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Controlling colloid charge in nonpolar liquids with surfactants

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The formation of ions in nonpolar solvents (with relative permittivity ε_r of approximately 2) is more difficult than in polar liquids; however, these charged species play an important role in many applications, such as electrophoretic displays. The low permittivities (ε_r) of these solvents mean that charges have to be separated by large distances to be stable (approximately 28 nm or 40 times that in water). The inverse micelles formed by surfactants in these solvents provide an environment to stabilize ions and charges. Common surfactants used are sodium dioctylsulfosuccinate (Aerosol OT or AOT), polyisobutylene succinimide, sorbitan oleate, and zirconyl 2-ethyl hexanoate. The behavior of charged inverse micelles has been studied on both the bulk and on the microscopic scale and can be used to determine the motion of the micelles, their structure, and the nature of the electrostatic double layer. Colloidal particles are only weakly charged in the absence of surfactant, but in the presence of surfactants, many types, including polymers, metal oxides, carbon blacks, and pigments, have been observed to become positively or negatively charged. Several mechanisms have been proposed as the origin of surface charge, including acid-base reactions between the colloid and the inverse micelle, preferential adsorption of charged inverse micelles, or dissolution of surface species. While most studies vary only the concentration of surfactant, systematic variation of the particle surface chemistry or the surfactant structure have provided insight into the origin of charging in nonpolar liquids. By carefully varying system parameters and working to understand the interactions between surfactants and colloidal surfaces, further advances will be made leading to better understanding of the origin of charge and to the development of more effective surfactants.

1 Introduction

Charges in aqueous solutions are ubiquitous, both in terms of their uses in applications as well as the energetics of formation. Forming charged species in nonaqueous, specifically nonpolar, solvents is energetically more difficult, but they are important in many applications. The earliest reports of charging in nonpolar liquids were in the 1950s, by van der Minne and Hermanie[1,2] and by Koelmans and Overbeek.[3] Charges in nonpolar liquids are an important concern in the petroleum industry, for both stabilizing components[4,5] and preventing explosions.[6] These charges are important in the understanding of fluid phenomena, such as flow electrification[7,8] and electrorheology.[9,10] They are also useful in applications as diverse as the developing of toner for printers and photocopiers[11] and the measuring the activity of enzymes.[12] In 1993, Morrison comprehensively reviewed the state of knowledge regarding the formation and applications of electrical charges in nonaqueous media.[13] In the intervening years, knowledge of the formation and mechanism behind nonaqueous charging of surfactant solutions and colloid surfaces has improved but still important gaps remain.

In recent years, the electrophoretic displays found in e-Reader devices, which make use of charging in nonpolar solvents, have appeared as an important and rapidly growing application.[14,15] These displays have the appearance of paper but can be refreshed to display different images, providing the benefits of both books and electronic displays. Electrophoretic displays consist of a colloidal suspension of charged pigment particles in a nonaqueous solvent sandwiched between two electrodes. ~~The application of a voltage causes the colloids to migrate in the cell, changing its appearance, as shown in Figure ??.[16]~~ When an electric field is applied, the particles migrate to the oppositely charged electrode, presenting either a white or black pixel, as shown in Figure 1. The electronic display devices currently on the market are very popular, but they only have monochromatic screens and have relatively slow refresh rates. Many approaches have been suggested for the development of future electronic paper technologies, to enable these displays to match the color gamut and popularity of printed paper. For many of these new technologies (vertical or horizontal electrophoretic, electrokinetic, liquid powder, electrowetting, or electrofluidic displays), controlling charge of either the dyed particles or the fluid is essential to the operation of the display.[17]

Charged ions have been generated in nonpolar solvents in several ways. Electrical charge has been observed in nonaqueous solutions with added salt, where the cation and anion are large organic molecules.[18] Fullerenes (both C_{60} and C_{70}) have been used to produced cations and anions through

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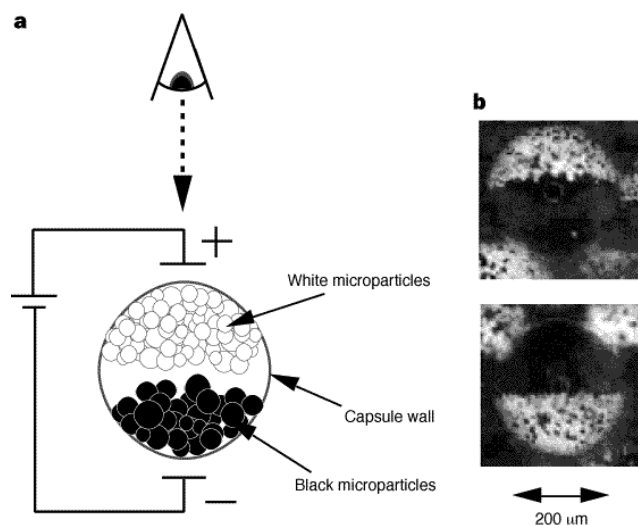
Fig. 1 An electrophoretic microcapsule. The white and black microparticles respond to the application of an electric field, giving either white or black text. The photomicrograph shows the experimental realization of this system. Reprinted with permission from Macmillan Publishers Ltd.: Nature, 1998.[14]

Table 1 Relative permittivity (ε_r) of common solvents at 293.2 K[26]

Solvent	ε_r
hexane	1.887
heptane	1.921
octane	1.948
decane	1.985
dodecane	2.012
cyclohexane	2.024
hexadecane	2.046
1,4-dioxane	2.219
benzene	2.283
toluene	2.379
water	80.100

γ-radiation induced charge transfer.[19] Surface modification of colloids has also been used to form charged species. Examples are gold nanoparticles functionalized by dodecane thiolate[20], TiO$_2$ particles milled with silane[21], and polymer colloids with charging agents added during the synthesis.[22,23] Charges have also been observed on colloidal particles in solutions containing bromocyclohexane due to self-decomposition of the solvent.[24,25] By far though, the most common approach to stabilizing charge in nonpolar solvents has been the addition of surfactant molecules, which is discussed in detail here.

There is nothing energetically prohibiting the formation of charges in nonpolar solvents, though it is a disfavored process. The stability of charges in polar and nonpolar media depends on the magnitude of the relative permittivity (denoted by ε_r). It is far lower in a nonpolar solvent than in water; values for common solvents are shown in Table 1. The inclusion of a charge in a nonpolar medium has a much longer range effect on any other charges present than in an aqueous medium. This is captured by the Bjerrum length (λ_B), which is defined as the distance between two charges where the Coulombic energy is equal to the thermal energy (k_BT).[27] In this expression, e is the elementary charge, and ε_0 is the permittivity of free space.

$$\lambda_B = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r k_BT} \tag{1}$$

As an example, given the values of ε_r and T above, two charged species in water would need to be 0.71 nm (the calculated value of λ_B) apart before the thermal energy would overcome the electrostatic energy at which point the ions would effectively not interact. In dodecane, the distance is 28 nm. Ions in nonpolar media must, therefore, be much larger before they could be stable.

Nonpolar solvents, as defined for this review, are solvents with values of ε_r approximately equal to 2. The polarity of the solvent has an important effect on the charge of the particle surface. In solvents with low values of ε_r, surfactants aggregate in solution and adsorb or interact with particle surfaces, causing them to become charged. In solvents with intermediate polarities ($\varepsilon_r \approx 25$), changing surfactant concentration has little effect on the charge of the particles.[28,29] The same effect has been observed for the aggregation of surfactants in solvents of widely different polarities; there is a region of intermediate "solvent quality" where no significant aggregation occurs.[30]

In this review, the nature of the surfactants in nonpolar solvents and their role in introducing charge into these systems will be considered. Given the tendency for surfactants to aggregate, the formation of inverse micelles and measurements of a critical onset concentration for micellization will be introduced first. It is possible to measure charge on colloids in the absence of surfactants, and while the average charge number is very low, the distribution is important to appreciate before considering the much higher number of charges present in surfactant solutions. The formation of charge, both with and without particles, will follow. After considering the sign and magnitude of charges on various type of particles in surfactant solutions in nonpolar liquids, possible mechanisms for the origin of charge and supporting evidence will be discussed.

Charges in nonpolar liquids are important and useful, as evidenced by the variety of fields in which they are employed. However, the potential for obtaining maximum charge on colloid surfaces and understanding the mechanism by which surfactants charge liquids has not yet been realized. This stems from two main limitations of previous studies. Few types of surfactants have been used to form charge in nonpolar liquids, and of those that have, some are nonionic which do not lead

to a readily understandable mechanism for charging. Also, beyond varying the concentration of surfactant, few previous studies have systematically varied parameters such as the particle surface chemistry or the surfactant structure. Addressing these issues in further research will provide much needed insight into the phenomenon and contribute toward better understanding of the underlying mechanism as well as the development of more effective charge control additives to benefit applications.

