



EVAPORATION OF BINARY MIXTURE DROPLETS ON STRUCTURED SURFACES

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ABSTRACT:

Evaporation modes of pure water, pure ethanol and their binary mixtures droplets on micro-pillared surfaces are experimentally investigated. The concentration of the binary mixture and the solid structure influences the initial droplet wetting behaviour and footprint as we recently reported and hence both play a paramount role on the evaporative behaviour. Investigation results show that droplets can evaporate in 3 different evaporative behaviours, which are consistent with the literature, the constant contact radius mode (CCR) or pinning, the constant contact angle (CCA) mode and stick-slip mode. Besides, in this work, we have observed a fourth additional evaporation mode not reported in the literature, the mixed-stick-slip mode. In this mode, both the contact angle and contact radius decrease with time while the droplet is in the stick-slip mode. The duration of each evaporation mode is dissimilar depending on the concentration of the binary mixture and the solid structure. For pure water and low ethanol concentration, higher pinning time is observed on the surfaces with a high solid fraction, i.e., short micropillar spacing. For the binary mixtures, droplets evaporate for a longer period time in the stick-slip mode independent on the solid fraction, while the longer mixed stick-slip mode evaporation time was observed for the higher ethanol concentration and pure ethanol on surfaces with high solid fractions. This investigation provides significant considerations and findings on applications considering the use of the micro-structured surfaces such as microfluidics, droplet diagnosis, etc.

1. BACKGROUND AND MOTIVATION

Evaporation of liquid droplets is a broad and rich topic of interest. Investigating the fundamentals and complex phenomena involved during droplets evaporation is of interest to many industrial, biological and biomedical applications. Furthermore, a great deal of research is undertaken to expand and improve everyday practices such as inkjet printing, painting, cooling and heating integrated devices, coating technology, combustion engines, crop dusting, desalination, power generation, etc. [1]-[3].

Liquid droplets in unsaturated atmosphere will undergo evaporation. Droplet evaporation typically ensues via three distinct evaporative modes: the constant contact angle (CCA), the constant contact radius (CCR) and/or the mixed-mode where both contact radius and contact angle decrease with time [3], [4]. On one hand, on smooth hydrophilic surfaces, the evaporation occurs in the CCR mode until certain evaporation and then evaporates in the mixed mode [4]; while in contrast, for rough hydrophilic substrates, evaporation occurs in the CCR mode completely [5]. On the other hand, on smooth hydrophobic surfaces, complete evaporation in the CCA mode is more likely to happen [3], [4]. However, if particles are added to the liquid, the droplets evaporate in a stick-slip mode with greater jumps of the contact line for higher nanoparticle concentration as reported by Orejon *et al.* [4]. Stick-slip evaporative behaviour of pure water droplets has also been reported on structured superhydrophobic surfaces[6]. During stick-slip evaporation, contact line pinning on the microstructures or on the

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nanoparticles takes place while the contact angle decreases, *i.e.*, CCR mode. Then the contact line jumps to the next microstructure and the contact angle increases. This stick-slip cycle repeats until complete evaporation [4]. Although the effect of surface structure on droplet evaporation of pure fluids has been addressed to some extent, its effect on binary mixture droplets evaporation has received lesser attention, which is of relevance to patterning and heat transfer amongst others. Binary droplets are ubiquitous and can appear upon the exposure of an organic solvent to the ambient [7].

From the above brief introduction, the importance of further understanding the fundamentals and basic science underlying the physical and physicochemical interactions taking place between solid surfaces and liquid droplets becomes clear. So, the objective of this investigation is to focus on the close interaction between structured solid surfaces and liquid droplets varying in composition on the mechanisms taking place during phase change.

2. EXPERIMENTAL METHODS

Fluid preparation: Pure water (W), pure ethanol (E) and their binary miscible mixtures at different concentrations on a volume basis: 100% E, 80% E-20% W, 60% E-40% W, 40% E-60% W, 20% E-80% W and 100% W were prepared, and good mixing via manual shaking is ensured.

