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Interfacial instability of growing drop: Experimental study and conceptual analysis

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ABSTRACT

Capillary pressure experiments were performed at the water/hexane interface including adsorption and mass exchange of hexanol under different conditions. The results from growing drop experiments show that instabilities due to Marangoni convection not only depend on the same parameters as have been reported for quasi-static interfaces, such as direction of mass transfer, distribution coefficient and ratio of diffusion coefficients, but also on the experimental conditions such as dispersed phase flow rate, capillary tip size, size of growing drop and its lifetime. Based on a new flow expansion model for mass transfer, a new approach is presented for data analysis, which includes the various parameters effecting interfacial instabilities. The proposed analysis considers the overall mass transfer coefficient ratio (k_1/k_2) which includes diffusion and convection effects instead of the pure ratio of diffusivities (D_1/D_2) under the condition of growing drops. The proposed analysis is verified on the basis of capillary pressure measurements.

1. Introduction

Carlo Marangoni was the first to correctly explain qualitatively the movement at a fluid interface caused by local variations in surface tension induced by differences in composition or temperature [1]. After this discovery in 1871, many papers, including those of the most famous scientists of the 19th century like Plateau, Gibbs, and Rayleigh, were dedicated to this phenomenon. Scriven and Sternling reported in 1960 [2] that Thomson was obviously the first who explained in 1855 the “tears of wine” in his paper entitled “on the certain curious motions observable at the surfaces of wine and other alcoholic liquors”.

Meanwhile the interfacial instability caused by Marangoni convection, due to variations of interfacial tension with temperature or surface composition, is a well-know phenomenon for gas–liquid and liquid–liquid systems. The transfer of a surface active solute across a liquid–liquid interface gives frequently rise to spontaneous perturbations at the phase boundary. These so-called solutal Marangoni effects have been attributed to interfacial tension gradients produced by local variations in solute concentration along the interface [3]. Because of the significantly enhanced mass and heat transfer caused by Marangoni convection, this phenomenon is an important topic for numerous scientific and technological applications, such as liquid–liquid extraction systems, foam and emulsion technologies, absorption, distillation, and crystal growth.

The present paper gives a brief overview on the Marangoni effect with emphasis on the very few attempts to apply the concept to growing drop conditions. First a review on the available interfacial instability criteria for planer interfaces and spherical droplet surfaces is performed, and then an experimental and conceptual analysis is proposed for instability criteria of Marangoni convection for growing drops, based on capillary pressure experiments.

2. General instability criteria

Most instability criteria for Marangoni convection have been derived for regular planar interfaces or without emphasis on any special interfacial geometry. The first attempts to find a relationship between Marangoni instability and interfacial turbulence was presented by Sternling and Scriven in 1959 [3], who applied a linear stability analysis to the transfer of a solute across a non-deformable interface. Their analysis showed clearly that solute transfer in one direction yields a stable, while transfer in the opposite direction produces an unstable interface. They also showed that there are systems where mass transfer in either direction produces instabilities. The analysis showed that instabilities are controlled also by other parameters such as direction of interfacial tension change with solute concentration, the signs of differences between the

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solute diffusivities and kinematic viscosities of the two phases. For example, systems are always unstable when the surfactant transfer is out of the phase of lower diffusion coefficient, or when both solute diffusion coefficient and kinematic viscosity are lower in the same phase. The stability analysis was further improved by Sørensen et al. [4]. Later Cho and Jones [5] added heat effects to the analysis, while Perez de Ortiz and Sawistowski [6] considered heat and mass transfer in binary liquid–liquid systems simultaneously. Also the physical conditions under which transfer of a surfactant through a fluid interface between two immiscible liquids may induce aperiodic convections were studied [7,8].

An extensive recent review on the different instability criteria of liquid interfaces has been presented by Kovalchuk and Vollhardt [9], where they discussed the development of spontaneous convective motion due to solute transfer via three different procedures: (i) gravitational (buoyancy) effect; (ii) Marangoni instability due to thermal effects and (iii) solutal Marangoni instability.

Recent progress in flow visualization, in particular development of Micro-PIV (Particle image velocimetry) provides an interesting opportunity for investigations of fluid flow in small-scales and in a close distance to solid and fluid interfaces. Via this technique [10] presented an experimental investigation of the self-induced liquid convection for an evaporating meniscus in small capillary tubes. According to the flow pattern in the liquid phase they reported a thermocapillary Marangoni convection in the horizontal diametrical sections of the horizontally oriented capillary tube as two contrarotating vortices of similar strength, whereas in vertical diametrical sections a single clockwise vortex was mostly observed.

The Marangoni convection and interfacial instabilities occurring at spherical interfaces are basically similar to those at planar interfaces, however, some additional aspects have to be considered due to the finite diffusion depth (drops) and deformable interfaces. The problem of the stability of a spherical interface (surface of a drop or bubble) was considered in the most general formulation by Sorensen and Hennenberg [11], in which a linear analysis of the stability was made with allowance for deformation of the surface. Recently Arendt and Eggers [12] investigated the influence of surfactant transfer and Marangoni convection in water–acetone–toluene systems, supported by Schlieren optics, and reported that only in case of the transfer direction from the droplet into the continuous phase a Marangoni convection is detected.