2 Aggregation of surfactants

In nonpolar solvents, surfactants have been observed to form aggregate structures. These are often similar to their aqueous counterparts, but given the different polarity of the background medium, the structures are inverted micelles (also called reverse micelles).[31] A schematic of an inverse micelle is shown in Figure ??. Inverse micelles form with the polar head groups associating in the middle and the hydrocarbon chains extending into the nonpolar solvent. In aqueous systems, the aggregation of amphiphilic surfactant molecules into micelles arises from the hydrophobic effect. The preference for aggregation arises not from the chemical similarity of the hydrocarbon tails but, rather, from the dissimilarity of water and the hydrophobic group. Hydrocarbons disrupt the hydrogen bonds of the water without forming any polar bonds, which results in aggregation.[32] The formation of inverse micelles in nonpolar liquids is due to a similar solvophobic effect, although the intermolecular forces between nonpolar molecules are weaker than the hydrogen bonds in water, providing less of a driving force for aggregation. This mechanism for inverse micelle formation can be seen with nonionic surfactants in hydrocarbon solvents, where increasing numbers of oxyethylene groups decreased the solubility of the surfactant.[33]

2.1 Surfactants used as charge control additives.

Few different surfactants have been used as charge control additives in nonpolar solvents in academic studies, although other types have been presented in the patent literature. These surfactants are useful for academic studies as they both form charged species in solutions and charge particle surfaces. Whether this is due to few surfactants being able to stabilize charge or lack of research is not clear. The four surfactants primarily used are shown in Table 2.

Surprisingly, two of these, polyisobutylene succinimide (PIBS)[34–51] and sorbitan oleate (Sorb)[41,48,52–56], are nonionic in nature. It is at first sight difficult to see how neutral additives can act as charge stabilizers. It has been proposed that ionizable impurities are the origin of charge when nonionizable surfactants are used.[54] However, while this offers some explanation of the charging mechanism, it does not account for the chemical nature of the charged species. PIBS, commercially distributed as OLOA, is a polymeric surfactant with a long hydrocarbon tail and a nitrogen-containing headgroup and is supplied dispersed in mineral oil. Although the structure of the commercial surfactant is not exactly known, effort has been made recently to systematically characterize the performance of the surfactant by careful synthesis.[50] Sorb, the other nonionic surfactant, commercially distributed as Span, consists of a five-membered oxygen-containing ring with differing numbers of hydrocarbon chains coming off it. The trioleate (Span 85) is shown in Table 2, but the monooleate (Span 80) has also been studied in this context.

The other two surfactants are anionic, which provides a more straightforward explanation for their ability to form and stabilize charge. Aerosol OT is the most common surfactant used in charging studies and is commonly employed in its sodium form,[41,47,53,54,57–73] though its calcium salt has also been used.[6] Zirconyl fatty acid salts have been used far less frequently, and normally only in one form, zirconyl 2-ethyl hexanoate $(Zr(Oct)_2)$.[47,63,66,74–77]
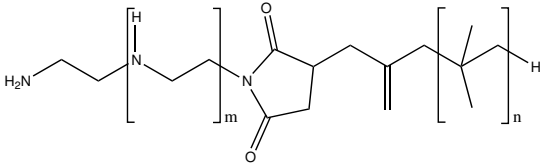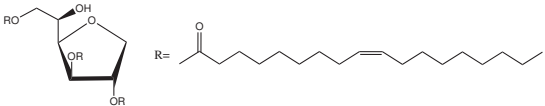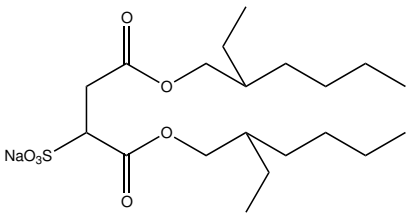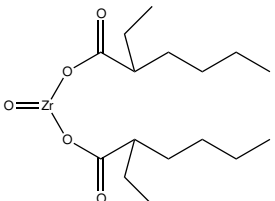
2.2 Inverse micelles.

The presence of even a small amount of impurities or water may provide a nucleus for the formation of inverse micelles. Eicke and Christen found that the critical micelle concentration (CMC) for the formation of inverse micelles of AOT in isooctane depended on the amount of water added.[78] It has been suggested, in a theoretical study making many assumptions, that in the limit of a completely water-free system of AOT in a nonpolar solvent that the surfactant would be insoluble.[79] Other authors have suggested in experimental work that water must be present to form inverse micelles.[44,80] The volume of the polar region in an inverse micelle is very small, and it is reasonable to assume that experimentally it will be impossible to remove any trace of impurity or water. It will be energetically preferable for the polar portion of the surfactant to associate around a nuclear site. Small traces of water, impurity, or added probe molecules mean that experimentally there will be sites which promote the formation of inverse micelles.

Some authors add water or other polar solvents to enable the measurement of properties of inverse micelles; however, as stated above, the presence of water can impact the formation of inverse micelles.[80–84] Although the addition of water does enable the formation of inverse micelles, such samples would be more accurately be described as microemulsions. In this review, systems with a minimal amount of water are considered so that charging will arise from inverse micelles rather than microemulsions.

The nature of inverse micellization is different in nonpolar solvents compared to polar solvents, and this had caused

Table 2 Surfactants discussed in this review

Structure	Type	Name
	Nonionic	Polyisobutylene succinimide (PIBS)
	Nonionic	Sorbitan trioleate (Sorb)
	Anionic	Sodium dioctylsulfosuccinate (Aerosol OT)
	Anionic	Zirconyl 2-ethyl hexanoate (Zr(Oct)$_2$)

several authors to refer to the critical micellization concentration measured as either the "reverse" CMC[80,85–87] or the "operational" CMC.[84,88–92] Several authors have even asserted that while aggregation does occur in nonaqueous solvents that there is no sharp transition from a monomeric to a micellar regime and that there is no CMC in these systems.[93,94] Altogether, this indicates the concept of inverse micellization and the existence of a critical onset concentration is not as well-understood or clear as in polar solvents. Although there is disagreement about whether or not a CMC exists for the formation of inverse micelles, for simplicity, the measured onset concentration for inverse micelles will be called the CMC throughout this review.

The value of the CMC measured depends strongly on the technique employed, a good indication that the measurements are studying different physical properties of the system. For AOT, direct measurements of the structure of surfactant aggregates gives the lowest values of CMC. The aggregation of AOT in nonpolar solvents has been reviewed by De and Maitra.[95] Using small-angle neutron scattering (SANS) results in a measured CMC of 0.225 mM in dodecane,[96] whereas measurements using addition of water results in a value of 5.7 mM in the same solvent.[81] As a comparison, the aqueous CMC of AOT has been calculated using the surface tension (drop volume technique) at different concentrations.

The value of 2.56 ± 0.03 mM is greater than the majority of measurements in nonpolar solvents, which indicates that AOT is likely more soluble as a monomer in water than in nonpolar solvents.[97] In general, the literature values measured in water show greater precision than in nonpolar solvents.

Of the additives used in charging studies, AOT is the most commonly studied surfactant. CMCs have been measured using techniques including solubilization of an optically active probe particle,[83,98–101] light scattering,[72,102] titration calorimetry,[99] interfacial tension with mercury,[103] positron annihilation,[104] NMR,[82] water solubilization,[81] and SANS.[96,105] The CMC of OLOA surfactant has been studied using optical probe particles[100,106,107] and transient current measurements.[45] The onset of micellization appears to occur at a lower, or at least similar, concentration to that of AOT. In water, there have been few studies on the behavior of the surfactant in water, which may be because it was found to be practically insoluble.[108] The CMC of sorbitan monooleate and trioleate have been studied using optical probe particles[109] and interfacial tension with water.[54] The CMC values measured in this two studies are similar, but it is difficult to tell whether this is coincidence or not. The solvents and structure of the surfactant are different, as are the methods employed. The CMC of Zr(Oct)$_2$ has been poorly studied, with reports only on the structure of inverse micelles in nonpolar solvents

using SANS and small-angle X-ray scattering[110] and CMCs reported by measuring the speed of sound in the surfactant solution in a semi-polar solvent.[111]

3 Charged colloids in nonpolar solvents

Before discussing the effects of added surfactants, it is worthwhile considering the charge on bare surfaces in nonpolar solvents with no additives. As expected, given that generating charge in nonpolar solvents is more disfavored than in aqueous ones, the number of charges per colloidal particle is low. Optical tweezers, along with sensitive detection and data analysis, provide a method to detect the small charge numbers present.[63,67,112–114]

Sainis *et al.* developed a method using blinking optical tweezers imaged with a high-speed digital camera.[112] The trajectories of the particles are recorded when the trap is off, enabling the motion of the particle to be studied, but by quickly reforming the trap, the particles are constrained. For PMMA spheres in hexadecane, there were 23 ± 3 charges on the surface to be, though the charge distribution was not studied.[67]

