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Electrohydrodynamic manipulation of particles adsorbed on the surface of a drop

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Abstract

In our previous studies we have shown that particles adsorbed on the surface of a drop can be concentrated at its poles or equator by applying a uniform electric field. This happens because even when the applied electric field is uniform the electric field on the surface of the drop is nonuniform, and so particles adsorbed on the surface are subjected to dielectrophoretic (DEP) forces. In this paper, we study the behavior of adsorbed particles at low electric field frequencies when the drop and ambient liquids are weakly conducting dielectric liquids, and model it using a leaky dielectric model. The electrohydrodynamic (EHD) flow which arises because of the accumulation of charge on the surface of the drop can be from pole-to-equator or equator-to-pole depending on the properties of the drop and ambient liquids. The flow however diminishes with increasing frequency and there is a critical frequency at which the drag force on a particle due to the EHD flow becomes equal to the DEP force, and above this critical frequency the DEP force dominates. When the fluid and particles properties are such that the EHD and DEP forces are in the opposite directions, particles can be collected at the poles or the equator, and also can be moved from the poles to the equator, or *vice versa*, by varying the frequency. Also, it is possible to separate the particles of a binary mixture when the critical frequencies of the two types of particles are different.

1. Introduction

Considerable attention has been given in recent years to understand the behavior of particles trapped at fluid-fluid interfaces because of the importance in a wide range of applications, e.g., the self-assembly of particles resulting in novel nano structured materials, micro/nano manufacturing, formation of Janus particles, the stabilization of emulsions, etc.[1-7]

The use of particle stabilized emulsions has increased in the food, biomedical and materials industries since they offer many advantages over those stabilized using surfactants.[8-9] For example, colloidal particles at the interface can be manipulated using external magnetic or electric fields[10], as we do in this paper, or by changing the temperature or the pH. The latter has been exploited to control particle stabilized capsules for controlled and targeted release of drugs. pH responsive particles can stabilize or destabilize emulsions depending on the pH value. Also, in biomass refining reactions, particles at the liquid interfaces can serve the dual purpose of stabilizing emulsions and acting as catalyst.[11] Future progress in this area will critically depend

upon our ability to understand and accurately control the particle arrangement for a broad range of particles of various types, sizes and shapes.[12,13]

It is known that a drop placed in a uniform electric field, under perfect dielectric conditions, deforms into an axisymmetric ellipsoid (prolate shape), with the major axis along the direction of the field.[14,15] The degree of deformation depends on the electric Weber number, which compares the stress due to electric field to interfacial tension between the two fluids. It was shown by Allen and Mason[14] and by Taylor[15] that there is a critical Weber number at which drops break apart or tip-stream.

However, under a leaky dielectric condition, where either or both fluids are weakly conducting, a drop can deform to a prolate or to an oblate shape. Deformation of a drop to an oblate shape has been noted to be due to a small but finite electrical conductivity of the fluids.[14-18] Due to this conductivity, charge migration to the drop's surface creates a transverse electric stress imbalance, which generates an electrohydrodynamic (EHD) flow, inside and outside of drop. The direction of the EHD flow depends on the ratios $R_r = \frac{R_d}{R_s}$, and $q = \frac{k_d}{k_s}$, where R_d and R_s are respectively the drop and ambient liquids resistivities, while k_d and k_s are dielectric constants of the drop and ambient liquids, respectively. When the EHD flow is from equator-to-pole the drop deforms into a prolate shape and when the EHD flow is from pole-to-equator into an oblate shape. The former is the case when $R_r q > 1$ and the latter is the case when $R_r q < 1$. The drop does not deform for $R_r q = 1$, since there is no induced flow in this case. This flow has been exploited in several recent studies to manipulate the distribution of adsorbed particles.[6,7,19,20] Particles collect at the poles when the EHD flow is from equator-to-pole and at the equator when the EHD flow is from pole-to-equator. The poles are defined as the two points on the drop which are nearest to the electrodes, and the equator is the curve at equidistance from the poles.

It has been shown that particles distributed on the surface of a perfectly dielectric drop immersed in a perfectly dielectric liquid can be concentrated at its poles or the equator by subjecting it to a uniform electric field, [21-24] and that this method can be used to separate on the surface of a drop those particles experiencing positive dielectrophoresis from those experiencing negative dielectrophoresis. The approach works also when the liquids are weakly conducting provided an ac electric field of sufficiently large frequency is used. In this paper, we show that the frequency of an electric field is an important parameter which can be used to adjust the intensities of the dielectrophoretic (DEP) and EHD flow induced forces on surface-absorbed particles, and thus control their distribution on the surface.

The key idea behind this study is that, under leaky dielectric conditions, surface-adsorbed particles can be effectively controlled by varying the frequency; by being able to move them to the poles or equator by applying electric fields with different frequency regimes. The EHD flow decays with increasing frequency and so the EHD flow induced drag force decreases with increasing frequency. The DEP force acting on particles depends on the real part of Clasius-

Mossati factor which does vary but varies relatively slowly with frequency. Therefore, there exists a critical frequency above which the DEP force dominates. A possible application is that when the two forces are directed in the opposite directions the approach can be used to move particles to poles or equator by tuning to the right frequency regime. The approach is superior to traditional dielectrophoresis since the critical frequency is a function of particle and fluids properties and the frequency can be varied easily which makes the approach easier to implement.

The paper is organized as follows: we first describe the various forces that act on an adsorbed particle, which is followed by a description of our experimental procedure, and then presentation of results.

2. Drops in ac electric fields

Torza *et al*. used the leaky dielectric model to calculate the axisymmetric flow induced outside and inside of a drop in an ac electric field.[18] The focus of this work is on the tangential component of the flow on the surface of the drop which can cause particles adsorbed on the surface to move towards the poles or the equator. The tangential velocity contains a steady component and a periodic component. The frequency of the latter is twice the frequency of the applied ac electric field. The periodic component causes particles to oscillate back and forth and so does not cause a net displacement. The steady component of the velocity on the surface of the drop which causes particles to collect at the poles or the equator (in spherical coordinates) is given by[18]

$$U_S = \frac{18\varepsilon_0 k_s E_0^2 b R_r \left(R_r q - 1\right)}{20\mu_s \left(1+\lambda\right)\left(2R_r+1\right)^2 + a^2\omega^2\left(q+2\right)^2} \sin\theta\cos\theta \ , \tag{1}$$

and the periodic component is given by

$$U_T = U_S \frac{\sqrt{R_r^{\,2} + a^2\omega^2}}{R_r} \cos\left(2\omega t + \alpha\right), \tag{2a}$$

where ε_0 is the permittivity of free space, E_0 is the amplitude of the ac electric field, b is the drop's radius, μ_s is the ambient liquid viscosity, λ is the drop to ambient liquid viscosity ratio, ω is the angular frequency of the field, $a = \varepsilon_0 R_d \mathrm{k}_s$, and θ is the azimuthal angle. The value and sign of α is defined by these expressions:

$$\sin\alpha = \frac{a\omega}{\sqrt{R_r^{\,2} + a^2\omega^2}} \frac{\left(2R_r+1\right)\left(1-2qR_r-2R_r\right) - a^2\omega^2\left(q+2\right)^2}{\left(2R_r+1\right)^2 + a^2\omega^2\left(q+2\right)^2} \tag{2b}$$

$$\cos\alpha = \frac{1}{\sqrt{R_r^{\,2} + a^2\omega^2}} \frac{\left(2R_r+1\right)^2 R_r - a^2\omega^2\left(q+2\right)\left(R_r q - 2R_r - 2\right)}{\left(2R_r+1\right)^2 + a^2\omega^2\left(q+2\right)^2} \tag{2c}$$

Notice that the sum of the steady and unsteady components changes direction during each period as the amplitude of the unsteady component is larger than that of the steady component. However, when $a\omega$ is much smaller than R_r, the amplitude of the periodic component is

approximately equal to the steady component, and so when the steady and unsteady components are in the same direction the net flow becomes about twice as large as the steady component and about zero when they are in the opposite directions. On the other hand, when $a\omega$ is comparable or larger than R_r, the amplitude of the periodic component can be much larger than the steady component, and so the velocity changes direction during each period. Thus, in the former case, the EHD flow causes particles adsorbed on the surface to move approximately steadily towards the poles or equator. In the latter case, they reverse direction for a part of the period, but the net motion during each period is towards the poles or equator depending on the direction of the steady component. The interfacial force keeps adsorbed particles on the surface as they move along the surface because of the flow.

