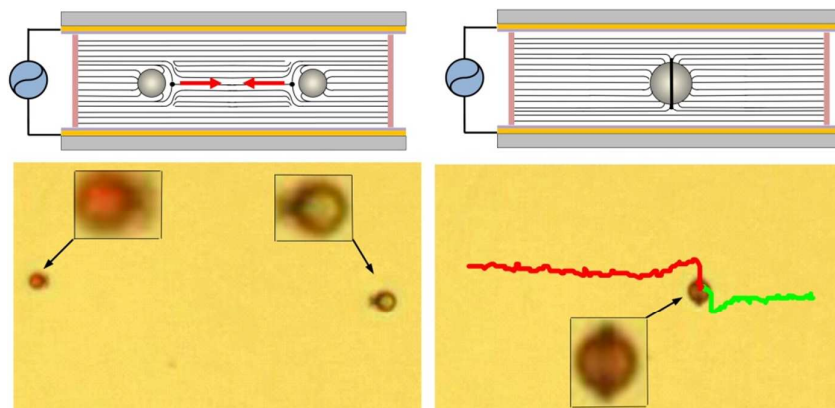RSCPublishing Soft Matter

AC Electrophoresis of Microdroplets in Anisotropic Liquids: Transport, Assembling and Reaction

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TOC:

Controlled motion of microdoplets in anisotropic fluids is a rich field of research which unveils new perspectives in the transport of water miscible chemicals or drugs. We demonstrate several strategies to transport, react and assemble in a controlled way microdroplets of aqueous solution in a nematic liquid medium. As an example, the images show the mixing of two different water soluble dyes (red and green) to give rise to a final droplet having brownish color.

ARTICLE TYPE

AC Electrophoresis of Microdroplets in Anisotropic Liquids: Transport, Assembling and Reaction

Sergi Hernàndez-Navarro,[a] **Pietro Tierno,**[*b] **Jordi Ignés-Mullol,**[a] **Francesc Sagués**[a]

We describe the realization and controlled transport of water-based microreactors dispersed in a nematic liquid crystal and transported by application of an alternating electric field through the mechanism of induced charge electrophoresis. We characterize the propulsion speed of these microreactors in terms of droplet size, strength and frequency of the applied field and show how to use them to transport and 10 coalesce microscale colloidal cargoes or water miscible chemicals. Controlled motion of microdoplets in anisotropic fluids is a rich field of research which unveils new perspectives in the transport of water miscible chemicals or drugs.

Introduction

Water based microemulsions in oil phases are of fundamental 15 importance in chemical and analytical sciences, due to the possibility to encapsulate and deliver chemical or biological entities otherwise immiscible in the dispersion medium. The controlled transport of these microdroplets is of crucial importance for many applications related with lab-on-a-chip,[1] 20 drug delivery,[2] or the realization of remotely addressable micromotors.[3] In contrast to simple oils as dispersion media, anisotropic fluids like liquid crystals offer the advantage of showing a variety of phases and structures which can be easily controlled and changed via temperature or external fields. These 25 features, in turn, could be used to manipulate the physical or chemical properties of the dispersed droplets.[4]

In this context, nematic liquid crystals (NLC) are complex fluids massively used in display technology, and characterized by rod shaped molecules which tend to orient their long axis along one 30 direction, called director field. When a microscale particle is dispersed in a nematic medium, the distortion of the director field caused by the inclusion leads to the formation of defects around the particle, which will mainly depend on the anchoring conditions at the particle surface.[5] For homeotropic anchoring, 35 i.e. when the nematic molecules align preferentially perpendicular to the surface of the particle, two main defects can arise: a point defect known as hyperbolic hedgehog,[6] or an equatorial Saturn-ring like defect[7] [Fig. 1(a)-(c)]. A recent breakthrough in electric field transport of colloidal microspheres[8] showed that colloidal 40 particles with point defects can be transported in a NLC by using alternating current (AC) electric fields through the mechanism known as induced-charge electrophoresis (ICEP).[9] The electrophoretic motion of the particles is due to the fact that the point defect, in contrast to the symmetric Saturn ring, breaks the 45 spatial symmetry, unbalancing the ionic flows created by the field around the particle. The main advantage of this technique,

compared to the standard capillary electrophoresis methods based on the use of a direct current (DC) field, is the absence of ion migration, avoiding electrochemical processes and steady flows,[10] 50 thus making it suitable to transport also liquid rather than solid inclusions. It is worth remarking that for ICEP to occur, the system must feature broken symmetries. For instance, this phenomenon has been also reported for Janus particles in aqueous solution, where the contrast between metallic and dielectric half 55 surfaces results in unbalanced ionic flow and in particle motion under AC fields.[9] In this respect, the use of NLC provides a more versatile strategy, compatible with droplets of any nature, since the introduction of structural anisotropies in liquid droplets is a technically challenging process.[11]

