The particle charging behavior of ion-exchanged surfactants in apolar media

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Graphical Abstract:

Abstract:

This paper investigates the effects of surfactant counterion electronegativity on the micellization and particle charging behavior of a series of ion-exchanged surfactants in apolar media. The sodium cation in Aerosol OT (AOT) was exchanged for four divalent cations and one trivalent cation, resulting in five AOT analogs. The critical micelle concentrations (CMCs) of each of these AOT analogs was measured by conductometric techniques. For each surfactant, dispersions were made with three different mineral oxides, spanning a range of points of zero charge (PZC), and their electrophoretic mobilities were measured. It was found that all five surfactants behaved as acids, charging all particles positively, with zeta potentials up to 201mV. It was also found, generally, that as the electronegativity of the surfactant head-group increased,

the imparted particle mobilities also increased. The trivalent AOT analog imparted higher mobilities than an electronegatively comparable divalent analog.

Keywords:

Reverse micelles; apolar media; particle charging; surfactant

1. Introduction:

Three major surfactant types have been of interest to the field of charging in nonpolar media: two non-ionic, viz. the Span series and polyisobutylene succinimides (PIBS), and one ionic, Aerosol OT. The Span series consists of an acidic sorbitan head-group, and varies in the length, number, and saturation of the tail groups. PIBS surfactants, such as the commercial OLOA 11000, impart charge to colloids through the basic, polyamine head-group. The ionic surfactant, Aerosol OT (NaAOT) is one of the most extensively studied. NaAOT has a head group consisting of a sodium ion bound to an SO_3^- group. This surfactant is of interest due to its hygroscopic nature, the ability to swell to large emulsion droplets, and its ability to form either normal or reverse micelles.[1] While NaAOT forms spherical reverse micelles in most apolar media[2], exchanging the sodium ion for another metal results in changes of the reverse micellar structure. Exchanging the sodium for divalent cations such as Mg^{2+} and Ca^{2+} still yields spherical reverse micelles, while Ni^{2+} and Zn^{2+} produce rod-like structures.[3] Upon swelling with water, the rod-like structures undergo a rearrangement to spherical droplets. The use of tri- and pentavalent cations- Al^{3+} , Fe^{3+} , and V^{5+} - yields reverse micelles that are ellipsoidal structures.[4]

These AOT analogs have been studied as viscosity modifiers in supercritical CO_2 systems[5–7], as templates for the synthesis of metal, polymer, and doped nanoparticles[8–10], as well as multi-phase reaction systems.[11,12] While NaAOT has been extensively studied as a particle charge control agent in apolar systems[13–15], the ion-exchanged analogs have only been briefly investigated. One study investigated Mn^{2+} and Co^{2+} analogs,[16] but was unable to determine a consistent particle charging mechanism for both analogs, suggesting that surfactant molecules could adsorb either head or tail down on the particle surface. A more recent study exchanged the Na^+ ion for four of the monovalent, alkali metals.[17] The authors did not find any trend in particle charging behavior with the size of the exchanged ion, instead finding that sodium was able to impart the largest charge to the polymer particles.

Given that NaAOT behaves as a slightly acidic surfactant, charging oxide particles similar to their charging in an aqueous medium with a pH of approximately 5, replacing the sodium ion with more electronegative, polyvalent cations, would be expected to yield AOT analogs of an increasingly acidic nature. Specifically, increasing the electronegativity of the head group, a surfactant should act as a stronger electron acceptor, and thus a stronger Lewis acid. The goal of this study was to test the extent to which ion-exchanged surfactants will charge mineral oxides, and to correlate their charging with effective acidity, as quantified by the electronegativity of the cation in the head-group. A secondary goal of this study was to determine the relative sizes of these reverse micelles to assist in the interpretation of the charging results.

2. Materials and Methods:

2.1 Synthesis of AOT Analogs

Solid sodium dioctyl sodium sulfosuccinate (NaAOT) was purchased from Fischer Scientific and used as received. The AOT analogs were synthesized using four divalent cations- Ba^{2+} , Mg^{2+} , Zn^{2+} , and Ni^{2+} - following increasing electronegativity from 0.9, to 1.2, to 1.6 and 1.9.[18] A final analog was prepared with a trivalent cation, Al^{3+} , with an electronegativity of 1.5. A saturated, ethanolic solution of NaAOT was slowly added to a saturated, aqueous solution of the metal nitrate salt and stirred continuously for one hour. The resulting mixture became cloudy with the insoluble analog surfactant. A liquid-liquid extraction into hexane was then performed to remove the AOT analog. This solution was then washed with deionized water five times to remove excess metal salt and unreacted AOT. The hexane solution was finally dried at 35°C for 72 hours, yielding a finished, waxy product.

