Coalescence of Electrically Charged Liquid Marbles

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In this work, we have investigated the coalescence of liquid water marbles driven by a DC electric field. We have found that two contacting liquid marbles can be forced to coalesce when they are charged by a sufficiently high voltage. The threshold voltage leading to the electro-coalescence depends sensitively on the stabilizing particles as well as on the surface tension of the aqueous phase. By evaluating the electric stress and surface tension effect, we attribute such coalescence to the formation of a connecting bridge driven by the electric stress. This liquid bridge subsequently grows and leads to the merging of the marbles. Our interpretation is confirmed by the scaling relation between the electric stress and the restoring capillary pressure. In addition, multiple marbles in a chain can be driven to coalesce by a sufficiently high threshold voltage that increases linearly with the number of the marbles. We have further proposed a simple model to predict the relationship between the threshold voltage and the number of liquid marbles, which agrees well with the experimental results. The concept of electro-coalescence of liquids marbles can be potentially useful in the use of liquid marbles as containers for chemical and biomedical reactions involving multiple reagents.

Introduction

Liquid water marbles are composed of water droplets in air encapsulated with a shell of particles.[1-5] They can be easily generated by depositing and rolling the water droplets on a layer of hydrophobic particles either manually[1] or automatically.[6] Similar to the particles adsorption on Pickering emulsions,[7-9] these hydrophobic particles can also irreversibly absorb on the liquid-air interfaces to the minimize surface energy,[1] making droplets non-wetting and non-sticky with the substrate. Therefore, liquid marbles are excellent carriers for transporting and handling small volumes of liquids in air.[5,10-14] They have been shown to be a promising platform for different droplet-based applications, including water pollution detection,[15] gas sensing,[16] as micro-pumps,[14] for optical absorbance detection[12] and for fabrication of color pigments.[17] In particular, liquid marbles are advantageous when used as miniaturized reactors for chemical reaction[11, 12] and bioassays.[18-20] The amount of reagents as well as the reaction time can be significantly reduced due to the small volume of liquids involved.[11] In these micro-reactor applications, each liquid marble encapsulates one type of reagent or ingredient. By manipulating them to coalesce, the encapsulated reagents can mix and the corresponding reactions or tests can be initiated.[11,18] Currently, most of these concepts and ideas are demonstrated by manually pushing the liquid marbles to move or coalesce. However, manual manipulation of liquid marbles is inefficient and tedious when a large quantity of sample is involved, hence limiting the realization of the potential of liquid marble-based liquid handling. Therefore, on-demand and fast coalescence of liquid marbles controlled by external forces is highly desired.[13] For instance, a magnetic field has been applied to initiate the coalescence between marbles coated by magnetic particles.[11, 12] However, this approach is only applicable to liquids which can be coated by specific magnetic particles. With the exception of a recently reported method that achieves the opening and closing of liquid marbles using acoustic levitation,[21] general approaches which do not rely on the unique properties of the coating particles or liquids for manipulating the liquid marbles in a controlled manner are rarely explored.

In this work, we propose to manipulate the coalescence of liquid marbles by applying an electric field. An electric field has been demonstrated previously as an efficient tool for deforming the liquid interface,[22-25] for demulsifying emulsions stabilized by surfactants[26,27] or colloidal particles[28] as well as for actuating liquid marbles.[2,13,29-31] A systematic study of the coalescence of liquid marbles driven by an electric stress is reported here for the first time. We found that two contacting liquid marbles can be forced to coalesce efficiently upon applying a voltage above a threshold value. We have systematically studied the dependence of this threshold voltage on various parameters and found it to be significantly influenced by the diameter of the coating particles and the surface tension of the liquid core. We attribute the electro-coalescence of liquid marbles to the electric stress that deforms the liquid interfaces to form a bridge and initiate coalescence. This interpretation is confirmed by evaluating the magnitude of the electric stress as well as the surface tension stress. In addition, we have found a sufficiently high voltage can also lead to the coalescence of multiple liquid marbles. By treating a chain of liquid marbles as a series of electric capacitors, we propose a simple model to predict the dependence of the threshold voltage on the number of liquid marbles; the model predictions agree well with the experimental results. Our approach of imposing an electric stress offers a general, robust and feasible way to manipulate the coalescence of liquid marbles, which is a breakthrough potentially needed to trigger liquid marble-based applications such as chemical or biomedical reactions.

