Dynamic fluid interface formation in microfluidics: Effect of emulsifier structure and oil viscosity

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ABSTRACT

Microfluidic devices are known for their accurate control of emulsification, but are less known for their suitability to investigate involved dynamic mechanisms. We previously showed that a microfluidic Y-junction can be used to measure interfacial tension in the millisecond time-scale, at high interface expansion rates, and under convective mass transport. In the present work, we further use this device to elucidate and compare dynamic adsorption behaviour of water- or oil-soluble surfactants, in combination with different alkanes. We found that oil viscosity affects adsorption of the oil-soluble surfactant Span 20 because surfactant transport is influenced by viscosity through the internal velocity. Conversely, adsorption of the water-soluble surfactant Tween 20 was not affected by oil viscosity. When comparing surfactant adsorption rates, it was clear that surfactant structure became more important when more surfactants were present at the interface; Tween 20 adsorption was slower than Span 20 because of steric repulsion at the interface.

1. Introduction

At an industrial level, emulsions are made in very large quantities, using devices that mostly impose large shear forces on droplets that are consequently broken up into smaller ones (Walstra, 2003). To characterise droplet formation, and to tentatively predict their size, dimensionless numbers are used, such as the Capillary number, Weber number, and Ohnesorge number (Rayner & Dejmek, 2015). What all these numbers have in common is that a value for the interfacial tension needs to be inserted, but the decision on which value to use is far from trivial. Droplet formation typically takes place at sub-millisecond time-scales, while interfacial tension measurements are not possible at such time-scales using conventional methods. The droplet volume tensiometer, which is the standard measurement technique, can measure at time intervals that are in the order of seconds or just below, which is thus an order of 3 slower than the time-scales relevant for large scale emulsification.

Although microfluidic and microstructured devices can be used for monodisperse emulsion production (Muijlwijk, Berton-Carabin, & Schroën, 2016; Vladisavljevic et al., 2012), the current low through-puts limit their application (Schroën, Bliznyuk, Muijlwijk, Sahin, & Berton-Carabin, 2015). Yet, since droplet formation in these devices can be very fast (Baret, 2012; Bremond & Bibette, 2012), they are of interest to investigate processes at time-scales relevant to the industrial scale. Recently, we have shown that it is possible to measure

the interfacial tension during droplet formation in the sub-millisecond to millisecond time-scale with a microfluidic Y-junction (Muijlwijk, Hinderink, Ershov, Berton-Carabin, & Schroën, 2016). Others have also used microfluidics for this purpose, albeit exploring slightly longer time-scales (Brosseau, Vrignon, & Baret, 2014; K. Wang, Zhang, Zhang, & Luo, 2016; X. Wang, Riaud, Wang, & Luo, 2014; Xu, Dong, Zhao, Tostado, & Luo, 2012). The steps beyond initial emulsifier adsorption can also be investigated by microfluidics, for example whether emulsifiers efficiently stabilise the oil-water interface and prevent droplet coalescence (Baret, Kleinschmidt, Harrak, & Griffiths, 2009; Krebs, Schroën, & Boom, 2012, 2013). Through these methods, more insights can be generated on how and how fast the interface is covered and stabilized by emulsifiers, which will ultimately help to optimise processing conditions and emulsion formulation.

In the present work, we focus on the initial stages of emulsifier adsorption using a microfluidic Y-junction, for which a relation between the interfacial tension at the moment of droplet formation (the acting interfacial tension), and the droplet size was derived using a balance between the continuous phase shear force and the interfacial tension. The acting interfacial tension (γ_a) can be calculated from the droplet volume (V) with Eq. 1, continuous phase velocity (v_c), dispersed phase flow rate (φ_d), continuous phase viscosity (η_c), and chip specific fitting parameters b and c, as described in detail in earlier work (Muijlwijk et al., 2016).

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$$\gamma_a = \eta_c v_c \left(\frac{V - \frac{c}{v_c}\varphi_d}{b} \right)^2$$

(1)

At a low expansion rate, emulsifier adsorption can take place over a longer period of time because droplet formation is slower (Muijlwijk et al., 2016), resulting in lower acting interfacial tensions. In previous work, we focussed on effects occurring in the continuous phase, and showed that the adsorption process is greatly influenced by the convective mass transport conditions while the Marangoni effect can be neglected because of the fast continuous phase velocity (Muijlwijk et al., 2016). Others have indicated that the dispersed phase viscosity also influences droplet size (Gu & Liow, 2011; Husny & Cooper-White, 2006; Nie et al., 2008; Yeom & Lee, 2011; Zhang & Stone, 1997), as does the droplet formation regime (Pathak, 2011; Wehking, Gabany, Chew, & Kumar, 2013), yet without establishing a direct link with the dynamic behaviour of surfactants.

In this paper, we systematically vary the viscosity of the oil phase and the droplet expansion rate, while using Span 20 and Tween 20 as oil- and water-soluble emulsifiers, respectively.