60 We here demonstrate the controlled motion of water microdroplets dispersed in a NLC and propelled in this medium via AC electric fields. Point defects generated by the microdroplets in the NLC break the fore-aft symmetry and enable controlled motion of the water droplets in the direction of the 65 defect, even if the field is symmetric in time and space. Moreover, we employ a NLC with negative dielectric anisotropy, which induces motion of the inclusions perpendicular to the electric field. We characterize the droplets velocity in terms of droplet size, frequency and strength of the applied field, and show 70 that these droplets can be used as microreactors to transport in the nematic medium nanoscale particles or to mix femtosized volumes of chemicals, ranging from 10^{-14} to 10^{-16} L.

Experimental part

The experimental cell was composed of two 0.7 mm thick 75 microscope slides of size 15×25 mm^2, coated with a layer of indium-tin oxide (ITO), with surface resistivity = 100Ω/square (VisionTeck Systems). The slides were cleaned with a Micro-90 (Sigma-Aldrich) solution, dried and spin-coated with polyimide (PI-2555, HD-Microsystems), baked at 300 ºC, and then rubbed

with a velvet cloth to obtain planar alignment in one direction. The two plates were then separated by a polyethylene terephthalate spacer (Mylar, Goodfellow, nominal thickness 23 µm) and glued together along two sides with the ITO layers facing inwards.
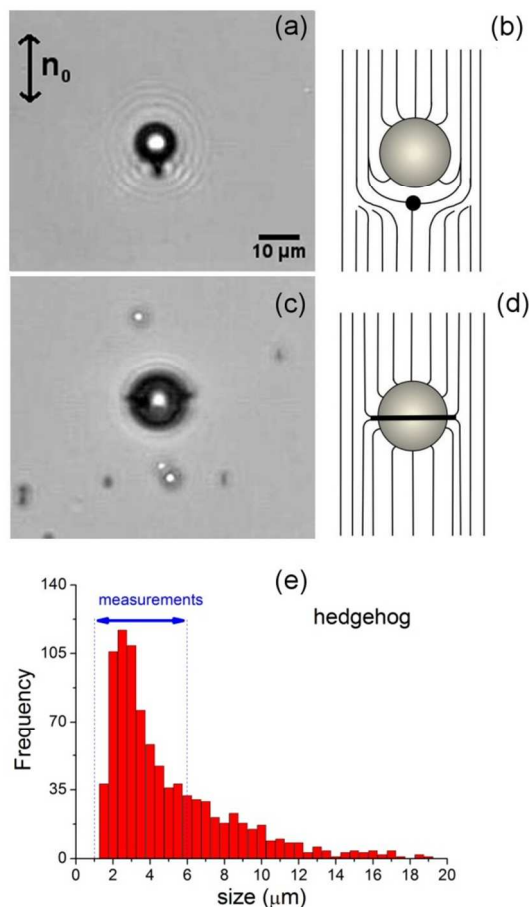

Figure 1. (a,c) Optical microscope images showing water microdroplets characterized by a hyperbolic hedgehog defect (a), and a Saturn-ring defect (c). In (a) the double arrow indicates the direction of the director field. (b) and (d) show schematics of the corresponding configurations of the nematic liquid crystal around the water droplets. (e) Histogram showing the typical population of particles with hedgehog defects in an experimental cell. The fraction of observed particles featuring a Saturn-ring was below 1%. Subsequent measurements were done for droplet size between 1 - 6 µm, as indicated in the image.

Actual thickness of cells was measured via interferometric techniques. Electrical contacts were made by eliminating part of the polyimide coating on the slides by using a suitable solvent (T9039, HD-Microsystems) and gluing wires with colloidal silver. Dispersions of aqueous microdroplets were created by adding 1 µL of Milli-Q water-based aqueous solution to 10 µL of a nematic liquid crystal (MLC-7029, Merck) with a negative dielectric anisotropy, $\Delta\varepsilon = -3.6$ at 1 kHz, followed by vortex agitation (IKA MS3 basic) for 3 minutes. Some tests were performed also by using the nematic liquid crystal MLC-2037 from Merk ($\Delta\varepsilon = = -3.1$ at 1kHz) and MBBA from Synthon Chemicals ($\Delta\varepsilon = = -0.53$ at 1kHz). The emulsions were stabilized using 0.01-0.05 M Sodium Dodecylsulphate (SDS, Sigma-Aldrich) which, in turn, induced homeotropic alignment of the nematic molecules at the LC/water interface. The experimental

cells were then filled by capillarity with freshly prepared dispersions and sealed with glue. With this protocol we obtained suspensions of polydispersed water droplets with sizes ranging from 1 to 20 µm in diameter and a distribution peaked at a diameter of 3µm (Fig. 1). Sinusoidal electric fields were applied to the experimental cell by using a function generator (ISO-TECH IFA 730) feeding a power amplifier (TREK model PZD700). The voltages were monitored by a multimeter (HP 34401A) and were in the range 0 to 30 Volts peak to peak, while the applied range of frequencies varied from 0 to 100Hz. Experimental observations were performed with an optical microscope (Nikon Eclipse 50iPol). Images and videos were captured with an AVT Marlin F-131C CMOS camera controlled with the software AVT SmartView 1.10.2. They were then treated and analyzed using the software packages ImageJ and IgorPro.

