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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

1 Charges in aqueous solutions are ubiquitous, both in terms
2 of their uses in applications as well as the energetics of for-
3 mation. Forming charged species in nonaqueous, specifically
4 nonpolar, solvents is energetically more difficult, but they are
5 important in many applications. The earliest reports of charg-
6 ing in nonpolar liquids were in the 1950s, by van der Minne
7 and Hermanie^{1,2} and by Koelmans and Overbeek.³ Charges in
8 nonpolar liquids are an important concern in the petroleum in-
9 dustry, for both stabilizing components^{4,5} and preventing ex-
10 plosions.⁶ These charges are important in the understanding
11 of fluid phenomena, such as flow electrification^{7,8} and elec-
12 trorheology.^{9,10} They are also useful in applications as diverse
13 as the developing of toner for printers and photocopiers¹¹ and
14 the measuring the activity of enzymes.¹² In 1993, Morrison
15 comprehensively reviewed the state of knowledge regarding
16 the formation and applications of electrical charges in non-
17 aqueous media.¹³ In the intervening years, knowledge of the
18 formation and mechanism behind nonaqueous charging of sur-
19 factant solutions and colloid surfaces has improved but still
20 important gaps remain.

21 In recent years, the electrophoretic displays found in e-
22 Reader devices, which make use of charging in nonpolar sol-

23 vents, have appeared as an important and rapidly growing ap-
24 plication.^{14,15} These displays have the appearance of paper
25 but can be refreshed to display different images, providing the
26 benefits of both books and electronic displays. Electrophoretic
27 displays consist of a colloidal suspension of charged pigment
28 particles in a nonaqueous solvent sandwiched between two
29 electrodes. ~~The application of a voltage causes the colloids~~
30 ~~to migrate in the cell, changing its appearance, as shown in~~
31 ~~Figure ??.~~¹⁶ When an electric field is applied, the particles mi-
32 grate to the oppositely charged electrode, presenting either a
33 white or black pixel, as shown in Figure 1. The electronic dis-
34 play devices currently on the market are very popular, but they
35 only have monochromatic screens and have relatively slow re-
36 fresh rates. Many approaches have been suggested for the
37 development of future electronic paper technologies, to en-
38 able these displays to match the color gamut and popularity of
39 printed paper. For many of these new technologies (vertical or
40 horizontal electrophoretic, electrokinetic, liquid powder, elec-
41 trowetting, or electrofluidic displays), controlling charge of ei-
42 ther the dyed particles or the fluid is essential to the operation
43 of the display.¹⁷

44 Charged ions have been generated in nonpolar solvents in
45 several ways. Electrical charge has been observed in non-
46 aqueous solutions with added salt, where the cation and an-
47 ion are large organic molecules.¹⁸ Fullerenes (both C₆₀ and
48 C₇₀) have been used to produced cations and anions through

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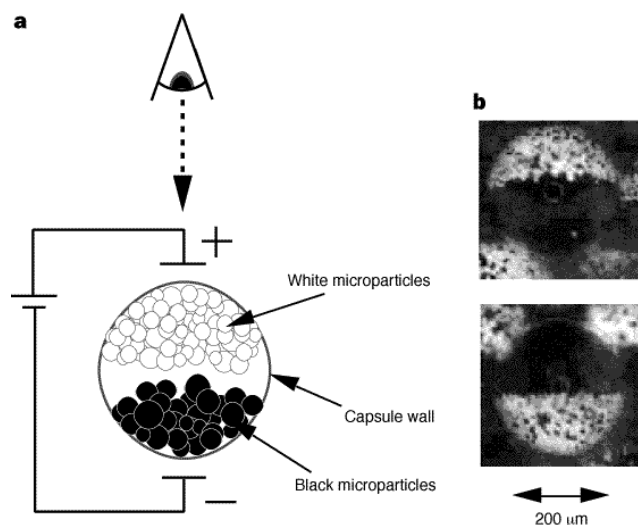


Fig. 1 An electrophoretic microcapsule. The white and black microparticles respond to the application of an electric field, giving either white or black text. The photomicrograph shows the experimental realization of this system. Reprinted with permission from Macmillan Publishers Ltd.: Nature, 1998.¹⁴

Table 1 Relative permittivity (ϵ_r) of common solvents at 293.2 K²⁶

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

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 ($\epsilon_r \approx 25$), 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

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 thiolate²⁰, TiO₂ particles milled with silane²¹, 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 ($k_B T$).²⁷ In this expression, e is the elementary charge, and ϵ_0 is the permittivity of free space.

$$\lambda_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T} \quad (1)$$

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

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). ~~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 ($\text{Zr}(\text{Oct})_2$).^{47,63,66,74–77}

