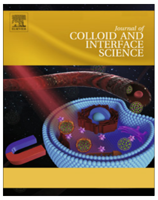
Journal of Colloid and Interface Science 516 (2018) 182–191

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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



Regular Article

Effect of soluble surfactants on pinch-off of moderately viscous drops and satellite size

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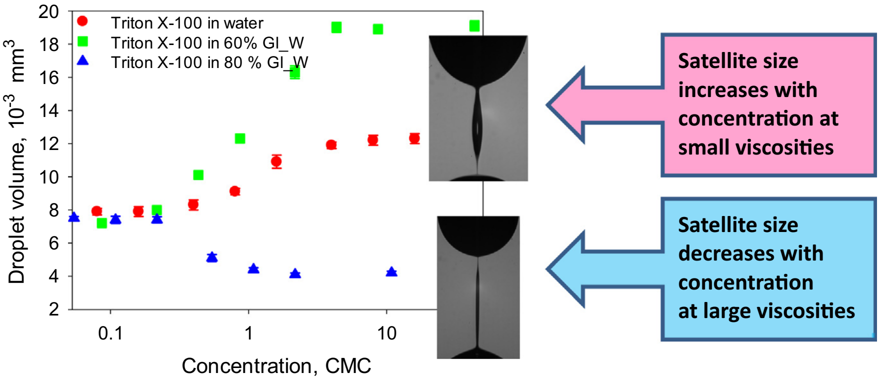
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 November 2017
Revised 9 January 2018
Accepted 10 January 2018
Available online 11 January 2018

Keywords:
Drop formation
Viscosity
Dynamic surface tension
Ohnesorge number
Kinetics near pinch-off
Satellite droplet
Diffusion coefficient

ABSTRACT

Hypothesis: Surfactant redistribution in a liquid bridge close to drop detachment depends on competition between the bridge deformation rate and surfactant equilibration rate. Surfactant effect can be different in situations when diffusion coefficient changes independently of thinning kinetics or in line with it. Using moderately viscous liquids should allow both situations to be explored experimentally.
Experiments: Formation of liquid drops at the tip of capillary is studied experimentally for silicone oils and for surfactant-laden and surfactant-free water/glycerol mixtures of moderate viscosity with particular attention to the kinetics of liquid bridge close to pinch-off and formation of satellite droplets.
Findings: Effect of surfactant depends on the dynamic regime of the bridge thinning. In the presence of surfactant, inertial kinetics slows down close to pinch-off demonstrating effective surface tension smaller than dynamic surface tension. An acceleration of thinning kinetics caused by depletion of surfactant from the liquid bridge was observed in viscous and visco-inertial regimes. The size of satellite droplets has a maximum versus viscosity; increasing with surfactant concentration at smaller viscosities and decreasing with an increase of surfactant concentration at largest studied viscosity, where inversion of the pinch-off point was observed for surfactant solutions.

1. Introduction

Liquid drops are ubiquitous in everyday life and applications are numerous, including medicine, food, pharmaceutical, agricultural

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https://doi.org/10.1016/j.jcis.2018.01.039
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Nomenclature

A_I	proportionality constant in scaling law for inertial kinetics of bridge thinning, Eq. (2)
A_V	proportionality constant in scaling law for viscous kinetics of bridge thinning, Eq. (4)
A_{VI}	proportionality constant in scaling law for visco-inertial kinetics of bridge thinning, Eq. (1)
CMC	critical micelle concentration
g	acceleration due to gravity
h_m	neck radius
I	inertial regime
L_v	viscous length scale $L_v = \frac{\mu^2}{\rho\sigma}$
Oh	Ohnesorge number $Oh = \sqrt{\frac{L_v}{R}} = \frac{\mu}{\sqrt{\rho\sigma R}}$
R	radius of capillary
R_d	drop radius
Re_L	local Reynolds number
t	time
V	viscous regime
VI	visco-inertial regime
v	drop volume
t_0	time of pinch-off
μ	dynamic viscosity of liquid
ρ	density of liquid
σ	surface tension
σ_0	surface tension of surfactant-free liquid
σ_d	dynamic surface tension of surfactant solution at the time of drop destabilisation
σ_e	effective surface tension, i.e. surface tension found from fitting the experimental data using one of the Eqs. (1), (2) or (4)
σ_{ef}	effective surface tension found from the fitting by Eq. (2) of experimental data for faster inertial kinetics found for surfactant solutions
σ_{es}	effective surface tension found from the fitting by Eq. (2) of experimental data for slower inertial kinetics found for surfactant solutions
σ_{eq}	equilibrium surface tension of surfactant solution