More actively applied forces, rather than just Brownian motion, can also be used to probe optically trapped particles. A technique dubbed single particle optical microelectrophoresis (SPOM) has been used to measure charges on the surface of sterically-stabilized poly(methyl methacrylate) (PMMA) in dodecane. Optical tweezers were used to trap a particle between two electrodes. By applying a periodic field, the particles moved electrophoretically in response to the field, providing a way to extract the number of charges on the surface (the magnitude of the motion of the particle depends on its charge number Z). For stabilized PMMA spheres in dodecane, there is a small, but nonzero, charge on the surface. The mean particle charge is $-2.9e$, but there is a broad, approximately Gaussian distribution of charges, indicating that there are both positive and negative surfaces.[63] It is possible to measure the charge number of a silica particle using a similar method with the application of a square voltage. By assuming that the particles have an elementary mobility (μ_e) originating from electrophoretic motion and that any errors in the mobility are due to Brownian motion, it is possible to assign the magnitude of the charge to the nearest whole number value. There is a broad distribution indicating that there are particles which have both positively and negatively charged surfaces.[113] This technique was extended to enable more accurate measurements of the charge of PMMA in dodecane. The amplitude of the movement of the particle was found to change in discrete steps, and these values, in terms of charge, were near the elementary charge. This enabled the production of a histogram of charge numbers; an example for PMMA in dodecane is shown in Figure 2 which is for one particle taken over 3000 s.[114]

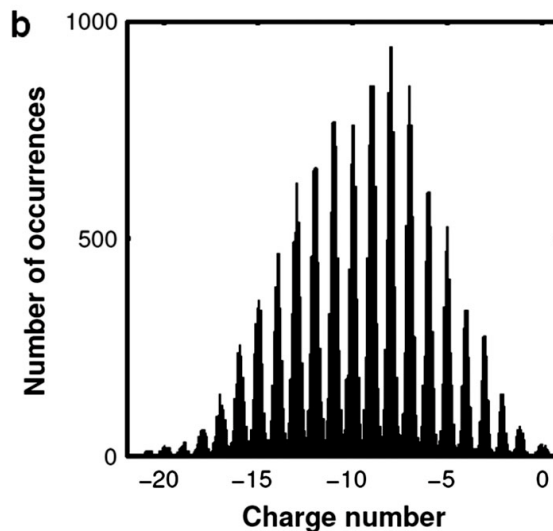In these systems in nonpolar liquids, charge numbers are

Fig. 2 Charge histogram for a PMMA particle in dodecane measured over 3000 s. The charge number is calculated by analyzing the electrophoretic motion of the particle when held in an optical trap. Reprinted with permission Beunis *et al.*.[114] Copyright 2012 by the American Physical Society.

very low and effectively zero. For comparison, the charge number of electrons on silica in pure water is estimated to be 700 ± 150.[115,116] For a silica sphere the same size as analyzed by Strubbe *et al.*[113] in water, there are 10^4 charges on the particle surface. In dodecane, there are ± 10. The number of charged sites on a colloid surface in a nonpolar liquids, therefore, is much lower than in water.

4 Charging with surfactants in nonpolar solvents

Surfactants are important in the stabilization of charge in nonpolar liquids. Section 2.2 discussed the literature regarding whether a CMC exists in nonpolar liquids, but the important consideration in terms of charging is that at sufficiently high concentrations, surfactants assemble in nonpolar liquids. These aggregates are important as the Bjerrum length (λ_B) is long, or equivalently the relative permittivity (ε_r) is low, for all solvents considered in this article. The values for ε_r for solvents discussed in this review are shown in Table 1, and the important similarity is that they are all significantly less than that of water.

The addition of surfactant to a nonpolar liquid can cause an electrical current. The surfactant molecules and aggregates are too small to be viewed directly using optical methods, which means other means must be used to study the system. By measuring transient currents,[117,118] the current remaining in

an electrical cell once a voltage has been modified, as they evolve in time, it is possible to draw conclusions about the nature of charged species and how they form.

4.1 Surfactant micellization studied by current measurements.

Studies of the current in nonpolar liquids can be used to make inferences about the structure and properties of the charge control additive. Transient current measurements offer a way of studying micelles in the environment in which they are employed in applications, such as electrophoretic displays. Although these methods often involve making many assumptions or simplifications, they are still useful for providing an additional way to characterize micelles. The specific conductance (K) of solutions of OLOA 371 in heptane can be used to calculate first the mobility of charge carriers (μ) and then estimate the Stokes radius (a). This involves assuming the carriers are rigid spheres and point charges. The extracted values of a range from 11 to 20 nm, compared to the radius from light scattering with peaks at 15, 160, and 620 nm. The authors propose that this disparity could be due to either the instability of large micelles as charge carriers, resulting in their failure to be noticed in the conductivity measurements, or the breakdown of the assumption that micelles are point charges.[40]

By using the Stokes–Einstein law, it is possible to calculate a conductivity determined radius for OLOA 371 in dodecane of 10 nm, which is independent of concentration. The geometrical structure of the micelles given the diameter is assumed to be either a spherical micelle and a water pool or a prolate spheroid with a radius of 10 nm and no water pool, but it is not possible to distinguish between these extremes. The reality must be somewhere between the two.[35] Similar approaches have obtained a Stokes radius of 6 nm.[49] The concentration of charge carriers is found to be far lower than the concentration of surfactant added. For a solution with 0.5 weight % surfactant (using OLOA surfactant prevents molar measurements), the charge carrier concentration is on the order of 10^{-5} mM.[35,49]

Transient current measurements enable the calculation of micellar properties, although certain assumptions must be made. The shape of the transient current function ($I(t)$) can be used to determine the average number of charged inverse micelles ($\bar{n}_\pm$). A potential difference step of 3 V is applied, which is large enough to separate the charged species. The transient current is integrated from time 0 to time τ, when the current reaches a steady state.

$$\bar{n}_\pm = \frac{1}{eSd} \int_0^\tau I(t)\mathrm{d}t \tag{2}$$

The number of charged micelles is approximately proportional to the surfactant concentration for polyimide coated electrodes

with a concentration dependence that does not depend on d. It is also possible to estimate the electrophoretic mobility of the charged micelles using the initial value of the transient current and find that it is roughly constant for all measurements. The effective radius of the OLOA 1200 micelles is calculated from this mobility using the following expression, which assumes that the viscosity of dodecane (η) is the same as in the absence of surfactant and that the micelles are univalent.

$$R = \frac{e}{6\pi\eta\mu} \tag{3}$$

This results in an effective inverse micelle radius of 7.6 nm, which is on the same order of magnitude, though somewhat smaller, than in other measurements. The authors also provide an estimate for the micellar aggregation number (N_{mic}) of 490 by assuming that the inverse micelles are spherical and have the same density as pure dodecane (ρ_m). It is also possible to calculate the equilibrium constant for micelle disproportionation and the CMC of surfactant molecules (c_{cmc}) by fitting a plot of $\bar{n}_\pm$ against surfactant weight fraction to the following equation. In this expression, m_{mol} is the mass of one surfactant molecule, and c is the concentration.

$$\bar{n}_\pm = \frac{\sqrt{K}}{1 + 2\sqrt{K}} \frac{\rho_m}{m_{mol}N} (c - c_{cmc}) \tag{4}$$

This approach results in a c_{cmc} value of 4.1×10^{-5} (as a weight fraction). By using the results from the more complex situation with an untreated electrode to estimate the CMC by accounting for surfactant first adsorbing onto the electrode surface before dissolving into the solution, the CMC is found to be 3.5×10^{-5}. The values measured using both techniques are similar.[45]

4.2 Structure of the electric double-layer.

An important consideration when studying charged species in the microscopic electrode cells used in electrophoretic displays or near particle surfaces is the nature of the electric double-layer. While the qualitative view of charged ions in solution being influenced by charged surfaces can be applied as in aqueous solutions, the different values for the relative permittivity, and consequently λ_B, along with the reduced number of charge carriers means that the nature of the double-layer is different in nonpolar liquids. Briscoe and Attard have considered the properties of the double-layer in the "counterion-only" limit where there is no ionic background in the solvent. Their model system consists of three parts: an infinitely large planar surface where some surface sites are ionized, a fluid between the plates where the only ionic species present is the same number of counterions, and a thermal reservoir. The number of charges and potential in the double-layer are obtained when the entropy of the system is minimized. As the

separation between the plates increases, the concentration of charge carriers at the mid-point between the two plates is equal to approximately 0.1 mM. This is four to six orders of magnitude greater than the background charge carrier concentration in a nonpolar medium, making the counterion-only approach reasonable. The result of the study is that the double-layer is characteristically different in nonpolar liquids than in aqueous solutions. At large separations, the interaction free energy decays as a power law in nonpolar solutions, whereas it decays exponentially in aqueous solutions. It also is long-ranged and weak, an order of magnitude lower than in water. [119]

Transient current measurements have been employed to extract the length of the electrostatic double layer, although these measurements are difficult both experimentally and theoretically. Two groups have used the same theoretical analysis, based on the Gouy–Chapman approximation, to provide a value of the Debye screening length (κ^{-1}). Kim *et al.* studied a OLOA 371 in dodecane with some carbon black also present in a 190 μm thick planar electrode. The conductivity (measured with a meter) and the value of I_0 (the initial current measured in a transient current measurement) are found to agree reasonably well. By using the measured value of the conductivity (K), the charged species concentration (C) can be calculated to determine κ^{-1} using the following expression, where z is the valency of charged species (± 1 in charged micellar solutions), RT is the thermal energy in terms of the gas constant R, and F is Faraday's constant.

