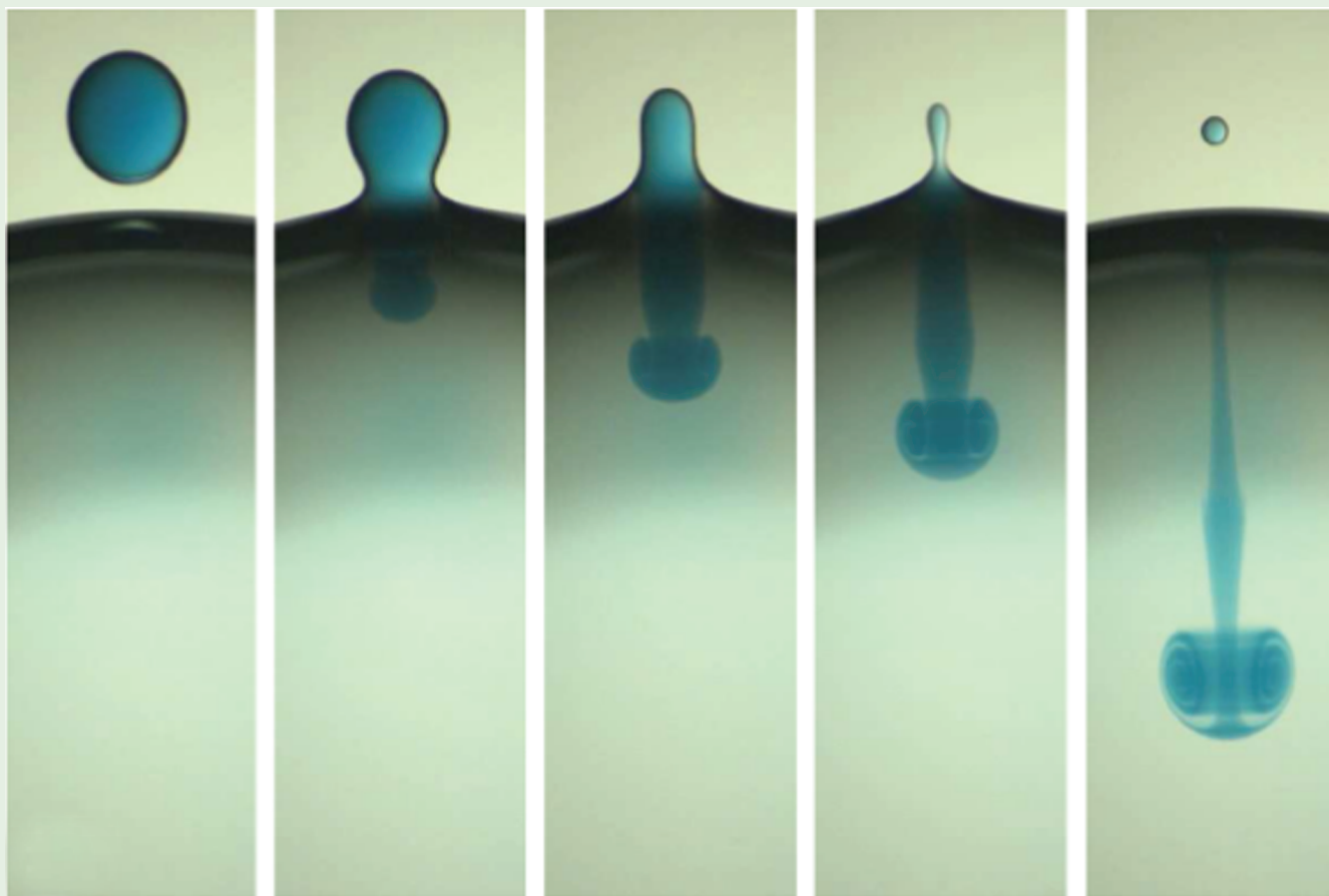


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Electrically Tunable Partial Coalescence of Oppositely Charged Drops

