Colloids and Surfaces A: Physicochem. Eng. Aspects xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Interfacial activity of amino acid-based glycerol ether surfactants and their performance in stabilizing O/W cosmetic emulsions

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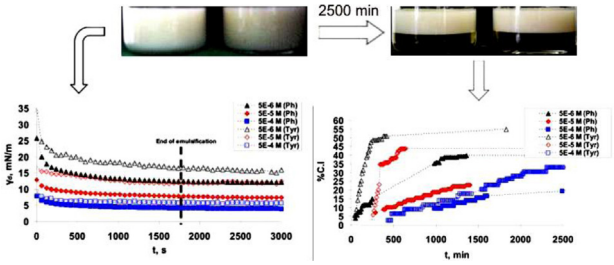
HIGHLIGHTS

- Emulsions containing $PhGE_{12}$ show better stability.
- Increase of surfactant's concentration lead to increased stability.
- $PhGE_{12}$'s emulsions have smaller droplets.
- Interfacial tension has approached its equilibrium value after 1800 s.
- Interfacial rheology seems not to affect emulsion's stability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 December 2013
Received in revised form 11 February 2014
Accepted 11 February 2014
Available online xxx

Keywords:
Dynamic interfacial tension
Dilatational viscoelasticity
Ecofriendly surfactants
O/W emulsions
Creaming Index
Droplet size distribution

ABSTRACT

Biocompatible and biodegradable molecules of Phenyl- and Tyrosine-glycerol ether surfactants are good candidates for eco-friendly cosmetic emulsions. Both molecules have a hydrophobic alkyl chain with 12 carbon atoms, but different amino acids in the hydrophilic head: phenylalanine ($PhGE_{12}$) and tyrosine ($TyrGE_{12}$). This study reports on the activity of liquid/liquid interfaces with the glycerol ether surfactants being dissolved in the organic phase (olive oil) and the aqueous phase containing the non-ionic poly(oxyethelene) (20) sorbitan monooleate (trade name Tween 80). Measurements refer to a) dynamic surface tension by drop profile tensiometry and drop volume tensiometry and b) interfacial dilatational viscoelasticity by oscillating drop profile analysis. It is shown that $PhGE_{12}$ attains much lower interfacial tension values and exhibits faster interfacial adsorption than $TyrGE_{12}$ whereas interfacial dilatational viscoelasticity values are comparable between the two surfactants. Oil-in-water emulsions are prepared and their stability is assessed by monitoring the time evolution of creaming index. To interpret observations, measurements of the emulsions' initial droplet size distributions and apparent bulk viscosity are employed. It is found that at similar surfactant concentrations, $PhGE_{12}$ emulsions exhibit better stability than $TyrGE_{12}$ emulsions. This might be attributed to the lower interfacial tension in $PhGE_{12}$ emulsions that yield droplet size distributions richer in intermediate (~50 μm) and small size (~0.5 μm) droplets and to their higher apparent viscosities. On the other hand, increasing the concentration of either surfactant leads to a substantial increase of emulsions stability which is in line with the lower interfacial tension and higher apparent viscosity measurements but does not agree with the insensitive versus surfactant concentration droplet size distributions and interfacial dilatational viscoelasticity.

1. Introduction

Emulsions are omnipresent. They dominate our daily life ranging from cosmetic products, foods, cleaning and pharmaceutical products to paint and oil industries [1]. Knowledge of the

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http://dx.doi.org/10.1016/j.colsurfa.2014.02.033
0927-7757/

physicochemical properties of such formulations is essential to optimize manufacturing conditions, provide cosmetic elegance and control the delivery of cosmetic agent to the skin.

Emulsions are heterogeneous mixtures consisting of at least two immiscible liquids [2]. Emulsions are made stable by the use of emulsifiers, i.e., surface active agents (surfactants), amphiphilic polymers or proteins, which sufficiently reduce interfacial tension [3]. Such molecules stabilize the oil droplets at the time of manufacture by the formation of an interfacial film, and also control the interfacial rheological properties of the formulation between wide limits. Therefore, many researchers in the physical-chemistry field have tried to assess the efficiency of emulsification and the stability of emulsions based on measurements of static/dynamic interfacial tension and of interfacial viscoelasticity [4–9]. However, in most cases systematic measurements over a broad range of interface lifetimes (using independent techniques) is missing and so results are rarely conclusive.

At the other end of the line, one can find a vast number of technology oriented publications where emulsification and emulsion stability are assessed by macroscopic quantities such as the propagation of the phase separation front, droplet size distribution, emulsion apparent viscosity etc. These quantities are often enough to appraise the production of emulsions and the subsequent phase separation due to the gradual flocculation and aggregation of the dispersed phase droplets leading ultimately to a cracked or separated emulsion. However, they cannot explain the mechanisms that dictate the specific properties and shelf-life of emulsions. It is apparent that a combination of physicochemical and macroscopic measurements is advantageous to shed light on the underlying mechanisms.

It has long been recognized that mixed emulsifying agents (co-surfactants) often yield more stable emulsions than single ones do, and, in most cases the high stability is ascribed to the complex formation at the interface, which results in an interfacial film of great strength which prevents coalescence of droplets. Usually, film strength is quantified by interfacial elasticity measurements. Nevertheless, when emulsifying agents are present in both phases of the emulsion then the situation is more complicated and the possibility cannot be excluded that there is interaction between molecules across the interfaces affecting also the bulk rheological properties of the system e.g. increase the emulsion apparent viscosity.