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_r RT}{2z^2 F^2 C}} \qquad (5)$$

The solutions of this equation give values for κ^{-1} of 332, 179, and 120 nm for C of 21.3, 73.2, and 164 μmol m^{-3}. The thickness of the double layer decreases with increasing ionic strength, as expected. [35] However, their fit to the data is not excellent due to their application of the Gouy–Chapman approximation. Given the conditions of their measurement, the charge carriers are separated, and the bulk electric field is not zero. [43] Prieve *et al.* studied the same surfactant (OLOA 371) in heptane in a 1.19 mm thick planar electrode. Using a similar theoretical background, including the use of Equation 5, κ^{-1} can be calculated using the following expression involving both the conductivity K and the decay time constant τ.

$$\kappa^{-1} \approx \frac{\varepsilon_r d}{2\tau K} \qquad (6)$$

In addition to this method using transient current measurements, κ^{-1} can be extracted from total internal reflection microscopy (TIRM) measurements by measuring the double layer repulsion between a microscopic sphere and a flat plate. Values of κ^{-1} from the two methods compare favorably and range between 500 and 40 nm for surfactant concentrations ranging from 0.1 to 10 weight %. [40]

Beunis *et al.* use a different approach to study the thickness of the double layer and present results for the thickness of the Stern layer (λ_s) rather than the Debye length (κ^{-1}). The experimental system consisted of OLOA 1200 in dodecane in a 14.8 μm thick layer. To analyze the experimental results, it is assumed that the electrode spacing is much greater than the thickness of the Stern layer and Debye lengths ($d \gg \kappa^{-1}, \lambda_s$). It is then possible to derive an expression for the current (I) in terms of λ_s and κ^{-1}. In this expression, ΔV is the voltage step before current measurements.

$$I = S\Delta V \frac{\varepsilon_r \varepsilon_0 D}{d(\kappa^{-1})^2} \exp\left(-\left(1 + \frac{\lambda_s}{\kappa^{-1}}\right)\left(\frac{2D}{d\kappa^{-1}}\right)t\right) \qquad (7)$$

It is only for the smallest voltage step measured ($\Delta V = 0.02$V) that the theory holds; larger voltage steps demonstrate nonlinear behavior. The exponential decay of the transient current was fit to Equation 7 by comparing the initial value and the time constant with the assumption that $\lambda_s = 0$. From the solution of these simultaneous equations, D and the number concentration ($\bar{n}$) can be extracted. (The Debye length depends on $\bar{n}$.) This fit is repeated for increasing Stern layer thicknesses, and the authors find a maximum value of λ_s of 10 nm. [39]

4.3 Bulk conductivity measurements.

Transient current measurements enable the study of the dynamics of particle motion across an electrode, but bulk conductivity measurements provide a simple way of determining the properties of micelles. By measuring the conductivity (K) over a wide range of concentrations (10^{-5} to 10^2 mM), it is possible to access both premicellar and micellar regimes. As can be seen in Figure 3, the results can be divided into three regions. In Region I, the conductivity scales as $K \propto \sqrt{c}$, where c is the concentration of surfactant; the square root dependence being consistent with the charge carrier being dissociated surfactant monomers. In Region III, the conductivity scales as $K \propto c$; the linear dependence being consistent with inverse micelles being the charge carrier. In between, the scaling is a combination of the two. [67,120]

The conductivity of nonionic surfactant in nonpolar liquids has also been studied. The conductivity of Span 85 in dodecane is similar to that of AOT, when both are expressed in molar concentrations, and increases with the addition of surfactant. [53] Dukhin *et al.* have also studied the conductivity of nonionic surfactants in kerosene, and while the increase of conductivity of the Span 85 surfactant as a function of concentration is not visible on the scale of their data, the conductivity of sorbitan monolaurate (Span 20) and Span 80 increases with the addition of surfactant. [52]

By measuring the conductivity of Span 85 over a wide range of concentrations, it is possible to distinguish two linearly-scaling regions, though these two regions have nearly indistinguishable slopes and intersect over a wide region from 5 to
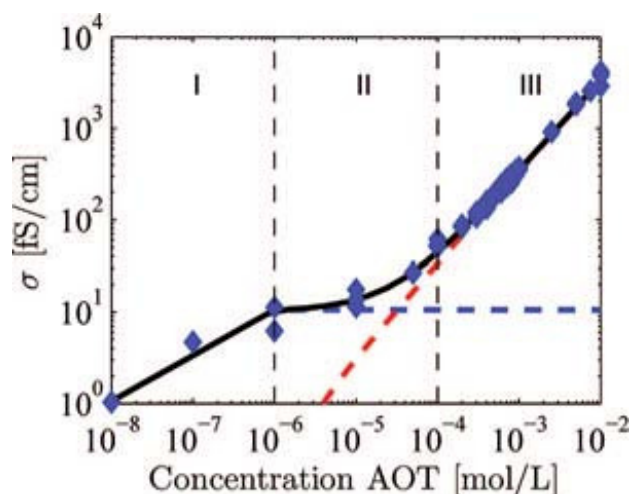
Fig. 3 Bulk conductivity of AOT in hexadecane as a function of surfactant concentration. The symbols indicate measurements. The blue line is the contribution of the monomer to the conductivity, and the red line is the contribution of inverse micelles. The black line is a sum of the contributions of the two species. Reprinted with permission from Sainis *et al.*[67] Copyright 2008 American Chemical Society.

25 mM. The different behavior in the two regions is attributed different structure of teh surfactant aggregates, in submicellar and micellar regimes. As the surfactant is nonionic, the presence of charged species is attributed to ionizable impurities in the solutions which are stabilized by surfactant aggregates. In the micellar region, uncharged micelles are proposed to divide into two oppositely charged micelles. In the submicellar region, the linear scaling indicates that the origin of charge is much different than in AOT, where the conductivity shows a square root scaling with concentration as shown in Figure 3. Given that the micelles themselves are not the origin of charge, premicellar aggregates are assumed to also stabilize the impurities present.[54]

4.4 Measuring particle trajectories.

Transient current measurements give an indication of how charged species move in a solution and are necessary to study micelles because they are too small to be viewed with a microscope. However, by placing larger, optically-visible colloidal particles in these suspensions, it is possible to study how the fluid flows by following their trajectory under an applied field. This has been achieved by following the motion of the colloids using video microscopy.

The exact nature of the trajectory that a silica particle takes in a cell between two planar electrodes depends on its z-position and the concentration of surfactant. In pure dodecane, the particles are found to move directly toward the attract-ing electrode with the same speed regardless of their initial z-position. When adding OLOA 1200 surfactant, the electric field is found to influence the trajectory. For concentrations of 0.01 and 0.025 weight % of surfactant, the trajectory monotonically moves toward the attracting electrode though does not do so at a constant speed. For a concentration of 0.1 weight % of surfactant, the trajectory is much more complex, varying in both speed and direction with time. This indicates that drift and diffusion alone cannot explain the motion of the particles, and electrohydrodynamic (EHD) effects may now be important.[42]

Planar electrodes provide a one-dimensional system which finds applications in horizontal electrophoretic displays, a proposed next-generation electronic paper technology.[121] Two-dimensional, in-plane electrodes or strip electrodes are more complicated, having an extra dimension, though are also found in applications. Carbon black in a 3–4 wt% solution of OLOA 371 in dodecane is found to move with a linear velocity until 30 μm away from the higher potential electrode when their velocity increased and they stuck to the electrode.[34] Strubbe *et al.* have attempted to simplify the analysis of this system by developing a one-dimensional approximation by separating the particle motion in the in-plane and out-of-plane axes. This model involves other simplifications—that colloidal particles do not contribute to the electric field, that uncharged micelles can be ignored, and that new charged micelles are not generated—but does compare favorably to the full two-dimensional model. By simulating the potential between the electrodes, the current density, and the particle trajectories for the in-plane and out-of-plane cases in both a low and high surfactant concentration system can be determined. In the low concentration case ($\bar{n} = 10^{17}$ m^{-3}), the in-plane and out-of-plane motion are very similar, with the only noticeable differences being between the shape of the potential. In the high concentration case ($\bar{n} = 5 \times 10^{18}$ m^{-3}), the potential between the electrodes evolves with time indicating that the system in a space-charge regime, but qualitatively the in-plane and out-of-plane behavior are similar.[51]

5 Surfactant induced charging of colloids

The addition of surfactant to a nonpolar liquid leads to the formation of charged species, much more so than is present on the surface of a colloid in a nonpolar liquid with no additives.

