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Silicone/vegetable oil Janus emulsion: Topological stability versus interfacial tensions and relative oil volumes

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ABSTRACT

Several aspects were studied of the formation and destabilization in bulk of silicone/vegetable oil, SO/VO, Janus emulsions, stabilized by Tween 80. In the formation of the emulsions, it was unexpectedly found that the dispersions tended to contain both single and flocculated drops irrespective of the emulsification intensity. Microscopy of the emulsions with no cover glass revealed flocculated drops of a large (200–500 μm) central SO drop with many small VO drops attached. Applying a cover glass did not significantly change the drop size; instead two-oil Janus drops of well-defined contact angle were found. The emulsions showed rapid creaming irrespective of the preparation method, but a few days storage did not significantly change the drop size in the creamed layer, nor was separation of the oils detected. The total interfacial free energy of the Janus drops at equilibrium was compared to the two relevant alternatives; engulfed and separate drops. The Janus drop free energies were found less for all volume ratios of the oils, when the surfactant concentrations in the aqueous phase was sufficient to prevent spreading of VO on SO. Changing the surfactant concentration to bring the interfacial tensions closer to the critical value for spreading gave declining interfacial free energy difference to that of engulfed drops.

1. Introduction

It is a true delight to be part of this collection of articles to honor Professor Darsh Wasan, who has been a friend to the senior author for some 40 years. His pioneering scientific contributions have been a constant inspiration; especially so, since his original approach created a necessary balance to the sometimes almost calcified traditional routine of "proper science". Among the examples may be mentioned the introduction of micelles as steric stabilizers [1] as part of his emphasis of structural forces in macro-dispersed systems [2]. His early interest in colloids and spreading [3] later developed into a series of investigations on superspreading [4]. In addition to his obvious leading role in colloid science, his generous and friendly personality, combined with an unusual energy and drive brings to mind the portrayal of Pierre Terrail, Seigneur de Bayard, "*Le chevalier sans peur et sans reproche*". A significant part of Wasan's scientific contributions have been concerned with the stability of liquid dispersions and in this early report we demonstrate some unexpected stability of two-oil emulsions with permanently flocculated drops, Janus emulsions, and evaluate the combined role of interfacial thermodynamics and relative volumes of the oils for the drop topology and behavior.

Thermodynamics of emulsions never attracted noticeable attention, with isolated exceptions of more special nature [5], because the dominant role of the interfacial component of the total free energy ensures these dispersions to be unfalteringly thermodynamically unstable. In fact, the thermodynamics plays no role in the primary steps in the destabilization of these emulsions; once the repulsive forces have been overcome in the process, the ex post facto release of the surface energy at the coalescence only causes an insignificant increase of the temperature. In summary, "emulsion stability" has become kinetically defined as a slower destabilization rate; an approach until recently applied also to multiple emulsions [6]. The focus away from thermodynamics was markedly changed with the introduction of the microfluidics method [7].

This emulsification method, with virtually no agitation, gave rise to a large number of new and original applications [8,9] but, more importantly from a fundamental point of view, offered systems, whose topology depended on the interfacial tension equilibrium at the three-liquid contact line. For the first time, thermodynamics became truly relevant in emulsion science; equilibrium topology could be compared with experimental results in a meaningful manner [9–11] and has recently given rise to advanced treatments [12]. In fact, the interfacial thermodynamics

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now actually began playing a decisive role; both in the formation of the emulsions and also in causing the topology to be retained to an unexpected degree during the destabilization process of the emulsions.

In addition, another recent event significantly contrived to redirect the research focus toward thermodynamics. Unexpectedly, Janus emulsions with silicone oil were also prepared by the traditional high energy emulsification process [13–15]. There is a less obvious – if any – correlation of such systems with equilibrium thermodynamics, giving additional impetus to correlating experimental results for the topology of aqueous multi-oil for systems [12,16,17] with the equilibrium configuration. Moreover, the discovery also indicated the potential for batch preparation of nano-particles with complex and uniform structure [18,19]; thereby potentially removing the volume constraints of the microfluidics method. In addition to these developments, publications have recently appeared on preparing Pickering Janus emulsions [20], by adding polydopamine particles (192 nm) to a hexadecane/water emulsion. Optical microscopy photos of the drops, combined with zeta potential measurements of the particles and of the emulsion drops, disclosed the Janus drop topology and its dependence on the pH of the aqueous solution. Finally, the Bormashenko marbles [21] should be mentioned; they actually are Janus drops in air with interesting behavior.

