, the situation is complex
as the ratio of the particle volume fraction to the surfactant volume fraction will increase as the dispersions are concentrated, at a fixed surfactant concentration. Therefore, it is possible that the reservoir of surfactant could be depleted. However, it is also known from the literature that the electrophoretic mobility will decrease in concentrated dispersions, even at constant $\zeta$ potential.\textsuperscript{31–35} For these charged colloids to be employed in an industrial setting, they will need to be used efficiently by loading the greatest concentration in dispersion as is possible.

In this paper, the functional and structural properties of dispersions of PHSA-stabilized PMMA latexes charged by AOT in dodecane have been studied as a function of particle volume fraction ($\phi$). The charge of the particles was measured using electrophoretic light scattering, specifically phase-analysis light scattering (PALS). The interaction between particles and the distribution of AOT were studied using small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS). SAXS is sensitive to the PMMA core and insensitive to the AOT surfactant, so it can be used to quantify interparticle interactions. SANS, in appropriate solvent contrast, arises only from deuterium-labeled surfactant, and it can be used to determine the distribution of the AOT. These measurements will show how increasing the concentration of latexes impacts both the structure and the electrokinetics. The focus is primarily on very small latexes, which are required for the SAXS and SANS experiments; these particles also tend to have a lower $\zeta$ potential, which has been observed in the literature,\textsuperscript{26} although not fully understood. By considering how the electrophoretic and structural properties vary as a function of particle concentration, it has been possible to determine the origin of any differences. This will impact both fundamental studies of these particles as model charged colloids and industrial applications of them as concentrated dispersions.
Experimental section

Materials

Aerosol OT surfactant

Commercial sodium dioctylsulfosuccinate (Aerosol OT or AOT) was obtained from Aldrich (98%) and was purified using dry diethyl ether before use. The synthesis and analysis of deuterium labeled AOT-$d_{34}$ has previously been reported.\textsuperscript{23}

PMMA latexes

Three dispersions of PHSA-stabilized PMMA latexes were studied. They were prepared by a classic dispersion polymerization process using the method described by Antl \textit{et al.}\textsuperscript{13} The synthesis of the small (76 nm diameter) and large (666 nm diameter) is provided elsewhere.\textsuperscript{36} The other latexes (412 nm diameter) were a gift from Merck Chemicals Ltd. The $Z$-average solvodynamic diameters ($d_Z$) and polydispersity indexes (PdIs) of the latexes were measured using a Malvern ZetaSizer Nano S90: GS1 ($d_Z = 76.1 \pm 0.5$ nm, PdI= 0.11), MC1 ($d_Z = 412 \pm 5$ nm, PdI= 0.07), and SF1 ($d_Z = 666 \pm 24$ nm, PdI= 0.13).

Volume fractions were determined by drying suspensions to determine the mass of dry particles in suspension. The mass densities ($\rho_m$) of dodecane ($\rho_m = 0.75$ g cm$^{-3}$)\textsuperscript{37} and the PMMA latexes ($\rho_m = 1.09$ g cm$^{-3}$)\textsuperscript{38} were used to convert the masses to densities to work out the volume fraction; this is the approach used by Pusey and van Meegan in their early papers on the phase behavior of PMMA latexes.\textsuperscript{39,40} The mass density of the latexes is a function of their size, as the PHSA stabilizer makes up a different fraction of the total volume. The core density of the latex is effectively independent of the particle size, although less than the density of PMMA homopolymer,\textsuperscript{36} and the density of the PHSA stabilizer is known from the literature.\textsuperscript{38} To distinguish the volume fraction determined using this method from the hard sphere volume fraction determined from small-angle scattering measurements, when used, it is referred to as $\phi_m$. 
Methods

Phase-analysis light scattering (PALS)

Electrophoretic mobilities ($\mu$) were measured using a Malvern Zetasizer Nano Z or ZS with a universal dip cell electrode. This cell consists of two parallel plate palladium electrodes separated by 2 mm, which enables high field strengths to obtained using low voltages. The applied field strength used was either $1.0 \times 10^4$ V m$^{-1}$ or $2.0 \times 10^4$ V m$^{-1}$, depending on the electrophoretic mobility of the sample being measured. The lowest field strength possible was used to avoid any effect of field dependent mobility. Six runs of at least 50 measurements were performed, and the average of these runs was used.

Phase-analysis light scattering (PALS) is a variant of Laser Doppler Velocimetry (LDV) that provides enhanced sensitivity compared to traditional measurements (down to $\mu = 1 \times 10^{-12}$ m$^2$ V$^{-1}$ s$^{-1}$). Rather than comparing the Doppler shift of the frequency of light as in LDV, the phase difference between the beam scattered from the electrophoretic particle and a reference beam is compared. The gradient of the phase difference as a function of time is related to the electrophoretic velocity ($\vec{v}$). The electrophoretic mobility is the constant of proportionality between $\vec{v}$ and the electric field strength ($\vec{E}$).

$$\vec{v} = \mu \cdot \vec{E}$$  \hspace{1cm} (2)

Small-angle neutron scattering (SANS)

Neutron scattering measurements were performed at the ISIS Pulsed Neutron Source. On Sans2d, a simultaneous $Q$-range of 0.003–0.43 Å$^{-1}$ was achieved using an instrument set up with the source-sample and sample-detector distances of $L_1=L_2=8$ m and the 1 m$^2$ detector offset vertically 60 mm and sideways $-290$ mm. The beam diameter was 8 mm. Raw scattering data sets were corrected for the detector efficiency, sample transmission and background scattering and converted to scattering cross-sections 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). Data have been fit to models as described in the text using the SasView small-angle scattering software package.

