

Aggregation and Coalescence of Oil Droplets in Water via
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Electrohydrodynamic (EHD) flows are known to cause rigid colloids to aggregate near electrodes. Here we report that EHD flows also induce immiscible oil droplets to aggregate and, for sufficiently strong field strengths, to coalesce. We measure the aggregation and coalescence rates of micrometer-scale oil droplets in water, and we find that the most effective way to induce coalescence is by suddenly decreasing the applied frequency. We interpret the results in terms of a balance between EHD flow and colloidal forces, and we discuss the implications for using EHD flows to separate trace oils from solution.

Electric fields have been used for almost a century to separate water-in-oil emulsions.¹ For example, electrostatic dehydrators, also known as electrostatic separators or electrocoalescers, are commonly used to remove dispersed water drops from crude oil^{2,3} and various vegetable oils.³ Separation occurs because the drops polarize upon application of the field, and the interaction between the induced dipoles⁴ causes the drops to arrange into chains aligned with the field.^{1–3,5} Provided the field strength is not too large,^{6,7} adjacent droplets in the chains then coalesce, hastening their rate of sedimentation and consequent separation.⁸

Oil-in-water emulsions, in contrast, have typically been considered to be more difficult to separate electrically. Because the continuous aqueous phase is conductive, the current densities required to induce significant chain formation are much larger compared to those required for water-in-oil emulsions.³ Consequently, modern electrostatic dehydrators are explicitly designed to minimize short-circuiting by water.⁸ Some electrocoagulation techniques instead take advantage of the resulting electrochemical reactions, which alter the pH and help to destabilize the droplets; the required current densities, however, are correspondingly large.⁹ Although some researchers have tested the electrocoalescence of oil-in-water emulsions at low applied voltages,^{10,11} measurable coalescence was achieved only with unstable emulsions (i.e., emulsions that tended to separate anyway within an hour or less after preparation). To date, no one has demonstrated a low-voltage technique for separating stable oil-in-water emulsions.

In this article, we describe a low-voltage approach to separate oil-in-water emulsions that exploits the tendency for objects near electrodes to aggregate via electrohydrodynamic (EHD) flows. It is well established that solid colloidal particles near electrodes form planar aggregates in response to steady or oscillatory electric fields, provided the particles do not adhere to the electrode.^{12–15} Early investigators led by Saville and co-workers^{12,16} explained the aggregation in terms of the EHD flow generated around each particle. In this model, the particles alter the local electric field near the electrode and the action of these perturbations on the electrode polarization layer yields fluid motion directed toward each particle. The adjacent particles become mutually entrained in their respective flows, and aggregation ensues. Because the charge in the polarization layer and the perturbation due to the particle both scale with the applied field strength E , the resulting EHD flow scales as E^2 . Ristenpart et al.^{17,18} developed more detailed models based on the EHD theory and found that measurements of the aggregation kinetics and direct flow visualization corroborated the theory for high-frequency fields (> 100 Hz) in the absence of faradaic reactions; a key finding was that the EHD velocity scales inversely with the applied frequency. Sides and co-workers expanded Trau et al.'s model for the case of low-frequency oscillatory faradaic currents and found a significant dependence on the nature of the electrolyte.^{19–21} As for steady fields, Solomentsev et al.^{15,22} proposed an alternative mechanism based on electroosmotic slip flow on the surface of the particle, and recent work by Ristenpart et al.²³

