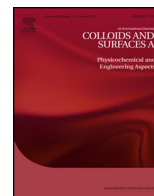




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Phase behavior of the ternary aqueous mixtures of two polydisperse ethoxylated nonionic surfactants

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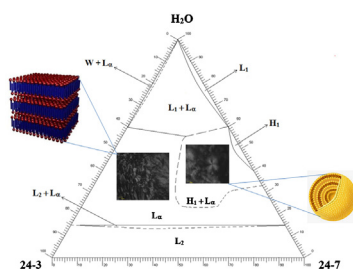
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HIGHLIGHTS

- The phase diagram of mixed commercial ethoxylated surfactants was developed.
- Considered surfactants are widely used in homecare detergent formulations.
- The LLC structures were identified by POM, SAXS and SANS.
- Effects of hydrophobic and hydrophilic chains polydispersity were highlighted.
- Relation of supramolecular structures with segregation phenomena was studied.

GRAPHICAL ABSTRACT



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ABSTRACT

The phase diagram of the ternary aqueous system composed by two polydisperse ethoxylated surfactants, commercially known as 24-3 and 24-7, with the average molecular formula corresponding to triethylene – and heptaethylene – glycol dodecyl ether, has been developed at 25 °C. The identification of the different lyotropic liquid crystalline (LLC) structures, whose range of stability has been preliminarily determined by visual inspection through cross-polarizers, has been performed using polarized optical microscopy (POM), small angle neutron and X-ray scattering (SANS, SAXS). Data have been analyzed in terms of the combined effects of the different length of poly(oxyethylene) chains of the two surfactants and hydration/dehydration of the polar headgroups, depending on the total surfactant concentration. Peculiar effects of both hydrophobic and hydrophilic chains polydispersity have been highlighted. Our results shed light on the aggregative behavior of surfactant mixtures widely used in homecare detergent formulations.

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1. Introduction

Polyethylene glycol alkyl ethers are typical nonionic surfactants, usually named C_nE_m . Their linear hydrophobic chain (formed by n carbon atoms) is linked to a polar head composed by m oxyethylene units. A variety of different mesoscopic phases appears in the aqueous mixtures of this class of surfactants, depending on temperature,

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composition and length of both hydrophilic and hydrophobic moiety [1–5].

Owing to their high biocompatibility, polyethylene glycol alkyl ether surfactants are widely used as emulsifying agents and detergents. Usually, commercial surfactants used in common detergent formulations are polydisperse raw materials. Polydispersity is a feature of most biological macromolecules and synthetic products. In the latter case, polydispersity depends on process parameters such as temperature [6], pH [7], concentration of reagents [8], and nature of catalysts used, and affects most of physico-chemical properties of the products [9–12]. Commercial C_nE_m surfactants show a wide length distribution of both alkyl and poly-oxethylene chains. This could strongly affect their self-aggregation behavior and the formation of lyotropic liquid crystalline (LLC) structures. As a consequence, the phase diagram of commercial C_nE_m surfactants can substantially differ from that of purified monodisperse analogues.

The phase diagrams of aqueous binary mixtures of a large number of polydisperse C_nE_m surfactants have been extensively characterized [13–22]. Ternary aqueous mixtures of one polydisperse C_nE_m surfactant and sodium dodecyl sulfate (SDS) have been also considered [23,24]. On the other hand, to the best of our knowledge, ternary systems containing two commercial polyethylene glycol alkyl ethers have not been investigated yet.

In this paper we present an investigation carried out on the ternary aqueous system composed by two polydisperse ethoxylated surfactants, with the average molecular formula corresponding to triethylene – and heptaethylene – glycol dodecyl ether ($C_{12}E_3$ and $C_{12}E_7$), respectively. In the industrial field, such substances are also named 24-3 and 24-7, where 24 indicates that the average length of the alkyl tail is composed by an average of 12–14 carbon atoms, while 3 and 7 indicate the average number of oxyethylene units in the polar head. They are two of the most commonly used surfactants in homecare detergent formulations, thus fully justifying the interest in the phase behavior of their mixtures.

The phase diagram of the ternary system 24-3/24-7/water has been developed in the whole composition range at 25 °C. The identification of the different lyotropic liquid crystalline (LLC) structures, whose range of stability has been preliminarily determined by visual inspection through cross-polarizers, has been performed using polarized optical microscopy (POM), small angle neutron and X-ray scattering (SANS, SAXS). Data have been analyzed with the aim to highlight the relation between the different supramolecular structures and the specific intermolecular interactions.

