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A Non-destructive Thermal Stimulus Method as a Tool for studying the Electrical Double Layer

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Abstract—When a liquid is put into contact with a solid, two charge layers of opposite signs appear at the interface. This Electrical Double Layer (EDL) is the result of electrochemical reactions occurring in the region separating the liquid and the solid. A bottleneck in understanding and quantifying the EDL and its behavior is the availability of direct methods allowing to fully measure the EDL charge and distribution. This paper concerns the use of the Thermal Step Method (TSM) as a tool for characterizing the EDL to complete the flow electrification method. Several dielectric liquids (cyclohexane, mineral oil and silicon oil) are subjected to thermal step measurements. The obtained results are analyzed and discussed with respect to literature and to numerical simulations.

Index Terms—space charge, liquid dielectric

I. INTRODUCTION

The issues of space charges in dielectric liquids are related to the reliability of power components (such as power transformers), but also for setting up electrostatic applications, for increasing the efficiency of existing ones and for reducing electrostatic hazard. This involves an in-depth understanding of the mechanisms leading to the creation of charges and to their distribution, requiring methods able to characterize the charge amount and distribution as precisely as possible. A non-destructive space charge measurement technique developed for dielectric solids is the subject of this paper. The aim is to assess its use on dielectric liquids, particularly for characterizing the Electrical Double Layer, which develops at the interface between a solid and a liquid and consists in two charged areas of opposite sign. The concerned technique is the Thermal Step Method, which has been widely used on solid insulating materials along the last decades. The theoretical aspects of the Electrical Double Layer and the method are first presented, then

results obtained on several dielectric liquids are presented and discussed.

II. PRINCIPLES

A. Electrical Double Layer (EDL)

At the interface between a solid and a liquid, the occurrence of chemical reactions leads to a space charge distribution in the liquid and to a layer of charges of opposite sign in the solid. This set is named the Electrical Double Layer. The area in the liquid is subdivided in two layers: the compact and the diffuse layer [1]. It is widely believed and accepted that the compact layer has a thickness of the order of the ionic radius and it is composed of charges unable to move, but so far there is no experimental evidence on this matter. The diffuse layer is developing from the compact layer toward the liquid bulk. This layer is defined by two parameters: the space charge density at the wall for a totally developed EDL ρ_{wd} and the diffuse layer thickness which is related to the Debye length δ_0 (1):

$$\delta_0 = \sqrt{\frac{\varepsilon_0 \varepsilon_r D_0}{\sigma}} \quad (1)$$

where ε_0 and ε_r are the vacuum permittivity and the relative permittivity of the liquid, D_0 is the mean ionic diffusion coefficient of the liquid and σ its bulk conductivity. The amount of charge in the diffuse layer is mainly estimated by flow electrification experiments [2] [3]. However, the charges close to the interface cannot be approached with such experiments as the velocity of the liquid near a motionless wall is nil, so these charges cannot be carried away by the liquid flow. New techniques are therefore needed to better characterize the amount and the distribution of the charges in the EDL.

B. Thermal Step Method (TSM)

The TSM is a non-destructive method for measuring space charge, using the thermoelectric properties of the material in order to generate a current when a temperature step is applied to

the sample surface. Fig. 1 gives the principle of the TSM for a flat sample. The sample is defined by its geometry (thickness D and surface S) and its dielectric properties (relative capacitance variation with the temperature α and permittivity ϵ). Because the sample is considered as infinitely flat and that thermal conduction is the main heat transfer mode in solids, the problem can be assumed as unidirectional.

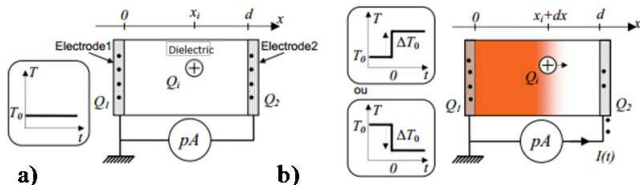


Fig. 1. Principle of the TSM ; sample at initial temperature (a) and after the thermal step (b).

