Electrocoalescence of paired droplets encapsulated in double-emulsion drops

Yankan Jia[a], Yukun Ren[a,b], Weiyu Liu[a], Likai Hou[a], Ye Tao[a], Qingming Hu[a] and
Hongyuan Jiang[a,b]

[a]*School of Mechatronics Engineering, Harbin Institute of Technology, Harbin, 150001, People's Republic of China*

[b]*State Key Laboratory of Robotics and System, Harbin Institute of Technology, Harbin, 150001, People's Republic of China*

Electronic Supporting Information (ESI)

This material gives supporting information of theoretical analysis and numerical simulation for the model studied in the paper.

Supplementary Material Contents:

Additional Supplementary Material:

Movie S1 Coalescing process of double-emulsion drops

Section 1 Electrical problem

Introducing phasor amplitude for electrical problem denoted by a tilde, electrostatic potential field within each fluid domain of uniform electrical properties satisfies the Laplace equation, $\nabla^2\tilde{\phi}_i = 0$. At the liquid-liquid interface, the integral form of Maxwell equations leads to continuity of normal component of Ohmic and displacement current

$$\left(\sigma_1 + j\omega\varepsilon_1\right)\tilde{E}_{1n} = \left(\sigma_2 + j\omega\varepsilon_2\right)\tilde{E}_{2n} \text{ or } \tilde{\varepsilon}_1\tilde{E}_{1n} = \tilde{\varepsilon}_2\tilde{E}_{2n} \tag{S1-a}$$

$$\tilde{\phi}_1 = \tilde{\phi}_2 \tag{S1-b}$$

where σ is the solution conductivity, ε the liquid permittivity, $\tilde{\varepsilon}$ the complex permittivity, j the imaginary unit, $\omega = 2\pi f$ angular frequency of the applied voltage, $\tilde{A}$ the phasor amplitude of its capped variable A, $E_n = \boldsymbol{n}\cdot\left(-\nabla\phi\right)$ the normal component of electric field amplitude, and ϕ the applied potential.

According to Guass law, the surface free charge density $\tilde{\sigma}_f$, at the liquid-liquid interface induced by the applied field is given by

$$\tilde{\sigma}_f = -\frac{\varepsilon_1\sigma_2 - \varepsilon_2\sigma_1}{\sigma_2 + j\omega\varepsilon_2}\tilde{E}_{1n} = -\frac{\varepsilon_1\tilde{\varepsilon}_2 - \varepsilon_2\tilde{\varepsilon}_1}{\tilde{\varepsilon}_2}\tilde{E}_{1n} \tag{S2-a}$$

Similarly, the surface polarization charge $\tilde{\sigma}_p$, total charge $\tilde{\sigma}_t$ is

$$\tilde{\sigma}_p = -\frac{\left(\varepsilon_0 - \varepsilon_1\right)\tilde{\varepsilon}_2 - \left(\varepsilon_0 - \varepsilon_2\right)\tilde{\varepsilon}_1}{\tilde{\varepsilon}_2}E_{1n} \tag{S2-b}$$

$$\tilde{\sigma}_t = -\frac{\varepsilon_0\left(\tilde{\varepsilon}_2 - \tilde{\varepsilon}_1\right)}{\tilde{\varepsilon}_2}E_{1n} \tag{S2-c}$$

Here ε_0 denotes the vacuum permittivity.

The induced bulk charge in the vicinity of interface, both free and bound, respond to the applied field, leading to a local time-averaged electric force $\langle \boldsymbol{F}_E \rangle$ acting around the interfacial region

$$\langle \boldsymbol{F}_E \rangle = \nabla\cdot\tilde{\tilde{T}}_E = \frac{1}{2}\mathrm{Re}\left(\tilde{\rho}_f\tilde{\boldsymbol{E}}^* - \frac{1}{2}\left|\tilde{\boldsymbol{E}}\right|^2\nabla\varepsilon\right) \tag{S3-a}$$