Results and discussion

In Fig. 1(a) and 1(c), we show optical micrographs of droplets featuring hedgehog (a) or Saturn-ring (b) defects. As shown in the corresponding schematics [Fig. 1(b) and 1(d)], the hedgehog defect is observed as a dark circular spot which appears on one side of the microdroplet, and oriented along the nematic director. As a result, the symmetry of the nematic director resembles that of an electric dipole. In contrast, the Saturn-ring defect displays a circular ring surrounding the microdroplet and features quadrupolar symmetry. In most of the experimental cells used in this work, we find that the distribution of defects around the microdroplets was predominantly of the hedgehog-type, while only a small fraction of inclusions (<1%) feature Saturn-ring defects. For the studies reported below, we restrict our analysis to droplets of diameter less than 6 µm. These constitute the majority of hedgehog particles [Fig. 1(e)] and are less prone to buoyancy effects, which tend to pin larger droplets.

In Fig. 2(a), we show the geometry of our experimental system. Water microdroplets were stabilized in the NLC matrix with sodium dodecyl sulphate (SDS). This surfactant provides strong homeotropic anchoring at the water/NLC interface, i.e. the NLC molecules tend to orient perpendicular to the surface of the inclusions. We observe that, once dispersed in the NLC, most of the water droplets display a point defect (hedgehog), arranged on one side of the particle, while few feature Saturn rings. The suspensions of SDS stabilized aqueous microdroplets were enclosed between two transparent electrodes, treated in order to induce planar (i.e. parallel) anchoring of the nematic molecules at the surface of the cell along a direction determined by the buffing of the polyimide layer. The cell spacing (23 µm) was chosen as a compromise to minimize the interactions with the cell substrates and to guarantee that most of the droplets where in the same observation plane.

In order to completely decouple the AC electrophoresis from any residual linear (DC) electrophoretic contribution, we choose to use a NLC characterized by a negative dielectric anisotropy, so the nematic director orients perpendicular to the direction of the applied field.[12,13] With this strategy, we transport the microdroplets always perpendicularly to the direction of the oscillating field. This has the further advantage that the motion

can be controlled along any arbitrary predesigned in-plane track in the NLC matrix.
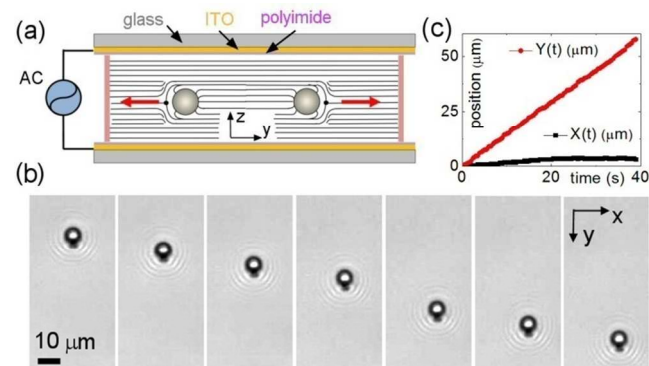

Figure 2. (a) Schematic of the experimental cell composed of water microdroplets dispersed in a nematic liquid crystal and enclosed between two transparent glass electrodes treated to induce surface planar anchoring. The water droplets are propelled by application of an AC electric field between the electrodes. (b) Optical micrographs taken every 4.5 s of a water droplet having 6.5 μm of diameter and propelled at a speed of 1.7 μm/s by an AC field with amplitude, $E = 0.7$ V/μm and frequency, $f = 10$ Hz. The corresponding video (Video 1) can be found in the Supporting Information. (c) Positions (x,y) versus time of the droplet shown in panel (b).

In our system application of an external AC electric field between both electrodes sets the droplets in motion always in the direction towards the point defect, Fig. 2(a). As it was reported by Lavrentovich and co-workers,[8] depending on the LC used the motion could be towards or against the point defect for the same particles and under the same conditions of applied field. After testing different liquid crystals, we found that the motion of the microdroplets was towards the point defects for MLC-7029 or MLC-2037, and against the point defect for MBBA.