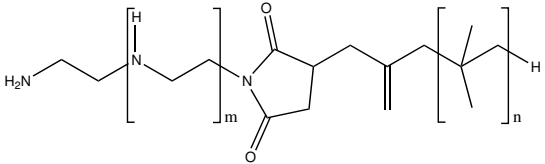
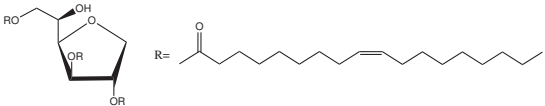
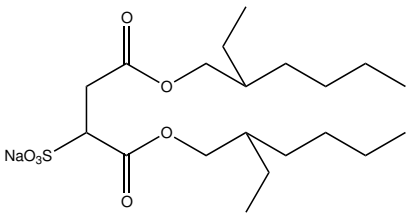
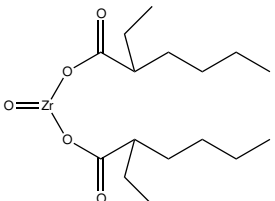
2.2 Inverse micelles.

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 isoctane 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

	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 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,^{96,255} 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 particles¹⁰⁹ and interfacial tension with water.⁵⁴ The CMC values measured in these 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

260 using SANS and small-angle X-ray scattering¹¹⁰ and CMCs
261 reported by measuring the speed of sound in the surfactant so-
262 lution in a semi-polar solvent.¹¹¹

263 3 Charged colloids in nonpolar solvents

264 Before discussing the effects of added surfactants, it is worth-
265 while considering the charge on bare surfaces in nonpolar sol-
266 vents with no additives. As expected, given that generating
267 charge in nonpolar solvents is more disfavored than in aque-
268 ous ones, the number of charges per colloidal particle is low.
269 Optical tweezers, along with sensitive detection and data anal-
270 ysis, provide a method to detect the small charge numbers
271 present.^{63,67,112–114}

272 Sainis *et al.* developed a method using blinking optical
273 tweezers imaged with a high-speed digital camera.¹¹² The tra-
274 jectories of the particles are recorded when the trap is off, en-
275 abling the motion of the particle to be studied, but by quickly
276 reforming the trap, the particles are constrained. For PMMA
277 spheres in hexadecane, there were 23 ± 3 charges on the sur-
278 face to be, though the charge distribution was not studied.⁶⁷

279 More actively applied forces, rather than just Brownian motion,
280 can also be used to probe optically trapped particles. A
281 technique dubbed single particle optical microelectrophore-
282 sis (SPOM) has been used to measure charges on the surface³¹⁰
283 of sterically-stabilized poly(methyl methacrylate) (PMMA) in³¹¹
284 dodecane. Optical tweezers were used to trap a particle be-³¹²
285 tween two electrodes. By applying a periodic field, the par-³¹³
286 ticles moved electrophoretically in response to the field, pro-³¹⁴
287 viding a way to extract the number of charges on the surface³¹⁵
288 (the magnitude of the motion of the particle depends on its³¹⁶
289 charge number Z). For stabilized PMMA spheres in dodecane,
290 there is a small, but nonzero, charge on the surface. The mean
291 particle charge is $-2.9e$, but there is a broad, approximately³¹⁷
292 Gaussian distribution of charges, indicating that there are both³¹⁸
293 positive and negative surfaces.⁶³ It is possible to measure the
294 charge number of a silica particle using a similar method with³¹⁹
295 the application of a square voltage. By assuming that the par-³²⁰
296 ticles have an elementary mobility (μ_e) originating from elec-³²¹
297 trophoretic motion and that any errors in the mobility are due³²²
298 to Brownian motion, it is possible to assign the magnitude of³²³
299 the charge to the nearest whole number value. There is a broad³²⁴
300 distribution indicating that there are particles which have both³²⁵
301 positively and negatively charged surfaces.¹¹³ This technique³²⁶
302 was extended to enable more accurate measurements of the³²⁷
303 charge of PMMA in dodecane. The amplitude of the move-³²⁸
304 ment of the particle was found to change in discrete steps,³²⁹
305 and these values, in terms of charge, were near the elementary³³⁰
306 charge. This enabled the production of a histogram of charge³³¹
307 numbers; an example for PMMA in dodecane is shown in Fig-³³²
308 ure 2 which is for one particle taken over 3000 s.¹¹⁴ 333