**Small-angle X-ray scattering (SAXS)**

SAXS measurements were performed using the instrument I22 at Diamond Light Source. Samples were measured in 1 mm capillaries, and data were recorded on a PILATUS 2M detector. The sample-detector distance was 9.4 m, and two X-ray wavelengths were used (1.77 Å, 7 keV, $Q = 0.001-0.11$ Å$^{-1}$ and 0.73 Å, 17 keV, $Q = 0.003-0.27$ Å$^{-1}$). Raw scattering data sets were radially integrated using YAX 2.0, a macro script for ImageJ, and the data were rebinned logarithmically using the Irena package for Igor Pro. Data have been fit to models as described in the text using the SasView small-angle scattering software package with data weighted by $|\sqrt{I(Q)}|$. Experimentally determined structure factors ($S(Q)$) were determined by, first, dividing all scattering curves by their scale factor. Then the scattering from concentrated dispersions was divided by the scattering from the dilute dispersion without AOT, and the curve normalized to 1 at high-$Q$.

**Results and Discussion**

The effect of varying particle concentration on the charge of particles will be considered in several steps. The concentration of surfactant will be kept constant to reduce the number of variables. This should fix both the total amount of charging agent to interact with the particles and the concentration of background inverse micellar electrolyte. Electrokinetic measurements will be discussed first to demonstrate how the electrophoretic mobility ($\mu$) varies with the latex volume fraction ($\phi$) for small (< 100 nm diameter) latexes. Two possible origins for these differences will then be explored: surfactant partitioning or charged particle...
interactions. Surfactant partitioning will be quantified using contrast-variation small-angle neutron scattering (CV-SANS) and small-angle X-ray scattering (SAXS), and solvodynamic and electrical interactions between particles will be quantified by modeling the electrokinetic data. By establishing the origin of the effect of varying the volume fraction on the electrophoretic mobility of small particles, it will be possible to consider these results in conjunction with electrokinetic measurements on larger particles to elucidate the effect that changing particle size has on the particle charge and $\zeta$ potential.

The electrophoretic mobilities ($\mu$) of small PMMA (DLS $d_z = 76$ nm) latex dispersions were determined as a function of volume fraction ($4 \times 10^{-4} \lesssim \phi \lesssim 2 \times 10^{-1}$) at a constant surfactant concentration (100 mM AOT). These dispersions were chosen because the amount of scattered light from the small latexes enabled measurements to be performed up to high volume fractions and because, as can be seen in Figure 1, the magnitude of the electrophoretic mobility varies dramatically across the range of particle concentrations studied. The values of $\mu$ were measured using phase-analysis light scattering (PALS) measurements. PALS is a form of Laser Doppler Velocimetry, enabling the electrophoretic velocity to be determined from a change in the light scattered from an electrophoretic particle compared to a reference beam. In a PALS experiment, the change in the phase of the scattered light is used.\textsuperscript{41–43} The reduced mobility ($\mu/\mu_0$, where $\mu_0 = e/(6\pi\eta\lambda_B)$ and $\lambda_B$ is the Bjerrum length, shown in Equation 1) is shown rather than the experimental mobility, to account for the viscosity of the AOT solution being greater than the pure solvent. The relative viscosities for the solutions ($\eta_r$) have been calculated using the Einstein relationship ($\eta_r = 1 + 2.5 \cdot \phi$),\textsuperscript{52,53} which has been shown to be appropriate for AOT solutions in dodecane.\textsuperscript{54}

For this system, the particle charge is indeed impacted by the addition of AOT surfactant. As these latexes are charged by an added small molecule charging agent, the decrease in mobility could be chemical or physical in origin. The possibility that this could arise from chemical interactions, namely the AOT reservoir being depleted by the large number of particles at large $\phi$, will be explored first using small-angle scattering.
Figure 1: Reduced electrophoretic mobilities ($\mu/\mu_0$) of 76 nm PMMA latexes as a function of volume fraction ($\phi_m$) at a constant AOT concentration of 100 mM. The magnitude of $\mu/\mu_0$ increases as the concentration of latexes decreases.

Interaction between latexes and AOT

As the particles are charged by interactions with an external species (AOT surfactant), the amount of surfactant incorporated into the particles will be at equilibrium. At fixed $\phi$, the partitioning of AOT has recently been studied as a function of solution concentration.\textsuperscript{10} The amount of surfactant absorption was found to vary as the solution concentration was changed, but the equilibrium constant of surfactant absorption was found to be constant.\textsuperscript{10} In this study, the concentration of AOT is fixed while $\phi$ is varied. From previous studies in the literature, it is not possible to determine whether the amount of surfactant will be constant in each sample or not. This has been studied, using SANS and SAXS, for the small PMMA latexes used for the electrophoresis measurements in Figure 1. These latexes are used because they have previously been shown to be amenable to analysis by small-angle scattering techniques.\textsuperscript{10}
Dispersions without AOT

SAXS measurements were performed on the 76 nm latexes with no added surfactant and with 100 mM AOT added. As X-rays are sensitive to differences in electron density, the technique is sensitive only to the PMMA core of the latexes. (The PHSA stabilizer and AOT surfactant have essentially the same electron density as the dodecane solvent.) It is important to consider core-sensitive scattering as this enables a comparison of form factors \((P(Q))\) and structure factors \((S(Q))\) for latexes at different \(\phi\).

