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Short communication

Physicochemical characterization of aqueous micellar systems formed by environmentally friendly salts

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ABSTRACT

In this work, environmentally friendly aqueous micellar two-phase systems containing nonionic surfactants (Triton X-114, Triton X-100 and Genapol X080) and organic salts (sodium citrate and sodium tartrate) were characterized. In order to accomplish this objective, the binodal diagrams (cloud point vs. surfactant concentration) were obtained for each condition. Additionally, critical micelle concentration (CMC) and micellar hydrodynamic diameter (D_H) were determined for each system. According to the obtained results, it was found that the presence of salts lowered the CMC (ΔCMC up to 0.15 mM) and cloud point values (ΔCP up to 18 °C) following the sequence: sodium citrate > sodium tartrate. In addition, the hydrodynamic diameters of the micelles were notoriously increased in presence of the studied salts, showing the high sensitivity of the described aqueous micellar two-phase systems to the medium condition. These results open perspectives for the use of greener aqueous micellar two-phase systems for bioseparation purposes.

1. Introduction

Surfactants comprise a group of amphiphilic molecules composed of a hydrophilic moiety and a hydrophobic moiety, known as head and tail, respectively. The surfactants can be classified onto anionic, cationic, zwitterionic or nonionic [1] according to the structural characteristic of their head. When these molecules are dissolved in a polar solvent above a critical micelle concentration (CMC), they are able to form nanometer-sized aggregates in which the hydrophilic heads remain on the outer surface and the hydrophobic tails flock to the interior in order to minimize their contact with the solvent [2,3]. The size and shape of these aggregates depend on surfactants properties and on the medium conditions such as temperature, total surfactant concentration, ionic strength, and pH.

For some micellar systems, a temperature increase [4,5] promotes a spontaneous phase separation, resulting in an aqueous micellar two-phase system (AMTPS). The mentioned phase-separation process, between a micelle-rich phase and a micelle-poor phase, is attributed to the temperature effect on the thermal motion of water molecules, thus affecting the interaction/solvation of micelles. At increasing temperature, micelles start to interact with each other, thus resulting in a micellar network [4]. The phase-separation temperature, so-called cloud point (CP), depends basically on the surfactant structure and concentration. The presence of additives such as inorganic salts, biopolymers, fatty acids, aliphatic alcohols, and phenols also affects the CP strongly [6–8]. Particularly, the addition of certain salts, drastically lower the phase-separation temperature due to strong electrostatic interactions between salts and water molecules, which prevail against the hydrogen bonds between the surfactant polar heads and water molecules [9]. This makes polar head–polar head (micelle–micelle) interactions more favorable than the polar head–solvent (micelle–water) ones.

The use of aqueous micellar two-phase systems (AMTPS) has been considered to be an attractive alternative in liquid–liquid extraction for years [10–13]. The first application of AMTPS as a separation methodology was reported by Watanabe and Tanaka for the concentration of zinc ions [14]. Afterwards, Bordier [15] demonstrated the differential partitioning of proteins within AMTPS phases.

Up to date, the use of AMTPS has been extended to the purification of different molecules such as aromatic hydrocarbons, viruses and antibodies [10,12]. Triton X-114 is one of the most

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Nomenclature

AMTPS	Aqueous micellar two-phase system
ANS	1-Anilino-8-naphthalene sulfonate
Cit	Citric acid
CMC	Critical micelle concentration
CP	Cloud point
ΔCMC	Critical micelle concentration variation
ΔCP	Cloud point variation
ΔG_{agg}	Free energy change associated with surfactant aggregation
D_H	Micellar hydrodynamic diameter
ΔS_{agg}	Entropic change associated with surfactant aggregation
GX080	Polyethylene glycol monoalkyl ether (Genapol) X-080
Tart	Tartaric acid
T_c	Critical temperature
TX100	Polyethylene glycol *tert*-octylphenyl ether (Triton) X-100
TX114	Polyethylene glycol *tert*-octylphenyl ether (Triton) X-114

widely used surfactant because of its slight protein denaturation index and biodegradability [16–18]. For example, Triton X-114 in combination with McIlavaine buffer (citrate/phosphate buffer) and an affinity ligand [19] has recently been used to purify an anti-electronegative LDL single-chain antibody fragment (recovery of 88% and purification factor of 2). On the other hand, surfactants belonging to the Genapol series are also widely used due to their low toxicity. In fact, the use of Genapol X-080 has been approved by the Food and Drugs Administration (FDA), extending their application to the processing of edible and pharmaceutical products. For example, liquid–liquid extraction with AMTPS, also known as cloud point extraction, using Genapol X-080 and NaCl has been used to purify polyphenols from wine sludge with recovery values close to 76% [20].