The flow causes a particle adsorbed on the surface to experience a drag force in the direction tangential to the interface. This electrohydrodynamic (EHD) flow induced drag can be computed using Stokes' law, since the velocity magnitude is relatively small, and it is given by

$$F_{eh} = 3\pi(\mu_d + \mu_s)R\left(U_S - U_p\right). \quad (3)$$

Notice that the EHD drag is computed in terms of the steady component U_S of the EHD velocity since it alone causes a net displacement of the particle. The fluid viscosity is taken to be the average viscosity of the ambient liquid and the drop liquid, R is the particle radius, and U_p is the particle velocity. Assuming that the particle velocity is zero, using equations (1) and (3), we obtain

$$F_{eh} = \frac{27\pi k_s \varepsilon_0 E_0^2 bRR_r\left(R_r q - 1\right)}{10\left(2R_r + 1\right)^2 + a^2\omega^2\left(q + 2\right)^2}\sin\theta\cos\theta. \quad (4)$$

Notice that the force decreases with increasing electric field frequency and increases with increasing drop radius and increasing electric field strength. For the cases considered in this paper, it was the dominant force at small frequencies. Therefore, at small frequencies, the final location of particles adsorbed on the surface of a drop was determined by the direction of the EHD force. The strength of EHD flow diminishes with increasing frequency since it takes a finite amount of time for charges to migrate to the surface. Equation (4) also implies that the EHD force is zero both at the poles $(\theta = 0, \pi)$ and at the equator $(\theta = \frac{\pi}{2})$, and maximum at $\theta = \frac{\pi}{4}$.

2.2 Dielectrophoretic force on adsorbed particles

A particle adsorbed on the surface is also subjected to a DEP force and to a buoyant weight. The DEP force becomes dominant when the frequency is increased above a critical value and the electric field strength is sufficiently large such that it is larger than the buoyant weight. The point dipole (PD) approximation can be used to obtain an expression for the dielectrophoretic (DEP) force that acts on a particle of radius R trapped on the surface of a spherical drop of radius b.[21] The tangential component of the DEP force (in spherical coordinates) is given by the following expression (see figure 1):

$$F_{DEP,\theta} = -12\pi R^3 \frac{1}{b}\varepsilon_0 k_s E_0^2 \beta' \beta(2+\beta)\cos\theta \sin\theta \,. \qquad (5)$$

Here, $\beta(\omega) = Re\left(\frac{\varepsilon_d^* - \varepsilon_s^*}{\varepsilon_d^* + 2\varepsilon_s^*}\right)$ is the drop's Clausius-Mossotti factor, and $\beta'(\omega) = Re\left(\frac{\varepsilon_p^* - \varepsilon_s^*}{\varepsilon_p^* + 2\varepsilon_s^*}\right)$ is the particle's Clausius-Mossotti factor with respect to the outer fluid. ε_p^*, ε_d^* and ε_s^* are the frequency dependent complex permittivities of the particle, the drop and ambient fluids, respectively. The complex permittivity $\varepsilon^* = \varepsilon - j\sigma/\omega$, where ε is the permittivity, σ is the conductivity and $j = \sqrt{-1}$. The above expression is also valid for a dc electric field in which case E_0 denotes the electric field intensity. Notice that the magnitude of force on a particle of given radius increases with decreasing drop size. Particles trapped on the interface also interact with each other via the dipole-dipole (D-D) forces,[24-28] which are not included in eq. (5). The PD model accurately predicts the DEP and D-D forces for small particles at small concentrations, but for larger particles, numerical computations based on the Maxwell stress tensor needs to be conducted to obtain accurate estimate of the force.[29]

Equation (5) implies that the DEP force is zero both at the poles $(\theta = 0, \pi)$ and at the equator $(\theta = \frac{\pi}{2})$, and maximum at $\theta = \frac{\pi}{4}$. Furthermore, it implies that if $\beta\beta' > 0$, particles aggregate at the poles because they are in a state of stable equilibrium at the poles and if $\beta\beta' < 0$, they aggregate at the equator where their equilibrium is stable (see figure 1b).

2.3. Total force on adsorbed particles

The total tangential force acting on a particle can be obtained by adding the contributions given by eqns. (4) and (5), and the buoyant weight of the particle

$$F_t = \left[\frac{27\pi R_r\left(R_r q - 1\right)}{10\left(2R_r+1\right)^2 + a^2\omega^2\left(q+2\right)^2}\left(\frac{b}{R}\right) - \left(\frac{R}{b}\right)12\pi\beta'\beta\left(2+\beta\right)\right] R^2\varepsilon_0 k_s E_0^2 \sin\theta\cos\theta + \frac{4}{3}\pi R^3(\rho_p - \rho_d)\,f_b \sin\theta \qquad (6)$$

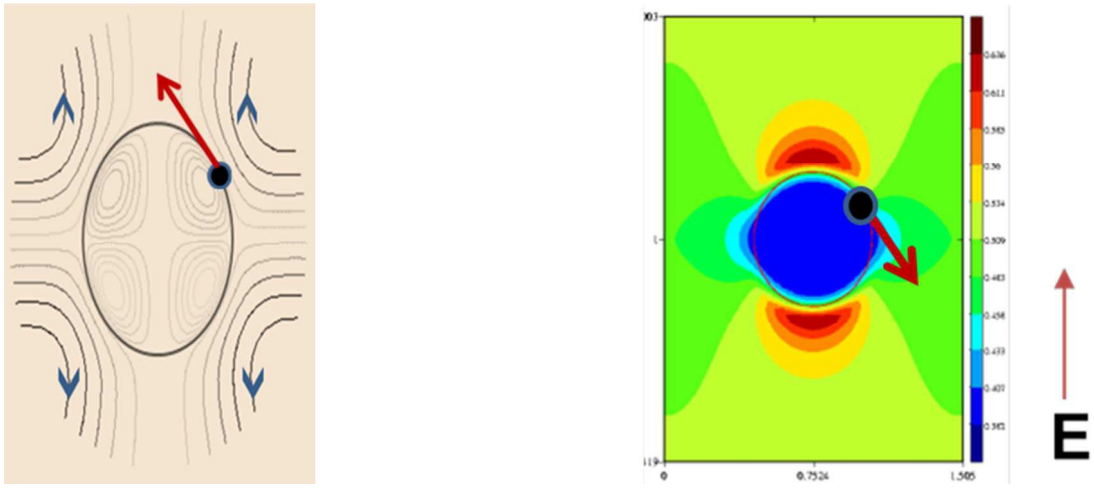
where f_b is the buoyancy coefficient which accounts for the fact that the particle is partially immersed in both ambient and drop liquids. In the absence of a strong electric field, the buoyant weight of the particle determines its position on the drop's surface. Notice that the three contributions may not be in same direction and that the total tangential force can be towards or away from the poles. We considered particles both denser than the ambient liquid and less dense than the ambient liquid. In the former cases, particles sedimented to the bottom surface of the drops, and in the latter cases, particles rose to the top surface of the drops. In a strong electric

field such that the buoyant force was relatively small compared to the electric force terms, the latter determined the location where particles collected.