Experimental

Materials

Liquid marbles were prepared by coating aqueous solutions with particles. The electrical conductivity of the liquid □was tuned by adding different concentrations (≤ 10^{-1} M) of sodium chloride (AR, Aladdin, China) in deionized water (Direct-Q, Merck Millipore, Germany) and measured using an electrical conductivity meter (CONT 610, EUtech Inc.). The viscosity of the liquid □was varied by dissolving different concentrations (≤ 2 wt.%) of sodium alginate (BioReagent, Aladdin, China) in water, and measured using a viscosity meter (µVISC, Pheosense Inc.). The surface tension of the liquids □was changed by dissolving different concentrations (≤ 8×10^{-3} M) of sodium dodecyl sulfate (AR, Aladdin, China) in water and measured using the pendant drop method.[32,33] The coating particles included PTFE grains (diameter = 35 µm, contact angle = 110° , Sigma-Aldrich, USA), silicone particles (diameter = 2.0 µm, 4.5

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μm or 6.0 μm, contact angle = 91°, Momentive Performance Material Inc., Japan) as well as silica particles (diameter = 92 μm, Qinhuang Glass Microsphere, China), the latter being rendered hydrophobic (contact angle = 112°) using trimethoxy(octadecy)silane (technical grade, Sigma-Aldrich, USA) following the protocol in ref.[34].

Liquid marble formation

To form liquid marbles, we deposited water droplets on a glass substrate covered by a layer of particles. The volume V of the liquid marble (from 3.6 μL to 16.1 μL) was precisely controlled by dispensing droplets vertically through nozzles with various diameters[35]. The droplets were then rolled around five times to ensure a full coverage of particles on the surface. After formation, these liquid marbles were transported to a PDMS substrate (Dow Corning, USA). Two marbles were pushed to contact each other for subsequent experiments.

Electro-coalescence of liquid marbles

To apply a DC voltage, we inserted electrodes made of metal wires into the liquid marbles to charge them using a high voltage supply (Tianjin Dongwen, China), as shown schematically in Figure 1(a).The applied voltage U was gradually increased until the liquid marbles coalesce (they are in contact before application of the field). The corresponding current I was monitored by an electrochemical workstation (660E, CH Instrument, USA). In the meantime, the morphology of the marbles was recorded by a high speed camera (Phantom v9.1, USA) coupled with a commercial lens (AF Nikkor, Nikon, Japan). The frame rate was set to be 500 fps. All the experiments were carried out at a temperature of 24 ± 1 °C and at a relative humidity of 50 ± 5%. For any pair of marbles, the experiments are repeated at least 10 times to determine U_c.

Results and discussion

Electro-coalescence of two liquid marbles

Two bare liquid droplets will coalesce into a single one following an initial contact, seeking to minimize the surface energy. When two liquid marbles contact each other however, such coalescence may be avoided since the presence of two particle layers prevents the direct contact of the liquid surfaces. To trigger the coalescence, we apply an increasing DC voltage to two contacting liquid marbles. When the applied voltage is small, the two contacting liquid marbles remain stable (Figure 1(b), insert: -4 ms). Such a stable state is also indicated by the nil current in the electric circuit shown in Figure 1(b). Interestingly, when the applied voltage is increased above a critical value U_c, the two liquid marbles coalesce into a single one. For instance, two water marbles coated with PTFE particles coalesce within several milliseconds at a threshold voltage of 300 V, as shown in Figure 1(b), inserts: 0 ms-8 ms. The coalescence event is also reflected by the significant increase in the current, also shown in Figure 1(b). The critical voltage for electro-coalescence of liquid marbles is much larger than that for w/o emulsions stabilized by surfactant, typically on the scale of 1V.[26,27,36] After electro-coalescence, the surface area of the marble is significantly reduced, leading to a more densely packed particle layer than in the two original marbles. Therefore, the coalesced liquid marble remains in the non-spherical shape for a long time as the relaxation of the liquid surfaces is resisted by the particle layer.

