Controlling breath figure patterns on PDMS by concentration variation of ethanol-methanol binary vapors

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Abstract. In this paper, the self-assembly of condensed droplets on smooth and constrained surfaces under saturated vapor atmosphere of ethanol and methanol binary system is reported. Hexagonally ordered array of pores are obtained on smooth surfaces with saturated vapors of binary liquids without the assistance of any additives. The results show that the addition of a small amount of ethanol to methanol plays a role very similar to that of surface active agents in inducing the formation of a regular droplet array. The effect of constraints on a self-assembled droplet pattern such as the movement of the contact line and the depinning of the contact line is also investigated. It is observed that the pore size, pore shape, pore depth and ring diameter are influenced by the atmosphere of binary vapors in addition to the commonly held attribution to the surface tension of the solvent. Contact angle studies of the patterned substrates show hydrophobicity with high adhesiveness and transitions between the Wenzel and Cassie impregnating state over the entire concentration region.

1 Introduction

The formation of a self-assembled droplet array on substrates (breath figure technique), an efficient bottom-up approach of templating, uses liquid droplets as sacrificial templates for the preparation of a micro-structured porous film [1–4]. This technique involves the self-assembly of condensing water droplets into hexagonal arrays on surfaces due to capillary and Marangoni forces. This process typically involves four steps as follows. Step 1) Casting of polymer solution on the substrate surface in the presence of humid air. Step 2) Condensation of water vapor into micro-droplets due to the evaporative cooling of the solvent. Step 3) Growth and self-assembly of droplets into an hexagonal array due to capillary and Marangoni forces. Step 4) Finally, complete evaporation of the solvent and water leads to an ordered array of pores [2,5–7]. The resultant droplet patterns on the polymer films are significantly affected by subtle changes in the casting conditions such as the polymer and its structure, solvent, air flow, humidity, surface temperature and substrate [5].

The influence of the polymer [8–11], solvent [9,12–16], temperature [9,17], substrates [9], and humidity [9,18,19] has been investigated in detail. However, very few reports investigated the influence of the vapor atmosphere on the self-assembly of droplets on surfaces. For instance, Ding et al. studied the influence of ethanol and methanol vapors on the formation of self-assembled droplet patterns on the polystyrene-block-poly-dimethyl siloxane (PS-b-PDMS) surface. They observed that the surface tension and the enthalpy of solvents in the atmosphere are responsible for the formation of porous films [5]. Xiong et al. reported the formation of microspheres on poly(styrene)-b-poly(butadiene) (PS-b-PB) co-polymers using solvent vapor atmosphere. They also stated that surface tension is a key parameter in the formation of patterns [20]. Bai et al. fabricated polymeric nano/microstructures on poly(9,9-dihexylfluorene) in mixed water and methanol vapor atmospheres [21]. Zhang et al. reported a modified process for preparing porous films in methanol vapor with conventional polymers, by adding a small amount of surface active agent into the casting solution, such as siloxane- and fluorine-containing block copolymers [22]. The previous studies are performed for either pure methanol or ethanol. It is observed from the above literature that the hexagonal array of pores with methanol vapors is obtained only with the addition of either high surface tension water
Fig. 1. Cartoon showing the effect of constraints with respect to the scale. (a) There is no influence of the constraint when the constraint is of the order of 50 μm. (b) Movement of the contact line as shown by the blue line when the constraint is of the order of capillary length or less.

in the environment or surface active agents to the casting solution.

Ethanol-methanol binary liquids are interesting because of their complex anomalous behavior that arises due to the molecular structuring of the moieties around each other in solution [23]. The interfacial structuring and hence the complex properties of the binary liquids are significant in affecting the formation of self-assembled droplets. In this paper, we present a strategy for obtaining ordered droplet arrays with a binary vapor of ethanol-methanol and a comprehensive description of the role of ethanol in stabilizing methanol droplets during the formation of self-assembled droplet arrays. The influence of constraints of the underlying substrate on the self-assembly process is also investigated.

The present work experimentally investigates the influence of saturated vapors of ethanol-methanol binary vapors (over entire concentration regions) on the self-assembled droplet patterns on PDMS surfaces over both smooth and constrained substrates. An attempt is also made to study the influence of constraints on the underlying surface and to explain the self-assembly of droplets in terms of the intermolecular interactions of the binary liquid vapors.

