Current Opinion in Colloid & Interface Science 25 (2016) 58–66

Contents lists available at ScienceDirect

Current Opinion in Colloid & Interface Science

journal homepage: www.elsevier.com/locate/cocis

Recent studies of Janus emulsions prepared by one-step vibrational mixing

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ARTICLE INFO

Article history:
Received 27 February 2016
Received in revised form 27 April 2016
Accepted 8 May 2016
Available online 15 May 2016

Keywords:
Multiple emulsions
Janus emulsions
Thermodynamic
Configuration
Application

ABSTRACT

Emulsion science has recently experienced several profound changes. At first, interfacial thermodynamics has been found to play a significant role in the behavior of multiple emulsions, leading to an unexpected effect on their traditional medium energy preparation as well as to an extension of their preparation into large volumes. In order to illustrate these changes, the present article is initiated by a brief review of the correlation between the equilibrium interfacial tensions and the configuration of Janus emulsions prepared by one-step vibrational mixing, and extends to the phase inversion of Janus droplets inside its interfacial tension range, followed by an assessment of the progress in the preparation of Janus emulsions and their application to fabricate complex anisotropic particles in scale.

1. Introduction

In the rich research area on emulsions [1–3], multiple emulsions have attracted particular attention due to their special structure, which has given rise both to fundamental research and a number of applications [4,5]. The investigations on these emulsions reach from the initial preparation, through their thermodynamic and kinetic stability [6–8], to subsequent application studies in fields such as foods, biology, cosmetics, and material synthesis [5]. Janus emulsions, composed of two mutually insoluble oils within the dispersed drops, attracted attention after being prepared by the method of microfluidics with one droplet at a time from a capillary, a process, virtually at equilibrium [9•]. As a result, the Janus emulsions immediately caused fundamental research to be initiated [10-12•,13•,14•,15], because their introduction meant that thermodynamics was found as a significant factor in their behavior, especially their intermediate stability.

Earlier investigations on multiple emulsions, as comprehensibly treated in a recent review [5], experienced problems with stability, because the spontaneous mixing of surfactants reduced the stabilization efficiency at individual interfaces. These attempts adhered to the common definition of "emulsion stability", which is exclusively defined by the colloid stability, i.e. the reduction of the coalescence rate [1–3], neglecting to take thermodynamics into consideration. This is certainly a justified position, since emulsions indubitably are thermodynamically unstable. In fact they possess an outsized free energy excess in comparison to the state of separated liquids, as illustrated by the fact that an average emulsion drop with a radius of 3 μm and an interfacial tension against the continuous phase of 4 mJ/m has an interfacial energy of 4.5E − 13 J, many orders of magnitude in excess of the value for kT = 4.11E − 21 J. This point is true also for multiple emulsions, but for these, as mentioned, the colloidal stability approach has been less directly successful [6–8]. As a contrast and outside the scope of the present contribution, thermodynamic stability is found in the micro-emulsions [16], which, in truth, are colloidal solutions; fundamentally different from macro-emulsions.

The interest in Janus emulsions was further enhanced, when Hasinovic and Friberg [17•,18•] as well as Ge et al. [19•] prepared Janus emulsions with the traditional medium energy vibrational methods; in so doing, substantially extending their application to a greater range [20•]. The present review begins with a brief outline of the potential relevance of interfacial thermodynamics for Janus emulsions prepared by one-step mixing, and then extends to topology control and phase inversion studies of these Janus emulsions, and finally the application of Janus emulsions in the batch-scale fabrication of anisotropic particles.

2. Interfacial tensions and formation of Janus emulsions

As mentioned, the attitude toward thermodynamics and emulsions recently changed, when the microfluidics emulsification process was introduced [9•] to produce Janus emulsions, but prior to review these, it is essential to emphasize that these emulsions only occupy a limited part of the interfacial tension range of multiple emulsions. These, as such, are

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http://dx.doi.org/10.1016/j.cocis.2016.05.001
1359-0294/

altogether comprised of droplets of two immiscible fluids, usually oils, O1 and O2, surrounded by a third liquid continuous phase, usually aqueous, Aq or W [13•, 14•, 15], resulting in three interfacial tensions, $\gamma_{O1/W}$, $\gamma_{O2/W}$ and $\gamma_{O1/O2}$. Local minimization of the interfacial energy of the system as a whole, the three possible states at local equilibrium are (Fig. 1) [21•,22•] (i) one of the dispersed phases completely engulfing the other one, forming double emulsions (complete engulfing); (ii) Janus droplets form, in which all three possible interfaces are present (partial engulfing) [14•] or (iii) distinct single oil droplets remain separated by the host phase (the non-engulfing configuration). The correlation between the entire range of interfacial tensions and the drop topology has recently been articulately illustrated [21•,22•].

There are two ranges of special interest in Fig. 1. The first range is limited by the transition of thermodynamically favored states from double emulsions to Janus emulsions, and the second boundary represents the corresponding change from the Janus topology to separate oil drops. Calculations of the interfacial free energy difference in favor of the double emulsion, used the interfacial tensions from Leonardi et al. [22•], combined with a drop size of $r = 10^{-5}$ m. The energy difference between a double emulsion drop and two separate drops for the system is decidedly significant [22•], even at a reduced drop size to the level of 10^{-6} m. The numbers offer a convincing indication that a thermodynamic approach to the preparation of double emulsions may be a helpful complement in the colloid stability attempts [4–8], although experimental evidence is still not available. An experiment would certainly be informative, in which the spontaneously increased coverage of the inner drop was measured as function of the reduced surfactant concentration.

