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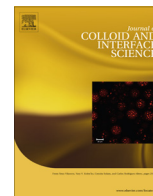
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Short Communication

The effects of counterion exchange on charge stabilization for anionic surfactants in nonpolar solvents



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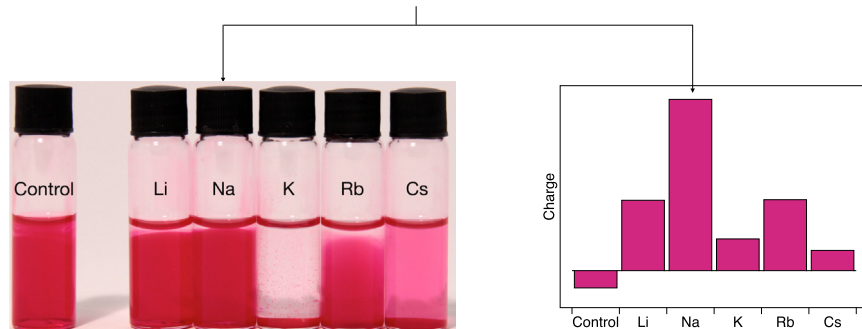
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GRAPHICAL ABSTRACT

Sodium AOT—Highly stable and highly charged PMMA latexes



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ABSTRACT

Hypothesis: Sodium dioctylsulfosuccinate (Aerosol OT or NaAOT) is a well-studied charging agent for model poly(methyl methacrylate) (PMMA) latexes dispersed in nonpolar alkane solvents. Despite this, few controlled variations have been made to the molecular structure. A series of counterion-exchanged analogs of NaAOT with other alkali metals (lithium, potassium, rubidium, and cesium) were prepared, and it was expected that this should influence the stabilization of charge on PMMA latexes and the properties of the inverse micelles.

Experiments: The electrophoretic mobilities of PMMA latexes were measured for all the counterion-exchanged AOT analogs, and these values were used to calculate the electrokinetic or ζ potentials. This enabled a comparison of the efficacy of the different surfactants as charging agents. Small-angle scattering measurements (using neutrons and X-rays) were performed to determine the structure of the inverse micelles, and electrical conductivity measurements were performed to determine the ionized fractions and Debye lengths.

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Findings: Sodium AOT is a much more effective charging agent than any of the other alkali metal AOTs. Despite this, the inverse micelle size and electrical conductivity of NaAOT are unremarkable. This shows a significant non-periodicity in the charging efficiency of these surfactants, and it emphasizes that charging particles in nonpolar solvents is a complex phenomenon.

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1. Introduction

Poly(methyl methacrylate) (PMMA) latexes stabilized by poly (12-hydroxystearic acid) (PHSA) brushes charged by the anionic surfactant Aerosol OT (NaAOT, sodium dioctylsulfosuccinate) are excellent model systems for studying the nature of charged colloids in nonpolar solvents [1–12]. Despite the many studies of these latexes using a variety of techniques, few variations to the surfactant structure have been explored [13]. There has been little attempt to study the highly polar portion of the surfactant molecule, the metal counterion. Octanoate surfactants with either calcium or zirconate surfactants have been used [2,4,14], but there has been no attempt to compare them in a single study. Kitahara et al. have studied varying the counterion of AOT surfactants, and they investigated a range of monovalent and divalent metals but without any control [15].

In this Short Communication, a systematic series of dioctylsulfosuccinate surfactants with different inorganic counterions are studied, including the commercially available sodium form. A series of counterion-exchanged AOT surfactants with alkali metals (lithium to cesium) have been prepared and used as charging agents for PMMA latexes in dodecane. Collectively these surfactants will be referred to as MAOTs (metal AOTs). These metals were chosen due to the high solubility of the surfactants in this nonpolar solvent. The electrophoretic mobilities of surfactant-charged latexes were measured, the structures of the surfactant aggregates were studied by small-angle scattering (both neutrons and X-rays), and the electrical conductivities of surfactant solutions were determined. Although sodium AOT is found to be the most effective charging agent, it is not apparent why this should be the case: sodium is not the largest or smallest alkali metal ion. The properties of MAOT surfactants in solution are insufficient to explain the differing abilities of the surfactants to charge latexes, and this emphasizes the complex interactions that dictate the charge of species of nonpolar solvents.

