

# Experimental device to measure the ionic conductivity anisotropy in liquid crystal hydrogel based in [EMIM] alkyl sulfate Ionic Liquids

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## ABSTRACT

We have built an experimental device with the aim to measure the expected electrical conductivity anisotropy in a liquid crystal, obtained from the gelation of the ionic liquid 1-ethyl-3-methyl imidazolium decyl sulfate, [EMIM][DSO<sub>4</sub>]. This ionic liquid has the particularity that it transits to a semi-solid gel state at room temperature when it contains water, naturally adsorbed from the environment until a balance is reached between the concentration of water in the IL and the atmospheric humidity grade. The quantity of water adsorbed to form the hydrogel at room temperature varies from about 5 to 30 wt%, each composition giving place to different smectic phases. In the gel state, the ionic liquid ions and the water molecules self-organize into micro-sized mesophases that resemble the structures of a liquid crystal. Our device is a closed 2D sample holder (with sides 150 times longer than its thickness), with a single narrow window open to the atmosphere, and four copper contacts on the sides. The dried ionic liquid is tempered at 40 °C to increase its fluidity when injected into the cavity, and then, it can only adsorb water through the narrow opening. Thus, water adsorption is unidirectional and slow, so the transition of the IL to the gel phase happens progressively. A metastable giant mesophase appears as an orientated macrodomain in the form of a striped pattern. In this state, we measure the electrical conductivity of the confined film in directions parallel and perpendicular to the observed strips, finding a difference of up to 26% between both values of the conductivity. If the sample freezes (below 10 °C) or it liquefies (above 50 °C) the meso structure is broken and the observed anisotropy destroyed. We can return the sample to gel state by varying the temperature, but the ordered macroscopic state is no longer recovered. This research must give clues to solve the charge transport mechanism quiz in ionic liquids and semi-solid conductors.

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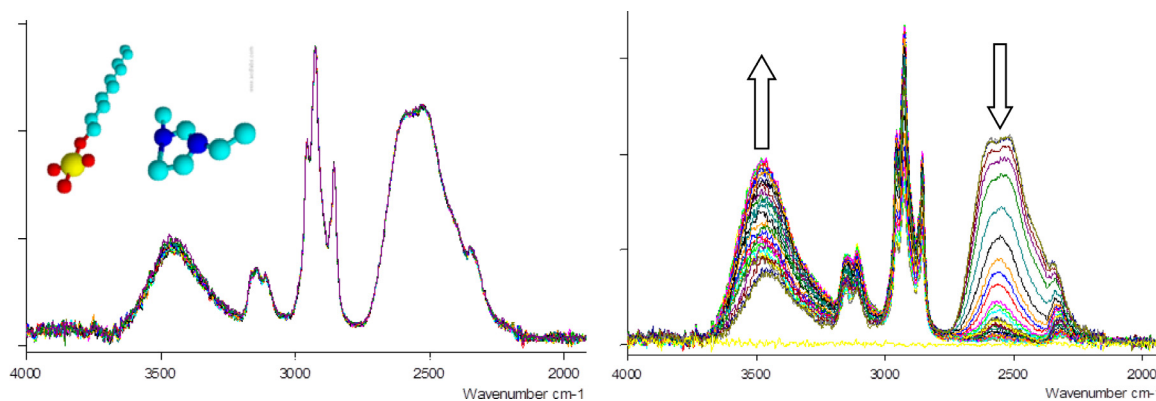
## 1. Introduction

In recent years we reported different studies about certain surface active ionic liquids (ILs) formed by the well-known 1-ethyl-3-methyl imidazolium, [EMIM]<sup>+</sup> cation an alkyl sulfate anion with eight [OSO<sub>4</sub>]<sup>-</sup> [1], nine [NSO<sub>4</sub>]<sup>-</sup> [2] or ten [DSO<sub>4</sub>]<sup>-</sup> [3] carbon atoms in the alkyl chain, the last two synthesized by us for the first time. The atomic formula of these ILs is C<sub>6+n</sub>H<sub>12+2n</sub>N<sub>2</sub>O<sub>4</sub>S, where n is the number of carbons in the alkyl chain. One of these ILs (in its semi solid gel phase) has been patented by some of us, specifically the hydrated [EMIM][DSO<sub>4</sub>] (Ref.: P201400476), whose constituent ions are represented in Fig. 1. These three ILs, have the peculiarity