Two amino-acid glycerol ether surfactants have been synthesised and chemically characterised in detail in previous work [10,11]. These are Phenylalanine ($PhGE_{12}$) and Tyrosine ($TyrGE_{12}$) with 12 carbon atoms in their hydrophobic chain. Air/water interfacial activity (dynamic surface tension and interfacial dilatational viscoelasticity) of both surfactants has been dealt with in two recent articles [12,13]. These molecules dissolve readily in water only at high pH value and this limits their use only to specific applications e.g., mercerization of fabrics. On the other hand, both molecules dissolve easily in organic solvents revealing strong potential for emulsions applications.

This work first examines the interfacial activity at the oil/water interface of Phenylalanine ($PhGE_{12}$) and Tyrosine ($TyrGE_{12}$) dissolved in olive oil in the presence of poly(oxyethelene) (20) sorbitan monooleate (Tween 80) in the aqueous phase. This includes measurements of dynamic interfacial tension by two independent techniques (drop profile tensiometry and drop volume tensiometry), which in combination cover a wide range of interface age, and of interfacial dilatational viscoelasticity. Then, emulsions particularly rich in oil content—such as those in skin and health care applications—are produced in a broad range of surfactants concentrations and their stability versus time is registered by monitoring the displacement of the creaming front (creaming index) in time. Measurements of initial droplet size distributions and initial emulsion apparent viscosity have been combined with measurements of oil/water interfacial properties to interpret observations. An effort is made to provide insight on what might explain the behavior of such oil rich surfactants.

2. Materials and methods

2.1. Preparation of solutions for interfacial measurements

Organic solutions of amino-acid glycerol ether surfactants ($PhGE_{12}$ and $TyrGE_{12}$) are prepared at concentrations of 1×10^{-6}–5×10^{-4} M (mol/L of oil phase). Due to an extra hydroxyl anion (phenolic group instead of a simple aromatic ring), $TyrGE_{12}$ is more hydrophilic than $PhGE_{12}$. Olive oil (Altis, Elanthy S.A., 2012) is the organic solvent. Olive oil is a high valued natural product typically used in foods and cosmetics. Dilution of surfactants in oil is carried out at low heating and mild stirring. Olive oil is purchased from the market and used as received, viz. purified from the company that bottled it.

Poly(oxyethelene) (20) sorbitan monooleate (Tween 80) (synthesis grade, Merck) is used at a constant concentration of 40% w/v in the aqueous phase for all measurements ($C = 3.05 \times 10^{-1}$ mol/L of aqueous phase). Its trade name, Tween 80, is used henceforth for convenience. It derives from polyoxylated sorbitol and oleic acid. It is a nonionic surfactant with HLB 15, which means that it is soluble in water and not in oil. Dilution of Tween 80 in Millipore water is accomplished at mild heating and stirring. The pH value of aqueous phase is 7.3 (at 24.2 °C).

2.2. Interfacial (liquid/liquid) measurements

2.2.1. Dynamic interfacial measurements

Measurements are conducted by two independent techniques spanning different ranges of interfacial lifetimes. This is important, first, to show that measurements are complementary and so are not technique dependent and, second, to extend information over a broad range interfacial lifetimes.

2.2.1.1. Drop volume tensiometry. Dynamic interfacial tension measurements at short interface lifetimes (less than 3 s) are performed with a drop volume tensiometer (DVT; TVT 2, LAUDA). DVT provides estimation of the interfacial tension of a freshly formed interface via an aqueous drop created into the oil phase. The instrument is calibrated against Millipore water and clearness of glass syringe and stainless steel capillary is checked with measurement with Millipore water. All measurements are carried out with freshly made solutions. The sample cell is filled with the organic solution of amino acid glycerol ether surfactant. A graded glass syringe (2.5 ml) with a stainless steel capillary, which has a diameter of 1.385 mm, is filled with Tween 80 aqueous solution. Then the syringe is adjusted to the test cell of the tensiometer. The temperature of both test cell and syringe is kept constant at 25 ± 0.1 °C. Initial drop time is 0.4 s and the subsequent drops time is 0.42 s. The experimental scenario consists of 3 drops per cycle for 10 consecutive cycles.

2.2.1.2. Drop profile analysis. Dynamic interfacial tension measurements at long adsorption times, (several seconds to hours), are employed via drop profile tensiometer (DPT; PAT-1S SINTERFACE). The instrument is placed on an anti-vibration table, (Halcyonics Micro 40/60/80). The tensiometer allows long-time experiments keeping either the volume or the surface area of a drop constant. Calibration took place against Millipore water. Due to the long times involved, surface lifetime is explicitly measured. The temperature of the solutions is kept constant at $T = 25 \pm 0.1$ °C. In this study a pendant drop ($V = 4$ mm^3) of Tween 80 aqueous solution is used. The drop is created by a computer driven dosing system at the tip

Please cite this article in press as: C.D. Ampatzidis, et al., Interfacial activity of amino acid-based glycerol ether surfactants and their performance in stabilizing O/W cosmetic emulsions, Colloids Surf. A: Physicochem. Eng. Aspects (2014), http://dx.doi.org/10.1016/j.colsurfa.2014.02.033