Colloids and Surfaces A: Physicochem. Eng. Aspects 482 (2015) 394–402

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Rheology of wormlike micelles in mixed solutions of cocoamidopropyl betaine and sodium dodecylbenzenesulfonate

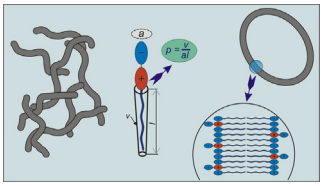
Sylwia Różańska*

Department of Chemical Engineering and Equipment, Faculty of Chemical Technology, Poznan University of Technology, ul. Berdychowo 4, PL 60-965 Poznan, Poland

HIGHLIGHTS

- Mixed wormlike micelles of zwitterionic/anionic surfactants were studied.
- CAPB/SDBS mixtures are highly viscoelastic gel-like systems.
- The rheological behavior of the CAPB/SDBS system strongly depends on the pH and temperature of a solution.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 March 2015
Received in revised form 6 June 2015
Accepted 28 June 2015
Available online 2 July 2015

Keywords:
Surfactant solutions
Maxwell model
Viscoelasticity
Wormlike micelles

ABSTRACT

The interactions between anionic and zwitterionic surfactants have been studied on different compounds systems at varied pH, temperature and concentration of anionic surfactant. These systems contained cocamidopropyl betaine, CAPB ($C_{19}H_{38}N_2O_3$), and sodium dodecylbenzenesulfonate, SDBS ($C_{18}H_{29}NaO_3S$) forms wormlike micelles in the concentration range of CAPB equal to 0.083 M and SDBS from 0.057 to 0.072 M. The synergism is significant when the concentrations of CAPB in the solution is 0.083 M and SDBS is 0.063 M. The wormlike micellar solutions show a viscoelastic characteristic and at low shear frequencies can be described by the Maxwell model with a single stress relaxation. A pronounced temperature effect on the wormlike micellar structures can be observed by rheological studies. With an increase in temperature, the samples become less structured due to shortening of the micelles. From measurements at zero shear viscosity η_0, plateau modulus G_0 and relaxation time τ it is evident that the highest values were achieved for 0.063 M SDBS solution. The rheological behavior of the CAPB/SDBS system strongly depends on the pH of a solution, which reflect the pH-dependence of the structural transformation of wormlike micelles. This is caused by the change in the acidity around the carboxylic acid headgroups as a function of pH. Studies of CAPB/SDBS mixtures at constant molar ratio of both surfactants (1.32) revealed that in the range of CAPB from 0.05 to 0.067 M the wormlike micellar network is formed. Above concentration of CAPB 0.067 M the network is completely constituted, however it disappeared completely below 0.05 M.

1. Introduction

Zwitterionic surfactants are surface active molecules that contain positive and negative charges in the headgroup. The main representatives of that type of surfactants are betaines, which in their structure contain the amino group and carboxyl group. Due to the presence of a quaternary atom, the zwitterionic surfactants in an acidic environment behave as the cation-active compounds, while in a basic environment as the anionic-active compounds. The anionic nature of zwitterionic surfactant molecules is usually decided by the presence of carboxyl or sulfonyl group [1]. That class of surfactants associate at low concentrations and aqueous solutions exhibit strong gel-like properties. These properties are attributed to the existence of an entangled network of micelles

* Fax: +48 61 6652789.
E-mail address: Sylwia.Rozanska@put.poznan.pl

http://dx.doi.org/10.1016/j.colsurfa.2015.06.045
0927-7757/

[2,3]. Wormlike micelle are formed in a mixture of anionic/cationic [4] and anionic/zwitterionic surfactants [5].

Surfactant solutions in which wormlike micelles forms are widely used in industry as viscosity modifiers and enhancers [6]. Moreover, they also become increasingly important in a wide range of industrial and commercial applications which include agrochemical spraying, inkjet printing, nanotemplating and also as drag-reduction additives in district heating systems [7–9].

Mixtures of zwitterionic and anionic surfactants exhibit a strong synergistic effect, which is manifested by a significant increase in the viscosity of the solution [10]. These mixed solutions are commonly used in soaps, shampoos and various liquid detergents because anionic surfactants are known for their cleansing properties and zwitterionic surfactants add conditioning and antistatic properties [10,11].

One of the best known and most commonly used zwitterionic surfactant is cocamidopropyl betaine (CAPB), which properties are dependent on the pH of solution [12,13]. Below the isoelectric point (at acidic pH) betaine is in the cationic form [14,15]. Due to the fact that this type of compounds is capable of accepting a proton, very often a stronger synergistic effect is shown by the anionic surfactants than by the cationic ones [16]. Strong electrostatic interaction between anionic and zwitterionic surfactants often result in the lower critical micelle concentration (CMC) [15,17].

