Supplementary information:

Droplet-based electro-coalescence for probing threshold disjoining pressure

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Correlation between the critical micelle concentration (CMC) and the surfactant concentration above which critical voltage converges

Surfactants can migrate to interfaces and form a physical barrier to prevent the direct contact of the emulsion droplets. The stability of emulsion is highly dependent on the surface concentration in addition to the properties of surfactants and the fluid phases. The surface concentration of the surfactant is in a dynamic equilibrium with the bulk concentration.[1-3] When the bulk concentration of surfactant is above a critical value, the surface concentration becomes saturated and does not increase further. The additional surfactants in the bulk solution will form micelles, instead of migrating to the interfaces; thus, they will not further enhance the stability of emulsion. The concentration where the micelles start to form is termed as critical micelle concentration (CMC). Based on our results, the specific concentration above which the critical voltage starts to converge is strongly correlated with the CMC of the surfactants.

Voltage drop across the oil film

We hypothesize that the voltage across the thin oil film is almost equal to the applied voltage. To confirm this, we first estimate the voltage drop on the two emulsion droplets through Ohm's law: $U_{droplets}=I \cdot R_{droplets}$. Before droplets' coalescence, the electric resistance of droplets $R_{droplets}$ can be calculated through analyzing the shapes of droplets. For example, when 0.01M potassium chloride (KCl) water is used as the droplet phase, the electric resistance is around: $R_{droplets} \approx 5 \cdot 10^6\,\Omega$. The corresponding current is measured using an electrochemical workstation. Before coalescence, the current is almost zero: $I < 10^{-9}$A. Thus, the voltage drop on the emulsions is less than: $U_{droplets} < R_{droplets} \cdot I = 5 \cdot 10^{-3}$ V, which is negligible compared with the applied voltage (ranging from 0.1V to 1.5V). This confirms our hypothesis that almost all voltage drop in the system takes place across the thin oil film (Fig S1 (a)). Indeed, if we use salty water with different concentrations of potassium chloride (KCl) as the dispersed phase and compare their critical voltages, we find that the critical voltages show low sensitivity to the ionic strength even as the ionic strength of the aqueous droplets changes from $5 \cdot 10^{-6}$ S/m to 0.12 S/m (Fig 1S (b)), confirming that there is negligible voltage drop within the aqueous droplets.

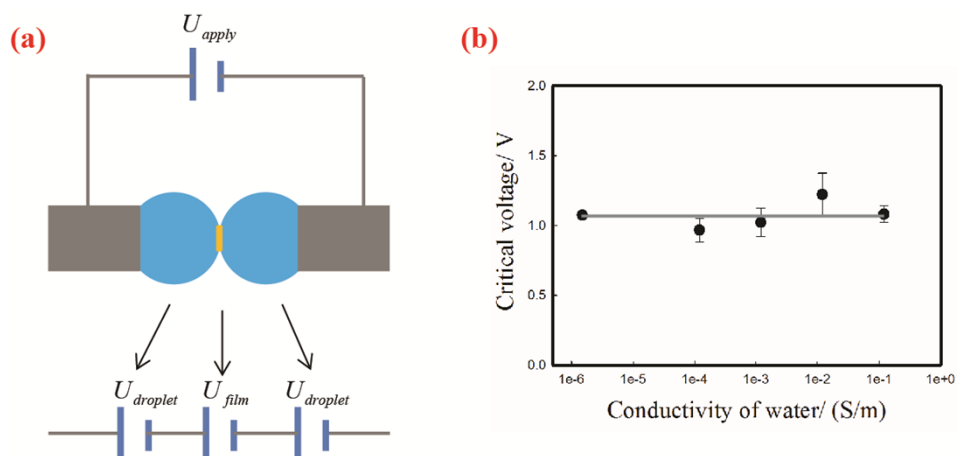**Fig. S1** (a) The applied voltage is the sum of the voltage differences in the droplets and across thin oil film: $U_{apply}=U_{droplets}+U_{film}$. (b) Influence of conductivity on critical voltage. The dispersed phases consist water with different concentrations of potassium chloride (KCl), while the continuous phases is liquid paraffin with 2% EM90.

References

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3. J. N. Phillips, Trans. *Faraday Soc.*, 1955, 51, 561-569.