Fluid Phase Equilibria 425 (2016) 358–364

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Phase equilibria of mixtures of surfactants and viscoelastic properties of the liquid crystal phases

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A R T I C L E I N F O

Article history:
Received 14 March 2016
Received in revised form
25 May 2016
Accepted 16 June 2016
Available online 17 June 2016

Keywords:
Mixtures of surfactant
Micelle
Liquid crystal
Viscoelasticity

A B S T R A C T

Mixtures of surfactants are widely used in many industrial and pharmaceutical products. Whereas diluted mixtures of surfactants have been studied in deep, much lesser studies at high surfactant concentrations have been made. A comparative study among the different systems of tetraoxyethylene dodecyl ether ($C_{12}E_4$) with different nonionic and anionic surfactants has been carried out. Four phase diagrams of $C_{12}E_4/C_{12}E_{10}$/water, $C_{12}E_4$/S40P/water, $C_{12}E_4$/SDS/water and $C_{12}E_{10}$/SDS/water systems at 30 °C are reported. In all of them, mixed micelles in water and reverse micelles have been found. Lamellar and hexagonal are the liquid crystals which appear in these ternary systems. Liquid crystals have been characterized by polarized light microscopy and rheology. Viscoelastic properties of the liquid crystals have been determined. Lamellar phase behaves like a gel with both mechanical moduli (G' and G'') independent on frequency. The elastic properties of the lamellar phase are strongly dependent of the presence of ionic charges. Lamellar liquid crystals for the mixture with the anionic surfactant (SDS) have the higher elastic modulus. For hexagonal phase, elastic and viscous moduli increase with increasing frequency but with different slopes. Its elastic properties are strongly dependent of critical packing parameter of surfactants. Hexagonal liquid crystals for the mixtures with $C_{12}E_4$ (surfactant with the smaller area of the head group) show the more important elastic properties.

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1. Introduction

Surfactants systems show a rich phase behavior. Surfactant molecules self-assemble at low concentration in water, forming an isotropic solution of micelles. At higher concentrations, one or several liquid crystal phases appear. Some of more common liquid crystals include the lamellar phase (which is constructed by stacking together bilayers), the various hexagonal phases (which result from assembling indefinitely long cylindrical units in a hexagonally close-packed array), and a variety of isotropic cubic phases. Conventional poly(oxyethylene) alkyl ethers are most popular nonionic surfactants. These surfactants form various self-organized structures in water, and their phase behavior has extensively been studied [1–3]. These self-organized structures are highly influenced by alkyl chain length, poly(oxyethylene) chain length, and temperature [2]. These polyoxyethylene alkyl ether surfactants have been also extensively studied in pharmaceutical systems due to their minimum toxicity [4–6].

Well-chosen mixtures of surfactants often show a synergistic interaction that means the interfacial properties of the mixture are more pronounced than those of the individual components by themselves. As a result, in many industrial products and processes mixtures of different types of surfactants, rather than individual materials, are used. For instance, the mixed micellar systems are more efficient than single micellar systems to improve some important properties such as the solubilization capacity.

On the other hand, the aqueous phase behavior of surfactants is subject of interest to industrial chemists. Up to now, the phase behavior of ternary systems composed by ionic surfactant/alcohol/water [7–10] and by surfactant/oil/water [3,7,11] has been extensively studied. Much lesser studies of ternary mixtures of two surfactants and water in the whole range of concentrations have been reported [12]. But diluted aggregates of mixtures of nonionic [13,14] surfactants, nonionic-ionic surfactants [15] and ionic-ionic [16–18] surfactants have been much more studied.

Moreover, in many practical applications it is important to control the flow behavior and viscoelastic properties of the system. The rheological aspects of these systems should be studied as shear flow has a strong influence on the structure of complex fluid due to

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http://dx.doi.org/10.1016/j.fluid.2016.06.030

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a mechanical deformation can alter the structure. Studies of the rheology of the highly concentrated surfactant system are seldom reported.

With these results in mind, we decided to expand our studies to mixtures of surfactants in the whole range of concentrations. We focus on the phase behavior of mixtures of nonionic surfactants in aqueous solution and on viscoelastic properties of the liquid crystals. We have studied ternary mixtures of two nonionic surfactants and water and ternary mixtures of nonionic surfactant, anionic surfactant and water. We have obtained the isothermal ternary phase diagrams. A comparative study among the different systems of surfactant of tetraoxyethylene dodecyl ether ($C_{12}E_4$) with different nonionic and anionic surfactants with n-dodecyl as the hydrophobic group ($C_{12}E_{10}$ and SDS) has been carried out. The mixture with a highly hydrophilic nonionic surfactant with a very bulky head group has been also studied. Liquid crystal phases have been characterized by polarized light microscopy and rheology. Knowledge about the formation and rheological properties of nonionic surfactant systems is important not only to obtain a better theoretical understanding of the systems, but also for practical applications such as in cosmetics and toiletry products, because of the absence of charged species and improved mildness to the skin.

