Flow Electrification During Melting of Frozen Dielectric Liquids

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Abstract—We already have presented experiments made with melting dodecane (ISEHD 2014, Okinawa, Japan). These previous experiments were made with a cone of dodecane frozen either in liquid nitrogen or in thermostatic bath. In both cases, moisture could deposit on the frozen cone during melting which may change the interface behavior. In order to avoid such situation, we decided to make a new setup in which the dielectric liquid or solid is never in contact with ambient air but remains inside a closed chamber. In this paper we will describe this new setup and the measuring protocol. Then we will present experiments made with cyclohexane doped with several concentration of additives. Even if it is very weak, the charge transported by the droplets seems indicate that a flow electrification process exists. Furthermore, we will examine the evolution of the resistivity with the concentration in additive.

Keywords—Flow electrification, charge transfer, melting process

I. INTRODUCTION

It is now well known for several decades that a liquid flowing past a solid surface leads to a transfer of electrical charges, this phenomenon being called either “streaming current” or “flow electrification” depending on the scientific community by which it was concerned. In the case of dielectric liquids, this phenomenon may lead to electrostatic hazards and has been first investigate with the goal to reduce these risks [1], at the same period of time but for more fundamental understanding of the phenomenon, investigations was made by the group of Dr. John Gibbings [2], even some investigations was also made in order to perform high voltage generators using such phenomenon [3]. Later many other researches were performed either for fundamental or applications [4]–[6]. An important part of applications concerns chemical industry and electrical appliances, especially, high power transformers. The research presented in this paper is mainly fundamental and concerns the origin of the double layer. Indeed, it is well known that at the contact between a liquid and a solid, an electrical double layer appears. Then, the streaming current, is due to the convection of a part of this double layer by the motion of the liquid relatively to the solid surface. Several assumptions have been presented to explain the origin of this electrical double layer. The most realistic in the case of dielectric liquids in contact with different solid surfaces seems to be a kind of physicochemical reaction appearing at the interface between the solid and the liquid [7], [8]. The origin of this reaction could be due to a preferential affinity of the solid to one ion issued from weakly dissociated impurities existing in the liquid. However it seems that even very pure liquid in contact with solid develops an electrical double layer. Thus, from a fundamental point of view, it seemed interesting to see if an electrical double layer exists at the interface solid/liquid of a melting solid. Indeed in that case the chemical composition of the liquid and the solid are the same. In fact, the research presented in this paper is a continuation of two previous researches [9], [10] concerning the specific case of melting solids. The first one has concerned water with some acidic or basic solutions; the second one has concerned a dodecane without any addition of additive. In the case of dodecane, melting at -9°C and which is an insulating liquid, even if we did not put inside additives and despite the precautions that we took to avoid humidity, we were not totally sure that moisture did not exist at the interface. This is the reason why we built a new experimental setup used in the present study. We are first going to describe this experimental setup, then the measuring protocols and the evolutions of the setup due to the experimental difficulties that we encountered.

II. EXPERIMENTAL SETUP

The previous experimental setup used for dodecane and described in a previous paper [10] has been widely improve. This improvement took a lot of time, nearly one year, responding to the measurement difficulties that we had to face in order to have reproducible experiments. Indeed, the currents that we have to measure are very low, in the range of 10^-14 A, and the liquids that we test, have electrical characteristics strongly affected by the amount of impurities.

The first perturbation that we had to avoid was the influence of humidity. The liquids used are dielectric liquids (alcanes) whose electrical resistivity is usually very high in the range of 10^12 Ωm. In the previous experiments [10] even with many care, numerous experiments had to be rejected due to the moisture reaching the cone and totally perturbing the experiment. So, taking into account these difficulties, we have performed a new setup in which the liquid and the cone all along the cycling process: freezing, melting, freezing again ..., is in a closed vessel surrounded by a neutral gas, generally argon. Thus, the first design of this new setup is presented in Fig. 1.