2. Experimental

2.1. Materials

As dispersed phase, decane ($\geq$ 99% pure from Sigma-Aldrich, USA), dodecane ($\geq$ 99% pure from Sigma-Aldrich, USA), or hexadecane (99% pure from Sigma-Aldrich, USA) were used either pure or with 0.05, 0.3, or 0.5 wt% Span 20 (sorbitan monolaurate, Sigma-Aldrich, USA). As continuous phase, filtered and deionised water (Milli-Q system Q-POD with Millipak Express 40 0.22 μm filter, Merck Millipore, USA) was used, either pure or with 0.05, 0.1, 0.3, or 0.5 wt% Tween 20 (polyoxyethylenesorbitan monolaurate, Sigma-Aldrich, USA). For model validation, liquid systems with a constant interfacial tension were used; the continuous phase consisted of pure water or of mixtures with 5, 9, or 28 wt% ethanol (99.9% pure from Merck, USA). All aqueous liquids were filtered with a 0.2-μm cellulose filter (13/0.2 RC, Whatman Spartan, UK) before use in microfluidic experiments.

2.2. Methods

2.2.1. Interfacial tension

Equilibrium interfacial tensions were measured at 20 °C with a droplet volume tensiometer (ADT, Teclis IRconcept, France) as described previously (Muijlwijk et al., 2016) and the results are shown in Table 1 and Table A2 in the Appendix.

2.2.2. Microfluidic set-up

Borosilicate glass chips (Micronit Microfluidics, The Netherlands) were used with a width (w) and depth (z) of 20 and 5 μm, respectively. The dispersed and continuous phase channels meet under an angle of

Table 1
Equilibrium interfacial tension measured at 20 °C with a droplet volume tensiometer. All measurements were done in duplicate and standard deviations were $\leq$ 0.6 mN/m.

Surfactant	Concentration (wt%)	γ (mN/m)	
		Hexadecane	Decane
None	0	44.0	48.3
Tween 20	0.05	7.3	7.9
	0.1	6.7	7.6
	0.3	6.8	6.8
	0.5	6.6	6.9
Span 20	0.05	7.6	7.2
	0.3	5.9	5.5
	0.5	5.2	4.3

97° in a Y-shape junction. Droplets were formed and recorded as described previously (Muijlwijk et al., 2016). The droplet formation time was typically 0.2–4.9 ms and the corresponding droplet formation frequency was 200–5000 s^{-1}.

Droplet volume (V), droplet formation time (t_{drop}), dispersed phase flow rate (φ_d), continuous phase flow rate (φ_c) and velocity (v_c), relative neck length ($L_{neck,r}$), and expansion rate were measured with a custom-written script for image analysis in Matlab with image processing toolbox (Mathworks, USA) as described previously (Muijlwijk et al., 2016). These parameters are needed to calculate the acting interfacial tension through Eq. 1, and for this only measurements in the dripping regime ($L_{neck,r} < 1\%$) were used. It is good to mention that parameters b and c were determined with very high accuracy before each experiment using a liquid system with a static interfacial tension; more details can be found in (Muijlwijk et al., 2016). The raw data used to construct the figures presented in this article are available as supplementary material in Appendix B.

3. Results and discussion

Some characteristics of the used liquids, including their interfacial tension are given in Table A2 in Appendix A. Model parameters b and c were determined for decane and dodecane droplets formed in water and validated using other continuous phase liquids of known interfacial tension, as was done previously for hexadecane (Muijlwijk et al., 2016). Droplet formation was characterised and compared, after which adsorption of water soluble (Tween 20) and oil soluble surfactants (Span 20) was measured.

3.1. Effect of dispersed phase viscosity on droplet formation

3.1.1. Model determination and validation

To establish model parameters b and c of Eq. 1, experiments were done with only water and the respective oil (Appendix A, Fig. A1). For both decane and dodecane, the droplet volume increased linearly with increasing the dispersed phase flow rate, as was previously found for hexadecane (Muijlwijk et al., 2016). The model parameters could be determined with great accuracy, and the parameters were not correlated (Appendix A, Table A1). The values may indicate that the b parameter is fairly constant, and that the c parameter is oil-dependent, but given small differences in channel dimensions between the different micro-chips, we cannot confirm that this conclusion holds.

The models were validated through experiments carried out with water/ethanol mixtures that had a range of viscosities and interfacial tensions (Appendix A, Table A2), and the experimentally determined droplet volumes (V_E) were compared with the predicted values (V_C) using Eq. 1 (Appendix A, Fig. A2). From the excellent agreement found for both oils we concluded that the two-step model is valid for a broader range of process conditions than previously investigated, therewith facilitating in depth exploration of surfactant adsorption.

3.1.2. Droplet formation

The Y-junction model (Eq. 1) is derived for the dripping regime where droplet formation occurs at the junction (i.e., $L_{neck,r} < 1\%$) (Muijlwijk et al., 2016). The dispersed phase viscosity has a pronounced effect on droplet formation, as illustrated in microscopy images taken just before droplet detachment, at an almost constant dispersed phase flow rate of 11–12 μL/h (Fig. 1). The relative neck length increased with increasing oil viscosity for a given dispersed phase flow rate and resulted in an earlier change in droplet formation regime from dripping to transition and ultimately jetting as indicated by the dashed lines in Fig. 1. Such changes have been linked to the viscosity ratio (λ), which is the ratio of dispersed phase (η_d) and continuous phase viscosity (η_c); at higher viscosity ratio the drag force increases and the droplets are more rigid resulting in an increased shear at the boundary of the two fluids (Milliken, Stone, & Leal, 1993; Pathak, 2011; Wehking et al., 2013). The