

# Effect of emulsifier diffusion and interaction on the stability of interfaces formed in WOW double emulsions

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## INTRODUCTION

Double emulsion systems and their applications have gained interest to food science and industry nowadays [1]. Various studies have been carried out to understand these types of systems [2]-[4] in order to produce low-fat foods and to encapsulate environmentally sensible ingredients in order to avoid poor food quality. However, several challenges in stability are still an issue. As described by Dickinson [5] many factors and variables affect the stability of reliable formulations for practical applications. Besides the emulsion preparation parameters, the molecular interaction between emulsifiers and all thermodynamic and hydrodynamic interactions have to be considered.

In this context, the movement of emulsifiers towards and through the interface and its influences on the stability has been both an important and an open question without a clear explanation [5]. There are several forces playing a role at the tiny scale in which the phenomenon is taking place. This project was designed to contribute to a better understanding of how interfaces in double emulsions behave and interact. We studied experimentally the diffusion of emulsifiers and the resulting changes in interfacial tension and coalescence process.

## EXPERIMENTAL METHODS

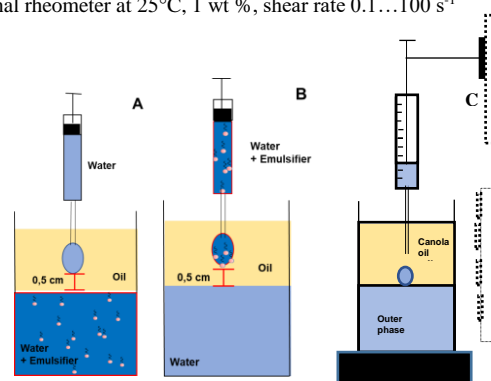
The study was divided in two parts. First, the interfacial tension was measured using the pendant drop method. Two different arrangements were set up to obtain the data as shown in figure 1a and 1b. In arrangement (A) one UV cuvette was filled with outer water phase and oil phase in a 6:4 ratio to resemble a real double emulsion distribution of phases like in Neumann et al [2]. The outer water phase in this arrangement contains polyvinyl alcohol (PVA) or Tween (table 1).

The inner water phase was created with a syringe in the oil phase as drop. This drop was suspended from a capillary with a diameter of 65  $\mu\text{m}$  and brought to the outer water phase at a distance of 0.5 mm from the interface. All measurements were conducted at 27 °C, during 7, 16 and 50 hours to follow changes caused by migration of emulsifier to the droplet of the inner water phase.

**Table 1.** Emulsifiers and components used in the formulation of every arrangement proposed.

Emulsifier	CMC (mg/L)	Concentration in experiment (mg/L)	Degree of Hydrolysis	Viscosity* (mPa.s)
PVA 99	800	1000	99	14.65
PVA 98	500	1000	98	3.18
PVA 88	800	1000	88	6.50
PVA 74	500	1000	74	3.80
Tween 20	60	1000	--	1.53
Tween 60	27	1000	--	1.41
Milli Q water	--	--	--	1.00

\* Viscosity was measured in a cylinder double gap geometry using a rotational rheometer at 25°C, 1 wt %, shear rate 0.1...100 s<sup>-1</sup>



**Figure 1.** Schematic of arrangements for measuring diffusion. a) Emulsifiers were added in the outer water phase. b) Emulsifiers were added in the inner water phase. c) coalescence experiment. The droplet is generated in the syringe and then release from it to fall on the outer water phase to get them in contact.

In arrangement (B) the setup is similar except emulsifiers are added in the droplet instead of the outer water phase. The measurements were performed for 1.5 hours. For coalescence experiments (C) water and oil phases were prepared in the same way as they were made for interfacial tension experiments. In this case, the drop, attached to the capillary, is slowly lift inside the oil phase to the oil-air-interface. The droplet is then released and sedimented gently on the interface of the outer water phase as is schematized in figure 1c.

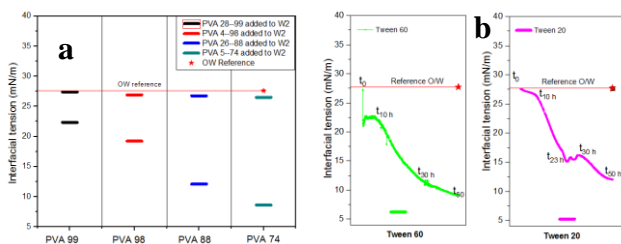
## RESULTS AND DISCUSSION

The use of PVA in the inner water phase showed a big change in interfacial tension (see figure 2a, lines at the bottom of the graph), since the emulsifier can diffuse directly to the interface. When added to the outer phase for long periods of

measuring no change was observed (figure 2a, lines at the top of the graph). The 0.5 mm oil film builds a barrier for the water-soluble polymer and inhibits the diffusion to the inner interface.

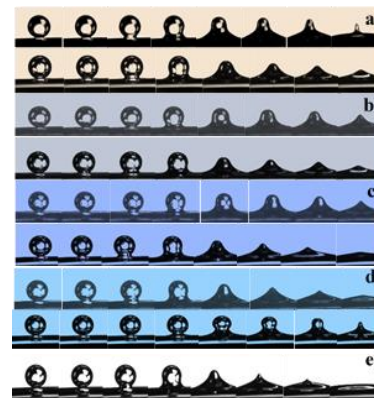
In order to explain this phenomenon, we need to understand the nature of the emulsifier used in the experiments. Amphiphilic molecules as polymers or proteins can associate with one another at the interface through van der Waals attraction, hydrogen bonding, or simply physical entanglement, forming a network [6]. The length of the chain of the polymer and their interactions between them and with the water interface are avoiding the free movement of molecules through the oil interface, although they have some affinity with this oil phase.

In contrast, it was observed that the use of non-ionic emulsifiers in the inner water phase showed a bigger change in interfacial tension value (lines showed at the bottom of the plots in figure 2b). This behavior was also observed after long time of conducting the experiment when surfactant was added to the outer phase.



**Figure 2.** a) Top lines are showing changes in interfacial tension of the droplet after adding PVA in the outer water phase. Bottom lines show changes in interfacial tension after adding PVA to the droplet. b) Top lines show the decreasing behaviour of interfacial tension of the droplet after adding different tweens in the outer water phase. At the bottom interfacial tension at the W/O interface after adding same emulsifiers to the droplet.

As a second result, changes in the shape of the droplet during coalescence were observed after adding emulsifiers either in the inner water phase or in the outer water phase. Sequences of images shown in figure 3 present how coalescence process took place after adding PVA and how the shape of the droplet was changing.



**Figure 3.** Time sequence of coalescence process for different PVA types added in the two different water phases. Each pair shows images for both arrangements when PVA was added to W1 (upper) or in W2 (lower). a) PVA 74, b) PVA 88, c) PVA 98, d) PVA 99, e) Without emulsifier.

The notable changes in the shape of droplet are demonstrating how the characteristics of interfacial behavior and physical forces change in presence of emulsifiers. The differences between the experiments with the same emulsifier added in different phases show, that diffusion is not taking place to equilibrium, even at this thin oil film between the interphases.

## CONCLUSION

This research project proves the potential of PVA as an emulsifier to stabilize WOW double emulsions. It decreases interfacial tension without migration through the oil phase. Short-chained non-ionic surfactants in contrary are present at both interfaces after a certain diffusion time. In future work, the molecular interaction between PVA and a lipophilic emulsifier, as well as other stabilizers found in commercial applications should be studied.

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