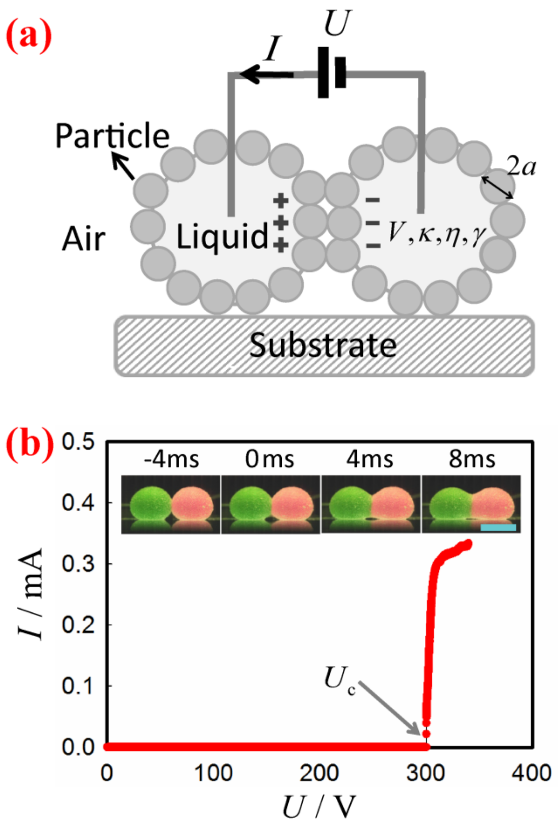

Figure 1. (a) Schematic of the coalescence of two charging liquid marbles resting on a PDMS substrate. V, □,□ □are the volume, electrical conductivity, viscosity and surface tension of the liquid core respectively; a is the radius of the stabilizing particles. The voltage U is applied through the electrodes inserted into the liquid marbles. The current I is monitored through an ammeter during the coalescence process. (b) Evolution of the current passing through the liquid marbles when the voltage applied to them gradually increases. Here, the liquid marbles are formed by coating water droplets of volume 8.8 μL with 35 μm PTFE particles. Coalescence occurs when the voltage exceeds a critical value, U_c = 300 V. Insert: optical images showing the coalescence (starting at 0 ms) between two liquid marbles at the critical voltage; scale bar = 2 mm. Dyes are added to the marbles for visualization.

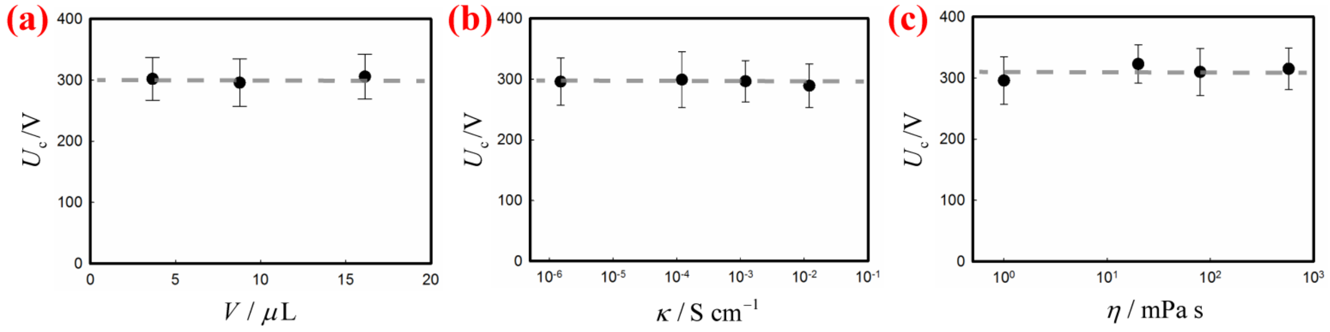

Figure 2. (a) Dependence of critical voltage U_c on the volume V of the liquid marbles. The liquid marbles are water droplets coated by 35 µm PTFE particles. (b) Dependence of critical voltage U_c on the electrical conductivity σ of the liquid. The liquid marbles of volume 8.8 mL are formed by coating droplets of aqueous sodium alginate with 35 µm PTFE particles. (c) Dependence of critical voltage U_c on the viscosity η of the liquid. The liquid marbles of volume 8.8 mL are aqueous NaCl droplets coated by 35 µm PTFE particles.