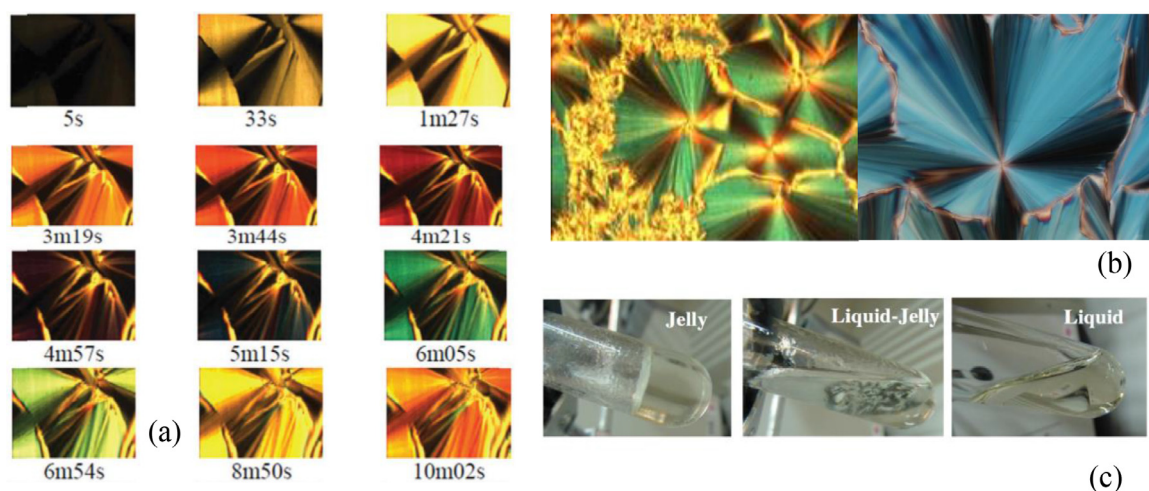
that they are in a semi solid gel phase at room temperature when they contain water, which is naturally adsorbed from the atmosphere due to its hygroscopicity. This same liquid-hydrogel transition occurs with surfactants based on long chain alkyl sulfates [4]. The water adsorption is a dynamic process, and the sample stabilizes in a composition when an equilibrium is reached between the concentration of water in the IL and the value of the relative humidity grade of the environment (it goes from 5 to 30% in weigh of water, which represent approximately a molar fraction of IL, from x<sub>IL</sub> ≈ 0.5 to 0.1). Thus, the water molecules are continuously exchanged between the compound and the atmosphere, so if we leave the sample in gel state in a dry chamber, over time the compound will become liquid by losing all the water previously adsorbed. For this reason, we assume it is an adsorption process and not absorption because it is reversible. To demonstrate this,

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**Fig. 1.** FTIR scans centred in the stretching peaks of H<sub>2</sub>O (about 3400 cm<sup>-1</sup>) and D<sub>2</sub>O (about 2600 cm<sup>-1</sup>) showing the time evolution of a sample hydrated with heavy water (32 scan series of 64 s each). At left with the sample closed to the atmosphere, and at right open to it. In this last case, we observe that the peak corresponding to the D-O bond decreases with time, while that corresponding to the H-O ones increases, indicated by arrows the scan temporal evolution for each peak. In the inset at left we represent the [EMIM][OSO<sub>4</sub>] ions, where the yellow sphere is for S, the red ones for O, dark blue ones for N and light blue ones for C (H atoms are not represented).



**Fig. 2.** (a) Time evolution of a sample of [EMIM][DSO<sub>4</sub>] at room temperature while it adsorbs water from atmospheric humidity observed using white light polarized microscopy (each picture covers an area of 400 × 290 μm<sup>2</sup>) extracted from Ref. [3]. (b) Micrographs of hydrated [EMIM][DSO<sub>4</sub>] (size 830 × 625 μm<sup>2</sup>). (c) Photographs of the gel-liquid transition of [EMIM][OSO<sub>4</sub>] at room temperature coming from the fridge.

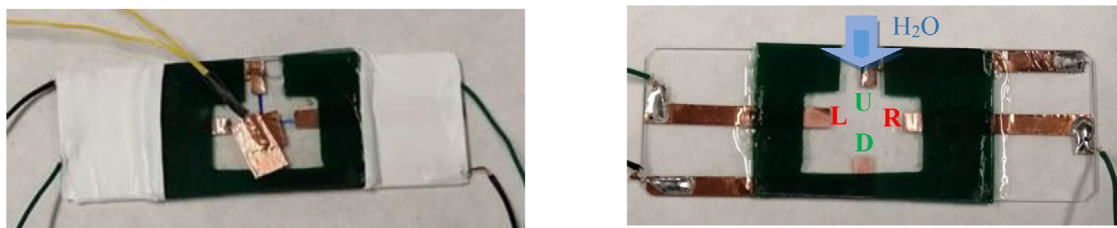
we have prepared a hydrogel by mixing [EMIM][OSO<sub>4</sub>] with heavy water (D<sub>2</sub>O) in a dry atmosphere chamber and we observed the infrared adsorption spectrum through FTIR, centred in the two most relevant peaks for H<sub>2</sub>O and D<sub>2</sub>O. Thus, in Fig. 1 we show 32 series of 16 scans each (4 s per scan) with the sample closed to the atmosphere (at left), and open to it (at right). In the last case can be seen how, as time passes, the peak corresponding to D<sub>2</sub>O (D-O stretching at 2600 cm<sup>-1</sup>) decreases, while that characteristic of H<sub>2</sub>O (H-O stretching at 3400 cm<sup>-1</sup>) increases. After the 34 min and 8 s that the experiment lasted, the D<sub>2</sub>O contained in the sample had been completely replaced by H<sub>2</sub>O.