It is composed of a stainless steel cylindrical block in which a tapered portion was dug. The closed vessel is made of a glass
tube placed between the cylindrical stainless steel block (at the bottom of the glass tube) and a flange of Teflon (at the top). Between this flange of Teflon and the glass tube and, as well, between the stainless steel cylinder and the glass tube, O-rings made of Viton provide sealing. Thus, the volume inside the glass tube is totally insulated from the surrounding air. This cavity is then filled with argon gas. In such configuration, the liquid or the frozen cone inside the glass tube is well protected against humidity and impurities. Three threaded spindles screwed into the stainless steel block and passing through the flange of Teflon can maintain (by using springs) the O-rings in compression, thus ensuring tightness. The liquid to test is introduced to the tapered hole of the stainless steel cylinder with a syringe fitted with a long needle introduced through a tube inserted in the flange in Teflon. One metallic hook with a ring attached to a vertical stainless steel small tube is immersed in the bulk of the liquid and hanged through a spring to another vertical stainless steel tube which passes through a tube inserted in the flange of Teflon. The glass tube has, on one side, one smaller size glass tube (2.5 cm in diameter) which allows to insert a video camera used to record the melting process. Indeed, when the liquid is totally frozen, after a few minutes (needed to increase a little the metalic block temperature in order to pull off the cone from the stainless steel) the frozen cone can be hanged facing the video camera and thus make possible control of the melting process (Fig. 2). With the help of O-rings around the vertical tube holding the cone, no passage exists between the argon which is inside the setup and the surrounding air. Two small tubes inserted in the Teflon flange make the communication possible between inside of the setup and the surrounding. One is used to either introduce the liquid or fill with argon gas. The other one is connected to a small balloon (photo in Fig. 3) which maintains a pressure inside the setup to prevent external air to come inside.

III. EXPERIMENTAL PROTOCOL

The experimental setup is placed in a glovebox under argon gas. The liquid is introduced inside the setup with a syringe connected to a stainless steel tube. Then, the setup is filled of argon gas until the balloon would be sufficiently inflated to maintain pressure to prevent the ingress of moisture. Then, the series of experiments with this liquid sample can begin.

The setup is placed in a thermostatic bath in order to freeze the liquid. Depending on the freezing temperature of the liquid sample, this operation takes between half an hour to one hour and half. We can detect when the liquid is totally frozen by pulling the thin tube connected, through the spring, to the hook holding the cone. The elasticity of the spring indicates that the liquid is frozen, and that the cone is stick to the stainless steel cylinder.

The setup is, then, taken out of the thermostatic bath and it is need to heat the stainless steel cylinder in order to speed up the detachment of the cone. The cone is placed in front of the video camera and all the setup is placed to another thermostatic bath in order to regulate the melting of the cone. All the apparatus is well shielded in Faraday cages. The hook, on which the melting cone is hanged, is connected to a Keithley electrometer.

The electrometer is itself connected to a data acquisition board and a computer. We used LatisPro to record the current. We record also the video of the melting of the cone. Fig. 4 is an example, in which we can easily see the droplet before falling.

IV. EXPERIMENTAL DIFFICULTIES

The experimental difficulties are mainly linked to the very small currents that we have to measure and also to the moisture, which inevitably, is deposited on cooler mounting
elements than the surrounding air. We had also some false results due to different artifacts. One example of such artifact was due to an hair dryer that we used to warm up the stainless steel cylinder when it was taken out of the cold thermostatic bath. We faced this problem, specially when using dodecane (we perfected the protocol with dodecane before using cyclohexane). The melting temperature of dodecane, is around -10°C, thus, the operational temperature of the cold thermostatic bath, was set at -30°C. Then, we use an hair dryer to warm up the cylinder. After, we found very high pulses, generally decreasing in time, not at all reproducible. After several attempts to understand what was at the origin of such behavior, we found that the hair dryer had deposited charges on the glass tube, which, then, charge the droplets. Thus, we put a grounded metallic grid around the glass tube and generally we avoid the use of the hair dryer. Another difficulty comes from the humidity which deposit on the glass tube then forms droplets which slide on the tube creating an induction on the frozen cone. Moreover, the charges existing on the insulating material covering the different cables create an induction. Thus, we must put all the setup inside a cage filled of dry argon gas and we must cover the cables with metallic sheaths.

