Colloids and Surfaces A: Physicochem. Eng. Aspects 326 (2008) 162–168

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Triolein solubilization using highly biodegradable non-ionic surfactants

E. Jurado*, V. Bravo, J.M. Vicaria, A. Fernandez-Arteaga, A.I. Garcia-Lopez

Departamento Ingeniería Química, Facultad Ciencias, Campus Universitario Fuentenueva, Universidad de Granada, Avda. Fuentenueva, s/n, 18.071, Granada, Spain

ARTICLE INFO

Article history:
Received 31 January 2008
Received in revised form 19 May 2008
Accepted 19 May 2008
Available online 24 May 2008

Keywords:
Phase diagram
Triolein
Alkylpolyglucoside
Ethoxilated fatty alcohols

ABSTRACT

Ternary, pseudo-ternary and binary water:triolein:non-ionic surfactant systems have been studied in order to establish the respective phase diagrams. Two non-ionic surfactants (an alkylpolyglucoside and an ethoxylated fatty alcohol) and a mixture of the two have been used. Microemulsions have been discovered in the ternary phase diagrams. A significant amount of triolein has been solubilized with long-term stability at slightly over the room temperature, using highly biodegradable surfactants without a co-surfactant. The conditions under which the microemulsion region has been found (low temperature, low oil concentration and low surfactant concentration) could be highly useful in detergency. Temperature-insensitive or temperature-sensitive O/W microemulsion formulations have been discovered by using alkylpolyglucoside or ethoxylated fatty-alcohol emulsions.

1. Introduction

REACH is a new European Community Regulation on chemicals and their safe use (EC 1907/2006) that deals with the registration, evaluation, authorization, and restriction of chemical substances. The aim of REACH is to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances. This regulation demands greater responsibility from industry to manage the risks from chemicals and to provide safety information on the substances produced. Manufacturers will be required to gather information on the properties of their chemical substances, which will allow safe handling. The regulation also calls for the progressive substitution of the most dangerous chemicals when suitable alternatives have been identified.

Among these chemical substances are industrial cleaning products, generally comprised of aqueous solutions of surfactants that contain coadjuvants, solvents, solubilizers, stabilizers, etc. The European Union has also established criteria for the concession of the so-called “EC ecological label for cleaning products of general use” (2001/523/CE). For all these reasons, due to their high use, these chemical substances need to be studied exhaustively in the near future, not only from the standpoint of their environmental security but also their use efficiency.

Some of the most widely studied surfactants are the alkybenzene sulfonates, but they are expressly forbidden in ecological detergent formulae. Also, alkylphenols present intermediate metabolites in their biodegradation that behave as hormonal disrupters and thus their use is also restricted [1]. Along this line, there is steadily growing use of non-ionic surfactants, such as alkylpolyglucosides and ethoxylated fatty alcohols, which are not only highly biodegradable and highly efficient on fatty soils [2] but also come from renewable sources.

Triolein or glycerol trioleate (GTO) is a liquid form of triglyceride and a major component of the natural fats from both plants and animals. It is present in many food products, such as cooking oil, margarine, and butter, and it is also one of the main constituents of olive oil. Being one of the most difficult oils to be removed from fabric, it is considered a good representative of triglyceride oily soil on clothes and kitchenware in detergency tests. In fact, triolein is considered to be a model triglyceride. It has a higher molecular weight than typical liquid hydrocarbon oils and a bulky structure with three branches, which makes solubilization more difficult with a common non-ionic surfactant such as an ethoxylated linear alcohol. Furthermore, triolein is a slightly polar oil so that its phase behaviour differs substantially from that of typical hydrocarbons.

Triglycerides significantly affect both solubilization and phase behaviour as a result of the large molecular size. Most published papers on triolein removal have involved non-ionic surfactants because triolein is extremely hydrophobic, leading to better solubilization in a lipophilic surfactant than in a hydrophilic surfactant. Lipophilicity is easy to attain with non-ionic surfactants. Studies on triolein removal by non-ionic surfactants have been reported

* Corresponding author. Tel.: +34 958 243307; fax: +34 958 248992.
E-mail addresses: ejurado@ugr.es (E. Jurado), vbravo@ugr.es (V. Bravo), vicaria@ugr.es (J.M. Vicaria), jandro@ugr.es (A. Fernandez-Arteaga), anaigl@ugr.es (A.I. Garcia-Lopez).

0927-7757/$ – see front matter
doi:10.1016/j.colsurfa.2008.05.024

for decades [3,4], whereas the phase behaviour and the detergency mechanism for triolein are not well understood [5].

By definition, the oil and water phases of a surfactant-oil-water (SOW) system are immiscible, and the role of the amphiphile is to reduce the miscibility gap, until the three components are eventually co-solubilized (normally into a so-called microemulsion). As is known, under appropriate conditions the aqueous surfactant solutions are able to dissolve relatively large amounts of oil by incorporating oil molecules into surfactant aggregates. Solubilization is an important element of detergency and finds various applications in micelle-enhanced separation, emulsion polymerization, and the preparation of various cosmetic, pharmaceutical, and agricultural products. Ionic surfactants are rather inefficient in solubilizing water-insoluble oils (such as triglycerides). By contrast, it has been found that some non-ionic surfactants can be good solubilizers of triglycerides. Frequently, the solubilization ability of the ethoxylated fatty alcohols (non-ionic surfactants) increases when the temperature of the system approaches the cloud point from below, but in detergency it is necessary to run at different temperatures, preferably at rather low ones.

