Gallery of Fluid Motion

Mysterious case of an evaporating binary drop

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When a sessile drop of water/1,2-hexanediol evaporates on a glass substrate, remarkable segregation dynamics occur (see Fig. 1), first observed by Li *et al.* [1]. Water is volatile and has a high surface tension, whereas 1,2-hexanediol is nonvolatile and has a low surface tension. This is very similar to water/glycerol, since glycerol is also nonvolatile and has a lower surface tension than water. Therefore, one might expect the evaporation dynamics to be similar. However, in contrast to an evaporating water/glycerol drop [2], which remains axisymmetric throughout the evaporation process, for water/1,2-hexanediol we observe that hexanediol-rich spots form at the rim, breaking axisymmetry.

Experimentally, we observe hexanediol-rich spots by adding a small amount of fluorescent dye to the drop and imaging it with a confocal microscope (Nikon A1). Dextran is a hydrophilic fluorescent dye, and therefore we expect that it will migrate to and accumulate in the water-rich regions in the drop. Nile red is a hydrophobic fluorescent dye that we expect to favor 1,2-hexanediol-rich parts of the drop. Additionally, the confocal microscope also provides a bright-field image of the drop, where strong compositional gradients are visible due to the difference in the refractive index of water ($n_w = 1.3326$) and 1,2-hexanediol ($n_{hd} = 1.441$) [3]. The two fluorescent and bright-field channels were recorded simultaneously by the confocal microscope, and they are shown in separate rows in Fig. 1. The following settings were used: Galvano scanner with laser illumination at wavelengths 561 and 488 nm using a 10 × magnification objective with a resolving power of 1.03 μm. The resulting images had a resolution of 2.50 μm/px and were taken at 3.9 s intervals.

Initially, the evaporation is axisymmetric. Then near the contact line, the hexanediol-rich spots appear and coalesce into larger spots until they engulf the whole drop. The behavior is reminiscent of phase separation, however water and 1,2-hexanediol are miscible in any ratio [1], ruling out this possibility. The effect of thermal Marangoni flow when solutal Marangoni flow is present is typically negligible. Furthermore, the dye is not the cause either, since the axisymmetry breaking is also observed with the transmission detection without any added dyes.

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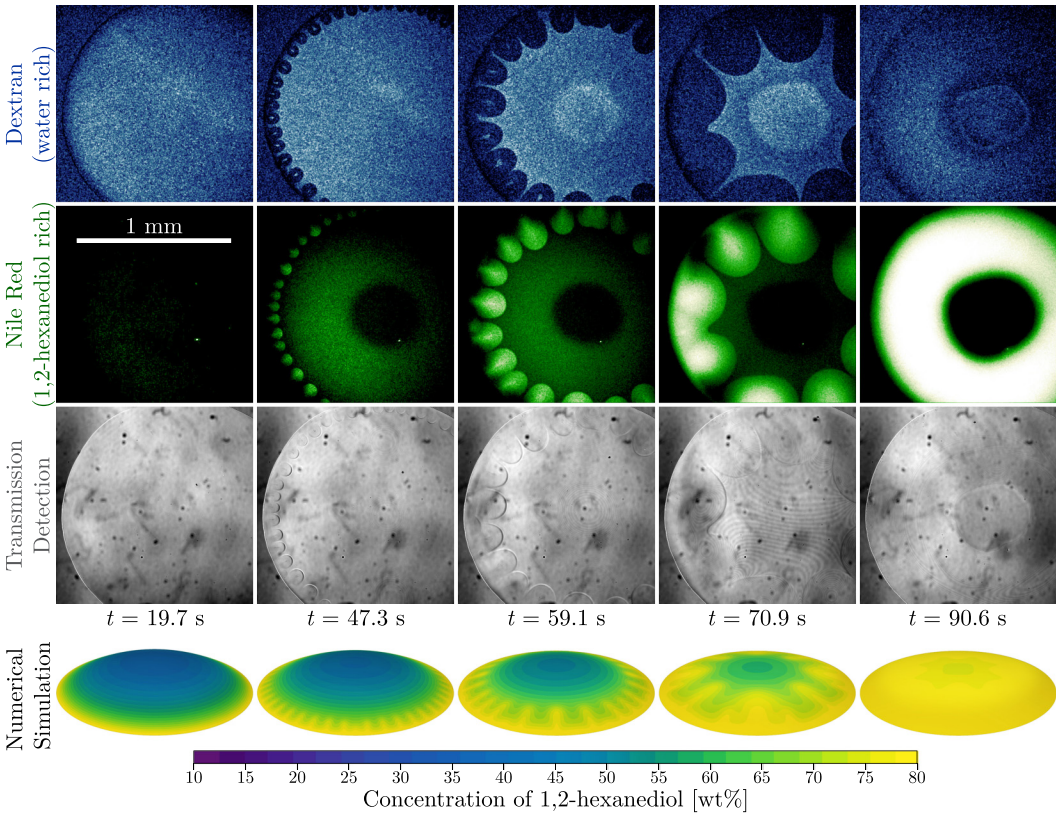