2 Experimental details

2.1 Materials

Polydimethyl siloxane (PDMS) of molecular weight 236.53 g/mol purchased from SIGMA Aldrich and chloroform (purity 99.9%) purchased from EMPLURA were used as polymer and solvent, respectively. Methanol and ethanol were purchased from Sigma Aldrich and Merck Emplura, respectively. The purities of methanol and ethanol were 99%. Commercially available SONY recordable DVDs were used as substrates. The DVD disc was cut into pieces of 1 cm × 1 cm. The two polymer layers were carefully peeled off. The polycarbonate support and the smooth polymer layer (the other one) were used as constrained and smooth surface, respectively. The width of the grooves is 0.74 μm and the geometry of the constrained surface is shown in fig. 2.

2.2 Preparation and characterization of binary liquids

Binary mixtures of ethanol and methanol were prepared by mixing the appropriate volume of each liquid in an air-tight stopper glass bottle. The accuracy of the binary system was ±0.1 mg and they were measured using a weighing balance. The surface tension of the binary systems for all the concentration range was measured using the Rame-Hart contact angle goniometer. The pendant drop method was used in calculating the polar and dispersive parts of the surface tension.

The infrared spectra of the binary system in the spectral range from 400 to 4000 cm⁻¹ were measured by the
FTIR Spectrometer of Perkin Elmer. The dielectric studies were carried out using the 40 GHz Vector Network Analyzer with the Dielectric Assessment Kit of Rhode and Scharwz. The refractive index measurements of the binary system were carried out using Abbe’s refractometer. Calibration was performed by measuring the refractive indices of doubly distilled water using Na light. All the experiments were done at room temperature.

2.3 Self-assembly of binary liquid droplets

In the current experiments, the mixture of ethanol and methanol at various volume ratios were chosen to produce vapor atmospheres. 3 ml of mixture of the binary liquid was added in a petri-dish and kept inside a sealed glass chamber to form a saturated vapor atmosphere. The smooth and the constrained surfaces were positioned at least 1 cm above the liquid. About 300μl of PDMS-chloroform solution was casted on the surface of the substrates using a micro-syringe under the binary liquid saturated vapor atmosphere at 26°C. After the complete evaporation of the solvent, a thin layer of polymer was left on the substrate surface. The actual experimental setup and its schematic diagram were shown in fig. 3.

To check the dissolutivity of chloroform with DVD, two experiments were performed. The substrates were treated with ethanol and checked for precipitates. It was found that within the given time of 1 minute, there was no formation of precipitate. To further confirm the dissolutivity, the DVD discs were treated with chloroform and the treated discs were used for patterning under saturated vapors of water. It was observed that the patterns formed on the chloroform treated smooth and constrained surfaces was similar to untreated patterned surfaces. Therefore it has been confirmed that within the time span of the experiment, chloroform does not dissolve the upper layer of DVD discs. The relevant images were given in the Supplementary material (see supplementary figs. 1 and 2).

2.4 Characterization of patterned surfaces

The patterns formed on the substrate surface were characterized using the Leica Confocal Laser Scanning Microscope TCS SP8 model. The transmission mode with the excitation wavelength of 561 nm was used to capture the images of the formed patterns. The Rame Hart contact angle goniometer equipped with a charge coupled device camera along with an advanced drop image program was used to measure the contact angle of water with the surfaces. 3μl drop of distilled water was placed on the substrates through a microsyringe which was placed onto the stage. The measurement was recorded after the drop reaches equilibrium. The substrate was moved to allow another drop to be placed on the substrate. At least 10 measurements were taken and all results were reproducible up to ±2°.

3 Results and discussion

Precise experimental conditions are required for the self-assembly of droplet patterns since evaporation and film formation occur in few seconds. To avoid the possibility of uncertainties with the dynamic method of self-assembly of droplets, the static method explained in the experimental section was employed to fabricate the structures on smooth and constrained substrates. This method is quite robust under the saturated vapor of water. Few works have systematically examined the self-assembly of droplet patterns on smooth surfaces in the ethanol and methanol environment [5]. In the present case the binary system of ethanol and methanol was employed as vapor atmosphere during the process of the self-assembly of droplets.

Most alcohols interact via strong repulsive forces and weak attractive forces. An important part of the interaction are the strong, directional hydrogen bonds they form which determine its structure. To understand the intermolecular interactions between methanol and ethanol, the properties like surface tension, refractive index and static dielectric permittivity of the binary system over the entire concentration range were studied and tabulated in table 1 and the density, polar and dispersive parts of the surface tension were given in fig. 4. From our recent work on the methanol-ethanol binary system, it was observed that all the properties show a deviation from the ideal behavior at 10% to 30% of methanol. The deviation in the properties of the binary system has been attributed to the increase of hydrogen bond strength with the increase in methanol concentration. At higher concentration of ethanol, the London dispersion forces dominate over the hydrogen bonds [23]. With these deviations, it is also expected a change in the self-assembly pattern of droplets over the substrates.