2. Experimental

2.1. Materials

2.1.1. Surfactant preparation

Counterion-exchanged surfactants were prepared using two different methods. Commercial sodium dioctylsulfosuccinate (NaAOT, 98%, Aldrich) was used as a precursor for all surfactants. LiAOT, KAOT, and RbAOT were obtained from an acid-base neutralization, by combining the acid form of NaAOT with an alkali metal hydroxide base [16]. CsAOT was obtained from a salt metathesis reaction between NaAOT and CsCl [17,18]. All surfactants were purified by dissolving in anhydrous diethyl ether centrifuging for 30 min at 6000 rpm (Centurion 3000) to remove any insoluble impurities. Methods and purity are given in the [Electronic Supporting Information](#).

2.1.2. Dispersion and solution preparation

MC1 and MC2 latexes were a gift from Merck Chemicals Ltd. and were prepared using the method described by Antl et al. [19]. Details are given in the [Electronic Supporting Information](#).

Latex dispersions and surfactant solutions were prepared in organic solvents as described in the text and left to equilibrate for 24 h before analysis. Dodecane ($\geq 99\%$, Sigma–Aldrich) was purified over basic alumina to remove polar impurities [20] and stored over molecular sieves prior to use. Cyclohexane ($\geq 99.7\%$, Sigma–Aldrich) and cyclohexane- d_{12} (>99.50 atom % D, Apollo Scientific) were used as supplied.

2.2. Methods

2.2.1. Phase-analysis light scattering (PALS)

Electrophoretic mobilities were measured using either a Malvern Zetasizer Nano Z or Nano ZS with a universal dip cell electrode. The applied field strength used was either 1.0×10^4 V m $^{-1}$ or 2.0×10^4 V m $^{-1}$ depending on the quality of the phase plots. Higher field strengths were preferred to measure mobilities of unstable samples. Five runs of 20 measurements were performed, and the average was used.

2.2.2. Small-angle scattering

Neutron scattering measurements were performed on two instruments at the ISIS Pulsed Neutron Source (UK): Sans2d [21], using a previously reported instrument configuration [22], and LOQ [23]. X-ray scattering measurements were performed using the beamline I911-SAXS at Max IV Laboratory (Sweden) [24]. Further details are given in the [Electronic Supporting Information](#).

2.2.3. Electrical conductivity

Conductivities in nonpolar solvents were measured using a model 627 conductivity meter (Scientifica, Princeton, NJ). The instrument consisted of a stainless steel cup probe that was fully immersed in a 2 mL volume of sample.

3. Results and discussion

The efficacy of MAOT surfactants as charging agents will be considered first. The electrophoretic mobilities were measured using PALS, and the stabilities of the latexes determined visually. Possible origins for the observed differences will then be considered. The sizes and shapes of the surfactant inverse micelles were determined using SANS and SAXS, and the electrical conductivity of solutions was measured.

3.1. Latex charge

The charge of PMMA latexes (MC1) was determined electrokinetically using PALS. The electrophoretic mobilities (μ) were then converted to the electrokinetic or ζ potentials. The ζ potential is a more direct comparison of the magnitude of the charge than the electrophoretic mobility, particularly in systems like these where the solution ionic strength varies dramatically (see Section 3.3). Mobilities were converted to potentials using the criteria given by Delgado et al. [25]. For ζ potentials with a magnitude <50 mV, the Henry equation with the Ohshima expression for $f(\kappa a)$ was used [26,27]. For ζ potentials with a magnitude >50 mV, the O'Brien and White method was used [28]. This is necessary