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- (1) Cottrell, F. G.; Speed, J. B. U.S. Patent 987,115, 1911.
- (2) Taylor, S. E. *Chem. Eng. Res. Des.* **1996**, *74*, 526–540.
- (3) Eow, J. S.; Ghadiri, M.; Sharif, A. O.; Williams, T. J. *Chem. Eng. J.* **2001**, *84*, 173–192.
- (4) Gast, A. P.; Zukoski, C. F. *Adv. Colloid Interface Sci.* **1989**, *30*, 153–202.
- (5) Chen, T. Y.; Mohammed, R. A.; Bailey, A. I.; Luckham, P. F.; Taylor, S. E. *Colloids Surf., A* **1994**, *83*, 273–284.
- (6) Ristenpart, W. D.; Bird, J. C.; Belmonte, A.; Dollar, F.; Stone, H. A. *Nature* **2009**, *461*, 377–380.
- (7) Bird, J. C.; Ristenpart, W. D.; Belmonte, A.; Stone, H. A. *Phys. Rev. Lett.* **2009**, *103*, 164502.
- (8) Eow, J. S.; Ghadiri, M. *Chem. Eng. J.* **2002**, *85*, 357–368.
- (9) Chen, G. H. *Sep. Purif. Technol.* **2004**, *38*, 11–41.
- (10) Ichikawa, T.; Itoh, K.; Yamamoto, S.; Sumita, M. *Colloids Surf., A* **2004**, *242*, 21–26.
- (11) Ichikawa, T. *Colloids Surf., A* **2007**, *302*, 581–586.

- (12) Trau, M.; Saville, D. A.; Aksay, I. A. *Science* **1996**, *272*, 706–709.
- (13) Bohmer, M. *Langmuir* **1996**, *12*, 5747–5750.
- (14) Yeh, S. R.; Seul, M.; Shraiman, B. I. *Nature* **1997**, *386*, 57–59.
- (15) Solomentsev, Y.; Bohmer, M.; Anderson, J. L. *Langmuir* **1997**, *13*, 6058–6068.
- (16) Trau, M.; Saville, D. A.; Aksay, I. A. *Langmuir* **1997**, *13*, 6375–6381.
- (17) Ristenpart, W. D.; Aksay, I. A.; Saville, D. A. *Phys. Rev. E* **2004**, *69*, 021405.
- (18) Ristenpart, W. D.; Aksay, I. A.; Saville, D. A. *J. Fluid Mech.* **2007**, *575*, 83–109.
- (19) Kim, J.; Anderson, J. L.; Garoff, S.; Sides, P. J. *Langmuir* **2002**, *18*, 5387–5391.
- (20) Fagan, J. A.; Sides, P. J.; Prieve, D. C. *Langmuir* **2006**, *22*, 9846–9852.
- (21) Hoggard, J. D.; Sides, P. J.; Prieve, D. C. *Langmuir* **2008**, *24*, 2977–2982.
- (22) Solomentsev, Y.; Guelcher, S. A.; Bevan, M.; Anderson, J. L. *Langmuir* **2000**, *16*, 9208–9216.
- (23) Ristenpart, W. D.; Aksay, I. A.; Saville, D. A. *Langmuir* **2007**, *23*, 4071–4080.

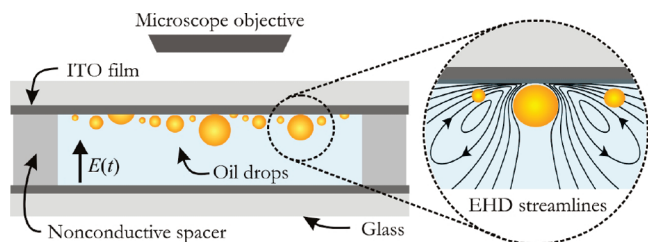


Figure 1. Sketch of the experimental apparatus (not to scale).

suggests that both EHD flow and electroosmotic flow (EOF) contribute significantly to aggregation in steady fields.

Although most of the experimental work to date has dealt with solid colloidal particles, nothing in the extant theories is predicated on the particle solidity. Rather, the key particle properties affecting aggregation are the electrokinetic properties: either the particle zeta potential for EOF or the particle dipole coefficient for EHD flow. Thus, nonsolid particles should also aggregate, and indeed there is some evidence to support this hypothesis. Various types of membrane-bound objects, including bacteria,²⁴ yeast,²⁵ and unilamellar vesicles,^{26,27} have been reported to aggregate near electrodes in response to oscillatory fields. In all of these systems, however, the interior liquid phase is surrounded by an elastic membrane that provides the electrokinetic surface for inducing flow. To date, no one has investigated whether liquid–liquid emulsions undergo similar EHD aggregation in an applied electric field.

