Effect of ethylene glycol on micellization and surface properties of Gemini surfactant solutions

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Using surface tension and conductivity measurements, micellization of didodecyl dicaticionic dibromide Gemini surfactants of different methylene spacer lengths, 12-s-12, 2Br− (where s = 2, 4-methylene groups), is investigated in water–ethylene glycol (EG) mixtures with vol. percent of EG changing within the range of 0–30.

Gibbs energy of mixed micellization (ΔGmic) is obtained from the critical micelle concentration (CMC) and degree of counter-ion dissociation (g) values. Differences in the Gibbs energies of micellization of Gemini surfactants between water and water–EG mixtures are calculated in order to monitor the influence of EG on the micellization process. We determine transfer free energy (ΔGtr) micelle formation for Gemini surfactants in mixed solvents using the Flory interaction parameter.

CMC and micellar ionization degree increase with increase in the vol. percent of EG. The surface excess concentration (Γmax) decreases and the minimum area per surfactant molecule (Amin) increases with increase in the amount of EG present in the mixture.

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1. Introduction

Conventional surfactants contain one hydrophilic and one hydrophobic group. Gemini are a special class of surfactants in which two monomeric surfactant groups (two hydrophilic and two hydrophobic) are coupled together via a spacer. Geminis have attracted considerable interest for their various surface-active properties superior to those of corresponding conventional surfactants [1]. They have much lower CMCs, better lime-soap dispersing, better wetting properties [2], much greater efficiency in reducing surface tension of water [1], and unusual aggregation morphologies [3]. This class of surfactants has wide range of applications because of its unique solution properties such as detergency, solubilization, and surface wetting capabilities in diverse areas such as mining, petroleum, chemical and pharmaceutical industries, and chemical as well as biochemical research and as catalyst in several organic and inorganic reactions. They are also used as preservatives and antimicrobial agents [3].

Various physicochemical properties of surfactants have been reported to be much sensitive to molecular architecture and environmental conditions such as temperature, pressure, and additives [4–9].

The self-assembly of surfactants in polar organic solvents such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), dimethyl acetamide, glycerol, EG and in some aqueous–organic mixed solvents has been investigated experimentally to explore how the solvent characteristics influence aggregation. All of these solvents have high cohesive energies and dielectric constants and considerable hydrogen bonding ability [10]. DMSO, DMF, and dimethyl acetamide are dipolar aprotic solvents with weak hydrogen bond donors, and are weakly acidic. Therefore, they may often act as strong bases. Previous studies have shown that the addition of these solvents has an inhibitory effect on the formation of micelles in aqueous solutions. The inhibitory effects of dipolar aprotic solvents on micelle formation can be explained in terms of a decrease in the hydrophobic forces in ternary system due to interaction between water and the co-solvent [11].

Among these solvents, one of the most widely studied ones is EG. Both inter- and intra-molecular hydrogen bonds are formed in EG, although not as strongly as those formed in water. Evans and Miller suggested that the ability of a solvent to form hydrogen bonds is a prerequisite for micellization [12].

Halogenated solvents were used for lubrication and grease-stripping. These solvents are generally toxic. Therefore, blending water with various polar organic solvents along with surfactants may be an effective formulation for various cleaning operations [13].

Changing the solvent quality provides an opportunity to study the role of the so-called solvophobic effect as opposed to the