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Circulation Inside a Methanol – Water Drop Evaporating in a Heated Atmosphere

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ABSTRACT

The oscillatory circulation inside an evaporating methanol – water mixture drop at various surrounding temperatures, is reported. The cyclic acceleration and deceleration of the flow inside and around the center of the drop, is termed oscillatory circulation. The volume fraction of methanol in the mixture was varied and the evaporation was recorded at various surrounding temperatures. The study finds that the oscillation diminishes as the temperature of the surrounding increases. The peak (i.e., maxima) frequency of the oscillation among all the volume fraction tested, is observed to be a strong function of the surrounding temperature. The variation of frequency with volume fraction shows that the peak shifts to the higher side of the volume fraction as the temperature is increased. The combined effect of the thermal Marangoni, solutal Marangoni, and solutal Rayleigh convection, was found to control the oscillatory circulation process.

The evaporation of a drop is important for the characterization of new fuels [1], in crystal growth formation of materials [2], to develop evaporation models [3], in semiconductor devices [4], etc. The process depends on the condition of the surrounding (temperature, pressure, etc.), flow outside the drop, concentration of components forming the drop, internal circulation, etc. The internal circulation in single as well as in multi-component drops was studied by many researchers [5–8]. Mandal and Bakshi [6] reported that the measured evaporation rate for a single component drop was significantly higher than that when predicted from the model of Abramzon and Sirignano [3], assuming a pure diffusion controlled evaporation. The cause was the internal circulation due to the combined Marangoni and Rayleigh convection. Both of the convections are caused by the temperature gradient, the first one takes place at the surface, and the other at the bulk. For the case of a drop evaporating in a convective environment, the Marangoni convection enhances the energy transport within the drop that causes faster evaporation and internal circulation compared to the case where the Marangoni convection is neglected [9]. The existence of the circulation was confirmed by others, as well [4,10,11].

For a multicomponent drop, the Marangoni convection is induced due to the surface tension gradient caused by both temperature and solute concentration gradient. For an evaporating sessile ethanol – water mixture drop, three distinct stages were identified for the internal flow [12]. The concentration gradient driven first stage, followed by the depletion of ethanol in the drop surface due to the rapid decay of the vortices at the second stage, and the radial flow towards the contact line in the third stage, were observed. Bennacer and Sefiane [13] reported that the surface tension gradients drive the vortices, whereas the viscous dissipation governs the transition of the flow and its dynamics. The stages of the internal circulation and the physics were confirmed by other researchers, as well [14].

Ha and Lai [5], in their theoretical investigation of a bi-component droplet, found that the onset of the thermal and the solutal Marangoni number are linearly related with a negative slope when the surface tension is assumed to be monotonically decreasing function of both temperature and the concentration of the higher volatility component. In such cases, the thermal and solutal effects are observed to supplement each other. However, Armendariz and Matalon [15] provided a theoretical study on the effects of thermal and solutal Marangoni convection of a multicomponent drop, and found that, they always oppose each other.

Probably the first experimental demonstration of the presence of oscillatory circulation was provided by Mandal and Bakshi [7] inside various evaporating ethanol – water mixture drops, and confirmed the existence of the opposing effect of solutal and thermal Marangoni convection, as a cause of the oscillation. Similar study for various methanol – water drops, was conducted by Kumar and Mandal [16], as well. Both of studies were conducted at normal temperature. The consequences of the variation of the surrounding temperature on the circulation have been unexplored so far. The temperature may be one of the governing parameter for the circulation, since the enhancement of evaporation rate increases the thermal and or solutal gradients at the

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surface and at the interior of the drop. Therefore, to fill the gap, the interaction of Marangoni and Rayleigh convection for various evaporating methanol-water drops at various temperatures, is studied here. An experimental setup was used.

The experimental setup and methodology were explained elsewhere [6]. In short, a drop was suspended centrally inside a test section (acrylic chamber of inner dimension 300 mm × 300 mm × 300 mm) with the help of a syringe, needle (outer diameter of 2.7 mm) and a stand to hold the syringe. The needle tip was placed centrally inside, to form a pendant drop whenever the liquid was pushed by the piston of the syringe. To form a symmetric drop about the vertical axis, the needle tip was made flat. The test section was provided with inlet and outlet lines for purging nitrogen gas to remove the moisture inside, before starting the experiment. A thermocouple, placed near the drop (about 10 mm away), was used to measure the temperature of the surrounding. For heating the surrounding, a radiant heater of 1500 W, controlled by a variable transformer, was placed at the bottom of the test section. Steady temperature of the surrounding was maintained while conducting the experiments. Four temperatures, 300, 306, 313, and 325 K, were used. The fluctuation was about ± 1 K, near the drop. The authors could not go beyond 325 K, to avoid reaching the boiling point of methanol.

To confirm the spatial uniformity of the surrounding temperature, two thermocouples were kept at several places around (about 10 mm away) a mixture drop of 0.5 volume fraction of methanol and separate experiments were conducted by setting the temperatures. The temperatures were recorded per second for duration of about 10 min. The fluctuation was the same as above (i.e., about ± 1 K). Therefore, it can be said that the surrounding temperature is spatially uniform while conducting the experiments.