The AOT analogs were then dissolved in Isopar™ L (Univar, Redmond, WA), a mixture of C_{11} to C_{14} isoparaffins. The Isopar was treated with molecular sieves for at least 24 hours prior to use in order to minimize the water content in the systems. For each of the five surfactants, a series of 15 concentrations was made ranging from 10^{-5} to 1wt% surfactant. The viscosity of these solutions was found to be independent of surfactant concentration under the range used in this study.

2.2 Characterization of AOT Analogs

Energy dispersive x-ray spectrometry (EDS) was performed on the synthesized surfactants in order to determine the coordination number of AOT^- tails to the metal cations. An FEI (Hillsboro, OR) Sirion-XL30 scanning electron microscope was used conjunction with an Oxford (Oxfordshire, UK) EDS instrument, and operated at 20kV and a working distance of 5mm. The elemental analysis measured the atomic percentages of the metal cation, as well as the single sulphur molecule in each AOT^- tail. Normalizing the percentages to those of the metal cations, one can determine the number of sulphur molecules per metal cation and therefore the tail coordination number of the synthesized surfactants. For each of the divalent cations, a sulphur-to-cation molar ratio of 1.9 ± 0.1 was measured, while the trivalent species had a ratio of 2.98 ± 0.02 was measured, indicating that the desired compounds had been produced.

Critical micelle concentrations (CMCs), in Isopar L, of the AOT analogs were measured using conductometric techniques, determined with a Dispersion Technologies DT700 Nonaqueous Conductivity Meter (Bedford Hills, NY), as outlined in a previous study.[19] The CMC was determined as the concentration at which the conductivity of the solution begins to scale linearly with surfactant concentration. In the pre-micellar region, the measured conductivities are low, but finite values which are independent of surfactant concentration. Other groups have measured pre-micellar conductivities which scale with the square root of the surfactant concentration[20–22] and it is likely that this region also exists in the present study, however the lower limit of detection of the DT700 prevents the accurate measurement of such behavior in these systems.

Structural information of the inverse micelles was obtained using small angle x-ray scattering (SAXS). A SAXS instrument (Anton-Paar, Austria) with a wavelength of 1.54 Å was used. Data were acquired using Fujifilm (Greenwood, SC) image plates and a Perkin-Elmer Cyclone (Covina, CA) image plate reader. The two-dimensional data were reduced to a one-dimensional,

intensity (I) versus scattering vector (q) plot using SAXSquantTM (Anton-Paar, Austria) software. It should be noted that this technique was used only to obtain qualitative trends with respect to reverse micellar core sizes. Due to the low- q limit of this instrument, quantitative values were not able to be obtained for several of the species.

2.3 Electrophoretic Mobility Measurements

Surfactant samples were prepared as previously described, with concentrations ranging from 10^{-5} to 1wt%. Three mineral oxide particles- 250nm silica (Fiber Optics Center Inc., New Bedford, MA), 300nm alumina (Baikowski, Charlotte, NC), and 300nm magnesia (US Nano, Houston, TX)- were used, with PZC's of 3, 7.5, and 10.7 respectively.[13] The particles were baked at 100°C for one hour before being added to the surfactant samples at loadings of 0.5mg per 25mL. These dispersions were allowed to sit for 12 hours before being sonicated and measured. Electrophoretic mobilities were determined using a Brookhaven Instruments (Holtsville, NY) ZetaPALS. Each sample was measured five times, and error bars were calculated using the average and standard deviation of the five measurements.

3. Results and Discussion

3.1 Characterization of the AOT Analogs

Figure 1 summarizes the CMCs of each of the AOT analogs. Figure 1a) is an example of the conductivity curve as a function of surfactant concentration, shown for the aluminum analog. For each concentration, the conductivity was measured 50 times, and error bars were calculated as the standard deviation of these measurements. Error bars cannot be seen on this plot, as they are of the order of 10^{-12} S/m, i.e., smaller than the data markers. Prior to the axis break at 10^{-3} mM, semi-log coordinates were used, and all conductivities were in the range of $3 \pm 2 \cdot 10^{-12}$ S/m, which is above the limit of detection of the instrument. At approximately 0.008mM, conductivity begins increasing linearly with concentration, indicating the formation and disproportionation of reverse micelles. Similar results were obtained for the other surfactants investigated.