309 In these systems in nonpolar liquids, charge numbers are³³⁴

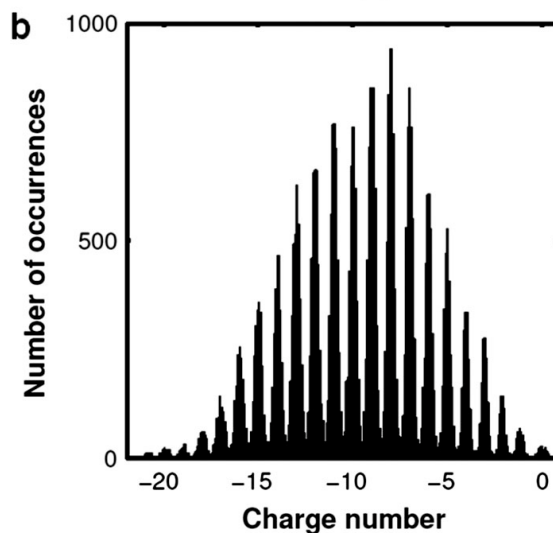


Fig. 2 Charge histogram for a PMMA particle in dodecane measured over 3000 s. The charge number is calculated by analyzing the electrophoretic motion of the particle when held in an optical trap. Reprinted with permission Beunis *et al.*¹¹⁴ Copyright 2012 by the American Physical Society.

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.

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

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.

$$R = \frac{e}{6\pi\eta\mu} \quad (3)$$

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.

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

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,⁴⁹¹ 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.

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

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 $\mu\text{mol m}^{-3}$. 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 .

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

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.

$$I = S\Delta V \frac{\epsilon_r \epsilon_0 D}{d(\kappa^{-1})^2} \exp\left(-\left(1 + \frac{\lambda_s}{\kappa^{-1}}\right)\left(\frac{2D}{d\kappa^{-1}}\right)t\right) \quad (7)$$

It is only for the smallest voltage step measured ($\Delta V = 0.02\text{V}$) 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 pre-micellar 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

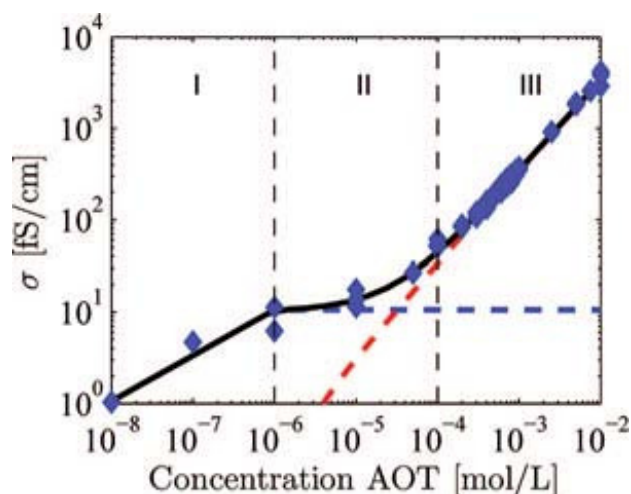


Fig. 3 Bulk conductivity of AOT in hexadecane as a function of surfactant concentration. The symbols indicate measurements. The blue line is the contribution of the monomer to the conductivity, and the red line is the contribution of inverse micelles. The black line is a sum of the contributions of the 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 to different structure of the 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, pre-micellar 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 ($\bar{n} = 10^{17} \text{ m}^{-3}$), 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 ($\bar{n} = 5 \times 10^{18} \text{ m}^{-3}$), the potential between the electrodes evolves with time indicating that the system is 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 non-aqueous solvents as well. It would be more appropriate to refer to the surfaces as polar or nonpolar, but given that that

595 the nomenclature is common in the literature, it will be main-
596 tained.

597 “Hydrophobic” surfaces are either polymeric colloids (pri-
598 marily PMMA or polystyrene (PS)), carbon black, or surfaces
599 treated with hydrophobic compounds. “Hydrophilic” surfaces
600 are oxides (primarily silica, TiO₂, alumina, or mica) or sur-
601 faces treated with hydrophilic compounds.

602 5.1 Hydrophobic surfaces.

603 Several approaches can be used to study charging of particle
604 surfaces. Some of these methods are not able to distinguish the
605 charge of the surface as they measure only the repulsive force
606 of the particles. Blinking optical tweezers measure the motion
607 of particles after the optical trap is turned off, and while repul-
608 sion is measured between polymer colloids and AOT, the
609 charge of the surface is not.^{41,67,69,112,122} There interparticle
610 repulsion does depend on surfactant concentration, and for
611 carboxylate-modified PS and PMMA in hexadecane, the force
612 is greater for 1 mM than for 10 mM AOT.^{41,112} Interparticle
613 forces have also been measured by following the motion of
614 an ensemble of particles with an optical microscope. In the
615 absence of surfactant, PMMA particles are found to aggregate
616 in dodecane, but the addition of AOT stabilizes the partic-
617 les. The magnitude of the surface potential is greatest at 12.5
618 mM.⁶¹ Atomic force microscopy (AFM) has also been used
619 to measure the surface force of hydrophobically-modified silica,
620 again without the ability to determine the sign of the surface
621 charge. High concentrations of surfactant were used, and the
622 magnitude of the surface potential was found to be greatest at
623 100 mM AOT.⁶⁰