Figure 2 shows SAXS curves of 76 nm latexes at different volume fractions fit to a core-shell sphere form factor with a hard sphere structure factor.\(^{55–58}\) Scattering from a core-shell (or concentric) sphere is defined in Equation 3. It is not possible to write a contrast-independent \(P(Q)\) for this geometry as scattering arises from the interaction between multiple components. The scattered intensity \((I(Q))\) depends on \(\phi\), the properties of the core of a sphere with radius \(r_c\) (volume \(V_c\) and scattering length density \(\rho_c\)), and the properties of the shell of the sphere with thickness \(t\) (scattering length density \(\rho_t\)). The radius of the entire sphere (shell plus core) is \(r_t\), and the volume of this sphere is \(V_t\). The scattering length density of the solvent medium is \(\rho_m\). \(j_1\) is the first order Bessel function \((j_1(x) = (\sin x - x \cos x)/x)\).

\[
I(Q) = \frac{\phi}{V_t} \left[ (\rho_t - \rho_m) \left\{ \frac{3V_t j_1(Qr_t)}{Qr_t} - \frac{3V_c j_1(Qr_c)}{Qr_c} \right\} + (\rho_c - \rho_m) \left( \frac{3V_c j_1(Qr_c)}{Qr_c} \right) \right]^2 \tag{3}
\]

The SAXS data on PMMA latexes without AOT are fit simultaneously to determine the global best \(r_c\) and \(t\). The scale factor and the volume fraction are allowed to vary independently. The width of the distribution in the particle radii \((\sigma_{Sch})\) are accounted for using the Schulz distribution.\(^{59}\) For SAXS measurements, where the stabilizer layer does not contribute to the scattering, the scattering function for core-shell spheres (Equation 3) reduces to that for simple spheres (Equation 4) in the dilute limit, with radius \(r_s\), volume \(V_s\), and
scattering length density $\rho_s$.\textsuperscript{60,61}

$$I(Q) = \frac{\phi}{V_s} \left[ \frac{3(\rho_s - \rho_m)V_s j_1(Qr_s)}{Qr_s} \right]^2$$  \hspace{1cm} (4)

It is important to use the scattering function of the core-shell spheres (Equation 3) to account for the thickness of the stabilizer layer when calculating the interaction lengthscale for the calculation of $S(Q)$. The details of the Percus–Yevick closure for hard spheres can be found in the literature.\textsuperscript{58} The interparticle potential ($U(h)$) for the hard sphere $S(Q)$ is defined in Equation 5 for center-center separation $h$ and radius $r$.

$$U(h) = \begin{cases} \infty & h < 2r \\ 0 & h \geq 2r \end{cases}$$  \hspace{1cm} (5)

Although there is no contrast between the solvent and the stabilizer, the core-shell model is required to describe the scattering for concentrated dispersions. The form factor is equivalent to that of a sphere, but the radius of closest approach for the structure factor for a sterically stabilized particle is given by $r_t$ rather than $r_c$.

This model described above gives a very good fit to the data. As a simultaneous fit was performed, the core radius ($r_c = 292$ Å), the shell thickness ($t = 32$ Å), and the width of the size distribution of the radius ($\sigma_{Sch} = 0.10$) are all equal. The shell thickness is less than previously reported in the literature.\textsuperscript{55,62} However, fitting data for a concentrated dispersion with a defined hard sphere interaction radius gives confidence in these fit values. The total diameter (65 nm) compares favorably to the $Z$-averaged diameter from DLS (76 nm). The fit volume fraction ($\phi_{fit}$) for the most concentrated dispersion ($\phi_{fit} = 0.21$) is greater than calculated using the solid state densities ($\phi_m = 0.16$). This is most pronounced in the most concentrated dispersion, and the fit of the experimentally determined structure factor by a hard sphere $S(Q)$ model is shown in Figure 2b. While unexpected, this is perhaps not surprising. Determining the volume fraction of these latexes is known to be a challenging
Volume fractions calculated using the solid state density do not include the contribution of the solvent in the stabilizer layer to the total volume of the latex. The ratio of the volume of a latex with a solvated shell to one with an unsolvated shell is found to be the same as the ratio of the SAXS determined volume fraction to that of the solid state density determined volume fraction (\(\sim 1.3\)), which explains this apparent discrepancy. This increases the apparent volume fraction (\(\phi_{\text{app}}\)), which is the value that will be used for the remaining data presented. Using the dimensions from these SAXS measurements, it is possible to fix the dimensions used for fitting scattering curves when surfactant is added.

Before considering contrast-variation SANS (CV-SANS) measurements with added AOT-\(d_{34}\), it is important to determine if there is any residual scattering in latex contrast-matched solvent. The scattering length density (SLD, \(\rho_n\)) of the latexes has been previously reported (\(\rho_n = 1.1 \times 10^{-6} \text{ Å}^{-2}\)).\(^{10,36}\) SANS has been measured for dispersions of 76 nm PMMA latexes in latex contrast-matched solvent (shown in Supporting Information) at the same concentrations used to study the absorption of AOT. A non-negligible amount of scattering is observed, particularly for the most concentrated dispersion. This residual scattering, however, does not come from a mismatch between the solvent and the particle. The data can be very well fit assuming the scattering arises from the small amount of contrast between the PHSA stabilizer shells with the PMMA cores and the solvent.\(^{36}\) The SLD of the latexes (measured at a volume fraction of 0.02) corresponds to the SLD of the PMMA core, which dominates at low \(\phi\), but at high \(\phi\), the contribution from the shell needs to be considered as well. The data have been fit to the same model as the SAXS data discussed previously, with dimensions fixed to the same as the SAXS fits and SLDs as determined from composition. The only parameters that were allowed to vary were \(\rho_t\) and a constant background. \(\rho_n\) of a multicomponent material is given
Equations:

\[ \phi_m = 0.16 \ (c=10^2) \]
\[ \phi_m = 0.051 \ (c=10^1) \]
\[ \phi_m = 0.025 \ (c=10^0) \]