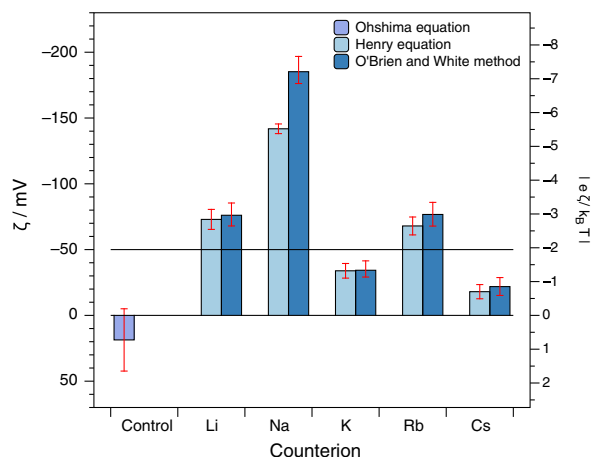


Fig. 1. The ζ potential of MC1 PMMA latexes both without surfactant and charged by 10 mM solutions of MAOT surfactants in dodecane. The electrophoretic mobilities were measured using PALS, and these values were converted to ζ potentials, using Ohshima's expression for charged colloids in a salt-free medium (for plain PMMA latexes) [29,30] or the Henry equation [26,27] and the O'Brien and White method [28] (for surfactant charged PMMA latexes). The data clearly demonstrate the differences in charging effectiveness between the different counterions: sodium is by far the most effective.

because the double layers become polarized for high ζ potentials, and the Henry equation underestimates the actual potential. For PMMA latexes without surfactant, the only ions in the background are counterions, and the unscreened Coulomb potential (ψ_s) can be regarded as the ζ potential. Ohshima has given analytical expressions to convert the electrophoretic mobility of charged colloids in a salt-free medium to the ζ potential; it now depends on the volume fraction [29,30]. This expression is appropriate for dilute dispersions and low surface charges, both of which are satisfied by the dispersion of plain PMMA latexes.

The ζ potentials for PMMA latexes both without surfactant and charged by 10 mM solutions of MAOT surfactants in dodecane are shown in Fig. 1. The line at -50 mV shows the ζ potential above which the O'Brien and White method must be used. This concentration of

surfactant is much greater than the CMC for inverse micelle formation of NaAOT in alkane solvents [22,31]. The latexes are charged with a negative polarity by all the surfactants, as might be expected from literature on NaAOT [1,2,4,5,9,11,12]. The effect of changing the surfactant counterion is immediately apparent, and sodium is by far the most effective charging agent. Lithium and rubidium are similarly effective, and potassium and cesium are relatively ineffective.

The difference in the charging abilities of the surfactants has a corresponding effect on the stability of the latexes. This has been observed on studies of PMMA latexes charged by NaAOT. For example, dispersions of latexes are known to be more ordered and particles more separated in the presence of NaAOT [1]. The sedimentation of magenta-dyed PMMA latexes (MC2) in 10 mM solutions of MAOT surfactants was followed over 24 h, and images of the latexes taken as a function of time are shown in Fig. 2.

LiAOT and NaAOT charged latexes are colloiddally stable. They sediment slightly over 24 h, but this is due to the density difference between the latexes and the solvent. This is unsurprising for NaAOT, in particular, given observations in the literature discussed above. Latexes charged by MAOT surfactants with counterions larger than sodium all sediment over 24 h. KAOT and CsAOT are particularly unstable. This is a consequence of both the low magnitude ζ potential as well as the short screening length (Section 3.3). The addition of surfactant, in the case of the LiAOT and NaAOT systems, should add an additional stabilizing potential arising from Coulombic repulsion, making the particles more stable than without surfactant. For the KAOT, RbAOT, and CsAOT systems, it is not clear why latexes with charging agent added should be less stable than the latexes without surfactant. This may be a consequence of the short screening length, which reduces the lengthscale of the Coulombic repulsion. The possibility that there may be a small number of charges on plain PMMA latexes has been proposed in the literature [2,6,32–34]. If present, these charges would be unscreened, adding a small but long-range repulsion to the plain latexes.

It is worthwhile considering LiAOT and NaAOT charged latexes further, as they are similarly stable (Fig. 2) and their inverse micelle properties are similar (Sections 3.2 and 3.3). The electrophoretic mobilities (μ) were measured as a function of concentration (1–32 mM) and were converted to ζ potentials using the

