Discharges near water-heptane interfaces: application to emulsion production

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Abstract: Discharge in liquid is a research field that has potential in many applications. Herein, spark discharges are produced at and near water-heptane interface. When produced at the interface, the breakdown voltage is lower and the discharge occurrence is higher as compared with those produced far from it. The discharges modified the solution's color, and the presence of heptane droplets in water, i.e. emulsion, was seen. The droplet size distribution is determined and the formation mechanisms are presented and discussed.

Keywords: Discharge in liquid, immiscible liquids, emulsion.

1. Introduction

Discharge in liquid is a research field that has great interest for many applications such as nanomaterial synthesis [1] and liquid processing [2, 3]. During the last two decades, many studies have been conducted to investigate in-liquid discharges, particularly those sustained in streamer mode [4] and spark mode [1]. Discharges in liquid have been recently studied with the presence of an interface that can be a gas or liquid. The former is encountered in the case of discharges in liquid with gaseous bubbles [2, 5], whereas the latter is encountered in the case of discharge in two immiscible liquids [6], which is the subject of this study. It has been observed that the probability of discharge occurrence significantly increases as the pin of the electrode is approached to the heptane-water interface [6]. Moreover, the influence of water electrical conductivity on the discharge properties was investigated, and a streamer-to-spark transition is observed when water electrical conductivity is > 500 µS/cm [7].

In the context of nanomaterial synthesis, it has been observed that the discharges at heptane-water interface produced carbonaceous nanomaterials [8], and discharges at water-hexamethyldisilazane interface produced H:SiOC nanomaterials [9]. Moreover, discharges in heptane in contact with Ag-nitrate solution produced Ag nanoparticles (5-10 nm) encapsulated in C-matrix in heptane side and larger Ag particles (10-100 nm) in solution side [10]. In addition to the production of nanomaterials, discharge at the interface of two immiscible liquids modified the solutions' colors to milky-like that disappears after resting the discharge cell [9]: this is a signature of emulsion production. The formation of emulsion is a research subject that is usually investigated by the fluid mechanics community, such as ultrasonic cavitation [11]. The mechanisms involved in the emulsification process are numerous and rather complex [11], but the bubble cavitation induced by acoustic field excitation remains the most important. In the context of in-liquid discharges, the ignition is usually followed by the formation of a bubble that oscillates by performing series of expansion-implosion dynamics [12].

In this study, we produce spark discharges at / near to the interface of two immiscible liquids, water and heptane, to investigate the formation dynamics of emulsion. The electrical characteristics of the discharges are acquired as a function of discharge number. Among many parameters of interest, we report the variation of breakdown voltage for discharges, and different trends are observed depending on the electrode position regarding the interface. Then, the liquid is characterized, and the droplet size distribution of the produced emulsion is determined.

2. Experimental setup

The experimental setup is shown in Fig. 1. It consists of a glass beaker that is filled with 60 mL of distilled water and 20 mL of heptane. Since the two liquids are immiscible, a stable interface was obtained. The electrodes are vertically mounted in the beaker, and their heads are bent in such a way that they are parallel to the interface. The interelectrode gap distance was fixed at 100 µm, and the distance between the electrode heads and the interface (z) was varied between –2 and +2 mm. z = 0 refers to the position where the electrode heads are at the interface, while the positive and negative values refer to electrode position is in heptane and water, respectively.

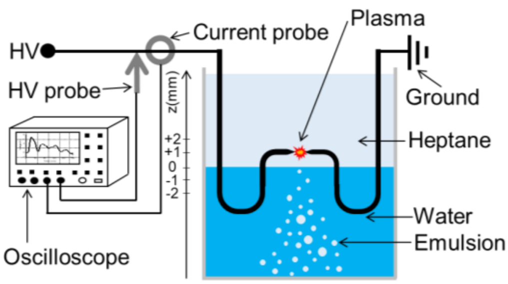

Fig. 1. Scheme of the experimental setup.

Spark discharges are generated using a positive polarity power source (NSP 120-20-P-500-TG-H; Eagle Harbor Technologies) at an amplitude of 20 kV, a pulse width of 500 ns, and a repetition rate of 5 Hz. The voltage and current waveforms of all the generated discharges were measured using a high-voltage probe (P6015A; Tektronix) and a current monitor (6585; Pearson), respectively, and both were displayed and acquired on an oscilloscope (MSO54, 2 GHz; Tektronix).

3. Results and discussion

The characteristics of 5000 successive discharges were recorded, and typical current-voltage waveforms are shown in Fig. 2. The drop of the voltage and the increase of the current to ~60 A are typical of an in-liquid spark [1]. The acquired data are processed using a previously developed algorithm (a detailed description can be found in [13]), and quantities of interest were extracted. Briefly, based on the voltage waveform, the algorithm detects if it corresponds to a failed or an occurred discharge. For occurred discharges, it determines the breakdown voltage, among other quantities.

