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# Morphology characterization of emulsions by differential scanning calorimetry

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## Abstract

This article is a review of some results obtained by Differential Scanning Calorimetry (DSC) for characterizing the morphology of emulsions. In a classical DSC experiment, an emulsion sample is submitted to a regular cooling and heating cycle between temperatures that include freezing and melting of the dispersed droplets. By using the thermograms found in the literature for various emulsions, how to get information about the solidification and melting, the presence of solute, the emulsion type, the transfer of matter, the stability and the droplet size is shown.

*Keywords:* Emulsion; DSC; Freezing; Melting; Mass transfer; Stability; Droplet size

## Contents

## 1. Introduction

In this introduction, the general background of emulsion properties will be reviewed. In the following sections, results found in the literature showing how these properties can be determined by Differential Scanning Calorimetry (DSC) will be discussed. Therefore, the references of articles dealing with DSC of emulsions will be given in the results sections.

According to IUPAC [47]: "an emulsion is a dispersion of droplets of one liquid in another one with which it is incompletely miscible. Emulsions of droplets of an organic liquid (an Oil) in an aqueous solution are indicated by the

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symbol O/W and emulsions of aqueous droplets in an organic liquid as W/O. In emulsions the droplets often exceed the usual limits for colloids' sizes".

This definition has to be broadened to include metal emulsions, which have been introduced around 1950 to study nucleation phenomena. For this type of emulsion, the droplets are made of molten metal dispersed in an oil phase [1,2]. Both W/O and O/W emulsions are found in various fields of application: petroleum industry, cosmetology, food, pharmacology ... since they are very good candidates for transporting hydrophobic material in a continuous water medium (O/W emulsion) or for trapping active materials in the droplets of the less common reverse system (W/O emulsion). Emulsions may also form naturally as the result of water injection during crude oil production. Another field, in which all types of emulsions are studied, including Metal/Oil emulsions, is in fundamental research. Metal/Oil emulsions have been considered as a convenient means for studying simultaneously the behavior of a large number of droplets. The main idea is that dispersing a liquid as droplets in a continuous medium should reduce drastically the possible influence of impurities since only a few droplets should be contaminated. The fundamental research made in this field concerns essentially the study of the solidification of the droplets. Due to undercooling phenomenon the nucleation shows a stochastic aspect and needs the study of a great number of samples. A review concerning the use of emulsions for such studies has been published some time ago [3].

Another type of emulsions made from simple ones and referred as either multiple or double emulsions or liquid membranes have been introduced more recently in the scientific community. Their structure, properties and applications are very well presented elsewhere [4]. They are described as being oil droplets or oil globules entrapping micro-sized water droplets and dispersed in a bulk aqueous phase. These emulsions are referred as W/O/W. When water globules entrapping oil droplets are dispersed in an oil medium, they are referred as O/W/O. Less known emulsions are those that are very close to simple emulsions as far as droplets are dispersed in a unique medium but the composition of the droplets differs. They are named mixed emulsions. They have been introduced in fundamental research as a way to obtain calibrated droplets [5]. In the results section, the actual composition and specific properties of these emulsions will be discussed in more detail.

Droplet size distribution is another important point to consider when dealing with emulsions. In the IUPAC definition, no precise information is given. Nevertheless, there is some information through the statement that "the droplets often exceed the usual limits for colloidal systems" combined with the definition of a colloidal particle: "any particle which has some linear dimension between $10^{-8}$ and $10^{-6}$ m is considered as a colloid" [6,1]. Generally, the droplet diameters are found between 1 and 50 μm. Nevertheless these limits, specially the lower one, are dependent on the apparatus used for particle size measurement since it can be assumed that smaller droplets are surely present in the emulsion. This is very important to stress out because phenomena specific to colloidal systems can occur. They are linked to the excess of pressure inside the droplets that is given by the Laplace equation. For 0.1 μm droplets, this excess is around 5 bars and cannot be neglected when time-evolution of the emulsion is studied. It can be shown that for such droplets there is an increase of the solubility which is droplet size dependent [7]. The smaller the droplet, the higher the solubility is. Therefore a possible matter transfer can occur from the smaller droplets towards the bigger ones. This mechanism is called Ostwald ripening and is responsible of the growth of the bigger droplets and the disappearance of the smaller ones. This mechanism does not need any contact between the droplets provided that the dispersed phase is at least partly soluble in the continuous phase. This phenomenon can be enhanced by the presence of micelles of surfactants within the continuous medium that can further increase the solubility. Another influence of the pressure excess is on the melting point of the solidified droplets that can be different from the one observed for bulk systems. However, this effect is hardly noticeable since it only concerns a very small number of droplets and, in addition, the melting point is not very sensitive to the pressure.

From the definitions of the emulsions recalled above, it appears clearly that these systems are complex ones. Furthermore they are not stable and their morphology can change with time. "Morphology changes" means that not only the droplet size but also the emulsion kind may change. The causes of these changes are various. One is Ostwald ripening in the case of very fine emulsion; more frequently, creaming or sedimentation of the droplets occurs followed or not by their coalescence. Temperature variations provoking freezing or melting of the droplets can also induce a change in morphology. Freezing is the result of nucleation phenomena and consequently all the droplets do not freeze at the equilibrium point: their freezing temperatures are scattered. Therefore, it can happen that some droplets are already frozen and others are not. In such a situation, it has been found that a matter transfer can occur from the still undercooled droplets to the already frozen ones. This matter transfer will induce a change in the droplet diameter and therefore in their morphology. This mechanism has been called "solidification ripening". More obvious is matter transfer due to composition ripening which is the result of a difference in the composition of either two droplet populations present within mixed emulsions or between the droplets trapped in the globules and the continuous phase in multiple emulsions. In that case, it is possible to observe changes of the emulsion kind, a W/O/W emulsion becoming an O/W one if all the dispersed droplets in the globules disappear. Finally, another mechanism that could create modification of the emulsion morphology is phase inversion which is described as being the process whereby a system changes from an O/W emulsion to a W/O emulsion or vice versa. The process is not