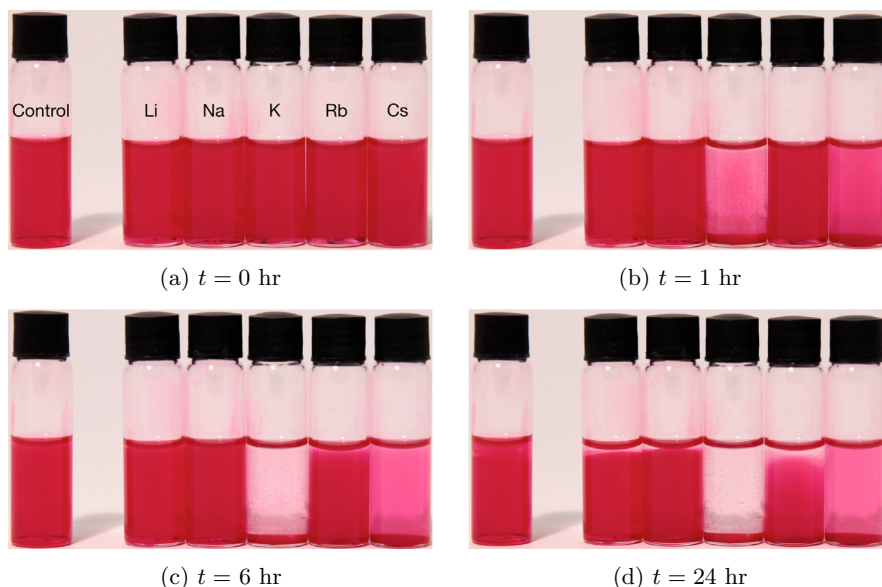


Fig. 2. Stability of dispersions of magenta-dyed MC2 PMMA latexes both without surfactant and charged by 10 mM solutions of MAOT surfactants in dodecane. The sedimentation of latexes was monitored over 24 h. LiAOT and NaAOT charged latexes are colloiddally stable and sediment slightly over the observation time due to the density difference between the latexes and the solvent. KAOT, RbAOT, and CsAOT charged latexes are unstable to differing degrees; this is due to the low magnitude ζ potential and the short screening length.

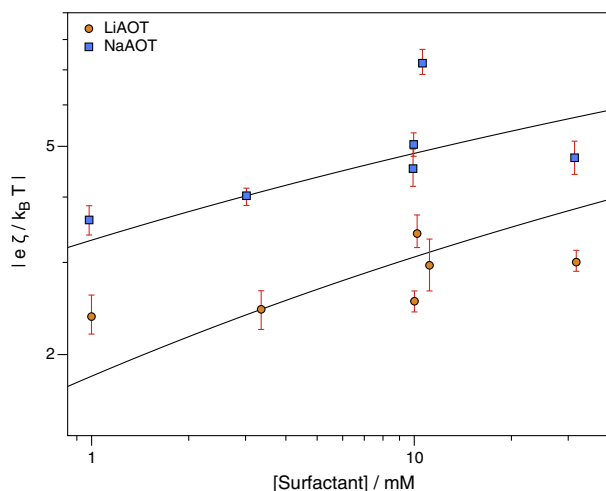


Fig. 3. The reduced ζ potentials ($|e\zeta/k_B T|$) as a function of concentration for LiAOT and NaAOT charged PMMA latexes in dodecane. The electrophoretic mobilities were measured using PALS, and these values were converted to ζ potentials using the O'Brien and White method [28]. The predicted ζ potentials are calculated using the equation given by Sainis et al. [6]. As in Fig. 1, NaAOT is the more effective charging agent.

O'Brien and White method [28], and the values are shown in Fig. 3. The calculated ζ potentials were calculated using an expression given by Sainis et al. [6] that relates changes in surface potential to inverse micelle concentrations. ζ_0 and c_0 are reference potentials and concentrations (3 mM in these calculations), and the equation is solved in terms of the Lambert W function, $W(z)$ [35].

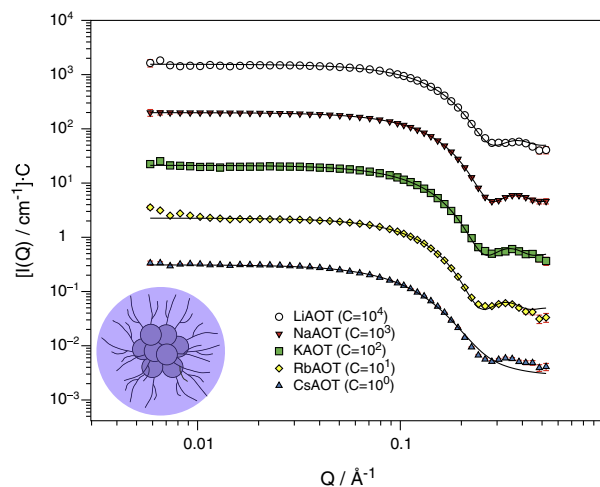
$$\left| \frac{e\zeta}{k_B T} \right| = 2W \left\{ \frac{1}{2} \left| \frac{e\zeta_0}{k_B T} \right| \cdot e^{\frac{1}{2} \left| \frac{e\zeta_0}{k_B T} \right|} \cdot \sqrt{\frac{c}{c_0}} \right\} \quad (1)$$