As an attempt at explaining the self-assembly of liquid droplets in terms of intermolecular interactions and the effect of constraints on the pattern formation, a drop of PDMS-chloroform solution was casted over smooth and constrained substrates in the vapor environment of the ethanol-methanol binary system. The solvent was allowed to evaporate. When the solvent evaporated completely, a porous film was left on the substrate. The experiment was repeated over the entire concentration range of methanol in ethanol in steps of 10% of volume.
Table 1. Variation of properties of the ethanol-methanol binary system with the concentration of methanol.

| Percentage of methanol | Surface tension (mJ/m²) (±0.02) | Refractive index (±0.001) | Dielectric permittivity (±2%) | Dielectric loss (±2%) |
|------------------------|----------------------------------|--------------------------|-------------------------------|-----------------------|
| 0                      | 22.00                            | 1.360                    | 24.80                         | 8.52                  |
| 10                     | 22.98                            | 1.363                    | 24.75                         | 10.00                 |
| 12                     | 22.14                            | 1.362                    | 24.65                         | 6.41                  |
| 14                     | 19.30                            | 1.362                    | 24.90                         | 8.16                  |
| 16                     | 19.46                            | 1.360                    | 25.33                         | 9.08                  |
| 18                     | 20.70                            | 1.358                    | 25.71                         | 9.98                  |
| 19                     | 19.88                            | 1.358                    | 25.58                         | 3.35                  |
| 20                     | 20.70                            | 1.357                    | 25.67                         | 4.07                  |
| 21                     | 19.01                            | 1.355                    | 26.72                         | 4.50                  |
| 22                     | 20.07                            | 1.355                    | 26.52                         | 11.33                 |
| 24                     | 19.76                            | 1.355                    | 26.85                         | 11.46                 |
| 26                     | 19.28                            | 1.353                    | 27.01                         | 11.20                 |
| 28                     | 19.94                            | 1.352                    | 27.18                         | 11.79                 |
| 30                     | 21.56                            | 1.352                    | 24.66                         | 9.26                  |
| 40                     | 21.47                            | 1.347                    | 24.79                         | 9.00                  |
| 50                     | 21.53                            | 1.342                    | 27.58                         | 8.15                  |
| 60                     | 21.45                            | 1.337                    | 29.20                         | 7.56                  |
| 70                     | 21.68                            | 1.333                    | 28.31                         | 8.06                  |
| 80                     | 21.53                            | 1.331                    | 29.82                         | 7.33                  |
| 90                     | 21.48                            | 1.324                    | 29.09                         | 7.67                  |
| 100                    | 22.10                            | 1.327                    | 34.38                         | 8.88                  |

Fig. 4. Top: variation of (left) density (ρ), (right) surface tension (γ); bottom: (left) dispersive part of surface tension (γd) and (right) polar part of surface tension (γp) with respect to concentration of methanol in the ethanol-methanol binary system.

The Confocal Laser Scanning Microscope (CLSM) images of the thus patterned smooth and constrained surfaces for pure liquids are shown in figs. 5 and 14, respectively. The CLSM images for various concentration of methanol in the ethanol-methanol binary system are shown in figs. 6, 12, 15 and 16 and the 3D CLSM images are also shown in figs. 7, 13, 18, 19 and 17. The shape, size and overall pattern of the pores prepared under various concentration ranges of ethanol and methanol were investigated. It is observed that there are variations in the size and shape of the pores on PDMS film patterned under various volume fractions of binary vapors of methanol and ethanol. The thickness of the PDMS film was measured to be 30 μm (see supplementary material, figs. 3 and 4).
3.1 Pattern formation on smooth surfaces

The images of a smooth surface patterned under pure and binary mixtures of ethanol and methanol are shown in fig. 5 and fig. 6, respectively. The size of the pores on the PDMS film prepared under ethanol-methanol binary vapors vary according to the concentration of methanol. The shape of the pore openings also vary from polygon to circular. Pores with irregular openings are formed on the polymer film patterned under various concentrations of methanol. 3D CLSM images are shown in fig. 7.