Figure 1. a) Conductivity vs Al(AOT)₃ concentration plot used to calculate the CMC. Open circles (○) indicate pre-micellar conductivities, while closed circles (●) indicate post-micellar conductivities. The dashed line represents the linearly increasing region. b) Summary of CMC's for all five AOT analogs.

As shown in Figure 1b) CMCs of the surfactants ranged from approximately 0.008 to 0.03mM. No systematic trend in CMC with respect to cation electronegativity was observed. It may be noted that the trivalent analog, Al(AOT)₃, displayed a lower CMC than any of the divalent compounds.

Small angle x-ray scattering (SAXS) was performed on all five AOT analogs with a concentration of 1wt%, at which the surfactants were fully dissolved and the samples did not display any turbidity. The x-ray contrast (scattering length density) in these experiments was primarily between the metal cations in the head group and the hydrocarbon solvent. This made it such that any fitting of these profiles resulted in the radius of the reverse micellar cores. The intensity vs scattering vector (I vs q) profiles for all five surfactants are shown below in Figure 2.

Figure 2. SAXS profiles of all five AOT analogs at concentrations of 1wt%.

These scattering profiles were fit to a sphere form factor, for which a levelling out of the intensity at lower q values is expected. It can be seen in Figure 2 that only Ba(AOT)_2 exhibits this behavior. When fit using SasView software (www.sasview.org), core radii of 2.2nm and 1.4nm were calculated for the barium and aluminum analogs respectively. A rise in the scattering intensity of the aluminum analog can be observed at low- q values. While this may be indicative of larger structures, such as undissolved surfactant, it is unlikely that this is the case. All samples measured in this study were entirely transparent, with no measurable turbidity. Dynamic light scattering was performed on these samples, but was unable to detect any structures, large or small, due to the small size of the reverse micelles and poor refractive index contrast. Previously, groups have observed that bulk electrostatic interactions, such as between charged reverse micelles, can lead to such low- q increases in scattering intensity.[23] The other three surfactants did not exhibit this levelling behavior necessary to fit the profiles. This is due to the fact that the low- q limit of the instrument was reached before the profiles could level out. What it appears can be said about these three surfactants, is that they form larger reverse micelles than either the barium or aluminum analogs. Again, it is important to note that the authors only intend to use these scattering profiles to note the qualitative size differences between the various reverse micellar species.

3.2 Particle Charging Behavior

Figure 3 summarizes the particle charging capabilities of the AOT analog surfactants. Figure 3a) is a typical example of the charging behavior as a function of surfactant concentration. At concentrations below the CMC, no measurable mobilities are observed since no reverse micelles are present to stabilize the charges. As the concentration increases past the CMC the particle mobility increases to a maximum value, before decreasing again due to electrostatic screening by charged reverse micelles in the bulk solvent. Figure 3b) summarizes the maximum particle mobilities for each surfactant-particle pairing.

Figure 3. a) The particle charging behavior of Ni(AOT)₂ with three different mineral oxides. No charging is observed before the CMC is reached. Particle mobility increases to a maximum value before decreasing due to micellar screening. b) The maximum particle mobilities plotted as a function of the particle PZC for each of the five surfactants.

For all surfactants but one, the trivalent, aluminum surfactant, as the PZC of the particle increased, the maximum mobility that the surfactant imparted also increased. Al(AOT)₃ imparted the largest mobility to the alumina particles, which had a moderate PZC. It is worth noting that all imparted mobilities in this study were positive, and, in many cases, extremely large. The zeta potentials of these particles can be calculated using the Hückel equation, [24]

$$\zeta = \frac{3\eta U_E}{2\epsilon\epsilon_0}, \quad (\text{Equation 1})$$

where ζ is the zeta potential, η is the solution viscosity, U_E is the electrophoretic mobility, ϵ is the dielectric constant of the solution, and ϵ_0 is the dielectric permittivity of free space. The viscosities of these systems were measured and found to be independent of surfactant concentration up to 1wt%, therefore the pure solvent viscosity was used in these calculations. The equation is valid in these systems due to the large electric double-layers and small particle size ($\kappa a < 0.01$, where κ is the Debye parameter and a is the particle radius).[24] Zeta potentials imparted by the barium analog ranged from 31 ± 3 to 39 ± 4 mV, a range commonly seen in apolar systems. The nickel analog, however, produced zeta potentials up to 201 ± 4 mV! Table 1 summarizes the maximum zeta potentials obtained for each surfactant-particle pairing.

