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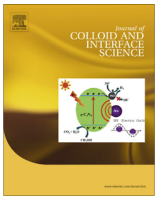

Interfacial tension measured at high expansion rates and within milliseconds using microfluidics

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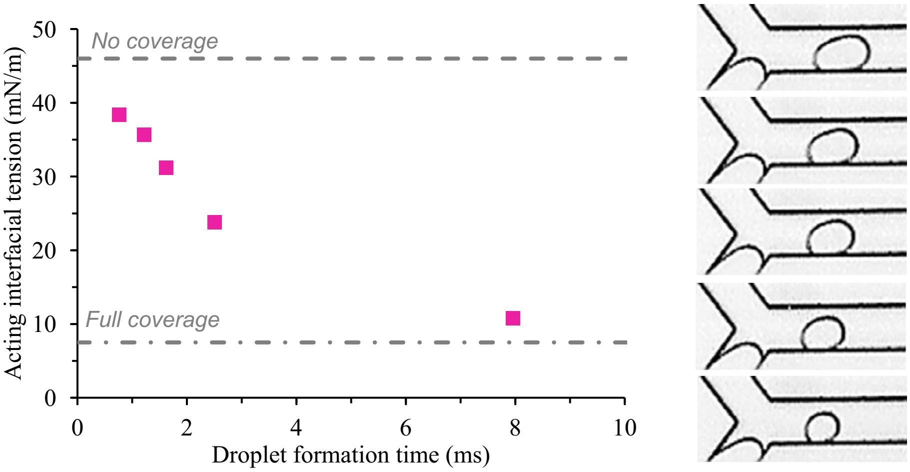
HIGHLIGHTS

- A two-step model was developed to describe emulsion droplet formation in a cross-flow microfluidic Y-junction.
- A microfluidic method was developed to measure the interfacial tension in the sub-millisecond to millisecond time scale.
- Probed time scales match those encountered in industrial emulsification processes.

GRAPHICAL ABSTRACT



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ABSTRACT

To understand droplet formation and stabilisation, technologies are needed to measure interfacial tension at micrometer range and millisecond scale. In this paper, microtechnology is used, and that allows us to access these ranges and derive a model for surfactant free systems. The predicting power of the model was tested, and we found that it can be used to accurately (validated with >60 experiments) describe droplet size for a wide range of flow rates, interfacial tensions, and continuous phase viscosities.

The model was used next to determine interfacial tensions in a system with hexadecane and sodium dodecylsulfate (SDS) solutions, and it was found that the model can be used for droplet formation times ranging from 0.4 to 9.4 ms while using a wide range of process conditions.

The method described here differs greatly from standard dynamic interfacial tension methods that use quiescent, mostly diffusion-limited situations. The effects that we measured are much faster due to enhanced mass transfer; this allows us to assess the typical time scales used in industrial emulsification devices.

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1. Introduction

Many products (e.g., milk, mayonnaise, dressings, paint, and shampoo) are emulsion-based systems. They are generally made using high shear devices that induce fast droplet break-up (i.e., in the sub-millisecond range) in the presence of surfactants [1]. Surfactants have two roles: they decrease the oil–water interfacial tension so that small droplets can be formed, and they further stabilise the droplets through formation of an interfacial layer that provides steric and/or electrostatic repulsion [1]. Surfactant adsorption can be divided into three steps: (1) transport (e.g., diffusion and/or convection) of the molecules towards the sub-interface, (2) diffusion through the sub-interface, (3) kinetic adsorption of the surfactant at the interface [2].

Depending on the interface expansion rate and surfactant adsorption time, the dynamic interfacial tension can be higher than the equilibrium interfacial tension during emulsification. The dynamic interfacial tension may even be equal to the interfacial tension of the corresponding bare liquid–liquid interface when surfactant adsorption takes more time than droplet formation. Conversely, when the adsorption time is in the same order of magnitude or faster than droplet formation, the dynamic interfacial tension ranges between that of a bare interface and that of a fully covered interface (i.e., the equilibrium interfacial tension).