Surface fabrication: Micro-structured surfaces were fabricated via Deep Reactive Ion Etching (DRIE) and coated with a hydrophobic self-assembled monolayer at the Scottish Microelectronic Centre (SMC) at the University of Edinburgh. **Figure 1** shows two surfaces of a total of 6 different structured surfaces studied. All microstructured surfaces have pillars with 10 μm height and 10 μm diameter, *i.e.*, height/diameter aspect ratio equals 1, and various spacing, $s = 5, 10, 20, 40, 80, 160 \mu\text{m}$.

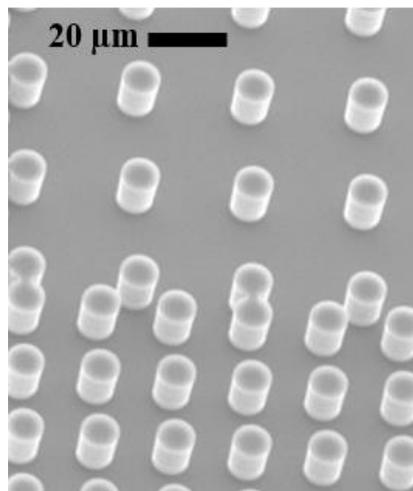


Figure 1: Scanning electron microscopy (SEM) of two of the surfaces used in this work $s = 20 \mu\text{m}$ spacing (top), $s = 10 \mu\text{m}$ spacing (down). Note that droplets are placed at the centre of each surface configuration and away from the boundary of different solid fractions.

Experimental Procedure: Small droplets of $3 \mu\text{l} \pm 0.2 \mu\text{l}$ of the various concentrations were deposited gently on the micro-pillared surfaces with varying spacing. All experiments were performed in ambient air pressure with an ambient temperature of $22 \text{ }^\circ\text{C} \pm 3 \text{ }^\circ\text{C}$ and relative humidity of $30\% \pm 10\%$. After droplet deposition, the evaporation behaviour was observed looking at the droplet from the side, and the contact angle, the volume, the height and the base radius of the droplets were analysed and extracted in time using the Drop Shape Analyser DSA100 and the DSA1 v1.9 software from KRÜSS (KRÜSS GmbH, Hamburg, Germany).

3. RESULTS

Evaporation modes:

Figure 2 presents the evolution of the (top) contact angle and (bottom) radius versus time for pure water, pure ethanol and their mixtures on (left) 5 μm spacing (shortest spacing in this study) and (right) 160 μm spacing (longest spacing in this study) micro-structured surfaces. Depending on the surface structure, the nature of the liquid, and the shape of the droplet, initial apparent contact angles vary between 50° and 145° . Refer to the work of Al Balushi *et al.*, for more details on the initial wetting regime and apparent contact angles reported function of the binary mixture concentration and the solid fraction underneath the droplets[8].

On 5 μm spacing **Figure 2** (left), the maximum intrinsic contact angle was 145° for water which is consistent with the Cassie-Baxter mode, whereas the minimum contact angle was 66° for pure ethanol. As ethanol concentration increases, the contact angle decreased as a consequence of the decrease in the liquid surface tension. For pure water and low ethanol concentrations, evaporation takes place initially in the CCR mode until certain time and then it transitions into the stick-slip mode, which ensues until the end of the droplet lifetime. For higher ethanol concentration (60%, 80% and 100%) for the same spacing of pillars, there was a steep decrease in the contact angle in the CCR mode followed by the mixed mode coupled with a stick-slip mode.