Figure 5(a) shows the pore formation on the smooth surface patterned under vapors of pure ethanol. It indicates that the ethanol vapors favor the hexagonal pore formation on PDMS films. The film is densely covered with pores that are nearly 3.25 μm in size. The pores are separated from each other by a distance of nearly 1 μm. With the introduction of 10% of methanol, the patterns on the film slightly deviates from their close arrangement of pores. Figure 6(a) indicates that, the introduction of 10% of methanol decreased the pore size and nearest-neighbor pore distance to 1.65 μm and 800 nm, respectively. Therefore, it is inferred from the observations that the pore diameter can be controlled by the percentage of methanol in the binary system forming the saturated vapor atmosphere.

A further increase in the concentration of methanol results in increased pore size and pore density as shown in fig. 6(c) and (d). It is also observed from the figure that at 30% of methanol, the pores are self-assembled into nearly hexagonal arrays. At higher concentration of methanol, the film is observed to have highly ordered hexagonal structures. A gradual change in the polymeric pore morphology is observed when the saturated vapor atmosphere is composed of pure methanol as shown in fig. 5(b). This result indicates that the intermolecular interaction between ethanol and methanol molecules increases with the increase in methanol concentration and is explained in detail as follows.

The evaporation rate of a droplet depends on its molecular weight and hence, to the first approximation, to its density. Lower molecular weight liquids evaporate faster. The density of alcohols and water is dependent on the extent of hydrogen bonding in the system. An increase in density is usually accompanied by an increase in the surface tension [35]. We have shown previously that the extent of hydrogen bonding in methanol-ethanol system is non-uniform with reference to concentration [23]. The variations of density and surface tension of the methanol-ethanol system over the entire concentration region are shown in fig. 4. Macleod showed that the addition of methanol to ethanol increases the evaporation rate of the binary liquid, in agreement with the above idea [35].

The diameter of the pores formed in breath figures depend on the surface tension of the solvent as well as that of the binary liquid. It is seen from fig. 8 that the pore size of the breath figures follows the same generic trend as the variation in the density/surface tension of the binary liquid. However, there is no perfect correlation between the two since other factors come into play when the breath figures are formed, namely the interaction of the binary liquid with the solvent, the dynamics of evaporation of the combined system along with the changes in the setting rates for PDMS in the presence of the solvent-binary liquid. Further the experimental results are compared with the computational results [23].
Fig. 8. Variation of the pore diameter for smooth and constrained surfaces patterned with various concentration of methanol in ethanol. Top: entire concentration region; bottom: concentration region from 10% to 30% of methanol.

Fig. 9. Variation of the pore depth for smooth and constrained surfaces patterned with various concentration of methanol in ethanol. Uncertainty is found to be less than the symbol size. Top: entire concentration region; bottom: concentration region from 10% to 30% of methanol.

Fig. 10. Variation of the depth-diameter aspect ratio for smooth (top) and constrained (bottom) surfaces patterned with various concentration of methanol in ethanol.

The current results indicate that the extent of hydrogen bonding in the system contributes significantly to the variation of the pore size with concentration. This is also seen from the fact that the addition of hydrophilic Rhodamine B dye to the solvent changes the breath figure pattern on the smooth surface from a perfect hexagon to a distorted hexagon (see supplementary material, fig. 4).

The pore aspect ratio ($P_{D/d}$) is defined as the ratio between the depth of the pores ($D$) and diameter ($d$) of the pores, i.e.,

$$P_{D/d} = D/d.$$  \hspace{1cm} (1)

Figures 9 and 10 give the variation of the pore depth of the breath figures formed and the aspect ratio of the pores, respectively. From fig. 10 it is observed that the maximum depth-diameter aspect ratio obtained with smooth and constrained patterned surfaces is 7.1 and 7.3, respectively.

For the smooth surface, this maximum value is achieved under 60% of methanol and for the constrained surface it is achieved under 12% of methanol. The pore aspect ratio is observed to be strongly influenced by the intermolecular interactions of binary vapors. These can be understood from the contribution of the polar and dispersive parts of the surface tension of the binary liquid and their interactions with the substrate. If a liquid has a higher polar component of surface tension, the contact angle increases implying a lesser spreading of the drop and hence a comparatively slower evaporation rate. On the other hand, higher dispersive forces imply a larger spreading and hence quicker evaporation rates.