2. Experimental

2.1. Materials and sample preparation

Polydisperse triethylene glycol dodecyl ether and heptaethylene glycol dodecyl ether (from this point on shortened as 24-3 and 24-7, respectively) were two SASOL Germany GmbH products. They were a gift of Procter & Gamble (Italian Research Center, Pomezia, Italy) and were used as had. Polydispersity of alkyl and poly(oxyethylene) chains for both surfactant samples was assessed at the Procter & Gamble analytical laboratories by gel permeation chromatography, following procedures well described in the literature [25]. Numeric distributions are reported in Fig. 1. 24-3 and 24-7 share the same alkyl tail distribution, in which only terms with even number of carbon atoms are present. This is due to the natural origin of the raw materials used for surfactant production. The C_{12} alkyl tail is by far the most represented, followed by a significant fraction of C_{14} . On the other hand, distributions of the number of oxyethylene units per surfactant molecule are much larger. As expected, they are centered around 3 for 24-3 and 7 for 24-7. In both surfactant samples, relevant fractions of non ethoxylated molecules

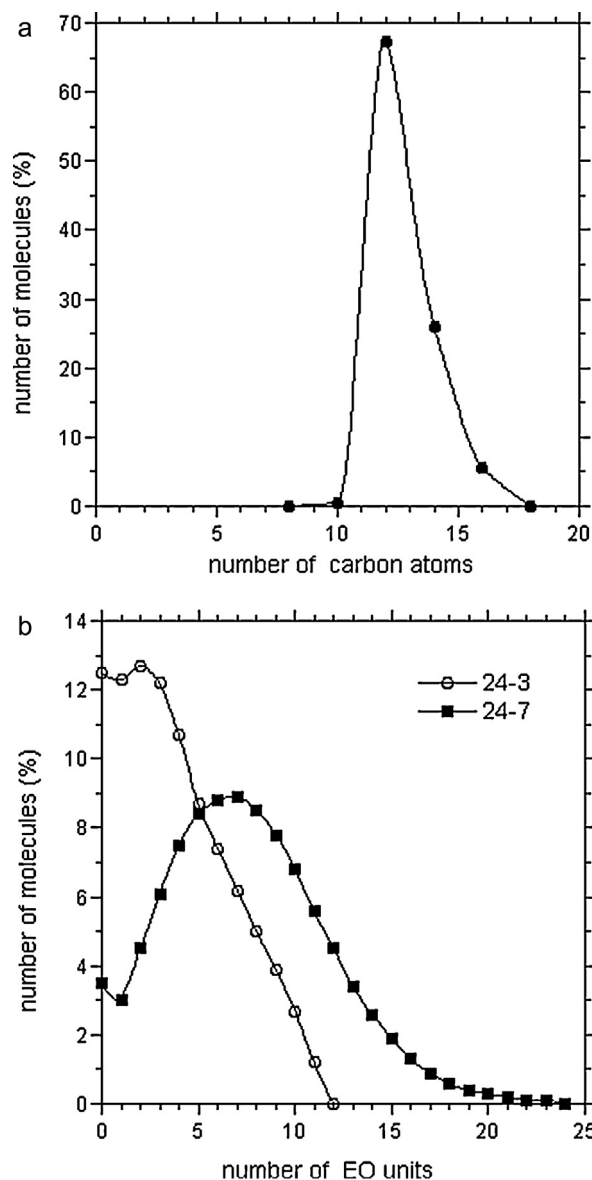


Fig. 1. Distributions of alkyl tail length (a) and poly(oxyethylene) chain length (b) in the 24-3 and 24-7 samples used in this work.

are present, while the maximum number of oxyethylene units is 11 and 23, respectively. From the distribution profiles, the polydispersity index of the molecular weight can be estimated as 1.7 for 24-3 and 1.3 for 24-7. Surfactant samples were also characterized in terms of critical micellar concentration (CMC) in aqueous solution, determined by tensiometry [26]. 24-7 presents a $CMC \approx 7 \cdot 10^{-5} \text{ mol kg}^{-1}$. In the case of 24-3, no homogeneous aqueous solution was obtained, even at very low concentration. This prevented CMC determination.

The binary and ternary aqueous mixtures of these surfactants were prepared by weighting all the components according to the desired composition, followed by a Vortex mixing. Double distilled water was used for all the investigations, except for SANS measurements, where water was replaced by heavy water (purchased from Sigma Aldrich, isotopic enrichment >99.8%) in order to reduce the incoherent contribution to the total scattering cross section and for enhancing the contrast between the scattering aggregates and the solvent [27]. Liquid crystalline samples were mixed by repeated centrifugation for several days, and samples in the solution regions were mixed by shaking overnight. Thoroughly mixed samples were

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