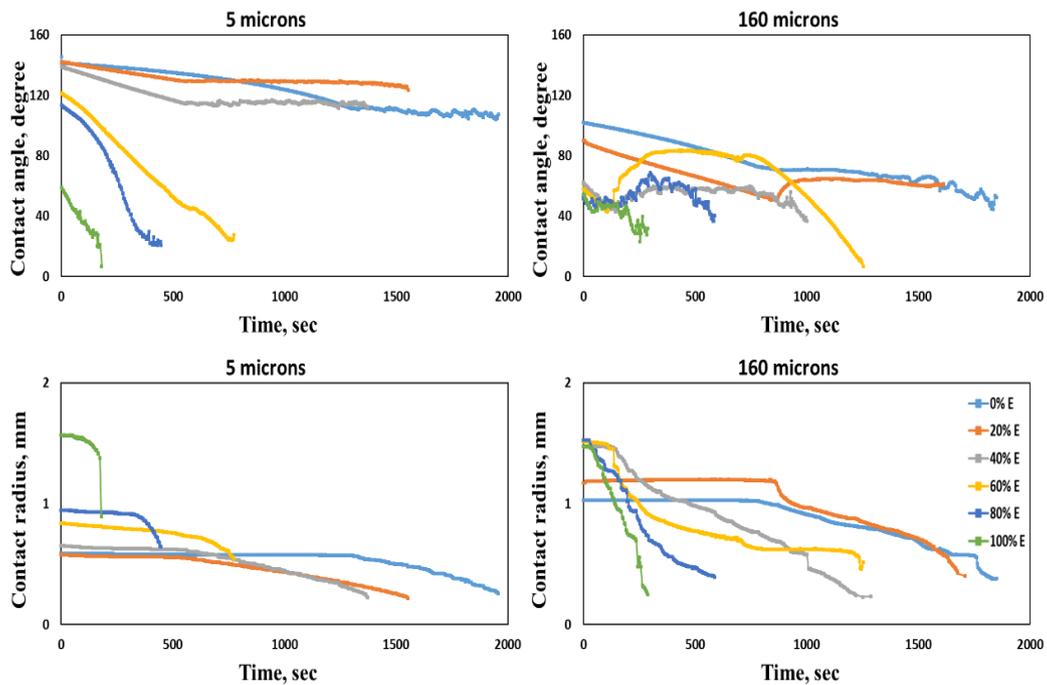


Figure 2: Evolution of (top) the contact angle ($^\circ$) and (bottom) the contact radius (mm) versus time (s), on (left) 5 μm spacing and (right) 160 μm spacing for the different binary mixtures studied.

On 160 microns in **Figure 2** (right), droplets evaporated initially in the CCR mode independent of the concentration, although different extents of pinning time were observed. For lower ethanol concentration, *i.e.*, 0% and 20% ethanol, pinning happened for the first 40% of the droplet lifetime time, while for higher ethanol concentration (40%, 60%, 80%, and 100% ethanol), it was about 4 to 15 % of the evaporation time. After that, the evaporation follows a stick-slip mode and in stick-slip mixed mode evaporation, where both contact angle and contact radius decrease as stick-slip ensues for the rest of the droplet lifetime. We note similar contact angles reported on 160 microns structured surface with those observed on a smooth flat hydrophobic surface.

Initial evaporation modes and duration:

The initial evaporation stage is very important as in the presence of colloidal particles, it does control the onset of the deposits. To provide further quantification of the duration of the initial evaporative behaviour dependence on the microstructure spacing and fluid concentration, **Figure 3** illustrates the normalised initial pinning time for all fluids on all microstructured surfaces as well as on the smooth flat hydrophobic surface. For large micropillars spacing $s \geq 40 \mu\text{m}$, the pinning times are relatively shorter than for short micropillar spacing $s \leq 20 \mu\text{m}$ independently of the binary mixture concentration. As the ethanol concentration increases, the initial pinning time decreases. On even shorter micropillar spacing, though, i.e., $s \leq 10 \mu\text{m}$, the trends and findings on the initial pinning time are not so clear when comparing the effect of pillar spacing. However, longer normalised initial pinning times are reported for lower ethanol concentrations and for pure water.