Marangoni phenomena were also studied during the formation and growing of droplets/bubbles, however, only very few investigations and explanations on the instability criteria and conditions for Marangoni phenomena were presented [13–15]. For example, Wong et al. [13] studied the motion of an expanding or contracting bubble pinned at a submerged tube tip covered with an insoluble surfactant. The motion was driven by a constant flow rate Q into or out of a tube. The physical properties and parameters considered were similar to typical air/water interfaces, and two important conclusions were obtained: (i) in spite of the larger area decrease at the apex upon contraction, the large Marangoni force drives a substantial convection, reduces the developing gradient and maintains a uniform concentration distribution; (ii) the resulting tangential velocity is higher than that of a corresponding clean bubble. Jin et al. [15] studied numerically the effect of soluble surfactants on droplet growth with particular attention to drop necking.

In the present work we analyse the conditions for the water drop formation in hexane in presence of the soluble surfactant hexanol, using a capillary pressure technique which provides simultaneously the droplet size. Our analysis is based on a recently presented flow expansion model for mass transfer during drop formation [16,17].

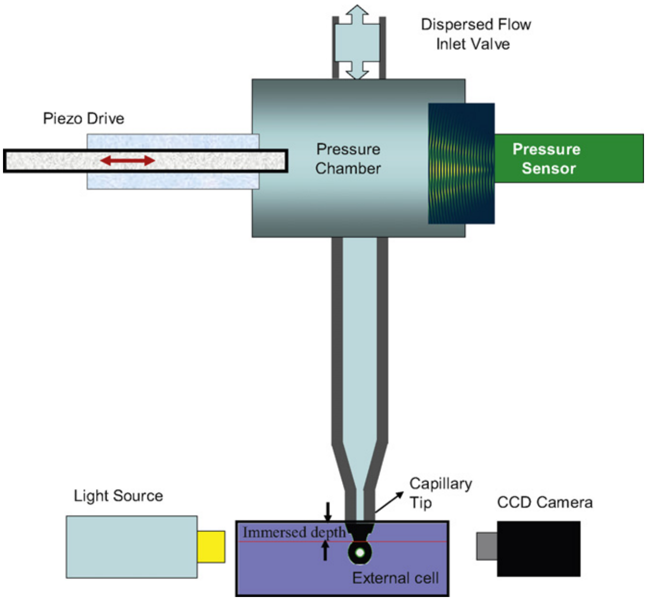

Fig. 1. Schematic view of the ODBA module (SINTERFACE Technologies, Berlin, Germany).

3. Experimental method

The capillary pressure measurements were performed with new developed setup based on the Drop Profile Analysis Tensiometer PAT-1 equipped with the Oscillating Drop Bubble Analyser module ODBA (SINTERFACE Technologies, Berlin). Using this experimental setup the capillary pressure can be recorded during the growth of a drop at the tip of a capillary in real time. The basis of this methodology has been described elsewhere and are developed to improve the measurement accuracy for short time conditions, high interface variations and to achieve a quantitative analysis for extracting the capillary pressure contribution in the measured total pressure [18–22].

The setup consists of four major components (Fig. 1): (1) pressure chamber, (2) piezo drive for drop/bubble expansion/contraction, (3) capillary tube and (4) external cell. The delivery of the liquid is provided by the dosing system of PAT-1, while fine tuning or drop oscillations are organised by the piezo actuator. Two major kinds of experiments can be performed with this experimental setup: continuous flow and sinusoidal oscillations.

The pressure sensor measures the difference between the pressure in the chamber and the outside atmosphere (Fig. 1). Under dynamic condition, the measured value contains the following terms [23]:

$$P(t) = P_{\mathrm{static}} + P_{\mathrm{visc}} + P_{\mathrm{inertial}} + P_{\mathrm{drag}} + P_{\mathrm{cap}} \tag{1}$$

P_{static} is the static pressure due to the liquid column height from the pressure chamber to the capillary tip. The droplet size, changing with time during the drop growth and the immersed depth of the capillary tip into the second liquid must be considered in this term. P_{visc} is the hydrodynamic pressure loss due to the liquid viscous flow through the pressure chamber, connections tubes and especially the narrow part of the capillary tip. This term can be evaluated experimentally and also theoretically using momentum shell balance equations [23]. The experimental results show that the contribution of the capillary tip can amount up to 90% of P_{visc} which is also in good agreement with the well-known model for Hagen–Poiseuille ($\Delta P = 8\,\mu LQ/\rho\pi R^4$) for viscosity loss in circular tubes where μ = viscosity of the fluid, π = 3.14, L = length of tube, Q = flow rate, P = pressure gradient, ρ = fluid density and R = tube