

Articles

Charging Behavior in the Silica/Aerosol OT/Decane System

Charging Behavior in the Silica/Aerosol
OT/Decane System

Roland I. Keir, Suparno, and John C. Thomas

Laser Light Scattering and Materials Science Group, School of
Electrical and Information Engineering, University of South Australia,
Mawson Lakes, Adelaide SA 5095, Australia

We report on the charging behavior of silica particles in a silica/aerosol OT/decane system. The major aim of the research was to determine the influence of Aerosol OT on the charging behavior of silica particles. Furthermore, the contribution of both the surfactant and the particle to the conductivity of the dispersion and also the location of the surfactant from measurements of the adsorption isotherm were of interest.

Introduction

An understanding of the interactions of surfactants at particle interfaces in aqueous media is important for a number of technologies, including "inks for magnetic printing applications" and the stabilization and charging of dispersions in display technologies.¹ Historically, and increasingly, methods in nonpolar media have been difficult to measure using conventional techniques such as microelectrophoresis or laser Doppler velocimetry. The development of the phase analysis light scattering (PALS) technique has enabled rapid and reproducible measurements of small electrophoretic mobilities.² We have developed a PALS system in our own laboratory and have recently reported results from this technique using triphenyl pigments in Isopar G.³

Whereas particle charging is well understood in aqueous systems, descriptions of charging mechanisms in nonpolar media are still problematic. General models of charging have been reported in the literature,^{4,5} however, in some systems, the particle charge can undergo a reversal as a function of surfactant concentration. This complicates the particle charging analysis, and it is especially important to understand this effect for practical ink formulations. In this paper, we report an investigation of a model system in which the particle charge was observed to undergo a change of sign in the presence of an increasing concentration of surfactant. The model system enabled close control over the chemistry, purity, and stoichiometry over the previously mentioned applied Ingalite Blue system. The specific system

particles, Aerosol OT (sodium bis(2-ethylhexyl) sulfosuccinate), and decane. The major aim of the research was to determine the influence of Aerosol OT on the charging behavior of silica particles. Furthermore, the contribution of both the surfactant and the particle to the conductivity of the dispersion and also the location of the surfactant from measurements of the adsorption isotherm were of interest.

Experimental Section

Decane (Aldrich, >99% pure) was used as supplied. Aerosol OT (AOT, Fluka, >98% pure) was purified by dissolution in methanol (Carbur, analytical grade) and tumbled with activated charcoal. This dispersion was filtered and centrifuged to obtain a clear supernatant. The methanol was extracted by rotary evaporation, and any remaining methanol was removed by heating in a vacuum oven at 120 °C for 24 h. The purified AOT was kept in a desiccator. Silica particles (Zorbaq SB, Mac-Med Analytical) with a diameter of 7 μm and a specific density of 2.2 g/cm³ were used in this research. The particles had a surface area of 305 m²/g and an average pore diameter of 70 Å.

AOT solutions for the electrophoretic mobility measurements were prepared from a stock solution of 1 M AOT in decane. The stock was agitated at 2 kHz for 60 s and then tumbled overnight. Dispersions were made by adding 10 mg of silica particles to 10 mL of the AOT solution in a clean, dry glass vial. The dispersions were then tumbled overnight. The water content in the systems was minimized by storing the silica particles in a clean, dry vial in an oven at 30 °C at all times. These particles were cooled in a desiccator for 10 min prior to sample preparation. The molar ratio of water to silica particles was found to be $X = [H_2O]/[SiO_2]$ in the system. Although water has an effect on the stability of aqueous dispersions in general,⁶ an in-depth study of water in this system will be the subject of a future paper.

