# **Supporting Information**

Manoj Prasad\*, Filip Strubbe, Filip Beunis and Kristiaan Neyts

Electronics and Information Systems, Ghent University, Technologiepark Zwijnaarde 15, 9052

Gent, Belgium

Center for Nano and Biophotonics (NB-Photonics), Ghent University, Technologiepark Zwijnaarde

15, 9052 Gent, Belgium

## **S1. Theoretical Model**

#### S1.1. Simulations

To interpret the electrical current measured in response to a triangular voltage, a simulation model based on the Poisson-Nernst-Planck (PNP) equations is developed. For the simulation, a non-polar dispersion containing charged inverse micelles (CIMs) and charged colloidal particles is considered. Since the overlapping area of electrodes ( $S = 4.93 \text{ cm}^2$ ) is much larger than the distance ( $d = 40 \text{ }\mu\text{m}$ ) between them, the device can be considered a 1D structure in which all quantities vary along the *x* axis. When a voltage *V* is applied, the flux due to the movement of the CIMs is given by<sup>9,21,22, 24, 25</sup>:

$$\Psi_{\pm} = \pm \mu n_{\pm} eE - \left(\frac{\mu k_B T}{ze}\right) \frac{\partial n_{\pm}}{\partial x}$$
(S1)

Here,  $\Psi_{\pm}$ ,  $\mu = \mu_{+} = -\mu_{-}$  and  $n_{\pm}$ , consecutively, are the flux, mobility and the concentration of the positive and negative CIMs, *e* is the electronic charge, *E* is the electric field,  $k_{B}$  is Boltzmann constant (J/K), *T* is temperature (K) and *z* is the valency of the CIMs. Since the size of Solsperse CIMs (*r* = 7

nm<sup>25</sup>) is four times smaller than the Bjerrum length, only a small fraction of inverse micelles (IMs) is charged which can have the maximum valency<sup>4,5,8,35</sup> of z = 1.

Similarly, the flux due to the charged particles is:

$$\Psi_p = n_p \mu_p e E - \left(\frac{k_B \mu_p T}{z_p e}\right) \frac{\partial n_p}{\partial x}$$
(S2)

$$\Psi_n = -n_n \mu_n e E - \left(\frac{k_B \mu_n T}{z_n e}\right) \frac{\partial n_n}{\partial x}$$
(S3)

In Eq. S2 & S3,  $\Psi_p$ ,  $\Psi_n$ ,  $\mu_p$ ,  $\mu_n$ ,  $n_p$ ,  $n_n$ ,  $z_p$  and  $z_n$  consecutively are the flux, mobility, concentration and valency of the positively and negatively charged particles. The continuity equations for the CIMs, the positively and negatively charged particles can be written as:

$$\frac{\partial n_{\pm}}{\partial t} = -\frac{\partial \Psi_{\pm}}{\partial x} \tag{S4}$$

$$\frac{\partial n_p}{\partial t} = -\frac{\partial \Psi_p}{\partial x} \tag{S5}$$

$$\frac{\partial n_n}{\partial t} = -\frac{\partial \Psi_n}{\partial x} \tag{S6}$$

In Eq. S4, we assume that the concentration of positive and negative CIMs is equal all the times and equal to that of equilibrium concentration. In Eqs. S5 and S6, we also assume that the average mobility, charge on each particle and the concentration of the charged particles are constant and do not change with time. The electric field between the electrodes is calculated using the Gauss equation:

$$\frac{\partial E}{\partial x} = \frac{\rho}{\varepsilon_0 \varepsilon_r} \tag{S7}$$

In Eq.S7,  $\rho = (e^n + -e^n - +e^{z_p n_p} - e^{z_n n_n})$  is the space charge density. In the simulations, Eq. S1-S7 are solved with initial homogeneous distribution of charges in the device with blocking boundary conditions. The current is calculated using Eq.<sup>35</sup>:

$$I(t) = \varepsilon_0 \varepsilon_r S \frac{\partial E}{\partial t} \Big|_{x=0}$$
(S8)