Where $\mathrm{Re}(A)$ is the real part of A, the asterisk is the complex conjugate operator and $\overleftrightarrow{T}_E$ is the Maxwell stress tensor. The electrokinetic force $\langle \boldsymbol{F}_E \rangle$ consists of two parts, viz. the Coulombian force due to free charge and the dielectric force due to polarized bound charge. For a two phase interface, where there is an abrupt jump in electrical properties, the complex Maxwell stress tensor in an oscillating field is

$$\tilde{\overleftrightarrow{T}}_E = \frac{1}{2}\varepsilon \operatorname{Re}\left(\widetilde{\boldsymbol{E}}\widetilde{\boldsymbol{E}}^* - \frac{1}{2}\widetilde{\boldsymbol{E}}\cdot\widetilde{\boldsymbol{E}}^* I \right) \tag{S3-b}$$

Where I is the unit tensor. The jump in electrical stress across the liquid interface, namely the net interfacial electrical stress, is $\boldsymbol{f}_E = \left\| \tilde{\overleftrightarrow{T}}_E \cdot \boldsymbol{n} \right\|$, where $\|A\|$ is the jump value of A across the interface, and $\|\ \| \equiv \text{'external'} - \text{'internal'}$. The interfacial electrical stress can be projected into normal and tangential components to the charged surface

$$\left\| \tilde{\overleftrightarrow{T}}_E \cdot \boldsymbol{n} \right\| \cdot \boldsymbol{n} = \frac{1}{4}\varepsilon_1 \left(\widetilde{\boldsymbol{E}}_{1n} \widetilde{\boldsymbol{E}}_{1n}^* \left(1 - \frac{\varepsilon_2}{\varepsilon_1} \frac{\tilde{\varepsilon}_1 \tilde{\varepsilon}_1^*}{\tilde{\varepsilon}_2 \tilde{\varepsilon}_2^*} \right) - \widetilde{\boldsymbol{E}}_t \widetilde{\boldsymbol{E}}_t^* \left(1 - \frac{\varepsilon_2}{\varepsilon_1} \right) \right) \tag{S4-a}$$

$$\left\| \tilde{\overleftrightarrow{T}}_E \cdot \boldsymbol{n} \right\| \cdot \boldsymbol{t} = \frac{1}{2}\varepsilon_1 \operatorname{Re}\left(\widetilde{\boldsymbol{E}}_{1n} \widetilde{\boldsymbol{E}}_t^* \left(1 - \frac{\varepsilon_2}{\varepsilon_1} \frac{\tilde{\varepsilon}_1}{\tilde{\varepsilon}_2} \right) \right) \tag{S4-b}$$

Where $\boldsymbol{n}$ and $\boldsymbol{t}$ are the unit vector for normal component and tangential component, respectively. And $\boldsymbol{E}_t = \boldsymbol{t} \cdot \boldsymbol{E}$ is the tangential component of the electric field.

It is noteworthy that local tangential electrical stress at the droplet surface (Fig.S3) causes a far-field electrohydrodynamic (EHD) flow field. The EHD flow dominates over electrostatic interaction as the drop pair is separated by more than several core diameters. The EHD flow is also strong when the drop pair is spaced very close.

Section 2 Fluid flow problem

Assuming the Reynolds number is sufficiently small, liquid motion in each Newtonian fluid phase obeys the full Stokes equation.
Momentum conservation:

$$\nabla \cdot \overleftrightarrow{T}_N = -\nabla p + \mu \nabla^2 \boldsymbol{u} = 0 \tag{S5-a}$$

Mass conservation:

$$\nabla \cdot \boldsymbol{u} = 0 \tag{S5-b}$$

Where $\overleftrightarrow{T}_N = -p\boldsymbol{I} + \mu\left(\nabla \boldsymbol{u} + \left(\nabla \boldsymbol{u}\right)^T\right)$ is the hydrodynamic stress tensor, μ the fluid viscosity, p the pressure and $\boldsymbol{u}$ the fluid velocity.