Langmuir[®]
The ACS Journal of Surfaces and Colloids

Corresponding author:

Roland I. Keir, r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

Fax: +61 8 8302 2222

Tel: +61 8 8302 2222

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

E-mail: r.keir@unisa.edu.au

Reprinted from
Volume 18, Number 5, Pages 1463-1465

The PALS system was used to measure the electrophoretic mobilities of the dispersion as a function of AOT concentration. This system was designed and built in our laboratory and used a fringe-crossing technique.⁷ A 10-mm-path-length cell was used as the sample cell. The tem-

Articles

Charging Behavior in the Silica/Aerosol OT/Decane System

Roland I. Keir, Suparno, and John C. Thomas*

Laser Light Scattering and Materials Science Group, School of Electrical and Information Engineering, University of South Australia, Mawson Lakes, Adelaide SA 5095, Australia

Received June 11, 2001. In Final Form: November 13, 2001

We report an investigation of the effect of Aerosol OT on the surface charge of silica particles suspended in decane. The electrophoretic mobilities were measured using phase analysis light scattering, and supporting evidence was provided by conductivity and adsorption isotherm measurements. The results showed that, as the Aerosol OT concentration was increased, a sign reversal of the electrophoretic mobility occurred. This observation is explained qualitatively by a site-binding model of the charging mechanism.

Introduction

An understanding of the interactions of surfactants at particle interfaces in nonpolar media is important for a number of technologies, including toners for nonaqueous printing applications¹ and the stabilization and charging of dispersions in display technologies.² Historically, electrophoretic mobilities in nonpolar media have been difficult to measure using conventional techniques such as microelectrophoresis or laser Doppler velocimetry. The development of the phase analysis light scattering (PALS) technique has enabled rapid and reproducible measurements of small electrophoretic mobilities.³ We have developed a PALS system in our own laboratory and have recently reported results from this technique using Irgalite Blue pigments in Isopar G.⁴

Whereas particle charging is well-understood in aqueous systems, descriptions of charging mechanisms in nonpolar media are still problematic. General models of charging have been reported in the literature,^{5,6} however, in some systems, the particle charge can undergo a reversal as a function of surfactant concentration. This complicates the particle charging analysis, and it is especially important to understand this effect for practical ink formulations.

In this paper, we report an investigation of a model system in which the particle charge was observed to undergo a change of sign in the presence of an increasing concentration of surfactant. The model system enabled more control over the chemistry, purity, and stoichiometry than the previously mentioned applied Irgalite Blue system. The specific system was composed of bare silica

particles, Aerosol OT [sodium bis(2-ethylhexyl) sulfosuccinate], and decane. The major aim of the research was to determine the influence of Aerosol OT on the charging behavior of the bare silica particles. Furthermore, the contributions of both the surfactant and the particle to the conductivity of the dispersion and also the location of the surfactant from measurements of the adsorption isotherm were of interest.

Experimental Section

Decane (Aldrich, >99% pure) was used as supplied. Aerosol OT (AOT) (Fluka, ~98% pure) was purified by dissolution in methanol (Univar, analytical grade) and tumbled with activated charcoal. This dispersion was filtered and centrifuged to obtain a clear supernatant. The methanol was extracted by rotary evaporation, and any remaining methanol was removed by heating in a vacuum oven at 120 °C for 24 h. The purified AOT was kept in a desiccator. Silica particles (Zorbax Sil, Mac-Mod Analytical) with a diameter of 7 μm and a specific density of 2.2 g cm⁻³ were used in this research. The particles had a surface area of 300 m² g⁻¹ and an average pore diameter of 70 Å.⁷

AOT solutions for the electrophoretic mobility measurements were prepared from a stock solution of 1 M AOT in decane. The stock was agitated at 2 kHz for 60 s and then tumbled overnight. Dispersions were made by adding 10 mg of silica particles to 10 mL of the AOT solution in a clean, dry glass vial. The dispersions were then tumbled overnight. The water content in the systems was minimized by storing the silica particles in a clean, dry vial in an oven at 90 °C at all times. These particles were cooled in a desiccator for 10 min prior to sample preparation. The molar ratio of water to purified surfactant was found to be $X = [\text{H}_2\text{O}]/[\text{AOT}] = 0.7$ using Karl Fischer titration. Although water has been shown to have an influence on the stability of inverse micelles⁸ and on particle charging in general,⁹ an in-depth investigation of the influence of water on this system will be the subject of a forthcoming paper.

Phase analysis light scattering (PALS) was used to measure the electrophoretic mobilities of the dispersions as a function of AOT concentration. This system was designed and built in our laboratory and used a fringe-crossing technique.³ A 10-mm-path-length quartz cuvette was used as the sample cell. The tem-

* Corresponding author.