#### **S1.2.** Analytical Approximation

In this section an equation for the current in a nonpolar liquid in response to a triangular voltage is derived. Depending on the peak value of the applied voltage and the frequency, the measured current can be categorized in two regimes, a linear and a non-linear regime. In the linear regime, the measured conductive current due to movement of charges varies linearly with the voltage. A linear relation between the applied voltage and the measured conductive current is possible when the charges in the system do not move much from their initial positions. In the non-linear regime, the charges move over a much larger distance from their initial positions, possibly all the way to the electrode, resulting in the formation of space charge layers that cause a non-linear voltage-current relation. The non-linear regime is observed for large voltages and small frequencies.

A period of a triangular voltage with frequency f and peak voltage  $V_p$  can be written as:

$$V(t) = \begin{cases} 4fV_pt, \ 0 < t < 1/4f \\ -4fV_p(t-1/2f), \ 1/4f < t < 3/4f \\ 4fV_p(t-1/f), \ 3/4f < t < 1/f \end{cases}$$
(S9)

The conductivity of a dispersion with CIMs and charged particles is given by:

$$\sigma = \sum_{i} Z_{i} e n_{i} \mu_{i} \tag{S10}$$

Here,  $Z_i$  and  $\mu_i$  are the values of the charge number and the mobility of the corresponding  $i_{th}$  charge carrier. The current measured in the external circuit in response to a triangular voltage can be interpreted as the superposition of a capacitive current and the conductive current. The conductive current is due to the movement of charges in between the electrodes in response to the applied voltage. In the linear regime, when the charges do not move much and hence do not affect the field between the electrodes, the total measured current can be expressed as:

$$I(t) = \left(\frac{S\varepsilon_0\varepsilon_r\partial V(t)}{d\quad\partial t} + \frac{\sigma SV(t)}{d}\right) \tag{S11}$$

Substituting the value of V(t) from Eq. S10 to Eq. S11, it gives:

$$I(t) = \begin{cases} -\frac{4 S \varepsilon_0 \varepsilon_r}{d} f V_p + \frac{4 \sigma S f V_p}{d} t, \ 0 < t < \frac{1}{4f} \\ -\frac{4 S \varepsilon_0 \varepsilon_r}{d} f V_p - \frac{4 \sigma S f V_p}{d} (t - 1/2f), \ \frac{1}{4f} < t < \frac{3}{4f} \\ \frac{4 S \varepsilon_0 \varepsilon_r}{d} f V_p + \frac{4 \sigma S f V_p}{d} (t - 1/f), \ \frac{3}{4f} < t < \frac{1}{f} \end{cases}$$
(S12)

In the non-linear regime, the charges move over a larger distance, depending on the magnitude of the applied voltage and the frequency. The movement and separation of charges in the device affects the field in the device and the field no longer remains V(t)/d.

The velocity of charged particles or CIMs in the linearly increasing field in the absence of space charge is given by:  $v(t) = \mu V(t)/d$ . From this, the distance travelled by the particles in time t

can be calculated as: 
$$\int_{0}^{t} v(t)dt \int_{0}^{t} (\mu V(t)/d)dt$$
.  
If the particles/CIMs travel over the entire distance between the electrodes, then the time taken by the particles/CIMs to reach the opposite polarity electrodes is given by  $t_{tr} = \sqrt{d^2/(2\mu V_p f)}$ . Knowing this transit time, the average value of the mobility of the particles can then be estimated by:

$$\mu = \frac{d^2}{2t_{tr}^2 V_p f}$$

## **S2.** Electrokinetics of Charged Inverse Micelles

#### S2.1. Material and Method

A suspension of the surfactant Solsperse with  $\phi_m = 0.0005$  (Lubrizol) in a carrier liquid is prepared. The carrier liquid is a mixture of organic solvents which has a relative permittivity:  $\varepsilon_r = 2$  and dynamic viscosity of 5.5 mPa. s. The electrical current measurement is performed using the high field toner cell (HFTC) combines a toner cell and a source meter. The toner cell consists of two parallel circular steel plates with surface area S = 4.93 cm<sup>2</sup> that are separated at a distance *d*. The lower plate of the cell is fixed and acts as a base while the upper plate is moveable. The two plates are placed parallel to each other in such a way that the electrode areas overlap completely, and then the distance between the plates is controlled by moving the upper plate up or down using a micrometer stage. The source meter is used to apply a voltage across the electrodes of the toner cell and to measure the corresponding current simultaneously. The distance between the plates is estimated by measuring the air capacitance *C* and applying the formula  $:d = (\varepsilon_0 \varepsilon_r S)/C$ , where  $\varepsilon_0$  is the vacuum permittivity (F/m) and  $\varepsilon_r$  is the relative dielectric constant.

The experimental procedure is as follows: firstly the distance between the electrodes is set by adjusting the air capacitance of the device to the desired value. Then, the device is opened and the space between the electrodes is filled with the prepared suspension. Afterwards, the upper electrode is placed back in its original position. Subsequently, a triangular voltage (peak amplitude  $V_p$  of 1 V to 400 V of frequency f = 5 Hz) is applied across the electrodes and the corresponding current is measured. The Schematic of the HFTC setup is shown in Fig. S1.



**Figure S1:** Schematic of the HFTC setup. The setup comprises the liquid toner cell with two circular electrodes. The space between the electrodes is filled with a prepared dispersion. A triangular voltage is applied and the corresponding current is measured simultaneously.

#### S2.2. Results

A comparison between the measurements and simulations for a triangular voltage of 5 Hz applied over a mixture of Solsperse with mass fraction  $\phi_m = 0.0005$  in the carrier liquid ( $\eta = 5.5 \text{ mPa. s}$ ) in the HFTC device with  $d = 40 \text{ }\mu\text{m}$  is shown in Fig. S2. The simulation parameters such as the mobility and the concentration of CIMs are estimated by matching the simulated currents with the measured currents for a small voltage ( $V_p < 20 \text{ V}$ ) or for at least the first half cycle (t = 0 to 0.05 s) of a large voltage. The obtained values of the mobility and the concentration of CIMs for the mixture are 210  $\mu$ m<sup>2</sup>/Vs and 7.5  $\mu$ m<sup>-3</sup>, respectively. The reported value of the mobility of CIMs for a solution of Solsperse with  $\phi_m = 0.001$  in dodecane ( $\eta = 1.38 \text{ mPa. s}$ ) is 760  $\mu$ m<sup>2</sup>/Vs<sup>25</sup>. If we assume that the mobility scales inversely proportional with the viscosity of the solvent (the carrier liquid versus dodecane), the expectation value for the mobility in the carrier liquid is 190  $\mu$ m<sup>2</sup>/Vs, which is similar to the value used in the simulations (210  $\mu$ m<sup>2</sup>/Vs).



**Figure S2:** The measured currents for a solution of Solsperse  $\phi_m = 0.0005$  in the carrier liquid using the HFTC setup with  $d = 40 \ \mu\text{m}$  and  $S = 4.93 \ \text{cm}^2$  are compared with simulated currents (black lines) for triangular voltages of frequency 5 Hz. The peak values of the applied voltages are (a)  $V_p = 5 \ \text{V}$  (b)  $V_p = 50 \ \text{V}$  (c)  $V_p = 100 \ \text{V}$  (d)  $V_p = 200 \ \text{V}$  (e)  $V_p = 300 \ \text{V}$  (f)  $V_p = 400 \ \text{V}$ .