Here we report that oil droplets in water do aggregate near electrodes in response to oscillatory electric fields. We show that the rate of aggregation scales as the square of the applied field, consistent with an aggregation mechanism based on EHD flow. More strikingly, we demonstrate that the droplets also coalesce into larger drops under appropriate conditions. A sudden decrease in frequency causes as much as 100% of the droplets in an aggregate to coalesce. Because larger droplets are easier to separate by conventional techniques (e.g., sedimentation or centrifugation), the observation of EHD-induced coalescence suggests a possible strategy for using low-voltage electric fields to separate emulsified oils from aqueous solutions.

The experimental apparatus is sketched in Figure 1. Two parallel electrodes composed of glass coated with indium tin oxide ($R \approx 6\Omega/\text{square}$, Delta Technologies) were separated by a layer of insulating electrical tape approximately $600\ \mu\text{m}$ thick. Oscillatory electric fields were applied with an Agilent function generator (33220A) and measured with an Agilent digital oscilloscope (DSO3152A). Emulsions were prepared by homogenizing (Ultra Turrax T25) a 0.1% by weight mixture of food-grade extra virgin olive oil (UC Davis Olive Center) in 1 mM NaCl. The olive oil was used as provided; the salt water was prepared from $18\ \text{M}\Omega/\text{cm}$ deionized water. No additional surfactants or emulsifying agents were added, but the emulsions were stable for more than 3 months as prepared without noticeable separation. Emulsions prepared at higher salt concentrations tended to separate rapidly (within a few days for 10 mM NaCl and within a few hours for 100 mM NaCl), indicating that the droplets were electrostatically stabilized in 1 mM NaCl. Optical microscopy measurements showed that the resulting emulsion had a log-normal size distribution with a mean diameter of approximately $2\ \mu\text{m}$.

To begin an experiment, the space between the two electrodes was filled with emulsion and left undisturbed for approximately 20 min; this delay allowed the oil droplets to float upward and form a dilute layer near the top electrode. The electric field was then applied, and the resulting droplet behavior was observed with an optical microscope (Leica) and recorded using a CCD camera at 25 frames/s. Low magnifications ($10\text{--}20\times$) were used to visualize 500–1000 droplets simultaneously, which allowed the behavior averaged over many droplets to be determined. Aggregation and coalescence rates were extracted from the digital movies using custom-written programs in Matlab.

A representative example of the aggregation behavior is shown in Figure 2 and in Supporting Information movie 1. Prior to application of the field, the droplets are randomly dispersed near the electrode and undergoing Brownian motion. Upon application of a 500 Hz, 4 V field, the droplets immediately begin moving toward one another. Within 20 s, the majority of droplets have joined an aggregate, and by 40 s, there are very few unaggregated droplets remaining. Qualitatively, the aggregation behavior is strongly reminiscent of the aggregation observed under similar electric field conditions for rigid colloids.^{12,16,17} A particularly important feature in Figure 2 is that little or no coalescence is observed under these electric field conditions. Although the droplets come into close proximity to one another within the aggregate, the electrostatic repulsion between adjacent double layers²⁸ helps maintain a nanometer-scale separation that prevents direct contact between the droplets.²⁹ A similar effect is observed with electrostatically stabilized colloids, which move into close proximity to one another while the electric field is applied but then separate by Brownian motion after the field is removed.^{12,17}

To test more quantitatively whether the observed aggregation is consistent with a mechanism based on EHD flow, we used the methodology developed by Ristenpart et al.¹⁷ to extract aggregation rates from the video data. Briefly, the concentration per unit area n of unaggregated single droplets (“singlets”) is tracked with time, and by assuming that at early times the disappearance of singlets is due primarily to binary collisions, one finds that n^{-1} increases linearly with time (i.e., $n_{\text{init}}/n \approx 1 + (k_E n_{\text{init}})t$). Here, n_{init} is the initial singlet concentration, and k_E is a rate constant (with dimensions of area/time) that reflects the influence of the electric field on singlet aggregation.