During large scale emulsification, surfactant adsorption occurs at similar time scales as droplet break-up [1], therefore also re-coalescence can occur when the interface is not timely stabilised, and this leads to over-processing [3]. Quantifying dynamic interfacial tension could be of great significance for emulsification processes, since this provides information on the adsorption time of surfactants and, related to that, the time needed for interface stabilisation. The dynamic interfacial tension can be measured with commercial techniques such as the oscillating jet and maximum bubble pressure method, that are both able to measure in the millisecond range [4]. Microfluidic devices can also be used for dynamic interfacial tension measurements [5–9]. The tensiometric measurements of Wang et al. [5] and Steegmans et al. [9] were both conducted in cross-flow microfluidic devices and were based on the relation between droplet size and interfacial tension; the former is able to measure in the millisecond range and the latter in the sub-millisecond range, due to differences in geometry. The method of Xu et al. [7], with a coaxial microfluidic device, is based on the same principle as those of Steegmans et al. [9] and of Wang et al. [5]. Other microfluidic methods to measure the dynamic interfacial tension are based on droplet deformability after formation [6] and on the pressure drop during droplet formation [8]. Only the method of Steegmans et al. [9] was able to measure the interfacial tension in the sub-millisecond to millisecond time-scale.

Please note that in most traditional methods used to elucidate interfacial tension the conditions are quiescent: the interfacial area remains the same and there is no flow of the surrounding liquid. In microfluidic methods adsorption during droplet formation is most probably measured under enhanced mass transfer conditions. Fast droplet break-up may cause the formation of eddies, resulting in local non-laminar flow conditions and thus convective transport towards the sub-surface. Transport towards the sub-surface is, therefore, assumed to be fast and adsorption is determined by diffusion through the sub-surface and interface expansion rate. Diffusion through the sub-surface might be enhanced during Y-junction emulsification because the shear force from the continuous phase reduces the sub-surface thickness [10] and diffusion might be enhanced because of the curved interface [11]. To distinguish the two methods, the interfacial tension measured under dynamic mass transfer conditions is referred to as the acting interfacial tension (γ_a).

In the present work, we used droplet formation in a microfluidic Y-junction as was done by Steegmans et al. [9], and we evaluated the droplet formation mechanism in detail. Van der Graaf et al. [12] proposed a two-step model to describe droplet formation in a cross-flow T-junction device, comprising of a growth and detachment step (Eq. (1)). The volume added during both steps depended on the capillary number (Ca), which is the balance between shear and interfacial tension forces (Eq. (2)). The volume added during the detachment step scaled linearly with the dispersed phase flow rate.

$$V = V_{crit,ref}\mathrm{Ca}^{x} + t_{neck,ref}\varphi_{d}\mathrm{Ca}^{x} \tag{1}$$

$$\mathrm{Ca} = \frac{\eta_c v_c}{\gamma} \tag{2}$$

where $V_{crit,ref}$ and $t_{neck,ref}$ are the reference critical volume and necking time, x a fitting parameter, η_c the continuous phase viscosity, v_c the continuous phase velocity, γ the interfacial tension, and φ_d the dispersed phase flow rate; for more details see Van der Graaf et al. [12].

In the work of Steegmans et al. [13] a Y-shaped junction was used, and for the rather limited experimental conditions that were probed it was suggested that the droplet size could be described with a one-step model, corresponding to Eq. (1) without the detachment step. Since we aim to extend the process conditions considerably compared to those used in earlier investigations, we consider both models, and investigate which one describes our situation best.

The current research aims to measure the acting interfacial tension in the sub-millisecond to millisecond range under dynamic mass transfer conditions. To do so, the method of Steegmans et al. [9] was used as a starting point, and further refined for a wide range of experimental conditions. The model for droplet formation in Y-junctions was statistically validated using >60 experiments. As a proof of concept, adsorption of sodium dodecylsulfate (SDS) at the oil–water interface was measured for various flow rates at the specified time scales. Flow rates, droplet volume and other data used to construct the figures presented in this article can be found in Appendix D.

2. Experimental

2.1. Materials

Anhydrous hexadecane >99% pure (Sigma-Aldrich, USA) was used in all experiments as the dispersed phase. Water was first filtered and deionised with a Milli-Q system (Q-POD with Millipak Express 40 0.22 μm filter, Merck Millipore, USA). For the continuous phase, water, 9 and 28 wt.% ethanol solutions, 20 and 30 wt.% glycerol solutions, and 20 and 25 wt.% sucrose solutions were used. Ethanol was 99.9% pure (Merck, USA), glycerol >99% pure (Acros Organics, USA) and sucrose ⩾99.0% pure (Fluka, Germany). Sodium dodecylsulfate >99% pure (Sigma–Aldrich, USA) was used as surfactant in aqueous solutions of 0.01, 0.05, 0.1, 0.3, 0.5 and 1 wt.%.

For microfluidic experiments, all aqueous liquids were filtered with a 0.2-μm cellulose filter (13/0.2 RC, Whatman Spartan, UK) before use.