The calculated potentials match the measured ones well, and the deviations at higher concentrations can be explained by a known asymptote for the potential at high surfactant concentrations [6,9]. It is immediately apparent that the surface potentials are greater for NaAOT than LiAOT at all surfactant concentrations. This demonstrates that the efficacy of NaAOT is not something specific to a solution concentration of 10 mM (Fig. 1) and that it is indeed the most effective alkali surfactant charging agent.

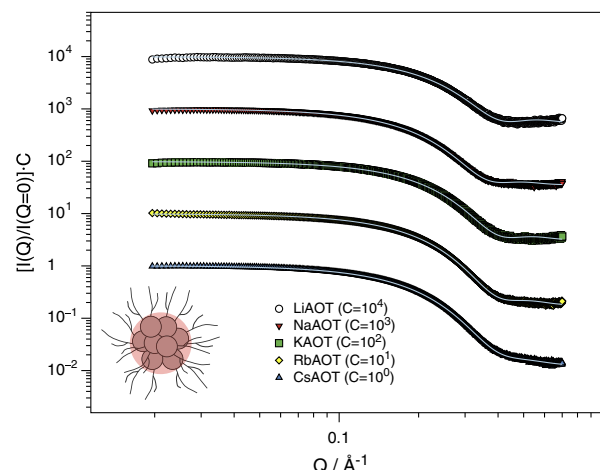
The data in Figs. 1–3 show clear differences between the charging abilities of the MAOT surfactants. Experiments were designed to keep all parameters, except the counterion, identical. This shows obvious counterion effects. The origin of these differences is not immediately apparent. As the organic dioctylsulfosuccinate anion is the same for all the surfactant charging agents, the interaction between this species and the PMMA latexes will be the same. The difference between the charge and stability of the different samples, therefore, must be due to the interaction between the metal counterions and the surfactant organic ions. Studying these interactions can be simplified by considering the surfactant solutions in the absence of particles. The properties of the solutions (inverse micelle structure and the electrical conductivity) will now be considered.

3.2. Inverse micelle structure

The structural properties will be considered first. Changing counterion is known to have an effect on the structure of water-in-oil microemulsions, specifically that metals with large hydrated radii tend to lead to elongated, non-spherical droplets [17]. The hydrated radii of the alkali ions increase with atomic number, as they are all monovalent metals; the ionic radii also increase [36].



(a) SANS of 10 mM MAOT solutions in cyclohexane- d_{12}



(b) SAXS of 10 mM MAOT solutions in cyclohexane

Fig. 4. SANS and SAXS curves for MAOT surfactant inverse micelles in cyclohexane (appropriately isotopically-labeled for the radiation used). SANS is sensitive to the entire inverse micelle size (polar cores plus the alkyl tails); SAXS is sensitive to the polar core size. The inset schematics show the sensitivity to the different contrasts for each technique. The curves are all fit to a spherical form factor [41,42] with a Schulz size distribution [43]. The inverse micelles have a radius between 13 and 17 Å from SANS fitting and a core radius of ~ 10 Å from SAXS. Curves are offset by a constant C (given in the legend) for clarity.

The structures of the surfactant inverse micelles are first determined in cyclohexane, as lower carbon number solvents are known to be better at solubilizing surfactants (for example, higher w -ratio microemulsions can be formed [37,38]). Both SANS and SAXS measurements were performed to fully characterize the inverse micelles. SANS is sensitive to the whole droplet (owing to isotopic contrast); SAXS is sensitive to the inverse micelle core (scattering arises from electron density differences). Performing both SANS and SAXS measurements is a powerful approach that can be used to determine the structure of dispersions in nonpolar solvents [39]. Scattering curves for all the surfactants using both types of radiation are shown in Fig. 4. The fit dimensions (a core of radius ~ 10 Å with a shell thickness of ~ 6 Å) are broadly consistent with the literature [40].