In order to understand the origin of the threshold voltage responsible for the electro-coalescence of liquid marbles, we first investigate the influence of the volume V and the electrical conductivity σ of the liquid core on the threshold voltage U_c. Considering that both V and σ can directly affect the electrical resistance of the liquid core, we expect U_c may change accordingly. Surprisingly, the results indicate that, for the liquid marble with a volume V ranging from 3.6 µL to 16 µL, the critical voltage U_c is more or less constant, as shown in Figure 2(a). Similarly, the critical voltage remains identical when the electrical conductivity of water is significantly increased from 1.5×10^{-6} S cm^{-1} to 1.2×10^{-2} S cm^{-1}, as shown in Figure 2(b). We attribute these results to the extremely high electrical resistance of particle layers compared to that of the water core considering that air[37] ($\sigma_{air} = 3\text{-}8\times10^{-15}$ S cm^{-1}) is much less conductive than water[38] ($\sigma_{deionized\ water} = 5.5\times10^{-6}$ S cm^{-1}). As such, the applied voltage mainly falls on the particle layers that separate the marbles rather than the liquid cores of the marbles. Therefore, any change in electrical resistance of the liquid core cannot affect the threshold voltage significantly. These results imply that it is the voltage drop across the particle layer (through air) that contributes to the electro-coalescence of liquid marbles. Moreover, we have studied the effect of the liquid viscosity η on the critical voltage U_c. The results also show that the critical voltage is independent of the liquid viscosity as U_c does not change considerably when η increases from 1 mPa s to 576 mPa s (Figure 2(c)). This suggests that the dynamic drainage of liquid does not contribute significantly during the electro-coalescence events.

By contrast, the threshold voltage U_c depends markedly on the radius a of the stabilizing particles as well as on the surface tension γ of the liquid. We systematically measure U_c of the liquid marbles fabricated by coating the surfaces of water droplets with silicone particles of various sizes and with hydrophobic silica particles of one large size. The results indicate that U_c increases significantly as the size of the particles increases, as shown in Figure 3(a). In addition, when the surface tension γ of water is varied by addition of SDS surfactant, the corresponding U_c decreases with decreasing γ (Figure 3(b)).