Figure 2: SAXS of 76 nm latexes in dodecane without AOT as a function of volume fraction \( \phi_m \) (2a) and the structure factor \( S(Q) \) of the most concentrated dispersion (2b). The data are fit simultaneously with a core-shell sphere form factor and a hard-sphere structure factor to determine the core radius \( r_c \), the shell thickness \( t \), and the volume fraction of the dispersed particles \( \phi_{app} \). The data can be well fit using this model, demonstrating that these latexes interact essentially as hard spheres in the \( Q \)-range studied.
as a volume fraction ($\phi_i$) weighted sum of the SLDs of each component ($\rho_i$).

$$\rho_n = \sum_i \rho_i \phi_i$$  

(6)

This equation can be used to determine the fraction of the shell that is polymer and that is solvent. The average volume fraction of the shell occupied by solvent is 0.84, which compares favorably to recent literature.\textsuperscript{36,62}

**Dispersions with AOT**

The scattering data of PMMA latexes in solutions of 100 mM AOT are are fit as a linear summation of two species: spherical AOT inverse micelles\textsuperscript{60,61} and hard core-shell spheres.\textsuperscript{55–57} This model does not account for the cross term that is observed in systems of binary spheres,\textsuperscript{64,65} but it is preferred as a binary sphere model would neglect the contribution from the PHSA shell. This assumption does not significantly modify the scattering curves, however (shown in Supporting Information). The SAXS data are insensitive the presence of AOT inverse micelles, the PMMA core dominates the scattering curves, whereas the CV-SANS data is sensitive to both species, in core contrast-matched solvent, as shown in Figure 3.

Unlike the scattering for PMMA alone, which can be well fit with a hard sphere $S(Q)$ (Equation 5 and Figure 2), the presence of AOT will modify the interparticle interactions to that of charged spheres. The scattering data has been fit using the Hayter–Penfold charged sphere $S(Q)$,\textsuperscript{66,67} which calculates the structure factor through a Fourier transform of the pair correlation function $g(r)$ for a system of charged, spheroidal objects in a dielectric medium, given the charge of the particle ($Z$) temperature ($25^\circ$C), $\epsilon_r$, and the background concentration of ions ($4.61 \times 10^{-5}$ mM, from the aggregation number and dissociation constant of AOT\textsuperscript{10}). A simultaneous fit was performed on the SAXS data (Figure 3a where the dimensions of the particle were fixed, and the scale, $\phi$, and number of charges allowed to vary. From this
simultaneous fit, a global best fit $Z$ of $2e$ is obtained. This charge number is only a guide, as it is not necessarily constant with varying $\phi$ as will be discussed later, and the $Q$-range of the scattering data is insufficient to resolve a charged sphere structure factor well. Figure 3a shows that a hard sphere and a charged sphere $S(Q)$ describe the data essentially the same.

For the CV-SANS data, at high-$Q$, the scattering from AOT-$d_{34}$ inverse micelles dominates, and the curves at different latex volume fractions overlap, as the same concentration of surfactant was added. At low-$Q$ scattering from AOT-$d_{34}$ absorbed in the PMMA latexes dominates. (The difference between adsorption and absorption of AOT surfactant has previously been discussed.) The AOT-in-latex scattering is fit using a core-shell form factor, as was done for the latexes themselves. In this case, however, the scattering is dominated by the isotopically-labeled surfactant rather than the latex. The best fit values of the difference in scattering length density with the solvent ($\Delta \rho_n^{\text{core}}$ and $\Delta \rho_n^{\text{shell}}$ are shown in Table 1.) There are contributions to the scattering from both the core and the shell. However, it is important to stress that the surfactant appears to be distributed throughout both regions of the latex, and the data cannot be fit if the surfactant is localized in any region of the particle. This differs from previous fits in the literature, where the surfactant was fit either as located entirely in the shell, in the core, or in a homogeneous sphere larger than the core. This proposal is an extension of the latter two, in particular the final one, which considered the surfactant occupying a volume larger than the core. The refinement is that the surfactant is considered to occupy a different fraction of the core and shell of the latexes but is located throughout the entire volume.

What is clear from the scattering data in Figure 3b is that the intensity of the contribution from the AOT-$d_{34}$ absorbed in the latexes increases proportionally with the volume fraction of latexes. From a qualitative analysis of the data alone, it is not possible to tell whether this is due to a larger amount of surfactant being absorbed in the latexes or the same amount of surfactant being absorbed in a larger concentration of latexes. The magnitudes of $\Delta \rho_n$ in each region of the latexes varies as a function of volume fraction,
Figure 3: Small-angle scattering, both SAXS (3a) and CV-SANS (3b), of dispersions of 76 nm PMMA latexes in solutions of 100 mM AOT (SAXS) or AOT-$d_{34}$ (CV-SANS) as a function of volume fraction ($\phi_{\text{app}}$). The SAXS measurements are sensitive to scattering from the PMMA core. Fits to the data show that the particles can be modeled successfully with a hard sphere $S(Q)$, although fits with a Hayter–Penfold $S(Q)$ for charged spheres are also shown. The CV-SANS measurements are performed in core contrast-matched dodecane and, thus, are sensitive only to the AOT-$d_{34}$ surfactant. Fits to the data show that the scattering can be modeled well as a linear sum of constant concentration of inverse micelles (at high-$Q$) and surfactant absorbed in core-shell latexes (at low-$Q$).
Table 1: CV-SANS data fitting parameters for AOT-\(d_{34}\) and PMMA latexes.

