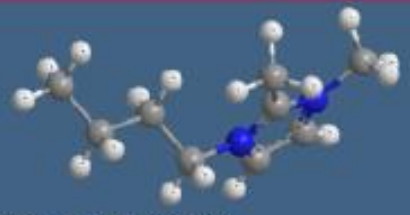

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Joint workshop of WG 2 and 3: „Ionic liquids at interfaces“
3rd -5th October 2015 in Belek (Turkey)

Rede Galega de Líquidos Iónicos (REGALIs)

Universidade de Vigo

USC UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

UNIVERSIDADE DA CORUÑA

SELF ORGANIZATION IN ALKYL SULFATE BASED IL HYDROGELS

Oscar Cabeza, Esther Rilo, Luisa Segade (UDC)
Luis Miguel Varela, Elena López-Lago (USC)
Emilia Tojo (Uvigo)

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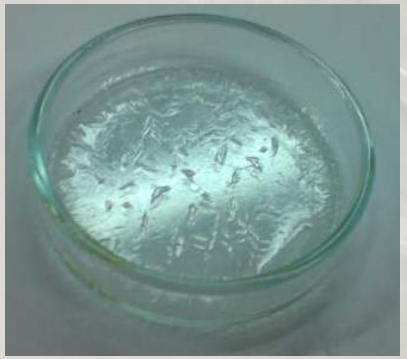
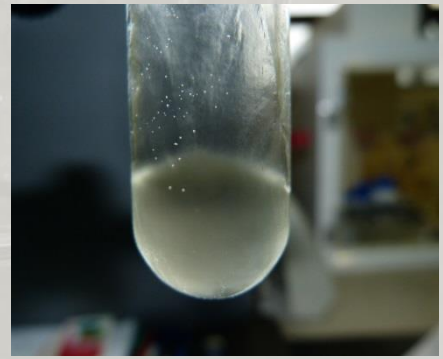
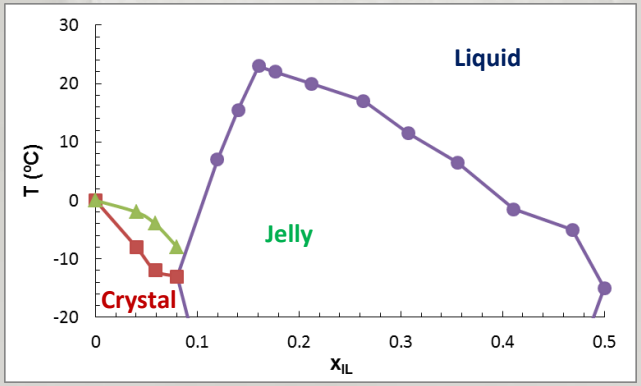
IN A RECENT PAPER WE PUBLISHED THE FORMATION OF A RIGID GEL FOR SOME AQUEOUS MIXTURES OF THE 1-ETHIL-3-METHIL IMIDAZOLIUM OCTYL SULFATE [EMIm][OSO_4]

Physical properties of aqueous mixtures of the ionic 1-ethl-3-methyl imidazolium octyl sulfate: A new ionic rigid gel.
O. Cabeza et al., *J. Chem. Thermodyn*. 75 (2014) 52-57.



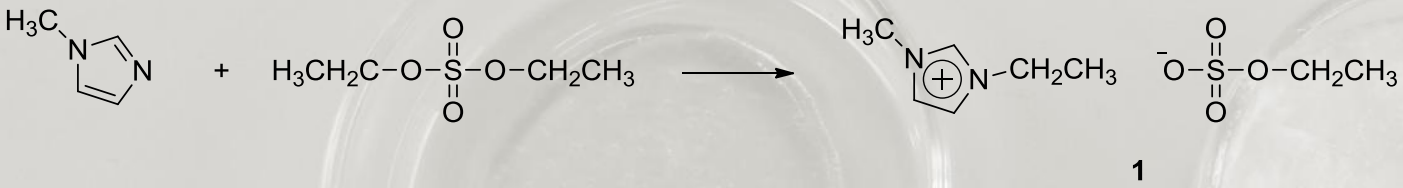




WE HAD NOT OBSERVED THAT MESOPHASE IN ANY OTHER IL (INCLUDING [EMIm] HEXYL SULFATE) AT ANY TEMPERATURE. IS THERE ANY OTHER GEL FORMER IL?