We characterize the transport properties of the microdroplets by measuring their average speed as a function of the strength E (Figure 3(a)) and frequency f (Figure 3(b)) of the applied field, and as a function of the diameter ϕ for a fixed value of E and f (Figure 3(c)). In the first case, we observe that the droplets start to move above a threshold field $E_0 \sim 0.5$ V/μm and that the speed increases quadratically with the field, $v \sim E^2$. This electrophoretic behavior in a nematic medium is in agreement with previous work,[8,12] where it was found that the first nonlinear term in the speed was quadratic rather than cubic like in isotropic fluids.

A quadratic term allows using a symmetric AC field to move the particles in the medium, since changing the field polarity does not affect the particle speed. We confirm this quadratic behavior by fitting the experimental values with $v=\beta(E-E_0)^2$, and we find $E_0 = 0.49$ V/μm. Also, we find that the dependence of the droplets velocity on the frequency of the applied AC field can be well described by invoking the induced-charge electro-osmosis (ICEO) model, which was originally developed for isotropic fluids.[14] This model is based in the electro-osmotic flow that appears when a tangential electric field is applied to a charged surface. If the surface charge is fixed, the electro-osmotic flow is linear with the applied field. In contrast, if the surface charge is induced by the same applied electric field, the nonlinear phenomenon of ICEO takes place. In ICEO, the first nonlinear term is quadratic with the electric field, thus allowing the use of AC and not only DC fields to generate electro-osmotic flow. If

we have a spherical polarizable inclusion immersed in a liquid electrolyte and subjected to an electric field, a quadrupolar electro-osmotic flow is formed around the inclusion, from its poles to its equator. The electric field first generates the induced-charge screening cloud on the inclusion, and then it drives the resultant electro-osmotic flow, so the dependence on the electric field is quadratic. When using AC fields, it must be noted that ICEO will only take place if the frequency of the field is low enough to let the induced-charge screening cloud form, but high enough to avoid screening of the electric field by the diffuse-layer charging at the electrodes.
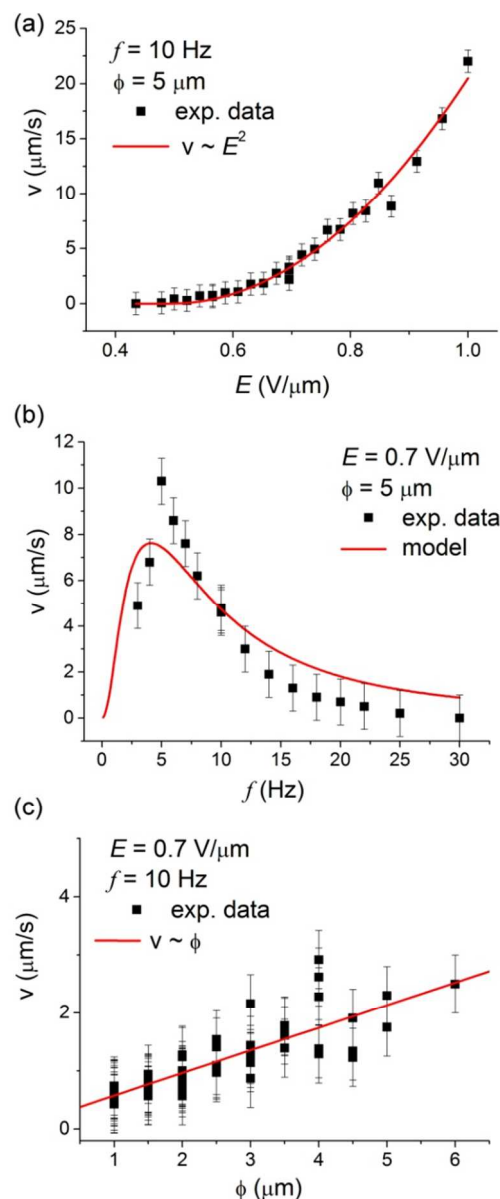

Figure 3. (a) Mean velocity v versus strength E of an applied AC field with frequency $f = 10$ Hz for a microdroplet with diameter $\phi = 5$ μm. (b) v versus frequency f of a $\phi = 5$ μm water droplet subjected to an applied AC field with strength $E = 0.7$ V/μm. (c) v versus size (ϕ) for microdroplets driven by an applied field with $f = 10$ Hz and $E = 0.7$ V/μm. For images (a) and (b), the continuous red lines denote fits following the equations described in the text, while in (c) it denotes a linear relationship between speed and size.