<table>
<thead>
<tr>
<th>Volume fraction</th>
<th>(\phi_{\text{app}})</th>
<th>(\Delta \rho_n^{\text{core}} / (10^{-6} \text{ Å}^{-2}))</th>
<th>(\Delta \rho_n^{\text{shell}} / (10^{-6} \text{ Å}^{-2}))</th>
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<td>0.03</td>
<td>1.36</td>
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<td>0.025</td>
<td>0.14</td>
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<td>0.25</td>
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<table>
<thead>
<tr>
<th>Volume fraction</th>
<th>(\phi_{\text{app}})</th>
<th>(\phi_{\text{AOT-}d}^{\text{core}})</th>
<th>(\phi_{\text{AOT-}d}^{\text{shell}})</th>
<th>(\phi_{\text{AOT-}d}^{\text{total}})</th>
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</table>

and therefore, the fraction of each that is occupied by surfactant needs to be calculated to determine the fraction of the entire latex that is occupied by surfactant. This can be done using Equation 6.

The core consists of PMMA and absorbed AOT-\(d_{34}\), and the fraction of surfactant \(\phi_{\text{AOT-}d}\) can be calculated from the known SLDs of the two \((\rho_{\text{PMMA}}\) and \(\rho_{\text{AOT-}d}\), respectively).

\[
\phi_{\text{AOT-}d} = \frac{\rho_n - \rho_{\text{PMMA}}}{\rho_{\text{AOT-}d} - \rho_{\text{PMMA}}} \tag{7}
\]

For the shell, this is calculation is more complicated because it is a ternary mixture and because the fraction of the shell occupied by PHSA \(\phi_{\text{PHSA}}\) is assumed to be constant. The surfactant displaces solvent, not PHSA. In this calculation, \(\phi_{\text{AOT-}d}\) is the fraction of the non-PHSA volume occupied by surfactant \((1 - \phi_{\text{PHSA}})\) rather than the total volume.

\[
\phi_{\text{AOT-}d} = \frac{\rho_n - \phi_{\text{PHSA}}\rho_{\text{PHSA}} - \rho_m + \phi_{\text{PHSA}}\rho_m}{\rho_{\text{AOT-}d} - \phi_{\text{PHSA}}\rho_{\text{AOT-}d} - \rho_m + \phi_{\text{PHSA}}\rho_{\text{PHSA}}} \tag{8}
\]

The amount of surfactant incorporated with the latexes, therefore, appears to be constant as the volume fraction is varied. Using the SANS data, it is possible to work out the degree of partitioning between the two parts of the system: inverse micelles and absorbed surfactant.\textsuperscript{10}
By comparing the volume fraction of inverse micelles ($\phi_{IM}$), equal to the scale factor from fitting, and the volume fraction of surfactant bound in the latex ($\phi_b = \phi_{total}^{AOT-d} \cdot \phi_{app}$), it is possible to determine the fraction of surfactant that partitioned between the two. Using the best fit values from SANS on the AOT-$d_{34}$ absorbed in the latexes and a value of $\phi_{IM} \approx 0.02$ (fit values were essentially the same as can be seen in Figure 3b), the amount of surfactant absorbed in the latexes ranges from 2% for the most dilute dispersion to 40% for the most concentrated dispersion. A non-trivial amount of the total AOT is, therefore, partitioning from the inverse micelles to the latexes. Higher concentrations of surfactant would have to be added to saturate the latexes, if it is even possible to reach this limit. A chemical origin for the mobility reduction, therefore, seems unlikely. The possibility that this could arise from physical interactions, namely the solvodynamic and electrical interactions between particles at large number concentrations ($n_i$), will be explored next using electrokinetic modeling.

**Electrokinetics**

If the amount of AOT that is absorbed by the particles is volume fraction independent, then another explanation of the origin of the reduction in electrophoretic mobility must be sought. As was stated earlier, it is known in the literature that the electrophoretic mobility can decrease for otherwise identically charged particles as the dispersions are concentrated due to electrostatic or solvodynamic interactions between particles.$^{31-35}$

Consideration of the finite volume fraction of dispersed solids can be introduced in the electrokinetic theory by means of cell models.$^{68,69}$ In these, the interactions (both electrical and solvodynamic) between particles are taken into account by solving the problem for a single particle (radius $a$) enclosed in a concentric sphere of solution, of radius $b$. This is chosen so as to ensure that the volume fraction $\phi$ in the cell and in the suspension are identical ($\phi = a^3/b^3$), and the interactions between neighbor particles are taken into account by proper selection of boundary conditions on the cell.

Under the action of the electric field, both the charged particle and the ions surrounding
it move while being subjected to gradients of electric potential, pressure, and concentration, and to viscous drag, and a steady state is reached in which the particle moves with the electrophoretic velocity \( v_e \) with respect to the laboratory frame. The electrophoretic mobility \( \mu \) is the constant of proportionality between the velocity and the electric field \( E_0 \) \( (v_e = \mu \cdot E_0) \).