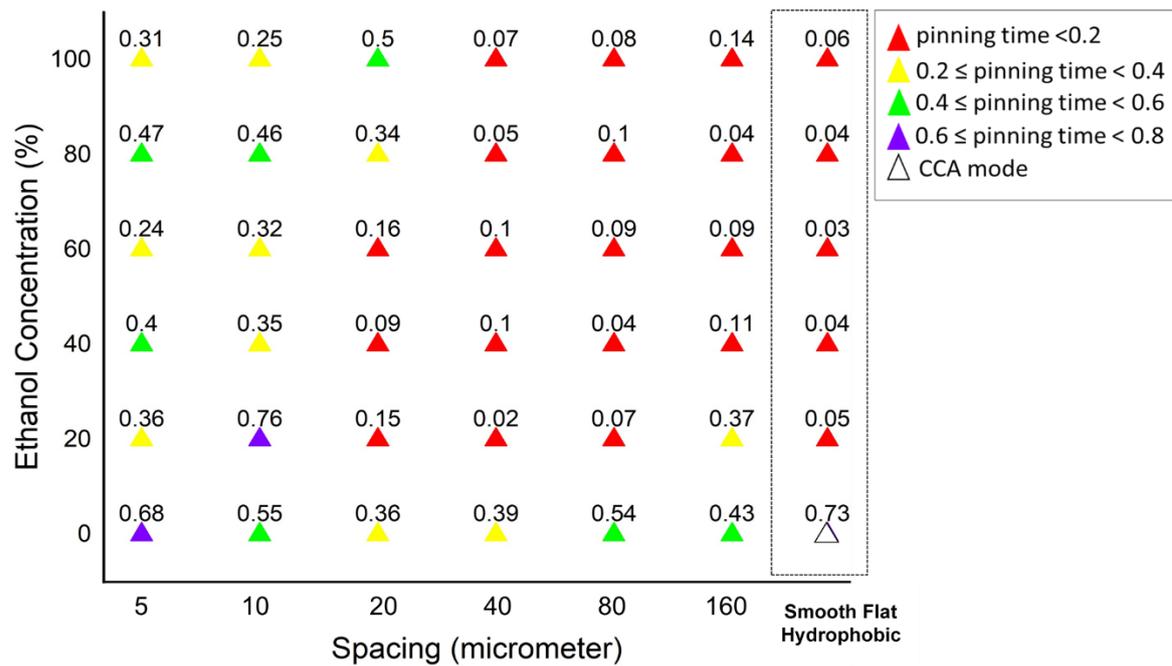


Figure 3: Initial pinning time normalised by the total droplet lifetime for different ethanol-water concentrations (%) on structured surfaces varying in micropillar spacing (s). CCA mode on flat hydrophobic surfaces is included for comparison.

Duration of the evaporation modes of complete evaporation process:

For the complete evaporation, we have compared our results to the results of Xu *et al.*, [9]. In their work, they used pure water only on different structured surfaces with similar solid fractions to those used in our work. **Figure 4** shows the duration of the different evaporation modes on different solid fractions, i.e., different spacing of (a) pure water from the literature [9], (b) pure water in this work, (c) 60%E, (d) pure ethanol.

