Supporting Information:
Phase separation of an evaporating ternary solution in a Hele-Shaw cell

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Geometry of the setup

Figure S1: Sketch of the a) side and b) bottom views of the experimental setup. The approximate distance between the chip holder and the nitrogen inlets are shown. A paper cylinder, used to prevent the nitrogen flow from directly impacting on the chip, is indicated with a dashed contour.

Figure S1 shows two sketches of the experimental setup with the locations of the nitrogen inlets and the sensor. To prevent the flow from impacting directly on the chip, a cylinder made out of paper was placed around the objective used for observation. The sensor was inside the cylinder. To isolate the chip from the surroundings we used plastic wrap around the microscope. The plastic wrap prevented strong air currents, but it did not provide an hermetic seal. Therefore air was still able to escape from different places around the gas volume. As a result, the pressure around the chip would still be atmospheric pressure.
Marangoni instability

Conditions for the appearance of the Marangoni instability

The spontaneous appearance of advective rolls at the beginning of the evaporation process suggests the presence of an instability. More specifically, a Marangoni instability given the preferential evaporation of ethanol and its lower surface tension. Sternling and Scriven predicted an unstable interface when a solute that decreases surface tension is transferred between two fluids. Specifically, transfer from a fluid of lower diffusion coefficient and kinematic viscosity, into another fluid of larger values of both quantities. This conditions are satisfied by our system since the transfer is from a liquid to a gas, in accordance with the presence of an instability, like in the case of ethanol–water mixtures.

Sternling and Scriven considered a purely two-dimensional system, however the drag caused by the walls of the Hele-Shaw cell have a stabilizing effect. The stability depends on a Marangoni number defined as

$$Ma^* = -\frac{E_l \delta^2}{D_l \mu_l} \frac{\partial \gamma}{\partial c_e},$$  \hspace{1cm} (S1)

where $\delta$ is the gap size between the walls, $E_l$ the gradient in solute concentration normal to the interface, $\gamma$ the surface tension, $c_e$ the mass fraction of solute, $D_l$ the diffusion coefficient of the solute, $\mu_l$ the dynamic viscosity, and $l$ indicates the liquid.

The Marangoni number given by (S1) corresponds to an evaporating binary mixture. Therefore, strictly speaking, it does not apply to ternary mixtures as used in our experiments. However, in many cases the initial concentration of either water or trans-anethole is small as compared to that of the other two components, in particular for the blue and green groups.

We will assume the mixtures in the blue group to be approximated by an ethanol-water solution and those in the green group by an ethanol–trans-anethole solution. The former case was already studied before, in particular for a 50 wt% solution. The corresponding
value of the Marangoni number was $Ma^* \sim 10^5$. In Table S1 we present the values of the different properties corresponding to the ethanol–water solution as used by Lopez de la Cruz et al.\textsuperscript{54} Those values were originally obtained by interpolating experimental data reported in the literature.\textsuperscript{56–58}

The properties of ethanol–trans-anethole mixtures are not available in the literature, however we can estimate their order of magnitude. For viscosity, we consider the value of pure trans-anethole given that it is the most viscous of the two components. The diffusion coefficient of ethanol in trans-anethole was estimated using the Stokes-Einstein equation

$$D = \frac{k_B T}{6\pi r_e \mu_l},$$

where $k_B$ is the Boltzman’s constant, $T$ is the temperature of the solution, $r_e$ is the radius of the ethanol molecule, and $\mu_l$ is the viscosity of the surrounding liquid (trans-anethole). The derivative of the surface tension with respect to the ethanol mass fraction was estimated by the difference in surface tension between the pure components, namely $\partial \gamma / \partial c_e \sim \gamma_{tA} - \gamma_e$.

Finally, the gradient of ethanol concentration normal to the interface $E_1$ was estimated from the volume flux $Q_{mix} = 0.005 \, \mu\text{L} / \text{min}$ to $Q_{mix} = 0.5 \, \mu\text{L} / \text{min}$ needed to keep the chip filled. Assuming that only ethanol evaporates, that there are no volume changes with concentration, and using Fick’s law, the normal gradient is estimated as $\partial c_e / \partial x \sim -Q_{mix} / (D_l A)$, where $A$ is the area where evaporation takes place, given by the gap thickness $\delta$ times the size of the open side of the chip of 29 mm. The corresponding values used for the estimation of the Marangoni number are shown in Table S1.