In this section, the nature of the surface is the important factor. The types of colloids studied can be loosely divided into two: "hydrophobic" and "hydrophilic". These terms are more appropriate when discussing aqueous solutions, but they make a useful way of distinguishing between particles in nonaqueous solvents as well. It would be more appropriate to refer to the surfaces as polar or nonpolar, but given that that

the nomenclature is common in the literature, it will be maintained.

"Hydrophobic" surfaces are either polymeric colloids (primarily PMMA or polystyrene (PS)), carbon black, or surfaces treated with hydrophobic compounds. "Hydrophilic" surfaces are oxides (primarily silica, TiO_2, alumina, or mica) or surfaces treated with hydrophilic compounds.

5.1 Hydrophobic surfaces.

Several approaches can be used to study charging of particle surfaces. Some of these methods are not able to distinguish the charge of the surface as they measure only the repulsive force of the particles. Blinking optical tweezers measure the motion of particles after the optical trap is turned off, and while repulsion is measured between polymer colloids and AOT, the charge of the surface is not.[41,67,69,112,122] There interparticle repulsion does depend on surfactant concentration, and for carboxylate-modified PS and PMMA in hexadecane, the force is greater for 1 mM than for 10 mM AOT.[41,112] Interparticle forces have also been measured by following the motion of an ensemble of particles with an optical microscope. In the absence of surfactant, PMMA particles are found to aggregate in dodecane, but the addition of AOT stabilizes the particles. The magnitude of the surface potential is greatest at 12.5 mM.[61] Atomic force microscopy (AFM) has also been used to measure the surface force of hydrophobically-modified silica, again without the ability to determine the sign of the surface charge. High concentrations of surfactant were used, and the magnitude of the surface potential was found to be greatest at 100 mM AOT.[60]

By following the motion of particles in an electric field, the effect applied in electronic paper displays, the sign of the surface charge can be extracted. Electrophoretic motion of hydrophobic particles in AOT has been measured using optical tweezer SPOM,[63,66,120] phase-analysis light scattering (PALS),[47,61,123] and differential-phase optical coherence tomography (DP-OCT).[64,70] These studies all agree that AOT induces a negative charge on hydrophobic surfaces and that the surface charge varies with surfactant concentration, although some studies find that the surface potential is constant.[61,66] Studies that report the ζ potential varying tend to calculate the value from the electrophoretic mobility (μ) measured with PALS or DP-OCT and do not account for the different nature of the double layer in nonpolar liquids. The screening length and particle radius are similar in magnitude ($\kappa\alpha \approx 1$) and the polarization of the charged cloud around the particle must be accounted for. When this is accounted for, the surface potential is apparently constant, as shown in Figure **??**.[61] For studies which examine the concentration dependence over a wide range, five or six orders of magnitude to include samples both with and without inverse micelles present, the value of ζ or
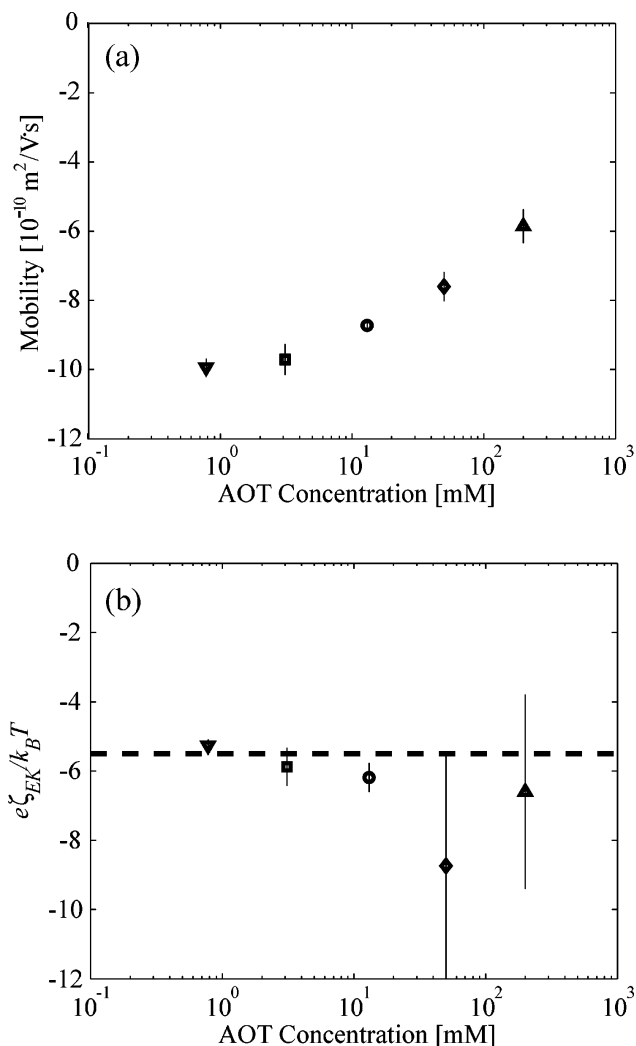

Fig. 4 The variation of (a) electrophoretic mobility and (b) dimensionless surface potential of PMMA particles of 780 nm radius in dodecane as a function of AOT concentration. The electrophoretic mobility is found to be negative and the magnitude decreases as surfactant concentration increases. The surface potential, which accounts for the polarization of the screening cloud by resulting from solutions of the Poisson–Boltzmann and Navier–Stokes equations, is constant. The error bars at high concentration are large because the electrophoretic mobility is less sensitive to the surface potential at high ionic strengths. Reprinted with permission from Hsu *et al.*[61] Copyright 2005 American Chemical Society.

μ is found to increase to a maximum, around 1 mM, when it either plateaus (in the case of ζ) or begins to decrease (in the case of μ).[47,67,120,123]

There have been fewer studies into charging hydrophobic surfaces with surfactants other than AOT, and the results do not agree as clearly. Span 85 surfactant was found to induce a positive charge on PMMA in hexane using PALS, except for low concentrations and high applied fields where the sign reverses. The zero-field μ is found to decrease with increasing concentration.[55] OLOA surfactant induces a negative charge on surfaces, and if the concentration is varied, it goes through a maximum in μ before decreasing.[34,47] There are conflicting results for the charging behavior of Zr(Oct)$_2$. It has been found to charge particles both negatively[47] and positively.[66,77] Given that these studies are on three different hydrophobic surfaces (PMMA, hydrophobically-modified silica, and carbon black), the results indicate that the interaction of the surfactant with the surface is important in determining the resulting charge.

5.2 Hydrophilic surfaces.

The surface charge of bare silica, a well-studied hydrophilic surface which obtains charge in nonpolar solvents, in a solution of AOT in decane has been found to reverse with increasing concentration, as shown in Figure 5. At very low AOT concentrations (0.001 mM), the electrophoretic mobility measured with PALS decreased to a minimum at a surfactant concentration 0.1 mM. The electrophoretic mobility became 0 again at 0.5 mM, increasing to a maximum near 5 mM when it again decreases to plateau at 0. The authors measure the conductivity of the dispersion and the supernatant fluid and find that the supernatant is uncharged until 0.5 mM, reasoning that this is the approximate point of full surface coverage.[58]

Other studies of bare silica support the observation of negatively charged surfaces at low concentrations; however, charge reversal is not repeated. These other studies do not examine such a wide range of concentrations, although they both reach a maximum concentration of 10 mM where, as can be seen in Figure 5, charge reversal should have occurred.[47,73] Silica surfaces treated with, for example, cyano, amine, or hydroxyl surfaces have been observed to be charged, although the sign of the charge depends on the surfactant and the surface functionalization. Cyano-treated silica with AOT surfactant has been observed to be negatively charged,[124] as has amino-treated silica in the presence of either PIBS or Span surfactants.[48] Hydroxyl-treated silica, on the other hand, has been observed to be positively charged in the presence of either PIBS or Span surfactants.[48]

From these treated surfaces, it is clear that the chemistry of the oxide surface plays an important role in determining the sign and magnitude of the charge. The electrophoretic mobility measured by PALS in a solution of AOT in isoparaffin has
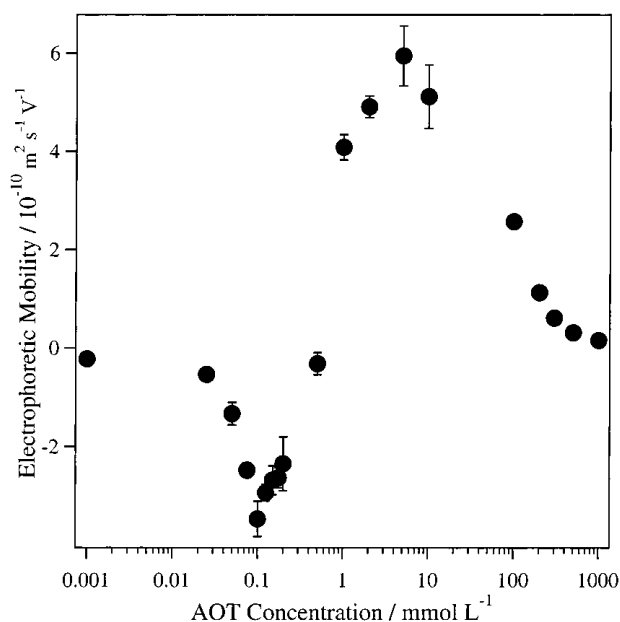

