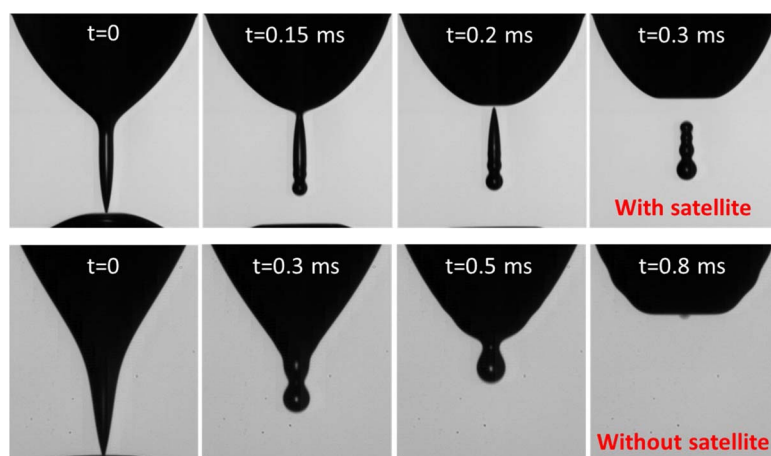# Effect of soluble surfactant on regime transitions at drop formation

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GRAPHICAL ABSTRACT

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ABSTRACT

Formation of surfactant-laden aqueous drops by liquid flow through a capillary is studied and compared with two reference pure liquids, water and low viscosity poly(dimethylsiloxane). Attention is paid to two transitions: (i) between regimes with and without satellite droplet formation and (ii) from dripping to jetting. It is shown that transition from dripping to jetting occurs at critical Weber number $We_J = 1.2 \pm 0.1$ based on dynamic surface tension on the flow timescale. Critical Weber number for transition to the regime without satellite droplets depends noticeably on the liquid surface tension and therefore cannot be used as a single parameter characterising this transition. Flow rate at transition decreases with decrease of surface tension for pure liquids and solutions of surfactants with critical micelle concentration, $CMC > 10$ mM. For solutions of surfactants with $CMC < 1$ mM transition to the regime without satellite droplets occurs at flow rates either larger or smaller than that of pure solvent depending on concentration. Anomalously high transition flow rates are related to surfactant redistribution during the time between the primary and secondary pinch-off.

1. Introduction

Drop formation is broadly used in industry: emulsification, spraying and ink jet printing are a few examples of the numerous applications which currently exist. Typical drop sizes required cover several orders of magnitude from micrometres to millimetres and the corresponding time scales of formation cover the range from sub-milliseconds to seconds. At small flow rates, liquid drops are formed in the dripping

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regime, when the time interval between subsequent drops is constant and drop size distribution is narrow. In what follows this regime is called a stationary dripping. As the flow rate increases, the drop formation becomes less regular with transition to regime called chaotic dripping [1] or dripping faucet [2]. Finally transition to jetting regime occurs where drops are formed due to the Rayleigh instability [1–4]. One more transition takes place inside the dripping regime. At small flow rates, formation of the main drop is accompanied by formation of a small satellite droplet, which is suppressed at larger flow rates [4–7].

Precise criteria for these transitions are vital for most applications, because transitions affect drop size and size distribution, determine the optimal throughput for a drop formation process and product quality. For example, technologies enabling avoidance of satellite droplets formation are of great demand in ink jet printing [8] and in spray-drying [9], because satellites or fines can be easily misdirected by electric field or air flow and therefore can considerably reduce the quality of final product. Another example is production of hydrogel capsules for 3-D cell culture, where capsules of mm-size were produced in dripping mode [10], whereas those of sub-mm size were produced in the jetting mode [11].

The behaviour of liquid flowing out of a nozzle is completely characterised by four dimensionless numbers [5,6], namely Weber number,

$$We = \rho u^2 R_{in}/\sigma = \rho Q^2/\pi^2 \sigma R_{in}^3 \qquad (1)$$

Ohnesorge number,

$$Oh = \mu/\sqrt{\rho \sigma R_{out}} \qquad (2)$$

gravitational Bond number,

$$Bo = \Delta\rho g R_{out}^2/\sigma \qquad (3)$$

and the ratio of inner and outer nozzle radius R_{in}/R_{out}, where u is the liquid velocity, σ is the surface tension, Q is the flow rate, μ is the dynamic viscosity of liquid, $\Delta\rho$ is the density difference between the liquid in the drop and ambient fluid ($\Delta\rho \sim \rho$, liquid density, if the ambient fluid is air) and g is the acceleration due to gravity [1]. If $R_{in}/R_{out} > 0.5$ the effect of the wall thickness on the dynamics of the process can be neglected [12].

The transition from dripping to jetting, which in fact is a transition from absolute to convective instability was intensively studied for pure liquids both theoretically and experimentally and summary of most important results is given in Ref. [1].