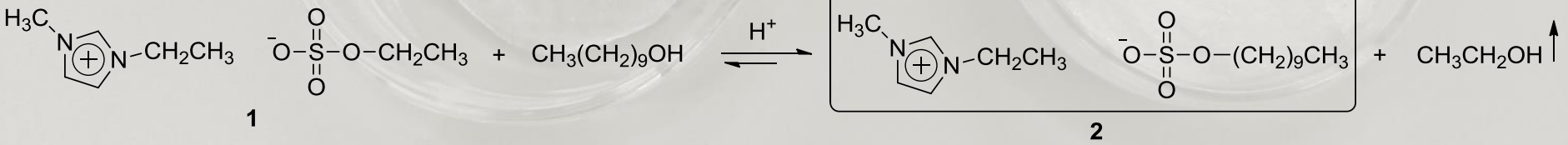
WE HAVE TRIED WITH [EMIm][DSO_4] AND [EMPyr][DSO_4] (TAILORED BY US BECAUSE THEY ARE NOT COMMERCIAL ILs) (Patent presented)

Etapa 1.- Cuaternización



1

Etapa 2.- transesterificación



1 2

SYNTHESIS HAS TWO STEPS:

- FIRST (QUATERNIZATION). WE OBTAIN [EMIm][ESO_4]
- SECOND (TRANSESTERIFICATION). ADDING DECANOL WE OBTAIN THE [EMIm][DSO_4]

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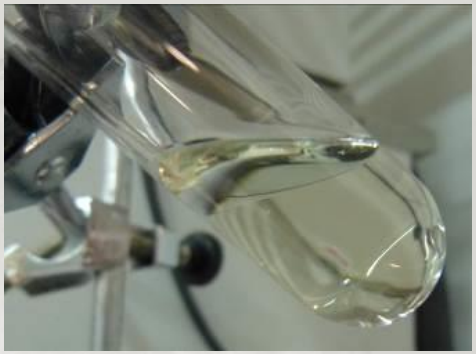
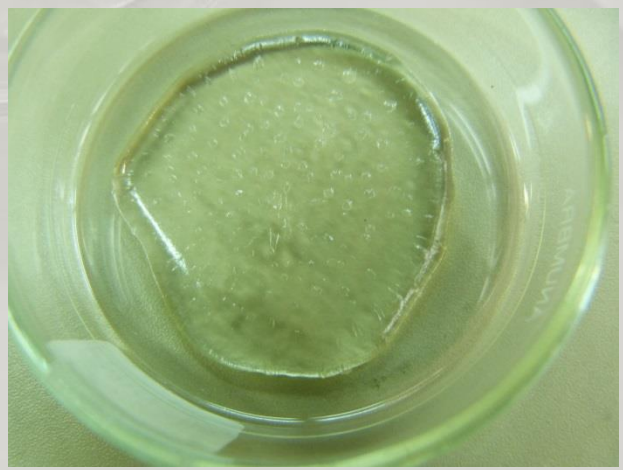
BOTH [DSO_4] ALSO CAN FORM A RIGID GEL. PURE THEY ARE VISCOUS LIQUIDS AT ROOM TEMPERATURE (OR CRYSTAL SOLID), BUT LEAVING OPEN TO THE ATMOSTHERE, THEY ADSORB WATER AND GET JELLY



The three states of the hydrated [EMIm][DSO_4] depending on temperature: From left to right: rigid gel (T between 15ºC and 60ºC), solid (T < 15ºC) and lIquid (T > 60ºC)



AT ROOM TEMPERATURE IT CAN BE A CRYSTALLINE SOLID OR A RIGID GEL, DEPENDIENG ON ITS THERMAL HISTORY!
WE WILL UNDERSTAND THIS LATER