In the present case, at the lower concentration of methanol, polar forces dominate while at higher concentration of methanol, especially at about 80%, dispersive forces dominate [23]. It is further noticed that the polar/dispersive components, like the total surface tension, do not have a direct correlation with concentration; all three components are specific to the concentration. Current data regarding pore diameter, pore depth and aspect ratio of pores with respect to concentration can be understood from Young’s equation:

$$\cos \theta_Y = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV},$$  \hspace{1cm} (2)

where $\gamma_{ab}$ are the interfacial tensions associated to each interface (SV, LV and SL) and $\theta_Y$ is Young’s contact angle [36]. A decrease in the surface tension $\gamma_{LV}$ implies a spreading of the drop, and hence it tends to increase the pore diameter. The pore diameter shows a trend similar to that of the surface tension. On the other hand, the spreading of the drop also implies as lesser time/solvent for the drop to penetrate into PDMS leading to smaller pore depths. The pore volume and pore volume per unit area are also calculated and shown in fig. 11. The similar variation as seen in other parameters is also reflected in pore volume and pore volume per unit area.
Fig. 11. Variation of pore volume and pore volume per unit area for constrained (top) and smooth (bottom) surfaces patterned with various concentration of methanol in ethanol.

Fig. 12. CLSM images of PDMS films over a smooth substrate prepared in various concentrations of binary vapors of ethanol-methanol. (a) 19% of methanol \((x = 0–60 \mu m, y = 0–60 \mu m, z = 0–6 \mu m)\) (b) 21% of methanol \((x = 0–45 \mu m, y = 0–45 \mu m, z = 0–6 \mu m)\) (c) 21% of methanol \((x = 0–120 \mu m, y = 0–120 \mu m, z = 0–6 \mu m)\) (d) 26% of methanol \((x = 0–60 \mu m, y = 0–60 \mu m, z = 0–6 \mu m)\).

Fig. 13. 3D CLSM images of PDMS films over a smooth substrate prepared in various concentrations of binary vapors of ethanol-methanol. (a) 12% of methanol \((x = 0–60 \mu m, y = 0–60 \mu m, z = 0–6 \mu m)\) (b) 19% of methanol \((x = 0–45 \mu m, y = 0–45 \mu m, z = 0–6 \mu m)\) (c) 21% of methanol \((x = 0–120 \mu m, y = 0–120 \mu m, z = 0–6 \mu m)\) (d) 26% of methanol \((x = 0–60 \mu m, y = 0–60 \mu m, z = 0–6 \mu m)\).

Fig. 14. CLSM images of PDMS films prepared on a constrained substrate under (a) pure ethanol and (b) pure methanol. (Scale bar: 100 \(\mu m\).)

To gain a better understanding of the role of surface tension in the patterns detailed studies were performed for the lower concentration of methanol in the ethanol-methanol binary system, where complexity in their properties has been reported [23]. Figure 12 shows the polymer films over a smooth substrate patterned under saturated vapors of 10% to 30% of methanol (in the ethanol-methanol binary system) and fig. 13 shows the 3D CLSM images of the same. It is observed that the pore parameters show a complex variation with varying the concentration of methanol. The maximum pore size and pore depth is observed for the films patterned under saturated vapor of 22% of methanol. The pores are found to be highly deformed from circularity and at 19%, 21% and 28% of methanol, the circularity of the pores increases. This further proves that the concentration of methanol in the ethanol-methanol binary system plays a major role in tuning the shape, size and distribution of the pores.

From the above analysis, it is observed that on smooth surfaces, pure ethanol forms an hexagonal array of pores, while disordered patterns are observed with pure methanol. With the addition of a small amount of ethanol to methanol, the droplets self-assemble into an hexagonal array. Thus the addition of a small amount of ethanol to methanol plays a role very similar to that of surface active agents in inducing the formation of a regular droplet array. A similar analysis is performed with the constrained surfaces to investigate the role of ethanol-methanol vapors. Interesting results are observed as follows.

3.2 Pattern formation on constrained surfaces

Figure 14(a) shows the self-assembled droplet pattern formed on the constrained surface under saturated vapor of pure ethanol. It is observed that the film is covered...
with distorted unclosed rings of pores. The ring size and pore size are approximately 36.4 μm and 3.8 μm, respectively. Pores of size 0.5 μm are found inside the distorted rings (size of the pores versus concentration of methanol is shown in fig. 8). On the addition of methanol, the pores self-assembles into patches of hexagons. Further addition of methanol favors the formation of hexagonal rings. The ring shape attains its hexagonal alignment at higher concentrations of methanol (fig. 15). The pore density inside the ring increases with the increase in methanol concentration. On examining the films patterned under 16%, 21% and 26% of methanol, ordered hexagonal ring of pores are observed (figs. 16 and 17). 3D CLSM images for various concentrations of methanol are shown in figs. 17 and 18.

