



Nanoemulsification in the vicinity of phase inversion: Disruption of bicontinuous structures in oil/surfactant/water systems



Kevin Roger

Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France

ARTICLE INFO

Article history:

Received 26 April 2016

Received in revised form 14 September 2016

Accepted 15 September 2016

Available online 30 September 2016

Keywords:

Nanoemulsion

Phase inversion

Bicontinuous

Low-energy

Self-assembly

Non-equilibrium

Surfactant

Emulsification

ABSTRACT

Oil/surfactant/water systems may undergo phase inversion upon tuning the preferred curvature of the surfactant layer. The longstanding relationship between nanoemulsification and phase inversion is discussed in view of recent mechanistic advances. The name “phase inversion emulsification” is shown to result from a historical confusion. Both nanoemulsification and phase inversion are controlled by the properties of the surfactant layer but phase inversion is shown to be unnecessary to obtain nanoemulsions. Nanoemulsions can be obtained in the vicinity of phase inversion through the disruption of equilibrium bicontinuous networks. A first pathway involves a change of the interaction between the surfactant layer and water at a precise location in the parameter space and under shear. A non-equilibrium micellar solubilization of oil, named superswelling, leads to an ideal nanoemulsion after quenching. All the surfactant is used to cover the interfaces and none is wasted in the continuous phase. The sub-PIT (Phase Inversion Temperature) method falls within this category. A second pathway involves the addition of water to a water-deprived system. Oil phase separates within a bicontinuous sponge phase matrix at a precise location in the parameter space and leads to a nanoemulsion upon further addition of water. Larger droplets are obtained and some surfactant is wasted, which demonstrates that this pathway is different and less efficient, although easier to implement. It is shown that the identification of the two access states in the nanoemulsification pathways, the superswollen microemulsion and the separating sponge phase, is essential when using surfactant blends. On the contrary, phase inversion is not only irrelevant but also damaging to the success of the emulsification process.

© 2016 Published by Elsevier Ltd.

1. Introduction

Mixing two liquids at the molecular scale is often desired to combine different molecular properties within a single matrix. However, it is rarely possible as the driving force for phase separation, the interaction energy, often overcomes the driving force for mixing, entropy. Two liquids are thus rarely fully miscible but rather possess a finite solubility into one another. Exceeding this solubility leads to phase separation. However, the experimentalist can still act by controlling the length scale of this phase separation. This is done by tuning the dispersion of one phase into the other, a process known as emulsification. In an emulsion, two immiscible liquids are forced into contact at the numerous interfaces formed through dispersion. Since these two liquids are immiscible, their interaction energy favors phase separation and interfacial contacts are energetically costly. The smaller the droplets, the larger the total interfacial area and thus the higher the free energy cost of producing an emulsion. The formation of emulsions consisting of droplets smaller than the hundreds of

nanometers, known as nanoemulsions, thus represents the ultimate emulsification challenge.

Mechanical methods largely prevail industrially in the preparation of emulsions. To access droplets' sizes below the hundreds of nanometers, it is necessary to use high pressure homogenizers, or microfluidizers [1]. Most of the energy input is dissipated in the fluid, which leads to increased temperatures and progressive wear of the chambers. Some species may be damaged by the large mechanical stresses and temperatures involved in the chambers. These devices also require frequent maintenance and a large energy supply. However, the most critical issue is the necessary use of large excesses of surfactant to produce nanoemulsions, which means that most of the surfactant is wasted as micelles in the aqueous phase, rather than adsorbed at oil/water interfaces. Using large excesses of surfactant is necessary because rapid recombination occurs after fragmentation, and can thus only be hindered by a faster adsorption of a surfactant monolayer.

Alternative methods rely on harvesting a system's free energy to create a large number of interfaces. If stabilizing species then cover these interfaces, a metastable nanoemulsion is obtained. One set of methods rely on triggering phase separation by a change in solvent

E-mail address: kevin.roger@ensiacet.fr (K. Roger).

quality for a solute dissolved in a good solvent. This can be performed through the addition of a bad solvent, a chemical reaction or a change in temperature, pH or salinity [2]. This article is dedicated to another set of methods, which rely on tuning the interactions within the surfactant layer separating oil and water.

This current opinion starts with a detailed historical perspective on these methods, commonly known as phase inversion emulsification methods. This will show how this unfortunate terminology arose from historical confusions over a half-century span of investigations. This current opinion argues that a quantitative description is now available to understand, describe and control this set of methods. The formation of nanoemulsions is shown to proceed through the disruption of bicontinuous structures, which exist in the vicinity of phase inversion. Undergoing phase inversion is an unnecessary step, which justifies a change of terminology. The practical gains of the mechanistic understanding are detailed in close connection with the engineering of these methods. It is emphasized that phase inversion can actually prevent successful nanoemulsification in complex mixtures.