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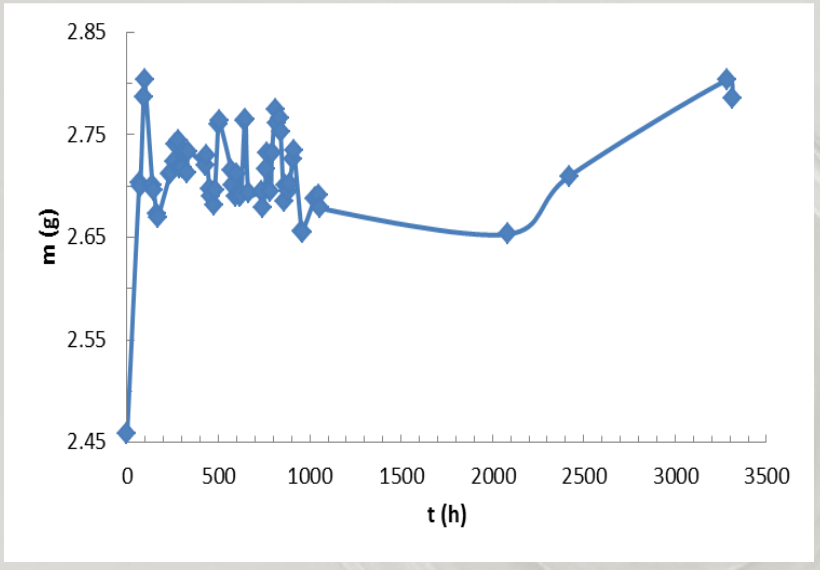
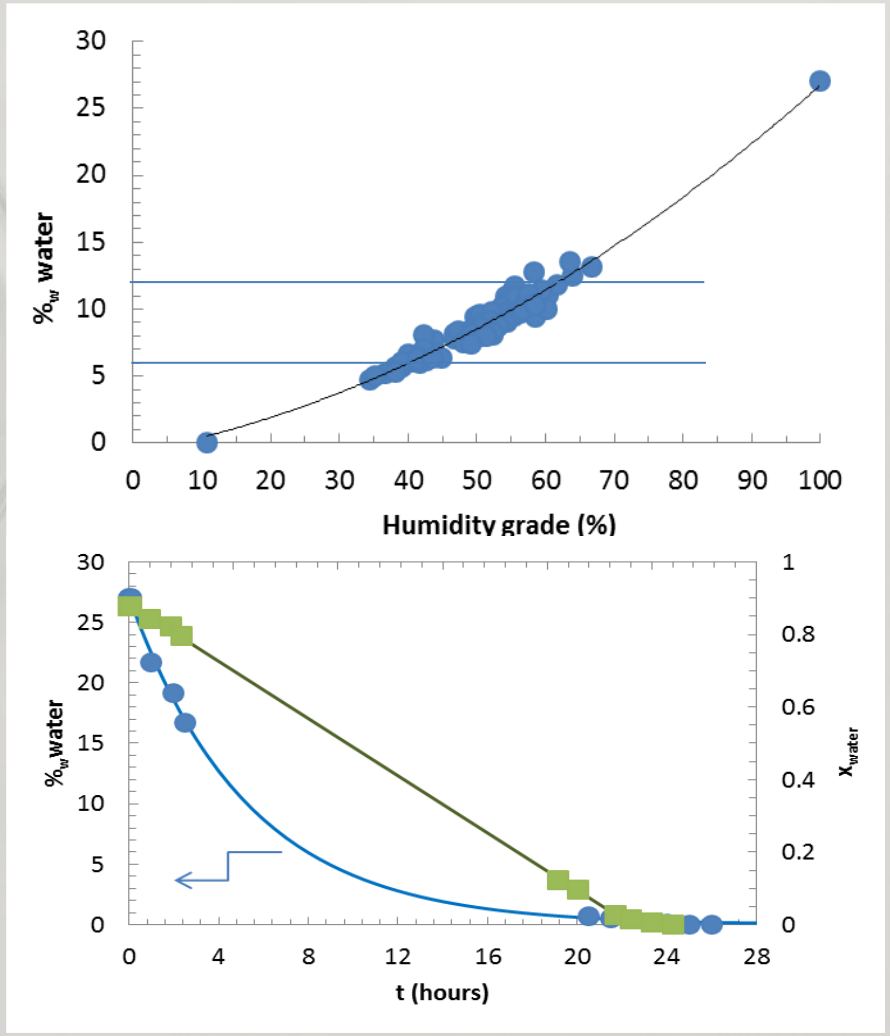
THESE COMPOUNDS ADSORB WATER FROM ATMOSPHERE. [EMIm][DSO_4] (≈ 9 ± 3%) DEPENDING ON HUMIDITY GRADE





Left: Variation of the hydrated [OSO_4] mass. Sample was left 5 months open to the ambient. Right up: Relation between mass percentage of water in [DSO_4] and relative laboratory humidity grade. Right down: Sample takes about 24 h to lose all water adsorbed at 100% humidity grade.