The effect of the applied potential and frequency on the rate of aggregation is shown in Figure 3. For small applied potentials (amplitude $\Delta\phi > 3\ \text{V}$), the aggregation rate scales linearly with the square of the applied potential, and for sufficiently high frequencies ($\omega > 500\ \text{Hz}$), the aggregation rate scales roughly inversely with frequency (inset, Figure 3). Note that the effect of frequency was tested at a slightly higher applied potential ($\Delta\phi = 3.5\ \text{V}$) to induce a measurable amount of aggregation at the higher frequencies. Both observed trends are qualitatively consistent with the EHD scaling analysis by Ristenpart et al.¹⁷ in which oscillatory fields between approximately 10^2 and $10^6\ \text{Hz}$ are predicted to yields flows that scale approximately as $u \sim (\Delta\phi)^2/\omega$. Notably, the aggregation rate constants observed here with oil droplets are on the order of $10\ \mu\text{m}^2/\text{s}$, which is comparable to the range of values obtained previously¹⁷ for polystyrene particles, $k_E \approx 5\text{--}50\ \mu\text{m}^2/\text{s}$.

There are two key differences, however, that complicate a direct comparison between the oil drops and solid particles. First, the emulsions are very polydisperse, so the measured rate constants represent only the average rate of aggregation for many

(24) Poortinga, A. T.; Bos, R.; Busscher, H. J. *Biotechnol. Bioeng.* **2000**, *67*, 117–120.

(25) Brisson, V.; Tilton, R. D. *Biotechnol. Bioeng.* **2002**, *77*, 290–295.

(26) Lecuyer, S.; Ristenpart, W. D.; Vincent, O.; Stone, H. A. *Appl. Phys. Lett.* **2008**, *92*, 104105.

(27) Ristenpart, W. D.; Vincent, O.; Lecuyer, S.; Stone, H. A. *Langmuir*, published online April 15, 2010, <http://dx.doi.org/10.1021/la100447m>.

(28) Russel, W. B.; Saville, D. A.; Schowalter, W. R. *Colloidal Dispersions*; Cambridge University Press: Cambridge, U.K., 1989; Section 4.5.

(29) Evans, D. F.; Wennerström, H. *The Colloidal Domain*, 2nd ed.; Wiley VCH: New York, 1999; Section 11.3.

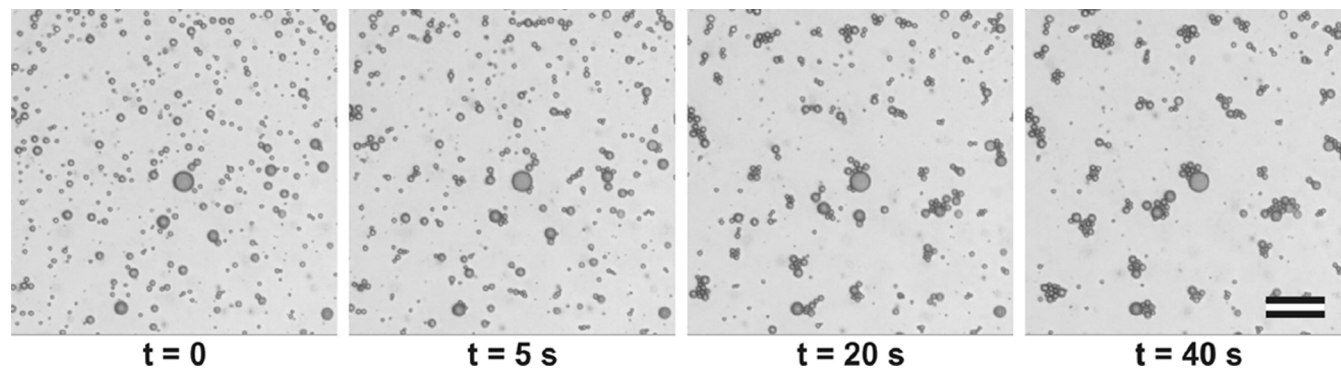


Figure 2. Low-magnification optical images showing the aggregation of olive oil droplets near an electrode in response to an electric field. The applied field is 4 V, 500 Hz and is oriented out of the page. The scale bar is 40 μm . Note that as aggregation proceeds the number of isolated drops (“singlets”) decreases with time.