In a few words, these recent developments have established interfacial thermodynamics as a relevant factor for the topology of multiple emulsions. In the following, the role of interfacial equilibria/relative volumes of the two oils in Janus drops will be examined.

2. Experimental

2.1. Materials

The materials used to prepare the systems were polydimethylsiloxane polymer 100 centiStokes (silicone fluid Xiameter® PMX-200), SO, kindly donated by Dow Corning (USA), olive oil of pharmaceutical grade, VO, polyoxyethylene sorbitan monooleate (Tween 80) acquired from Synth, Av Dr. Ulysses Guimarães, 3857 – Villa Mary – Diadema/SP – Brazil – CEP: 09990-080 and distilled water.

2.2. Interfacial tension

The interfacial tensions of the combinations oil/aqueous solution (0–10% surfactant) and oil/oil interfaces were measured by the pendant drop method, using a Traker-S tensiometer (Teclis, France) at 25 °C. The interfacial tension values were recorded after having reached a constant value.

3. Janus emulsion preparation

Janus emulsions were prepared by first mixing vegetable oil (VO), silicone oil (SO) and Tween 80 (Tw) to form a pre-emulsion. To this mixture was gradually added an aqueous phase with 0–10 wt% Tween at different agitation level to form emulsions of 8 wt% VO, 32 wt% SO and 60 wt% aqueous phase (Aq). A first array of emulsions were prepared from once turning a test tube upside down and back, while a second set of emulsions were mixed for 5 min on a Vortex Mixer AP 56 (Phoenix Luferco, Brazil, Fig. 1.

Subsequently, part of the samples were placed in a mini rotator (Glas-Col, USA) mixer, Fig. 1, at the lowest speed (4 min^{-1}), while the remaining set was stored at rest at room temperature. The test tubes were sealed with a plastic cap to avoid water evaporation.

Fig. 1. The rotator with one test tube attached.

Aliquots of each sample were removed for microscopy observation and photograph recording were taken until 2 weeks.

3.1. Microscopy

A small sample of each emulsion was removed and placed on a microscopy slide Bioslide, 26 × 76 mm, one set under a cover glass, 18 × 18 mm and a second group observed without cover on an optical microscope model Primo Star (Zeiss, Germany) with a yellow coded objective EPIPLAN 10×/0.2. (Images from without cover to the left in all subsequent figures.)

4. Results

The results will be presented in the order of fundamental relevance. Those of the interfacial tensions are first described, followed by the formation of the Janus emulsions under different levels of agitation, by their destabilization with the creaming prevented and, finally, by the total destabilization process, including creaming.

4.1. Interfacial tensions

The interfacial tensions are the central aspect of Janus emulsions [15], because they determine the contact angle at the contact line [9–12,16,17] and, as a consequence, are one of the two vital factors for the drop topology. Hence, they will be initially reported, Fig. 2, with some comments.

The interfacial tension between water and the silicone oil was extremely high with no surfactant present with a distinctly positive difference $\gamma_{SO/Aq} - \gamma_{VO/Aq} + \gamma_{VO/SO}$. The initial reduction of the tensions with addition of the surfactant was steepest for $\gamma_{SO/Aq}$ and the critical factor $\gamma_{SO/Aq} - \gamma_{VO/Aq} + \gamma_{VO/SO} = 0$ was reached at small surfactant concentrations. The exact surfactant concentration for this point, $[S]_{crit}$, was attained by interpolation of an empirical function $\Delta\gamma = \gamma_{SO/Aq} - \gamma_{VO/Aq} + \gamma_{VO/SO}$. This function, as well as that of the individual tension values, was monotonically decreasing versus $[S]$ and the application of traditional empirical functions as polynomials is highly unsatisfactory. Instead, the inverse of the surfactant percentage, $1/[S]$, was chosen as the variable giving 1st order equations with high accuracy both for the interfacial