Table 1. Summary of maximum zeta potentials (in mV) for each surfactant particle pairing

	Maximum Zeta Potential (mV)				
	Ba(AOT) ₂	Mg(AOT) ₂	Zn(AOT) ₂	Ni(AOT) ₂	Al(AOT) ₃
Silica	31±3	84±4	85±5	118±4	96±7
Alumina	35±3	98±4	110±4	156±6	153±6
Magnesia	39±4	118±4	144±3	201±4	144±4

The observed behavior in these systems can be explained by the acid-base nature of charging events in apolar media. For systems in which the effective pH of the surfactant is less than the PZC of the particle, the particle will charge positively.[25] The magnitude of this charge is a function of several parameters: the relative acidity-basicity of the surfactant and the particles, the probability of a charge-transfer event, the ability of a micelle to sequester a charge, and the affinity of the micelles to undergo disproportionation. In this study, the goal was to determine if the acidity of the surfactant could be controlled by adjusting the electronegativity of the cation in the head-group. If the maximum particle mobilities are plotted as a function of the surfactant electronegativity, as in Figure 4, a trend can be observed.

Figure 4. Maximum particle mobilities for silica, alumina, and magnesia as a function of the electronegativity of the cation in the surfactant.

What becomes apparent is that, generally, as the electronegativity of the surfactant counterion increases, the maximum particle mobility also increases. This behavior was expected, given that a more electronegative cation acts as a stronger electron acceptor, and thus a stronger Lewis acid. It should be noted that one surfactant did not follow this trend. The Zn(AOT)_2 surfactant, with an electronegativity of 1.6, imparted lower mobilities to the alumina and magnesia particles than the less electronegative Al(AOT)_3 , with an electronegativity of 1.5.

As mentioned previously, the maximum mobility imparted to a particle depends not only on the relative acidity-basicity of the surfactant-particle pairing, but also on the propensity for the reverse micelles to undergo disproportionation. If more reverse micelles disproportionate, more charge exists in the bulk, thus screening out charges on the particle surface. At 6.1mM, the Al(AOT)_3 and Zn(AOT)_2 surfactants had conductivities of $2.83 \cdot 10^{-8}$ and $3.51 \cdot 10^{-7}$ S/m respectively. This suggests that reverse micelles of the zinc analog have a significantly higher propensity to undergo charging events in the bulk. This is further corroborated by the SAXS results in Figure 2. Al(AOT)_3 reverse micelles were found to have core radii of 1.4nm, while the Zn(AOT)_2 reverse micelle cores were significantly larger. The zinc analog's scattering profile, while unable to be fit, was shifted approximately an order of magnitude to lower q values, suggesting a comparable increase in core radius. Larger core sizes have been found to undergo increased disproportionation in the bulk, measured by increased system conductivities.[19,25]

Previous studies have found that NaAOT, not tested here, charges silica, alumina, and magnesia to mobilities of -0.06, 0.05, and 0.07 $\mu\text{m cm/V s}$, respectively.[13] Given that Na has an electronegativity of 0.93, comparable to that of Ba, one would expect similar charging behavior if the maximum mobility relied only on cation electronegativity alone. It is evident that other factors must be involved. One must note that the maximum measured mobility of a particle does not necessarily describe the extent to which it is charged. Screening by reverse micelles in the bulk will decrease the measured particle mobility, resulting in artificially lowered values. The maximum particle mobility is still a worthwhile metric to describe the particle charging behavior

in apolar systems, not just due to its practical applicability, but because it does correlate with predictions.

Figures 4b) and 5 show that the $\text{Al}(\text{AOT})_3$ surfactant deviated from its expected behavior by imparting the highest magnitude of mobility to the alumina particles, which have a lower PZC than the magnesia particles. It could be possible that this surfactant-particle pairing undergoes a charge transfer event which involves the Al^{3+} cation becoming part of the particle structure. This cation may be able to replace the hydrogen of a surface hydroxyl group, thus leaving an overall +2 charge on the particle surface.

