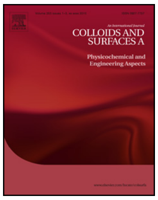
Colloids and Surfaces A: Physicochem. Eng. Aspects 498 (2016) 50–57

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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



Langmuir films and mechanical properties of polyethyleneglycol fatty acid esters at the air-water interface

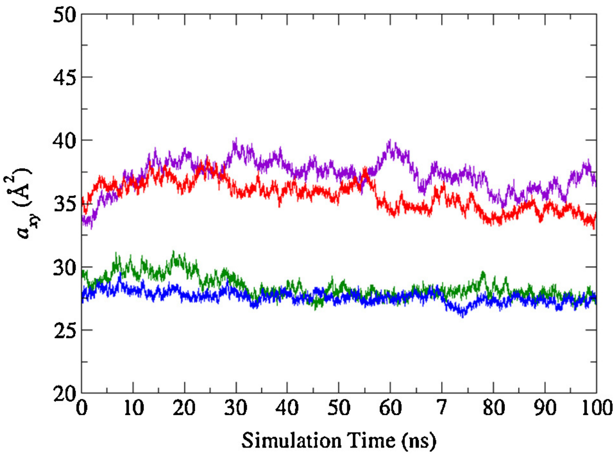
Stephanie Ortiz-Collazos[a], Yan M.H. Gonçalves[a,c], Bruno A.C. Horta[c], Paulo H.S. Picciani[d,e], Sonia R.W. Louro[b], Osvaldo N. Oliveira Jr[d], André S. Pimentel[a,*]

[a] *Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, RJ 22453-900, Brazil*
[b] *Departamento de Física, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, RJ 22453-900, Brazil*
[c] *Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ 21941-909, Brazil*
[d] *Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, SP 13566-590, Brazil*
[e] *Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ 21941-598, Brazil*

HIGHLIGHTS

- This study is a comprehensive theoretical and experimental study of the Langmuir films of Polyethyleneglycol Fatty Acid Esters.
- It is possible to associate a correlation between the tail group and hydrophilic chain and the ensuing physicochemical properties.
- Shorter polyoxyethylene polar chains lead to more ordered films, but longer chains may be more effective in stabilizing the monolayer film.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 December 2015
Received in revised form 25 February 2016
Accepted 11 March 2016
Available online 19 March 2016

Keywords:
PEG fatty acid esters
Langmuir films
Molecular dynamics
Compression modulus
PM-IRRAS
BAM

ABSTRACT

Polyethylene glycol (PEG) fatty acid esters are used in various industries for their interfacial properties, especially because their emulsifying characteristics can be varied considerably by altering the size of the PEG or fatty acid chains. In this study, we combine experimental surface-specific methods and molecular dynamics (MD) simulations to probe the effects from changing both the hydrophilic and hydrophobic chain sizes. PEG fatty acids containing either stearic or palmitic acid ethoxylated PEG chains of average molecular weight 200 or 400 g mol^{-1} (referred to as PEG200 and PEG400, respectively) had critical aggregation concentrations between 30 and 50 μM, and formed Langmuir films at the air/water interface with compressibility modulus typical of liquid-expanded phases. The area per molecule was consistently smaller for the PEG200 series owing to an increased ordering of the hydrophilic chains inferred from the polarization-modulated infrared reflection absorption (PM-IRRAS) spectra, which was corroborated by MD simulations. With PM-IRRAS and MD simulations, we also noted that the hydrophobic chain had increased order when its size increased from palmitic to stearic acid, which was attributed to a higher melting temperature for longer saturated hydrocarbon chains.

---

* Corresponding author.
E-mail address: a_pimentel@puc-rio.br (A.S. Pimentel).

http://dx.doi.org/10.1016/j.colsurfa.2016.03.032
0927-7757/

1. Introduction

Polyethyleneglycol (PEG) fatty acid esters are nonionic surfactants used in the food, pharmaceutical, cosmetic and oil industries [1]. In this class of surfactants, polyethylene glycol comprises the hydrophilic part of the surfactant while the fatty acid is the lipophilic part. By varying the molecular weight of PEG and the fatty acid, surfactants covering a wide range of hydrophilic-lipophylic balance (HLB) values can be produced. Typically, those with an HLB below 13 are oil soluble and water dispersible while those above are water soluble. They exhibit a range of accessible polarities owing to the large number of possible hydrophilic chain and tail group structures and their combinations. PEG esters, particularly PEG oleates and stearates, are excellent emulsifiers, better than alcohol ethoxylates or nonyl phenol ethoxylates (NPE), being therefore promising for NPE replacement in industry [1]. Furthermore, PEG ester surfactants are a closer match to NPE with respect to solubility and emulsifying characteristics than are alcohol ethoxylate surfactants. They have low foaming tendency, good wetting/dispersing properties, excellent biodegradability, good stability (hydrolyzing only on alkaline conditions), low hazard, and low toxicity [1]. With such properties, they are used in cosmetics and toiletries, also because they are excellent emollients, moisturizers, anti-irritants or mildness increasers, very mild cleansers and can confer slipperiness to shampoo, body washers and bubble baths [1]. Their water/oil emulsifying properties are exploited in lubricants for textile processing, cutting oils and metalworking fluids, solvent cleaners, emulsifiable degreasers, emulsifiers for self-emulsifying herbicides, insecticides, fungicides, and polymer latex production [1].