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

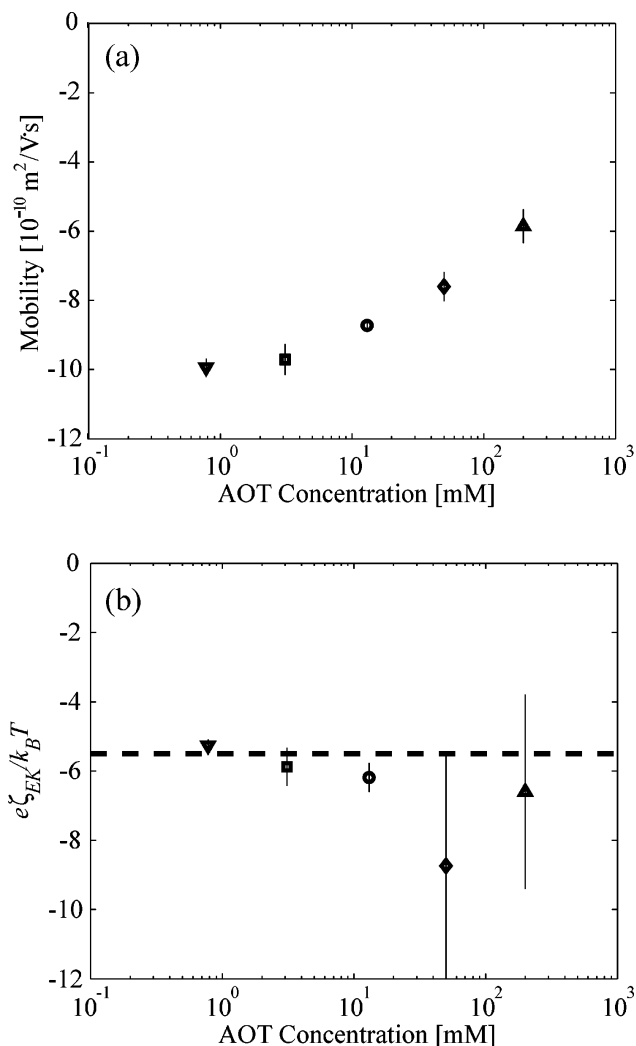


Fig. 4 The variation of (a) electrophoretic mobility and (b) dimensionless surface potential of PMMA particles of 780 nm radius in dodecane as a function of AOT concentration. The electrophoretic mobility is found to be negative and the magnitude decreases as surfactant concentration increases. The surface 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.

645 μ is found to increase to a maximum, around 1 mM, when it
646 either plateaus (in the case of ζ) or begins to decrease (in the
647 case of μ).^{47,67,120,123}

648 There have been fewer studies into charging hydrophobic
649 surfaces with surfactants other than AOT, and the results do
650 not agree as clearly. Span 85 surfactant was found to induce
651 a positive charge on PMMA in hexane using PALS, except
652 for low concentrations and high applied fields where the sign
653 reverses. The zero-field μ is found to decrease with increasing
654 concentration.⁵⁵ OLOA surfactant induces a negative charge
655 on surfaces, and if the concentration is varied, it goes through
656 a maximum in μ before decreasing.^{34,47} There are conflicting
657 results for the charging behavior of $Zr(Oct)_2$. It has been found
658 to charge particles both negatively⁴⁷ and positively.^{66,77} Given
659 that these studies are on three different hydrophobic surfaces
660 (PMMA, hydrophobically-modified silica, and carbon black),
661 the results indicate that the interaction of the surfactant with
662 the surface is important in determining the resulting charge.

663 5.2 Hydrophilic surfaces.

664 The surface charge of bare silica, a well-studied hydrophilic
665 surface which obtains charge in nonpolar solvents, in a so-
666 lution of AOT in decane has been found to reverse with in-
667 creasing concentration, as shown in Figure 5. At very low
668 AOT concentrations (0.001 mM), the electrophoretic mobility
669 measured with PALS decreased to a minimum at a surfactant
670 concentration 0.1 mM. The electrophoretic mobility became 0
671 again at 0.5 mM, increasing to a maximum near 5 mM when it
672 again decreases to plateau at 0. The authors measure the con-
673 ductivity of the dispersion and the supernatant fluid and find
674 that the supernatant is uncharged until 0.5 mM, reasoning that
675 this is the approximate point of full surface coverage.⁵⁸