With pure methanol as saturated vapor, the rings are found to be highly ordered (3D image of pure methanol on a constrained surface is shown in fig. 19) and densely populated with pores of size 1 μm (fig. 14(b)) whereas ethanol results in a distorted pore array. These results are completely opposite to what is observed in a smooth surface. The pore diameters and depth in the case of drops on the depinned contact line over grooved substrates are considerably larger than those over a smooth surface. The depinning leads to the coalescence of drops over the de-pinned line leading to larger drops. The pore diameter of drops
formed in regions enclosed by the depinned contact line are seen to be smaller than that over a smooth substrate. Accurate measurements of these could not be made since they are in the limit of resolution of the instrument used. The smaller diameter inner drops are those formed due to re-nucleation in this region, but whose formation is stalled by the completion of breath figure formation due to factors such as the complete evaporation of the solvent etc.

On a constrained surface, despite the role of surface tension of the ethanol-methanol binary system, the effect of constraints on the underlying surface dominates in the formation of pore patterns. It is evident from these results that not only Young’s unbalanced force but also the force due to constraints has its role in determining the alignment of pores. Figure 17 shows the 3D CLSM images of patterns on constrained surfaces. Thus, it is observed that the pore diameter depends on the concentration of methanol in the ethanol-methanol binary liquid and pore patterns are influenced by the pinning/depinning of contact lines in addition to the commonly attribution of the properties of the solvent.

3.3 Formation mechanism of self-assembled droplet patterns under saturated binary vapors

To explain the differences in the pattern formation prepared under the saturated vapor atmosphere of the ethanol-methanol binary system, the physical properties of liquids forming the saturated vapor atmosphere, solvent and polymer are taken into account. The droplet placed on a surface spreads to a certain extent until the equilibrium is reached. At equilibrium, the total free energy is minimized and the droplet shape stops varying. It is well known that the droplet shape is determined by the interfacial tension between the polymer and the droplet and the intermolecular interactions within the droplet [37]. And the spreading co-efficient in terms of these two factors is given by

$$S = \gamma_p - (\gamma_d + \gamma_{pd}), \quad (3)$$

where $\gamma_p$, $\gamma_d$ and $\gamma_{pd}$ are the surface tension of the polymer solution, surface tension of the droplet, and interfacial tension of the polymer solution and droplet, respectively.

The spreading co-efficient is used to characterize the spreading of droplets and it defines different regimes of wetting. $S > 0$ indicates complete wetting and $S < 0$ indicates partial wetting. The interfacial tension of the polymer solution is measured using the pendant drop method and is measured to be 17.11 mJ/m$^2$ and the surface tension of the binary liquid of various concentrations of methanol is shown in table 1.

The spreading parameter for the droplets of the binary liquid for all concentrations is positive, implying that the droplet impinging on the polymer surface will spread. The formation of an intervening polymer layer due to the condensation of the saturated vapor prevents the coalescence of the thus-formed droplets. As the droplets grow, they are attracted to each other through the capillary forces and after complete evaporation of the solvent, the self-assembled droplet arrays are formed. The surface tension of the vapor droplets determines the shape of the pores. It is known that a larger surface tension leads to spherical pores. The decrease in the surface tension leads to the deformation of the spherical shape. Ethanol and methanol with surface tension values of 22 mJ/m$^2$ and 22.1 mJ/m$^2$, respectively form deformed spherical pores as shown in fig. 5. This is true of the pores formed by the binary liquid droplets of ethanol and methanol whose surface tension values varying between 22.98 mJ/m$^2$ and 19.00 mJ/m$^2$ yield deformed pores. In addition to these factors roughness plays an important role in the formation mechanism of self-assembled droplet patterns on constrained surfaces and is explained in the following section in detail.

3.4 Effect of roughness on self-assembly process

In order to further probe the differences in the pore morphology of constrained surfaces, the effect of the depinning/pinning of the contact line is investigated in detail. A bare/smooth surface uniformly coated with the polymer layer has no effect on the movement of the contact line of condensed droplets. Whereas the spreading of the liquid on surfaces is strongly influenced by chemical heterogeneities and roughness of the surface [38,39]. The contact angle of a drop on a heterogeneous surface is determined solely by the interactions occurring at the three-phase contact line. The wetting of heterogeneous surfaces is controlled by the three-phase structure at the contact line and not by the interfacial contact area [40].