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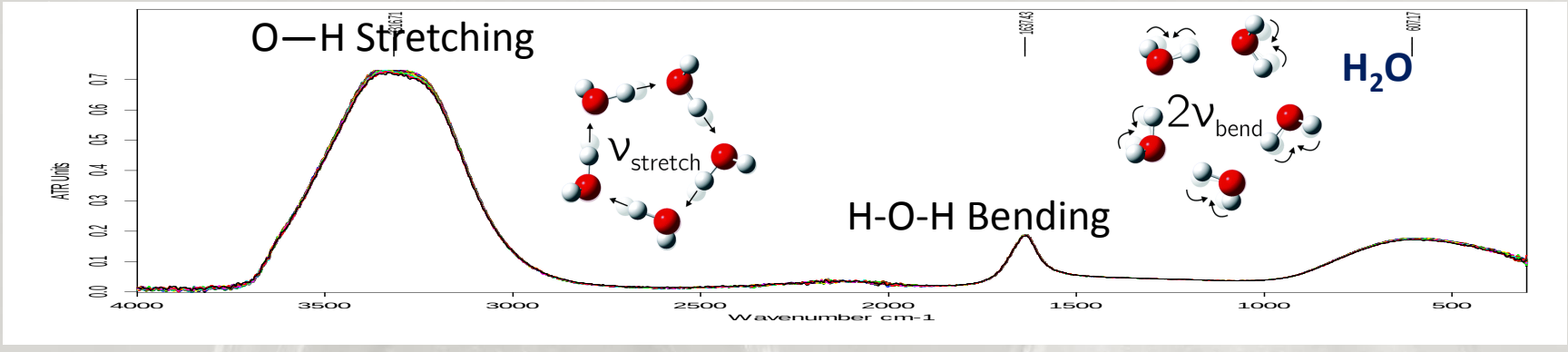
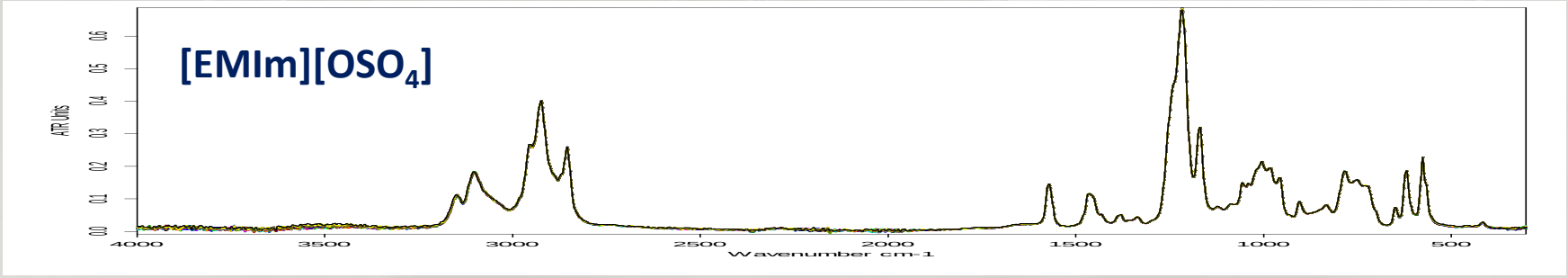
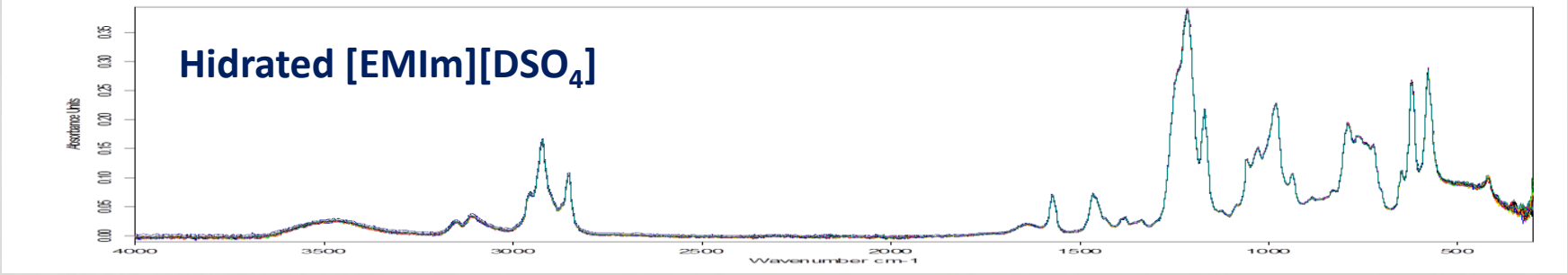
LET'S SEE THE GELIFICATION PROCESS FROM FTIR SPECTRA!



FTIR OF PURE H_2O AND [EMIm][OSO_4] AND [DSO_4]