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We report the existence of a critical ionic conductivity below which oppositely charged drops only partially coalesce. The extent of coalescence between dissimilarly sized water drops in oil can be tuned from complete coalescence at low electric field strengths to complete noncoalescence at high field strengths, thus providing external control over the daughter droplet size. Strikingly, the size and charge of the daughter droplet are both independent of the ionic conductivity. We present evidence suggesting the charge transfer is instead strongly influenced by convection associated with the capillary-driven penetration of a vortex into the larger drop, and we demonstrate that the size of the daughter droplet is consistent with a scaling model based on a balance between capillary-driven inertia and electrostatic repulsion.

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A combined drop has less surface energy than two separate drops, so drops of the same liquid normally coalesce upon contact. Application of an electric field, however, can prevent even oppositely charged droplets from completely coalescing [1–6]. Electrically driven partial coalescence was first reported by Torza and Mason [1], who used electric fields to drive mutually immiscible droplets together; their photos show a daughter droplet being ejected, but they did not elaborate. Ristenpart *et al.* observed similar partial coalescence with charged water droplets moving through a variety of viscous oils [2]. Importantly, no daughter droplets were formed unless an electric field was applied, suggesting that this behavior is distinct from the ‘coalescence cascades’ that are driven by inertial recoil in sufficiently inviscid systems [7–9]. More recently, Aryafar and Kavehpour performed a systematic investigation of electrically induced partial coalescence, and they demonstrated that a critical field strength must be exceeded for a daughter droplet to be ejected [4]. They interpreted their observations in terms of the stability of a liquid jet, and they hypothesized that the daughter droplet results from a competition between the electric field and inertial-capillary forces. Although it is well established that the field strength [4,5] and interfacial tension [6] affect the partial coalescence process, the details of the charge transfer process into the daughter droplet have remained obscure. Most importantly, a fundamental question has remained unanswered: what controls the size and charge of the daughter droplet?

In this Letter, we report the existence of a critical ionic conductivity that governs the response of a small charged droplet contacting a larger, oppositely charged droplet. Below the critical conductivity, the droplets partially coalesce; above the critical conductivity, the droplets bounce off one another. In both cases charge transfer occurs, but counterintuitively the size and the charge of the resulting

daughter droplet are independent of the ionic conductivity. We present evidence that the charge transfer is instead strongly influenced by convection associated with the capillary-driven penetration of a vortex into the larger drop. The observations have important implications for practical applications where electric fields effect droplet coalescence, including, for example, electrostatic demulsifiers [10,11] and lab-on-a-chip devices [12–15].

The experimental apparatus is similar to that used by Ristenpart *et al.* [2]. A container with the bottom half filled with water and the top half with an immiscible and poorly conducting oil [polydimethylsiloxane (PDMS)] has metal wires inserted into each liquid (at top and bottom) to serve as electrodes (Fig. 1, left). The conductivity of the aqueous phase is controlled by varying the concentration of KCl. A high-voltage power supply provides a potential difference of the order of 1 kV over approximately 5 mm; the total current density is low despite the high potential because of the insulating oil. After application of the field, an approximately 1 μL water drop is pipetted manually into the oil near the top electrode. For a sufficiently strong field, dielectrophoretic effects [16] cause the drop to move towards and contact the top electrode, thereby providing the drop a net charge. The drop then moves downward toward the oppositely charged oil/water meniscus. Drop motion is recorded with high-speed video.

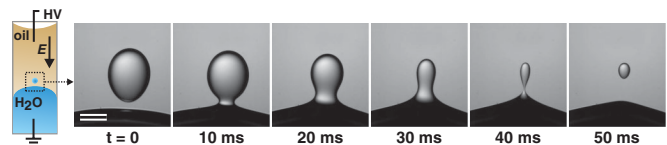


FIG. 1 (color). Left: diagram of the experimental apparatus. Right: time lapse images of a water droplet (1 mM KCl) undergoing electrically driven partial coalescence in 500 cSt PDMS oil. Field strength is 1.5 kV/cm; scale bar is 1 mm.