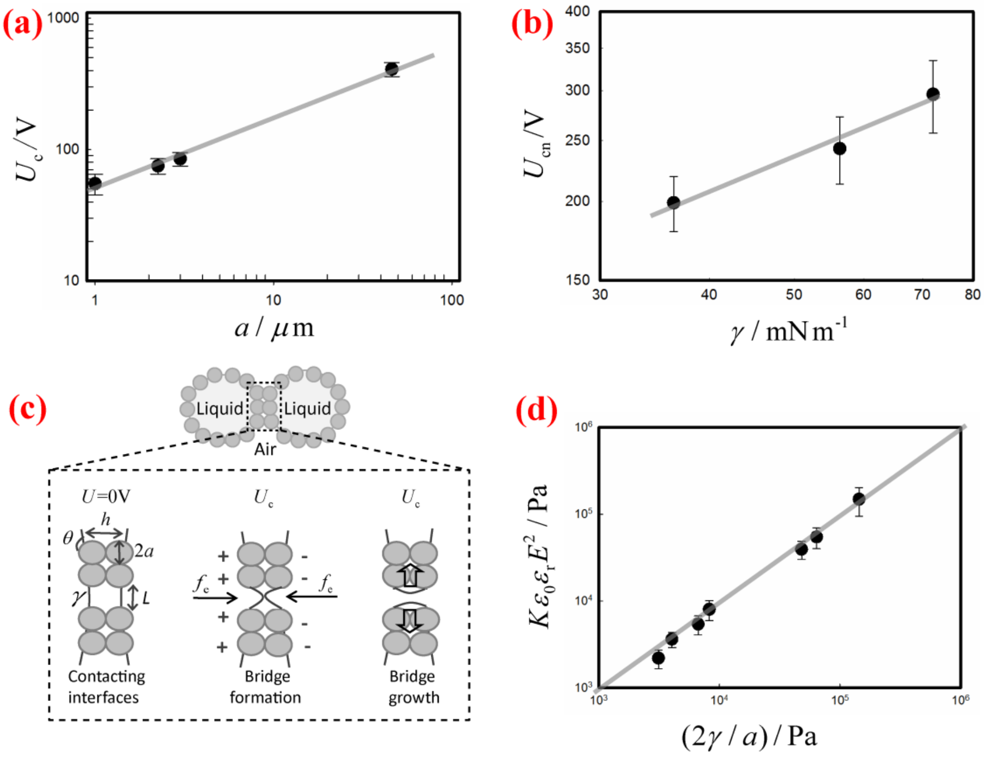

Figure 3. (a) Log-log plot demonstrating the dependence of threshold voltage U_c on the radius a of the stabilizing particles. The line has a slope of 0.5. The liquid marbles are formed by coating water droplets of volume 8.8mL with silicone or hydrophobic silica particles of different radii a. (b) Log-log plot demonstrating the influence of surface tension γ of the liquid on the critical voltage U_c. The plot is logarithmic. The line has a slope of 0.5. The liquid marbles are formed from water with or without surfactant coated of volume 8.8mL with 35 mm PTFE particles. (c) Sketch of the electro-coalescence process of liquid marbles. The electric stress f_e deforms the liquid interfaces within the particle shells to form a liquid bridge against the surface tension γ. (d) Log-log plot of the electric stress $K\varepsilon_0\varepsilon_r E^2$ *versus* the capillary pressure $2\gamma/a$ for all the systems of (a) and (b). Here, K = 0.3 is a dimensionless pre-factor; the line has a slope of unity.

To understand the threshold voltage U_c responsible for the electro-coalescence of liquid marbles, we analyze the stresses on the particle-stabilized interfaces by referring to recent work on Pickering emulsions.[28] When a voltage U is applied between the two contacting liquid marbles, the opposing particle-stabilized liquid interfaces are oppositely charged with most of the applied voltage drop occurring across them, as shown schematically in Figure 3(c). The charging induces an electric stress f_e on the liquid interfaces, which scales as $\varepsilon_0\varepsilon_r E^2$, where $\varepsilon_0\varepsilon_r$ is the permittivity of the liquid and E is the local electric field strength defined as U/h. The separation distance h between liquid interfaces can be estimated as $h \sim 2a(1-\cos □)$ with a being the radius of the particles and □ being the contact angle they exhibit with the interface measured through water. Such an electric stress would deform the liquid interface to form a conical tip within the particle shells. When the electro-deformation is pronounced enough, a liquid bridge would form and subsequently grow to cause coalescence,[28,39] as shown schematically in Figure 3(c). However, the electro-deformation of the liquid interfaces is resisted by a restoring capillary pressure that scales as $2□L$, where L is the local radius of the formed tips (Figure 3(c)). Typically, the coating particles are closely packed at the liquid-air interfaces in a hexagonal pattern.[40] Recent work on Pickering emulsions indicates that some defects exist randomly at the interfaces,[28] with a size on the same scale as the particle diameter. Such defects are the most likely places where the coalescence starts. Similarly, these defects also exist in our formed liquid marbles. By inputting $L \sim a$, and values of $□_r$ U_c, a, and □ we can evaluate the competition between the electric stress $□_0□_r E^2$ and the restoring capillary pressure $2□a$. Following this, we re-plot the data in Figure 3(a) and Figure 3(b) with axes of $K□_0□_r E^2$ and $2□a$ in Figure 3(d), where K = 0.30 is a dimensionless pre-factor. Indeed, the electric stress and the restoring capillary pressure are of the same order of magnitude and all the results collapse onto a line with a slope of unity, in agreement with our hypothesis. Considering our scaling relation is modified from the work of Chen *et al.*[28] by including the role of contact angle, we have also compared the dimensionless pre-factor between liquid marbles and Pickering emulsions. Using typical values of the relevant variables in Pickering emulsions ($□_r$ = 78.5, U_c = 80 V, a = 3 mm, □ = 133° and □ = 30 mN/m)[28] in our modified scaling relation, we deduce K = 0.24, which is close the value obtained for liquid marbles. Moreover, following the scaling relationship $□_0□_r E^2 \sim 2□a$, we can deduce the dependence of the threshold voltage on the particle diameter and surface tension as U_c µ $a^{0.5}$ and U_c µ $□^{0.5}$ respectively. Indeed, these two predicted relations agree well with our experimental data, as indicated by the solid lines in Figure 3(a) and Figure 3(b). Therefore, we conclude that it is the electro-driven deformation of the liquid interface at the defects that triggers the electro-coalescence between two touching liquid marbles. W

Electro-coalescence of multiple liquid marbles

Apart from two marbles, a sufficiently large voltage can cause the coalescence of a chain of multiple marbles. By simply applying a sufficiently high voltage to the liquid marbles at the two ends of the chain, we can trigger the electro-coalescence of 3, 4 and 5 marbles as shown in Figure 4(a). We find that the threshold voltage required for coalescence simply increases with the number of marbles: U_c = 664 ± 23 V for 3 marbles, U_c = 950 ± 26 V for 4 marbles and U_c = 1224 ± 43 V for 5 marbles respectively.