The scattering curves for all MAOT surfactants are very similar, as shown in Fig. 4. All curves are well fit using a spherical form factor [41,42], and there is a relatively narrow size distribution (Schulz distribution [43]). The fit numerical values are shown in the Electronic Supporting Information. The similarities between

Table 1
Electrical conductivities and ionic parameters of MAOT surfactants in dodecane (10 mM).

Surfactant	$\sigma/(\text{pS cm}^{-1})$	Ionization fraction, $\chi/10^{-5}$	$\kappa^{-1}/\mu\text{m}$
LiAOT	28.2 ± 0.8	2.2 ± 0.3	0.78 ± 0.03
NaAOT	26 ± 1	2.2 ± 0.3	0.80 ± 0.03
KAOT	62.3 ± 0.5	10 ± 1	0.47 ± 0.01
RbAOT	114.9 ± 0.8	18 ± 2	0.347 ± 0.009
CsAOT	1264 ± 8	870 ± 60	0.086 ± 0.001

the surfactant inverse micelles are clear. The size distribution of the entire droplet (SANS) is low; all surfactants (except cesium) do not require including size dispersity to fit the data. The core radii (SAXS) are also essentially identical (10 Å). As the size of the metal increases there are two effects. The size of the whole droplet (SANS) increases slightly. However, instead of an increase in size, cesium AOT seems to increase in size distribution. Additionally, the width of the size distribution of the core (SAXS) increases with ion size. The surface area per molecule at the surfactant chain-oil interface also varies (calculated using the method of Eastoe et al. [17] and shown in [Electronic Supporting Information](#)), and this is known to relate to the morphology of the aggregates. For spherical microemulsion droplets, for example, the area of a surfactant molecule at this chain-oil interface is $\sim 200 \text{ \AA}^2$, decreasing for cylindrical microemulsion droplets [17]. LiAOT, NaAOT, and KAOT all have surface areas at the interface of $\sim 200 \text{ \AA}^2$, whereas RbAOT and CsAOT have interfacial areas of $\sim 180 \text{ \AA}^2$. These values are not as low as calculated for cylindrical water-in-oil microemulsions and inverse micelles [17], which have values approaching 100 \AA^2 , but it does show that the interfaces are different when larger metals are used as counterions. This suggests that larger metals do modify the interface between the core and the inner layer of the alkyl tails, but for the most part, the surfactant tails can accommodate any differences.

SANS measurements were also performed in dodecane- d_{26} , the solvent used for the electrophoresis measurements (Section 3.1). Scattering curves and fit numerical values are shown in the [Electronic Supporting Information](#). The scattering of LiAOT, NaAOT, KAOT, and RbAOT are all similar, whereas the scattering of CsAOT is qualitatively different. The surfactants, CsAOT excluded, are fit to spherical form factors [41,42] without any distribution in the size. The scattering from CsAOT was best fit by an ellipsoidal form factor [44,45]. These results are similar to those in cyclohexane: droplet radii increase as the size of the metal ion increases.

There are counterion effects on the structure of inverse micelles, but these are not dramatic. Larger metals form slightly larger inverse micelles with less well-defined cores. Sodium, however, does not seem exceptional in terms of the size of inverse micelles. This seems unlikely to be the origin of its increased ability to charge PMMA latexes.

3.3. Electrical conductivity

The electrical conductivity of inverse micellar solutions of MAOT surfactants in dodecane will now be considered. The conductivity of NaAOT in alkanes has been previously studied by several groups [1,4,6,9,46]. Few have studied surfactants other than NaAOT [4,46,47]. There are very limited studies in the literature exploring counterion effects on the conductivity of AOT-based surfactants as dry inverse micelles or water-in-oil microemulsions [48,49]. The conductivities of 10 mM MAOT solutions in dodecane are shown in [Table 1](#). The conductivities of LiAOT and NaAOT are similar, but the magnitudes of the conductivities significantly increase for larger metals. This can be clearly seen in [Table 1](#), where the conductivities jump an order of magnitude per step between KAOT and CsAOT.