Across the electrical liquid-liquid interface, the flow velocity is continuous, $\boldsymbol{u}_1$=$\boldsymbol{u}_2$, and force balance is met along the drop surface[1]

$$\left\| \widetilde{\overleftrightarrow{T}}_E \cdot \boldsymbol{n} \right\| + \left\| \overleftrightarrow{T}_N \cdot \boldsymbol{n} \right\| = \gamma \boldsymbol{n} \nabla_s \cdot \boldsymbol{n} \tag{S6}$$

Here $\nabla_s \equiv (\boldsymbol{I} - \boldsymbol{nn}) \cdot \nabla$ is the surface gradient operator and $\nabla_s \cdot \boldsymbol{n}$ is the mean curvature of the interface.

For the leaky dielectric material studied in this work, tangential electrical stress is non-negligible. The equation of stress balance is decomposed along both normal and tangential direction to the electrical liquid interface

Normal:

$$\frac{1}{4}\varepsilon_1 \left(\widetilde{\boldsymbol{E}}_{1n} \widetilde{\boldsymbol{E}}_{1n}^* \left(1 - \frac{\varepsilon_2}{\varepsilon_1} \frac{\tilde{\varepsilon}_1 \tilde{\varepsilon}_1^*}{\tilde{\varepsilon}_2 \tilde{\varepsilon}_2^*} \right) - \widetilde{\boldsymbol{E}}_t \widetilde{\boldsymbol{E}}_t^* \left(1 - \frac{\varepsilon_2}{\varepsilon_1} \right) \right) + \left\| -p \right\| + \left\| \mu \left(\nabla \boldsymbol{u} + \left(\nabla \boldsymbol{u} \right)^T \right) \cdot \boldsymbol{n} \right\| \cdot \boldsymbol{n} = \gamma \nabla_s \cdot \boldsymbol{n} \tag{S7-a}$$

Tangential:

$$\frac{1}{2}\varepsilon_1 \operatorname{Re} \left(\widetilde{\boldsymbol{E}}_{1n} \widetilde{\boldsymbol{E}}_t^* \left(1 - \frac{\varepsilon_2}{\varepsilon_1} \frac{\tilde{\varepsilon}_1}{\tilde{\varepsilon}_2} \right) \right) + \left\| \mu \left(\nabla \boldsymbol{u} + \left(\nabla \boldsymbol{u} \right)^T \right) \cdot \boldsymbol{n} \right\| \cdot \boldsymbol{t} = 0 \tag{S7-b}$$

Section 3 Nondimensionalization

It is convenient to make all the variables nondimensional before making an analysis. We employ particle radius R as the distance scale, $\frac{\phi_0 R}{L}$ as the characteristic voltage scale, $E_\infty = \frac{\phi_0}{L}$ as the scale of field intensity, reciprocal charge relaxation time of droplet $\frac{\sigma_1}{\varepsilon_1}$ as the angular frequency scale, $u_0 = \frac{\varepsilon_1 E_\infty^2 R}{\eta_1}$ as flow velocity scale, $\frac{\eta_1 u_0}{R}$ as the stress scale.

The nondimensionalization process gives rise to the following dimensionless parameters,

$$\overline{\sigma}_{i1} = \sigma_i/\sigma_1\,,\ \overline{\varepsilon}_{i1} = \varepsilon_i/\varepsilon_1\,,\ \text{（i=1,2,3）}\ \overline{\mu}_{21} = \mu_2/\mu_1\,,\ Bo = \frac{\varepsilon_1 E_\infty^2 R}{\gamma} \qquad \text{(S8)}$$