A set of partial differential equations where the unknowns are the distributions of electric potential \( (\Psi(r)) \), fluid velocity \( (\mathbf{v}(r)) \), and ionic concentrations \( (n_j(r)(j = 1, \ldots, N)) \) must be solved. Without going into details, further discussion can be found in previous publications\(^{68,70–72} \) the following starting conditions must be considered.

(a) Navier–Stokes and incompressibility equations for the Newtonian fluid velocity, where \( \eta_m \) is the fluid viscosity and \( P \) is the pressure.

\[
- \nabla P + \eta_m \nabla^2 \mathbf{v} - \sum_{j=1}^{N} e z_j n_j \nabla \Psi = 0 \\
\nabla \cdot \mathbf{v} = 0
\]  
(9)  
(10)

(b) Poisson’s equation.

\[
\nabla^2 \Psi = - \sum_{j=1}^{N} \frac{e z_j n_j}{\epsilon_r \epsilon_0}
\]  
(11)

(c) The ions fulfill the continuity equation at any point of the space, where \( \mathbf{v}_j \) is the velocity of the \( j^{th} \) ionic species, given by convective, diffusive, and electric field contributions.

\[
\nabla \cdot [n_j \mathbf{v}_j] = 0
\]  
(12)

The latter two are represented by the gradient of the electrochemical potential \( (\mu_j) \).

\[
v_j = \mu - \frac{D_j}{k_B T} \nabla \mu_j
\]  
(13)

\[
\mu_j = \mu_j^\infty + e z_j \Psi + k_B T \ln n_j
\]  
(14)
It will be assumed that all quantities can be expressed as the sum of an equilibrium (superscript “0”) and a field-dependent perturbation terms. For low field strengths, as it is the case in the electrophoresis problem considered, the perturbations are linearly dependent on the field.\textsuperscript{73,74}

\[
\Psi(r) = \Psi^0(r) + \delta \Psi(r) = \Psi^0(r) - \Xi(r)E_0 \cos \theta 
\]

\[
\mathbf{v}(r) = \begin{pmatrix} -\frac{2}{r} f(r)E \cos \theta \\ \frac{1}{r} \frac{d}{dr} [rf(r)] E_0 \sin \theta \\ 0 \end{pmatrix} 
\]

\[
\mu_j(r) = \mu_j^0(r) + \delta \mu_j(r) = \mu_j^0 - z_j e \phi_j(r) E_0 \cos \theta 
\]

Here, \( \theta \) is the angle between the position vector and the field, \( r = |r| \), and \( \Xi(r), \phi_j(r), \) and \( f(r) \) are auxiliary functions.

The problem can be solved by setting boundary conditions on the rigid particle surface and the outer boundary of the cell according the following physical constraints.

(d) The equilibrium electric field must satisfy Gauss’s Law, for a given surface charge density \( \sigma \).

\[
-\epsilon_r \epsilon_0 \frac{d\Psi^0}{dr} \bigg|_{r=a} = \sigma 
\]

From this condition, the surface charge on the particle can be fit. Alternatively, the value of electric potential on the particle surface can be used as a boundary condition, setting in this case the zeta potential.

\[
\Psi^0 \bigg|_{r=a} = \zeta 
\]

(e) The cell is electroneutral.

\[
\frac{d\Psi^0}{dr} \bigg|_{r=b} = 0 
\]
Note that this equation does not imply that the potential goes to zero on the cell boundary, so that electric double layer overlap is automatically taken into consideration if it happens to be significant.

(f) Continuity of the potential and displacement perturbations on the particle surface can be written, if $\epsilon_p$ is the relative permittivity of the particles.

\[
\begin{align*}
\delta \Psi(a^-) &= \delta \Psi(a^+) \\
\epsilon_p \frac{\partial \delta \Psi}{\partial r} \bigg|_{a^-} &= \epsilon_r \frac{\partial \delta \Psi}{\partial r} \bigg|_{a^+} \\
\end{align*}
\]

Continuity of the potential and displacement perturbations on the particle surface can be written, if $\epsilon_p$ is the relative permittivity of the particles.

\[
\delta \Psi(a^-) = \delta \Psi(a^+) \\
\epsilon_p \frac{\partial \delta \Psi}{\partial r} \bigg|_{a^-} = \epsilon_r \frac{\partial \delta \Psi}{\partial r} \bigg|_{a^+} \\
\rightarrow \frac{d\Xi}{dr} \bigg|_a - \frac{\epsilon_p}{\epsilon_r \alpha} \Xi(a) = 0 \quad (21)
\]

(g) The fluid cannot slip on the particle surface.

\[
v(r = a) = 0 \rightarrow \begin{cases} 
  f(a) = 0 \\
  \frac{df}{dr} \bigg|_{r=a} = 0 
\end{cases} \quad (22)
\]

(h) The particle is impenetrable to ions.

\[
v_j(r) \cdot \hat{r} \bigg|_{r=a} = 0 \rightarrow \frac{d\phi_j}{dr} \bigg|_{r=a} = 0, j = 1, \ldots, N \quad (23)
\]

(i) The cell volume averages of the gradient of the potential perturbation, the ionic concentration perturbation, and the pressure can then be written as follows.