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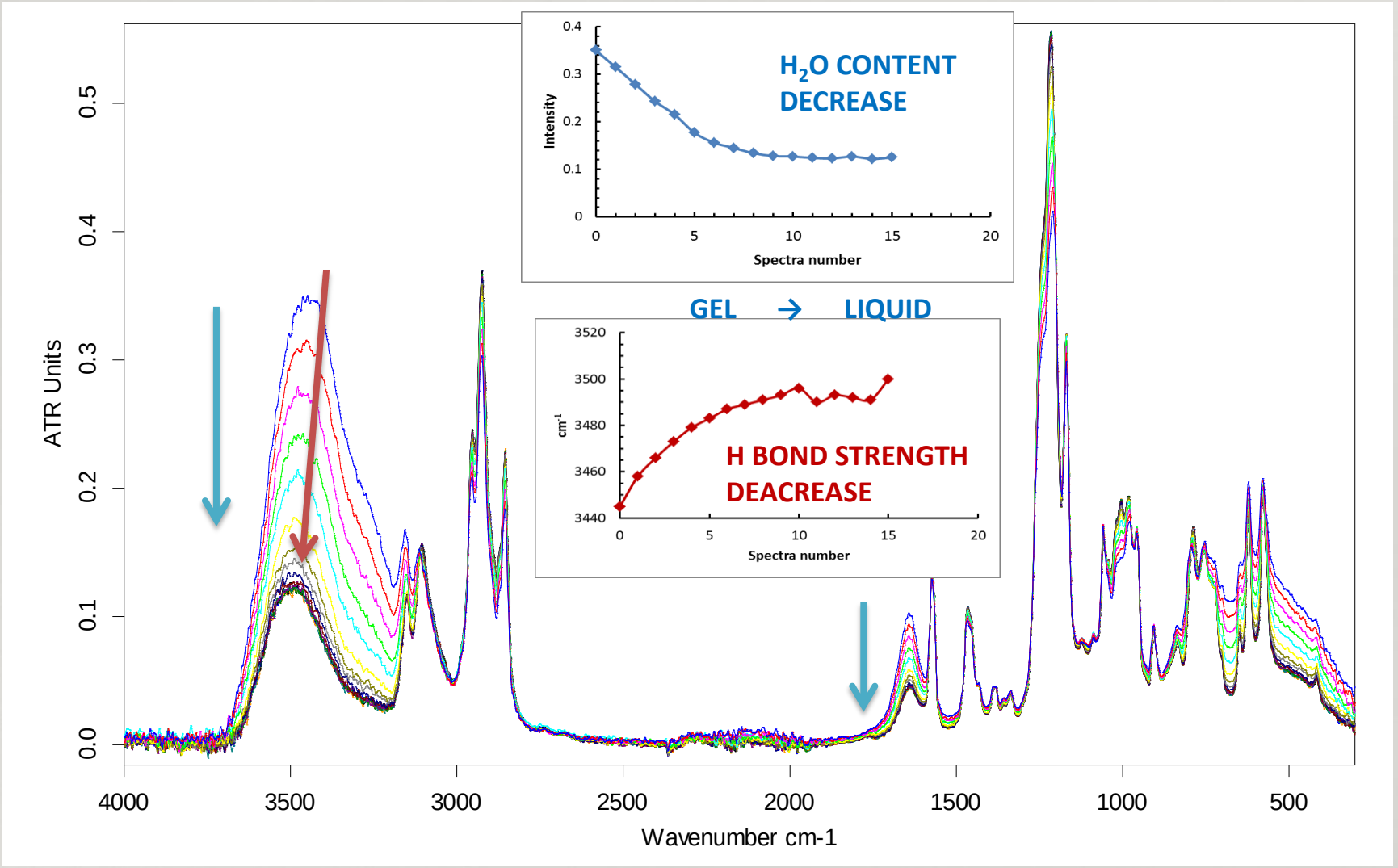
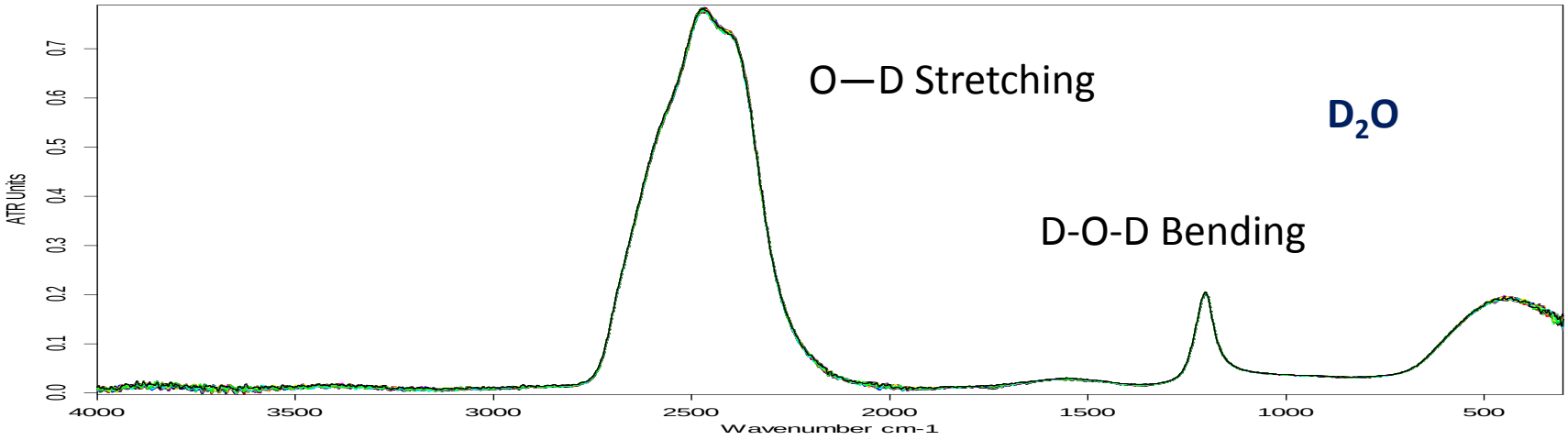
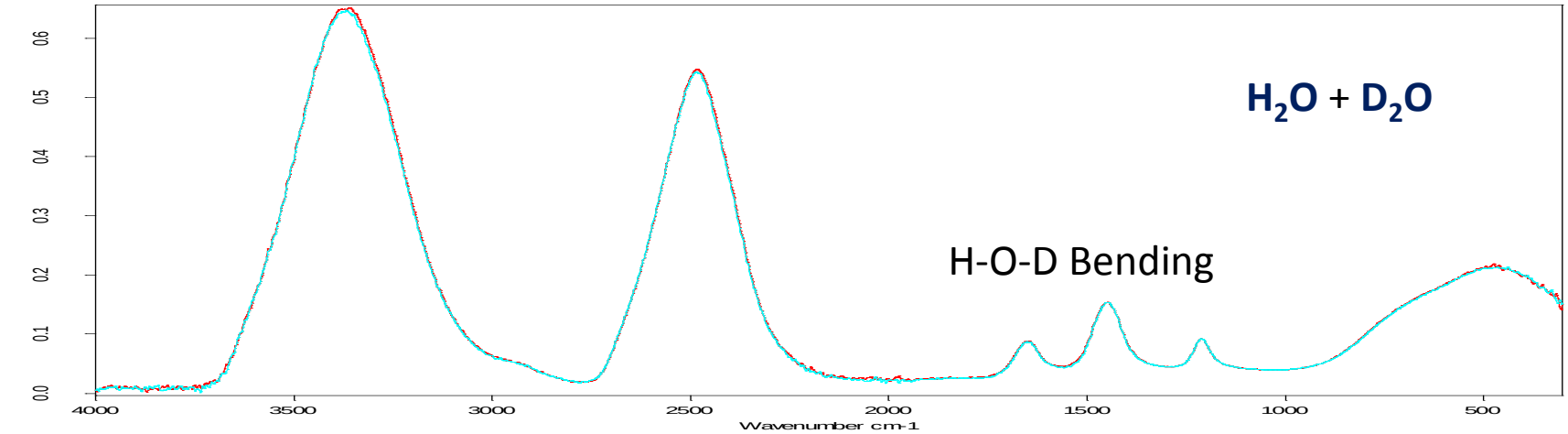
FTIR OF [EMIm][OSO_4] + H_2O (X_{IL} = 0.2) FROM THE FRIDGE TO ROOM TEMPERATURE

