

Physicochemical characterization of cationic gemini surfactants and their effect on reaction kinetics in ethylene glycol–water medium

Deepti Tikariha^a, Namrata Singh^a, Manmohan L. Satnami^a, Kallol K. Ghosh^{a,*}, Nadia Barbero^b, Pierluigi Quagliotto^b

^a School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur (C.G.) 492010, India

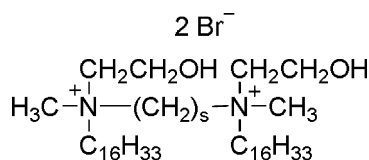
^b Dipartimento di Chimica e Centro di Eccellenza NIS, Università degli Studi di Torino, Via Pietro Giuria 7, 10125 Torino, Italy

HIGHLIGHTS

- ▶ The critical micelle concentration and degree of micellar ionization of gemini surfactants increases with increasing percentage concentration of ethylene glycol and temperatures.
- ▶ The kinetics of carboxylate and phosphate ester hydrolysis using some α -nucleophiles was studied in the presence of gemini surfactants spectrophotometrically.
- ▶ Effect of spacer of the gemini surfactants on the rate of hydrolysis was discussed and 16-6-16 MEA 2Br⁻ was the most efficient micellar catalyst for the hydrolysis of PNPA/PNDPPP.

GRAPHICAL ABSTRACT

The micellar and surface properties of gemini surfactants, in aquo-organic mixtures, have been investigated by conductance and surface tension measurements and were used as micellar catalysts for esterolytic reactions.



(C₁₆-s-C₁₆, MEA 2Br⁻, s = 4, 6)

ARTICLE INFO

Article history:

Received 5 March 2012

Received in revised form 26 June 2012

Accepted 28 June 2012

Available online 7 July 2012

Keywords:

CMC
Gemini surfactant
Kinetic hydrolysis
Ethylene glycol
Surface tension
Nucleophiles

ABSTRACT

Micellar and surface properties of two cationic gemini surfactants viz. alkanediyl- α,ω -bis(hydroxyethylmethylhexadecylammonium bromide) (C₁₆-s-C₁₆, MEA 2Br⁻, where s = 4, 6) in aqueous and ethylene glycol–water medium (0–20%, v/v) have been investigated by conductivity and surface tension measurements. The values of critical micellar concentration (CMC) and degree of micellar ionization (α) increase by increasing the concentration of ethylene glycol and the spacer chain length of gemini surfactants. The standard Gibbs free energy changes (ΔG_m°), enthalpies (ΔH_m°) and entropies (ΔS_m°) of micellization of gemini surfactants, determined by studying the variation of critical micelle concentration with temperature, revealed spontaneous and exothermic micellization behavior. The large rate enhancement for the hydrolysis of *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenyl diphenyl phosphate (PNDPPP) by α -nucleophiles such as, benzo hydroxamic acid (BHA), acetohydroxamic acid (AHA), salicylhydroxamic acid (SHA) and butane-2,3,-dione monooxime (BDMO) were obtained in the presence of gemini surfactants over the monomeric surfactant i.e. cetyltrimethylammonium bromide (CTAB). Kinetic constants were observed to be dependent on spacer chain length of gemini surfactants as well as on the nature of nucleophiles used. Ethylene glycol retarded the rate of reaction and C₁₆-6-C₁₆, MEA 2Br⁻ showed better catalytic effect for phosphate ester hydrolysis.

Crown Copyright © 2012 Published by Elsevier B.V. All rights reserved.

1. Introduction

Gemini surfactants have received wide attention not only due to their unique physicochemical properties but also for their

* Corresponding author. Tel.: +91 771 2263146/2262249; fax: +491 771 2262583.

E-mail address: kallolkghosh@yahoo.com (K.K. Ghosh).