FIG. 1. Snapshots of an evaporating water/1,2-hexanediol droplet on a glass substrate at different times t after deposition. Initial volume $V = 0.10 \pm 0.01$ µL, contact radius $R = 0.781 \pm 0.002$ mm, and initial contact angle $\theta = 15.2^\circ \pm 1.5^\circ$. A small amount of fluorescent dye is added to indicate the local composition in the drop. First row: Dextran dye (hydrophilic) highlights the water-rich regions in the drop. Second row: Nile red dye (hydrophobic) highlights the 1,2-hexanediol-rich regions in the drop. The third row is the transmission detection channel, which shows the bright-field image of the drop. Strong compositional gradients are visible due to the difference in the refractive index of water and 1,2-hexanediol. The scale of all the images is identical. Finally, the bottom row shows snapshots of a numerical simulation with the same parameters and conditions as in the experiments.

The key observation that led to the definitive explanation is the similarity with the work of De La Cruz *et al.* [4], who studied the evaporation of water/ethanol in a Hele-Shaw cell, which confines the flow to a small gap between two parallel plates. In that work, water-rich spots form near the opening of the Hele-Shaw cell, which closely resemble the 1,2-hexanediol-rich spots. Moreover, the water-rich spots also merge in a similar way to the 1,2-hexanediol-rich spots. Crucially, in a water/ethanol binary droplet, ethanol is the more volatile component, and it has a *lower* surface tension than water. This is the opposite of a water/1,2-hexanediol binary droplet, where the more volatile component (water) has a *higher* surface tension than 1,2-hexanediol.

The surface tension for water/1,2-hexanediol was measured before by Romero *et al.* [5]. However, in that work, the focus was on the dilute aqueous mixtures, with no data for high concentrations of 1,2-hexanediol. Numerical simulations [6] reveal that, with a nonmonotonic surface tension, a similar pattern in the composition of an evaporating water/1,2-hexanediol drop emerges [7], as shown in the bottom row of Fig. 1. Careful subsequent measurements of the surface tension of

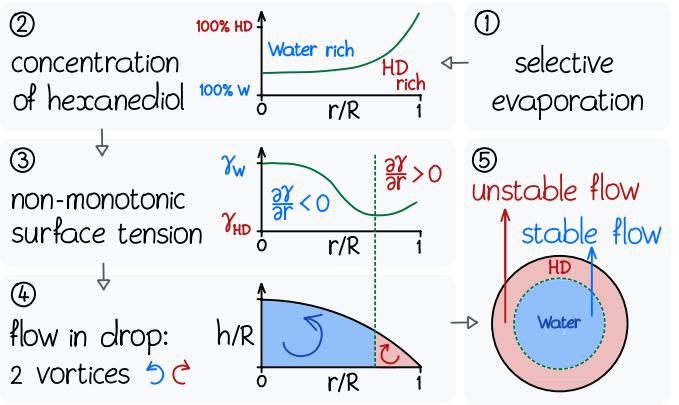

FIG. 2. Schematic of the mechanism leading to the breaking of axisymmetry. (1) Due to selective evaporation and the nonuniform evaporative flux, the concentration of 1,2-hexanediol is increased near the rim of the drop. (2) Sketch of the vertically average concentration of 1,2-hexanediol in the drop vs that of the radius r normalized by the drop contact radius R. (3) Starting at the drop center and moving toward the rim of the drop, the surface tension γ is initially decreasing, i.e., the surface tension gradient $\frac{\partial\gamma}{\partial r}$ is negative. However, close to the rim, where the concentration of 1,2-hexanediol is sufficiently large, the surface tension increases again, since it depends nonmonotonically on the composition. (4) This gives rise to two counter-rotating vortices in the drop, one in the water-rich region, where the liquid is pulled towards the drop apex, and one in the 1,2-hexanediol-rich region, where the liquid is pulled towards the rim. This is illustrated using arrows in the side view of the drop, with the interface at height h. (5) Top view of the drop. Whereas Marangoni flow in the water-rich region is stable (axisymmetric), the Marangoni flow in the 1,2-hexanediol-rich region is unstable (breaking of axial symmetry), similar to the breaking of axial symmetry in evaporating water/ethanol binary droplets.

water/1,2-hexanediol binary mixtures, including all concentrations, confirm that the surface tension is indeed nonmonotonic, with a minimum surface tension around $c_{\mathrm{hd,min}} = 40$ wt.% [7].