Fig. 5 The electrophoretic mobility (μ) of untreated silica particles of 3.5 μm radius at a concentration of 1 mg mL^{-1} in decane as a function of AOT concentration. The sign of μ is negative until the silica surface is saturated with adsorbed AOT when the sign of the charge reverses to positive. Reprinted with permission from Keir *et al.*[58] Copyright 2002 American Chemical Society.

been found to scale with the aqueous isoelectric point or point of zero charge for five oxide particles: acidic particles in aqueous solutions are negatively charged in nonpolar liquids and basic particles are positively charged in nonpolar liquids.[73]

There is disagreement about the sign of the charge of other oxide surfaces. Titania has been found to both positively[28,64,73] and negatively[29] charged in solutions of AOT in toluene and hexane. Given that the "effective" acidity of titania is similar to AOT and therefore it is poorly charged,[73] experimental errors may be explain this discrepancy. Alumina surfaces have been found to be negatively charged in solutions of AOT in nonpolar solvents,[29,73] although at high concentrations the charge reverses.[29] If a different surfactant (Span) is used, alumina surfaces are found to be positive.[52] The electrophoretic mobility of these systems was measured either using PALS,[73] DP-OCT,[64] or electroacoustic measurements.[28,29,52] Using a surface force apparatus, mica has been observed to be charged in a solution of AOT, although PALS and FTIR measurements were required to confirm that surfaces were negatively charged.[57,59,125]

6 Systematic studies of charged colloids

Given the range of charging behavior observed, it is important to study how the magnitude and sign of charge on colloidal surfaces varies with the chemistry of the particle and the surfactant in solution. In order to identify the origin of these differences, systematic studies of different types of colloids and surfactants are essential to distinguish between the influences of each component. Several recent publications have made systematic variations of either the surfactant or colloid surface in a nonpolar liquid, and a few examples are highlighted here.

Two studies by Berg *et al.*[48,73] exemplify how systematic modifications of the surfactant and particle can be used to support acid-base interactions as the origin of charge on oxide particles in nonpolar liquids. By using one surfactant (AOT) to charge a variety of mineral oxides, it is possible to determine how the relative aqueous acidity of the particle determines the charge in nonpolar liquids. The results, shown in Figure 6, indicate that the sign and magnitude of the electrophoretic mobility of the oxides in isoparaffin depends on the aqueous isoelectric point (IEP). The authors find similar results for the aqueous point-of-zero charge. By performing a study where only one variable is changed, it is possible to assign an "effective pH" for the AOT-isoparaffin system of 4, the IEP where the electrophoretic mobility equals 0.[73]

By modifying both the surfactant and the particle, a relationshiop between relative aqueous acidity or basicity and the charge in nonpolar systems has been determined. Acidic (Span 80) and basic (OLOA 11000) surfactants are mixed with acidic and basic silica particles in isoparaffin. The basic silica surface is positive in the presence of the acidic surfactant.
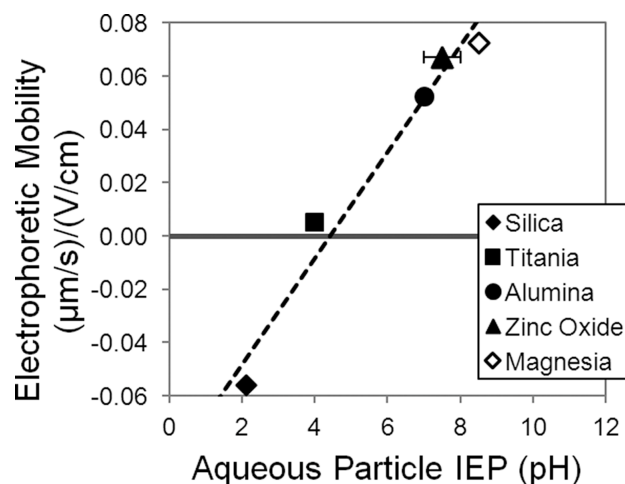

Fig. 6 The maximum electrophoretic mobility of a series of metal oxides in isoparaffin as a function of their isoelectric point (IEP). There is a nearly linear correlation between the mobility in nonpolar solvents and the aqueous acidity or basicity. Reprinted with permission from Gacek *et al.*[73] Copyright 2012 American Chemical Society.

However, the acidic particle is also positive in the presence of Span 80. In a solution with the acidic surfactant, both the acidic and basic particles are negatively charged. These results can be seen in Figures 7 and 8, emphasizing that the relative acidity or basicity is an important parameter. Both of the surfactants are relatively more acidic or basic than the particle surfaces, which is the reason that the sign of the charge does not change when altering the particle surface, only the magnitude does.[48]

As stated in Section 2.1, few different surfactants have been used to charge colloids, and consequently, the effect of minor differences in surfactant structure is not well understood. Parent *et al.* have attempted to understand how the structure of PIBS surfactant influences its ability to electrophoretic inks. Normally PIBS is used as a commercial formulation, but the authors synthesized a suite of PIBS analogues and so were able to control the exact chemical structure. The primary variable in controlling the ability of the surfactant to form charges in nonpolar liquids and to stabilize electrophoretic ink dispersions is the length of the amine chain in the headgroup, as shown in Table 2. There is a trend in the ability of the surfactant to charge surfaces for larger PIBS; for amine chain lengths between two and four, the ζ potential of the ink decreases with increasing chain length. However, the results for the anhydride and the single amine forms do not demonstrate clear results. The single amine form has a very low ζ potential, and the anhydride form has a ζ potential near that of the di-amine form, despite it not forming charged micelles in so-

Fig. 7 Electrophoretic mobility of basic and acidic silica particles of 125 nm radius at a concentration of 2.5 mg mL^{-1} in the presence of basic OLOA 11000 surfactant. While both particle surfaces are negatively charged, the magnitude of the charge on the acidic surface is greater. The error bars are derived from an average of three measurements. Used with permission from Elsevier. [48]
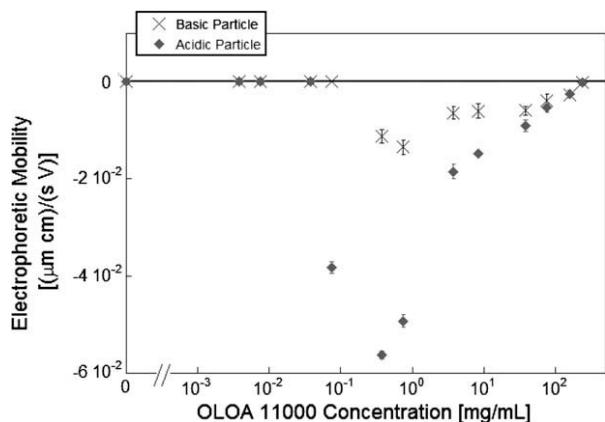

Fig. 8 Electrophoretic mobility of basic and acidic silica particles of 125 nm radius at a concentration of 2.5 mg mL^{-1} in the presence of acidic Span 80 surfactant. While both particle surfaces are positively charged, the magnitude of the charge on the basic surface is greater. The error bars are derived from an average of three measurements. Used with permission from Elsevier. [48]
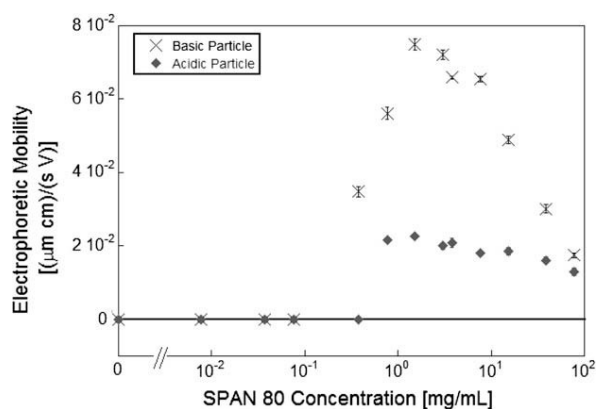
lutions on its own. These inconsistent results with low amine numbers suggest that it is difficult to decouple the influence of the ability surfactant to stabilize charge and the size of inverse micelles. [50]

7 Insights into charging mechanism

Morrison, in reviewing the field of charging in nonaqueous solvents, identified three possible mechanisms which could lead to the formation of charged colloidal species in nonpolar media. [13]

- The preferential adsorption of dissociated anions or cations, which could be charged micelles,

- The dissociation of surface anions or cations, which are stabilized in inverse micelles, or,

- The adsorption of a solute onto colloids, followed by formation a complex with a surface species, which then desorbs from the surface as a charged complex.