Thorough studies on the formation of satellite droplets during dripping of surfactant-free liquids have been published [5–7,12,13] including both numerical simulations and experiments. The behaviour of a satellite drop is determined by recoiling speed of the bridge after primary pinch-off and the rate of secondary pinch-off. During dripping from thin capillaries it is noted that the speed of recoil is sufficiently large to repress secondary pinch-off thus no satellite droplet is formed. An increase in the capillary size results in formation of a satellite drop moving upward and often coalescing with the liquid remaining on the capillary. At further increase of capillary size, the upward motion of the satellite slowed down and after a certain threshold capillary size the satellites moving downward were observed [12]. Suppression of satellite formation due to an increase of flow rate was not observed in this study due to flow rate limitations, but was predicted in numerical simulations and found experimentally in subsequent studies [5–7].

In line with Ref. [12] it was found in Ref. [7] that the ratio of inner and outer capillary diameter is an important parameter for formation of the satellite drops, which are formed only if this ratio exceeds 0.48. If this is the case the transition to the regime where formation of satellite drops is suppressed is determined by Weber number and depends much less upon Bond number. From analysis of numerical and experimental data for the drops of pure water ($Oh < \ < 1$) a parameter

$$K = We \cdot Bo^{0.3921} \qquad (4)$$

was proposed to best characterise this transition. Satellite droplets cease to form at K > 0.0125 [7]. In the more general case, the critical Weber number for transition to regime without satellite droplets depends also on Ohnesorge number [6].

Despite a very broad use of surfactants in industrial processes involving drop formation, there are relatively few publications focussing on surfactant-laden rather than surfactant free drops, with most attention paid to kinetics of drop formation and the size of satellite drops [12,14–19]. The effect of soluble surfactant on the dripping to jetting transition and the transition to regime without satellite drops has not been considered in the published literature. The work presented in this paper addresses this issue using a series of cationic surfactants, alkyltrimethylammonium bromides with chain length C10-C16.

2. Experimental

The surfactants, decyltrimethylammonium bromide ($C_{10}TAB$), Acros organics, 99%; dodecyltrimethylammonium bromide ($C_{12}TAB$), Acros organics, 99%; hexadecyltrimethylammonium bromide ($C_{16}TAB$), Sigma, BioXtra, $\geq 99\%$; as well as sodium bromide, Sigma, BioUltra, $\geq 99.5\%$ and Poly(dimethylsiloxane) (PDMS), Sigma, density $820\,\mathrm{kg/m^3}$, were used as purchased. All solutions in concentration range from 0.2 to 10 critical micelle concentrations (CMC) were prepared in double-distilled water produced by water still Aquatron A 4000 D, Stuart. The values of CMC of surfactant solutions and equilibrium surface tension, σ_e at concentrations above CMC are given in Table 1.

The densities of studied solutions were measured by weighing 10 mL of solution dosed by Eppendorf pipette and were found to be similar to those of water for all surfactants solutions except $C_{10}TAB$ at concentrations above CMC. However, the deviation of the density of $C_{10}TAB$ at the maximum studied concentration 10 CMC from that of water was below 1% and therefore can be neglected. The viscosities of studied solutions were measured by a TA instruments Discovery-HR-2 rheometer in flow mode using cone and plate geometry with the angle $2^O\ 0'\ 29''$ and a truncation of 55 μm. Viscosities of solutions of $C_{16}TAB$ were similar to that of water. Noticeable increase in viscosity was found only for solution $C_{12}TAB$, 10 CMC and $C_{10}TAB$ 5 and 10 CMC (see Supplementary material, S1). The dynamic surface tension was measured using a maximum bubble pressure tensiometer BPA-1S (Sinterface, Germany).

The experiments were performed as follows: drops were formed continuously at the tip of stainless-steel capillary with outer radius $R_{out} = 0.905$ mm, inner radius $R_{in} = 0.735$ mm and length $L_c = 43$ mm at flow rates in the range from 0.1 mL/min to 40 mL/min using a syringe pump Al-4000, World Precision Instruments, UK. The syringe pump was equipped with 10 mL syringe (BD Plastipak^{TM}) for flow rates up to 10 mL/min and with 60 mL syringe for higher flow rates. The maximum Reynolds number in this study based on inner diameter of capillary, D_{in}, was $Re = \rho u D_{in}/\mu \sim 580$, i.e. flow conditions are well within the laminar flow regime. As the hydrodynamic entrance length $L_h = 0.05 Re D_{in}$ [21] ~ 42.5 mm for the maximum flow rate of 40 mL/min, fully developed flow is assumed at the capillary exit at all flow rates studied. Flow rate was changed always from lower to higher values and after any change in the flow rate, the system was left for 0.5–5 min for stabilisation depending on flow rate.

Table 1
Properties of surfactants used [17,20].

Surfactant	$C_{10}TAB$	$C_{12}TAB$	$C_{16}TAB$	$C_{16}TAB$ + 10 mM NaBr
CMC, mM	60	15	0.9	0.1
σ_e, mN/m	39	39	37.5	37.2

Note, surface tension of PDMS is 17.2 mN/m, i.e. much lower than the minimum surface tension of all studied surfactant solutions.