The free energy difference from the double emulsion drop is still the feature of interest, even within the range of $\gamma_{O1/W} < \gamma_{O2/W} + \gamma_{O1/2}$, in which thermodynamics supports a partial drop enclosure to form a Janus drop. The lower interfacial free energy of the Janus drop for critical surfactant concentration $[S]_{cr} > 0.3240$ in reference [22•] is well illustrated. The results make clear that even a small increase of [S] in excess of the $[S]_{cr}$ value of 0.3240 (aqueous phase weight %) leads to a strong thermodynamic preference for the Janus topology. As shown in Fig. 2, the free energy ratio reaches unity for volume fraction of $\varphi = V_{O2}/(V_{O2} + V_{O1}) = 1$; a trivial result, since the drop consists of only one oil; the O2 at these values. As a contrast, when the VO volume equals zero; the ratio is not equal to unity, in spite of the fact that the drop volume now consists entirely of O1. The explanation to this "anomalous" result lies with the fact that although the surface of O2 has no volume per se, the infinitely thin layer fully contributes to the interfacial free

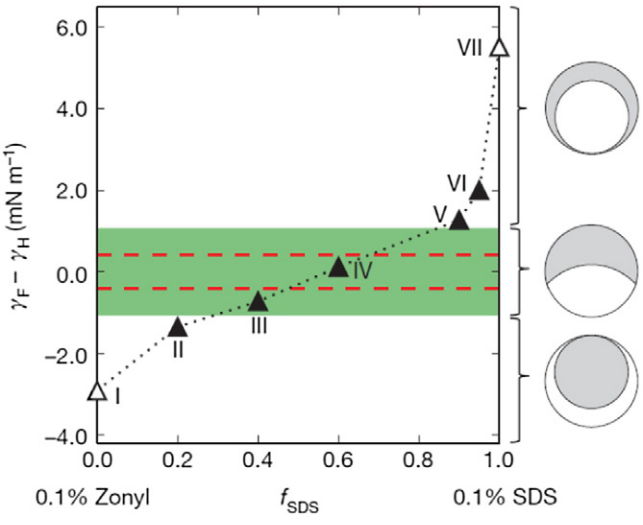

Fig. 1. Configurational stability diagram for the hexane–perfluorohexane–water system showing $\gamma_F - \gamma_H$ as a function of the fraction of 0.1% SDS, f_{SDS}, where the other fraction is 0.1% Zonyl (reproduced with permission from ref. [21•]).

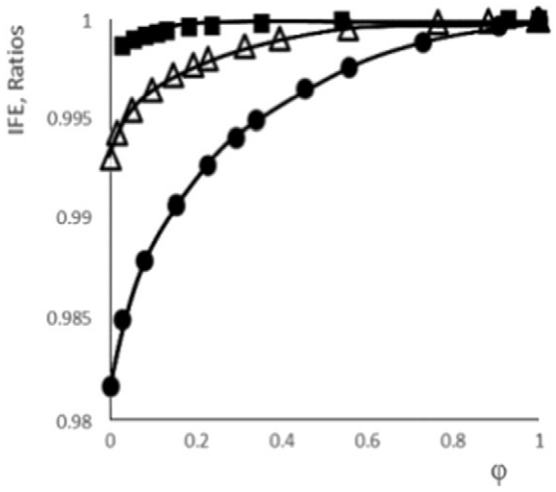

Fig. 2. The ratio between total interfacial free energy between Janus and engulfed drops versus the volume fraction of, $V_{O2}/(V_{O2} + V_{O1})$, φ. Symbol [S], wt.%: ● 0.3333; △ 0.3275; ■ 0.325 (reproduced with permission from ref. [22•]).

energy. Prior to examining some specifics of Janus emulsion thermodynamics, it cannot be overemphasized that the stability minima of these emulsions are temporary. Any macro-emulsion system will finally separate into distinct liquid layers.

3. Topology of Janus drops—Contact angle, volume ratio and surface coverage

Optical microscopy is the most simple and useful technique to provide topology information of complex emulsions [14•,15,23•,24•]. However, the correlation between the morphology of the Janus droplets in bulk and the microscopy images between the planer slide and the cover glass has to be established because of the specific effect of the shear on the sample, and of the wetting effect of the glass surface on the emulsion droplets. Initial work to draw attention to this problem was performed by Hasinovic et al. [25•], and the investigation supported a conclusion that the microscopy images actually provide realistic information about the drop topology, though with greater drop size in the image between a planner slide and a cover glass than with the image of the diluted emulsion in bulk. In addition, they called attention to that the image value of contact angles is a factor of the true contact angle, the size in bulk, and the orientation of the drop.

As mentioned, the topology of partial engulfing Janus droplets is more complex in comparison to separated homogeneous single droplets and to the double emulsion droplets. The additional degrees of freedom of Janus droplets allow for rational tuning of the geometry, such as 1) the volume ratio of two separated domains; 2) the curvature of the interface between two immiscible inner phases; and 3) the position of the three-phase contact circle on the outer surface of the droplet. The fundamental study of the affecting factors and, more importantly, of their ability to the control of the topology of Janus droplets is of vital importance to the subsequent emulsion application, because these factors determine the droplet topology and with it the properties of the emulsion. The following narrative examines the recent studies on the fundamentals and illustrates their effects.

The microfluidic method forms Janus emulsions with virtually no agitation and, in addition, separates the drops from mutual interaction. As a result, the conditions in individual drops may be studied without interference and experiments could, for the first time, independently establish the topology of a single Janus drop with virtually no external forces of significance. The outcome demonstrated the configuration of the drops to be dictated by the interfacial tensions at the drop surface contact line and attention focused on the correlation between topology and interfacial tension equilibrium in a number of pioneering