7.1 Acid-base mechanism.

Acid-base interactions between particles and surfaces are one proposed mechanism for the formation of charged surfaces, introduced by Fowkes. [126,127] The sign and magnitude of the charge depend on the relative acidity and basicity of the surfactant and the particle surface, and the particle obtains a charge through a three-step process. Neutral micelles adsorb onto particle surfaces, there is then a charge transfer from the surface to the micelle, and finally, the now charged micelle desorbs from the surface leaving an oppositely charged surface behind. This mechanism is particularly applicable for the case of nonionic surfactants, where in the absence of an ionizable group it is difficult to determine an origin for the observation of charged surfaces. Espinosa *et al.* use this model to explain the observation of positively charged PMMA surfaces in hexane solution of nonionic Span 85 surfactant. PMMA is considered to be a basic surface, and Span surfactants are considered acidic. An acid-base reaction between the two surfaces would result in a positively charged surface, as observed. [55] As discussed in Section 6, this mechanism has also been used to explain the charge on acidic or basic treated silica surfaces with Span 80 or OLOA 11000. [48] In another study, the authors investigate the charge on untreated and hydrophobically modified silica particles in isoparaffin in the presence of three surfactants (AOT, OLOA 11000, and Zr(Oct)$_2$). Both surfaces are negatively charged in the presence of all three surfactants. Given that the bare silica did not acquire the charge of ionic surfactants counterion (Na$^+$ or ZrO$^+$), it does not seem that preferential adsorption of these "hard" ions, which would be expected, could be the origin of charge. However,

the suitability use of this acid-base interaction model is not clear as the authors are only able to make a claim on the basicity of OLOA 11000 and are unsure of the acidity or basicity or AOT or Zr(Oct)$_2$. There are also problems in using this model with the hydrophobically treated silica, where it would be expected that no ionizable groups would be present. The authors attribute the presence of surface charge, which does have a lower magnitude than the bare silica, to an incomplete surface coverage of hydrocarbon groups which results in the silanol groups remaining on the surface.[47] Rather than primarily varying the acidity of surfactant, another group studied the effect of changing the acidity of the surface of the particle. Various metal oxides with isoelectric points (the pH where the surface is uncharged) varying between 2 for silica and 8.5 for magnesia were used. In solutions of AOT in isoparaffin, silica is negatively charged and that the other surfactants are positively charged. The relationship between the aqueous isoelectric point and the surface charge is approximately linear. Using an acid-base model, the positive charge on silica is attributed to its relatively acidic surface and the negative charge on the remaining oxides to their relatively basic surfaces. By analyzing so many different surfaces, the authors are able to assign an "effective pH" of AOT in isoparaffin of 4; this being the aqueous isoelectric point of an oxide which would also be uncharged in this nonpolar system.[73] However, this being only one pair of surfactant and solvent, it is not apparent that this concept of an "effective pH" could be extended to other systems.

For bare silica in dodecane, McNamee *et al.* observed a repulsive force between two silica surfaces in dodecane measured by AFM. As no charge control species were added, the measured repulsion is attributed to the following acid-base process. The presence of a small amount of water impurity in the system enables the formation of charged species on the acidic silica surface. Surface sites are denoted by S, and a basic molecule in solution is denoted by B

$$S + B + H^+OH^- \rightleftharpoons SOH^- + B + H^+ \qquad (8)$$

The experimental repulsive force fits a description of the interaction as a sum of the constant surface charge boundary condition and the van der Waals force.

Acid-base interactions have been applied to correctly describe the sign of charge on surfaces based on the relative acidity or basicity of the surfactant and particle surface. However, this explanation for surface charge is chemically most appropriate, and predictive, for surfaces such as bare metal oxides which have dissociable groups on their surface.

7.2 Preferential adsorption mechanism.

The acid-base mechanism involves the transfer of an ionic species between an inverse micelle and a particle surface. The preferential adsorption model also involves the partitioning of charged species, but the charges are contained in inverse micelles which adsorb onto the surface, which makes this explanation most appropriate for systems without transferable groups.

Hydrophobically modified silica would not be expected to interact in this way given its inability to dissociate, although some authors have observed dissociation as consistent with the acid-base charging mechanism.[47] McNamee *et al.* found that hydrophobic silica can become charged in the presence of a surfactant such as AOT. The authors assume that the surface charge is negative, given that a proton exchange is unlikely for a hydrophobic silica surface. The surface charge is attributed to preferential adsorption of the "soft" AOT anion. The following equilibrium describes this surface reaction in the specific case of AOT but can be generalized to any surfactant attaining charge which demonstrates preferential adsorption.

$$S + AOT^-Na^+ \rightleftharpoons SAOT^- + Na^+ \qquad (9)$$

As the concentration of AOT is increased, the surface potential begins to decrease, a characteristic of the preferential adsorption model. The decrease in surface potential occurs because, above some threshold concentration, the counterions in solution begin to adsorb onto the charged surface sites, neutralizing them, as described the following equilibrium.[60]

$$SAOT^- + AOT^-Na^+ \rightleftharpoons SAOTNa + AOT^- \qquad (10)$$

The preferential adsorption model has been used to explain the observation of charge measured on different particle surfaces and for different surfactants. For a system of alumina particles in a solution of Span 80 in kerosene, the conductivity of suspension of particles is significantly less than a surfactant solution, and the authors assume that the anions and cations are of a different size. If they were the same size, the conductivity would only be expected to decrease by a factor of two. The cations are small and preferentially adsorb on the surface; above a threshold concentration, the cations are no longer adsorbed on the surface and remain in solution to contribute to the increased conductivity. The surface charge decreases at a certain concentration, and this is theorized to be due to the particle double layers overlapping.[52] Their application of a model involving small cations is questionable given that the size of the ions would be much less than λ_B; the cations are calculated to be approximately 1 nm in diameter. Given that an acidic surfactant is used, the positive charge agrees with the acid-base results described above.

Other recent examples employing the preferential adsorption explanation study PMMA latexes, treated oxide surfaces, and carbon black, all of which should be less able to dissociate and participate in acid-base reactions. A recent thermodynamic model attributes the charged surface to the difference

in the number of positive and negative micelles adsorbed on the surface. A fluctuation in the surface charge will change the affinity for either positive and negative to preferentially adsorb. The main quantity determining the particle charge is the surface coverage (θ) and that the calculation of the surface potential varies depending if the system is in a low surface coverage ($\theta \ll 1$) or a high surface coverage ($\theta \lesssim 1$).[66]

The charge on hydrophilic and hydrophobic TiO_2 as well as carbon black can be explained using a preferential adsorption model. Bare TiO_2 is found to be positively charged with a decreasing ζ potential with increased concentration. The oxide surfaces have a higher affinity for water or the "hard" ion Na^+ and so obtain a positive charge. AOT^- hemimicelles form on the surface with the charged head group attached to the cations. As the surfactant concentration increases, the water on the surface is displaced and migrates into inverse micelles. The AOT chains adsorb on the surface to form a monolayer atop the Na^+ cations. For the hydrophobic TiO_2, the preference for adsorption is reversed, and the surface charge is now negative with an increasing ζ potential with increased concentration. At low surfactant concentrations, the surfactant adsorbs on the particle surface forming hemimicelles. The negative surface charge arises from the Na^+ ions preferring the inverse micelle core to the hemimicelle boundary. As the surfactant concentration is increased, a more concentrated layer of surfactant forms on the surface. This layer can extend beyond one monolayer and can sustain dissolved counterions in the increasingly hydrophilic environment, leading to the decrease in the ζ potential.[64] A similar variation is found for the ζ potential with surfactant concentration in a suspension of carbon black in a solution of AOT in toluene. The same model was found to be appropriate.[70] A preferential adsorption model can also explain the charge of PS colloids in solutions of AOT in dodecane by considering the monolayer packing of adsorbed inverse micelles.[123]