A high-speed camera was used to capture the internal circulation at 10 frames per second and at a resolution of 0.10 pixel/μm. A continuous wave, 532 nm, 5 mW laser was used to illuminate the drop, which was seeded with aluminium particles of about 3 μm size. The laser focusing the drop was placed perpendicular to the axis of the camera and the drop. The diameter of the beam was about 3 mm adjacent to the bulb and to the drop. The beam was passed through a slit of 0.5 mm thickness. The distance between the drop and the slit was about 180 mm. The path-lines become visible after adjusting the position of the laser, and the camera settings (exposure time, etc.).

For conducting experiments, nitrogen gas was purged inside the test section and the desired temperature of the surrounding was maintained. The syringe was then filled with the desired mixture. Methanol – water mixtures of various volume fractions were used. A pendant drop was formed. The initial diameter was nearly 3 mm for all drops. The laser and the camera were adjusted and the experiment was started. The maximum duration of the experiment was about 5 min.

As demonstrated in Mandal and Bakshi [6], for the measurement of the velocity of internal circulation, a region inside the drop (of a given image) was marked using Matlab. The path-lines, which completely lie within the region, were selected. A second-order polynomial was fitted to obtain the length. The instantaneous velocity was obtained by dividing the average length with the exposure time of the camera (exposure time: 50 to 80 ms).

The maximum error in the velocity measurement is 9%. A standard uncertainty analysis, which estimates the uncertainty in the value of the measured velocity due to unavoidable errors, is used. The detail of the analysis is provided in the supporting material.

The variation of the instantaneous velocity with time shows intense oscillatory internal circulation for various evaporating methanol – water mixture drops (see the supporting material). The circulation reported here, is a cyclic process, where the acceleration and deceleration of the flow inside and around the center of the drop, is observed. Therefore, the process is termed oscillatory. Movies demonstrating the circulation at various surrounding temperatures are attached in the supporting material. The oscillation can be confirmed from the squared modulus of the instantaneous velocities (see the Supporting material). The circulation at normal temperature, was demonstrated by Kumar and Mandal [16]. For the present case, the oscillation is observed at elevated surrounding temperature, as well. However, the frequency of oscillation for a drop of given volume fraction of methanol, is observed to reduce sharply at elevated temperatures (306, 313 and 325 K, see Fig. 1). For a given experiment, the variations of the peak frequencies are within 10% when the measurement location is altered (see the supporting material). The peak occurs when the volume fraction is 0.5, 0.5, 0.6, and 0.7 for the surrounding temperatures of 300, 306, 313, and 325 K, respectively (see Fig. 1). The peak moves to the higher volume fraction side, as the temperature increases. The oscillation is zero for pure methanol and water, since, pure methanol shows steady circulation, and for pure water the circulation is negligible. So, there are three issues to address; the cause of the oscillation, the reduction of frequency at elevated temperatures, and the shift in peak frequency with temperature. The oscillation comes from the opposing effect of thermal and solutal Marangoni convection, as reported earlier [7,16,17], whereas, the present study shows that the reduction of frequency and the shift in peak frequency, result from the complex interaction of thermal Marangoni, solutal Marangoni and solutal Rayleigh convection.

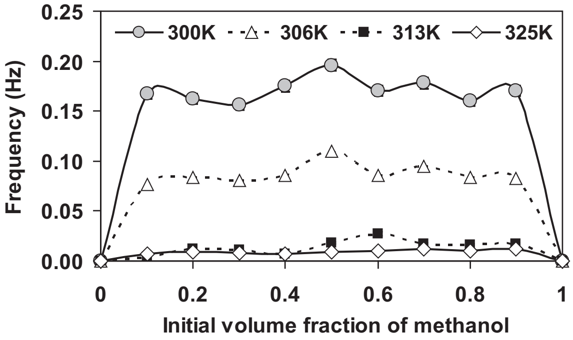

Fig. 1. Frequency of oscillation as a function of initial volume fraction of methanol. All data for 300 K are taken from Kumar and Mandal [16]. Lines are used for clear demonstration.

The opposing nature of the thermal and solutal Marangoni convection (as reported in Mandal and Bakshi [7]; Armendariz and Matalon [15]; Mandal [17]; Machrafi et al. [18]) is found responsible for the oscillation. Since, methanol evaporates faster, a liquid concentration gradient is setup along the surface. The surface tension of methanol (24 mN/m at 300 K) dominates in the region where the concentration of methanol is higher. Hence, the solutal Marangoni convection drives the liquid from lower surface tension region (i.e., methanol dominated region) to higher surface tension region (i.e., water dominated region, surface tension is 72 mN/m at 300 K). But, the thermal Marangoni convection drives the liquid in the opposite direction. The higher evaporation in the region where methanol concentration is higher lowers the regional temperature. The comparatively lower temperature will have higher surface tension. The thermal Marangoni convection drives the liquid from higher temperature region (lower surface tension) to the lower one (higher surface tension). Hence, the opposing effect develops and results in the oscillatory internal circulation.

In order to get the variation of the solutal Marangoni, thermal Marangoni, solutal Rayleigh, and thermal Rayleigh convection, with initial volume fraction of methanol, the numbers are obtained from the equations below [6,16,17].

$$Ma_S = \frac{R}{D_L}\sqrt{\frac{\sigma_C \dot{R}}{\mu}} \tag{1}$$

$$Ma_T = \frac{R}{\alpha}\sqrt{\frac{\sigma_T \dot{R} h_{fg}}{\mu C_P}} \tag{2}$$