The resulting Marangoni number ranges from $10^3 - 10^5$ depending on the volumetric flux considered. For the green group the flux needed to keep the chip filled was of $Q_{mix} = 0.005 \, \mu\text{L} / \text{min}$, corresponding to $Ma^* \sim 10^3$.
Critical Marangoni number

A critical Marangoni number was obtained by means of a linear stability analysis, as based on previous works. It is defined by

$$ \text{Ma}^* = 24 \left( 1 + \frac{c_{\text{sat}} a_1 \rho_g D_g}{\rho_l D_l} \right), \quad (S3) $$

with $\rho$ the density, and the subscript g indicating the gas phase. The saturation concentration of ethanol was obtained as $c_{\text{sat}} = p_{e,\text{sat}}(T) M_e/(RT \rho_g)$, with $p_{e,\text{sat}}(T)$ the saturation pressure of ethanol at temperature $T$, $M_e$ the molar mass of ethanol, and $R$ the universal gas constant. The constant $a_1$ results from taking a Taylor expansion of the molar fraction $n_e = n_e(c_e)$ around $c_e(t = 0) \equiv c_{e,0} \neq 0$, such that $n_e = (1 + (1/c_e - 1) \mathcal{M})^{-1} \approx a_0(c_{e,0}, \mathcal{M}) + a_1(c_{e,0}, \mathcal{M}) c_e + O(c_e^2)$. Then $a_0 = c_{e,0}(c_{e,0} + \mathcal{M}(1 - c_{e,0}))^{-1} - c_{e,0} \mathcal{M}(\mathcal{M}(c_{e,0} - 1) - c_{e,0})^{-2}$, and $a_1 = \mathcal{M}(\mathcal{M}(c_{e,0} - 1) - c_{e,0})^{-2}$, where $\mathcal{M} = M_e/M_s$ with $M_s$ the molar mass of the second component, either water or trans-anethole. The values of the different properties are shown in Table S1. For the gas phase, the density of air at 50 % relative humidity and the diffusion coefficient of ethanol in air were used as shown in Table S1.

For the ethanol–trans-anethole mixture, the liquid density was estimated by $\rho_l = c_{e,b} \rho_e + c_{tA,b} \rho_{tA}$, with the subscript b indicating a binary solution. We consider a case of $c_{e,b} = 0.14$ which is close to the mixture with the highest oil content in the ternary mixtures. Finally, $c_{tA,b} = 1 - c_{e,b}$.

For both ethanol–water and ethanol–trans-anethole mixtures $\text{Ma}^* \sim 10^2$. This value is below the estimated Marangoni numbers for both mixtures. Therefore, a Marangoni instability is to be expected, which is indeed what we observe in experiments. For the groups with intermediate values of the three components, this analysis is not valid anymore, however, it seems that as long as one of the three components is present at a low concentration, the results of the binary analysis could be used as a first approach to determine if a Marangoni instability could arise.
Table S1: Values of the properties used to calculate the Marangoni number and its critical value for two binary mixtures. For the ethanol–water mixture we did not estimate the diffusion coefficient, therefore we added a hyphen (-) in the properties needed for the calculation of $D_l$. *Estimated values. †Value for pure trans-anethole at 20 °C. ‡Obtained from Song et al. $^{10}$

| Property       | Ethanol–water | Ethanol–trans-anethole |
|----------------|---------------|------------------------|
| $D_l$ [m$^2$s$^{-1}$] | $3.65 \times 10^{-10}$ | $3.90 \times 10^{-10,*}$ |
| $D_g$ [m$^2$s$^{-1}$] | $1.35 \times 10^{-5}$ | $1.35 \times 10^{-5}$ |
| $\mu_l$ [kg m$^{-1}$s$^{-1}$] | $2.49 \times 10^{-3}$ | $2.45 \times 10^{-3,*}$ |
| $\rho_l$ [kg m$^{-3}$] | $9.11 \times 10^2$ | $9.61 \times 10^2,*$ |
| $\rho_g$ [kg m$^{-3}$] | 1.2 | 1.2 |
| $\frac{d\gamma}{dc}$ [kg s$^{-2}$] | $-1.85 \times 10^{-2}$ | $-1.37 \times 10^{-2,*}$ |
| $p_{sat}$ [kg m$^{-1}$s$^{-2}$] | $6.57 \times 10^3$ | $6.57 \times 10^3$ |
| $M_e$ [kg mol$^{-1}$] | $4.61 \times 10^{-2}$ | $4.61 \times 10^{-2}$ |
| $M_s$ [kg mol$^{-1}$] | $1.80 \times 10^{-2}$ | $1.48 \times 10^{-1}$ |
| $a_1$ | $8.08 \times 10^{-1}$ | 1.88 |
| $T$ [K] | $2.95 \times 10^2$ | $2.93 \times 10^2$ |
| $R$ [kg m$^2$K$^{-1}$mol$^{-1}$s$^{-2}$] | 8.31 | 8.31 |
| $\gamma_e$ [kg s$^{-2}$] | - | $2.18 \times 10^{-2}$ |
| $\gamma_{TA}$ [kg s$^{-2}$] | - | $3.55 \times 10^{-2}$ |
| $k_B$ [kg m$^2$ K$^{-1}$ s$^{-2}$] | - | $1.38 \times 10^{-23}$ |
| $r_e$ [m] | - | $4.5 \times 10^{-10,\text{c}}$ |
| $A$ [m$^2$] | - | $5.80 \times 10^{-7}$ |
Power law exponents during the Marangoni instability stage

Figure S2: Power law exponent versus initial oil mass fraction.