PEG esters may exhibit high interfacial affinity when dispersed in aqueous solutions, depending on their molecular structure [1]. However, they exhibit very low solubility in water because of their pronounced hydrophobic effect. Consequently, they self-assemble into multilamellar vesicles even at extremely low concentrations [2], forming aggregates that are generally significantly less surface-active than their monomers in solution. Indeed, their adsorption at the air-water interface is energetically unfavorable due to the interaction of the hydrophobic chains with water [2]. On the other hand, these unfavorable interactions no longer prevail as the structures are self-assembled, and bulk aggregates may be transferred to the interface [3,4]. Various adsorption mechanisms have been suggested for soft materials [5–9], normally with three consecutive steps in which vesicles diffuse to the interface, adhere, and finally disintegrate into superficial mesophases [3]. It is also possible that there is first a partial dissociation of aggregates into monomers, which are indeed surface-active, very similarly to micelles [10–12]. In both cases, the kinetics of these multistep processes depends mostly on the ability of amphiphiles to move to the interface, which is determined by the temperature and physical state of the aggregate, i.e. gel-like or liquid-crystalline [10–14]. The first state has a high binding energy of the individual molecules and a slow molecular motion [13,14], which should prevent vesicles from adsorbing at an interface. In contrast, the mobility of the liquid-crystalline state is much higher and adsorption is favored energetically. The transition from the gel-like to liquid-crystalline state occurs by simply increasing the temperature above the chain melting phase-transition temperature (T_m) of the aggregate dispersion, which is usually around 32 °C. Below this temperature, aggregates are predominantly in the gel-like state, where the mobility of individual molecules is very slow.

The aim of the present study is to investigate the mechanical properties of PEG fatty acid ester monolayers, which are investigated in the air-water interface below the melting phase-transition temperature, 32 °C. With such a system we can address the following issues: (1) produce Langmuir films with PEG fatty acid esters to determine whether they are in the gel-like or liquid-crystalline state below 32 °C; and (2) correlate the surface structure to compressional modulus. Our experimental approach to examine these issues is described as follows. We first spread a monolayer of PEG fatty acid ester using the Langmuir technique to investigate its structural and interfacial compressional modulus. Also, the critical aggregation concentration is measured by using fluorescence spectroscopy. We selected polyethylene glycol fatty acid esters consisting predominantly of stearic or palmitic acids (tail group) ethoxylated with polyethylene glycol (PEG) chains of average molecular weight 200 or 400 g mol^{-1} (hydrophilic chain), since the size of fatty acids and the PEG attached may have an important role on hydrophilic-lipophilic balance (HLB) which is a determinant for future applications. From now on, we shall refer to the PEG fatty acid ester investigated as PEGXXXSA or PEGXXXPA, where XXX is 200 or 400 to indicate the average PEG molecular weight, and SA and PA are stearic and palmitic acid, respectively.

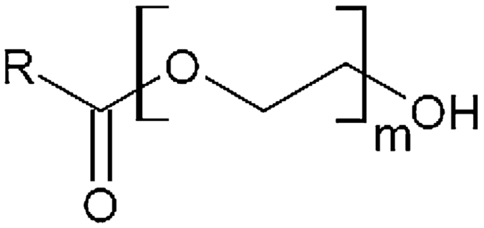


Fig. 1. Chemical structure of PEG fatty acid esters. R is $C_{17}H_{35}$ for stearic acid (SA) and $C_{15}H_{31}$ for palmitic acid (PA). m is 4 or 9, representing PEG with molecular weight 200 g mol^{-1} (PEG200) and with molecular weight 400 g mol^{-1} (PEG400), respectively.

2. Experimental

2.1. Materials and methods

The PEG fatty acid esters were synthesized by using well-established organic synthesis procedures [15]. Their structures are shown in Fig. 1. The reactants used were PEG as a mixture of oligomers with average molecular weight of 200 or 400 g mol^{-1}, and stearic or palmitic acids. The reactants were used without further purification and may contain trace amounts of impurities. The reaction was carried out by standard esterification using a Dean Stark apparatus with small excess of PEG. The reaction product was a mixture with a majority of monoesters and small amount of diesters. The PEG fatty acid esters were purified with the standard salting out procedure to remove the catalyst and unreacted PEG.

Surfaces and glassware were cleaned with chloroform (purity >99.4% HPLC-UV grade) and acetone (purity >99.5% PA ACS grade) from Sigma-Aldrich, Brazil. Water employed as subphase and for the preparation of surfactant solutions was obtained from a Milli-Q purification system (Millipore, Brazil). Stock solutions of pyrene (Sigma-Aldrich, Brazil) were used to perform the fluorescence measurements to evaluate the critical aggregation concentration. For the spreading experiments in the Langmuir trough, chloroform PEG fatty acid esters solution were prepared with concentrations of 0.3–0.5 g L^{-1} and 20 μL of these solutions were spread over the ultrapure water subphase (Milli-Q purification system from Millipore with resistivity 18.2 MΩ-cm).

2.2. Physical and chemical analysis

The melting point of PEG fatty acid esters was measured using a melting point apparatus, Model Q340S (QUIMIS, Brazil), which contained a microscope to observe the melting process. PEG fatty acid