From Eq. (6) we note that the EHD contribution decreases with decreasing $\frac{b}{R}$, but the DEP contribution increases with decreasing $\frac{b}{R}$. The EHD contribution also decreases with increasing frequency as $\frac{1}{\omega^2}$, whereas the DEP contribution varies only because β and β' vary with ω. For the cases considered in this paper β and β' varied slowly with ω. Therefore, there was a critical frequency (ω_c) such that below it the EHD force dominated and above it the DEP force dominated. The equilibrium location of a particle depended on the direction of the dominant force. At small frequencies, the first term in the square brackets of eq. (6) was larger, and so, it determined where the particles adsorbed on the surface of a drop would collect. Above the critical frequency, the second term became the dominant term, and so it determined where the particles collected. The critical frequency is given by

$$\omega_c = \left(\frac{1}{a^2 (q+2)^2} \frac{9R_r (R_r q - 1)}{4\beta\beta'(2+\beta)} \left[\left(\frac{b}{R} \right)^2 - \frac{40\beta\beta'(2+\beta)}{9R_r (R_r q - 10)} (2R_r + 1)^2 \right] \right)^{\frac{1}{2}}. \quad (7)$$

This dependence on the frequency of ac electric field can be exploited to manipulate particles on the surface of drop. Notice that the critical frequency for a given drop and ambient fluid combination is not fixed, as it also depends on the ratio b/R.



(a) $(R_r q > 1)$ (b) $(\beta\beta' < 0)$

Figure 1. Streamlines of EHD flow in a leaky dielectric fluid which determine the direction of EHD force and isovalues of electric field intensity which determine the direction of DEP force: (a) streamlines of EHD flow for $R_r q > 1$, (b) isovalues of the electric field intensity around a drop subjected to a uniform electric field generated by the electrodes placed at the top and

bottom of the domain for $\beta\beta' < 1$ (see ref. [16] for details). Notice that the EHD and DEP forces are not in the same direction.

The drop and ambient liquids properties determine the direction of circulating flow. For $R_r q < 1$, the direction of the EHD flow is from equator to pole, and for $R_r q > 1$ it is from pole to equator. The DEP force moves particles to either pole or equator depending on the sign of the factor $\beta\beta'$, see Fig. 1, and it is the dominant force at frequencies above the critical value. If the DEP and EHD forces are in the same direction, the net force acting on particles does not change direction when the frequency is increased above the critical frequency. But, when the DEP and EHD forces are not in the same direction, the direction of the net force changes and this can be used to move particles as well as separate particles for which the critical frequencies are different.

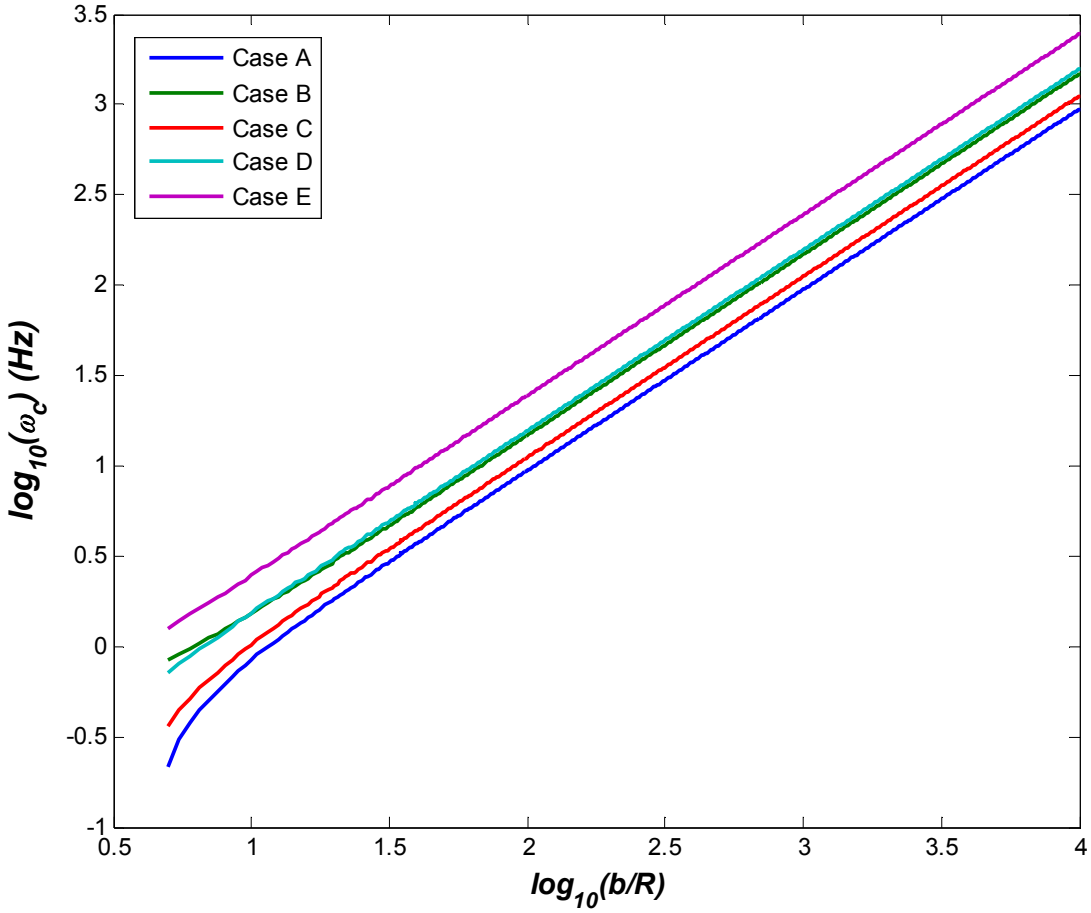


Figure 2. The critical frequency at which the EHD and DEP forces are equal as a function of $\frac{b}{R}$ for cases A-E described in Table 3.

The above equations can be used to describe the behavior of particles when the frequency of the electric field is varied. The properties of the liquids and particles considered in our experiments are described in Table 1-3. We considered five liquid-particle combinations which

are denoted as cases A-E. The properties for cases A, C and D were such that the EHD and DEP forces were in the opposite directions, and for cases B and E those two forces were in the same direction. The dependence of the critical frequency, ω_c, for these cases is shown in Figure 2. The parameter $\frac{b}{R}$ was varied between 5 and 10^4. The figure shows that the critical frequency increases with increasing $\frac{b}{R}$. The EHD force varies directly with $\frac{b}{R}$ whereas the DEP force varies inversely with $\frac{b}{R}$. Therefore, if the particle radius is kept constant and the drop radius is decreased, the DEP force increases while the EHD force decreases. For the DEP force to dominate the EHD force at a fixed $\frac{b}{R}$, the EHD force can be reduced by increasing the frequency. Thus the frequency of the electric field is a convenient control parameter. Furthermore, larger particles have a lower ω_c than smaller particles, and thus they can be separated by varying the frequency even when they are of the same type.

3. Experimental setup

Experiments were conducted in a rectangular prism-shaped device shown in Fig. 3. The voltage was applied using transparent electrodes placed on the top and bottom surfaces so that the motion of particles could be monitored using a microscope camera. The electric field inside the device was uniform and in the vertical direction. The distance between the electrodes was 5.5 mm, which was the same as the depth of the ambient liquid. An insert which matched the dielectric properties of the ambient fluid was placed at the bottom of the device to help maintain uniform electric field. A variable frequency ac signal generator (BK Precision Model 4010A) was used along with a high voltage amplifier (Trek Model 5/80) to apply voltage to the electrodes. The motion/deformation was recorded using a digital color camera connected to a Nikon Metallurgical MEC600 microscope.