The conductivity values are instructive, but more information can be gained by calculating other ionic properties of solution: the fraction of inverse micelles that are ionized (χ) and the Debye screening length (κ^{-1}). These properties account for differences in the ion size, which is important to make a more direct comparison between the surfactants.

The fraction of ionized inverse micelles can be calculated using Eicke's fluctuation theory, formulated for water-in-oil microemulsions [50]. The conductivity (σ) is a function of the elementary charge (e), the solvodynamic radius and volume of the charged species (r_i and v_i), the solution viscosity (η), the volume fraction of surfactant (ϕ), and χ .

$$\sigma = \frac{e^2}{6\pi r_i \eta v_i} \chi \phi \quad (2)$$

Previous conductivity measurements of NaAOT solutions in alkanes have calculated a value of χ of $\sim 10^{-5}$ [1,4,9,46]. The value for χ for NaAOT shown in [Table 1](#) is consistent with the literature. The values of χ are similar for LiAOT and NaAOT, and they increase rapidly as the counterion is changed from K to Cs, consistent with the increase in conductivity.

The Debye length (κ^{-1}) can also be determined from conductivity measurements, and this value is important as it relates to the lengthscale over which charges interact. All else being equal, more ions in solution decrease the Debye length due to increased ion screening. It can be determined from measuring the conductivity and, for monovalent ions in solution, can be defined either in terms of the number concentration of ions (n_i) or the conductivity (σ) and solution and ion properties (η and r_i) [25,46].

$$\kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{e^2 n_i}} \equiv \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{6\pi \eta r_i \sigma}} \quad (3)$$

Previous studies of NaAOT solutions in alkanes have calculated a value of κ^{-1} of $\sim 1 \mu\text{m}$ [1,4,7]. The value for NaAOT shown in [Table 1](#) is similar. As with the calculated values of χ , LiAOT and NaAOT are similar, and the Debye length decreases rapidly for larger counterions. This helps explain seemingly counterintuitive results discussed in Section 3.1. LiAOT and RbAOT charged latexes have similar ζ potentials ([Fig. 1](#)), but RbAOT charged latexes are slightly unstable whereas LiAOT charged latexes are not ([Fig. 2](#)). Even though they have the same charge, with a shorter screening length, the Coulombic repulsive barrier is less effective.

There are indeed counterion effects on the electrical conductivity of MAOT solutions in dodecane, but these do not correlate with the charging ability of the surfactants. NaAOT is not the most effective electrolyte, but AOT analogs with larger counterions are better electrolytes and worse charging agents. NaAOT is a much more effective charging agent than LiAOT, but they are equally good electrolytes. Therefore, this seems unlikely to be an origin for its effectiveness as a charging agent.

4. Conclusions

The selection of sodium as a counterion for the popular charging agent dioctylsulfosuccinate (AOT) seems a providential choice. Counterion-exchanged analogs of this surfactant (with all other alkali metals) are notably less effective charging agents. However, the origin of the enhanced ability of sodium to charge colloidal polymeric particles is unclear. Properties of surfactant solutions (inverse micelle size and electrolytic conductivity) do show counterion effects, but these tend to be monotonic. Sodium, in the middle of the alkali group, is unexceptional in both the size of inverse micelles and ion properties. Monotonically varying properties are expected based on fundamental chemical principles. For example,

ion size [36], first ionization energy [51], and infinite dilution ionic conductivity [52] are all periodic properties. Not all properties are periodic though. Both ΔH° and ΔG° for ion formation in aqueous solution for alkali metals are least negative for sodium [53]. This is not necessarily the origin of the ability of NaAOT to charge PMMA latexes, but it does show that properties of ions are not intrinsically periodic.

Charging particles in nonpolar solvents is a complex process and requires consideration of interactions between many species (surfactant inorganic and organic ions, surfactant organic ions and polymer particles, surfactant inorganic ions and polymer particles). The charge on particles arises from non-stoichiometric compositional imbalances in the particles, and this is controlled by the relative affinity of the inorganic and organic portions of the surfactant ions. Therefore, it seems that sodium represents an optimum balance between the two, making it a highly effective charging agent when used in combination with the dioctylsulfosuccinate anion.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcis.2015.11.062>.

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