



Evaporation of aqueous dispersed systems and concentrated emulsions formulated with non-ionic surfactants



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ABSTRACT

Vacuum evaporation of aqueous surfactant systems and concentrated oil-in-water (O/W) and water-in-oil (W/O) emulsions was studied as a function of the base oil (castor oil, heavy mineral oil and light mineral oil), and the kind of non-ionic surfactant (Tween and Span series) used in their formulation. Water evaporation rates were measured from aqueous surfactant solutions/dispersions (5% w/w surfactant), and O/W emulsions (5% w/w surfactant) in 1:1 water/oil weight ratio. Vacuum evaporation of W/O emulsions was also investigated, since a W/O emulsion is formed when the emulsion inversion point is surpassed during the evaporation of O/W emulsions. Surface tension, conductivity and particle/droplet size distribution were measured to characterize the formulated systems. Three simple models were tested to fit the evaporation rate data and their consistency depends on the system under consideration.

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1. Introduction

The study of water evaporation in presence of organic compounds is of growing interest in areas such as the treatment of hazardous fluids, drying, release of volatile compounds from commercial products, and the retardation and evaporation control from colloidal microstructured emulsions for drug delivery applications [1–12].

The treatment of metalworking fluids and other oily waste effluents from food or cosmetic industries, which are considered hazardous fluids, is frequently carried out by vacuum evaporation.

Moreover, the use of water-based synthetic fluids and semi-synthetic emulsions is increasing in industrial processes due to their low (or any) oil content. Their treatment is more difficult either because of the very small oil droplet size (semi-synthetic emulsions) or no droplets present (synthetic fluids). Evaporation is more effective than other alternative processes and the presence of surfactants and dispersed nanostructures has a big influence on the evaporation process [6].

In previous works [5,7] the effect of surfactants on the water evaporation rate of surfactant solutions and oil-in-water (O/W) emulsions with 3% w/w oil, formulated with a surfactant content close to its critical micelle concentration (CMC) was studied. The effect of the surfactant on the water evaporation rate and the

quality of the final water condensate were examined in the presence of non-ionic and ionic surfactants.

Surfactants reduce the water evaporation rate [1,8,13,14]. This is especially noticeable for non-ionic surfactants [3].

Vacuum evaporation of surfactant solutions and O/W emulsions can be described as a three-step sequence [7]:

1. Transport of water vapour bubbles to the top of the liquid sample, a process controlled by mass transfer. Repulsive forces between oil droplets, surfactant micelles or niosomes play an important role in this step.
2. Transport of water vapour bubbles through a thin layer of a secondary phase formed by oil or surfactant, which is also controlled by mass transfer [2,3]. This step does not occur for solutions of surfactants highly soluble in water or for highly stable O/W emulsions, during the entire evaporation process.
3. Water vapour bubbles transfer from the liquid–vapour interface into the vapour phase.

Evaporation rates of surfactant solutions are controlled by either the first or the second step, depending on surfactant water solubility and surfactant concentration. For O/W emulsions, the controlling steps are more difficult to ascertain, depending on the emulsion composition, i.e. the second step becomes less important when the O/W emulsion is very stable [7]. However, it is difficult to establish which of the first two steps is the most significant in the

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evaporation process since the oil and surfactant concentrations are frequently very low in these systems.

In this work, evaporation rates of surfactant solutions/dispersions with 5% w/w of surfactant, and emulsions with 1:1 water/oil weight ratio were studied using several base oils. Non-ionic surfactants of the Tween series (high water solubility) and Span series (low water solubility) were used for the formulation of solutions, dispersions and emulsions. Water-in-oil (W/O) emulsions were formulated to investigate the evaporation process when water is present as droplets in a continuous oil phase, as occurs at the end of O/W emulsions evaporation when the emulsion inversion point has been surpassed. Attempts have been made to determine the controlling step in the evaporation process. Evaporation rates have been fitted to zero order, first order and diffusional models, depending on the system.

The main purpose of this work is to understand the behaviour of evaporation process of oily and dispersed systems found in several industries, which generate large amounts of waste effluents that cannot be treated by conventional methods (i.e. sedimentation, centrifugation and flotation).