The drop and ambient liquids were chosen so that the drop density was slightly larger, which ensured that the drop did not float or move freely. The properties of the liquids are shown in Table 1 (as provided by the supplier). A drop with particles distributed on its surface was formed using the following procedure. The first step was to form a dilute suspension by mixing particles in the liquid that was to be used to form the drop. Concentration of particles in the suspension was kept small to ensure that the concentration of particles on the surface of the formed drop was small. Drops of various sizes were formed at a small distance from the bottom surface by injecting a given amount of the drop liquid into the ambient liquid with a micropipette. Since the drop liquid was denser than the ambient liquid, the drop, along with particles inside the drop, sedimented to the bottom surface. The bottom surface and the drop were in contact along an approximately circular contact line as seen through the microscope. We then waited several minutes until all particles suspended inside the drop reached either the bottom or the top surface of the drop, depending on the density of the particles compared to that of the drop. Once a particle was trapped at the two-fluid interface, it remained trapped due to the interfacial tension,

even when the electric field was switched on. The position of a particle within the interface was determined by the three-phase contact angle on its surface and its buoyant weight.

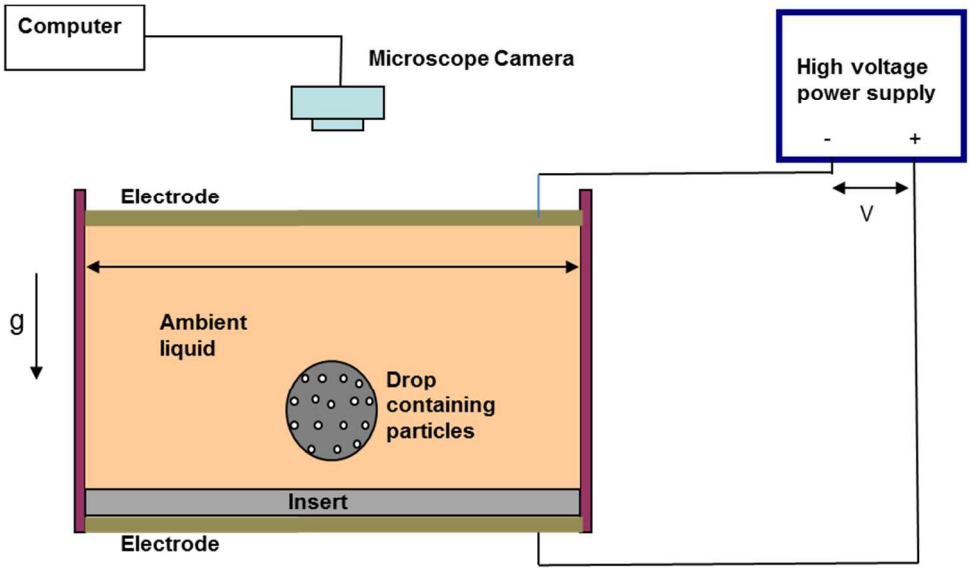


Figure 3. A schematic of the setup used in our experiments. The electrodes were mounted on the top and bottom of the device. The resulting electric field was in the vertical direction.

Table 1: Liquid properties.

Liquid	Density $\boldsymbol{\rho}$ $(\boldsymbol{kg\ m^{-3}})$	Viscosity $\boldsymbol{\mu}$ $(\boldsymbol{Pa\ s})$	Dielectric constant $\boldsymbol{k_p}$	Conductivity $\boldsymbol{\sigma}$ $(\boldsymbol{S\ m^{-1}})$	Supplier
Castor oil	961	1	4.7	32×10^{-12}	Sigma-Aldrich, (83912)
Silicone-I oil	1270	0.30	6.85	56×10^{-12}	Dow Corning, (FS 1265)
Silicone-II oil	960	0.05	2.75	3.6×10^{-12}	United Chemical Technology (UCT), (PS040)

Table 2: The properties of the particles used in experiments. Particles were approximately spherical.

Type	Density $\boldsymbol{\rho_p}$ $(\boldsymbol{kg\ m^{-3}})$	Diameter $\boldsymbol{2r}$ $(\boldsymbol{\mu m})$	Dielectric constant $\boldsymbol{k_p}$	Supplier
Soda lime glass	2500	$1-3$	6.9	MO-SCI, (GL-0191)
Hollow glass	600	$6-32$	1.2	Potters Industries, (60P18)
Polystyrene	1000	4	2.0	Invitrogen, (580/605)

Table 3: Properties for the cases considered in our experiments.

	Case A	Case B	Case C	Case D	Case E
Ambient liquid	castor oil	castor oil	castor oil	castor oil	castor oil
Drop liquid	silicone oil-I	silicone oil-I	silicone oil-I	silicone oil-II	silicone oil-II
Particle	Hollow glass	Soda lime glass	Polystyrene	Hollow glass	Soda lime glass
$\boldsymbol{R_r q}$	0.832	0.832	0.832	5.20	5.20
$\boldsymbol{\beta}$	0.132	0.132	0.132	-0.160	-0.160
$\boldsymbol{\beta'}$	-0.330	0.135	0.237	-0.330	0.135
$\boldsymbol{\beta\beta'}$	-0.044	0.018	-0.031	0.053	-0.022

4. Results

As discussed above, an EHD flow arises on the surface of a drop suspended in an ambient fluid when it is subjected to a uniform ac electric field. The flow is driven by an electric stress imbalance on the surface that arises because of the accumulation of electric charge on the surface. The particle laden drops in our experiments were denser than the ambient liquids and so they along with the suspended particles settled to the bottom of the device and formed a contact

line with the bottom surface. Thus, the EHD flow near the bottom surface was weaker and particles could not migrate to the bottom pole since the velocity on the drop's surface surrounded by the contact line, which was in contact with the bottom surface, was zero. Although the presence of a solid boundary altered the EHD flow around the drop, there was a poles-to-equator or equator-to-poles EHD flow depending on the properties of the drop and ambient liquid similar to that for a freely suspended drop.

Our aim was to study how this flow and the DEP force influence the distribution of particles adsorbed on the surface of the drop. As the drops in our experiments were stationary on the bottom surface, we were able to observe the migration of particles adsorbed on their surfaces under the action of an applied electric field over longer periods of time compared to that for an approximately density matched case where the drop slowly sediments in the ambient liquid. The motion of an adsorbed particle consisted of steady and time periodic components as the EHD flow and the electric field intensity were time periodic. Furthermore, the particles adsorbed on the surface also moved because the drop shape pulsated with time. The size of the drop, the properties of the liquids, and the electric field intensity determined the strengths of the periodic and steady flow components. The EHD flow and the pulsations of the drop shape diminished as the frequency of electric field was increased.

4.1 Drops containing a single type of particles

We first describe the results for the cases in which only one type of particle was present. We considered the five different combinations of liquids and particles described in Table 3. These cases were selected to understand the dependence of the distribution of adsorbed particles on the frequency of electric field. The EHD flow for cases A, B, and C was towards the poles. The DEP force for case B was also towards the poles, but for cases A and C, it was towards the equator. For cases D and E, the EHD flow was towards the equator. For case D, the DEP force was towards the poles and for case E it was towards the equator.