The sample is short-circuited between the electrodes located at $x = 0$ and $x = d$, so when a temperature step $\Delta T = T - T_0$ is applied to electrode 1, the influence charges at electrodes are redistributed through the external circuit, creating a capacitive current (Fig. 1) measured by a current amplifier. By considering first order variations of the capacitance and by neglecting the conductivity of the dielectric, the resulting current can be written as [4]:

$$I(t) = -\alpha C \int_0^d E(x) \frac{\partial \Delta T(x, t)}{\partial t} dx \quad (2)$$

where C , $E(x)$ and $\frac{\partial \Delta T(x, t)}{\partial t}$ are respectively the sample capacitance at initial temperature, the electric field distribution and the variation of temperature distribution in the sample. The space charges distribution is given by the Poisson law (3) after the current signal has been processed to get $E(x)$ [5]:

$$\rho(x) = \nabla \cdot (\epsilon E(x)) \quad (3)$$

For a cylindrical sample of radii R_{int} and R_{ext} , the expression of the thermal step current is [5]:

$$I(t) = -\alpha C \int_{R_{int}}^{R_{ext}} E(r) \frac{\partial \Delta T(r, t)}{\partial t} dr \quad (4)$$

C. Measurement conditions

A complete measurement installation (cell and bench) has been developed with the aim to test the application of the TSM to dielectric liquids. The stainless steel cylindrical cell (Fig. 2) holds the sample in the intermediate room (2). The inner one (1) is used to produce the temperature step: ethanol (the cooling fluid) circulates from the top of the cell (A) to the bottom (B) and the temperature diffuses radially through the cell. The outer cavity (3) is used as a buffer to maintain the initial temperature at the edge of the sample and as a Faraday cage to insulate the cell from electromagnetic noise. To ensure good measurement conditions and purity of the sample, the cell is cleaned with heptane (a solvent with the ability to dissolve oil), then dried and filled with gaseous nitrogen. After that, by using a filling system, the liquid sample is pushed by nitrogen and enters into the cell from the bottom and pushes the gas to the outside environment through holes on the top of the cell. This procedure avoids the presence of gas bubbles in the liquid. After the filling

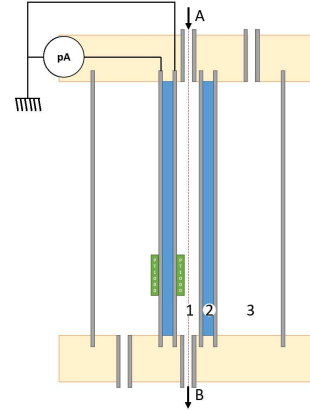


Fig. 2. Measurement cell - (A) Cooling inlet, (B) Cooling outlet - (1) Cooling fluid cavity, (2) Sample cavity, (3) Air cavity.

procedure, the liquid sample is left in contact with the stainless steel walls for several hours to allow the EDL to fully develop. During EDL development, the cylinders holding the sample are put in short-circuit. While the EDL is developing, the sample is brought at the initial temperature ($T_{amb} \approx 293.15 K$). Once the set-point is reached, the temperature step is applied and the response signal is measured with a current amplifier *nf CA-5350*. After the measurement, the cell is brought back to its initial temperature so as other measurements can be performed. In order to ensure a good reproducibility, for each temperature set-point the measurement is made 10 times and once the reproducibility is checked for each signal, the measured signals are averaged to reduce the noise.

D. Studied liquids

Three different liquid samples have been used in this work. The reference sample is mineral oil, a common dielectric liquid used in the industry, which develops a positive layer of charges in the liquid. The second one is silicon oil, which is known to develop a negative layer of charges in the liquid, but of a much lower amount than mineral oil [6]. The last sample is cyclohexane, which has a lower viscosity than the two other samples, so it is much more prone to thermal convection effects.

III. RESULTS AND DISCUSSION

A. Experimental results

The measured TSM current is proportional to the temperature step ΔT (eq.2) [7]. In order to make sure the TSM works on liquids in the same way it works on solids, experiments have been made on a sample of mineral oil by varying ΔT . For a temperature step of +1.5 K, a current with an amplitude of +4.5 nA is measured, and for $\Delta T = -2 K$, the current amplitude is -6 nA (Fig. 3). Both measurements have an amplitude of 3 nA/K, thus confirming the good functioning of the TSM on liquid samples such as mineral oils. The TSM currents measured on silicon oil with a $\Delta T = \pm 20 K$ have lower amplitudes than for mineral oil. Even though the signal/noise ratio is low, we observe that changing the sign of the temperature step also changes the sign of the current (Fig. 4). To ensure that the measured signals do not come from a reaction of the measurement cell to the application of the temperature step, empty cell currents are compared to silicon oil measurements