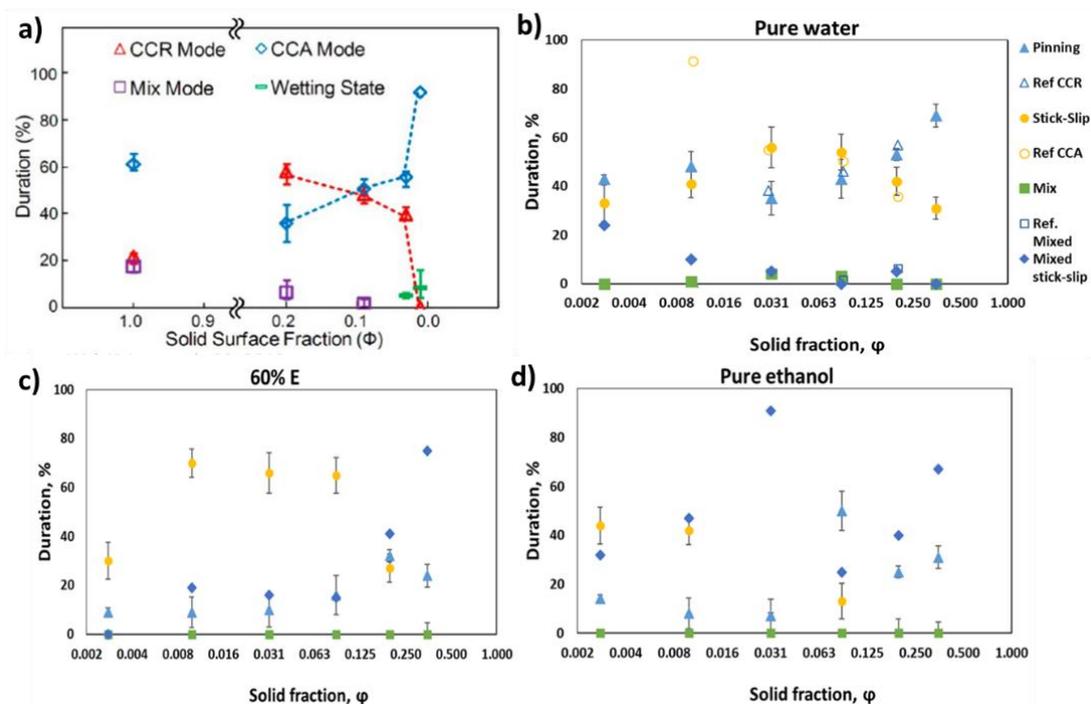


Figure 4: Duration in (%) of the evaporation modes for the complete evaporation lifetime of a) pure water from reference [9] b) Pure water from this work and reference [9], c) 60% ethanol, and d) pure ethanol on different structured surfaces with different solid fractions φ studied.

The duration of the pinning mode (filled blue triangles) is found to be longer for pure water on higher solid fraction surfaces, *i.e.*, shorter spacing, which agrees both quantitatively and qualitatively with the work of Xu *et al.*, (empty blue triangles)[9]. When looking into the stick-slip behaviour, the longest stick-slip duration (filled yellow circles) is observed for the binary mixture and intermediate solid fractions **Figure 4 (c)**. Moving to the mixed stick-slip mode, the longest duration is found to be for pure ethanol and high ethanol concentrations (60%E and 80%E) on short spacing ($5\mu\text{m}$, $10\mu\text{m}$, $20\mu\text{m}$ and $40\mu\text{m}$). In these specific cases, droplets initially wet the structure surface adopting polygonal shapes upon deposition as reported in Al Balushi *et al.*, [8]. These polygonal shapes are retained until the end of the droplet evaporation lifetime as a consequence of the presence of structures and increased roughness and the decrease on the fluid surface tension not allowing the droplet to form a spherical shape upon contact line depinning. Further analysis on the surface free energy and the droplet behaviour is undergoing to further understand the relationship between initial wetting droplet geometry and the dynamic evaporative behaviour both of them function of the surface structure and fluid interfacial tension.

4. CONCLUSIONS

The evaporation behaviour of pure fluids and their binary mixtures on the structured surfaces has been experimentally investigated. Three different evaporative behaviours have been noticed: pinning, stick-slip, and mixed-mode, which are consistent with the literature; while a mixed stick-slip mode is further reported here for the first time. The extent of these evaporative modes depend greatly on the binary mixture concentration and on the micropillars spacing, which condition both the initial wetting regime as well as the dynamics of evaporation. It is concluded that by choosing the proper structure spacing coupled to the liquid properties and concentration, the initial pinning time, the droplet shape and the different durations of the evaporation modes can be tailored for specific applications and objectives, which can prove to be beneficial to many biological, microfluidics or medical applications.

5. ACKNOWLEDGMENT

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