In the gel state, the compound would be in the category of water-in-salt electrolytes, because the water content is low (it goes from 9 to 1 molecules of H<sub>2</sub>O per each IL ion pair, but between 3 and 4 in the samples self-hydrated) and it presents a mesostructure similar to a liquid crystal. This can be observed through microscopy with white polarized light, as seen in Fig. 2(a), similar to that published by some of us in Ref. [3], where the structural evolution is observed as long the sample adsorbs water. In the first photo of the series (up on the left) the sample is water free, i.e., it is in an isotropic liquid state (and therefore it is opaque to the polarized white light), in a few seconds the sample adsorbs water from the atmosphere and transits to the gel state, while after 10 min in air, it is saturated of water and an aqueous film appears

on the sample, that blurs the micrographs. Fig. 2(b) shows details of the liquid-crystal textures that form in the gel phase made with polarized white light microscopy. Finally, in Fig. 2(c) the gel-liquid transition is observed in a macroscopic scale. All the micrographs were performed at room temperature (about 20 °C). We believe that the formation of the observed “malt-cross” structures is due to the growth of a smectic H<sub>1</sub>-type hexagonal mesoscopic phase [5], although the specific liquid-crystal structure strongly depends on the water content of the sample [6,7].

The objective of this work was to create an ordered macrodomain, where we can measure the possible anisotropy in the electrical conductivity along two orthogonal directions, parallel and perpendicular to the observed strips (which are shown in Fig. 2(b)). These measurements will help us to understand the charge transport in ILs and in semi-solid conductors. According to the hopping conduction model in a pseudo-lattice [8], we bet that electrical conductivity is higher parallel to the strips than perpendicular to them, due to the enhancement of high mobility regions in the direction of entering water.

As a precedent to this work, it should be noted that some of the authors have managed to generate ordered macrodomains with these ILs, and we have observed optical anisotropy in the refraction index between the parallel and perpendicular directions to those strips [9]. Unfortunately, the method used there to obtain



**Fig. 3.** Experimental device conceived to measure the anisotropy in the electrical conductivity of liquid crystals based on hydrogels, with the Pt1000 used to measure temperature (left), and without it (right), where it can be seen the four internal electrical contacts, U, up (at the water entry indicated by an arrow), D, down, L, left and R, right.

the macro ordered domain in the liquid crystal was not suitable for the measurement of electrical conductivity, mainly because of the required electrical contacts. In what follows in this paper, we will first explain the construction of the sample holder that will allow us to align the [EMIM][DSO<sub>4</sub>] hydrogel strips (i.e., obtain macro liquid crystal domains), then we will show evidences of the ordered macrostructures obtained and the method performed to measure the possible anisotropy in the electrical conductivity, dependant on whether the direction of the current is parallel or perpendicular to the mentioned strips. Finally, we will set out our conclusions and the future research lines focused on this family of IL hydrogels.

## 2. Experimental device

The experimental device made is shown in Fig. 3, on the left, with a Pt1000 thermometer to measure the temperature of the sample in situ, while on the right it is shown without it. The humidity inlet direction is indicated with a blue arrow, and also the four electrical contacts are shown (the current between U and D being parallel to the humidity inlet, and between L and R perpendicular to it). Specifically, the sample holder device is made of two glass microscope slides, in one of them four electrical contacts have been placed by means of an adhesive copper tape. In the central part, the contacts are facing each other, with a distance between them (U-D or L-R) of about 10 mm. On this slide with contacts, a 100  $\mu\text{m}$  thick plastic masque of polypropylene is glued, creating a  $15 \times 15 \times 0.1 \text{ mm}^3$  cavity with a single window of 10 mm width, as seen in Fig. 3. The other microscopic slide glass is cut to the size of the masque and adhered to it. The glue used in all cases was a thermal adhesive that ensures a tight seal of all surfaces in contact. A fine copper wire has been tin soldered to each of the contacts, as shown in Fig. 3 on the right. The contact resistance obtained is lower than  $1 \Omega$  for each. Then, we cover the electrical contacts with Teflon and then place the Pt1000 thermometer with self-adhesive copper film on the area where the ionic liquid will be confined, being the final appearance of the device shown in Fig. 3 at left.