To interpret the dependence of threshold voltage U_{cn} on the number of marbles n, we first investigate the voltage drop for each pair of liquid marbles. When a voltage is applied across two liquid marbles, most of the voltage drop is across the air gap between the liquid surfaces. Therefore, we can treat the air gap that exists between each pair of neighboring marbles as a capacitor. Based on this, when n liquid marbles in a chain are charged by a voltage U, the corresponding analogous circuit is (n-1) capacitors in series connected to the power source, as shown schematically in Figure 4(b). For each capacitor, the corresponding voltage drop is $U/(n-1)$. The liquid marbles start to coalesce when the voltage drop on each capacitor exceeds the threshold voltage of two marbles: $U/(n-1) > U_c$. Therefore, the critical voltage leading to the coalescence of multiple marbles can be written as $U_{cn} = (n-1)U_c$. To vindicate this simple model, we measured the threshold voltages for different numbers of water marbles. Indeed, the results show that the critical voltage U_{cn} increases linearly with the number of the marbles n as seen in Figure 4(c), which agrees well with our model. Moreover, the slope of the line is around 300 V, which is equal to the threshold voltage U_c of two marbles, in excellent agreement with our prediction.

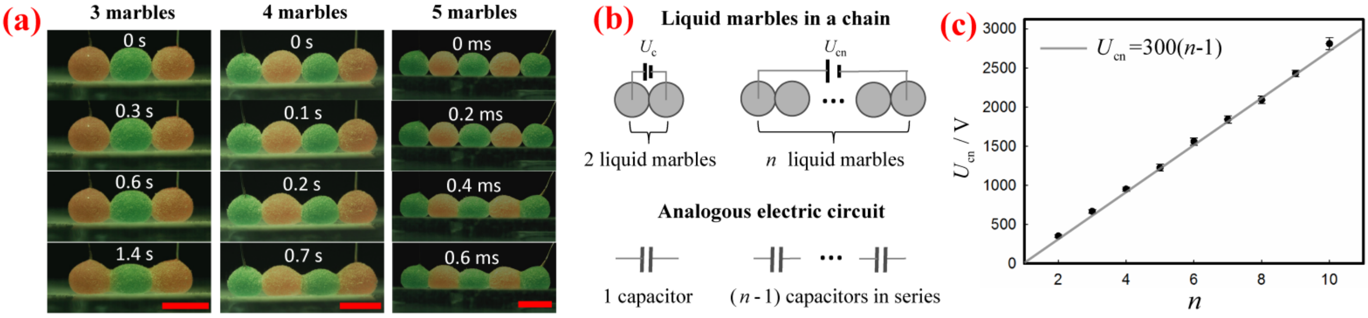

Figure 4. (a) A chain of liquid marbles can be driven to coalesce under a sufficiently high applied voltage across them. Here, the electro-coalescence of 3, 4 and 5 marbles is demonstrated. Scale bars = 3 mm. (b) Sketch of a chain of liquid marbles charged by a voltage and its analogous electric circuit. (c) A plot of the critical voltage (U_{cn}) for coalescing multiple marbles *versus* the number (n) of marbles. The line represents U_{cn} = 300(n-1). All the liquid marbles are fabricated by coating 2 wt.% aqueous sodium alginate droplets of volume 8.8 mL with 35 µm PTFE particles.

Conclusions

In this work, we have investigated the electrically-controlled coalescence of two and multiple liquid marbles in a chain. We have found that two oppositely charged liquid marbles coalesce above a threshold applied voltage. We show that such coalescence occurs when the electric stress exceeds the surface tension and deforms the liquid interface to form a liquid bridge connecting the liquid marbles. This bridge subsequently grows and eventually leads to the coalescence of the marbles. Moreover, we have extended our approach of the electro-coalescence of two marbles to multiple marbles. By treating a chain of liquid marbles as a series of electrical capacitors, we put forward a simple model to predict the threshold voltage for electro-coalescence based on the number of liquid marbles, with excellent agreement with experiment. Our approach as well as understanding of electro-assisted coalescence of liquids marbles facilitates a more widespread use of large number of liquid marbles as containers for chemical and biomedical reactions where controllable mixing of liquid reagents represents a current limitation.

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