(1) Bartchser, G.; Breithaupt, J. *J. Imaging Sci. Technol.* **1996**, *40*, 441.(2) Comiskey, B.; Albert, J. D.; Yoshizawa, H.; Jacobson, J. *Nature* **1998**, *394*, 253.(3) Miller, J. F.; Schätzel, K.; Vincent, B. *J. Colloid Interface Sci.* **1991**, *143*, 532.(4) Keir, R. I.; Quinn, A.; Jenkins, P.; Thomas, J. C.; Ralston, J.; Ivanova, O. *J. Imaging Sci. Technol.* **2000**, *44*, 528.(5) Kitahara, A.; Amano, M.; Kawasaki, S.; Kon-no, K. *Colloid Polym. Sci.* **1977**, *255*, 1118.(6) Caruthers, E. B.; Gibson, G. A.; Larson, J. R.; Morrison, I. D. In *IS&T's Tenth International Congress on Advances in Non-Impact Printing Technologies*; Society for Imaging Science and Technology (IS&T): Springfield, VA, 1994; p 204.

(7) Mac-Mod Analytical, Chadds Ford, PA, 1997.

(8) Eicke, H. F.; Christen, H. *Helv. Chem. Acta* **1978**, *61*, 2258.(9) Jenkins, P.; Basu, S.; Keir, R. I.; Ralston, J.; Thomas, J. C.; Wolffenbutter, B. M. A. *J. Colloid Interface Sci.* **1999**, *211*, 252.

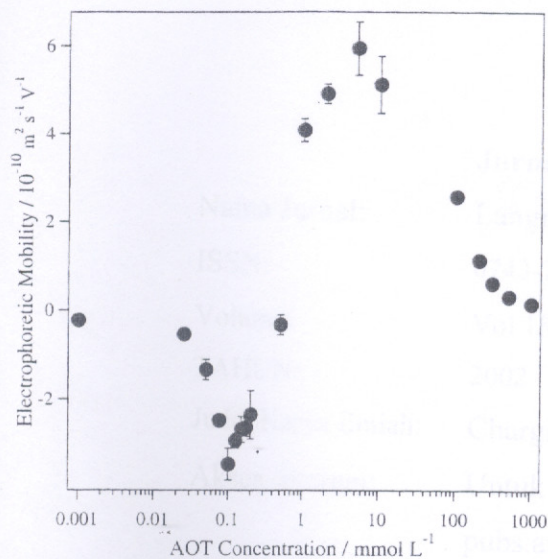


Figure 1. Electrophoretic mobility of bare 7- μm silica particles suspended in decane as a function of Aerosol OT concentration.

perature was maintained at 25 °C using a Peltier element. The scattering angle of the crossed laser beams in air was 15.6°. The crossed beams were driven at 80 MHz and 80 MHz + 2 kHz using an acousto-optic driver and Bragg cells to form the moving fringe pattern. The bright palladium electrodes were driven with a sinusoidal electric field of 1800 V cm⁻¹ at 30 Hz by a function generator. The scattered light signal was collected using a single-mode fiber-optic probe and a photomultiplier. Each sample was measured three times (an average of five 30-s measurements) to obtain an estimate of the experimental uncertainty (on the order of 1–2%).

Conductivities of the dispersions and supernatants were measured using a conductivity probe (model 600, Scientifica) at 25 °C. The adsorption isotherms were determined using the solution-depletion technique, and the concentrations were measured using FTIR spectroscopy (via the carbonyl stretching frequency of Aerosol OT) after calibrating with standard concentrations using a fixed-path-length NaCl cell.

Results

Figure 1 shows the measured electrophoretic mobility of the bare silica particles suspended in decane as a function of Aerosol OT concentration. Initially, the silica particles were only slightly negatively charged. A small increase in the Aerosol OT concentration resulted in a more negative mobility (reaching a maximum negative value at 0.1 mM). As the concentration of the Aerosol OT increased, the mobility passed through zero (the point of zero charge occurring at approximately 0.5 mM) and increased rapidly to a maximum positive value at 5 mM. Finally, any further increase in the Aerosol OT concentration resulted in a decrease of the electrophoretic mobility value. This behavior was quite reproducible.

Similar behavior was observed in our previous studies of Irgalite Blue systems^{4,9} using a different particle charging agent (Nuxtra). However, a change in sign was not observed. Other researchers have also observed maxima in the particle charge as a function of surfactant,¹⁰ but again, a sign reversal has not been observed.