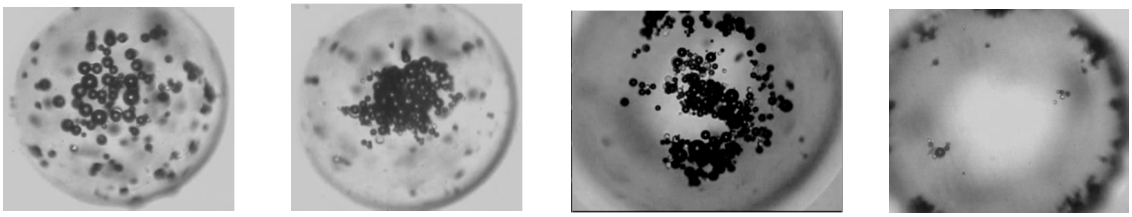
The critical frequency for the cases considered in our experiments was O(10-100), and so the frequency was varied between 0.01 to 1000 Hz. The periodic component of flow varied with a frequency that was twice the frequency of the applied electric field. Since the critical frequency (ω_c) depends on the particle size, when particles were not monodispersed there was a range of ω_c; for smaller particles, ω_c was larger and for larger particles ω_c was smaller. Similarly, non-spherical particles moved to the equator or the poles depending on the direction of the net force which depended on their size.

4.1.1. Silicone oil-I drop in castor oil

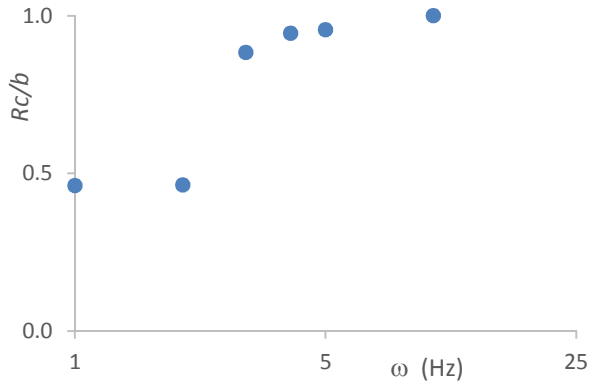
We first discuss cases A, B and C which have silicone oil-I as the drop liquid and castor oil as the ambient liquid. For this liquid combination, the EHD flow was towards the poles. This is in agreement with Eq. (1) since for this case $R_r q < 1$. Thus, at small frequencies particles migrated to the poles because the drag due to the EHD flow was the dominant force. The critical

frequencies for the three types of particles depended on the properties of the liquids and particles, and $\frac{b}{R}$. Above the critical frequency, the motion of particles was dominated by the DEP force.

In case A, the silicone oil-I drop contained hollow glass particles which were less dense than the drop and ambient liquids. Thus, initially, before the field was applied, particles rose to the top of the drop. The diameter of the silicone oil drop in Fig. 4 was approximately 436 μm. Taking a mean particle size of 18 μm, our theoretical analysis predicted $\omega_c = 2.12$ Hz. After a voltage was applied at a frequency less than about 2 Hz, the EHD drag dominated the DEP force for all particle sizes. Below this critical frequency, particles were drawn towards the pole since the direction of flow circulation was equator-to-pole, as shown in Fig. 4b. The frequency in Fig. 4b was 0.4 Hz. The particle velocity contained a steady component and a periodic component.



(a) (b) (c) (d)



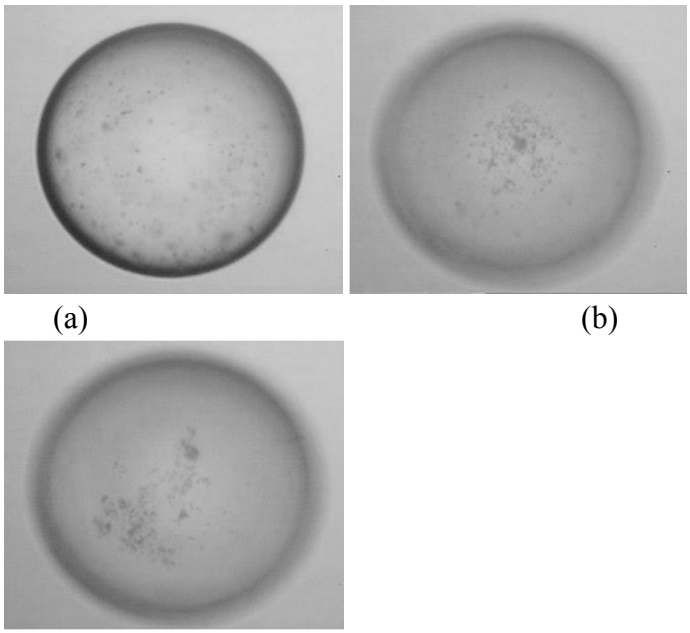
(e)

Figure 4. Distribution of hollow glass particles on silicone oil-I drop in castor oil. The mean particle diameter was 18 μm and the drop diameter was 436 μm. The voltages and frequencies were (a) 0 V; (b) 2000 V at 0.4 Hz; (c) 3000 V at 3 Hz; (d) 3000 V at 20 Hz; (e) the radius of the region around the equator within which particles were confined (*Rc*), nondimensionalized with the drop radius, is shown as a function of the frequency. The critical frequency $\omega_c = 2.12$ Hz.

The strength of the EHD flow diminished with increasing frequency. When the frequency was larger than about 2 Hz, the DEP force started to dominate the EHD flow induced drag for the larger sized hollow glass particles causing them to move towards the equator. Since ββ' was negative, this implied that the DEP force was greater than the EHD flow induced drag. However, only when the frequency was increased to about 5 Hz smaller particles moved to the equator. This can be seen in Fig. 4e where the dimensionless radius of the region around the pole within

which particles were confined is plotted as a function of the frequency. Notice that the radius increases with increasing frequency as particles progressively move towards the equator. This is a consequence of the fact that when the DEP and EHD forces *exactly* balance each other the buoyant weight of particles cannot be neglected. The tangential component of the buoyant weight which is zero at the poles increases as a particle moves towards the equator, and therefore the DEP force must overcome this increase in the buoyant weight. The DEP and EHD forces also vary with the angular position but they have a different functional dependence (see eq. (6)).

In case B, the silicone oil drop contained spherical soda lime glass particles which were denser than the drop and ambient liquids. Thus, particles sedimented to the bottom of the drop, see Fig. 5. The diameter of the drop was approximately 400 μm. After a voltage was applied, as shown in Fig. 5, particles collected at the poles at both low and high frequencies. This was because the EHD flow was from equator to pole, and so it dragged particles to the poles. In addition, since $\beta\beta' > 0$, the DEP force also moved particles to the poles. Therefore, at higher frequencies, particles continued to collect at the poles as the two forces were directed toward the poles. An increase in the frequency above the critical value did not change the distribution since the direction of the net force on the particles did not change. Using a mean particle diameter of 2 μm, our analysis predicted that the critical frequency at which the DEP force became the dominant force was around 33.0 *Hz*, but this could not be measured experimentally as the EHD flow and the DEP force were in the same direction. However, unlike in the EHD flow dominated regime, the DEP force moved particles to poles in a steady manner, without a significant periodic component.



(a) (b)

(c)

Figure 5. Distribution of soda lime glass particles on silicone oil-I drop in castor oil. The mean particle diameter was about 2 μm and the drop diameter was 400 μm. Particles appear as small dots in the photographs due to their small size. Particles collected at the poles as both the DEP

and EHD forces are directed towards the poles. The voltages and frequencies are (a) 0 V; (b) 2 kV at 0.4 Hz; and (c) 3 kV at 60 Hz. In (b) and (c), particles collected at the poles.