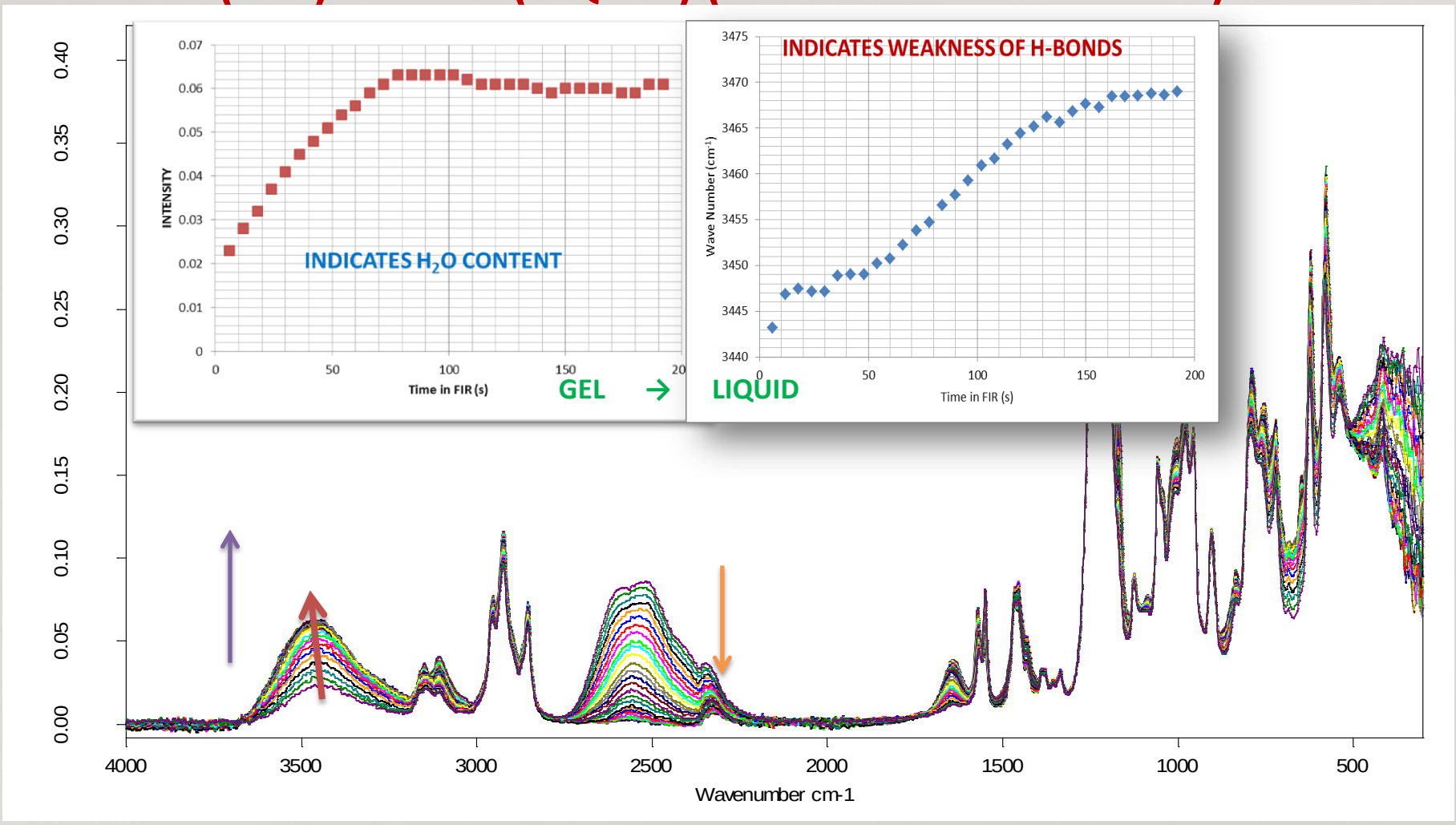


FTIR OF D_2O AND $D_2O + H_2O$





FTIR OF [EMIm][OSO_4] + D_2O (X_{IL} = 0.20) FROM THE FRIDGE (GEL) TO R. T. (LIQUID) (32 SERIES OF 16 SCANS)



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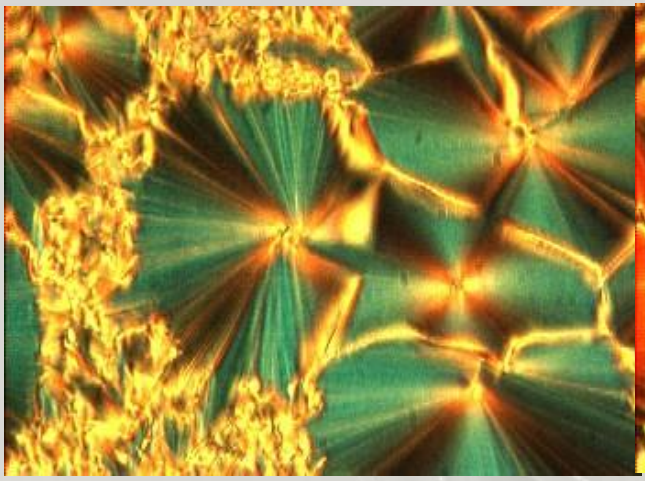