676 Other studies of bare silica support the observation of nega-
677 tively charged surfaces at low concentrations; however, charge
678 reversal is not repeated. These other studies do not examine
679 such a wide range of concentrations, although they both reach
680 a maximum concentration of 10 mM where, as can be seen in
681 Figure 5, charge reversal should have occurred.^{47,73} Silica sur-
682 faces treated with, for example, cyano, amine, or hydroxyl sur-
683 faces have been observed to be charged, although the sign of
684 the charge depends on the surfactant and the surface function-
685 alization. Cyano-treated silica with AOT surfactant has been
686 observed to be negatively charged,¹²⁴ as has amino-treated
687 silica in the presence of either PIBS or Span surfactants.⁴⁸
688 Hydroxyl-treated silica, on the other hand, has been observed
689 to be positively charged in the presence of either PIBS or Span
690 surfactants.⁴⁸

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

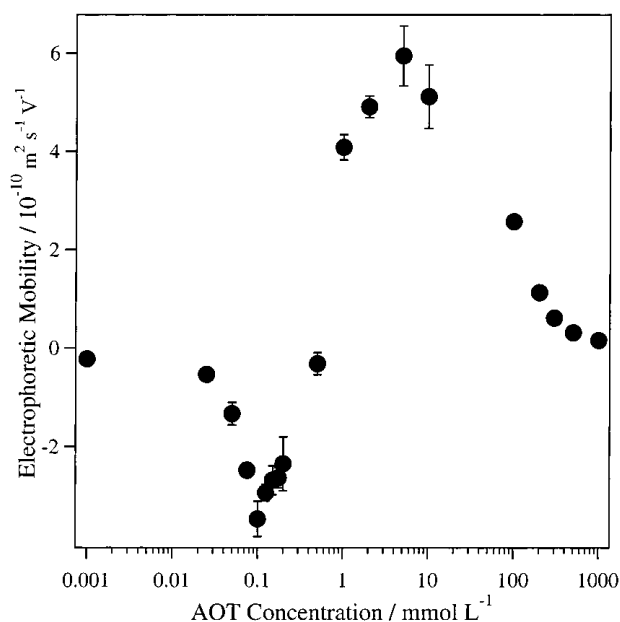


Fig. 5 The electrophoretic mobility (μ) of untreated silica particles of $3.5 \mu\text{m}$ radius at a concentration of 1 mg mL^{-1} in decane as a function of AOT concentration. The sign of μ is negative until the silica surface is saturated with adsorbed AOT when the sign of the charge reverses to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

695 been found to scale with the aqueous isoelectric point or point
696 of zero charge for five oxide particles: acidic particles in aque-
697 ous solutions are negatively charged in nonpolar liquids and
698 basic particles are positively charged in nonpolar liquids.⁷³

699 There is disagreement about the sign of the charge of
700 other oxide surfaces. Titania has been found to both posi-
701 tively^{28,64,73} and negatively²⁹ charged in solutions of AOT in
702 toluene and hexane. Given that the “effective” acidity of tita-
703 nia is similar to AOT and therefore it is poorly charged,⁷³
704 experimental errors may explain this discrepancy. Alu-
705 mina surfaces have been found to be negatively charged in
706 solutions of AOT in nonpolar solvents,^{29,73} although at high
707 concentrations the charge reverses.²⁹ If a different surfactant
708 (Span) is used, alumina surfaces are found to be positive.⁵²
709 The electrophoretic mobility of these systems was measured
710 either using PALS,⁷³ DP-OCT,⁶⁴ or electroacoustic measure-
711 ments.^{28,29,52} Using a surface force apparatus, mica has been
712 observed to be charged in a solution of AOT, although PALS
713 and FTIR measurements were required to confirm that sur-
714 faces were negatively charged.^{57,59,125}

715 6 Systematic studies of charged colloids

716 Given the range of charging behavior observed, it is important
717 to study how the magnitude and sign of charge on colloidal⁷⁴⁵
718 surfaces varies with the chemistry of the particle and the sur-⁷⁴⁶
719 factant in solution. In order to identify the origin of these dif-⁷⁴⁷
720 ferences, systematic studies of different types of colloids and⁷⁴⁸
721 surfactants are essential to distinguish between the influences⁷⁴⁹
722 of each component. Several recent publications have made⁷⁵⁰
723 systematic variations of either the surfactant or colloid surface⁷⁵¹
724 in a nonpolar liquid, and a few examples are highlighted here.⁷⁵²