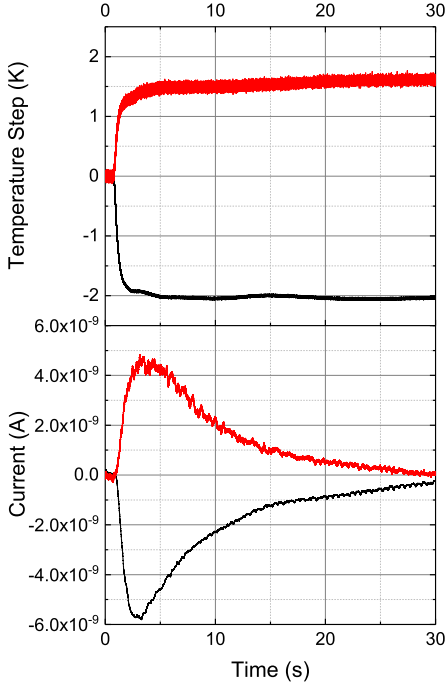


Fig. 3. TSM currents and temperature step on mineral oil for $\Delta T = \pm 2$ K.

with the same temperature steps. We can see that, even if the sign of the step changes, the current is not modified on empty cell currents. This means that the signals issued from silicon oil (Fig. 4) are relevant, although the signal/noise ratio is low, so it is difficult at this point to carry out interpretations. However, we can assume that silicon oil contains less charges than mineral oil, as it has been shown in the literature [6]. Literature also shows that silicon oil develops an EDL of opposite sign than the mineral oil. Here, TSM currents have not shown such results, but the difference can come from the sign of the α coefficient, which can be different for these two liquids. Calibration measurements could be useful to determine this coefficient [8]. With cyclohexane, two aspects which are different from the previous samples are observed (Fig. 5). First, the sign of the current is opposite to the one of the temperature step. Second, the current maximum is reached a few seconds after the step has been applied, while for mineral oil it happens simultaneously. To better observe and compare this behavior, let us define $Temperature^*$ and $Current^*$ the dimensionless temperature and current with a maximum amplitude of 1. For mineral oil, the current increases until the temperature reaches the set-point (Fig. 3 and Fig. 6), although for cyclohexane the current first slightly decreases and then increases to reach its maximum (Fig. 7). A possible cause could be the presence of thermal convection in this particular liquid, as its dynamic viscosity is about 20 times lower than that of mineral oil and about 50 times lower than that of silicon oil. The Rayleigh number for mineral oil (≈ 850) is lower than the critical value for the Rayleigh-Bénard instability (presuming the absence of convection), while the Rayleigh number of cyclohexane is 17000, much higher than the stability limit.

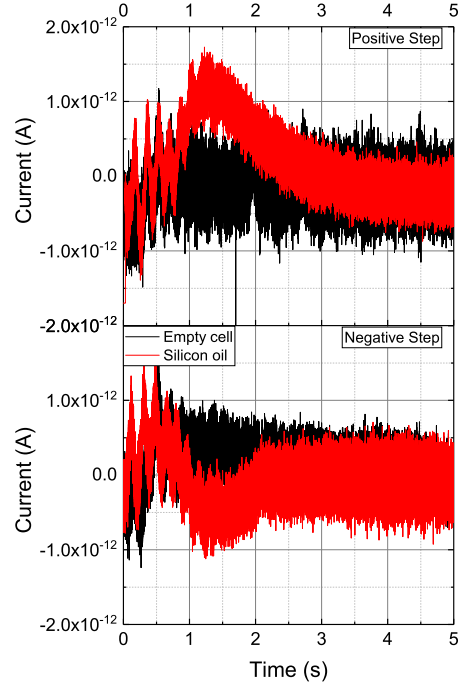


Fig. 4. TSM currents on silicon oil versus empty cell for a positive and a negative temperature step $\Delta T = \pm 20$ K.

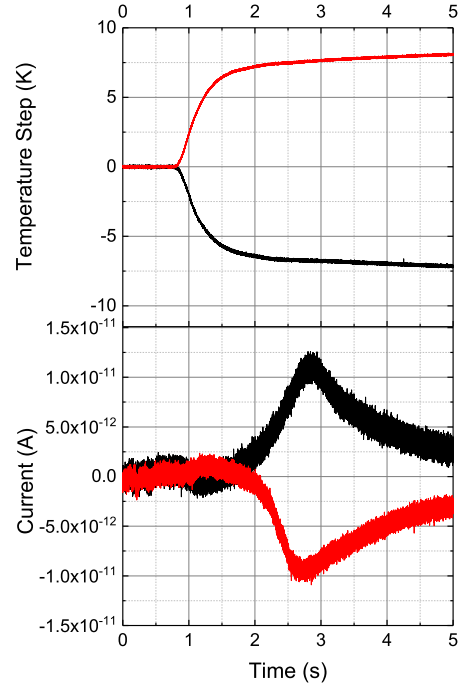


Fig. 5. TSM currents and temperature step on cyclohexane $\Delta T = \pm 8$ K.