The good match between the measurements and simulations for small voltages indicates that the currents can be described well by drift and diffusion of CIMs in response to the applied voltage. In the linear regime in which  $V(t) \propto I(t)$ , the currents are approximated well by Eq.14, an example shown in Fig. S2 (a), in which the current approximately follows the applied voltage. For the other voltages in Fig. S2 (b - f), the measured currents match well with the simulations from 0 to 0.1 s. After 0.1 s there is a discrepancy in the form of a peak in the measured current. For intermediate voltages up to  $V_p = 100$  V, the integral of the measured current peak after the first half cycle of the voltage is larger than the integral of the simulated current peak, see Fig. S2 (b - c). This can be explained since the charges from the measurements are completely separated while the charges in the simulation are not completely separated. For very large voltages  $V_p = 100$  V to 400 V as shown in Fig. S2 (d, e and f), the integrals of the peaks for  $V(t) \rightarrow -V(t)$  or  $-V(t) \rightarrow V(t)$  are the same: 40 nC (excluding the capacitive currents). The integral of measured current is calculated using Eq.:

$$\int_{0}^{t} |(I - I_c)| dt$$
, here *I* is the measured current while *I<sub>c</sub>* is the capacitive current. However, the peak in the measured current occurs much earlier than the peak in the simulated current, see Fig. S2 (d, e and f).

The triangular voltage starts at t = 0 s, when the CIMs are distributed uniformly in the device. The measured current for the first half cycle ( $0 < t \le 0.1$  s) of the triangular voltage can be explained as follows: for a linearly increasing voltage and neglecting the effects of space charge, the time required for a CIM to drift from one electrode to the other is given by Eq. 12. For a fixed frequency the transit time varies as  $t_{tr} \propto 1/\sqrt{V_p}$  (see Eq. 13). For very low voltages ( $V_p < 20 V$ ,  $t_{tr} \gg 1/4f$ ) in Fig. S2 (a), the CIMs do not move much from their initial positions. For example, the distances travelled by the CIMs when  $V_p = 1$ , 5 and 10 V are 2.3, 5 and 7 µm respectively, which are much smaller than the distance between the electrodes, i.e. 40 µm. Therefore, the field in the device remains approximately V(t)/d and the linear approximation is valid, Fig. S2 (a). For intermediate voltages ( $\sim 20 V < V_p < 100 V$ ,  $t_{tr} > 1/4f$ ) the CIMs move over a larger distance and the resulting space charge affects the field in the device resulting in a nonlinear current. For large voltages ( $V_p > 100 V$ ,  $t_{tr} \approx 1/4f$ ) the CIMs move all the way to the electrodes until the bulk is depleted of CIMs. The separation of CIMs (up to t = 0.03 s for  $V_p = 400$  V) results in an increasing current while during the depletion phase the current decreases due to the arrival of CIMs at the opposite polarity electrodes. The discrepancies between the measurements and simulations for larger voltages just after first half cycle (t > 0.1 s, in Fig. S2 (b to f)) can be attributed to electrohydrodynamic (EHD) instabilities that are likely to occur for the reversal voltages with a value of  $V_p > 20$  V. For intermediate voltages ( $20 \text{ V} < V_p < \sim 200 \text{ V}$ ) in Fig. S2 (b – c), the mismatch in the integral of the measured and simulated current peak is also a consequence of the EHD flow in the bulk: due to the EHD flow, practically all charges are transported to the opposite electrode in a faster time than expected from the simulations. For the largest voltages in Fig. S2 (d – f), the integral of the measured current peak matches with the simulation because the field is strong enough so that also without EHD flow all the bulk charge is transported to the electrodes before the voltage starts decreasing. The measured current peak is much larger and has a shorter duration than the simulated current peak ( $V_p > 200$  V). The reason for this is that, due to the EHD flow, the CIMs are transported faster to the opposite polarity electrode, resulting in a larger current with a shorter duration than in the simulation, where the CIMs are transported only according to drift and diffusion.

# **S3.** The Estimation of Mobility and Size of the Individual Liquid Toner Particles

Here we describe how the mobility and radius of individual toner particles are determined by observing the particle motion under influence of an electric field with a microscope using a method which has been described elsewhere in detail<sup>27</sup>.

#### **S3.1.** Experiment



**Figure S3:** A single particle tracking set up consisting two parallel gold coated electrodes at a distance *d*. The Space between the electrodes is filled with a diluted dispersion of liquid toner in the carrier liquid and then a particle is focused and images of the particle are acquired without or with an applied ac voltage.