In the literature, it is possible to find information about the properties of amphoteric surfactants mixed with sodium dodecylsulfate (SDS) in aqueous solutions [5,12,18,19]. In these systems the formations of large rodlike micelles were reported at a relatively low total surfactant concentration [5]. Rosen and Zhu [20] explained the significant intermolecular attractions between anionic and betaine surfactants by the strong electrostatic attractions between them.

Another anionic surfactant which is frequently used in the production of cosmetics, liquid dishwashing and laundry detergents is sodium dodecylbenzenesulfonate (SDBS). The research conducted by the author show that the solutions of CAPB/SDBS mixture are characterized by a complex rheological properties. The aim of this study was to determine the influence of the weight ratio, total concentration, pH and temperature on the rheological properties of the aqueous solutions of various CAPB/SDBS mixtures.

2. Theory

According to the mean-field theory, the average linear contour length $\bar{L}$ of neutral wormlike micelles is described by [21]:

$$\bar{L} \sim \phi^{1/2} \times \exp\left[\frac{E_s}{2k_B T}\right] \tag{1}$$

where φ is the volumetric fraction of surfactant, E_s is the scission energy required to break a wormlike micelle into two parts, k_B is the Boltzmann's constant and T is the temperature. For neutral or screened wormlike micelles, the scission energy E_s is equal to the end-cap energy E_c, i.e., the excess free energy of the hemispherical caps compared to the curvature free energy of the cylindrical part.

In the case of charged micelles, the scission energy has an additional electrostatic component, E_e, due to the repulsion of the charges along the cylindrical part that favors shorter worms. MacKintosh et al. [22] have proposed a model to demonstrate that the electrostatic repulsion reduce the scission energy and therefore favor the breaking of micelles:

$$\bar{L} \sim \phi^{1/2} \times \exp\left[\frac{1}{2k_B T}(E_c - E_e)\right] \tag{2}$$

In the semi-dilute regime very long and flexible wormlike micelles form an entangled network analogous to that of polymers [23,24]. Their behavior in oscillatory flow (in the range of low and intermediate frequency) can be described by the single-mode Maxwell model [23]:

$$G' = G_0 \frac{\omega^2 \tau_M^2}{\omega^2 \tau_M^2 + 1} \tag{3}$$

$$G'' = G_0 \frac{\omega \tau_M}{\omega^2 \tau_M^2 + 1} \tag{4}$$

where: ω is the oscillation frequency, G_0 is the elastic modulus extrapolated to infinite frequency (plateau modulus), and τ_M is the Maxwell relaxation time of the system. G_0 is proportional to the density of the entanglement points, so it characterizes the network structure. Relaxation time τ_M is obtained from the critical angular frequency ω^* at which the curves of G' and G'' intersect according to the equations:

$$\tau_M = \frac{1}{\omega^*} \tag{5}$$

The parameters G_0 and τ_M for the Maxwell fluid are related to $\eta_{0,M}$ by following relation:

$$\eta_{0,M} = G_0 \times \tau_M \tag{6}$$

For the semi-dilute wormlike micelles solutions Cates and Candau [21] proposed the model that predicts the single relaxation time as follows:

$$\tau_M = (\tau_b \times \tau_r)^{0.5} \tag{7}$$

where: τ_b is the micellar breaking time, i.e., the expected survival time of a chain of the mean length L before it breaks into two pieces, τ_r is the micellar reptation time. According to Cates and Candau [21] the Maxwell-type behavior is only observed when the τ_b is much shorter than the τ_r.The Maxwellian behavior is ascertained by a semicircular shape of the cole–cole plot with the normalized storage modulus, G''/G_0, plotted against the normalized loss modulus, G''/G_0. The rheology of wormlike micelles deviates from the Maxwellian behavior at high frequencies. These deviations are due to the transition of relaxation mode from the reptation at longer time-scales to the "breathing" or Rouse modes at shorter time-scales. According to Cates and Candau [21] a frequency at which G'' shows a deviation is around $1/\tau_b$ [21,25]. The local minimum of G'' in the high frequency region is related to the micellar contour length according to the following relation [26]:

$$\frac{G_0}{G''_{min}} \approx \frac{\bar{L}}{l_e} \tag{8}$$

where: l_e is the entanglement length, i.e., the contour length of the section of wormlike micelles between two entanglement points. The ratio of $\bar{L}/l_e$ defines the average number of entanglements per micelle. For flexible micelles, the correlation length, which gives the mesh size ξ of the micellar network, is related to l_e according to the relation [27,28]:

$$l_e \approx \frac{\xi^{5/3}}{l_p^{2/3}} \tag{9}$$

The persistence length, l_p, gives an estimate of micellar flexibility. The micelles act as rigid entities over length scales close to l_p and are flexible at longer length scales (typically $\bar{L} \gg l_p$). The parameter ξ is the hydrodynamic correlation length, typically identified with the network mesh size [27,28]:

$$\xi = \left(\frac{k_B T}{G_0}\right)^{1/3} \tag{10}$$