3.3 Proposed Charging Mechanisms

The surfactants that were used in this study differ from the standard apolar surfactants used in previous particle charging studies. Span 80 and OLOA 11000, the standard acidic and basic surfactants currently used, have the chemical functionality to form a classical acid-base adduct on the surface which can then dissociate to donate or accept a proton (H^+). The acidic Span surfactants have hydroxyl groups in the head group, while the basic OLOA has a polyamine head group. NaAOT can form an adduct which can dissociate to either donate its Na^+ ion or to accept a proton from the surface. After the surfactants donate or accept a charge, the now-charged surfactant can be stabilized within a reverse micelle in the bulk. It should be noted that reverse micelles can only stabilize a single, monovalent charge due to the small radii of their polar cores. As discussed in Guo et al.[26], the probability of reverse micelles undergoing charging events scales as $\exp(-Z^2\lambda_B/2a)$, where Z is the valence of the charge in the core, λ_B is the Bjerrum length ($\sim 28\text{nm}$ for nonpolar systems), and a is the radius of the polar core. This suggests that reverse micelles are 54 times less probable to become charged to a valence ± 2 , and 8100 times less probable to become charged to a valence of ± 3 .

The di- and tri-valent AOT analogs do not have the chemical functionality to donate or accept a proton from a particle surface, which would appear to prevent these surfactants from engaging in the full range of acid-base charging mechanisms as described above. However, this study showed that these surfactants still charge particles as would a highly-acidic, aqueous solution. It is possible that the acidic, associated head group forms an acid-base adduct with a surface functional group on the particle. The dissociation event could involve the uptake of one of the negative, AOT^- tails by a reverse micelle in the bulk. In the case of the magnesium-AOT analog, this would leave a monovalent $\text{Mg}(\text{AOT})^+$ species on the particle, thus imparting an monovalent, positive charge to the surface. This process is shown schematically in Figure 5. While it is possible that the presence of trace water on the particle surfaces could influence particle charging events and the mechanisms by which they occur, both the particles and solutions were dried prior to being tested. The low water contents, below 250ppm, and intermediate surfactant concentrations at which the maximum zeta potentials occurred are indicative of a region where water has minimal influence on the charging behavior.[27]

Figure 5. Schematic of the proposed acid-base particle charging mechanism. An $\text{Mg}(\text{AOT})_2$ molecule would form an adduct with a surface hydroxyl group on the particle. A dissociated AOT^- group could then be stabilized in a nearby reverse micelle. The remaining $\text{Mg}(\text{AOT})^+$ species would impart a positive charge on the particle surface.

4. Conclusions

Aerosol OT undergoes ion-exchange reactions with divalent and trivalent cations, resulting in surfactants with a range of counterion electronegativities. These surfactants were synthesized and dissolved in the apolar solvent, IsoparTM L, and able to form reverse micelles of varying core radii.

These AOT analogs behaved in an acidic manner, charging mineral oxide particles to produce positive electrophoretic mobilities for every particle-surfactant pairing. Generally, as the PZC of the particle increased, the magnitude of the particle mobility increased as well. The $\text{Al}(\text{AOT})_3$ surfactant imparted the largest electrophoretic mobility to the alumina particles, which had a moderate PZC of 7.5. It was also found, generally, that as the electronegativity of the surfactant counterion increased, the magnitude of the imparted particle mobilities increased as well. The $\text{Al}(\text{AOT})_3$ surfactant, with an electronegativity of 1.5, imparted larger mobilities than the $\text{Zn}(\text{AOT})_2$ surfactant, with an electronegativity of 1.6.

Micellar core sizes were investigated using small angle x-ray scattering (SAXS) and it was found that the trivalent $\text{Al}(\text{AOT})_3$ formed the smallest reverse micelles, while the divalent-exchanged analogs increased in core radii with an increase in cation electronegativity. The three largest reverse micelles were unable to be fit to a sphere form-factor due to the low- q limit of the instrument used in this study. Thus it is speculated that the high mobility of the aluminum surfactant was due to the fact that the reverse micelles of this compound had a significantly smaller core size, resulting in less bulk disproportionation and therefore less electrostatic screening of the particle charges.

This study is significant for researchers who wish to tune the magnitude of particle charges. By simply exchanging the cation in the surfactant head-group, one can vary the magnitude of the particle zeta potentials between 39 and 201mV. It appears that exchanging sodium for a trivalent cation creates reverse micelles with smaller core sizes than those of divalent cation exchanged surfactants. This makes it such that trivalent surfactants of similar electronegativities are likely to impart higher electrophoretic mobilities than their divalent counterparts.

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Notes

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