Microemulsion systems with short-chain oils have been extensively studied [6–9], and a large range of surfactants and additives can be used to control their microstructural properties. However, the development of microemulsions of molecularly large and partially amphiphilic oils such as triglycerides is difficult and there is possibly a lack of reported studies on this subject, although most results to date are encouraging for using surfactant-based microemulsions as organic-solvent replacements, vegetable-oil extraction, detergency, micelle-enhanced separation, etc. Thus, for vegetable-oilseed extraction, the formation of microemulsions with triolein has been challenging for decades due to the extremely polar and hydrophobic regions of the triglyceride molecule. Recently, ultra-low IFT and Winsor Type-IV microemulsions have been detected for the first time with triglyceride oils at ambient temperature [10,11] using extended surfactants [12].

Present report examines the solubilization process of these types of molecules using environment-friendly resources. Here, we study the phase behaviour of systems prepared with water, triglyceride (triolein), and biodegradable non-ionic surfactants. Our aim is to search for areas of higher triglyceride oil solubilization, at temperatures low enough to be applied in detergency, preferably thermodynamically stable ones, containing reduced proportions of surfactant. We have studied the phases present in binary systems (non-ionic surfactant–water, non-ionic surfactant–triglyceride, a mixture of non-ionic surfactant–water, a mixture of non-ionic surfactant–triglyceride) and ternary ones (a mixture of non-ionic surfactant–water–triglyceride). These studies will contribute to the design of detersive formulae containing both efficient and environment-friendly surfactants.

2. Materials and methods

The oil used was triolein or glyceryl trioleate, purchased from Sigma Chemical Co. (Milwaukee, WI) as technical grade (purity of 65 wt.% - CASN: 122-32-7). It also contains 1,3- and 1,2-diglycerides, monoglycerides and its fatty-acid chain composition is 90 wt.% as oleic acid and 10 wt.% as linoleic acid (density = 0.91 g/cm^3; refractive index = 1.469). Triolein, 1,2,3-tri(cis-9-octadecenoil)-glycerol ($C_{57}H_{104}O_6$, molecular weight 885.5 g/mol), has a three-branched structure. This oil is frequently used in detergency as a soil model. The choice of triolein in technical purity was dictated by the fact that these formulations are of applied interest. Generally, very pure materials are not used for industrial purposes. Moreover, the presence of different chain lengths, unsaturation, and mono- or diglycerides in GTO particularly is important since these “impurities” play a synergetic role in emulsion stabilization [13]. In practical applications, triolein and other liquid triglycerides are rarely pure, containing fatty acids formed by the hydrolysis of ester bonds [14].

Two non-ionic surfactants were used, an ethoxylated fatty alcohol, Findet 1214N/23 (supplied by Kao-Chemical Europe, average molecular formula $C_{12.6}E_{11}$, estimated HLB value of 14.4, water content less than 0.3 wt.%) and an alkylpolyglucoside, Glucopon 650 (supplied by Henkel-Cognis, average molecular formula $C_{10.7}G_{1.4}$, estimated HLB value of 11.9, 50 wt.% in water). The alkylpolyglucoside water content was reduced to less than 2 wt.% by freeze drying, following the procedure described by Platz et al. [15]. The samples were frozen at −42 °C for 35 h and then vacuum dried (5 mmHg) for 2 days.

The samples used for the phase-diagram determination were prepared with distilled water from a Milli-Q water purification system (Millipore Inc.).

2.1. Sample preparation and phase diagram determination

The binary and ternary phase diagrams were made by preparing samples in ampoules with several weight compositions of water:surfactant, triolein:surfactant, water:mixture of surfactants, triolein:mixture of surfactants and water:triolein:mixture of the surfactants. To avoid solvent evaporation, the mixtures were quickly flame sealed. The samples were mixed and repeated cycles of heating and centrifugation at 3000 rpm were made. The compositions are expressed in wt.% ratios between components and also as wt:wt ratio. Before being examined, the samples were kept frozen for 24 h and then allowed to equilibrate in a thermostatic bath at 30 °C for several days. The phases were identified by visual observation (turbidity, viscosity), polarizers (birefringence), and optical microscope (characteristic textures). In some cases, the solvent-penetration-scan method (or inversely, partial evaporation) was used to identify phases by microscopy.

The phase behaviour as a function of the temperature was determined in binary systems (alkylpolyglucoside:water and ethoxylated fatty alcohol:water). The procedure used to prepare the samples was the same. The samples were allowed to equilibrate in a thermostatic bath at different temperatures (in the range 0–70 °C) for 1 day prior to observations.

The examination of the macroscopic properties of the samples (isotropy, turbidity, homogeneity, and birefringence) at 30 °C allowed a preliminary phase-diagram characterization. The phase boundaries were determined by visual observation. Liquid crystals were detected by using crossed polarizers and the type of liquid crystal was also identified by a polarizing microscope. The anisotropic liquid-crystal phases were observed and the corresponding optical microphotographs were taken by optical microscopy (TOPIC-CETI) in polarized light at 30 °C. The patterns found for lamellar (Maltese crosses or disclination with four dark brushes) and hexagonal (fan-shaped texture or fan-texture) phases were compared with the typical textures and classical patterns of these phases shown by systems containing other related surfactants [13,16].

3. Results and discussion

3.1. Binary systems: influence of the temperature

Glucopon 650 has different carbon chains (C_8–C_{18}) and a glycosidation number varying between 1 and 5 [17,18]. Their behaviour was therefore complex and influenced by the individual behaviour of each of the constituents. Fig. 1 shows the phase diagram of water/Glucopon 650. Below 20 °C a precipitate began to appear over