Next, we describe case C for which the silicone oil drop contained polystyrene particles which were denser than silicone oil-I and so they sedimented to the bottom of the drop. The diameter of the silicone oil drop in Fig. 6 was approximately 400 μm. After a voltage was applied at small frequencies, the EHD flow induced drag dominated and so particles were drawn towards the poles. The critical frequency in this case was around 10 Hz, above which the DEP force dominated. Since $\beta\beta' < 0$, particles were moved from the pole to the equator, as shown in Fig. 6b. In comparison to the experimental value, our theoretical analysis predicted $\omega_c = 15.8$ Hz.

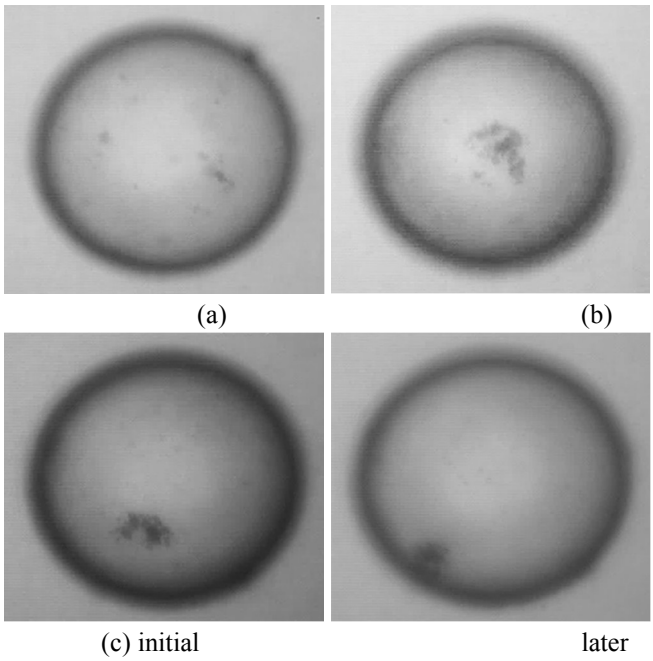


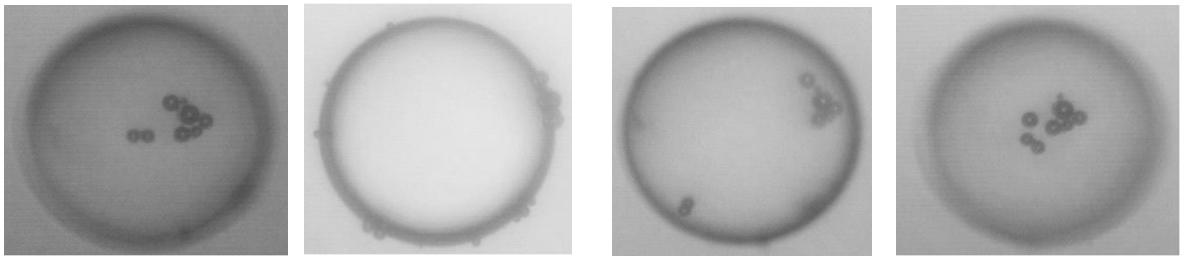
Figure 6. Distribution of polystyrene particles on silicone oil-I drop in castor oil. The mean particle diameter was 4 μm and the drop diameter was around 400 μm. Due to their small size, particles appear as dots in the images. The voltages and frequencies are (a) 0 V; (b) 4 kV at 4 Hz; (c) 4 kV at 40 Hz. The two photographs show particles migrating towards the equator.

It is noteworthy that the critical frequency for case A was about 2 *Hz*, but for case C, it was about 15.8 Hz. This is due to the fact that the size of hollow glass particles was larger and the critical frequency decreases with increasing particle size (see fig. 3). Also, the critical frequency depends on the value β' for the particle which was different for hollow glass particles and polystyrene particles.

4.1.2. Silicone oil-II drop in castor oil

For cases D and E, silicone oil-II was used as the drop liquid and castor oil as the ambient liquid. Unlike the cases discussed in the previous subsection, for these cases $R_r q > 1$ since the two silicone oils have different physical properties. Thus, the EHD flow was towards the equator, and so at small frequencies for which the EHD flow provided the dominant force particles migrated to the equator. Also, as before, the motion of particles towards the equator had a steady and a periodic component. Both of these components diminished as the frequency was increased.

In case D, a silicone oil-II drop with hollow glass particles was suspended in castor oil. Initially, hollow glass particles rose to the top of the drop, since they were less dense, as shown in Fig. 7a. The diameter of the drop was approximately 400 μm.



(a) (b) (c) (d)

Figure 7. Distribution of hollow glass particles on silicone oil-II drop in castor oil. The mean particle diameter was 18 μm and the drop diameter was around 400 μm. The voltages and frequencies were (a) 0 V; (b) 3 kV at 0.2 Hz; (c) 3 kV at 16 Hz; (d) 8 kV at 20 Hz.

Figure 7b shows a snapshot of the particles as they moved from the poles to the equator at a frequency of 0.2 Hz. This was due to the fact that the EHD flow in this case was from poles-to-equator. In Fig. 7b, particles have moved to the equator, but are not clearly visible because of the drop's curvature. We observed that below $\sim 10\ Hz$, the EHD flow induced drag force was the dominant force and so all particles were dragged towards the equator.

The value of $\beta\beta'$ for hollow glass particles was positive and so the DEP force was towards the poles. Thus, above 10 Hz, for which the DEP force became the dominant force, all particles were dragged towards the poles. Fig. 7c shows that particles moved away from the equator when the frequency was increased to 16 Hz. Our theoretical analysis predicted ω_c to be 7.65 *Hz* for a mean particle size of 18 μm (Note that the hollow glass particles were not monodispersed). Fig. 7d shows that particles moved to the poles when the frequency was 20 Hz.

For case E, the silicone oil-II drop contained soda lime glass particles. Initially, before an electric field was applied, the particles sedimented to the bottom surface of the drop, as shown in Fig. 8a. The diameter of the drop was approximately 430 μm. The EHD flow and the DEP forces in this case were in the same direction, i.e., from pole-to-equator. Therefore, as can be seen in

Fig. 8b and 8c, the particles moved towards the equator for both low and high frequencies. According to our analysis the critical frequency at which the DEP force became the dominant force was around 110 *Hz*, but this could not be verified experimentally, as the two forces were in the same direction.

An increase in the frequency above the critical value did not change the distribution since the direction of the net force on the particles did not change. In this sense, this case was similar to the case reported in Fig. 5, where position of the particles did not change when the frequency was increased above the critical value. Particles collected at the poles for both low and high frequencies. The values of $R_r q$ and $\beta\beta'$ for the two cases were such that the EHD and DEP forces acted from equator-to-pole in Fig. 5 and from pole-to-equator in Fig. 8.

