Novel type of pattern formation in droplet systems

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Introduction

In nature we can observe pattern formation on various spatial and temporal scales; various patterns like spots, stripes, waves, spirals or dendrites could appear in both the inanimate word and in biological systems. The spontaneous formation of spatial or spatio-temporal patterns under homogeneous external conditions is a characteristic feature of systems far from equilibrium. The most familiar patterns are Rayleigh-Bénard convection[1], Taylor vortexes[2], snowflakes or ice crystal growth[3], fingering in the Hele-Shaw cell[4, 5], Turing patterns[6], Belousov-Zhabotinsky reaction-diffusion system[7] or pattern formation in a layer of starving *Dictyostelium* cells[8, 9, 10]. Although we exemplified only a few examples of pattern formation, it is obvious that there are plenty of systems where the evolution of patterns in time has been intensively studied both experimentally and theoretically. The present work focuses on a novel type of pattern formation that, to the best of our knowledge, had not been described before.

In our previous work, we have studied the behaviour of microliter-sized decanol droplets floating in a thin layer of sodium decanoate solution[11]. We have found that the droplet is able to perform an oriented movement in an externally imposed salt concentration gradient. This phenomenon mimics the chemotaxis of living cells or organisms, which also move directionally in chemical gradients[12]. This observed process is complete within a few minutes. However, in the same system without a macroscopic salt concentration gradient, we can observe that the decanol droplets undergo intriguing shape changes over much longer time scales. Recently we started to focus on the study of pattern formation of decanol droplets in the presence of sodium chloride and sodium decanoate solution that is slowly evaporating in air under laboratory conditions over a time scale in the order of hours[13]. Present paper describes the macroscopic and microscopic patterns observed in the system consisting of decanol droplets in the presence of decanoate solution. Further the effect of salts will be shown.

Experimental

Experiments were performed as follows: 500 µl of aqueous 10mM decanoate solution was spread over a round cover glass with a diameter of 24 mm. A decanol droplet containing oil red O as a colorant was placed by a micropipette on the decanoate layer and then the 6.5M salt solution was added to the decanoate solution (Figure 1). The experiment was performed under laboratory conditions at temperature around 23 °C and the evaporation of water from the decanoate solution occurred due to natural convection. The pattern formation of decanol droplets could be clearly seen with the naked eye, however the experiments were monitored using an ImagingSource video-camera (DFK 23U274) from the top view and processed later by 4.3 version of NIS-Element software (Laboratory Imaging s r.o., Czech Republic). For microscopic observation, the polarized microscope Brunel NP-107A was used.

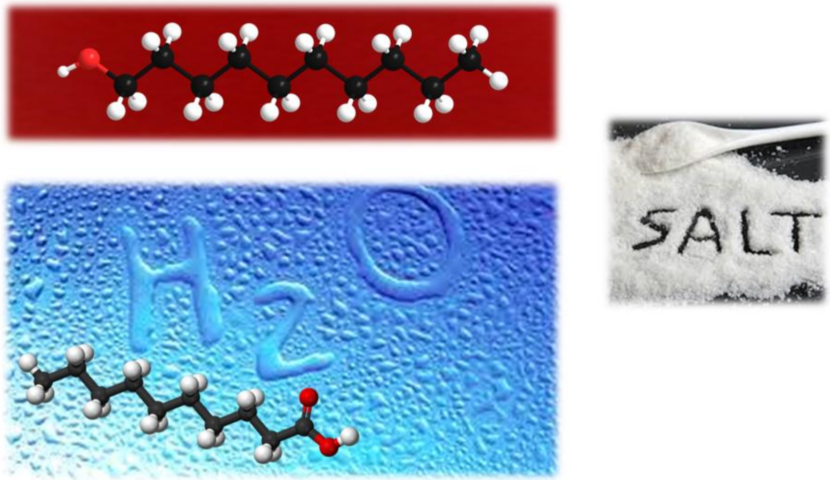

Figure 1: *Substances used for our experiments. 1-decanol (colored by Oil Red O), aqueous solution of sodium decanoate (pH 12-13) and salt.*

Results and discussion

We have observed interesting pattern formation in the system consisting of decanol droplet placed in an aqueous solution of sodium decanoate (Figure 2). Such finger-like branching patterns share some properties with well-known Hele-Shaw patterns[14]. However, in Hele-Shaw experiments the fingering occurs when a less viscous fluid displaces a more viscous one confined between two parallel plates. In our case we place a decanol droplet (more viscous) into thin layer of 10mM decanoate solution (less viscous), which is opposite to the typical Hele-Shaw experiment. This observation leads us to the hypothesis that during the evaporation of water from the decanoate solution the concentration of decanoate is increasing, reaching and later overreaching critical micelle concentration (CMC) and thus the viscosity is increasing. Originally less viscous decanoate solution is getting to be more viscous than decanol and the typical Hele-Shaw fingering can begin. However, this is just our hypothesis in this moment and to prove it more experiments and measurements are needed. Anyway, to the best of our knowledge, such an evaporation-controlled Hele-Shaw experiment has not been described yet.