\[
\begin{align*}
E_0 &= \langle -\nabla \delta \Psi(r) \rangle \\
\langle \nabla \delta n_j(r) \rangle &= 0 \\
\langle \nabla \delta p(r) \rangle &= 0 \\
\Xi(b) &= -b \\
\delta n_j(b) &= 0 \rightarrow \phi_j(b) = b \\
\frac{d}{dr} [r L(f)] \bigg|_{r=b} &= \frac{\sum_{i=1}^{N} z_i e_i n_i(b)}{\eta_m} \\
L(\cdot) &= \frac{d^2(\cdot)}{dr^2} + \frac{2}{r} \frac{d(\cdot)}{dr} - \frac{2(\cdot)}{r^2} \quad (24)
\end{align*}
\]

(j) A final condition is equivalent to Kuwabara’s condition that the radial velocity of the fluid on the cell coincides (except for a change of sign) with the component of the
electrophoretic velocity in the same direction.

\[
v_r(b) = -\mu E_0 \cos \theta
\]

or

\[
\langle v(r) = 0 \rangle \rightarrow \mu = \frac{2f(b)}{b}
\]  

(26)

This set of equations is completed with that for the force balance on the cell. A Matlab routine was written for solving the described differential equations and boundary conditions. The inputs are the particle radius, the volume fraction of latexes, and the ionic concentrations, valencies and diffusion coefficients, and the output is the zeta potential or electrokinetic surface charge density.

By performing this routine for all experimental data points, the electrophoretic mobility was calculated at each value of \( \phi \) measured with a varying \( \zeta \) potential until the calculations best matched the entire set of data. As can be seen in Figure 4, using a constant, \( \phi \)-independent \( \zeta \) potential of \(-65\) mV gives a good match to the experimental data.

![Figure 4: Reduced electrophoretic mobilities (\( \mu/\mu_0 \)) of 76 nm latexes as a function of corrected volume fraction (\( \phi_{app} \)). The data were previously shown in Figure 1. The values of \( \mu/\mu_0 \) were calculated assuming a constant \( \zeta \) potential of \(-65\) mV.](image)

This provides an explanation for the reduction in electrophoretic mobility shown in Figure
1. There is sufficient surfactant to charge the particles, up to a volume fraction of $\sim 20\%$ at least. When the content of suspended particles is high enough (beyond a volume fraction of $\sim 2\%$) interactions between particles must be taken into account for the correct interpretation of the experimental data of electrophoretic mobility. In the model used in this work, the interactions between particles and the possibility of double layer overlapping are considered by means of the proper choice of boundary conditions in the cell model as above described. Other works$^{75,76}$ allow to qualitatively understand the dependence between mobility and volume fraction, showing that there are two main reasons for the electrophoretic mobility reduction. The first and stronger one is the solvodynamic perturbation induced by the motion of neighbor particles on a given one, consisting of a back flow of the surrounding fluid and subsequent hindering of its movement. The second interaction is of electrical origin: the polarized double layers of the particles in the vicinity of any of them alter the local electric field acting on the particle. It is the combination of both effects that determines the decrease of the mobility with the increase of volume fraction. The $\zeta$ potential, however, is constant. This analysis shows that, for small particles at least, electrophoresis measurements over a range of volume fractions are required to determine the $\zeta$ potential. If any one of these samples were analyzed with an electrophoresis model that assumes infinite dilution, such as the Henry equation or the O’Brien and White method that are regularly used in studying charged colloids in nonpolar solvents,$^{77\text{-}79}$ the magnitude of the $\zeta$ potential would be underestimated. It is only when accounting for the volume fraction of the particles as well that the the correct $\zeta$ potential can be determined.

**Extension to larger particles**

The magnitude of the $\zeta$ potential for these 76 nm latexes is lower than has been found for AOT-charged PMMA latexes with a larger size, an observation that has been reported by a meta-analysis of the literature before.$^{26}$ Having performed these electrophoresis measurements at a wider range of volume fractions than previously reported in the literature,
and consequently determining the $\zeta$ potential of the small particles with a larger amount of accuracy, it is worth considering if this can provide insight into this observation. PALS measurements were performed on larger latexes as a function of volume fraction (shown in Supporting Information), although due to the greater amount of light scattered by these larger particles, it was only possible to perform measurements on dilute dispersions. At these volume fractions, the electrophoretic mobility is essentially concentration independent, perhaps with a slight decrease in magnitude for the most concentrated dispersions studied. The electrophoresis can be analyzed using the same model as used for the 76 nm latexes, and the volume fraction dependent electrophoretic mobility calculated assuming a constant $\zeta$ potential. As for the smaller latexes, the magnitude of the electrophoretic mobility decreases at higher volume fractions, although this is shifted to higher $\phi$ when the particles are larger. The magnitude of the $\zeta$ potential is also found to be greater ($-95$ mV for both). This agrees with an analysis of the literature,$^2$ although the difference in this study is lessened by accounting for the volume fraction.

These PMMA latexes have generally been considered to have a size-independent $\zeta$ potential, and a report in the literature studying a series of latexes using a single technique came to that conclusion.$^8$ These data suggest that this is not entirely the case but that very small latexes must be studied to see any difference. Large latexes do have a constant potential, but small latexes have a lower potential. What could the origin of this be?

