Journal of Molecular Liquids 216 (2016) 565–570

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Aggregation of diester-bonded cationic gemini surfactants in the presence of ethylene glycol: An electrical conductivity study

Hai-lin Zhu, Zhi-yong Hu, Dong Liang, Jian-long Wang, Duan-lin Cao

School of Chemical Engineering and Environment, North University of China, Taiyuan 030051, China

ARTICLE INFO

Article history:
Received 9 August 2015
Received in revised form 6 December 2015
Accepted 21 January 2016
Available online xxxx

Keywords:
Gemini surfactant
Ethylene glycol
Critical micelle concentration (CMC)
Degree of counterion association (β)
Thermodynamic properties

ABSTRACT

Aggregation behavior and thermodynamics of micellization of diester-bonded cationic gemini surfactants (12-Z1-12, 14-Z1-14, 12-Z2-12, 14-Z2-14) have been studied in ethylene glycol–water (EG–water) binary mixtures by conductometric method in the temperatures ranging from 298.15 to 313.15 K. With increasing length of hydrophobic chain and spacer, the values of critical micelle concentration (CMC) decrease, and degree of counterion association (β) increases. While with increasing temperature and concentration of ethylene glycol, the values of CMC increase, and β decrease. The thermodynamic parameters of micellization were determined from the temperature dependence of CMC values. The Gibbs energy values were found to be negative, and the negative values increased with the increase in the length of hydrophobic chain and spacer of surfactant, and with the decrease in temperature and volume fraction of ethylene glycol.

1. Introduction

Surfactants are widely used due to efficient solubilization, dispersion and suspension properties [1,2]. These are amphipathic molecules that consist of a polar portion attached to a non-polar portion. The process of micellization is induced by the hydrophobic interaction between the non-polar hydrocarbon portion and water, thereby reducing the free energy of the system. Recently, a novel class of surfactants, gemini surfactants, consisting of two hydrophobic chains and two polar head-groups covalently linked by a spacer (that may be hydrophilic, hydrophobic, flexible or rigid) [3,4], have been the subject of interest to many researchers [5–7].

Gemini surfactants show different properties in their solution due to the difference in chain length, head-group and spacer structure [8,9]. Previous studies have shown that the aggregation behavior of gemini surfactants is affected by the rigidity of the spacer in aqueous solution [10–12]. Xie et al. [10] found that at low concentrations (≤8 mmol L^{-1}), gemini surfactant containing a *p*-biphenyl group spacer could form large size aggregation, while gemini surfactant with a spacer containing a single phenyl group only forms spherical micelles. Zhang et al. [11] found that gemini surfactants with flexible spacer formed micelles in aqueous solutions, while the gemini surfactants featuring semi-rigid spacer could form micelles and vesicles. Zhu et al. [12] obtained a similar conclusion, that gemini surfactants featuring semi-rigid spacers are prone to form micelles and vesicles at low concentration and vesicles at high surfactant concentration, while gemini surfactants with long fully rigid spacers preferred to form vesicles.

The environment effects, such as additives, temperature, and pH [13,14] also affect the aggregation behavior and thermodynamic parameters of gemini surfactants. There are various reports on the aggregation behavior of gemini surfactants in the presence of water–organic solvents mixed media [15–19]. Although several studies well documented the micellization properties of gemini surfactants containing flexible spacers in the presence of water–organic solvents mixed media, nevertheless, this field still has potential for researchers, especially for gemini surfactants containing rigid or semi-rigid spacers.

So in this paper, four cationic gemini surfactants with the spacers containing two ester groups and a benzene ring were synthesized and the aggregation behavior of these synthesized gemini surfactants were studied in ethylene glycol–water (EG–water) binary mixtures. Ethylene glycol (EG) is one of the normally used as a cosolvent because of its miscibility with water, intra- and intermolecular hydrogen bonding ability, high dielectric constant and cohesive energy [20]. The chemical structure of the synthesized gemini surfactants is shown in Fig. 1.

2. Experimental

2.1. Materials and instruments

The synthesis of studied surfactants was carried out by reacting chloroacetyl chloride and hydroquinone or 1,4-Benzenedimethanol, and the products was then reacted with N,N-Dimethyldodecylamine or N,N-Dimethyltetradecylamine. Details of the synthesis procedure and purification are provided in the Supporting Information. Ethylene

---

E-mail address: zhuhailin99@126.com (H. Zhu).

http://dx.doi.org/10.1016/j.molliq.2016.01.067

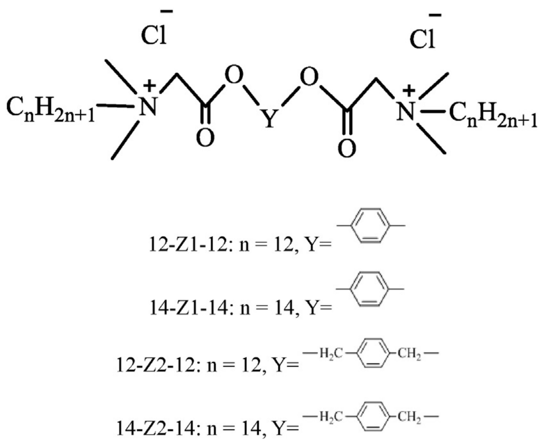

Fig. 1. Structures of synthesized gemini surfactants.

glycol (Aladdin Industrial Corporation, >99.5%) and Ultra-pure water (AXL Corporation, China) were used to prepare the mixed solutions. The volume ratio of EG to water in the mixed solution was 0:1, 1:20, 1:15, 1:10 and 1:5.