2. Experimental

2.1. Materials

All surfactant solutions, surfactant dispersions and emulsions were prepared using deionised water (Millipore Elix 5 deionizer).

The surfactants used were non-ionic ones of the Tween and Span series, supplied by Sigma–Aldrich (USA). Their chemical structures are shown in Fig. 1.

All Tween surfactants have the same hydrophilic part, but a different lipophilic part, corresponding to specific hydrophilic–lipophilic balances (HLB): Tween 20 (HLB = 16.7), Tween 40 (HLB = 15.4) and Tween 60 (HLB = 14.9). Tween 80 (HLB = 15) shows an unsaturated bond. Similarly, Span 20 (HLB = 8.6), Span 40 (HLB = 6.7) and Span 60 (HLB = 4.7) surfactants differ in the length of their lipophilic part. Span 80 (HLB = 4.3) also has an unsaturated bond.

Three different oils supplied by Sigma–Aldrich (USA) were tested: castor oil, heavy mineral oil and light mineral oil, with viscosities of 0.541, 0.099 and 0.016 Pa s, respectively. Mineral oils are frequently used in metalworking industries and castor oil in food and cosmetic industrial processes.

Two dyes (Sigma–Aldrich, USA) were employed to visualise the external phase of the formulated emulsions: water-soluble copper (II) phthalocyanine-tetrasulfonic acid tetrasodium salt (blue), and oil-soluble fat red bluish (red).

2.2. Preparation of surfactant systems

Surfactant dispersions were prepared with a 5% w/w surfactant in deionised water by mechanical stirring on a hot plate at 50 °C for three hours.

2.3. Preparation of emulsions

Emulsions were prepared with 5% w/w surfactant content in a 1:1 water/oil weight ratio. Deionised water with 1% w/v NaCl to increase its conductivity was used as the aqueous phase. The surfactants were first dissolved in the phase in which they are

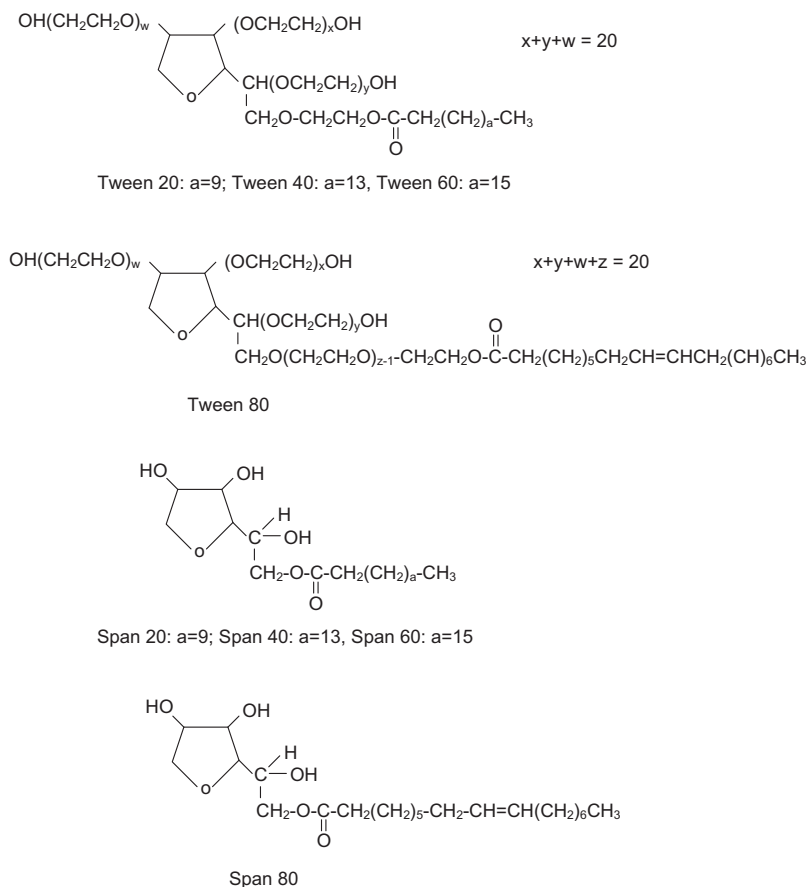


Fig. 1. Chemical structures of Tween and Span surfactants series.

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