# Supporting information

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## Estimation of interfacial energies

Upon phase separation, a significant portion of the Gibbs free energy is used up in forming three interfaces: 1) solid-liquid interface between water-rich subphase and substrate, 2) solid-liquid interface between water-lean subphase and substrate, and 3) liquid-liquid interface between the two subphases. The energy required to form the three interfaces can be estimated by the difference between the interfacial energies between the mixture and the substrate before and after phase separation. Prior to phase separation, the interfacial energy between the unstable ternary mixture and the substrate ($E_1$) is given by the product of interfacial tension ($\gamma_{ternary-S}$) with contact area ($A$),

$$E_1 = \gamma_{ternary-S} A$$

Once phase separation takes place and the three interfaces form, the total interfacial energy ($E_2$) becomes the sum of the product of interfacial tensions and contact areas:

$$E_2 = \gamma_{L1-S} A_1 + \gamma_{L2-S} A_2 + \gamma_{L1-L2} A_{interface}$$

$L1$, $L2$, and $S$ denote water-lean subphase, water-rich subphase and substrate, respectively. The $\gamma$ denote the interfacial tensions between respective interfaces. $A_1$ and $A_2$ denote the contact area of water-lean and water-rich subphases with the substrate, respectively, such that $A = A_1 + A_2$. $A_{interface}$ is the interfacial area between the two subphases (See Figure S2). The energy $E$ required to form the three interfaces is then the difference between the two states $E = E_2 - E_1$.

Because the composition of each subphase is not exactly known, here we estimate the interfacial energy for the extreme case of an oil droplet (i.e. 1-octanol) surrounded by

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water. Therefore, in the following discussions, octanol and water are taken as $L_1$ and $L_2$, respectively.

With this assumption, $\gamma_{L_1-S}$ and $\gamma_{L_2-S}$ can be obtained using the Young's equation as shown below (see also Figure S2):

$$\gamma_S = \gamma_{L_1} cos(\theta) + \gamma_{L_1-S} = \gamma_{L_2} cos(\theta) + \gamma_{L_2-S}$$

where the surface tensions of octanol ($\gamma_{L_1}$) and water in air ($\gamma_{L_2}$), and the surface tension of OTS-coated substrate ($\gamma_S$) in air are known from literature. The static contact angle ($\theta$) of each liquid on the substrate with air as the surrounding is $\theta_{octanol} \sim 42\ ^o$ and $\theta_{water} \sim 110\ ^o$. Table S3 lists the values of surface tension as well as solid-liquid interfacial tensions for each liquid. The interfacial tension between the liquids is also known from literature.

Once the interfacial tensions are known, the total energy can be calculated by multiplying the $\gamma$ values with the contact area. Here, the volume of surrounding phase (i.e. water) is estimated to be 100 times that of the oil, based on the ratio of the two subphases from phase separation along a tie line, see Figure 1a and the reference.[1] Thus, with an oil droplet of 2.5 $\mu m$ in radius, the contact areas with the substrate for both oil and water are $A_1 \sim 1.96 \times 10^{-11}\ m^2$ and $A_2 \sim 1.34 \times 10^{-10}\ m^2$, respectively. The interfacial area between the two liquids is $A_{interface} \sim 5.4 \times 10^{-12}\ m^2$.

With these values, the total energy required for forming the three interfaces is $E = E_2 - E_1 \sim 0.49\ J/mol$. The energy approximated here is likely to be higher than the actual interfacial energy since the experimental value for interfacial tension between the subphases is very small (i.e. $\sim$0.2 $mN/m$ for oleic acid, ethanol, water mixture). However, this analysis demonstrates that most of the energy from phase separation is spent for the formation of new interfaces, in addition for overcoming the inertial.