The behavior of a representative droplet is shown in Fig. 1 (right); see also the movies in the Supplemental Material [17]. The charged droplet initially moves downward electrophoretically, but the behavior following contact with the oil/water interface depends on the applied field strength. At sufficiently high field strengths the droplet ‘bounces,’ i.e., it briefly touches and immediately moves away [2]. At the other extreme of sufficiently low field strengths, the droplet completely coalesces. At intermediate field strengths, as shown in Fig. 1, the droplet only partially coalesces. Here the meniscus bridge initially forms and the droplet begins to coalesce, but partway through coalescence the meniscus bridge pinches off and a small daughter droplet is ejected. The daughter droplet moves away upward, indicating that it acquired the opposite charge following contact.

The behavior illustrated in Fig. 1 is qualitatively similar to previous observations of partial coalescence [1,2,4–6], but the following question remains: what controls the size of the daughter droplet? Since the electric field provides the driving force against coalescence, one might expect the daughter droplet size to scale simply with field strength. Our systematic quantitative measurements, however, indicate that the situation is not so simple. Figure 2(a) shows

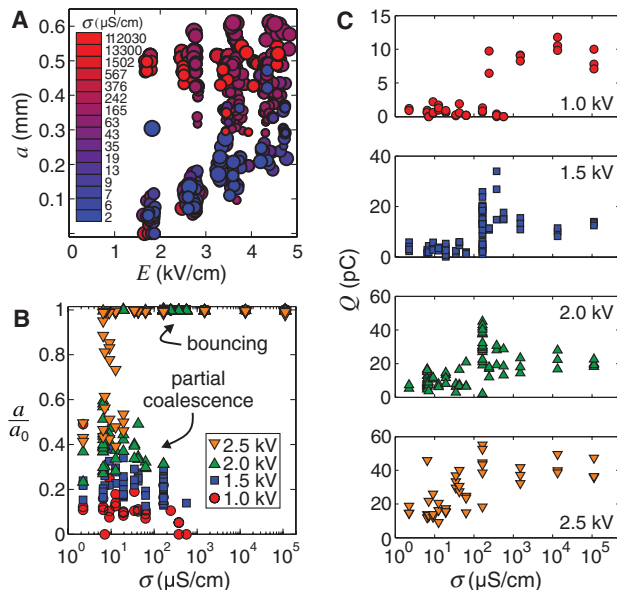


FIG. 2 (color). (a) The daughter droplet radius versus applied field strength in 500 cSt PDMS oil. Marker size is proportional to the initial droplet radius a_0 ; color indicates the conductivity of the aqueous phase as denoted at left. (b) The ratio of the daughter droplet radius to initial radius versus the ionic conductivity for different applied electric potentials: 1 kV (circles), 1.5 kV (squares), 2.0 kV (up triangles), 2.5 kV (down triangles). Note $a/a_0 = 0$ indicates complete coalescence, $a/a_0 = 1$ indicates bouncing, and intermediate values indicate partial coalescence. (c) The daughter droplet charge magnitude versus conductivity; note the varied vertical scales.

the observed daughter droplet radius a as a function of applied field strength E for 751 separate experiments. Two key trends are apparent. First, it is clear that the daughter droplet size does indeed increase with field strength, but only for some of the droplets. The second and more important observation is that the ionic conductivity of the aqueous phase has a tremendous impact on the behavior of the droplets. Specifically, the daughter droplet size varied with field strength for ‘low’ conductivity droplets [$\leq 100 \mu\text{S}/\text{cm}$, the blue to purple markers in Fig. 2(a)], but was less sensitive to field strength for more conductive droplets (purple to red markers). In other words, lower conductivity droplets tended to partially coalesce, whereas higher conductivity droplets tended to bounce.