The above studies infer the mechanism of charge formation indirectly; however, it is useful to directly probe the location of the surfactant in colloid-surfactant mixtures. SANS was recently used to study the adsorbed surfactant layer. PMMA particles were contrast-matched with the solvent by preparing them in a mixture of H-dodecane ($C_{12}H_{26}$) and D-dodecane ($C_{12}D_{26}$) so that no scattering from the particle is observed. By observing the scattered intensity of a solution of AOT alone and of AOT in the presence of PMMA particles, it is possible to ascertain the structure of the adsorbed layer. Figure 9 shows the results from this experiment. As can be seen, at a higher AOT concentration, the scattered intensity at low-q values is much greater, due to the adsorbed surfactant. By assuming that the AOT layer is the thickness of one molecule, the inner radius of the shell can be calculated and correlates with the inner radius of the PMMA particle. This indicates that the AOT adsorbs within the stabilizing PHSA layer. In
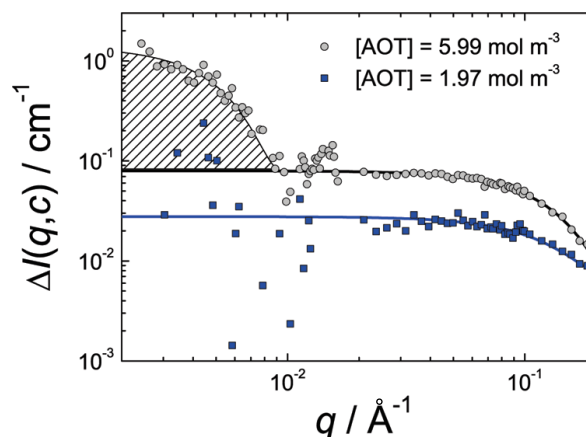

Fig. 9 The difference between the intensity scattered by a mixture of PMMA/AOT at two AOT concentrations. The PMMA particles are 46 nm in diameter at a volume fraction of 0.02. The scattering at high q is due to micelles, and the solid line shows shows the expected scattering due to this species alone. The low-q data for the less concentrated solution is noisy due to the solvent contrast-matching. The scattering at low-q for the more concentrated sample is clearly higher and is beleived to be due to the presence of adsorbed surfactant. Reprinted with permission from Kemp *et al.*[120] Copyright 2010 American Chemical Society.
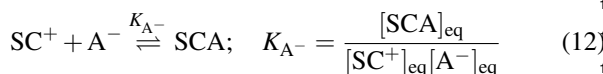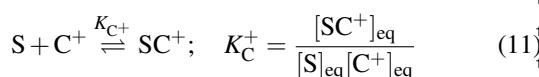
this system, the AOT molecules are concluded to have adsorbed individually within the stabilizing layer rather than as micelles. The mechanism of charge formation, therefore, is that individual AOT molecules adsorb onto the PMMA surface which becomes charged when the Na^+ counterion is solubilized in an inverse micelle.[120]

7.3 Site-binding mechanism.

A site-binding model has recently been employed the describe the mechanism of charging, employing ideas from both acid-base interactions and preferential adsorption. The charge reversal of silica in a solution of AOT in decane, shown in Figure 5, can be explained using this model. At low surfactant concentrations, the surface is negatively charged. Even at low concentrations, there are assumed to be small aggregates of one, two, or three surfactant monomers, so-called "premicellar aggregates", which through a disproportionation mechanism can stabilize charge. At low concentrations, the negatively charged micelles preferentially adsorb to the particle surface, which is attributed to acid-base interactions. As the surfactant concentration increases, positively charged species begin to adsorb, neutralizing the surface. As the concentration increases further, positively charged species begin to adsorb, although the authors do not offer an explanation for the pref-

erence of positively charged species at higher concentrations. Then at even higher concentrations, the negatively charged species in the double layer neutralize the positive surface.[58]

This explanation is qualitative, though two groups have employed a more quantitative site-binding model. This model was first proposed by Kitahara *et al.* and considers the equilibrium constants for binding at surface sites.[128] Recent studies have used this approach to explain the charge induction of $Zr(Oct)_2$ in isoparaffin with copper phthalocyanine (CuPc) with PVA or resin[74,76] or in silicone oil with carbon black.[77] The explanation for the presence of charge is similar in the three papers, so only the mechanism as discussed by Jenkins *et al.* will be presented. The system consists of surface groups S and an ionizable, dissociating surfactant CA, where the cation C^+ adsorbs first. There is water in the system, but it is not considered to adsorb and only serves as a catalyst for the formation of charge. The chemical equilibria and related equilibrium constants for this generalized system are given below.

$$S + C^+ \overset{K_{C^+}}{\rightleftharpoons} SC^+; \quad K_C^+ = \frac{[SC^+]_{eq}}{[S]_{eq}[C^+]_{eq}} \quad (11)$$

$$SC^+ + A^- \overset{K_{A^-}}{\rightleftharpoons} SCA; \quad K_{A^-} = \frac{[SCA]_{eq}}{[SC^+]_{eq}[A^-]_{eq}} \quad (12)$$

It is possible to express the surface charge density (σ_s) in terms of these equilibrium constants, and σ_s is defined as the product of the elementary charge (e), the number of surface sites (N_s), and the fraction of charged sites (θ_{charge}) which can be defined in terms the equilibrium constants and concentrations.

$$\sigma_s = eN_s\theta_{charge} \quad (13)$$

From measurements of σ_s as a function of surfactant concentration, it is possible to determine values for the equilibrium constant for the surface reaction to form charged species and neutralized species. Two assumptions were required to do this: that $Zr(Oct)_2$ dissociated into three ions (ZrO^{2+} and two Oct^-) and the equilibrium concentration of $Zr(Oct)_2$ was equal to that in the bulk due to the large Debye length. The calculated equilibrium constant for the adsorption of ZrO^{2+} is approximately 11 orders of magnitude lower than for the adsorption of two Oct^- ions to neutralize the surface, which would be expected given that the formation of charged species in nonpolar media would not be favored. By adjusting the concentration of water in the system, the formation of charged ZrO^{2+} surface sites was found to be more favorable in the presence of higher concentrations of water. This could propose two mechanisms (either surface water or micellized water enhancing the dissociation of surfactant), though the two could not be distinguished.[76]

7.4 Surface dissolution mechanism.

The dissociation of a surface ion into an inverse micelle has been infrequently used to explain the observed charge in nonpolar solvents. Briscoe and Horn investigated mica surfaces in a solution of AOT in decane using surface force apparatus. Mica is more chemically complex than the silica, titania, or alumina surfaces discussed previously. A small amount of water will be present, even in "dry" solvents, which will be located in the inverse micelles. The potassium ions, part of the mica surface, will migrate from the surface to the core of the inverse micelles resulting in a negatively charged surface.[57]

8 Conclusions

The nature of charging in nonpolar media is still an active area of research 60 years after first being reported,[1–3] promoted not only by recent interesting applications[4–12,14,15] but also by considered use of experimental techniques. The use of transient current measurements provides not only a method to describe the motion of particles in the electrophoretic cells where they are employed in electrophoretic displays[121] but also enables a way of extracting properties of micelles electrochemically.[35,40,45,49] The reduction in size of electrochemical cells also enables a way to study the nature of the double layer and has revealed that some common assumptions may be inappropriate in small devices.[43,119] Sensitive optical techniques enable the measurement of a single charge on the surface of a colloid.[63,113,114] The same techniques along with more established methods, such as PALS or bulk conductivity measurements, have been successfully applied to the measurement of electrophoretic mobilities, surface potentials, and surface charge numbers. A wide variety of surface chemistries have been shown to demonstrate charging in nonpolar media.[28,29,34,41,47,48,52,55,57–61,63,64,66,67,69,70,73,77,112,120,122,124,125]

However, there are still outstanding issues, primarily relating to the charge control additive, the surfactant. Few surfactants have been employed in academic studies of nonpolar charging and exploring surfactants with related chemistries is important to improving their ability to stabilize charge and find use in applications. A key parameter involved in the consideration of surfactants in nonpolar media is their ability to aggregate into inverse micelles.[31] However, this process is still not well understood and is mainly inferred from experimental results when intensities drop below the resolution of the technique. A precise value for a critical micelle concentration for the formation of inverse micelles has not been determined, indicating that there may not be one "critical" concentration where micelles begin to form. The purity of all components present (solvents, surfactants, and particles) is another important consideration for characterizing these systems. The formation of inverse micelles, for example, is known to be de-

pendent on the presence of water.[78] Recent results have also shown that variation in the amount of trace water present can influence both surfactant solution conductivity and particle electrophoretic motion.[129] As water or other polar impurities can be introduced from solvents, surfactants, or particles, it is crucial to control the purity of all chemicals to ensure that the observed results are due to intentionally varied parameters and not impurities.

The mechanism of charge induction has still not been determined, though it is clear that the origin of the charge will be system dependent. Three major mechanisms were proposed by Morrison in his 1993 review of the field: acid-base interactions between inverse micelles and particle surfaces, dissolution of surface species into inverse micelles, and preferential adsorption of charged inverse micelles onto particle surfaces.[13] No new possible mechanisms have been suggested since. However, some recent results indicate the benefit of systematic variation of the chemistry of either the particle surface or charge control additive structure to provide a deeper understanding of the interactions resulting in the formation of charge in nonpolar solvents. Direct investigations of the surface of the charged species, using techniques such as SANS,[120] have also resulted in knowledge about the location of charge controlling components.

In order to better understand the origin of charging in these systems, experimental work which directly probe the structure of the surfactant is sorely needed. Given the academic and industrial interest in charge stabilization in nonpolar media, it seems certain that future research will provide insight into these unresolved issues.

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