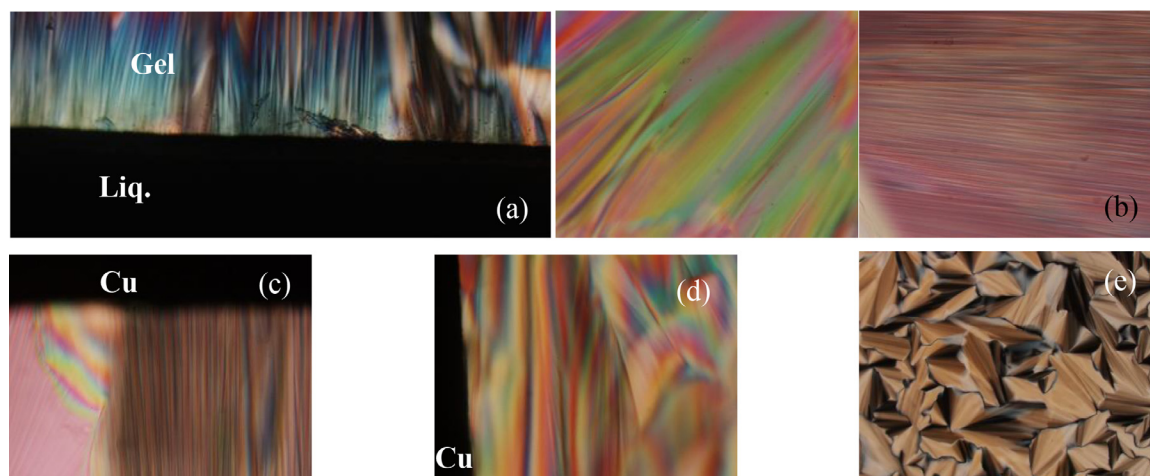
## 3. Formation of an ordered macrostructure

The quasi 2D cavity described above is filled with pure [EMIM][DSO<sub>4</sub>] being the compound completely dry and warm (to keep it in liquid state and with fluidity enough to flow into the narrow cavity). To do that, the IL, the syringe that we will use, and the sample holder are tempered at  $60 \text{ }^\circ\text{C}$  in a laboratory oven. The filling process is carried out under an argon jet on the open window, to avoid the early adsorption of water from the sample. Once filled, taking care not to leave argon bubbles inside the cavity, the sample holder is placed in the environment to adsorb moisture naturally, and so the water molecules will enter into the IL sample in a quasistatic and unidirectional way from the open window, and it slowly transits to an ordered semi-solid state, even with tiny quantities of water. The formation of the gel is invisible to natural

light, not even appreciating the border between both states within the sample holder. However, it is very easy to follow the state transition process through polarized white light microscopy. The image seen through the microscope is dark when in the isotropic liquid state, while the gel sample is multicoloured due to optical interference, as seen in Fig. 4(a). It is necessary for the sample to remain open to the atmosphere in the laboratory for a minimum of three days (with a degree of humidity of approximately 65%) to achieve its full gelation. We have tried to accelerate the water adsorption process by introducing the sample holder into a chamber with 100% humidity grade, or even by placing a drop of water on the cavity window. However, the phase transition is still very slow and we have not reduced significantly the time necessary to have all the sample in gel state. This is due to the kinetics of the process itself, which is slower than the water adsorption capacity because it implies an ionic arrangement due to the adsorbed water molecules. Once the sample is hydrated, we can deduce its water content knowing the temperatures of solidification ( $T_S \approx 5 \text{ }^\circ\text{C}$ ) and liquefaction ( $T_G \approx 55 \text{ }^\circ\text{C}$ ). Thus, from the phase diagram we deduce that the water content of our hydrated sample is approximately 7% in weight (i.e., a mole fraction of [EMIM][DSO<sub>4</sub>],  $x_{IL} \approx 0.4$ , which means three H<sub>2</sub>O molecules for a pair of ions) [3]. The transition between the liquid and gel states requires the formation of a mesostructure with long-distance ion ordering, promoted by the presence of H<sub>2</sub>O. If the unidirectional adsorption process has been successful, we obtain large ordered structures that are aligned with the direction of the incoming water, as shown in Fig. 4(b). The border between the Cu electrodes and the gel can be observed in Fig. 4(c) and 4(d). In the first one, obtained in the direction of the open window (contacts U and D), the strips tend to grow perpendicular to them, while in those electrodes that are perpendicular to the water inlet, L and R, the strips grow parallel to the edge (see Fig. 4(d)). Finally, if the sample melts due to reaching a temperature above its melting point and re-gels on cooling, the ordered structure is not recovered, as shown in Fig. 4(e), obtaining patterns similar to when the adsorption of water is not unidirectional, (shown in Fig. 2(b)).