Following the model developed in Ref. [14], the velocity of the induced flow can be described by the following equation:

$$v(\omega) = v_0 \frac{\omega^2\tau_e^2}{(1+\omega^2\tau_c^2)(1+\omega^2\tau_e^2)} \tag{1}$$

being $\omega = 2\pi f$. As proposed in Ref. [8], this equation can be also used to describe the velocity of a particle in ICEP, where v_0 contains a quadratic dependence with the amplitude of the applied electric field, consistently with the data trend shown in Fig. 3(a). In Eq. (1), $\tau_c = \lambda_D \phi/2D$ is the droplet charging time and $\tau_e = \lambda_D L/2D$ is the electrode charging time. Here $\phi = 5$ μm, and the distance between the electrodes is $L = 23$ μm, which gives the ratio $\tau_e/\tau_c = L/\phi = 4.6$. Unknown parameters are λ_D, which is the Debye screening length of the droplet in the NLC, and D the diffusion coefficient of the ions. From the nonlinear fit of the experimental data, we find $v_0 = 11.5$ μm/s, $\tau_e \sim 0.09$ s, and $\tau_c \sim 0.02$ s, which gives a ratio $\lambda_D/D = 0.008$ s/μm. We estimate the Debye length λ_D, considering $\varepsilon_r=5.4$, T=298K, and a number density of monovalent ions in the LC of the order of $[10^{19} - 10^{20}]$ m^{-3},[15] which leads to $\lambda_D \sim [0.3 - 0.9]$ μm. Our fitted value λ_D/D is consistent with the previous range of values of λ_D, giving typical values of D in the range of $[10^{-10} - 10^{-11}]$ m^{2}s^{-1}.[16]

By varying the size of the microdroplets, we observe a linear increase of v with ϕ, at fixed strength and frequency of the applied field, which is consistent with the fact that larger droplets induce stronger distortion of the nematic director and thus enable larger electrophoretic speed.

We next demonstrate that these liquid droplets can be effectively used as microcarriers to transport, mix or disperse solid particles or femtoliter volumes of aqueous solutions. First, we observe that microdroplets with Saturn ring defects, although immobile, distort the motion of neighbouring droplets with point defects. The attraction between dipolar and quadrupolar droplets is long range and mediated by the elastic distortion of the nematic medium.[17] We use this property to realize a localized cargo release operation, as shown in Fig. 4(a). In particular, one microdroplet was previously loaded with polystyrene particles having 1.7 μm in diameter, and driven by an AC field towards a larger droplet characterized by a Saturn ring defect. The large droplet attracts the small one, and they coalesce releasing the colloidal cargo into a larger volume of fluid.

Droplets with point defects feature highly anisotropic interactions. In particular, a microdroplet with a point defect can be considered as a dipole, with one charge located on the point defect and the
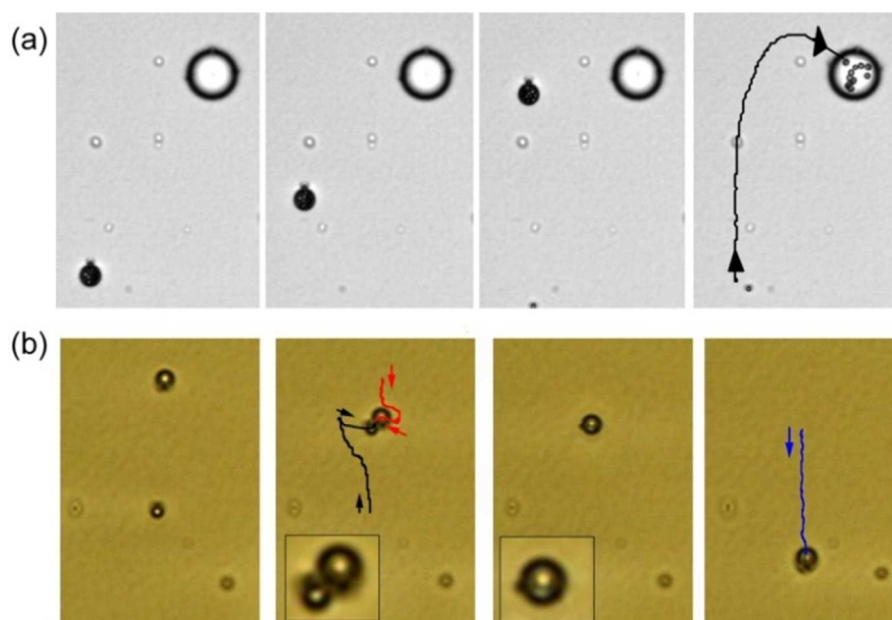