Optical measurements are used to estimate the mobility, the charge, the size of the individual colloidal particles. The experimental setup consists of a camera (Pulnix TM-6740L) mounted on a microscope with a 40 times objective, two gold coated parallel electrodes separated by a distance  $d = 70 \mu m$ , a data acquisition device used to apply a sinusoidal voltage across the electrodes and all parts of the setup are controlled using a graphic user interface. The gold coated electrodes are specifically used to generate a uniform one dimensional field between the electrodes. The experimental sequence is as follows: firstly a 1:100 diluted dispersion of liquid toner in the carrier liquid is prepared. Then, the

space between the electrodes is filled and the electrodes are covered with a cover glass plate to minimize the effects of the surrounding perturbation on the setup as shown in Fig. S3. Afterwards, the setup is short circuited for at least 100 s to ensure a homogeneous distribution of the charge between the electrodes. Then a particle is brought into focus and images of the particle are acquired in the absence of an electric field for 2 s. Subsequently, a sinusoidal voltage (amplitude 50 V with a frequency of 10 Hz) is applied across the electrodes and images are acquired at a frequency of 100 Hz. The whole experiment is controlled by a LabVIEW program using a graphical user interface. By image analysis of the acquired images, the discrete positions of the particle are extracted in the *xy*-plane (*x*, *y*). The *x*-direction is chosen perpendicular to the electrodes and parallel to the direction of applied electric field. From the acquired position data of the particle in the absence of a voltage the hydrodynamic radius of the particle is estimated while from that acquired in the presence of a voltage the average mobility of the particle is estimated using a method which has been described elsewhere.

#### S3.2. Results



**Figure S4:** (a) The trajectory of a single liquid toner particle in the 'x' direction without and with a sinusoidal voltage of  $V_p = 50$  V with a frequency of 10 Hz. (b) Histogram of the hydrodynamic radius of 100 liquid toner particles estimated from the Brownian motion of particles for a duration of 2 s. (c) The mobility histogram of 90 liquid toner particles. The particles with zero mobility are not included in the mobility histogram.

The measured *x* position of a liquid toner particle as a function of time is shown in Fig. S4 (a). From t = 2 s to t = 7 s a sinusoidal voltage of frequency f = 10 Hz and peak voltage  $V_p = 50$  V is applied across the electrodes separated at a distance  $d = 70 \,\mu\text{m}$ . In the absence of an electric field, the change in the position of the particle is due to Brownian motion while in the presence of an electric field, the particle oscillates in the direction of the electric field, i.e. the *x* direction. From the position data of the particle is estimated<sup>27</sup>. In Fig. S4 (b), a histogram for the size of 100 particles is shown; the mean size of the particles is  $0.9 \,\mu\text{m}$ . The mobility distribution of 90 particles, calculated from their motion in a sinusoidal electric field, in Fig. S4 (c). In the mobility histogram Fig. S4 (c), the particles have a positive mobility which means that they are positively charged. The mean value of the mobility is around  $30 \,\mu\text{m}^2/\text{Vs}$ . Using Eq.:  $\mu = Ze/(6\pi\eta r)$ , the average charge on a particle is estimated and is found to be 18 *e*.

A similar type of study has also been performed on quina- cridone pigment particles (Paliogen Red Violet L5100 from BASF) dispersed in n-dodecane with poly- isobutylene succinimide (PIBS or commonly known as OLOA 1200 from Chevron Oronite) as a charging agent<sup>27</sup>. In this study, the authors find that the particles are negatively charged with the mobility ranging from -10 to -600  $\mu$ m<sup>2</sup>/Vs. These findings are consistent with the other reported studies in the literature<sup>3,10,32</sup> and have been explained on the basis of acid-base interactions<sup>3,7,10,32</sup>. However, in our study, we find most of the particles are positively charged with a relatively low value of the mobilities which may be linked to the nature of surfactant Solsperse and the particles surface.