## 4. Measurement of the electrical conductivity anisotropy

To measure the electrical conductivity due to the ionic movement, we use a Crison GLP31 conductivity metre, replacing the measuring cell connections with those of the sample holder shown in Fig. 3. This conductivity metre uses ac electrical conductivity with a frequency of 500 Hz and a voltage of 0.5 V rms. Before measuring the possible anisotropy of the sample, we must calibrate our device to obtain quantitative data of the measured conductivity. Although this is not the objective of the present work, nor is this device the most suitable for it, we find it interesting to be able to compare the values obtained here with those previously published for the same hydrogel [3]. To calibrate the sample holder, we carefully filled the cavity with Crison's certified standard liquid, a solution 0.01 M of potassium chloride in water, which has



**Fig. 4.** Polarized white light micrographs of a [EMIM][DSO<sub>4</sub>] sample in the sample holder shown in Fig. 3. (a) Boundary between the liquid (bottom black) and hydrogel (top multicoloured) states. (b) Two micrographs of different parts of the sample showing ordered domains. (c) and (d) Growth of the strips at the border of the copper electrodes, aligned with the opening of the sample holder and perpendicular to it, respectively. (e) Structure of the gel after it has melted and re-gelled. The height of picture (a) represents 320  $\mu\text{m}$ , while the rest of the micrographs represent  $830 \times 625 \mu\text{m}^2$ .

an electrical conductivity of  $1413 \mu\text{S}/\text{cm}$  at  $25 \text{ }^\circ\text{C}$ . We placed the sample holder in a Julabo F25 thermostat to stabilize the temperature within an uncertainty of  $25.0 \pm 0.1 \text{ }^\circ\text{C}$ . On the other hand, the temperature of the sample was measured with the platinum thermometer, type Pt1000, adhered with copper tape to the sample holder, as shown in Fig. 3 on the left. This thermometer was previously calibrated in melting ice ( $R_0 = 1001.5 \Omega$ ) and boiling water ( $R_{100} = 1383.1 \Omega$ ), using a calibrated electronic thermometer as a patron and a Keithley 2000 Vmeter to measure the 4 wires resistance of the Pt1000.

Then we proceed with the calibration of the sample holder with the mentioned certified solution, obtaining a mean value of  $\kappa = 7.1 \mu\text{S}/\text{cm}$  at  $25.0 \text{ }^\circ\text{C}$  for the electrical conductivity. At the time of measurement from the calibration of the standard measurement cell in the Crison GLP31 conductivity metre, the cell constant was  $C = 1.161 \text{ cm}^{-1}$ . Dividing the conductivity value with the standard measurement cell by that measured with our device, we obtain a cell constant of around  $C' \approx 200 \text{ cm}^{-1}$  for our sample holder. Remember that  $C$  is a geometric parameter, being its value obtained as the coefficient of the distance between the electrodes and its surface (thus, if  $C \approx 1 \text{ cm}^{-1}$  are equal both parameters, in cm and  $\text{cm}^2$ , respectively). The value measured for our sample holder is consistent with the geometry of the opposing contacts, which are located at a distance of about 10 mm between them, with the surface of the edge of the copper tape being  $0.05 \times 5 \text{ mm}^2$  (so the theoretical cell constant would be  $C_t = 400 \text{ cm}^{-1}$ ). Note that this last value is roughly approximate, since the edge surface is not a perfect flat rectangle (as observed in Fig. 4(c) and (d)) and so effective area must be higher than expected. On the other hand, measuring in the same direction but opposite orientations (L-R and R-L), we observe a slight difference in the results of 1%, for which we have no explanation. In addition, there are higher differences between both directions, L-R (perpendicular to the direction of entry of the water) and U-D (parallel to it) of around 10%, possibly associated with small differences in the distance and section of the edge amongst the four copper contacts (i.e., its cell constant is different). In any case, the consistency of the measured result (with all its experimental uncertainties) and the calculated one indicates that our device, connected to the GLP31 conductivity metre, is suitable for quantitatively measuring electrical conductivity, although obviously the experimental uncertainty is larger than that obtained using the commercial standard probe. In addition, chemical reactions could happen on the surface of the copper electrode

**Table 1**

Electrical conductivity measured in the perpendicular (U-D) and parallel (L-R) to the strips of the hydrogel [EMIM][DSO<sub>4</sub>]. In the fourth column we include the percentage difference of the measured values between both directions.