The electrostatic potential is governed by Laplace equation $\overline{\nabla}^2\overline{\phi}_i = 0$, subjected to fixed potential phasor $\overline{\phi} = L/R$, $\overline{\phi} = 0$ on the electrode surface, $n\cdot\overline{\nabla}\overline{\phi} = 0$ on insulating channel wall. At both the electrical medium/shell and drop/shell interface, continuity of normal component of total current accounts for the structural polarization because of a jump in ionic concentrations $\left(\overline{\sigma}_{i1} + j\overline{\omega\varepsilon_{i1}}\right)\boldsymbol{n}\cdot\overline{\nabla}\overline{\phi}_i = \left(\overline{\sigma}_{(i+1)1} + j\overline{\omega\varepsilon_{(i+1)1}}\right)\boldsymbol{n}\cdot\overline{\nabla}\overline{\phi}_{i+1}$, where i=1,2,3 represents the domain occupied by the droplet, liquid PDMS and suspension medium, respectively. Surface charge, both free $\tilde{\sigma}_f$ and bound $\tilde{\sigma}_b$, are induced at the electrical liquid interface, as a consequence of electrical field being discontinuous, so as to render the current density continuous across the polarizable surface.

The applied field acting on its own induced bipolar charge produces a pondermotive electrical stress $\boldsymbol{f}_E = \left\|\widetilde{\overleftrightarrow{T}}_E \cdot \boldsymbol{n}\right\|$ at the drop surface, with the Maxwell stress tensor given by (S3-b).

Because of the sufficiently small Reynolds number, liquid motion in each Newtonian fluid phase obeys the full Stokes equation

For the droplet phase:

$$-\overline{\nabla}\,\overline{p}_1 + \overline{\nabla}^2\overline{u}_1 = 0 \qquad \text{(S9-a)}$$

For the liquid PDMS phase:

$$-\overline{\nabla}\,\overline{p}_2 + \overline{\mu}_{21}\overline{\nabla}^2\overline{u}_2 = 0 \qquad \text{(S9-b)}$$

where gravity effect is neglected.

The total stress, including, electrical $\overline{\boldsymbol{f}}_E$ and hydrodynamic one $\overline{\boldsymbol{f}}_N$ are balanced by interfacial tension at the droplet surface, in terms of the equilibrium condition along the normal and tangential direction, respectively,

Normal:

$$\frac{1}{4}\left(\overline{\boldsymbol{E}}_{1n}\overline{\boldsymbol{E}}_{1n}^{*}\left(1-\frac{\varepsilon_2}{\varepsilon_1}\frac{\tilde{\varepsilon}_1\tilde{\varepsilon}_1^{*}}{\tilde{\varepsilon}_2\tilde{\varepsilon}_2^{*}}\right)-\overline{\boldsymbol{E}}_t\overline{\boldsymbol{E}}_t^{*}\left(1-\frac{\varepsilon_2}{\varepsilon_1}\right)\right)+(\overline{p}_2-\overline{p}_1)+\overline{\boldsymbol{f}}_N\cdot\boldsymbol{n}=\frac{1}{Bo}\overline{\nabla}_s\cdot\boldsymbol{n} \qquad \text{(S10-a)}$$

Tangential:

$$\frac{1}{2}\mathrm{Re}\left(\overline{\boldsymbol{E}}_{1n}\overline{\boldsymbol{E}}_t^{*}\left(1-\frac{\varepsilon_2}{\varepsilon_1}\frac{\tilde{\varepsilon}_1}{\tilde{\varepsilon}_2}\right)\right)+\overline{\boldsymbol{f}}_N\cdot\boldsymbol{t}=0 \qquad \text{(S10-b)}$$

where

$$\overline{\boldsymbol{f}}_N=\left(\left(\overline{\nabla}\overline{\boldsymbol{u}}_1+\left(\overline{\nabla}\overline{\boldsymbol{u}}_1\right)^T\right)\right)\cdot\boldsymbol{n}-\overline{\mu}_{21}\left(\overline{\nabla}\overline{\boldsymbol{u}}_2+\left(\overline{\nabla}\overline{\boldsymbol{u}}_2\right)^T\right)\cdot\boldsymbol{n} \qquad \text{(S10-c)}$$

For leaky dielectric fluids considered in this work, the non-zero surface tangential electrical stress $\overline{\boldsymbol{f}}_E\cdot\boldsymbol{t}=\frac{1}{2}\mathrm{Re}\left(\overline{\boldsymbol{E}}_{1n}\overline{\boldsymbol{E}}_t^{*}\left(1-\frac{\varepsilon_2}{\varepsilon_1}\frac{\tilde{\varepsilon}_1}{\tilde{\varepsilon}_2}\right)\right)$ always need a non-zero hydrodynamic shear stress to enable a force balance, arouses EHD flows of circulative patterns both inside and outside the droplet, which even evolves in the stable stage of electrical-induced droplet deformation.