A comparison of the electrophoretic mobility data and conductivities for the system is given in Figure 2. The adsorption isotherm for Aerosol OT is given in Figure 3 and shows that full surface coverage occurred at ap-

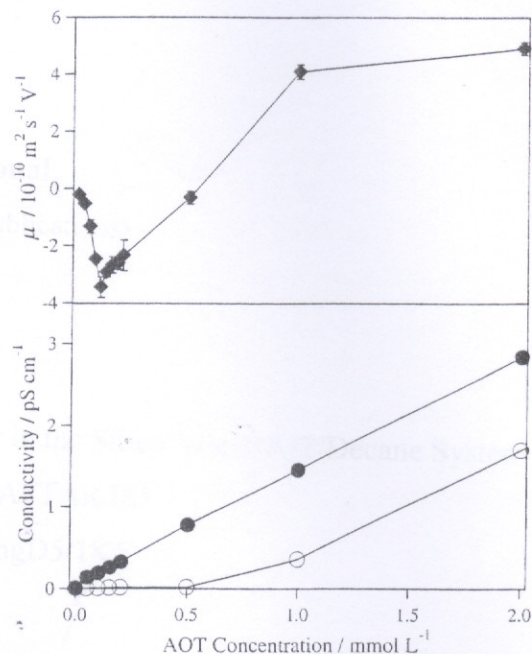


Figure 2. Plot of electrophoretic mobility and conductivity of the silica/Aerosol OT/decane system. The electrophoretic mobility data are a subset of the data presented in Figure 1. The conductivity data includes measurements of the silica dispersion (●) and of the supernatant (○). The AOT concentrations here are the total amount of AOT added to the systems.

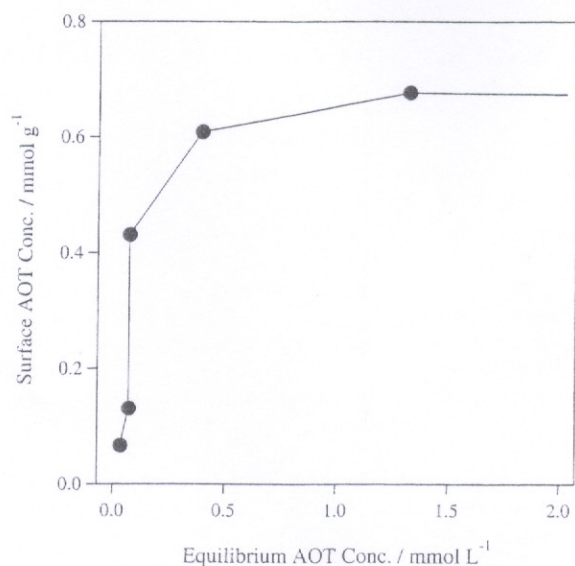


Figure 3. Adsorption isotherm of the Aerosol OT/silica/decane system plotted as the surface concentration of AOT per gram of silica against the equilibrium concentration of AOT.

proximately 0.5 mM. Hence, sign reversal of the electrophoretic mobility (Figure 1) correlated with the observed point of full surface coverage. In addition, the shape of the graph revealed that the AOT molecules formed only a monolayer on the silica surface in this range of concentration.

The conductivity data for the dispersions and corresponding supernatants are given in Figure 2b. There was a linear increase in the conductivity of the dispersion. For the supernatant, the conductivity remained at a low value until an Aerosol OT concentration of 0.5 mM and then increased. This was due to the availability of more charged species in solution after full surface coverage was reached at this concentration.

(10) Kitahara, A. In *Electrical Phenomena at Interfaces. Fundamentals, Measurements and Applications*; Kitahara, A., Watanabe, A., Eds.; Marcel Dekker: New York, 1984; p 119.

Discussion

Figure 1 shows that the electrophoretic mobility, and hence the surface charge, had a minimum (maximum negative) value at an AOT concentration of 0.1 mM and a maximum (positive) value at 5 mM. Furthermore, the figure shows that, at high AOT concentrations, the mobility of the dispersions decreased with increasing AOT concentration. Figure 1 also shows a sign reversal that occurred at an AOT concentration of approximately 0.5 mM. These results imply that there was competition between negative and positive charging processes with increasing AOT concentration.