| T( $^\circ\text{C}$ ) | $\kappa_{\text{L-R}}$ ( $\mu\text{S}/\text{cm}$ ) | $\kappa_{\text{U-D}}$ ( $\mu\text{S}/\text{cm}$ ) | % dif. |
|-----------------------|---|---|--------|
| 45.0                  | 84.6  | 95.7  | 13.1   |
| 42.0                  | 75.8  | 85.4  | 12.7   |
| 40.0                  | 71.5  | 82.3  | 15.1   |
| 35.0                  | 65.7  | 77.9  | 18.6   |
| 30.0                  | 57.7  | 67.7  | 17.3   |
| 25.0                  | 49.1  | 58.9  | 20.0   |
| 20.0                  | 40.6  | 47.7  | 17.5   |
| 15.0                  | 33.6  | 41.0  | 22.0   |
| 10.0                  | 22.7  | 28.6  | 26.0   |
| 5.0                   | 10.85   | 11.23   | 3.5    |
| 0.0                   | 4.09  | 3.77  | -7.8   |

after measurements. In fact, we used a new holder sample device, previously calibrated, for every sample.

## 5. Results

Now, we can measure the possible anisotropy between opposing contacts, both parallel (U-D) and perpendicular (L-R) to the direction of entry of moisture into the sample. We proceed with a clean and dry sample of [EMIM][DSO<sub>4</sub>], as described in Section 3. After a week open to the atmosphere, and observing that we have obtained a strip ordered pattern (as observed in Fig. 4(b)), we proceed with the measurement of the electrical conductivity of the hydrated liquid crystal sample as a function of temperature and in the two directions commented. The results obtained for a sample in a range of temperatures from  $45 \text{ }^\circ\text{C}$  to  $0 \text{ }^\circ\text{C}$  appear in Table 1, where the average of the results obtained in the same direction, but opposite orientations, is reflected (the discrepancy is lower than 3%). The sample is in the gel phase down to  $10 \text{ }^\circ\text{C}$ , below this temperature it solidifies and crystallizes. During the change of state, the sample turns from transparent to translucent white, and appears dark when viewed under white light polarized microscopy. Furthermore, conductivity decreases sharply when changing from a gel to a solid crystal state, as occurs with ionic liquids [10]. In the gel state, the sample has a VTF-like behaviour with temperature, as happens to the majority of ILs in liquid or gel state [11], including

those studied here [1,2,3]. An anisotropy is clearly observed between the data measured in both directions, greater conductivity in the water inlet direction (U-D) than in the perpendicular to it (L-R), which could be related to the preferred orientation of the strips in the mesoscopic structure formed observed with polarized light. The liquid-crystal type structure formed has not been elucidated due to the metastable state of the ordered pattern, in addition, structure changes with the amount of water in the sample (and it can also change with temperature) [6,7], although the evidences point to a smectic hexagonal structure type  $H_1$  [12]. From the point of view of cell theory for liquids, charge transport in ILs in general, and in this hydrogel in particular, is mainly due to the jump of ions between holes in a pseudo-lattice, with a minor contribution (if any) from classical diffusion mechanisms, as has been discussed in previous papers [2,8]. Therefore, it seems reasonable that charge conduction along the strips would be easier than perpendicular to them. Table 1 also indicates the percentage difference between the conductivities in both directions. This increases as the temperature decreases, up to a maximum difference of 26% at 10 °C, being about 20% difference at room temperature. When the sample crystallizes, below 10 °C, the anisotropy practically disappears (less than 10%), and even reverses at 0 °C (although the electrical conductivity values are much smaller and so uncertainties are of the same order of those differences). As the sample crystallizes, its liquid crystal type mesostructure in the gel state is destroyed and, as a consequence, the crystalline solid state is isotropic, contrarily to the ordered hydrogel state.

If the data given in Table 1 are normalised respecting the cell constant measured for our device,  $C' = 200 \text{ cm}^{-1}$ , we can estimate the real conductivity (i.e., that measured with the standard cell) let it be  $\kappa'$ ,

$$k' = k \cdot C' / C \quad (1)$$

Remember that  $C$  is the cell constant value given by the last calibration of the standard measurement cell ( $C = 1.161 \text{ cm}^{-1}$ ). Carrying out the calculations, we will obtain a conductivity of the sample in L-R configuration of 14.6 mS/cm at 45 °C, 8.5 mS/cm at 25 °C and 3.9 mS/cm at 10 °C. These data are double to those previously published for this same compound with a similar degree of hydration (10% by weight in water in the published version, compared to 7% estimated in ours, which represent approximately,  $x_{IL} \approx 0.3$  and 0.4, respectively) [3]. Thus, the published conductivities at those same temperatures were, respectively, 7.7 mS/cm, 4.0 mS/cm and 2.1 mS/cm. Fig. 5 shows, on a semi-logarithmic scale, the data calculated using Eq. (1) and the values measured for both directions, as well as those published for a macroscopic sample with 10% weight in water [3]. In all three data series the solid lines represent the best fit of a VTF-type curve to the data when in the gel state (above 10 °C) [11]. It can be seen that the order of magnitude is similar, as well as the temperature behaviour for the three series. Below 10 °C our sample solidifies, giving place to a crystal rigid structure, and so its conductivity decreases respecting that expected from the VTF plot [10]. Observe that our sample has a crystallization temperature higher than that published in Ref. [3], due probably to their water content but also to their different geometry.