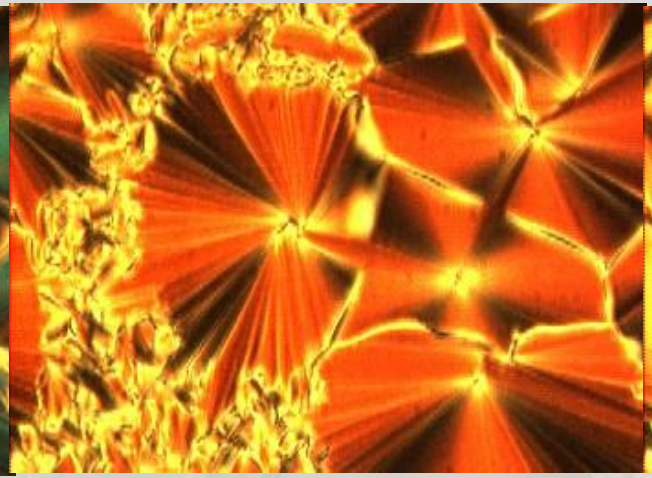
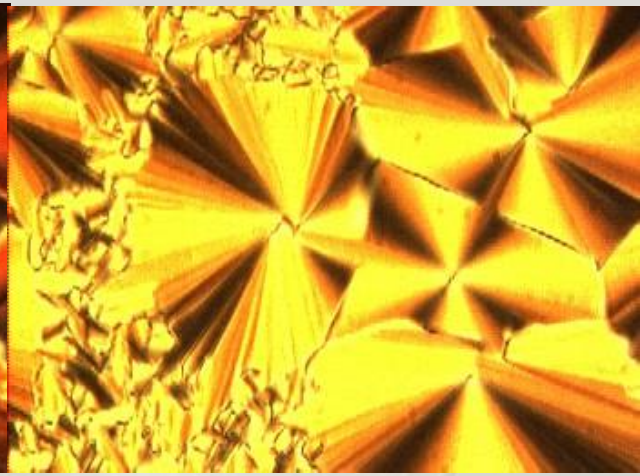
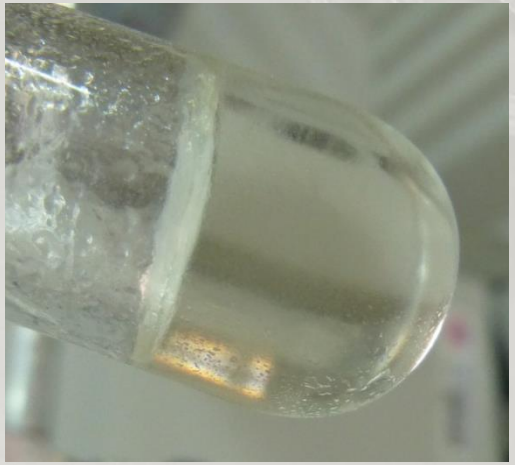
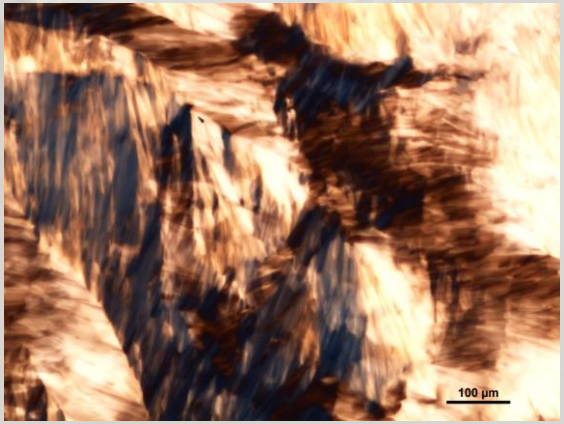
MICROGRAPHS MADE WITH WHITE POLARIZED LIGHT