Figure 4. (a) Sequence of images showing the absorption of a microdroplet ($\phi = 7.3$ μm), filled with 11 polystyrene particles (1.7 μm diameter), by a larger droplet ($\phi = 18$ μm) with a Saturn ring defect ($E = 0.7$ V/μm, $f = 10$ Hz). Time interval between images is 17.2 s. (b) Microscope images showing two water microdroplets ($\phi = 2.7$ μm and 3.7 μm) driven in opposite directions by an AC field ($E = 0.70$ V/μm, $f = 10$ Hz) and containing the separated reactants, potassium ferrocyanide [hexacyanoferrate (II)] (0.2 M) and ferric ions [Fe3+] solution (0.3 M). The droplets approach and coalesce in a larger one ($\phi = 4.3$ μm), forming Prussian blue as a precipitate. In this particular example, the field was momentarily switched off to facilitate the assembly of the droplets. The AC field was then used to prompt coalescence and to drive the resulting droplet away from the reaction zone. The corresponding videos (Video 2 and Video 3) can be found in the Supporting Information

other, of opposite sign, located inside the droplet. In general, two approaching inclusions in the NLC will thus try to assemble with the defects in opposite sides.[18] In our case, we find that when driven towards each other, the microdroplets deviate from their collision trajectory. After crossing, their dipolar defects are in antiparallel configuration, and the two droplets attract and can

coalesce into a larger one. In Fig. 4(b) we use this feature to realize a chemical reaction by coalescing two water droplets doped with aqueous solutions of the reactants, potassium ferrocyanide [hexacyanoferrate (II)] and ferric ions [Fe3+] solution, in order to obtain Prussian blue,

$$4FeCl_{3(aq)} + 3K_4[Fe(CN)_6]_{(aq)} \rightarrow Fe_4[Fe(CN)_6]_3 \downarrow + 12KCl_{(aq)}$$
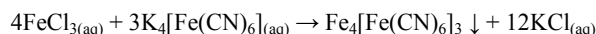
The resulting droplet shows the typical dark-blue precipitate of ferric ferrocyanide, and initially features a Saturn-ring defect, which quickly transforms back into a hedgehog defect, allowing to drive the reaction product to a desired location of the experimental platform. The process shown in Figure 4(b) is only an example of localized microreactions which can be performed with this technique. Our system also allows to explore a self-assembly scenario under AC fields. In particular, by modifying the experimental protocol by introducing the ultrasonication of the NLC emulsions, we are able to further reduce the size of the microdroplets. We find that smaller water droplets, with diameters below 1 μm, were less prone to coalesce. In particular, we show in the Supporting Information (Video 4) that application of the AC field was able to accumulate smaller droplets, while decreasing the frequency releases them in the nematic medium covering a larger area.

Conclusions

In conclusion, we have shown several strategies to transport, react and assemble in a controlled way microdroplets of aqueous solutions in a nematic liquid medium driven by AC electric fields. Although the process can be described in a semiquantitative way by the model of induced charge electroosmosis, the actual mechanism driving the liquid inclusions has still some pending questions, such as how the nature of the NLC determines the direction of motion of the dipolar droplets with respect to the position of the hedgehog defect. Using NLC with negative dielectric anisotropy allows driving the liquid inclusions in the direction perpendicular to the cell electrodes, which can include any predesigned track in the NLC matrix. For example, one could establish the direction of motion by locally altering the in-plane orientation of the NLC by means of an optical field in the presence of photosensitive confining layers. Controlled motion of microdoplets in anisotropic fluids is a rich field of research which unveils new perspectives in the transport of water miscible chemicals or drugs.

Acknowledgements

Notes

a Universitat de Barcelona, Departament de Química Física, Av.Diagonal 647, Barcelona Spain.
b Universitat de Barcelona, Departament d'Estructura i Constituents de la Matéria, Av. Diagonal 647, Barcelona Spain.
E-mail: ptierno@ub.edu
† Electronic Supplementary Information (ESI) available:
four videos files (3 .AVI 1 . WMV format). See DOI: ...

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SUPPORTING VIDEO FILES.

With the article there are four video files as support of the experimental results.

Video 1 (.AVI): Movie showing a water droplet with 6.5 μm of diameter and propelled at a speed of 1.7 μm/s by an AC field with amplitude, E = 0.7 V/μm and frequency, f = 10 Hz, Fig. 1(b) of the article.

Video 2 (.AVI): Movie showing the absorption of a microdroplet (ϕ = 7.3 μm), filled with 11 polystyrene particles (1.7 μm diameter), by a larger droplet (ϕ = 18 μm) with a Saturn ring defect (E = 0.7 V/μm, f = 10 Hz), Fig. 3(a) of the article.

Video 3 (.AVI): Movie showing two water microdroplets (ϕ = 2.7 μm and 3.7 μm) driven in opposite directions by an AC field (E = 0.70 V/μm, f = 10 Hz) and containing the separated reactants, potassium ferrocyanide [hexacyanoferrate (II)] (0.2 M) and ferric ions [Fe^{3+}] solution (0.3 M). The droplets approach and coalesce in a larger one (ϕ = 4.3 μm), forming Prussian blue as a precipitate. In this particular example, the field was momentarily switched off to facilitate the assembly of the droplets. The AC field was then used to drive the resulting droplet away from the reaction zone, Fig. 3(b) of the article.