For the typical background field intensity E_∞ =40V/mm employed in experiment, $O(Bo)\sim 0.005$, being negligibly small. However, by taking a direct numerical simulation of the nondimensional physical model developed in this work (see Fig. S1), great enhancement of local field occurs in the insulating PDMS gap between the neighboring drops, field intensity even grows beyond $1.5\times10^6\,\mathrm{V/m}$ and yields a large value of $O(Bo)\sim 10$, implying it is indeed the interfacial electrokinetic force that drives both the rotational and translational motion of droplet pairs. The nondimensional electrical bond number is expressed as $Bo=\frac{\varepsilon E^2 R}{\gamma}$, being on the order of O(10), where the water permittivity is $\varepsilon=80\varepsilon_0$, the local field intensity in the gap region $E=1.5\times10^6\,\mathrm{V/m}$, the core radius R=72.5 μm, the surface tension coefficient γ on the order of 0.01N/m[2].

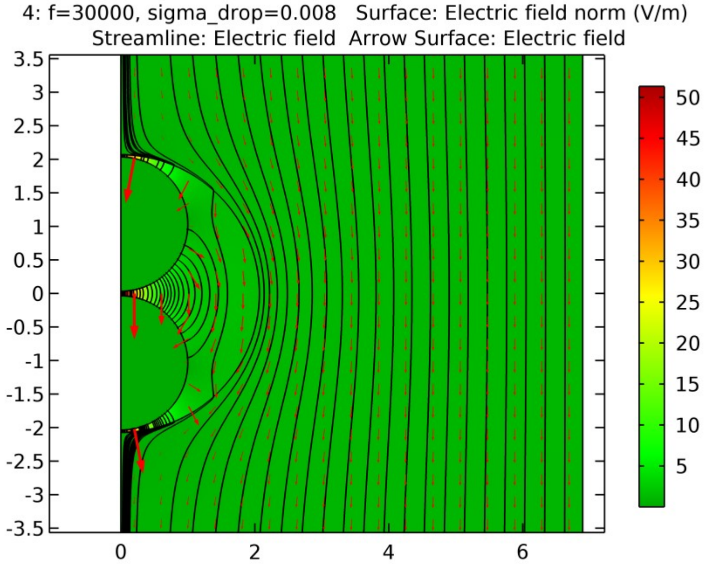

Fig. S1. A streamline and surface plot of nondimensional electric field

Section 4 Global electrostatic interaction

The net electrostatic force acting on the interfacial induced charge tends to transport the fluid with higher polarizability (core) to occupy regions of higher field intensity, namely the DEP phenomenon. For neighboring droplets placed parallel with the applied field, there is an area of enhanced field intensity in the insulation gap between the cores, positive DEP force induces a translating of drops towards one another, favoring the merging phenomenon. From the perspective of induced dipolar interactions, the opposite charges formed on their nearest surfaces generate an attraction effect between the drop pair. The dipole force induces a droplet velocity decaying with interdroplet distance h as $\overline{U}_{dipole} = O\left(\frac{R^4}{h^4}\right)$, while the frequency-dependence is still unclear.