**Table S1.** Characteristic group volume ($R_k$) and surface area ($Q_k$) parameters for each chemical group in our ternary systems. Here A represents an aromatic group. Data are taken from Dortmund Data Bank (DDB)[2]

| | $R_k$ | $Q_k$ |
|---|---|---|
| $CH_3$ | 0.9011 | 0.8480 |
| $CH_2$ | 0.6744 | 0.5400 |
| $COO$ | 1.3800 | 1.2000 |
| $ACOH$ | 0.8952 | 0.6800 |
| $ACH$ | 0.5313 | 0.4000 |
| $AC$ | 0.3652 | 0.1200 |
| $OH$ | 1.0000 | 1.2000 |
| $H_2O$ | 0.9200 | 1.4000 |

**Table S2.** Group interaction parameters ($a_{mn}$) for the functional groups found in the system. Here A represents an aromatic group. Taken from Dortmund Data Bank (DDB)[2]

| | $CH_3$ | $CH_2$ | $COO$ | $ACOH$ | $ACH$ | $AC$ | $OH$ | $H_2O$ |
|---|---|---|---|---|---|---|---|---|
| $CH_3$ | 0 | 0 | 387.1 | 1333 | 61.13 | 61.13 | 986.5 | 1318 |
| $CH_2$ | 0 | 0 | 387.1 | 1333 | 61.13 | 61.13 | 986.5 | 1318 |
| $COO$ | 529 | 529 | 0 | -167.3 | 317.6 | 317.6 | 88.63 | 284.4 |
| $ACOH$ | 275.8 | 275.8 | -494.2 | 0 | 25.34 | 25.34 | -451.6 | -601.8 |
| $ACH$ | -11.12 | -11.12 | 103.5 | 1329 | 0 | 0 | 636.1 | 903.8 |
| $AC$ | -11.12 | -11.12 | 103.5 | 1329 | 0 | 0 | 636.1 | 903.8 |
| $OH$ | 156.4 | 156.4 | 190.3 | -259.7 | 89.6 | 89.6 | 0 | 353.5 |
| $H_2O$ | 300 | 300 | -197.5 | 324.5 | 362.3 | 362.3 | -229.1 | 0 |

**Table S3.** Surface and interfacial tensions of octanol ($L_1$), water ($L_2$) and OTS-Si substrate ($S$)

| | mN/m | |
|---|---|---|
| $\gamma_S$ | 20.7 | ref. [3] |
| $\gamma_{L_1}$ | 27.5 | ref. [4] |
| $\gamma_{L_2}$ | 72 | |
| $\gamma_{L_1-L_2}$ | 8.4 | ref. [4] |
| $\gamma_{L_1-S}$ | 0.26 | calculated |
| $\gamma_{L_2-S}$ | 45.3 | calculated |

**Table S4.** Energies associated in the process: Excess Gibbs free energy during phase separation ($\Delta G_{exc}$) from UNIFAC calculation and average kinetic energy of self-propelled droplets ($E_{kinetic}$)

| Paraben concentration | $\Delta G$ ($J/mol$) | E$_{kinetic}$ ($10^{-11}$ $J/mol$) |
|---|---|---|
| 8% | 1.89 | 45.3 ± 13.3 |
| 10% | 1.66 | 8.93 ± 4.75 |
| 15% | 1.19 | 6.47 ± 1.0 |

