Colloids and Surfaces A: Physicochem. Eng. Aspects 417 (2013) 146–153

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Effect of headgroups on the aggregation behavior of cationic silicone surfactants in aqueous solution

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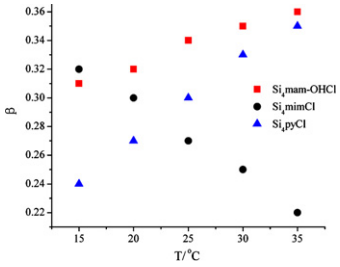
HIGHLIGHTS

- Cationic silicone surfactants with the same hydrophobic group and different headgroups were synthesized.
- Cationic silicone surfactants have higher surface activity compared with common hydrocarbon surfactants.
- The β values for Si_4pyCl and Si_4mam-OHCl increase with increasing the temperature in the investigated temperature range.

GRAPHICAL ABSTRACT

Aggregation behaviors of three novel cationic silicone surfactants are investigated. The figure of β–T for Si_4mimCl, Si_4pyCl and Si_4mam-OHCl shows that the values of β for Si_4pyCl and Si_4mam-OHCl increase as the temperature increases.



ARTICLE INFO

Article history:
Received 30 August 2012
Received in revised form 22 October 2012
Accepted 24 October 2012
Available online 30 October 2012

Keywords:
Cationic silicone surfactants
Electrical conductivity
Degree of counterion binding
Entropy-driven
Enthalpy-driven

ABSTRACT

Three cationic silicone surfactants, 1-methyl-3-[tri-(trimethylsiloxy)]silylpropyl-imidazolium chloride (Si_4mimCl), (2-hydroxyethyl)-*N*,*N*-dimethyl-3-[tri-(trimethylsiloxy)]silylpropylammonium chloride (Si_4mam-OHCl), 1-methyl-1-[tri-(trimethylsiloxy)]silylpropylpyrrolidinium chloride (Si_4pyCl), with the same hydrophobic group and different headgroups were synthesized. Their aggregation behavior in aqueous solution was systematically investigated by surface tension, electrical conductivity, and steady-state fluorescence. Surface tension of water can be reduced almost to 20 mN m^{-1} with the addition of the cationic silicone surfactants. This result indicates that all the three surfactants exhibit remarkable surface activity. Because of the effect of the headgroups, the critical micelle concentrations (CMC) values increase following the order Si_4pyCl < Si_4mimCl < Si_4mam-OHCl, and Si_4pyCl packs more tightly at the air/water interface compared with Si_4mimCl and Si_4mam-OHCl. Electrical conductivity measurements show that all the three cationic silicone surfactants have low degree of counterion binding (β) and the β values for Si_4pyCl and Si_4mam-OHCl increase with increasing the temperature in the investigated temperature range. Thermodynamic parameters (ΔH_m^0, ΔS_m^0, and ΔG_m^0) of micellization indicate that the micellization for Si_4mimCl in aqueous is enthalpy-driven, and that for both the Si_4pyCl and Si_4mam-OHCl entropy-driven.

1. Introduction

Silicone surfactants consist of a permethylated siloxane group coupled to one or more polar groups, which can be nonionic, cationic, anionic, or zwitterionic. They are widely used in industrial fields, such as agricultural adjuvant, polyurethane foam additives, paint additives, emulsifiers in cosmetics, and textile conditioning [1–6]. The characteristics of silicone surfactants are that they have surface activity in both aqueous and nonaqueous solutions [7]. This extraordinary quality is attributed to three properties of silicone surfactant: (i) its flexibility enables it to pack more compactly and efficiently at various interfaces,

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http://dx.doi.org/10.1016/j.colsurfa.2012.10.041