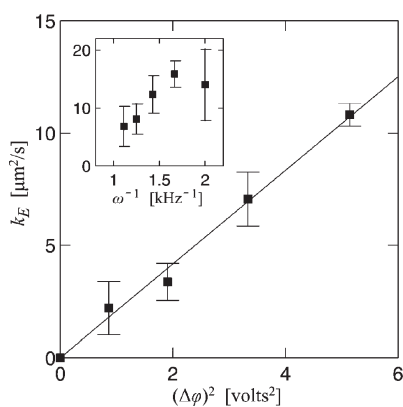


Figure 3. Effect of the applied amplitude on the aggregation rate constant for oil droplets in 1 mM NaCl with $\omega = 500$ Hz. The solid line was derived by linear regression. (Inset) Effect of frequency on the aggregation rate constant, with $\Delta\phi = 3.5$ V. Each point is the mean of three separate experiments performed at the specified voltage or frequency; error bars represent the standard deviation.

different drop sizes; a more precise comparison would require monodisperse emulsions. Second, and more importantly, the oil droplets exhibited a pronounced tendency to adhere irreversibly to the electrode when sufficiently high field strengths were applied (as evidenced by their sudden cessation of motion, including Brownian motion). Experiments at applied amplitudes much larger than 3 V or lower than 500 Hz caused variable degrees of “sticking”, thereby preventing meaningful measurements of the aggregation rate. Apparently, the electrostatic double-layer repulsion that helps stabilize the droplets in the absence of an applied field is overcome by the applied field; notably, drops suspended in higher salt concentrations (> 10 mM NaCl) adhered upon contact with the electrode even in the absence of an applied field. For rigid colloids, the electric field is known to induce small-amplitude oscillations in the particle position,²⁰ and a similar electrophoretic effect might help drive the droplets into contact with the electrode despite the double-layer repulsion.

The key point, however, is that sufficiently high field strengths destabilize the droplets with respect to the electrode, raising the question of whether higher field strengths could also destabilize the droplets with respect to each other (i.e., to cause coalescence). Accordingly, we conducted a series of experiments in which low field strengths were first used to bring the droplets into close proximity, and then the electric field was increased to determine the effect on the droplets. The result of one such experiment is shown in Figure 4 and in Supporting Information movie 2. Here,

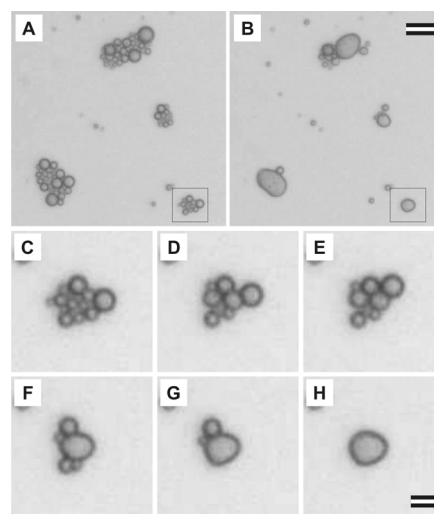


Figure 4. Optical micrographs showing the coalescence of oil droplets near an electrode in response to changes in the applied electric waveform. (A) The droplets initially aggregated in response to a 500 Hz, 3 V field without any coalescence. (B) After the applied field was changed to 50 Hz, 5 V, a large fraction of the droplets coalesced. The scale bar is 20 μm . (C) Magnification of the cluster indicated by the boxes in A and B, shown here at $t = 0$. (D) Approximately 0.08 s after the applied amplitude was suddenly increased to 5 V, about 50% of the drops initially visible in the cluster have coalesced. (E) After another 20 s at 500 Hz, 5 V, no further coalescence is observed. (F–H) Time-lapse sequence of the same cluster showing droplet coalescence after the applied frequency was suddenly decreased to 50 Hz. Images were taken 0.16, 0.4, and 0.92 s after the frequency decrease. The scale bar is 5 μm .