Figure S2 shows the average exponent of the power law fitted to the initial arch growth, before \( x_F \) reaches the plateau. The error bars correspond to one standard deviation, obtained from fitting different realizations at the same initial oil mass fraction \( c_{tA} \).

For the group 1, the exponent is close to 0.5, however for larger oil concentrations the exponent goes up to 0.7. This corresponds to the cases for which bulk phase separation takes place, except for the last two points. This suggests that the extra interface could accelerate the growth process. For the two points with the highest oil mass fraction, we only have a small period over which to make the fit, therefore the value obtained might not properly reflect the growth rate of the initial period.
Confocal images and intensity profiles of case h, $c_{tA} = 0.417$

Figure S3: Intensity profiles obtained from a realization of case h ($c_{tA} = 0.417$) dyed with perylenne. a) Shortly after the arches merged. A sharp interface is still developing. b) Once a sharp interface has formed and flattened. The insets in both cases show the intensity field from which the profiles were obtained. Note that the snapshot in b) was rotated to make the liquid-liquid interface vertical. The profiles are averages taken in between the red horizontal lines shown in the insets. In both cases a red arrow points to a minimum in the intensity just after the liquid-liquid interface, suggesting a lower oil concentration. The scale bars correspond to 500 µm. The black region to the left corresponds to air phase.

One repetition of case h (specifically $c_{tA} = 0.417$) was dyed with perylenne to highlight the regions of higher oil concentration. Figure S3 shows average intensity profiles taken close to the air–liquid interface once phase separation has taken place and the oil-rich phase has covered the whole edge. Figure S3a was obtained shortly after the visible arches merged. A sharp interface is present only in the region where the merging took place. Figure S3b was obtained when the sharp liquid–liquid interface has extended over the whole field of view.

In the averaged intensity profiles of both cases, marked with a red arrow, a minimum in intensity is visible to the right of the interface. While perylenne might not perfectly follow the concentration of oil, the dip in intensity suggests that there is a local decrease in oil mass fraction. The minimum in intensity is in agreement with our hypothesis that the concentration just to the right of the liquid–liquid interface has a lower oil mass fraction than the original mixture far away from and to the right of the interface.
Description of case i, $c_{tA} = 0.599$

In this section we show an example of case i (yellow group) because it presents some extra interesting characteristics that are not seen in cases g and h. In Figure S4a a series of snapshots taken at increasing times are shown. Like in all cases, the initial stage presents the Marangoni instability with growing and merging arches. Inside the arches water rich droplets nucleate, but eventually disappear. Once the oil rich phase has covered the whole edge, a series of fingers appear to the right of the liquid–liquid interface. As in the case shown in the main text, the finger grow in length and reduce in number over time.

From the snapshot at 999.5 s it is clear that there is a change in the light intensity at the areas that separate the fingers. Such a change in intensity indicates a change in the composition of the liquid. More specifically, given that the oil-rich phase has a darker color, it is possible that the lighter areas in between fingers have a lower oil mass fraction. Such a depletion of oil to the right of the liquid–liquid interface further supports the scenario proposed in the main text with regards to the composition changes in the mixture along the $x$ direction.

Figure S4b-d show zooms to the fingers at the three different times. One difference with cases g and h of the yellow group is that initially the fingers are not formed by surface droplets, but by a continuous stream of new phase. Close to the liquid–liquid interface, bulk droplets nucleate, which once large enough travel away from the liquid–liquid interface. On the contrary, at later times, surface droplets pinch off from the streams and travel toward the liquid–liquid interface. Even later, the surface droplets become large enough to span trough the whole gap of the cell (from the glass plate to the silicon plate), creating columnar droplets, which from the bottom look like circles with a sharp interface. The columnar droplets also travel toward the interface. Since bulk droplets travel to the right, while surface droplets travel to the left, we can conclude that the interaction with the wall has a strong effect on the direction of the droplet displacement.
Figure S4: Main characteristics of case i ($c_{tA} = 0.599$). (a) Snapshots taken at increasing times. The scale bar at 1s is 500 µm in length and applies to all the snapshots in the time series. In all cases, the gas phase is to the left of the image. (b) Zoom (4x) to two fingers taken from the snapshot at $t = 499.5$ s. Bulk droplets travel away from the interface. (c) Zoom (4x) to two fingers taken from the snapshot at $t = 999.5$ s showing surface droplets pinching from fingers and traveling towards the interface. (d) Zoom (4x) to one finger taken from the snapshot at $t = 2499.5$ s. Surface droplets have grown into columnar droplets which also travel towards the interface.
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