## 6. Discussion

The objective of the sample holder that we have made is threefold. The first one is to try to order the [EMIM][DSO<sub>4</sub>] hydrogel strips in a macrodomain with a liquid crystal-like structure, from the unidirectional adsorption of water by the sample after being confined in the quasi 2D cavity. This objective has been fulfilled, at least in part, since we are able to get ordered domains in regions with millimetre sizes, although not yet the entire ordered structure

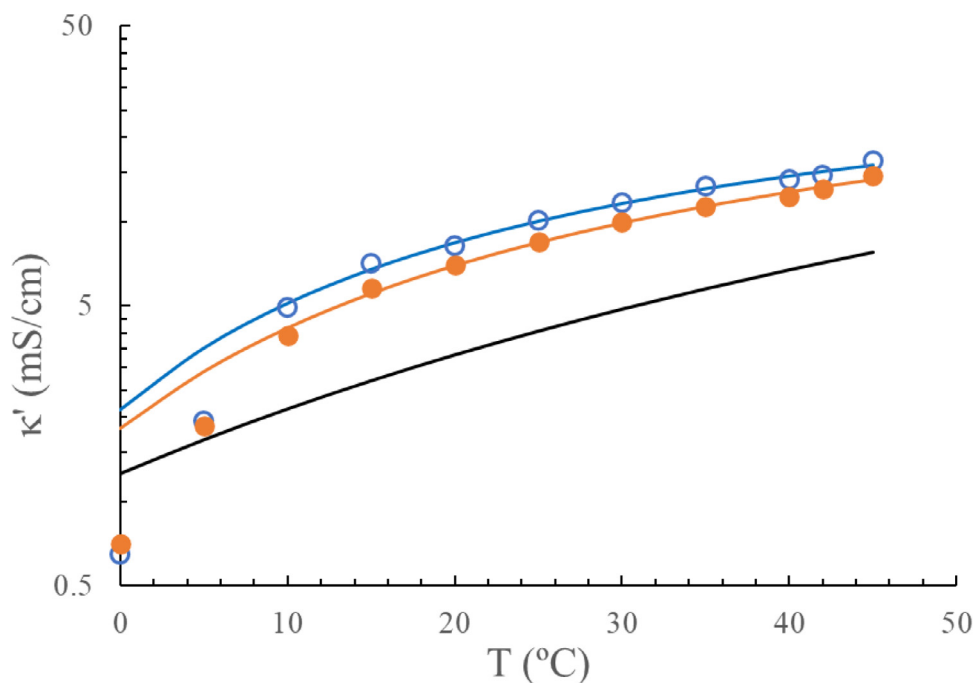
between the electrodes. This ordered structure remains unchanged as long as the sample does not liquefy or freeze due to the effect of temperature. Although those state transitions are reversible, the alignment observed in the millimetre domains is lost and randomly orientated microdomains appear in the re-gelled state, as seen in Fig. 4(e).

A second objective, once the first had been attained, was the measurement of the possible anisotropy between the directions parallel and perpendicular to the observed strips. Although this effect has been measured by us in some samples, we cannot be sure that it is due to the differences in charge conduction along or perpendicular to those strips. A possible cause of the observed conductivity anisotropy could be inhomogeneity in the water content within the sample. In this line, it is logical that the region parallel to the water inlet direction contains more water than the region perpendicular to it. As we know, the presence of water greatly increases the electrical conductivity of ILs [13]. Another factor that must be taken into account is that the device is not perfectly symmetrical, and discrepancies between both directions are observed through electrical conductivity, even using a completely homogeneous liquid such as the calibration patron. A third effect that could influence the measurements, is the occurrence of percolation phenomena for the conductivity. Actually, as long as there was a more favourable path for charge conduction, which would electrically join the opposing electrodes, we would measure a given value for the electrical conductivity, while the majority of the sample being of little relevance to that measured result. The formation of these connecting paths has been qualitatively observed with a simple experiment, but with direct current. Thus, when injecting a dc current between two sample electrodes, a narrow path (about 1 mm with) was formed connecting them after a while, which is visible under a polarized light microscope because the hydrogel was liquefying due to Joule effect, thus observing a black path in the multicoloured back. These studies are preliminary, but indicate that charge transport could not to be uniform and homogeneous across the entire width of the electrode.