the droplets were first subjected to a 3 V, 500 Hz field for 2 min to cause aggregation; no coalescence was observed (Figure 4a). After first increasing the amplitude to 5 V and then reducing the frequency to 50 Hz, the vast majority of the droplets have coalesced (Figure 4b). The exact sequence of coalescence events for one particular cluster is shown in more detail in Figure 4c–h. Initially, the cluster has at least 17 individual droplets that are optically resolvable at this magnification (Figure 4c). Following an instantaneous increase in the amplitude from 3 to 5 V at a constant 500 Hz, approximately half of the droplets coalesce within 80 ms (Figure 4d). Notably, the coalescence then ceases; no further coalescence is observed at 5 V, 500 Hz for the next 20 s (Figure 4e). To get the remaining droplets to coalesce, the frequency was then decreased to 50 Hz at constant field strength and within 1 s all of the remaining droplets coalesced (Figure 4f–h).

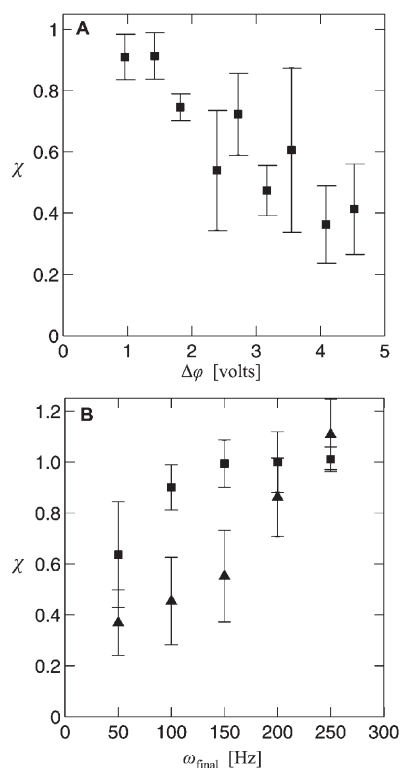


Figure 5. (A) Coalescence efficiency in response to a sudden frequency jump of 500 to 50 Hz for different applied potentials. The applied potential remained fixed at the specified voltage. (B) Coalescence efficiency in response to changes in the applied frequency, with an initial frequency of 500 Hz. The amplitude remained fixed at 4.5 V. (■) Gradual decrease of -25 Hz/10 s to the final frequency and (▲) sudden decrease to the final frequency. Error bars are standard deviations of at least three different clusters from each trial.

Notably, the coalescence occurred at higher applied potentials and lower applied frequencies, which are conditions that tend to increase the velocity of the EHD flow (which scales roughly as $u \sim \Delta\phi^2/\omega$). Thus, a plausible explanation for the coalescence is that the EHD flow “pushed” the droplets into close enough proximity, past the primary maximum,²⁸ for van der Waals interactions to become dominant and for coalescence to proceed by capillarity. Given the nanometer scale of the double layers, however, a more elaborate experimental setup will be required to probe the competition between colloidal scale forces and the EHD flow. Moreover, consistent with our previous observations, it appeared that most of the resulting large drops were adhered to the electrode.