Despite of the successful results above mentioned, the use of non biodegradable salts should be avoided because of their negative environmental effect. The replacement of inorganic salts by biodegradable and non-toxic ones, such as citrate and tartrate, has been reported to be a good alternative [21–23]. For example, sodium citrate and sodium tartrate has been widely used in aqueous two phase systems with polyethylene glycol (PEG), ionic liquids (IL) and Ucon [22–24]. Nevertheless, up to our knowledge, the use of these organic salts to form AMTPS with nonionic surfactants has been poorly explored. There are just a few reports about liquid–liquid equilibrium of Tween 20/sodium citrate [25] and Triton X-100/sodium citrate [26] aqueous two-phase systems in which the reported phase separation data only involve the concentration of the system components at a fixed temperature [2,27]. However, the knowledge of temperature effect on phase-separation behavior, necessary for a better understanding and exploitation of the AMTPSs in purification processes, has not been further explored.

Taking into account the mentioned above, the main aim of this work was to determine the main characteristics of AMTPSs containing nonionic surfactants (Triton X-114, Triton X-100 and Genapol X080) and organic salts (sodium citrate and sodium tartrate). To accomplish that, the binodal diagrams (cloud point vs. surfactant concentration) were obtained for each case. Additionally, critical micelle concentration (CMC) and micellar diameter (D_H) were determined for each system. This characterization represents a start point to a further application of these systems in bioseparation purposes.

2. Materials and methods

2.1. Materials

The nonionic surfactants, polyethylene glycol *tert*-octylphenyl ether (Triton) X-100 and X-114 (TX100 and TX114, respectively) and polyethylene glycol monoalkyl ether (Genapol) X-080 (GX080), were purchased from Sigma–Aldrich and used without further purification (see Table 1). Tartaric acid (Tart), citric acid (Cit), sodium hydroxide and 1-anilino-8-naphthalene sulfonate (ANS) were supplied by Sigma–Aldrich and used as received. All the other reagents were of analytical grade and used without further purification.

Sodium citrate and sodium tartrate stock solutions (500 mM) were prepared by dissolving the acid in water and adjusting the pH to 5.00 with sodium hydroxide.

2.2. Experimental procedure

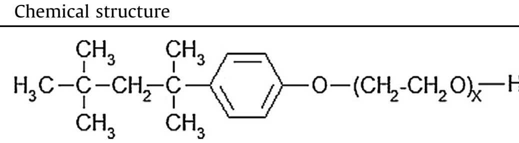
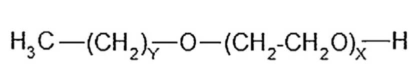
2.2.1. Critical micelle concentration (CMC)

The critical micelle concentration of the surfactant was determined by using 1-anilino-8-naphthalene sulfonate (ANS) as hydrophobic probe ($\lambda_{excitation}$ 382 nm, $\lambda_{emission}$ 470 nm, [ANS] 0.1 mM, temperature 22 °C) [28]. Fluorescence measurements were performed on an Aminco Bowman S2 spectrofluorometer with a thermostated circulating water bath and each measurement was performed by triplicate.

2.2.2. Cloud point (CP) determination

Cloud point determination of surfactant solutions was performed by the method described by Watanabe and Tanaka [14], which consist in visually identifying the temperature at which solutions with known concentrations of a given surfactant become cloudy. To accomplish that, 5 mL-systems containing surfactant (0–8% w/w) and sodium citrate/sodium tartrate (50, 100 and

Table 1
Chemical structure and purity of surfactants.

Compound	Chemical structure	Mass fraction purity
Triton X-100, $x = 9$–10 Triton X-114, $x = 7$–8		≥0.99 ≥0.99
Genapol X-080, $x = 8$; $Y = 12$		≥0.99