and fine chemicals industries, 2-D and 3-D printing, and cooling [1–5]. For most applications, control of drop size and size distribution as well as elimination of normally undesirable satellite droplets is of great importance. Predictive control is only possible on the basis of thorough understanding of the complex physics underlying drop formation. Considerable scientific attention has been given to the processes close to the pinch-off point, where a liquid bridge connecting the forming drop to the feeding liquid breaks up [6,7]. This is a singularity point where the capillary pressure, being the driving force of bridge thinning, and the liquid velocity diverge as the radius of the neck of the bridge goes to zero.

Surfactants are used in most industrial drop formation processes as a part of formulation and/or as drop stabilisers [8,9]. Addition of surfactant lowers the interfacial tension and therefore results in a decrease of the drop size, a fact used for a long time to measure interfacial tension by the drop weight/drop volume method [10–13]. As a rule, drop formation in industrial applications is rapid, with characteristic times being in the second and even sub-second range. Adsorption and redistribution of surfactant under such highly dynamic conditions affects the drop formation process and drop size distribution. That is why understanding the surfactant dynamics during the drop formation process is of high importance.

Especially strong dynamic effects are expected in the vicinity of pinch-off, when liquid is expelled from the thinning liquid bridge at high velocity. Due to continuity the flow is transferred to the interface where it sweeps the surfactant away from the thinnest part of the bridge (neck) as shown in Fig. 1. As the velocity is directed along the bridge, the replenishment of the surfactant occurs mostly by diffusion from the bulk. Therefore, the resulting surfactant distribution is determined by the rate of the bridge thinning, availability of surfactant in the bulk phase and the surfactant diffusion coefficient. On the other hand, non-uniform surfactant distribution at the interface will result in Marangoni stresses (Fig. 1) which slow down the bridge thinning. The complicated surfactant redistribution takes place also immediately after pinch-off. The bridge recoil [14,15] can result in the local increase of the surfactant concentration and generation of Marangoni stresses accelerating or slowing down the secondary pinch-off and therefore affecting the size of the satellite drop.

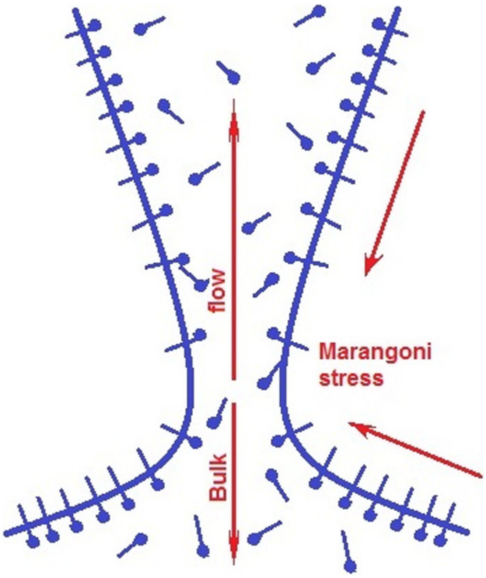

Fig. 1. Sketch of thinning liquid bridge at formation of surfactant-laden drop.

Most theoretical/numerical studies on surfactant-laden liquid bridges have been carried out using insoluble surfactants [16–18]. Although these studies do not account for surfactant exchange between the liquid bulk and the interface, many of the obtained results are of general importance, in particular predicted depletion of surfactant from the liquid bridge. It has been shown that a liquid bridge stretched between two discs which are slowly moved apart can be stabilised by Marangoni stresses caused by non-uniform surfactant distribution under conditions of high liquid viscosity and low surface diffusion coefficient [16]. Study on the break-up of viscous liquid threads covered by insoluble surfactant in the long wavelength approximation has shown that the self-similar solution for the kinetics of a surfactant-free liquid bridge close to the pinch-off is still valid [17]. The results of numerical simulations for bridges covered by an insoluble surfactant were validated by using spread monolayers of octadecanol [18].