Judging from these observations, it should be possible to derive a site-binding model that can accommodate both negative and positive charging descriptions of the system. In previous work, a site-binding model was used by Keir et al.⁴ and proved to be useful in describing the charging behavior of toner particles in a nonpolar-based printing ink. At the present time however, we present simply a qualitative discussion of the possible mechanisms that can occur in this system.

Negative Charging Model. At low concentrations, the AOT molecules dissolve in decane to form premicellar species such as dimers and trimers. At concentrations far below the critical micelle concentration (CMC, ~0.73 mM),¹¹ there is an equilibrium among monomers, dimers, and trimers.¹² Neutral premicellar species can collide to form negatively and positively charged species via sodium ion (Na⁺) transfer.¹³ These processes are represented by eqs 1 and 2, respectively.



Here, n is the number of AOT molecules; AOT is a single AOT molecule; M is a neutral premicellar aggregate; and M⁻ and M⁺ are the negatively and positively charged premicellar aggregates, respectively.

The charged species can adsorb onto the surface of the silica particles, and they are the dominant charging species at concentrations below 0.5 mM. The negatively charged premicellar species are adsorbed more strongly via acid-base interactions than the positively charged premicellar aggregates at very low concentrations. This process is represented by



where S is a neutral, unbound site on the silica surface and SM⁻ is a negatively charged site.

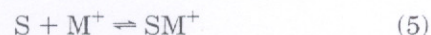
As the concentration of positively charged species, M⁺, in the electrical double layer increases, some of the excess M⁺ ions begin to neutralize the negatively charged sites on the surface of the particle. This charge neutralization process is given by



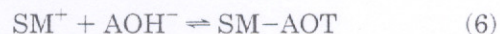
where SMM is the neutralized surface site.

The adsorption of the positively charged species continues until all of the negatively charged sites are neutralized at a concentration of approximately 0.5 mM (corresponding to full surface coverage by AOT).

Positive Charging Model. Further changes in the surface charge must be due to a positively charged species whose adsorption continues to increase the amount of AOT on the surface. This is likely to be a positively charged micellar species.



Consequently, negatively charged headgroups, AOT⁻, become the counterions and form an electrical double layer around the particle (presumably as micelles). As the concentration of AOT molecules increases, the AOT⁻ counterions overcrowd the positively charged silica surface. Some of the AOT⁻ counterions in the proximity of the positive sites can adsorb and neutralize the surface. This process is described by



where SM-AOT is the neutralized surface site due to adsorbed AOT⁻.

Conclusion

In summary, the charging behavior of silica particles suspended in dispersions of Aerosol OT in decane was investigated. This system showed a reversal in the sign of the particle charge as a function of increasing surfactant concentration, and the electrophoretic mobilities were investigated over 5 orders of magnitude in Aerosol OT concentration. A general qualitative discussion of possible particle charging mechanisms in this system was outlined, although a full site-binding model that can accommodate charge reversal has yet to be developed.

Acknowledgment. This research was supported by the Australian Research Council (ARC) through the Large Grants Scheme and through an ARC Collaborative Research Grant with Research Laboratories of Australia. Financial assistance for Suparno was provided by the Department of Education of the Republic of Indonesia. Discussions with Dr. Gary Bryant from the RMIT, Melbourne, Australia, are gratefully acknowledged.

LA0108757

(11) Assih, T.; Larché, F.; Delord, P. *J. Colloid Interface Sci.* **1982**, *89*, 35.

(12) Eicke, H. F.; Hopmann, R. F. W.; Christen, H. *Ber. Bunsen-Ges. Phys. Chem.* **1975**, *79*, 667.

(13) Eicke, H. F.; Deniss, A. In *Solution Chemistry of Surfactants*; Mittal, K. L., Ed.; Plenum Press: New York, 1979; Vol. 2, p 699.

Jurnal Internasional

Nama Jurnal: Langmuir (ACS Publications)
ISSN: 0743-7463
Volume: Vol 18. No 5
TAHUN: 2002
Judul Karya Ilmiah: Charging Behavior in the Silica/AerosolOT/Decane System
Akses internet: Untuk masuk ke DAFTAR ISI
pubs.acs.org/toc/langD5/18/5