This effect is seen more directly in Fig. 2(b), which shows the daughter droplet radius (normalized by the initial droplet radius a_0) as a function of conductivity. Figure 2(b) makes clear that above a critical ionic conductivity, the droplets invariably bounce, but below the critical conductivity they partially coalesce. The exact value of the critical conductivity depends on the applied electric potential. At 1 kV, the transition to bouncing occurred near $\sigma \approx 10^3 \mu\text{S}/\text{cm}$, whereas at 2.5 kV the transition occurred at the much lower value $\sigma \approx 50 \mu\text{S}/\text{cm}$.

The transition from partial coalescence to perfect bouncing likely stems from the increased probability of the droplet forming a Taylor cone with an angle unfavorable to coalescence (as discussed in detail elsewhere [2,3]); this interpretation is consistent with the observation that Taylor cones form more readily in fluids with higher conductivity [18]. Here we focus on the most surprising feature of Fig. 2(b), which is the pronounced insensitivity of the daughter droplet size to the conductivity. Although there is some scatter in the data, it is clear that for each measured voltage there is little variation in daughter droplet size with respect to conductivity. For example, at 1.5 kV the daughter droplet size was roughly $a/a_0 \approx 0.25 \pm 0.1$ over almost 3 orders of magnitude in conductivity.

This result is surprising because the droplets clearly acquire charge of the opposite sign during the partial coalescence event (as evidenced by their upward migration following pinch-off), and one normally would expect the ionic conductivity to control how much charge is transferred. Since the size of the daughter droplet presumably depends on how much electrical driving force is provided by the daughter droplet charge, the implication of Fig. 2(b) is that the daughter droplet charge is likewise independent of conductivity. Indeed, our measurements of the daughter droplet charge (estimated via droplet velocimetry, cf. Ref. [2]) indicate that the charge is insensitive to the droplet conductivity [Fig. 2(c)]. The daughter droplet charge magnitude Q depends on the applied potential and whether the droplet partially coalesces or bounces; aside for the transition between partial coalescence and bouncing, however, there is little variation in the charge transferred.

Thus, the key question is as follows: how can the charge (and hence size) of the daughter droplet not depend on the conductivity? Insight is provided by considering how charge transfer takes place during the partial coalescence event. In general, charge transfer through an aqueous phase consists of the motion of ionic species (e.g., K^+ or Cl^-) via three different mechanisms: diffusion, electromigration, and convection. The relative influence of convection is gauged by the Péclet number $Pe = \lambda_D u / D$, where u is a characteristic velocity, D is the ionic diffusivity, and $\lambda_D \approx 1$ to 100 nm is the Debye length scale that characterizes the width of the nonelectroneutral region where free charge resides. For typical electrokinetic problems in aqueous systems, $Pe \ll 1$ and the effect of convection on charge transfer is negligible [19–21].

Our high-speed video observations, however, indicate that convection during the partial coalescence event is far from negligible (Fig. 3). To visualize the fluid motion following contact, we added 0.01 g/mL of blue food coloring to the droplet and otherwise followed the same experimental procedure. As made clear in Fig. 3 (and in the movie in the Supplemental Material [17]), after the droplet makes contact a jet of fluid rapidly erupts downward from the coalescing drop. The leading edge of the jet develops a vortex, which moves downward at a velocity much higher than the initial velocity of the droplet prior to contact; the vortex continues to move downward even after the daughter droplet (in the oil phase) has pinched off and begun to migrate upward. Additional experiments with other types of dyes and tracer particles (not shown) confirm that the vortex generation is robust and insensitive to the particular type of dye used.