Since a 2D axisymmetric model is employed, we quantify the global DEP interaction force with the expression $\overline{F}_{depz} = 2\pi\oint_{\partial drop} \overline{\boldsymbol{f}}_E \cdot \boldsymbol{e}_z d\bar{l}$ by DNS, as neighboring induced dipole pairs are in parallel orientation with the background field (Fig.S1). DEP force $\overline{F}_{depz}$ changes insensitively for the lowest solution conductivity as field frequency increases from DC limit to 500kHz. For higher conductivity 0.15 and 1.5S/m, $\overline{F}_{depz}$ even increases gradually with frequency and shares identical magnitude (Fig.S2). Theoretically, for an individual non-shelled particle placed in a non-uniform AC field, DEP force reaches a low-frequency conductivity plateau and decays around the reciprocal interfacial charge relaxation time. The particular increasing trend with frequency in current case originates from simultaneous emergence of both electrical medium/shell and drop/shell interfaces. The opposite charges induced at neighboring interfaces actively interact, making the two hemispheres of each drop suffer from electrokinetic force in reverse directions (Fig. 3 (d)).

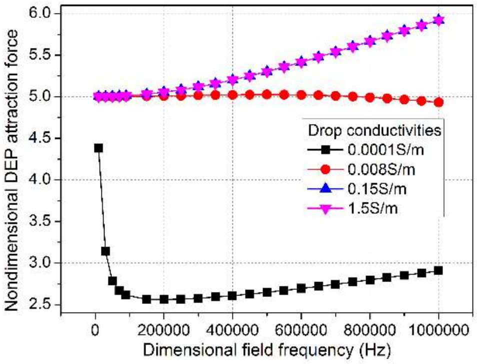

Fig. S2. Frequency-dependency of nondimensional global DEP attraction force acting on a single core for different drop conductivities

Section 5 EHD flow

A distribution of local tangential electrical stress along the leak dielectric drop surface gives rise to active EHD flow. Far-field theory indicates that flow velocity diminishes with increasing distance **as** $\overline{U}_{EHD} = O\left(\frac{R^2}{h^2}\right)$, and hence merely dominates over DEP attraction for a large drop separation. However, according to a recent numerical study in DC, similar convective flow plays a significant role especially as neighboring droplets are in close proximity. In current analysis, the interdrop gap size is even much smaller than an individual radius, and the circulatory flows outside a droplet stream away from the droplet and meet at the gap center, which has a propensity to push apart the two droplets, hindering the coalescence process (Fig.3).

The circulative EHD vortex is largest for the lowest droplet conductivity, since it is much closer to a real leak dielectric (Fig.S3). With increasing ionic concentration, the droplet tends to become an ideal conductor, and EHD flow weakens as the tangential stress diminishes for a more conducting drop. Besides, as frequency increases, EHD flow for various of drop conductivities increases, due to a charge relaxation process.

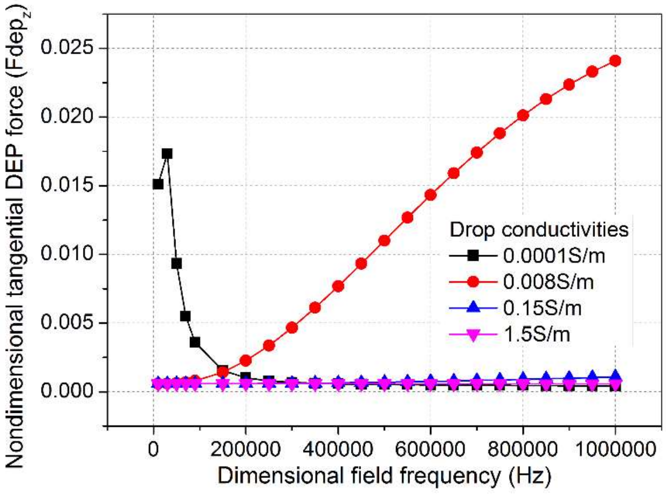

Fig. S3. Frequency-dependence of nondimensional tangential DEP force for distinct drop conductivities

Section 6 Structural polarization at the shell/medium interface

Another action that favors the coalescence is the droplet deformation or elongation in the horizontal direction, which reduces the interdrop separation and eventually causes them to collide with one another, and this effect is greatly enhanced by electrokinetically squeezing the PDMS shell. The non-uniform electrical surface stress felt by the shell of liquid PDMS (Fig.3) cannot be compensated by a pressure gradient, thus induces viscous fluid flow that makes it deform, squeezing its shape to become a prolate ellipse, which facilitates the merging process at moderate voltages.