The interaction between the fluid interface and the heterogeneities results in the movement of contact lines. This dynamics of the contact line is determined by the upper length scale of the droplets and the lower length scale set by the characteristic size of the constraints/grooves [41, 42]. For a surface with infinitely long grooves close to each other like that of the number of lines normal to the axis in a capillary, the contact line can lie either parallel to the grooves or at an angle $\phi$ to the grooves. The contact line gets pinned when it is parallel to the grooves and it moves continuously without any pinning when it lies at an angle $\phi$ [38].

![3D CLSM image of PDMS films prepared in pure methanol vapor on a constrained surface (x = 0–400 μm, y = 0–400 μm, z = 0–16 μm).](image-url)
When the contact line moves over the surface there are often points that remain pinned, inducing the contact line to suddenly jump to a new position [43, 44]. The velocity of the contact line based on calculating the energy dissipation per length of the unit line is given by Brochart-Wyatt and de Gennes as [45, 46]

\[ V = \frac{\theta \sigma}{6 \eta \ln(L/a)} (\cos \theta_0 - \cos \theta), \]

where \( \theta \) is the dynamic contact angle, \( \sigma \) is the liquid-vapor surface tension, \( \theta_0 \) is the equilibrium contact angle, \( L/a \) is the ratio of macroscopic to microscopic length scales and \( \eta \) is the dynamic viscosity. From the above equation it is clear that the contact line velocity is determined by the dynamic viscosity and surface tension of the liquid. The contact line velocity is high for liquids of high surface tension. So it is expected a difference in the pattern formation on the constrained surface with condensing droplets of various surface tension.

The dynamic viscosity of ethanol and methanol is \( 0.001095 \text{Ns/m}^2 \) and \( 0.00056 \text{Ns/m}^2 \), respectively. With low dynamic viscosity, methanol droplets show a high contact line velocity. This results in the formation of more aligned hexagonal rings compared with ethanol of comparatively low dynamic viscosity. (Supporting 3D image of pure methanol on a constrained surface is shown in fig. 19.) Thus, highly ordered hexagonal ring patterns are obtained with saturated vapors of higher concentration of methanol as shown in fig. 20. It should also be noted that when the horizontal component of the force caused by the Marangoni stress overcomes Young’s force, the Marangoni effect also has its influence on the depinning of the contact line.

3.5 Contact angle studies

Contact angles of 3 \( \mu \)l of distilled water over the various surfaces were measured using a goniometer and are given in table 2 and table 3. In tables 2 and 3, \( \theta \) and \( \theta^* \) correspond to the Young contact angle and the apparent contact angle over a rough surface which are attributed in the present case to contact angles over unpatterned PDMS coated surfaces and patterned surfaces, respectively. The values given are averaged over ten readings.

It is found from tables 2 and 3 that

\[ \theta_{UPS}, \theta_{UPC} < \theta_{PS}, \theta_{PC}, \]

e.g., water has a higher contact angle over patterned surfaces compared to smooth surfaces. If the roughness factor

\[ r = \cos \theta^* / \cos \theta > 1, \]

the Wenzel state of wetting is preferred [47, 48]. The three possible states of wetting are shown in fig. 21. Of these three states, the Cassie state has the highest energy barrier and the Cassie impregnating state the lowest [48]. In the present studies, water over all patterned surfaces was seen to be in a sticky Wenzel state, as seen from fig. 22. The drop inverted from the patterned surface was seen to remain without falling for over 30 minutes, thus proving the absence of Cassie states. However, it is not possible to differentiate between the two lower energy states, namely Wenzel and Cassie impregnating states.
Table 2. Contact angle studies of unpatterned substrates. BS/BC: Bare surface Smooth/Constrained. UPS: UnPatterned Smooth surface. UPC: UnPatterned Constrained surface.

| Surfaces                  | Contact angle – smooth (°) (±1°) | Contact angle – constrained (°) (±1°) |
|---------------------------|----------------------------------|--------------------------------------|
| Bare DVD surface          | 86.0 (θ_{BS})                    | 74.0 (θ_{BC})                        |
| Surface coated with PDMS  | 101.0 (θ_{UPS})                  | 103.0 (θ_{UPC})                      |

Table 3. Contact angle studies of substrates patterned under various concentration of methanol in the ethanol-methanol binary system.