2. Nanoemulsification and phase inversion: a historical perspective

The development of emulsification methods based on a change in the surfactant layers properties naturally follows the advances of surfactant science. In the 1960s, it was recognized that the Hydrophilic/Lipophilic Balance (HLB) concept, which only takes into account the isolated molecular structure of amphiphiles, failed to predict the phase behavior of oil/water/surfactant systems. Nonetheless, the effect of molecular structures on phase behavior could be efficiently described through the phase inversion parameter. This quantity corresponds to a parameter value, typically temperature or composition, at which a system switches from water continuous structures to oil continuous structures. This concept was developed in systems containing oxyethylenated surfactants, the structure of which consists of a hydrophobic alkane chain and a hydrophilic oligomeric ethylene oxide chain. Shinoda and Saito were pioneers in the use of this class of surfactants [3], which possesses unusual hydration properties. Increasing the temperature notably decreases the hydration of the hydrophilic head, due to changes in the interaction between this head and surrounding water molecules [4]. The opportunity to devise new emulsification methods closely followed the studies of phase behavior. In their 1969 founding paper, Shinoda and Saito described an emulsification method based on stirring an oil/water/surfactant system in the vicinity of its phase inversion, followed by a rapid cooling. They showed that this method, named emulsification by the PIT method, leads to the formation of much smaller droplets than stirring at any other temperatures. They stated that the optimal temperature for stirring was “about 2–4 °C below” the phase inversion temperature. They also compared their method to emulsification through crossing of the phase inversion temperature and found that emulsification by the inversion method is not as good as emulsification by the PIT-method. Therefore, they dismissed phase inversion itself as the mechanism for emulsification. Unfortunately, this subtle distinction in their terminology was generally missed. Also contrary to some beliefs, they did not obtain nanoemulsions at that time. This is probably due to the high oil/surfactant ratio they used in their composition (48.5% water, 48.5% oil, 3% surfactant). Five years later, Lin, Kurihara and Ohta investigated a different pathway in which water is added to a solution of oil and surfactant [5]. They emphasized its similarity to Shinoda and Saito emulsification method despite a different trigger, a composition change, and the crossing of the phase inversion composition (PIC). They observed micrometric droplets with optical microscopy.

The two following decades witnessed only a few contributions. Sagitani and coworkers [6] described an emulsification method combining two triggers, temperature and water addition. Salager and coworkers [7] conceptualized the notion of phase inversion. They divided it into two categories: transitional, induced by intermolecular interactions changes, and catastrophic, induced by changes in the oil/water volume ratio. At the same time, progresses were made linking the phase inversion parameter to a mesoscopic quantity, the preferred curvature of the surfactant layer, and a macroscopic quantity, the interfacial tension. The interfacial tension was shown to be minimal at the phase inversion parameter. This added to the incorrect idea that the emulsification method described by Shinoda and Saito proceeded through an easier fragmentation in the vicinity of phase inversion.

In the 1990s, Förster and coworkers were the first to detail a nanoemulsification method inspired from the original method of Shinoda and Saito [8,9]. A coarse oil/water emulsion was heated above the phase inversion temperature, which Shinoda and Saito described as “emulsification above the inversion method” in opposition to “emulsification by the PIT-method” (a few degrees below the PIT). The inverted emulsion was then quickly cooled down to room temperature, which resulted in the formation of a nanoemulsion. Since this pathway crossed the phase inversion temperature, a tentative explanation based on the ultra-low interfacial tensions in the vicinity of phase inversion was put forward. However, Förster et al. also noticed that their system self-assembled at equilibrium, in the vicinity of the PIT, into microemulsions (equilibrium mixtures of oil, water and surfactant). They also stated that “the influence of stirring and cooling was comparatively small”. Minana-Perez, Salager and coworkers later emphasized that this microemulsion phase was actually required in order to obtain nanoemulsion by stating that “no miniemulsion was formed in absence of microemulsion at optimum formulation” [10].

Solans, together with several co-workers (Esquena, Gutierrez, Izquierdo, Forgiarini, Solé...), recognized the importance of phase behavior in respect to nanoemulsification. In the 2000s, they extensively studied both the temperature-controlled process first discovered by Shinoda and Saito, later developed by Förster, and the composition process of Lin and coworkers [11–15]. They demonstrated the relevance of establishing phase diagrams, which contain the variations of the preferred curvature of surfactant films, to classify the different emulsification pathways they encountered. Quantitative data was obtained and showed notably that the surfactant concentration was a key parameter to control the nanoemulsification process. However, the exact link between the pathway taken and the emulsification outcome remained elusive in the absence of a quantitative model.

Meanwhile, Salager postulated an emulsification mechanism based on the disruption of bicontinuous structures in microemulsions. However, the size of the droplets he obtained through inversion was much larger than the size of the microemulsion domains [16]. Undertaking a similar study as the original one by Shinoda and Saito confirmed that the minimum droplet sizes were actually obtained a few degrees below the phase inversion temperature. In parallel, an experimental study by Sajjadi showed that water addition could lead to transitional or catastrophic inversion but that only transitional phase inversion leads to nanoemulsions [17]. The postulated mechanism was fragmentation at low interfacial tensions in the vicinity of the PIT. Anton and coworkers observed that multiple heating/cooling cycles were improving the emulsification when undergoing phase inversion [18]. Taisne and Cabane monitored the phase inversion pathway, changing temperature, using small angle neutron scattering in an attempt to unveil the structural transformations taking place [19] and confirmed that several pathways existed. Fragmentation at the phase inversion was also proposed as the mechanism for nanoemulsification. This was latter

Download English Version:

<https://daneshyari.com/en/article/6984785>

Download Persian Version:

<https://daneshyari.com/article/6984785>

[Daneshyari.com](https://daneshyari.com)