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Colloids and Surfaces A: Physicochemical and Engineering Aspects

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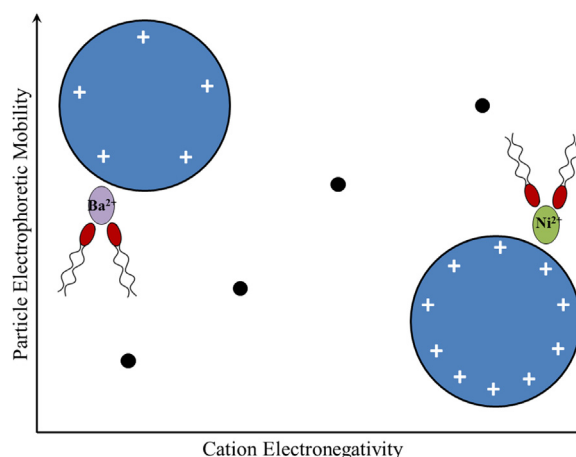
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HIGHLIGHTS

- Ion exchange reactions are performed on Aerosol OT to synthesize a series of surfactants with a range of counter-ion electronegativities.
- The AOT analogs are used to charge a series of mineral oxide particles in apolar media.
- The AOT analogs undergo acid-base charging mechanisms with the particles, resulting in particle zeta potentials up to 200 mV.

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 201 mV. 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.

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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 hygro-

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scopic 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 multiphase 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 h, 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 h 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 1 wt% 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 20 kV and a working distance of 5 mm. 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 premicellar 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 SAXSquant™ (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 1 wt%. Three mineral oxide particles- 250 nm silica (Fiber Optics Center Inc., New Bedford, MA), 300 nm alumina (Baikowski, Charlotte, NC), and 300 nm 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 0.5 mg per 25 mL. These dispersions were allowed to sit for 12 h 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

Fig. 1 summarizes the CMCs of each of the AOT analogs. Fig. 1(a) is an example of the conductivity curve as a function of surfactant