For the lowest ionic concentration, the deformation of PDMS shell caused by interfacial electrical stress is slightest, thus imposing the smallest impact on the drop movement (Fig.S4). With increasing field frequency, the electrokinetic force acting on the shell decays rapidly, therefore the PDMS shell is unable to deform regardless of the voltage amplitude beyond 200kHz. However, for higher drop conductivities, the interfacial electrical stress becomes larger, which more easily squeezes the liquid PMDS to deform, greatly accelerating the merging process.

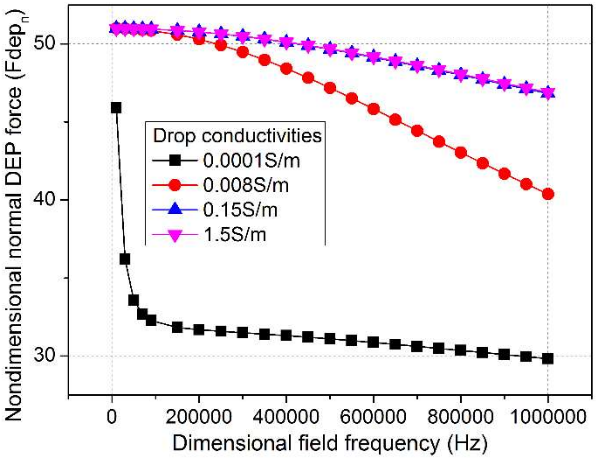

Fig. S4 Frequency-dependence of nondimensional normal DEP force exerted at the shell/medium interface for distinct drop conductivities

Section 7 Impact of the medium conductivity

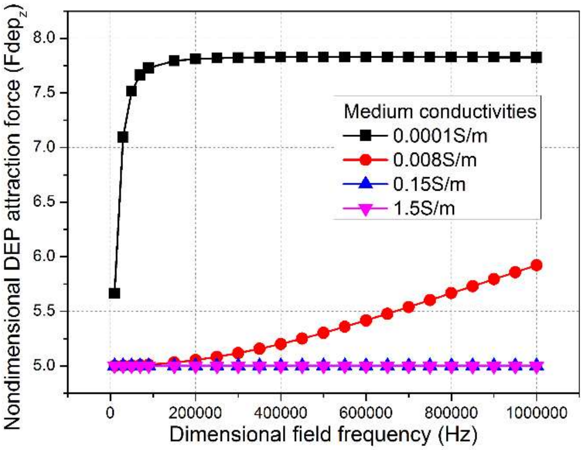

Fig. S5 Frequency-dependency of nondimensional global DEP attraction force acting on a single core of conductivity 0.15S/m, for different medium conductivities.

As medium conductivity decreases from the standard 0.008S/m to the level of DI water 0.0005S/m, the DEP attraction force increases a lot, favoring the merging process. However, by adding more KCL electrolyte to the medium, thus increasing the ionic strength, the DEP attraction force decreases to a plateau, and does not vary with increasing field frequency at 0.15 and 1.5 S/m.

Reference

1 Baygents, J.C., Rivette, N., and Stone, H.: 'Electrohydrodynamic deformation and interaction of drop pairs', Journal of Fluid Mechanics, 1998, 368, pp. 359-375

2 Utada, A.S., Lorenceau, E., Link, D.R., Kaplan, P.D., Stone, H.A., and Weitz, D.A.: 'Monodisperse double emulsions generated from a microcapillary device', Science, 2005, 308, (5721), pp. 537-541

Movie Legend

Movie S1. This movie demonstrates the coalescing process of a group of double-emulsion drops. Additionally, the detailed coalescing process of one specific drop is displayed.