Nonetheless, these observations confirm that coalescence occurs under appropriate electric field conditions. To determine the optimal conditions for maximizing coalescence, we systematically varied the change in electrical conditions and observed the resulting coalescence behavior. Here we define the coalescence fraction $\chi \equiv (N_{\text{final}} - 1)/(N_{\text{init}} - 1)$, where N represents the number of droplets in an individual cluster. Note that $\chi = 0$ corresponds to 100% coalescence and $\chi = 1$ corresponds to no change in the number of droplets. An important caveat is that it is possible to have $\chi > 1$ if, for example, little coalescence occurs but additional droplets join the cluster following the change in electric field conditions. Because of that complication, we emphasize that χ serves here as a semiquantitative indication of the coalescence efficiency.

The effect on χ for a sudden decrease in the frequency from 500 to 50 Hz at constant applied amplitude is shown in Figure 5a. Here, the droplets underwent aggregation for several minutes at

500 Hz and the specified applied potential and then the frequency was suddenly dropped to 50 Hz with no change in potential. Although some of the error bars are sizable, the overall trend is clear: more coalescence occurs for a sudden frequency decrease when the applied potential is higher. Again, one source of variability appears to stem from the enhanced tendency for the droplets to stick to the electrode at high field strengths during the aggregation phase, which prevents the drops from getting close enough for coalescence to occur.

The effect of the magnitude of the frequency jump is shown in Figure 5b, where two different types of frequency decrease are compared: gradual and sudden. In both cases, the drops underwent aggregation for several minutes at 500 Hz and 4.5 V and then the frequency was decreased to the indicated final frequency at constant applied potential. In the case of a sudden decrease, the frequency was dropped instantaneously (i.e., on a timescale of less than microseconds, limited by the response time of the function generator), but for the gradual decrease, the frequency was decreased instantaneously by 25 Hz every 10 s until the final frequency was reached. In both cases, lower final frequencies yielded lower values of χ . However, even for identical values of ω_{final} the coalescence fraction was significantly lower for the sudden frequency decrease, with approximately a factor of 2 difference for $\omega_{\text{final}} < 200$ Hz. This result suggests that the frequency “path” plays a role in the coalescence efficiency, possibly because the gradual decrease provides more opportunity for the droplets to stick to the electrode and impede coalescence. It is also possible, however, that the sudden decrease in frequency induces a surge in the EHD flow or another effect that provides an additional driving force for coalescence. Additional experiments are necessary to probe the cause of this frequency path dependence in more detail, but the key practical implication is that sudden frequency decreases are more effective at inducing coalescence.

To summarize, we have demonstrated that oil droplets in water aggregate and coalesce in response to oscillatory fields in a manner that is qualitatively consistent with a mechanism based on EHD flow. Several questions remain to be answered. First, the key difference between solid particles and liquid drops is that, in principle, slip velocities might occur at the oil/water interface.³⁰ If so, then a fundamental question is how the slip velocity affects the far-field EHD streamlines and the consequent rate of aggregation. Intriguingly, there is also the possibility that circulatory flow occurs inside the droplets themselves in a manner analogous to Taylor’s classic observations of flow inside leaky dielectric droplets.³¹ On a more practical level, the primary result here is that the electric field can induce droplet coalescence of micrometer-scale droplets. Because larger droplets are easier to separate by sedimentation, centrifugation, and membrane filtration, the results here suggest that EHD flow might serve industrially as a precursor step to initiate coalescence and simplify the removal of trace oils from solution. For example, a wastewater stream with emulsified oil droplets that must be removed could first be passed through a series of parallel electrodes (e.g., an EHD separator) with an oscillatory field applied between them. Provided that the droplets do not adhere to the electrode, aggregation and coalescence would occur and larger drops would be output from the separator. Future experiments will clearly benefit from an improved apparatus that substantially prevents droplet adhesion to the electrode; experiments along these lines are currently in progress.

(30) Baygents, J. C.; Saville, D. A. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1883–1898.

(31) Melcher, J. R.; Taylor, G. I. *Annu. Rev. Fluid Mech.* **1969**, *1*, 111–146.

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Supporting Information Available: Two movies. This material is available free of charge via the Internet at <http://pubs.acs.org>.