The schematic in Fig. 2 illustrates how the nonmonotonic surface tension leads to symmetry breaking. The evaporative flux is nonuniform and diverges close to the contact line [8] since the contact angle θ of a water/1,2-hexanediol binary drop on a glass substrate is very low ($\theta < 15^\circ$). In combination with selective evaporation, this leads to an increased concentration of 1,2-hexanediol near the contact line, which is still axisymmetric. When the local concentration of 1,2-hexanediol in the drop is still below the minimum in surface tension, $c_{\mathrm{hd,min}}$, the Marangoni flow is similar to a system with a monotonic surface tension such as water/glycerol. The surface tension decreases from the apex to the rim, and this causes the solutal Marangoni forces to pull the liquid from the rim along the interface to the apex. Since the drop must retain a spherical cap, the liquid must return to the rim to resupply the liquid, leading to a vortex in the drop.

However, when the local concentration of 1,2-hexanediol exceeds the minimum in surface tension, $c_{\mathrm{hd,min}}$, close to the rim, the surface tension will increase again, causing a second vortex in the drop to emerge that rotates in the opposite direction. This limits the mixing of water and 1,2-hexanediol between the first vortex near the drop center, which is water-rich, and the second vortex near the drop rim, which is 1,2-hexanediol-rich, resulting in a sharp concentration difference where the two vortices meet.

So far, the flow in the drop is still axisymmetric, but as the concentration of 1,2-hexanediol keeps increasing, the region where the surface tension is nonmonotonic keeps growing larger. In this region, the evaporation is inherently unstable, analogous to an evaporating drop of water/ethanol [9]. At a given point, the axisymmetry will spontaneously break due to the unstable flow inside the 1,2-hexanediol-rich region near the contact line.

The remarkable evaporation dynamics of water/1,2-hexanediol illustrates the beauty of evaporating drops and the surprises that can be uncovered. Furthermore, we emphasize that it was only the combination of experiments, numerics, and theory that enabled us to solve this complex and nonintuitive problem. Although we have explained the symmetry breaking for evaporating water/1,2-hexanediol drops, the molecular cause of the nonmonotonic surface tension remains elusive and will be a subject of future investigation.

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Data availability. The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

[1] Y. Li, P. Lv, C. Diddens, H. Tan, H. Wijshoff, M. Versluis, and D. Lohse, Evaporation-triggered segregation of sessile binary droplets, Phys. Rev. Lett. **120**, 224501 (2018).

[2] L. Thayyil Raju, C. Diddens, Y. Li, A. Marin, M. N. van der Linden, X. Zhang, and D. Lohse, Evaporation of a sessile colloidal water–glycerol droplet: Marangoni ring formation, Langmuir **38**, 12082 (2022).

[3] D. Dragoescu, F. Sirbu, and L. Almásy, Study of the thermophysical properties for aqueous alkanediols binary mixtures, J. Mol. Liq. **335**, 116150 (2021).

[4] R. A. L. De La Cruz, C. Diddens, X. Zhang, and D. Lohse, Marangoni instability triggered by selective evaporation of a binary liquid inside a hele-shaw cell, J. Fluid Mech. **923**, A16 (2021).

[5] C. M. Romero, M. S. Páez, J. A. Miranda, D. J. Hernández, and L. E. Oviedo, Effect of temperature on the surface tension of diluted aqueous solutions of 1,2-hexanediol, 1,5-hexanediol, 1,6-hexanediol and 2,5-hexanediol, Fluid Phase Equilib. **258**, 67 (2007).

[6] Simulations were performed by a sharp-interface moving mesh finite element method using the framework PYOOMPH [10]. The weak formulation is a three-dimensional version of the method described in the supplementary information of Ref. [11] using a quarter droplet with symmetry boundaries and >600 000 degrees of freedom.

[7] C. Diddens, P. J. Dekker, and D. Lohse, Non-monotonic surface tension leads to spontaneous symmetry breaking in a binary evaporating drop, arXiv:2402.17452.

[8] Y. O. Popov, Evaporative deposition patterns: spatial dimensions of the deposit, Phys. Rev. E **71**, 036313 (2005).

[9] C. Diddens, H. Tan, P. Lv, M. Versluis, J. G. M. Kuerten, X. Zhang, and D. Lohse, Evaporating pure, binary and ternary droplets: thermal effects and axial symmetry breaking, J. Fluid Mech. **823**, 470 (2017).

[10] C. Diddens and D. Rocha, Bifurcation tracking on moving meshes and with consideration of azimuthal symmetry breaking instabilities, J. Comput. Phys. **518**, 113306 (2024).

[11] M. Jalaal, B. Ten Hagen, H. le The, C. Diddens, D. Lohse, and A. Marin, Interfacial aggregation of self-propelled Janus colloids in sessile droplets, Phys. Rev. Fluids **7**, 110514 (2022).