725 Two studies by Berg *et al.*^{48,73} exemplify how systematic⁷⁵³
726 modifications of the surfactant and particle can be used to sup-⁷⁵⁴
727 port acid-base interactions as the origin of charge on oxide⁷⁵⁵
728 particles in nonpolar liquids. By using one surfactant (AOT)⁷⁵⁶
729 to charge a variety of mineral oxides, it is possible to deter-⁷⁵⁷
730 mine how the relative aqueous acidity of the particle deter-⁷⁵⁸
731 mines the charge in nonpolar liquids. The results, shown in⁷⁵⁹
732 Figure 6, indicate that the sign and magnitude of the elec-⁷⁶⁰
733 trophoretic mobility of the oxides in isoparaffin depends on⁷⁶¹
734 the aqueous isoelectric point (IEP). The authors find similar⁷⁶²
735 results for the aqueous point-of-zero charge. By performing⁷⁶³
736 a study where only one variable is changed, it is possible to⁷⁶⁴
737 assign an “effective pH” for the AOT-isoparaffin system of 4,⁷⁶⁵
738 the IEP where the electrophoretic mobility equals 0.⁷³⁷⁶⁶

739 By modifying both the surfactant and the particle, a re-⁷⁶⁷
740 lationship between relative aqueous acidity or basicity and⁷⁶⁸
741 the charge in nonpolar systems has been determined. Acidic⁷⁶⁹
742 (Span 80) and basic (OLOA 11000) surfactants are mixed with⁷⁷⁰
743 acidic and basic silica particles in isoparaffin. The basic sil-⁷⁷¹
744 ica surface is positive in the presence of the acidic surfactant.⁷⁷²

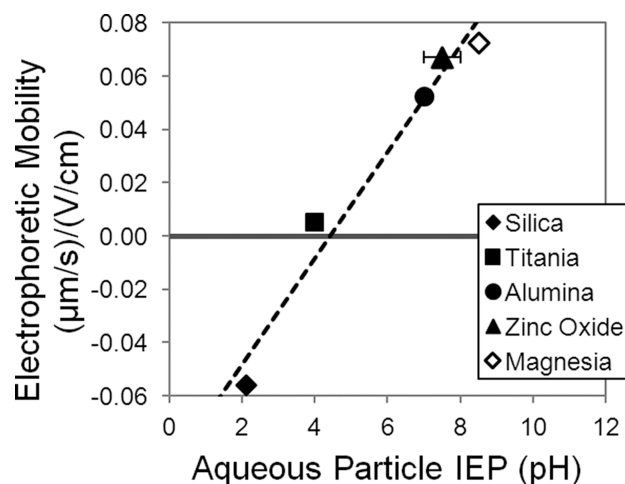


Fig. 6 The maximum electrophoretic mobility of a series of metal oxides in isoparaffin as a function of their isoelectric point (IEP). There is a nearly linear correlation between the mobility in nonpolar solvents and the aqueous acidity or basicity. Reprinted with permission from Gacek *et al.*⁷³ Copyright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

745 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 parti-
cle 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. Par-
ent *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 vari-
able in controlling the ability of the surfactant to form charges
in nonpolar liquids and to stabilize electrophoretic ink disper-
sions is the length of the amine chain in the headgroup, as
shown in Table 2. There is a trend in the ability of the sur-
factant to charge surfaces for larger PIBS; for amine chain
lengths between two and four, the ζ potential of the ink de-
creases 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 poten-
tial, and the anhydride form has a ζ potential near that of the
di-amine form, despite it not forming charged micelles in so-

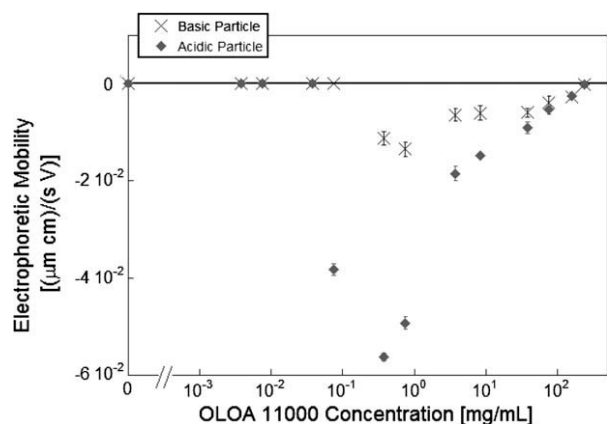


Fig. 7 Electrophoretic mobility of basic and acidic silica particles of 125 nm radius at a concentration of 2.5 mg mL^{-1} in the presence of basic OLOA 11000 surfactant. While both particle surfaces are negatively charged, the magnitude of the charge on the acidic surface is greater. The error bars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