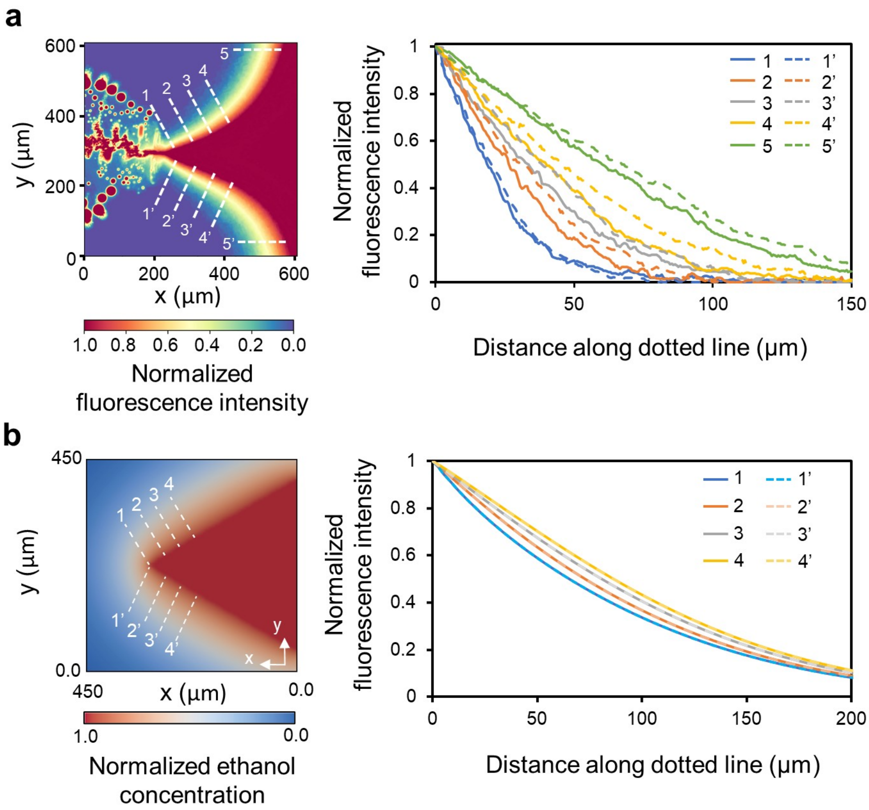

**Figure S1.** Concentration profiles are symmetric along the y-axis

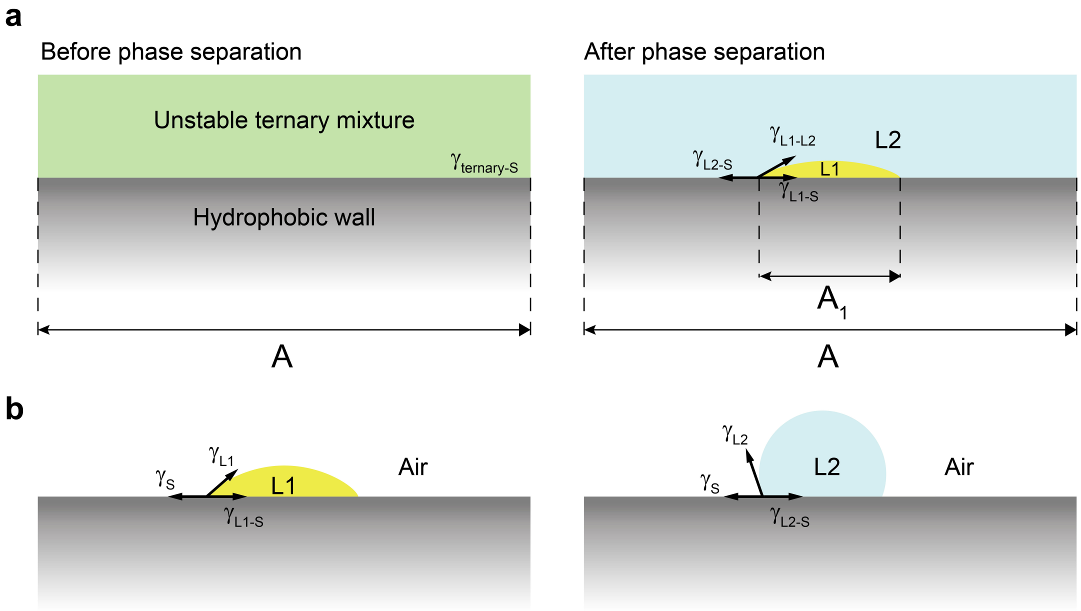

**Figure S2.** **a.** Schematic showing the interfaces before and after phase separation and their respective interfacial tensions. **b.** Schematic showing the force balance on oil and water droplets on the hydrophobic substrate surrounded in air.

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