2. Material and methods

2.1. Sample preparations

A summary of the studied materials is given in Table 1. All materials were used as supplied.

For the determination of the phase behavior, samples of 2–4 g were weighed into test tubes and homogenized by vigorous shaking and gentle heating. Afterward, the samples were left in a 30.0 ± 0.1 °C bath. The samples then were monitored for at least 4 weeks and examined by optical inspection and polarization optical microscopy to obtain the different phase diagrams. The difference in composition between two samples was below 5% in weight in the third component.

2.2. Polarization optical microscopy (POM)

Birefringent textures of lyotropic liquid crystals were investigated by using a Nikon ECLIPSE 50i optical microscope equipped with crossed polarizers and a Nikon Coolpix 8400 digital camera. Using polarized light and viewing the samples through cross polarizers gives a black picture for isotropic phases, whereas anisotropic ones give bright image. The patterns in a polarization optical microscope are distinctly different for different anisotropic phases and can therefore be used to identify the phases. Lyotropic liquid crystal structures were assigned to the different samples according to the textures observed. These observations were pursued at least for two months as the aggregation state of the sample may change with time. Selected samples in the single phase regions were considered for further characterization.

2.3. Rheology

Rheological measurements were performed at 30 °C, in a Carri-Med $CSL^2{}_{100}$ controlled stress rheometer with cone-plate configurations (4 cm 1° and 2 cm 2°, depending on the samples viscosity). Two different experiments, steady flow (shear stress weep mode) and oscillation were performed. In flow experiments logarithmic series of increasing stress were applied. Apparent viscosity values (η) were calculated as the ratio of shear stress to shear rate. The elastic modulus G' and the viscous modulus G'' were measured as a function of stress to obtain the linear viscoelastic region. When the linear viscoelastic region was established, measurements were performed as a function of frequency at constant stress.

3. Results

3.1. Phase equilibria

The phase behavior of different ternary systems of nonionic surfactants were determined over the whole range of concentrations at 30 °C. The effects on $C_{12}E_4$/water system of two more hydrophilic nonionic surfactants than $C_{12}E_4$ and of one anionic surfactant have been studied. Moreover, the effect of the anionic surfactant on phase behavior of nonionic surfactants was enlarged to $C_{12}E_{10}$/water system. The ternary systems $C_{12}E_4$/$C_{12}E_{10}$/water, $C_{12}E_4$/S40P/water, $C_{12}E_4$/SDS/water and $C_{12}E_{10}$/SDS/water were studied. Theirs phase diagrams can be observed in Fig. 1a–d, respectively.

Firstly, we study the ternary system composed by $C_{12}E_4$/$C_{12}E_{10}$/water (Fig. 1a). The only difference between both surfactants is the oxyethylene content in the head groups. As the oxyethylene content increases, hydrophilicity of the surfactant increases. This system shows two liquid crystal phases (H_1: hexagonal and L_α: lamellar) and two isotropic and transparent phases of direct and reverse micelles (L_1 and L_2 phases).

The $C_{12}E_4$ surfactant in water shows two uniphasic regions (lamellar liquid crystal and reverse micelles). The solutions of $C_{12}E_4$ in water at low surfactant content are slightly turbid. This turbid solution did not separate in two phases in two months. But when these solutions are centrifuged at 4000 rpm during 10 min, a lamellar phase separates from aqueous solution. This kind of samples extends to surfactant content close to 35% as it would correspond to highly diluted lamellar phases that we can consider like a dispersion of the lamellar phase in water ($W + L_\alpha$). The micrograph of one of these samples (30% $C_{12}E_4$) can be seen in Fig. 2a. The boundary between the dispersion of lamellar phase in water and the lamellar phase is not easy to determine. The tendency of lamellar aggregates to separate depends on their state of subdivision, and a wide variety of interesting dispersed system can be produced. Mitchell and co. [19] located this limit phase close to 25% of $C_{12}E_4$ between 20 °C and 50 °C. In our study, we have employed commercial surfactant (Brij 30: $C_{12}E_{\sim 4}$) whose main component is $C_{12}E_4$. Lamellar phase is thermodynamically stable at higher amount and a micrograph for 70% of surfactant and it can be seen in Fig. 2b. We can observe the texture of “Maltese crosses” to characterize lamellar phases.

Table 1
Origin and formula of the surfactants employed in this work.

Compound	Supplier	Acronym	Formula
Brij 30	Sigma Aldrich	$C_{12}E_4$	$C_{12}H_{25}(OCH_2CH_2)_{\sim 4}OH$
Polyoxyethylene (10) lauryl ether	Sigma Aldrich	$C_{12}E_{10}$	$C_{12}H_{25}(OCH_2CH_2)_{10}OH$
Acid S 40 P	Evonik	S40P	$C_{17}H_{35}CO(OCH_2CH_2)_{40}OH$
Sodium lauryl sulfate	Sigma Aldrich	SDS	$C_{12}H_{25}OSO_3^- Na^+$

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