Video 4 (.WMV): Movie showing several small microdroplets (ϕ ~ 1 μm) which are accumulated without coalescence around a larger one (ϕ ~ 7 μm) with a Saturn ring defect via application of an AC field with strength E = 0.65 V/μm and frequency f = 20 Hz. Later on they are dispersed by decreasing the frequency of the field to f = 3 Hz. To better visualize the small droplets, the video was recorded with crossed polarizers.

Dr Ian Coates
Publishing Editor
Royal Society of Chemistry,
Soft Matter

Pietro Tierno
Departament de ECM
Universitat de Barcelona
Av. Diagonal 647, 08028
Barcelona, Spain
Tel.: 0034-934020138
ptierno@ub.edu

Barcelona, 21/06/2013

Dear Dr. Coates,

enclosed please find our revised manuscript (ID SM-COM-03-2013-050757) entitled :

AC Electrophoresis of Microdroplets in Anisotropic Liquids: Transport, Assembling and Reaction.

by Sergi Hernàndez-Navarro, Pietro Tierno, Jordi Ignés-Mullol, Francesc Sagués

that we wish to publish in *Soft Matter*. We follow all recommendations of the referees, and our changes and responses are outlined in what follows. In particular, one of the main concerns of the referees (1 and 4) was that the article did not present enough novelty to be considered as a *Communications*, while both referees suggest that an extended version could be suitable as a *Paper*. We follow their recommendations, and provide with this submission an extended version with more details on the experiments and the model employed in the paper. We also ask You to consider this version as a *Paper*. Moreover, we have addressed the other criticisms, raised by referees 3 and 4, who asked for a better description of eq. 1, and the fitting procedure. We have rewritten the relevant paragraphs in order to improve their clarity.

We hope that with these changes the manuscript is now suitable for Soft Matter.

Sincerely yours,

Pietro Tierno

Answers to the Referees.

We thank the referees for their exhaustive comments which help to improve this manuscript. Here we list the response to their queries and the corresponding changes made in the paper.

Referee: 1
the authors describe AC electrophoresis of droplets forming dipolar director structures in liquid crystals. They first characterize general features of this AC electrophoresis, which they find to be similar to the ones recently reported in Ref. 8 of the manuscript. They then give examples of how they can make droplets coalesce (provided that the droplets move in different directions due to topological dipole orientations) and cause mixing or reactions between different fluid contents of droplets. Only the last part is novel as AC electrophoresis was already reported and characterized in Ref. 8. However, I do not see why it would be useful to go through such complicated procedures just in order to obtain droplet coalescence. Especially since controlling defect configurations while also varying droplet content (which can be only of very limited types) is very difficult. Droplet coalescence can be achieved by many much more simple but also robust and universal ways (such as optical manipulation & microfluidics) without having to involve complications with electrodes, liquid crystals, surface treatment, and, most importantly, having droplets with just right defects just opposite of each other...

Answer: As we state in the revised manuscript, we believe that the main advantage of LC-based AC electrophoresis is realised in droplet transport, since only Janus solid inclusions could be transported through the same phenomenon inside an isotropic liquid. Regarding the technical difficulty, we may argue that, although understanding the physichochemical processes involved may be an open challenge, the experimental procedures and setup required for LC-based AC electrophoresis feature some advantages with respect to microfluidics or optical techniques. In particular, LC-based AC electrophoresis did not require the use of photolithographic process or clean room facilities like in microfluidics. Optical methods are usually based on the use of focalized laser beams which could damage biological or chemical samples transported by the droplets due to local heat.

I feel that what is described in this manuscript has insufficient novelty and potential impact as compared to what we expect from publications in soft matter, especially as communication.

Answer: We have taken into account the reviewer's suggestion and reformatted our manuscript as a regular article, including additional material left out in the original submission.

Referee: 2
This is an excellent paper in the new field of liquid crystal electrophoresis. The authors demonstrate that by placing microdroplets of water and water-based solutions in a thermotropic liquid crystal, they can manipulate the transport of these particles by an AC electric field. The most impressive result is the demonstration of a coalescence of two droplets, one electrophoretically active and one inactive and the resulting mixing of their content. The quality of experiments is superb. I have the following minor remarks.

1. The drops are relatively large, ranging from 1 to 20 microns. Since the densities of the liquid crystal and water are different, they might sediment. The authors should discuss the issue, as it might be very detrimental to the entire idea of AC electrophoresis.

Answer: Although droplets in the size range 1 to 20 microns in diameter are produced with our preparation methods, only droplets of 6 microns or less are taken into account in our analysis of the electrophoretic motion. Larger droplets tend to pin on the substrate, probably due to buoyancy effects as suggested by the reviewer. We have included a statistical study of the droplet size distribution in Fig.1 of the revised manuscript.