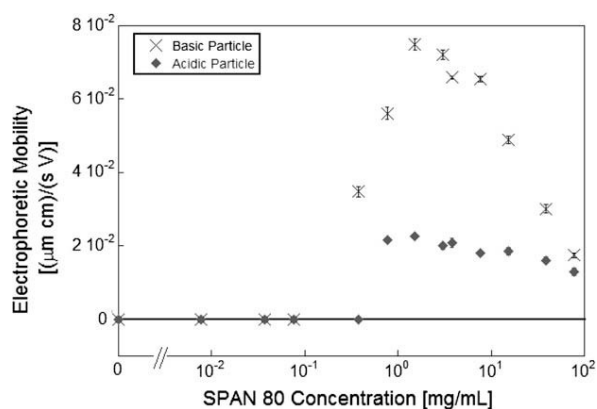


Fig. 8 Electrophoretic mobility of basic and acidic silica particles of 125 nm radius at a concentration of 2.5 mg mL^{-1} in the presence of acidic Span 80 surfactant. While both particle surfaces are positively charged, the magnitude of the charge on the basic surface is greater. The error bars are 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 $\text{Zr}(\text{Oct})_2$). 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



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.



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



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

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

921 The charge on hydrophilic and hydrophobic TiO₂ as well as
922 carbon black can be explained using a preferential adsorption
923 model. Bare TiO₂ is found to be positively charged with a de-
924 creasing ζ potential with increased concentration. The oxide
925 surfaces have a higher affinity for water or the “hard” ion Na⁺
926 and so obtain a positive charge. AOT⁻ hemimicelles form
927 on the surface with the charged head group attached to the
928 cations. As the surfactant concentration increases, the water
929 on the surface is displaced and migrates into inverse micelles.
930 The AOT chains adsorb on the surface to form a monolayer
931 atop the Na⁺ cations. For the hydrophobic TiO₂, the prefer-
932 ence for adsorption is reversed, and the surface charge is now
933 negative with an increasing ζ potential with increased concen-
934 tration. At low surfactant concentrations, the surfactant ad-
935 sorbs on the particle surface forming hemimicelles. The nega-
936 tive surface charge arises from the Na⁺ ions preferring the
937 inverse micelle core to the hemimicelle boundary. As the sur-
938 factant concentration is increased, a more concentrated layer
939 of surfactant forms on the surface. This layer can extend be-
940 yond one monolayer and can sustain dissolved counterions in
941 the increasingly hydrophilic environment, leading to the de-⁹⁶⁶
942 crease in the ζ potential.⁶⁴ A similar variation is found for⁹⁶⁷
943 the ζ potential with surfactant concentration in a suspension⁹⁶⁸
944 of carbon black in a solution of AOT in toluene. The same⁹⁶⁹
945 model was found to be appropriate.⁷⁰ A preferential adsorp-⁹⁷⁰
946 tion model can also explain the charge of PS colloids in solu-⁹⁷¹
947 tions of AOT in dodecane by considering the monolayer pack-
948 ing of adsorbed inverse micelles.¹²³

949 The above studies infer the mechanism of charge formation
950 indirectly; however, it is useful to directly probe the location⁹⁷³
951 of the surfactant in colloid-surfactant mixtures. SANS was⁹⁷⁴
952 recently used to study the adsorbed surfactant layer. PMMA⁹⁷⁵
953 particles were contrast-matched with the solvent by preparing⁹⁷⁶
954 them in a mixture of H-dodecane (C₁₂H₂₆) and D-dodecane⁹⁷⁷
955 (C₁₂D₂₆) so that no scattering from the particle is observed.⁹⁷⁸
956 By observing the scattered intensity of a solution of AOT⁹⁷⁹
957 alone and of AOT in the presence of PMMA particles, it is⁹⁸⁰
958 possible to ascertain the structure of the adsorbed layer. Fig-⁹⁸¹
959 ure 9 shows the results from this experiment. As can be seen,⁹⁸²
960 at a higher AOT concentration, the scattered intensity at low-⁹⁸³
961 q values is much greater, due to the adsorbed surfactant. By⁹⁸⁴
962 assuming that the AOT layer is the thickness of one molecule,⁹⁸⁵
963 the inner radius of the shell can be calculated and correlates⁹⁸⁶
964 with the inner radius of the PMMA particle. This indicates⁹⁸⁷
965 that the AOT adsorbs within the stabilizing PHS layer. In⁹⁸⁸

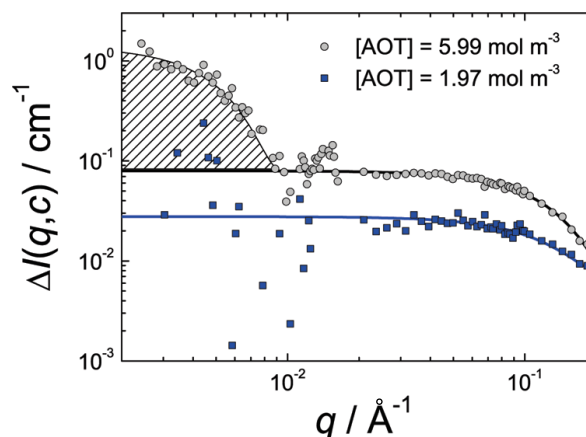


Fig. 9 The difference between the intensity scattered by a mixture of PMMA/AOT at two AOT concentrations. The PMMA particles are 46 nm in diameter at a volume fraction of 0.02. The scattering at high q is due to micelles, and the solid line shows the expected scattering due to this species alone. The 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 believed to be due to the presence of adsorbed surfactant. Reprinted with permission from Kemp *et al.*¹²⁰ Copyright 2010 American Chemical Society.