| Surfaces patterned with various concentration of methanol | Contact angle θ_{PS}-smooth (°) ±1° | Contact angle θ_{PC}-constrained (°) ±1° | $R_{\text{Smooth}} = \frac{\cos \theta_{PS}}{\cos \theta_{PS} - \cos \theta_{PC}}$ | $R_{\text{Constrained}} = \frac{\cos \theta_{PC}}{\cos \theta_{PS} - \cos \theta_{PC}}$ |
|--------------------------------------------------------|-------------------------------------|----------------------------------------|-----------------------------------|-----------------------------------|
| 0                                                      | 116.0                               | 107.6                                  | 2.3                               | 1.3                               |
| 10                                                     | 126.0                               | 96.9                                   | 3.1                               | 0.5                               |
| 12                                                     | 113.8                               | 108.9                                  | 2.1                               | 1.4                               |
| 14                                                     | 108.4                               | 106.9                                  | 1.6                               | 1.2                               |
| 16                                                     | 119.2                               | 101.8                                  | 2.5                               | 0.9                               |
| 18                                                     | 121.8                               | 101.7                                  | 2.7                               | 0.9                               |
| 19                                                     | 115.4                               | 110.7                                  | 2.2                               | 1.5                               |
| 20                                                     | 127.0                               | 101.2                                  | 3.1                               | 0.8                               |
| 21                                                     | 102.8                               | 115.8                                  | 1.1                               | 1.9                               |
| 22                                                     | 110.2                               | 106.8                                  | 1.8                               | 1.2                               |
| 24                                                     | 108.5                               | 100.2                                  | 1.6                               | 0.7                               |
| 26                                                     | 118.1                               | 105.3                                  | 2.4                               | 1.1                               |
| 28                                                     | 107.6                               | 102.0                                  | 1.5                               | 0.9                               |
| 30                                                     | 118.5                               | 104.6                                  | 2.5                               | 1.1                               |
| 40                                                     | 117.5                               | 110.7                                  | 2.4                               | 1.5                               |
| 50                                                     | 124.5                               | 105.8                                  | 2.9                               | 1.2                               |
| 60                                                     | 119.7                               | 105.0                                  | 2.6                               | 1.1                               |
| 70                                                     | 108.0                               | 111.0                                  | 1.6                               | 1.5                               |
| 80                                                     | 120.5                               | 106.0                                  | 2.6                               | 1.2                               |
| 90                                                     | 110.8                               | 119.3                                  | 1.8                               | 2.1                               |
| 100                                                    | 120.2                               | 117.9                                  | 2.6                               | 2.0                               |

![Figure 22](image1.png)  
**Fig. 22.** The droplet adheres to the surface when the smooth (a) and the constrained (b) patterned surface with the droplet is turned upside down.

Figure 23 shows the variation of the energy barrier with respect to concentration from which it is seen that the system oscillates between two states: Wenzel and Cassie impregnating. The overall variation in the contact angle is similar to the variation in pore parameters.

![Figure 23](image2.png)  
**Fig. 23.** Variation of the energy barrier for smooth and constrained surfaces patterned with various concentrations of methanol in ethanol.
4 Conclusion

In conclusion, six main results are observed from this study. 1) It has been demonstrated that it is possible to form an ordered array of self-assembled droplets of methanol by the addition of a small amount of ethanol without the use of any surfactants/water. This is attributed to the hydrogen bond between the ethanol and methanol and the ability of ethanol to bind strongly to water since it is more hydrophilic than methanol. 2) The difference in pattern formation over smooth and constrained substrates indicates a strong influence of the depinning of the three-phase contact line formed between substrate, binary liquid vapor and PDMS solution. 3) The pore diameter is observed to be a function of the surface tension of the ethanol-methanol binary concentration. 4) The pore area ratio is influenced by intermolecular interactions of binary vapors. 5) The complex variation in the shape, size and distribution of the pores is observed in the same concentration range where the complex anomalous variation in the properties of the ethanol-methanol binary system is reported earlier. 6) The contact angle studies indicate that the hydrophobicity/hydrophilicity can be achieved by the proper choice of the concentration of methanol. In the present study the pore parameters are understood in terms of surface tension, density and other properties of the binary liquid. Since some of the comparisons are between computational results and experimental data [23] and also the fact that experiments have additional weak/hydrogen bonds between solvent, vapor and polymer, a perfect correlation between the results was not achieved. This work can find its applications in self-cleaning surfaces, microfluidic devices, and water-repellant surfaces.

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Author contribution statement

All the authors were involved in the preparation of the manuscript. All the authors have read and approved the final manuscript.

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