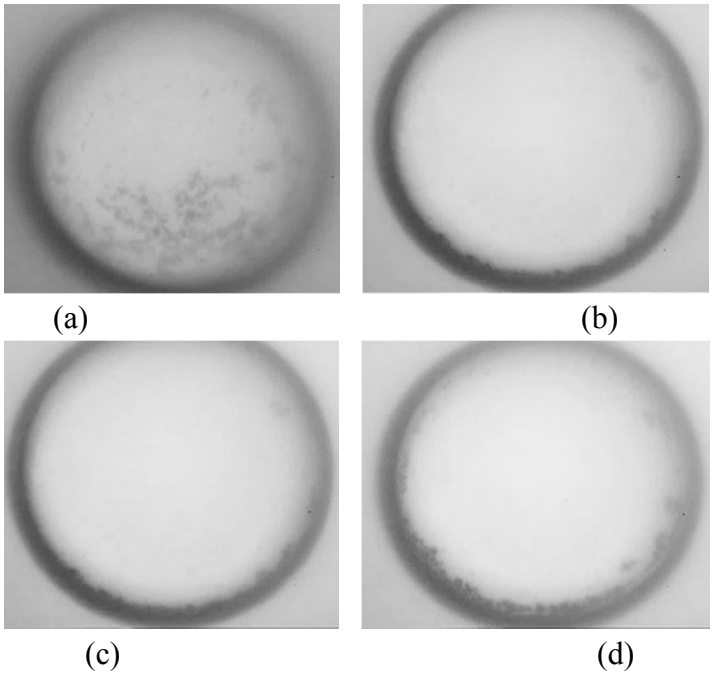


Figure 8. Distribution of solid glass particles on silicone oil-II drop in castor oil. The mean particle diameter was 4 μm and the drop diameter was around 430 μm. Due to their small size, particles appear as dots in the images. In (b)-(d) they are concentrated near the equator. The voltages and frequencies are (a) 0 kV; (b) 2 kV at 0.2 Hz; (c) 4 kV at 1 Hz; (d) 4 kV at 120 Hz. The photographs show that in (b)-(d) particles collected near the equator.

4.2. Drops containing two types of particles

We next consider cases in which two different types of particles were placed on the surface of a drop. First, we consider the case of a silicone oil-I drop in castor oil. The aim was to determine when the two types of particles can be separated and concentrated in different regions on the surface of the drop by adjusting the frequency of electric field. This is analogous to fractional distillation of a mixture into its components parts based on their boiling points. But, in this case, particles are separated based on their critical frequencies.

4.2.1. Silicone oil-I drop with mixture of hollow glass particles and polystyrene particles in castor oil

A silicone oil-I drop, with mixture of hollow glass particles and polystyrene particles, was suspended in castor oil as shown in Fig. 9. The diameter of the drop was approximately 410 μm. Initially, prior to the application of electric field, both hollow glass particles and polystyrene particles rose to the drop's top surface since they were less dense than the drop.

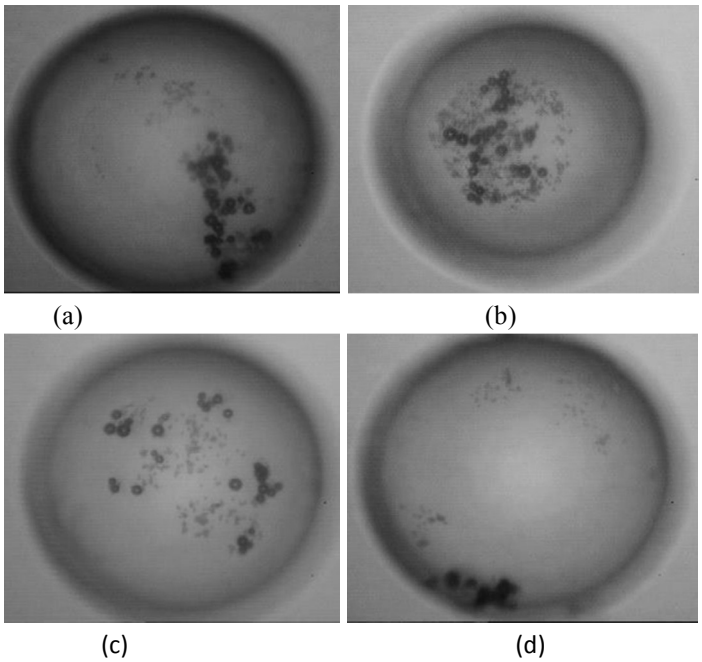


Figure 9. Distribution of a mixture of hollow glass and polystyrene particles on a silicone-I oil drop immersed in castor oil. The mean diameter of the glass and polystyrene particles was 18 μm and 4 μm, respectively, and the drop diameter was 410 μm. The voltages and frequencies were (a) 0 V; (b) 2.5 kV at 0.1 Hz; (c) 3 kV at 6 Hz (d) 3 kV at 20 Hz.

After a voltage was applied at a frequency of 0.1 Hz, as shown in Fig. 9, particles collected at the poles. This was because the EHD flow was directed from equator to pole, and so it dragged both types of particles to the poles. This case was interesting because $\beta\beta' < 0$ for both type of particles and so the DEP force caused particles to move towards the equator, but the critical frequencies for them were different. From section 4.1.1, we know that the critical frequency at which the DEP force became the dominant force was about 2.12 Hz for hollow glass particles and about 15.8 Hz for polystyrene particles.

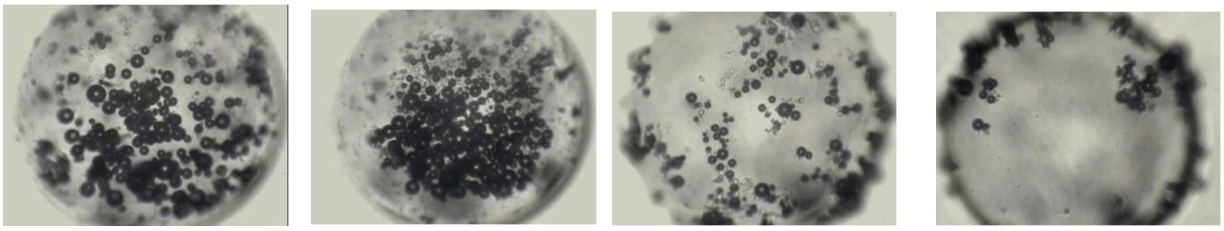
Thus, when the frequency was increased to 6 Hz the hollow glass particles began moving to the equator, but the polystyrene particles remained at the poles. When the frequency was increased to 20 Hz, above the critical frequency of about 15.8 Hz for polystyrene particles, those particles also started to move towards the equator and both types of particles collected at the

equator. This shows that the frequency of the applied electric field can be used to selectively move particles to the different regions on the surface of a drop.

4.2.2. Silicone-1 oil drop with spherical hollow glass particles and soda lime glass particles in castor oil

We next considered the case of silicone oil-I drop with a mixture of hollow glass particles and soda lime glass particles suspended in castor oil. The diameter of the drop was approximately 430 μm. The aim was to separate the two types of particles from each other by varying the frequency. This case is different from the previous case as the DEP force on hollow glass particles was towards the equator, while the force on solid glass particles was towards the poles.

At small frequencies, as Fig. 10b shows, both particle types collected at the poles, since the motion of particles in this regime is determined by the EHD flow. When the frequency was increased to 6 Hz, all particles started to move away from the poles, and some hollow particles collected at the equator. Notice that solid glass particles became attached to hollow glass particles (see Fig. 8c). This happened because glass particles were positively polarized and hollow glass particles were negatively polarized. The DEP force between them was attractive, and the net force on a pair containing a solid glass particle and a hollow glass particle was small, and, thus, the pairs remained between the pole and the equator. This, however, changed when the frequency was increased to 20 Hz. Both individual particles and the pairs moved to the equator. This behavior was different from what happened in Fig. 9 where both types of particles were negatively polarized and did not attract each other.



(a) (b) (c) (d)

Figure 10. Distribution of hollow and solid glass particles on the surface of a silicone oil-I drop immersed in castor oil. The mean diameter of the hollow and solid glass particles was 18 μm and 2μm, respectively, and the drop diameter was 430 μm. The voltages and frequencies are (a) 0 V; (b) 2 kV at 0.4 Hz; (c) 3 kV at 6 Hz (d) 3 kV at 20 Hz.