We can compare the measured anisotropy in the conductivity with the previous results published on the refractive index of a similar sample, but with a higher water content of about 58 wt%, and so the IL molar fraction was  $x_{IL} = 0.54$  [9]. In this case, the mesoscopic phase seems to be lamellar instead smectic, as seems to happens in our confined gel, with much lower quantity of water. In that study we have performed a similar approach and analysed the behaviour of the optical anisotropy under changes of the temperature in both directions (parallel and perpendicular to the lamellar planes). The optical anisotropy is much smaller than that measured here, nearly a 1% ( $\Delta n \approx 4.1 \cdot 10^{-3}$ ), but it is easily detected.

The final conclusions agree in both works, thus in Ref. [9] says that the anisotropy is caused by the process of adsorption of water and not only the presence of it. During the process, the ionic liquid self assembles in a lamellar structure that favours the adsorbed water molecules diffusion inside the liquid. The images of white polarized light microscopy show a strip structure while the sample is organized. Finally, we can say that the presence of water creates an assembly state of the molecules, but only through the specified process, the anisotropy can be perceived macroscopically.

In this manner, we can conclude that both anisotropies (optical dispersive and electrical conductivity) are caused by the self-organization on the liquid through the process of diffusion on water along the IL. Further studies on how both magnitudes correlate to each other are needed as the optical anisotropy can be easily detected without disturbing the sample during the process, which may allow to indirectly quantify the conductivity on both axis without undesired side effects (including Joule heating).



**Fig. 5.** Electrical conductivity,  $\kappa'$ , calculated from Eq. (1) for [EMIM][DSO<sub>4</sub>] hydrated with 7% water in parallel, d-U (blue open circle), and perpendicular, l-R (orange solid circle), to the direction of the humidity inlet in the measuring cell. The lines above the data show the corresponding VTF fits in the liquid zone. The solid black line represents the VTF equation for a bulk sample with 10 wt% water content published in Ref. [3].

Assuming that our data have not been affected by those spurious effects commented above, and so we are really measuring the anisotropy of the charge transport in line or through the observed strips, which are a reflect of an smectic H<sub>1</sub>-type hexagonal macroscopic order [12]. We can explain it based in the theoretical framework developed by some of us [8]. Indeed, the enhanced conductivity in the direction parallel to the gradient of water can be attributed to the occurrence of percolative nanopaths of high mobility cells within the polar regions. Those paths present high frequency jumping for cations parallel to the water gradient than perpendicular to it. Remember that in this hydrogel anions are the surfactant part of the IL, which form mesoscopic structures due to the water molecule presence. In contrast, imidazolium cations are free to jump and transport charge, more efficiently in the strip direction than crossing them [12].

The future objective to be achieved with this device is the measurement of anisotropy in a single ordered domain, for that we will approach the electrodes distance to a maximum of 1 mm and with a good quality electrode surface with perfect control of its thickness, made with metal deposition techniques.

## 7. Conclusions

We have built an original experimental device to measure the anisotropy in the electrical conductivity of hydrogels. It has a quasi 2D cavity (15 × 15 × 0.1 mm<sup>3</sup>), connected to the outside by a single window of approximately 0.1 × 10 mm. Inside the cavity we have 4 contacts facing each other, two in a direction perpendicular to the water inlet, and two in parallel to it. The compound used, 1-ethyl-3-methyl imidazolium decyl sulfate, [EMIM][DSO<sub>4</sub>], undergoes a transition from a liquid to a hydrogel state by adsorbing water from the atmosphere, at room temperature. Thus, its structure changes from an isotropic liquid to an ordered liquid-crystal type. By only being able to adsorb water in one direction, the stripped meso-structures that form the liquid-crystal domains grew to form ordered strip millimetre macrod domains. The measurement of the electrical conductivity in a direction parallel and perpendicular to

the strips, parallel to the water inlet, shows anisotropy in the physical magnitude, which can reach 26% at low temperatures (but in the gel state) and a difference of 20% at room temperature. Once the semisolid hydrogel sample is frozen or melted, the anisotropy disappears and it is no longer recoverable, because the water distribution in the sample has become homogenized at the beginning of the gel formation process. Our first observations published here encourage us to continue developing our ability to order the structure of these hydrogels and to continue with the measurement of anisotropy in perfectly ordered domains and trying to understand the percolation phenomena that is probably behind the measured data.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## CRediT authorship contribution statement

**D. Portela:** Conceptualization, Investigation, Data curation. **L. Segade:** Formal analysis, Writing – review & editing, Visualization. **Y. Arosa:** Validation, Formal analysis. **E. López Lago:** Conceptualization, Investigation, Writing – review & editing. **L.M. Varela:** Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition. **E. Tojo:** Investigation, Resources, Writing – review & editing. **O. Cabeza:** Conceptualization, Formal analysis, Investigation, Writing – original draft, Supervision, Project administration, Funding acquisition.

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