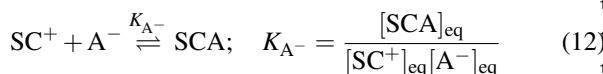
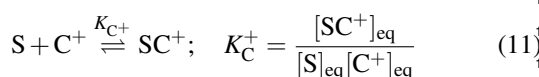
this system, the AOT molecules are concluded to have adsorbed individually within the stabilizing layer rather than as micelles. The mechanism of charge formation, therefore, is that individual AOT molecules adsorb onto the PMMA surface which becomes charged when the Na⁺ counterion is solubilized in an inverse micelle.¹²⁰

972 7.3 Site-binding mechanism.

A site-binding model has recently been employed to 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-

989 erence of positively charged species at higher concentrations¹⁰³¹
990 Then at even higher concentrations, the negatively charged
991 species in the double layer neutralize the positive surface.^{58 1032}

992 This explanation is qualitative, though two groups have em-
993 ployed a more quantitative site-binding model. This model¹⁰³³
994 was first proposed by Kitahara *et al.* and considers the equi-
995 librium constants for binding at surface sites.^{128 1036} Recent stud-
996 ies have used this approach to explain the charge induction¹⁰³⁷
997 of Zr(Oct)₂ in isoparaffin with copper phthalocyanine (CuPc)¹⁰³⁸
998 with PVA or resin^{74,76} or in silicone oil with carbon black.^{77,1039}
999 The explanation for the presence of charge is similar in the¹⁰⁴⁰
1000 three papers, so only the mechanism as discussed by Jenk-
1001 ins *et al.* will be presented. The system consists of surface
1002 groups S and an ionizable, dissociating surfactant CA, where¹⁰⁴²
1003 the cation C⁺ adsorbs first. There is water in the system, but it
1004 is not considered to adsorb and only serves as a catalyst for the¹⁰⁴³
1005 formation of charge. The chemical equilibria and related equi-
1006 librium constants for this generalized system are given below.¹⁰⁴⁴
1045



1007
1008 It is possible to express the surface charge density (σ_s) in terms¹⁰⁵⁴
1009 of these equilibrium constants, and σ_s is defined as the product¹⁰⁵⁵
1010 of the elementary charge (e), the number of surface sites (N_s),¹⁰⁵⁶
1011 and the fraction of charged sites (θ_{charge}) which can be defined¹⁰⁵⁷
1012 in terms the equilibrium constants and concentrations.
1058

$$1059 \sigma_s = eN_s\theta_{\text{charge}} \quad (13) \quad 1060$$

1061
1013 From measurements of σ_s as a function of surfactant concen-¹⁰⁶²
1014 tration, it is possible to determine values for the equilibrium¹⁰⁶³
1015 constant for the surface reaction to form charged species and¹⁰⁶⁴
1016 neutralized species. Two assumptions were required to do this¹⁰⁶⁵
1017 that Zr(Oct)₂ dissociated into three ions (ZrO²⁺ and two Oct⁻)¹⁰⁶⁶
1018 and the equilibrium concentration of Zr(Oct)₂ was equal to¹⁰⁶⁷
1019 that in the bulk due to the large Debye length. The calculated¹⁰⁶⁸
1020 equilibrium constant for the adsorption of ZrO²⁺ is approxi-¹⁰⁶⁹
1021 mately 11 orders of magnitude lower than for the adsorption¹⁰⁷⁰
1022 of two Oct⁻ ions to neutralize the surface, which would be ex-¹⁰⁷¹
1023 pected given that the formation of charged species in nonpolar¹⁰⁷²
1024 media would not be favored. By adjusting the concentration¹⁰⁷³
1025 of water in the system, the formation of charged ZrO²⁺ sur-¹⁰⁷⁴
1026 face sites was found to be more favorable in the presence of¹⁰⁷⁵
1027 higher concentrations of water. This could propose two mech-¹⁰⁷⁶
1028 anisms (either surface water or micellized water enhancing the¹⁰⁷⁷
1029 dissociation of surfactant), though the two could not be distin-¹⁰⁷⁸
1030 guished.^{76 1079}

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 non-polar 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 displays¹²¹ 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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