4.2.3 Silicone oil-II drop with spherical hollow glass particles and soda lime glass particles in castor oil

Finally, the case of a silicone oil-II drop with a mixture of hollow glass particles and soda lime glass particles suspended in castor oil was considered. The diameter of the drop was approximately 405 μm. The aim was not just to separate the two types of particles from each

other by varying the frequency, but also to observe the opposite of what was described in Fig. 10 in terms of where particles collect. This is because the use of silicone oil-II as drop liquid caused both EHD and DEP forces on both particle types to act in directions opposite to their previous directions when the drop liquid was silicone oil-I, as shown in Fig. 10, due to differences in the properties of the two silicone oils.

Initially, before applying voltage, the hollow glass particles rose to the pole and solid glass particles sedimented to the bottom. At frequencies below ~10 Hz, both particles moved away from the pole and collected at the equator as shown in Fig. 11b, since the motion of particles was determined by EHD flow in this regime. As the frequency was increased to 10 Hz and above, hollow particles collected at the pole (see Fig. 11c-d), while the solid glass particles remained at the equator as seen in Fig. 11c-d. However, the opposite polarizations of the two types of particles, as mentioned above, also created an attraction between the two particle types; some solid particles became attached to hollow particles and moved to the pole in Fig. 11c, when they are expected to be at the equator.

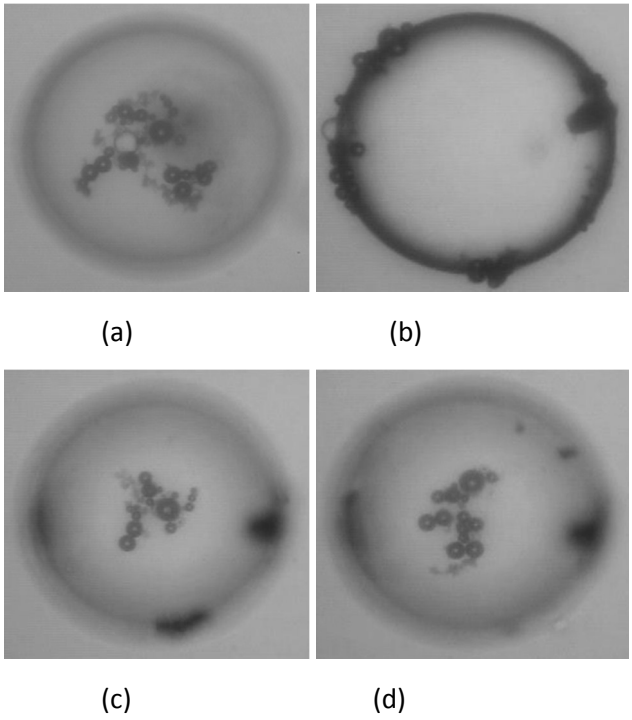


Figure 11. Distribution of hollow and solid glass particles on the surface of silicone oil-II drop immersed in castor oil. The mean diameter of the hollow and solid glass particles was 18 μm and 2 μm, respectively, and the drop diameter was 405 μm. The voltages and frequencies are (a) 0 V; (b) 2 kV at 0.2 Hz; (c) 4 kV at 10 Hz (d) 4 kV at 20 Hz.

5. Conclusion and discussion

We have shown that the distribution of particles adsorbed on the surface of a weakly conducting drop, immersed in another weakly conducting liquid, can be modified by subjecting it to an ac electric field. The problem of manipulation of particles on liquid-liquid interfaces has received considerable attention in recent years because of its importance in a wide range of applications. For example, several recent studies have been conducted in which a dc electric field is applied to manipulate the distribution of particles. The field gives rise to an EHD flow on the surface of the drop. The direction of the EHD flow can be pole-to-equator or equator-to-pole depending on the properties of the drop and ambient liquids. The flow causes particles adsorbed on the surface of the drop to move in its direction, and so the approach can be used to concentrate particles near the poles or the equator of the drop depending on the direction of flow.

In our earlier studies, we have shown that when the drop and ambient liquids are perfect dielectric liquids, particles can be concentrated around the poles or equator of the drop by applying a uniform electric field. This happens because even when a uniform electric field is applied to a drop the field on the surface of the drop is nonuniform, and thus particles adsorbed on its surface are subjected to dielectrophoretic (DEP) forces. The motion of particles in this case is driven by the DEP forces *alone* because when the drop and ambient liquids are perfect dielectrics the electric field does not cause any fluid flow.

The focus of this paper is on the forces that act on a particle when the drop and ambient liquids are weakly conducting and the drop is subjected to a uniform ac electric field. The forces that act in an ac electric field are: (i) DEP force; (ii) buoyancy force; and (iii) EHD flow induced drag force. The net force acting on a particle, which is the sum of these three forces, determines the particle's direction of motion.

The frequency of electric field is an important parameter which can be used to adjust the magnitude of the EHD flow induced drag such that it is larger or smaller than the DEP force. This is due to the fact that the EHD flow diminishes with increasing frequency and that there is a critical frequency at which the EHD flow induced drag on a particle becomes equal to the DEP force. For a frequency above the critical value, the DEP force dominates. When the fluid and particles properties are such that the EHD and DEP forces are in the opposite directions particles can be collected at the poles or the equator, and also can be moved between the poles and the equator by varying the frequency of electric field. For example, the EHD flow for cases A, B, and C was towards the poles, and for cases D and E, the EHD flow was towards the equator. All of the cases considered were such that the influence of buoyancy force was negligible when a sufficiently intense electric field was applied. At low frequencies particles movements were determined by the EHD flow. However, as the frequency was increased, the EHD flow diminished and the DEP force started to influence the motion of particles. The critical frequency at which the transition occurred was different for each of the cases; since the critical frequency is a function of particle and fluids properties. The experimentally measured critical frequency ω_c values were in good agreement with the theoretical values given by equation (7), especially

considering that the drops in our experiments were in contact with the bottom surface whereas in deriving equation (7) it is assumed that the drops are suspended in the ambient liquid. We demonstrated that particles can be manipulated to move in different directions in a certain frequency regime as determined by ω_c, provided the DEP force and the EHD drag force are not in the same direction.

It was also shown that it is possible to separate the particles of a binary mixture when the critical frequencies for the two types of particles are different. However, it was not possible to separate the particle pairs in which one type of particle was positively polarized and the other negatively as in this case there was dipole-dipole attraction between the particles which prevented them from moving apart. We were able to separate a mixture of polystyrene particles and hollow glass particles. The critical frequency ω_c for the latter particles was smaller, and so they were moved away from the poles by applying a frequency that was larger than the critical frequency for hollow glass particles, but smaller than that for polystyrene particles. It is also possible to separate particles based on their sizes. This is possible because larger particles have a lower ω_c. Larger particles were separated from smaller particles by using a frequency that caused larger particles to move away from the poles while smaller particles remained at the poles. The approach is thus superior to traditional dielectrophoresis for which the frequency dependence is weak.

In conclusion, we have shown that when the directions of the EHD flow and the DEP force are different it is possible to collect particles at the poles or the equator of a drop by selecting a suitable frequency and that particles can be moved from the poles to the equator, or vice versa, by selecting a suitable frequency. Also, when the critical frequencies of the particles forming a binary mixture in a particular combination of drop and ambient liquids are known, the two types of particles can be separated, in a fractional manner, by tuning to corresponding critical frequencies of particle types that make up the mixture.

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Author Contributions
E.A., I.F. and P.S. designed experiments. E.A. and K.S. performed experiments; E.A. and P.S. analyzed data. E.A., I.F. and P.S. wrote the paper.

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A method for concentrating particles at the poles or the equator of a drop and for moving them between the poles and the equator by selecting a suitable frequency of the electric field, and for forming Janus drops by separating particles with different dielectric properties on the surface of the drop.