2. The definitions of tau_c and tau_e on page 2 are misprinted, ad "D" in the denominator should be apparently a subscript, not an independent variable.

Answer: We thank the reviewer for bringing this typographical error to our attention. We have corrected it in the revised manuscript.

3. The authors use a liquid crystal with a negative dielectric anisotropy for electrophoresis. There is a recent publication by Lazo et al on the same approach, Phil. Trans. R. Soc. A 371, 20120255 (2013)

Answer: A reference to this recent work is present in the revised manuscript.

<u>*Referee: 3*</u>
In this work, the authors report a method to control the flow of water droplets in a liquid crystal phase using an AC electrical field. They show how changing the field parameters and droplets size can affect droplet mobility and be used to control droplet coalescence.
The paper seems interesting and well-done but I regret this is outside my field and I haven't read any of the related topics to be able to comment on its novelty or impact. Indeed I wonder if Soft Matter is the best outlet for this kind of work. The manuscript is very clearly presented and the figures and videos are informative.

Minor Points
P1L45: This is outside my expertise but I didn't understand the terms point defect and Saturn ring. On the next page the authors note these defects on their droplets but I'm not sure what they are or how they were seen. It might be worth more explanation for the general reader.

Answer: We have included a new figure in the revised manuscript with the definition and structure of the director field in the two types of defects observed in the inclusions with homeotropic NLC anchoring.

When Equation 1 was fit to the data I wasn't clear which were the adjustable parameters. Is this a typical Debyle length in a non-polar complex fluid? A citation would be helpful.

Answer: We provide an estimation for the value of the expected Debye length in this material, based on known material parameters and estimated ion concentrations as found in the literature (a new reference is added in the revised manuscript).

How were different-sized emulsion droplets made?

Answer: In all the experiments, we prepared the same type of emulsion, featuring a distribution of droplets sizes. We focus on droplets of small diameters since they give the most reproducible results. We have rewritten some sentences in the Experimental Section for clarity, and included an histogram plot in Fig.1 reporting the experimental droplet size distribution.

P2L18: I don't think these are microemulsions.

Answer: We have renamed our system "dispersion of water microdroplets" instead of microemulsions in order to avoid confusion.

Referee: 4
The authors study the movement of water droplets in a nematic liquid crystal. The approach builds on a recent paper (their reference 8 which showed similar manipulation for particles). The present paper seems to me to fall short – the basic ability to manipulate particles in nematic liquid crystals has already been shown, as the authors indicate in their introduction. Moreover, I can't tell if this is hype about using nematic liquid crystals in a controlled way in analytical and chemical devices or if there are serious possibilities and I think this should be more clear. There are nice scientific ideas to be explored here. To me the basic weaknesses are the incompleteness of what is actually shown, and that along with the major idea of particle movement being known, makes this version of the paper not suitable for a "communication".

Answer: We believe, as we answered to Referee 1, that this technique features several advantages compared to other methods related with the realization of analytical and chemical devices. For instance, the system we demonstrate here features the collective nature of microfluidics and it can offer the control of optical manipulation. In fact, we are currently experimenting with the reversible patterning of photosensitive substrates that will allow designing arbitrary tracks to guide droplet flow.
We follow the reviewer's advice and have reformatted our original manuscript, and included additional material in order to resubmit it as a regular article.

As far as "weaknesses" go, equation (1) is really incomplete. What sets v0?
Also, there should be one equation, of the form of (1) but also including the electric field dependence.

Answer: We have included an additional paragraph in the revised manuscript that summarizes the physical origin of equation (1) in the context of non-linear electro-osmosis, where it had been derived to describe the flow velocity induced by the AC field. As we clearly indicate in the revised manuscript, Lavrentovich and co-workers showed that the same equation can be empirically fitted to the velocity induced on colloidal particles by an AC field (non-linear electrophoresis). Since eq. 1 has to be considered an empirical expression, the parameter v0 must be considered as a characteristic scale for droplet speed, and one can expect that this parameter is

proportional to the square of the amplitude of the AC field, as we experimentally demonstrate.

The paper needs to do a better job of more completely comparing experiments and theory and such a revised paper could make a good normal article if done well. Moreover, I do not think showing coalescence is so significant as to merit a communication.

Answer: We take the reviewer's advice into consideration and have revised the manuscript into a normal article. Regarding the significance of showing the possibility to induce droplet coalescence through the mechanism reported here, this is clearly a matter of debate. Our view, strongly shared by reviewer 2, is that devising a strategy for the transport and coalescence of droplets with dissimilar cargo is what can lead to the applicability of the reported phenomenon in the context of lab-on-a-chip, or chemical reactions at small scales.