B. Analysis of thermal convection hypothesis

Given that cyclohexane is the fluid with the lower viscosity in our study and that its behavior is different from the two other liquids, the effect of thermal convection in this liquid has been simulated. We have represented the measurement cell in Comsol Multiphysics® in a 2D axisymmetric geometry. We have set an exponential profile of EDL with $\rho_{wd} = 10^{-4} C.m^{-3}$ and a Debye length of $\delta_0 = 183 \mu m$, with respect to known values of cyclohexane parameters. In order to allow the circulation of

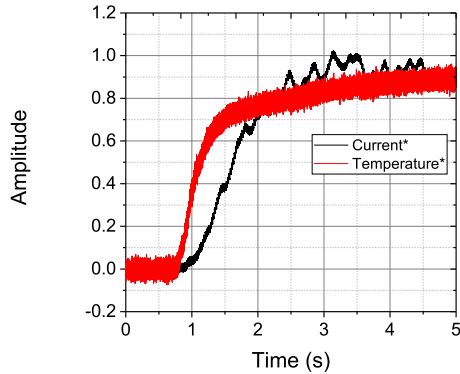


Fig. 6. Current* and Temperature* for $\Delta T = 2 K$ on mineral oil.

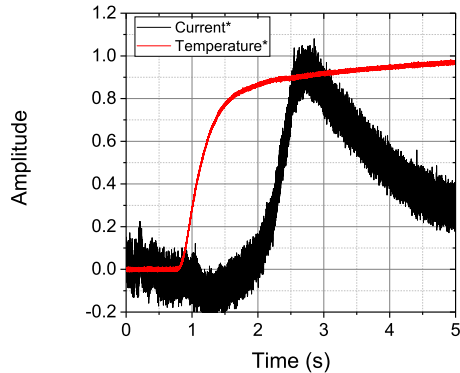


Fig. 7. Current* and Temperature* for $\Delta T = 8 K$ on cyclohexane.

fluid, we took into account the variations of density due to the variation of temperature. We also included a transport equation which links the velocity field \vec{u} of the sample to the space charge density ρ :

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\vec{u}\rho) = 0 \quad (5)$$

Simulation results are plotted in Fig. 8. The time constants are not the same as for the experimental results from Fig. 7 due to the difficulty to determine the velocity of the cooling fluid in the experimental bench. If we focus on the dimensionless currents, a first negative peak appears when the step is applied, then a higher positive peak occurs. By comparing the experimental results and the simulations, it seems that the first peak is the response of the space charges from the electrical double layer and the second peak is the result of the thermal convection occurring during the measurement. The main reason for the occurrence of this phenomenon in cyclohexane but not in mineral oil is the difference of dynamic viscosity, which is the ability of a fluid to resist to a laminar flow. At ambient temperature, this parameter is about $10^{-3} Pa.s$ for cyclohexane and about $2 \cdot 10^{-2} Pa.s$ for mineral oil. This means that more energy is needed to set into movement mineral oil than cyclohexane, and so the convection is more likely to occur in cyclohexane.

IV. CONCLUSIONS

In this work, several liquid samples have been subjected to TSM experiments to assess the applicability of this method for space charge measurements in dielectric liquids. Measurable

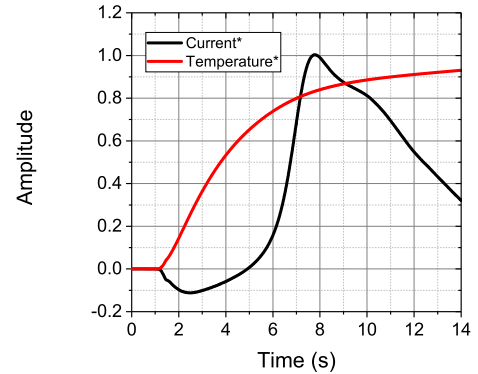


Fig. 8. Current* and Temperature* simulated on Comsol for $\Delta T = 8 K$ on cyclohexane.

and reproducible signals have been obtained from mineral oil, silicon oil and cyclohexane. These results seem to confirm the possibility of adapting the TSM to charge measurements in liquids. However, even if the obtained results are in accordance with the presumable amounts of charge in the liquids and with their thermal and mechanical properties, more work is to be done on the physical modeling and the experimental implementation in order to reach a full direct characterization of space charge distributions in liquids.

ACKNOWLEDGMENT

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