With all these precautions and several Faraday cages, we could measure currents in the order of 10^{-14} A.

V. EXPERIMENT

We made experiments with cyclohexane without additives and with several concentrations of AC60C. The experiments made without additive has given currents so small that they were not measurable.

L’AC60C is an Alkylsalicylate of calcium (Fig. 5).

This additive added to others additives are generally used as lubricants.

Two sets of experiments were made: one with a rapid melting and another one with a slow melting. This can be obtained by varying the temperature of the second thermostatic bath. The rapid melting occurs for a bath temperature of 35°C and the slow melting for a bath temperature of -10°C.

For experiments at 35°C we used five different concentrations of AC60C: 100ppm, 200ppm, 500ppm, 1000ppm and 5000ppm. For experiments at -10°C we used only the three first previous concentrations. Some examples, among numerous recording, are presented in Figs. 6–14. They represent the current due to the fall of the droplets. In all the experiments, the droplets were negative, thus, as we measure the current generated on the cone due to the separation of each droplet, this current is positive and opposite of what we see on the figures because the output signal of the electrometer is opposite to its input signal. In fact, the figures could correspond to the current measured on the vessel in which the droplets are falling; but we could not measure this current, because the collecting vessel (the stainless steel cylinder) is grounded. In reality, the current on the cone increases very rapidly when the droplet detaches itself the cone (because the droplet is negative), then it slowly decreases with a time constant due to the resistance and the capacity of the setup, the wires and the electrometer. Of course, as there is an inversion, we see on the figure a rapid decreasing and then a relaxation. The time origin on the figures has been adjusted in order to start at “0” on the figure. As well, the currents origin has been shifted in order to show values around “0”, but in reality often there is an offset due to multiple causes.

We can notice that all the signals are noisy due to their very low level. Every rapid decreasing, corresponds to the fall of a droplet. Obviously, we can notice that the fall frequency is more rapid for rapid melting (35°C) than for slow melting
Fig. 7. Example of current record obtained for a cone containing 200ppm of AC60C and melting at 35°C.

Fig. 8. Example of current record obtained for a cone containing 500ppm of AC60C and melting at 35°C.

Fig. 9. Example of current record obtained for a cone containing 1000ppm of AC60C and melting at 35°C.

Fig. 10. Example of current record obtained for a cone containing 5000ppm of AC60C and melting at 35°C.

Fig. 11. Example of current record obtained for a cone containing 100ppm of AC60C and melting at -10°C.

Fig. 12. Example of current record obtained for a cone containing 200ppm of AC60C and melting at -10°C.

Furthermore, it seems that the charge of each droplet is, generally, greater for slow melting. This could be due to a more complete development of the diffuse layer in that case.

The mean values of all the experiments made for each concentration in additive and for the two different temperatures of melting are gathered in Figs. 14-17. Figs. 14 and 15 correspond to the results obtained with a melting at 35°C for the five additive concentrations: 100ppm, 200ppm, 500ppm,
1000ppm and 5000ppm. Fig. 14 shows the peak current reaches when a droplet detaches itself the cone and Fig. 15 the charge on the droplet. Figs. 16 and 17 correspond to the results obtained with a melting at -10°C for the three concentration of additive used in that case. Fig. 16 shows the peak current and Fig. 17 the charge of the droplet.

The evolution in terms of the concentration in additive is not obvious; however, it seems to pass by a maximum for 200ppm of additive. In order to see if this corresponds to a critical micelle concentration (CMC), we have measured the evolution of the conductivity.

Indeed, at the CMC the slope of the conductivity in terms of the additive concentration must change. For this measurement we used the IRLAB tester as it was described in a previous paper [10]. The results are shown in Fig. 18. It seems that there is no clear change of the slope of the conductivity, or, at least not for a concentration of 200ppm.
In order to analyze the behavior of the conductivity at the freezing process we have measured the resistance between the hook and the stainless steel block during freezing. We can see this evolution in Fig. 19, the resistance decreases rapidly then stabilizes.

VI. CONCLUSION

A very weak electrical double layer seems to exist at the interface of a melting cyclohexane doped with additive but without additive we could not detect any flow electrification.

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REFERENCES