Qualitatively similar vortices, albeit without applied electric fields, were observed more than a century ago by J. J. Thomson [22], who investigated the complicated vortex dynamics and instabilities resulting from the impact of various types of liquid droplets (e.g., milk or ink) into another liquid reservoir. Thomson focused on droplets impinging with high kinetic energy, but subsequent work [23–25] has demonstrated that similar vortices can form even for zero impact velocity, provided there is a sufficient capillary pressure within the droplet. Specifically, in the

situation of interest here, there is a large disparity in the curvature of the freely moving droplet and the water below ($a_0 \ll a_{\text{bot}} \approx 7$ mm). Upon contact, the capillary pressure in the droplet is therefore larger by approximately $2\gamma/a_0$, where γ is the oil/water interfacial tension. This pressure difference will tend to drive fluid toward the bottom reservoir. If the cone angle upon contact is sufficiently small [2,3], then the curvatures and associated capillary pressures are favorable to growth of the neck, and fluid will begin flowing from the drop to the reservoir. Following Anilkumar *et al.* [23], the corresponding velocity may be estimated by assuming that the surface energy of the droplet is of order $a_0^2\gamma$, and that this energy is transformed into kinetic energy of order $\rho a_0^3 u^2$. Equating the two energies indicates the vortex velocity just following coalescence is of order $u \sim \sqrt{\gamma/\rho a_0}$. For 1-mm water droplets moving through PDMS oil ($\gamma \approx 30$ mN/m), the estimated velocity is 0.17 m/s.

Our high-speed video measurements of the vortex velocity yielded an average velocity of approximately 0.1 m/s, in accord with the scaling estimate [17]. Importantly, the applied electric field strength had little effect on the observed vortex velocity, at least over the experimentally relevant range of 0 to 5 kV/cm. This observation suggests that electrostatic effects contribute little to the vortex velocity. Moreover, the lack of electric field dependence, and corresponding impact velocity dependence (since drops travel more quickly in larger electric fields), suggests that the capillary energy overwhelms whatever kinetic energy the droplet has prior to coalescence. The key point is that our observations are consistent with the well-established phenomenon of vortex generation via a large difference in capillary pressure.

What has not been considered heretofore, however, is the effect of the jet on charge transfer and corresponding partial coalescence in the presence of an applied field. The tremendous velocity of the jet means that the Péclet number here is of order 1 to 10, indicating that convection is comparable in magnitude to diffusive effects. A more detailed scaling analysis of the relative magnitudes of electromigration and convection likewise indicates that convective effects are 1 to 2 orders of magnitude greater than the conductive contribution to charge transfer [17]. These estimates, coupled with the observed lack of dependence on the conductivity (cf. Fig. 2), suggest that convection and diffusion, not conduction, play the dominant role in the charge transfer process.

Because the direction of the convection is, at least initially, directed away from the droplet, a key implication of convective charge transfer is that charge primarily *leaves* the droplet rather than entering it. How, then, does the daughter droplet acquire the opposite charge? Note that prior to contact the droplet is highly polarized, i.e., the top half of the droplet already contains charge of the opposite sign. (For a sphere in an infinite medium, the surface charge varies as $\cos\theta$, where θ is the angle with respect

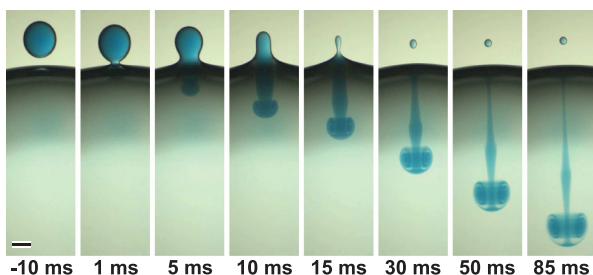


FIG. 3 (color). Time lapse images of vortex penetration during electrically driven partial coalescence. The oil is 350 cSt PDMS and the water has 1 mM KCl; the small drop contains 0.01 g/mL of blue food dye. The applied potential is 2.9 kV. Scale bar is 0.5 mm. See also the movie in the Supplemental Material [17].