2.2. Electrical conductivity measurements

The conductivity measurements were performed by using a low-frequency conductivity analyzer (Model DDS-307, Shanghai Precision & Scientific Instrument Corporation). KCl solution (0.1 M and 0.01 M) was used for calibration of conductivity cell. The conductivity was recorded when its value fluctuated less than 1% over a 5 min interval. Super thermostatic cistern SX-CH1015 was used to control the temperature varied from 298.15 to 313.15 K, and the temperature fluctuation was ±0.5 °C.

3. Results and discussion

In this study, the critical micelle concentration (CMC) and degrees of counterion association (β) were evaluated from the conductivity method. The electrical conductivity (κ) versus concentration (c) in various compositions of EG–water at different temperatures was shown in Figs. S1–S4. The electric conductivity value increases with the increase in temperature and surfactant concentration. With surfactant concentration increasing, the electric conductivity increases quickly first and changes slowly after a certain concentration. The concentration at the break point was the critical micelle concentration (CMC) of the surfactant. As this method may introduce greater uncertainties in the values of CMC, in this work, a nonlinear fit method proposed by Carpena [21] was used to determine the CMC and β values. This method is based on the fitting of the κ as a function of c to the integral of a Boltzmann-type sigmoidal equation as follows:

$$\kappa(c) = \kappa(0) + A_1 c + \Delta c (A_2 - A_1) \ln\left(\frac{1 + e^{(c - c_0)/\Delta c}}{1 + e^{-c_0/\Delta c}}\right) \quad (1)$$

where κ(0) is the value of κ in pure solvent solution. A_1, A_2, △c and c_0 represent the pre-micellar slope, the post-micellar slope, the width of the transition and the central point of the transition region (CMC), respectively. Data fitting was carried out by making use of a software naming Matlab. The values of A_1, A_2, △c and c_0 were calculated by using the function of nlinfit, and the errors were calculated by using the function of nlparci. The confidence interval was chosen to be 95%. A respective plot of fitting using Carpena's method was shown in Fig. 2.

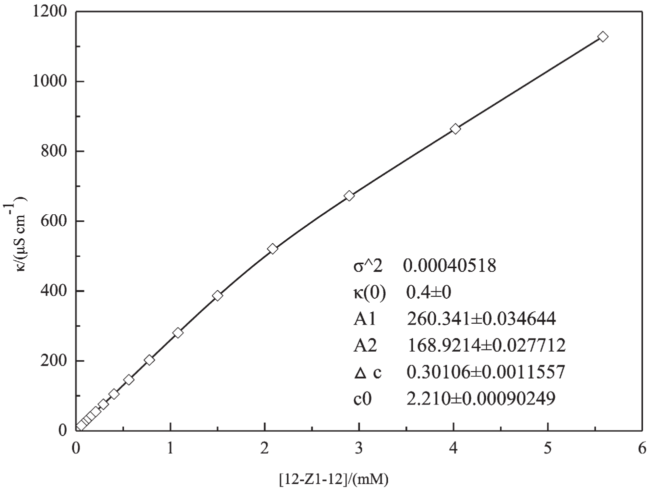

Fig. 2. Representative plot of specific conductance (κ) versus [12-Z1-12] in EG–water mixed solvent (V_{EG}:V_{Water} = 1:5) at 313.15 K.

From the ratio A_2/A_1, the degrees of counterion association (β) could be calculated from Eq. (2),

$$\beta = 1 - A_2/A_1 \quad (2)$$

3.1. Critical micelle concentration (CMC)

The CMC values of four synthesized gemini surfactants (12-Z1-12, 14-Z1-14, 12-Z2-12 and 14-Z2-14) in various volume percentages of EG–water mixed media have been determined by applying Carpena method. The obtained CMC values are listed in Table 1.

The data in Table 1 show that with an increase in the hydrophobic chain length of the gemini surfactants from 12 to 14, the CMC values decrease significantly (Fig. 3). The observed CMC values for 12-Z1-12 and 14-Z1-14 were 1.308 and 0.249 mM at 298.15 K in aqueous medium, respectively. The long hydrophobic tails are favor to form micelles, and as a result the CMC decreases. Self-aggregation of investigated gemini surfactants is also influenced by the spacer. The CMC values decrease slightly with an increase of the spacer length by two methylene units. This may be attributed to the fact that benzene ring is hydrophobic and rigid and tends to lay on the surface when it is adsorbed at the water–air interface. Adding a methylene to each side of the benzene ring, on the one hand, the minimum surface area per surfactant increases, resulting in adsorption saturation is more likely to achieve; on the other hand, the spacer becomes more flexible and more hydrophobic with increasing two methylene units to the spacer, which is favorable for micellization and thus decreases the CMC.

As can be seen from Tables 1 and 4, the addition of EG resulted in an increase in the CMC, making a progressive delay for micellization. The dielectric constants of EG and water were 37.7 and 78.5 at 298.15 K, respectively. The addition of EG decreases the polarity of the solvent, which makes the bulk phase a better solvent for gemini surfactant, thus, the transfer of the surfactant tail and the alkyl chains in the head groups and in the spacer from the bulk phase into the micellar core becomes less favorable [22].

At a fixed composition of EG–water, the CMC values for a certain surfactant increased with increasing temperature (Fig. 4). The effect of temperature on CMC values can be interpreted by two opposite effects [23,24]. On one side, the increase in temperature causes the decrease in hydration of hydrophilic ionic head group, which is in favor of the formation of micelles. On the other side, with the temperature increase, the solvent structure around the hydrophobic group is gradually disrupted, which is unfavorable for micellization. In addition, for ionic surfactants, as the temperature rises, the thermal motion of surfactant molecules