Figure 2: *Example of pattern formation of decanol droplet in the absence of salt. In time t=0, decanol droplet (20 µl, coloured in red) is placed in the solution of sodium decanoate (500 µl, 10mM, pH 12.4). No salt present. As water evaporates the decanol droplet starts to form dendrites. Diameter of the glass slide substrate 2.4 cm. Scale bar corresponds to 1 cm.*

Different and also very intriguing pattern formation is observed, if the salt is added into the decanoate solution. Figure 3 shows which patterns we can observe when a 2.5 μl decanol droplet is placed in 500 μl of 10mM decanoate solution after the addition of 10 μl of 6.5M salt solution. At the beginning of the experiment, the decanol droplet has a round shape, and at around 30 minutes from the beginning of the experiment, the first small protrusions on the droplet surface are observable. A few minutes later, several protrusions dominate over the others and start to prolong and grow. The droplet adopts a star-like shape with further elongation at the leading edges to form prominent tentacular structures. The tentacles are long and rarely branched.

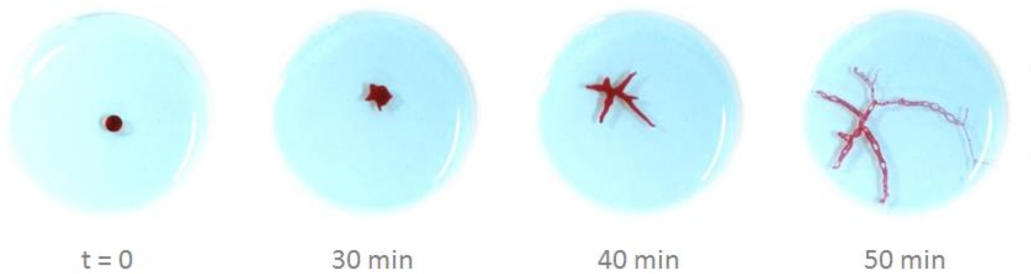

Figure 3: *Example of pattern formation of decanol droplet in the presence of salt. In time t=0, decanol droplet (2.5 μl, coloured in red) is placed in the solution of sodium decanoate (500 μl, 10mM, pH 12.4) containing salt (NaCl, 10 μl of 6.5M solution). As water evaporates the decanol droplet starts to form tentacular structures. Diameter of the glass slide substrate 2.4 cm. Scale bar corresponds to 1 cm.*

Supplementary movie (https://youtu.be/hAXmJ8k97P0) shows the comparison of decanol droplets behaviour in the absence and presence of sodium chloride. Various sized decanol droplets (namely 0.6 μl; 1.3 μl; 2.5 μl; 5 μl; 10 μl and 20 μl) in 500 μl of sodium decanoate were observed 6.5 hours until the evaporation of water from decanoate solution was completed. From this experiment it is evident, that in the absence of salt the decanol droplets remain their spherical shape much longer in comparison with droplets affected by salt ions. We can observe in all six sizes that droplets are without shape changes two hours after beginning of experiment. Smaller droplets divide into several pieces and bigger droplets form usually three tentacles. In all cases the Hele-Shaw-like fingering is observable.

In the case with salt, the droplet with volume 0.6 μl starts to form tentacular structure about ten minutes from the beginning of experiment. With the increasing size of decanol droplet the time of the start of droplet shape changes increases. However, the droplet with volume 20 μl does not show the growth of tentacles. It has been shown, that the composition of the system, namely molar ratio decanol/decanoate/salt is the main factor affecting the pattern formation of decanol droplets.[13]

Conclusion

Present paper describes the novel kind of pattern formation in droplet system. Recently, we have found that decanol droplets are able to form complex morphological patterns when they are placed on a thin layer of decanoate solution at far-from-equilibrium initial conditions. Intriguing patterns are observable depending on the initial composition of the system, namely the molar ratios of decanol and decanoate and salt. Nevertheless, no conclusions regarding the mechanism of patterning were found yet. It seems that this phenomenon is a novel kind of pattern formation that needs to be studied more in detail in both experimental and theoretical approach.

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