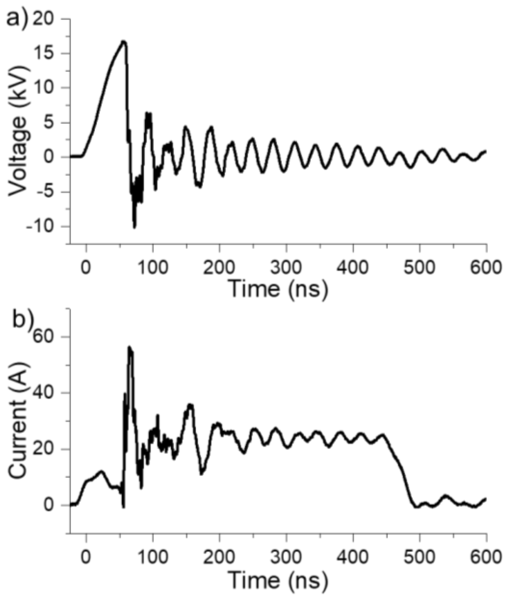

Fig. 2. Typical voltage-current waveforms of a spark discharge at the water-heptane interface (z = 0).

Fig. 3 shows the percentage of successful discharges among the 5000 applied pulses. It is noticeable that for electrode position far from the interface (z = ±1 and ±2 mm), one obtains successful discharges between ~40 and 60%. However, when positioned at the interface (z = 0), the percentage of successful discharges is close to 100%.

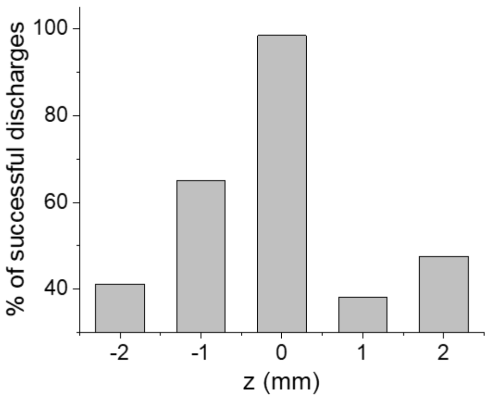

Fig. 3. Percentage of successful discharges for 5000 applied pulses at different z = 0, ±1, and ±2 mm.

The variation of breakdown voltage as a function of discharge number for two z-conditions are shown in Fig. 4. One remarks that the initial few discharges occur at a voltage value (~16 kV at z = 0 and ~18 kV at z = -1 mm), that is smaller than that of the pre-set plateau value (20 kV). This means that the discharges have occurred in the rising period of the pulse. Far from the interface (z = -1 mm), one notes a monotonous increase of the breakdown voltage that reaches ~20 kV (plateau value) after ~1500 discharges and remains so for the following discharges. Such an increase is due to the reduction of the E-field induced by the increase of the gap distance (due to electrode erosion). However, the variation of breakdown voltage for the discharges that occurred at the interface (z = 0) exhibits a significant drop (from ~16 to 12 kV) in the period of 100-150 discharges. Then, it increases monotonously to reach that of the plateau after ~2000 discharges. The trend observed at z = 0 indicates the occurrence of phenomena at the interface that facilitate the discharge occurrence and lower the breakdown voltage.

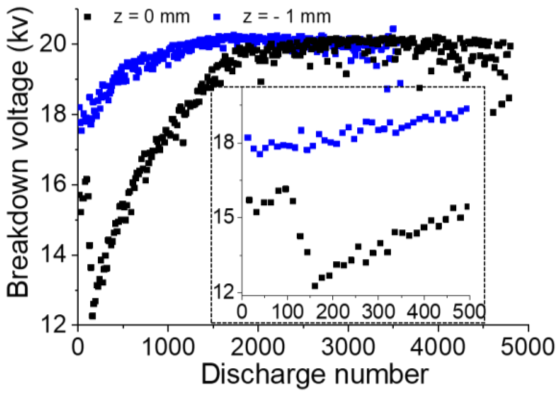

Fig. 4. Variation of the breakdown voltage as a function of discharge number for z = 0 and -1 mm.

In fact, during discharges at the interface (z = 0), we remarked that the water colour changes significantly, as it becomes less transparent and turbid; light transmittance measurement has been conducted as a function of time to report such a modification (not shown here). We also extracted liquid samples from water and imaged using optical microscope. Fig. 5 shows a typical image of the solution after 5000 discharges. This image clearly shows the presence of spherical micrometer-size objects, i.e. microdroplets of heptane in water—an emulsion.

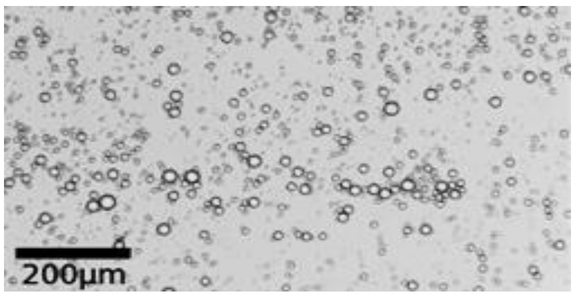

Fig. 5. Optical image microscope of solution sample after 5000 discharges at z = 0 mm.