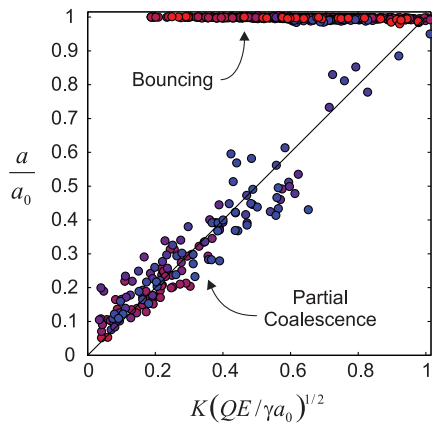


FIG. 4 (color). The daughter droplet size versus the electrocapillary scaling prediction, using the same data and color code as in Fig. 2(a). Here $K = 0.85$ is a dimensionless prefactor; the solid line has slope equal to one.

to the applied field [26].) While the charge at the leading (bottom) edge of the droplet is pulled away via convection, charge of the opposite sign remains near the top. This ‘residual’ dipolar charge becomes the net charge on the droplet, providing the electrophoretic driving force for pinch-off and the eventual migration away. A similar residual-dipole-charge mechanism was recently invoked to explain charge buildup in airborne solid particulates [27]; here we have the added complexity of changes in the droplet size during the charge transfer.

This interpretation suggests that the daughter droplet results from a competition between two opposing effects: an electrophoretic driving force that pulls the drop away, and the capillary-pressure-driven inertial acceleration in the opposite direction. A full description of these effects is challenging since the charge distribution on the moving, elongating droplet changes dynamically as it approaches contact. Nonetheless, we note that the electrophoretic force must scale as $F_E \sim QE$, where Q is the charge remaining on the daughter droplet following pinch-off and E is the applied field strength in the oil phase. Assuming that the initial cone angle favored coalescence, then the droplet starts penetrating the bulk liquid and forming a vortex. In this situation, the instantaneous inertia of the droplet scales as $\rho u^2 a(t)^2$. The kinetic energy of the vortex is ultimately dissipated by viscous shear stress as it penetrates the bulk liquid, but our measurements of the vortex velocity indicate that the velocity varies little during the course of coalescence [17]. Thus, to good approximation $u \approx \sqrt{\gamma/\rho a_0}$ is constant. Assuming that inertia balances the electrophoretic force when the droplet shrinks to size of order a , we obtain the scaling estimate

$$\frac{a}{a_0} \sim \left(\frac{QE}{\gamma a_0} \right)^{1/2}. \quad (1)$$

All of the experimentally measured daughter droplet sizes from Fig. 2(a) are replotted in Fig. 4 versus Eq. (1).

We see that the electrocapillary-inertial scaling prediction provides an excellent estimate of the daughter droplet size over a wide range, using the dimensionless prefactor $K = 0.85$ as the only adjustable parameter. One surprising consequence of this scaling argument is that the size of the daughter droplet is independent of the oil viscosity. Our measurements confirm that, provided the oil viscosity is sufficiently high so that inertial recoil does not occur in the absence of an applied field (i.e., for Ohnesorge numbers greater than 1), the daughter droplet size is indeed insensitive to the oil viscosity [17]. Although the probability of bouncing appears to increase at higher viscosities, when daughter droplets do form the size is insensitive to the magnitude of the viscosity. This observation suggests that the inertia in the aqueous phase overcomes the increased viscous drag in the oil phase, at least over the viscosity range tested.

In summary, we have demonstrated that oppositely charged, dissimilarly sized drops partially coalesce below a critical conductivity, and that a high velocity vortex generated by the large mismatch in capillary pressure plays an important role in both the charge transfer into and final size of the resulting daughter droplet. The observations presented here thus represent a rare instance of convectively mediated charge transfer in an aqueous system. In terms of practical implications, the use of more conductive liquids will be beneficial in applications where partial coalescence is undesired (such as in electrocoalescers [10]). Contrariwise, the electrically tunable size of the daughter droplet at low conductivities could be useful in lab-on-a-chip applications where specific droplet sizes are desired.

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