



Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Short Communication

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



Gregory N. Smith^{a,1}, Paul Brown^{a,2}, Craig James^{a,3}, Roger Kemp^{b,4}, Asad Muhammad Khan^{a,5}, Tomás S. Plivelic^c, Sarah E. Rogers^d, Julian Eastoe^{a,*}

^aSchool of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, United Kingdom

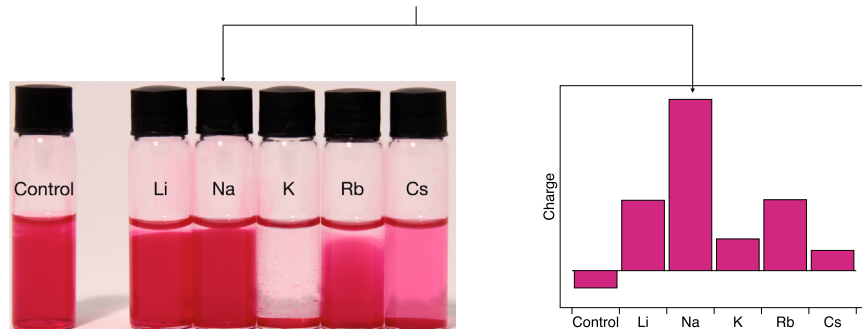
^bMerck Chemicals Ltd, University Parkway, Chilworth, Southampton SO16 7QD, United Kingdom

^cMAX IV Laboratory, Lund University, Box 118, SE-221 00 Lund, Sweden

^dISIS-STFC, Rutherford Appleton Laboratory, Chilton, Oxon OX11 0QX, United Kingdom

GRAPHICAL ABSTRACT

Sodium AOT—Highly stable and highly charged PMMA latexes



ARTICLE INFO

Article history:

Received 19 October 2015

Revised 25 November 2015

Accepted 25 November 2015

Available online 2 December 2015

Keywords:

Electrophoresis

Nonpolar solvents

Surfactants

Polymer latexes

Small-angle scattering

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.

* Corresponding author.

E-mail addresses: g.n.smith@sheffield.ac.uk (G.N. Smith), julian.eastoe@bristol.ac.uk (J. Eastoe).

¹ Current address: Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, South Yorkshire S3 7HF, United Kingdom.

² Current address: Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.

³ Current address: Department of Chemistry and CSGI, University of Florence, 50019 Sesto Fiorentino, Firenze, Italy.

⁴ Current address: Battelle UK, Hampshire PO9 1SA, United Kingdom.

⁵ Current address: COMSATS Institute of Information Technology, Abbottabad, Pakistan.

<http://dx.doi.org/10.1016/j.jcis.2015.11.062>

0021-9797/© 2015 The Authors. Published by Elsevier Inc.

This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

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.

© 2015 The Authors. Published by Elsevier Inc. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

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

Download English Version:

<https://daneshyari.com/en/article/6994970>

Download Persian Version:

<https://daneshyari.com/article/6994970>

[Daneshyari.com](https://daneshyari.com)