The droplet size distribution was determined by processing the images recorded by the microscope (such as

Fig. 5) using ImageJ software. Fig. 6 shows the droplet size distribution after 5000 discharges. This distribution shows that the average droplet diameter is ~8 µm with a tail up to ~25 µm.

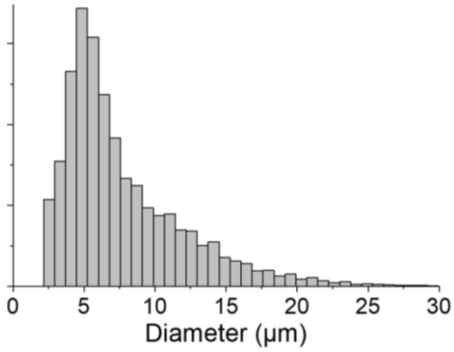

Fig. 6. droplet size distribution obtained by analysing the images recorded by the microscope (such as Fig. 5) using ImageJ software.

The presence of microdroplets of heptane in water induces discontinuities in the properties of water, mainly in density (ρ_{water} = 1 vs. $\rho_{heptane}$ = 0.7 g/cm^3) and in dielectric permittivity (ε_{water} = 80 vs. $\varepsilon_{heptane}$ = 2). The discontinuity of ε significantly modifies the distribution of the E-field and, therefore, the discharge occurrence and its characteristics. To quantify this modification, we performed a 2D simulation to numerically resolve Laplace's equation ($\vec{\nabla} . \varepsilon \vec{\nabla} V = 0$) and to determine V as a function of position (*x*,*y*). Then, the E-field distribution across the *x-y* plane is deduced via $\vec{E} = -\vec{\nabla} V$. The emulsion is simulated using a Monte Carlo approach, where a given number of spherical droplets of heptane are uniformly distributed in water, and the droplets' diameter was chosen randomly from the experimental distribution (Fig. 6). The results of the simulation are shown in Fig. 7; the right-hand side represents the case without droplets and the left-hand side represents the case with droplets.

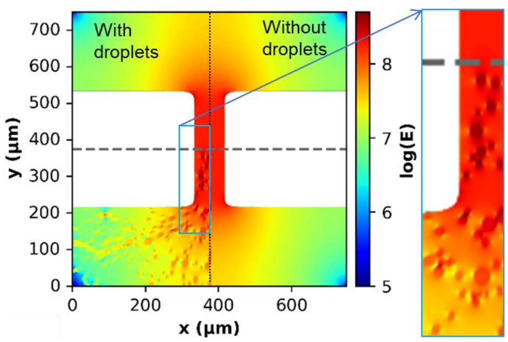

Fig. 7. Simulation of the E-field distribution without (right-hand) and with (left-hand) droplets.

The simulation displayed in Fig. 7 clearly shows that the presence of heptane droplets in the gap creates zones with high E-field (almost one order of magnitude higher) as compared to the case without droplets. This finding explains the behaviour of both, the high percentage of successful discharge (Fig. 3) and the drop of the breakdown voltage after ~100 discharges (Fig. 4).

Concerning the formation mechanism(s) of the emulsion by in-liquid discharges, it is important to recall those identified using ultrasonic cavitation in a medium containing two liquids [11]. In such cases, the acoustic field produces bubbles oscillation (explosion-implosion) near the interface and, depending on the relative viscosity and density of the two liquids, the bubble implodes asymmetrically towards the denser liquid under the action of the Kelvin impulse. The strong shear flow at the interface produces instabilities which will result in a distortion of the interface and formation of small droplets, i.e. an emulsion. In the present study, the emulsion is produced by spark discharges at water-heptane interface. In such systems, it is well known that after discharge ignition, a shock wave is emitted, and an oscillating bubble, series of expansion-implosion, is observed [12]. Although the expansion phase produces a well-defined gas-liquid interface, instabilities (such as Kelvin impulse, Rayleigh-Taylor, etc.) develop during implosion phase [14] and lead to the formation of droplets of heptane in water. Although this mechanism may be the principal one, other mechanisms could also contribute to emulsion production, such as droplet fragmentation by shock wave. This subject will be further investigated by analysing the droplet size distributions (using optical imaging as well as dynamic light scattering) produced by different discharge number, particularly between 100 and 200, where a significant decrease in the breakdown voltage is measured.

4. Conclusion

Discharge in liquid is an expanding research field that has great potential in many fields. In this study, we produced spark discharges at / and near the interface of two immiscible liquids, water and heptane. We find that the discharge occurrence is enhanced when the electrodes are positioned at the interface. After discharges, the solution becomes turbid, and the imaging of solution samples by optical microscope showed the presence of microdroplets of heptane in water, i.e. an emulsion. The droplet size distribution ranges from few microns to ~25 µm, with an average size of ~8 µm. The continuous recording of the electrical characteristics showed that the breakdown voltage increases monotonously for discharges occurred far from the interface. However, when they are produced at the interface, a significant drop in the breakdown voltage is observed after ~100 discharges. The simulation of the E-field distribution by considering the presence of droplets showed the existence of zones with high electric field in the gap, which may explain the high percentage of discharge occurrence and the drop in the breakdown voltage for discharges produced at the interface.

5. Acknowledgements

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