There are models in the literature that report size dependent electrostatic properties for charged particles. Strubbe et al. found that surface potential and charge can depend on the size of the particle if the particles are charged by ionization equilibrium of surface sites and the number of surface sites decreases.$^{80}$ From the electrokinetic model used to analyze the electrophoresis of these latexes, the surface charge density can be determined as well as the $\zeta$ potential. The $\zeta$ potential is a volume fraction independent property, but the surface charge density decreases as $\phi$ increases. Therefore, the surface charge at a very low concentration ($\phi = 10^{-5}$) will be compared; at this concentration, the surface charge density has reached
an asymptote. (The relation between surface charge density and volume fraction is shown in the Supporting Information.) This demonstrates that the charged sphere structure factor used to model the SAXS and CV-SANS data shown in Figure 3 is insensitive to the charge of the latexes in the $Q$-range analyzed, as good fits to the scattering data can be obtained using a constant charge for all the latexes.

The $\zeta$ potential and the total surface charge $Z$ are shown in Figure 5 as a function of size for the three latexes. As was discussed in the previous section, the $\zeta$ potential is lower for the smallest of the latexes, but it is the same for the larger latexes. The surface charge, however, is essentially a linear function of the radius. This is qualitatively the same as the observation of Strubbe et al.$^{80}$ For a near maximum number of surface sites, the charge is an approximately linear function of particle size, and the surface potential is constant for larger particles but decreases for the smallest particles. The similarity between the two studies suggests that the charging of PMMA latexes by AOT surfactant in nonpolar solvents may be governed by the equilibrium of ionization at the surface. The ionization of surfactant adsorbed at the surface appears to give rise to the particle charge, but AOT does not need to entirely be located at the surface of the latexes. In fact, our recent studies, along with this one, show that AOT surfactant appears to be absorbed throughout the whole volume of the latexes.$^{10,23,24}$ However, it is the ionic groups at the surface that dictate the charge of the particle.

**Conclusions**

The electrophoretic mobilities of dispersions of PMMA latexes charged by AOT surfactant have been studied as a function of particle volume fraction, a variable that has not been explored for this system before.$^{26}$ The mobility was found to decrease as the particle volume fraction was increased. Two possible origins for this were considered: the equilibrium partitioning of surfactant between inverse micelles and PMMA latexes and the solvodynamic
Figure 5: The surface charge $Z$ (at $\phi = 10^{-5}$) and the $\zeta$ potential of PMMA latexes of different sizes (diameters given in the legend) at a constant AOT concentration of 100 mM. The charge is an approximately linear function of size, whereas the magnitude of the potential is greater for larger latexes than a small one.
and electrical interactions between charged particles. Small-angle neutron scattering measurements showed that the amount of AOT-$d_{34}$ absorbed into the latexes was essentially independent of the volume fraction, and this was, therefore, not a viable explanation for the observation. In fact, the reduction in mobility is due to the solvodynamic and electrical interactions between particles, a consequence of the fact that small particles have a much greater number concentration than larger particles at the same volume fraction. This is the first study, as far as we are aware, to observe this for AOT-charged PMMA latexes. A reduction in the electrophoretic mobility for concentrated dispersions has previously been seen for ionic monomer charged latexes\textsuperscript{27} and for latexes charged by autoionized solvents.\textsuperscript{28}

This observation is significant for enabling accurate analysis of the electrophoresis of these types of particles. For small latexes, it is challenging to measure electrophoretic mobilities at dilute enough concentrations that the double layers do not interact. Performing measurements at a range of volume fractions and determining what $\zeta$ potential best matches the data, therefore, becomes a preferable way to characterize the electrokinetic data. From the data presented in this study, it appears that dispersions of the same latexes have a constant, volume fraction independent $\zeta$ potential. However, as has been proposed in a recent analysis of the literature on these PMMA latexes,\textsuperscript{26} the potential does seem to vary as a function of particle size, whereas the surface charge is roughly linear. This correlates with theoretical analysis of the origin of the charging of particles being due to surface equilibria,\textsuperscript{80} and this is an explanation that merits further study in the future.

The significance is not only relevant to studies of the fundamental electrokinetics of particles in nonpolar media. For particles used in applications, it is desirable to use concentrated dispersions to make efficient use of materials. Also, for application in electrophoretic displays,\textsuperscript{3,81} for example, concentrated dispersions are desirable to maximize the amount of reflected light. However, concentrating the dispersions has a penalty, as the electrophoretic mobility of the particles is reduced, and particle motion is hindered. Therefore, for either fundamental or applied studies of surfactant-charged particles in nonpolar solvents, the de-
pendence of the particle charge on particle concentration must be appreciated to optimally use them.

Supporting Information

Fitting parameters for SAXS data, scattering curves of excess SANS scattering in contrast-matched solvent, electrokinetics of larger PMMA latexes.

Acknowledgement

GNS acknowledges Merck Chemicals Ltd. UK, an affiliate of Merck KGaA, Darmstadt, Germany, and the UK Engineering and Physical Sciences Research Council (EPSRC) for the provision of a CASE PhD studentship. GNS also acknowledges a Santander research mobility award to fund a visit to Universidad de Granada. Professor P. Bartlett and Dr. S. D. Finlayson are kindly acknowledged for assistance with materials. The authors thank the UK Science and Technology Facilities Council (STFC) for allocation of beamtime at ISIS and Diamond and grants toward consumables and travel. This work benefited from the use of the SasView application, originally developed under NSF Award DMR-0520547. SasView also contains code developed with funding from the EU Horizon 2020 programme under the SINE2020 project Grant No 654000.

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Constant concentration of Aerosol OT surfactant
Increasing volume fraction of latexes
Decreasing electrophoretic mobility

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