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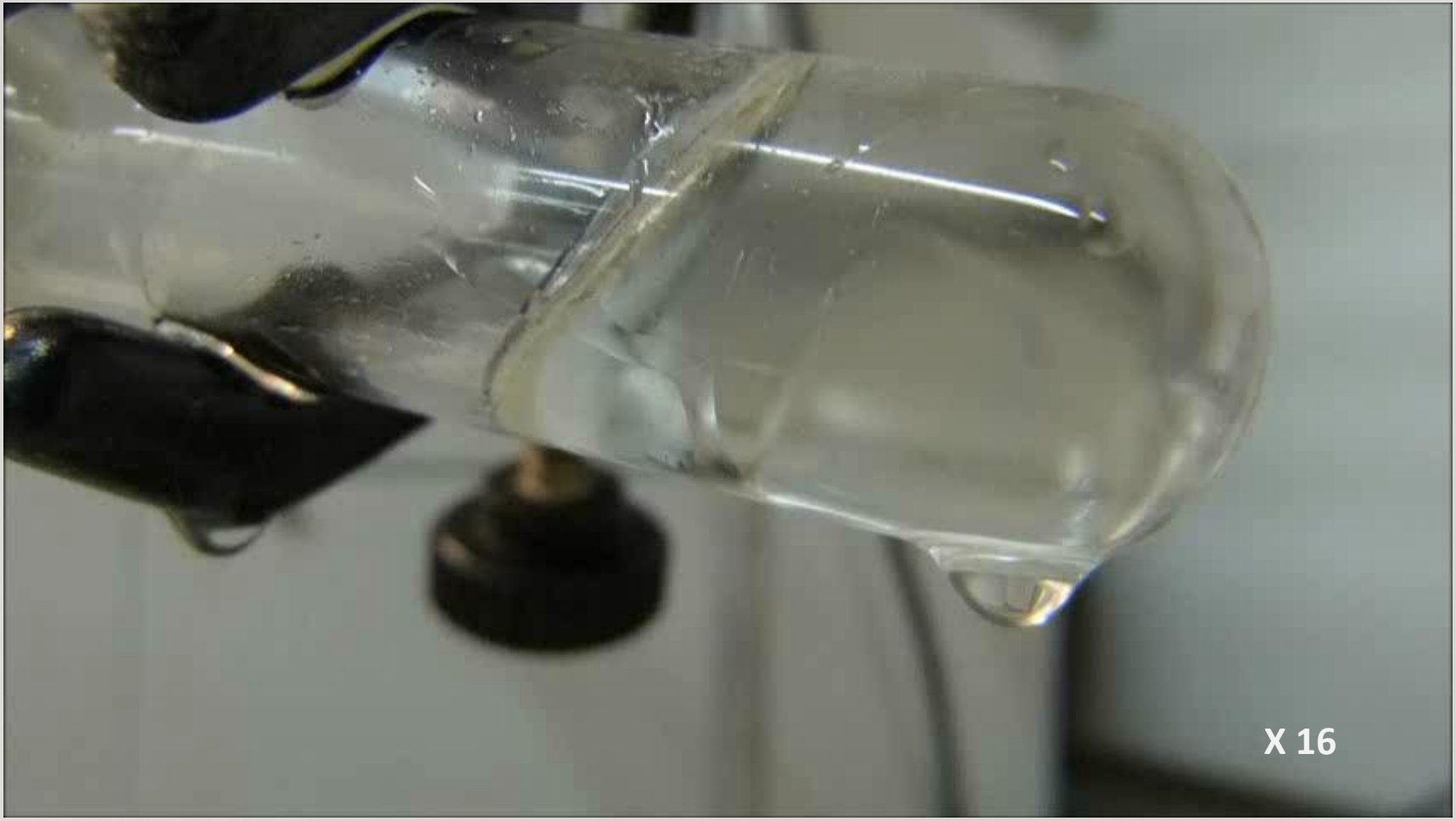
MELTING OF A [EMIm][OSO_4] SAMPLE (T_G = 15 ºC)



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GELIFICATION FOR [EMIm][DSO_4] WHEN ADSORBING MOISTURE IN mm SCALE

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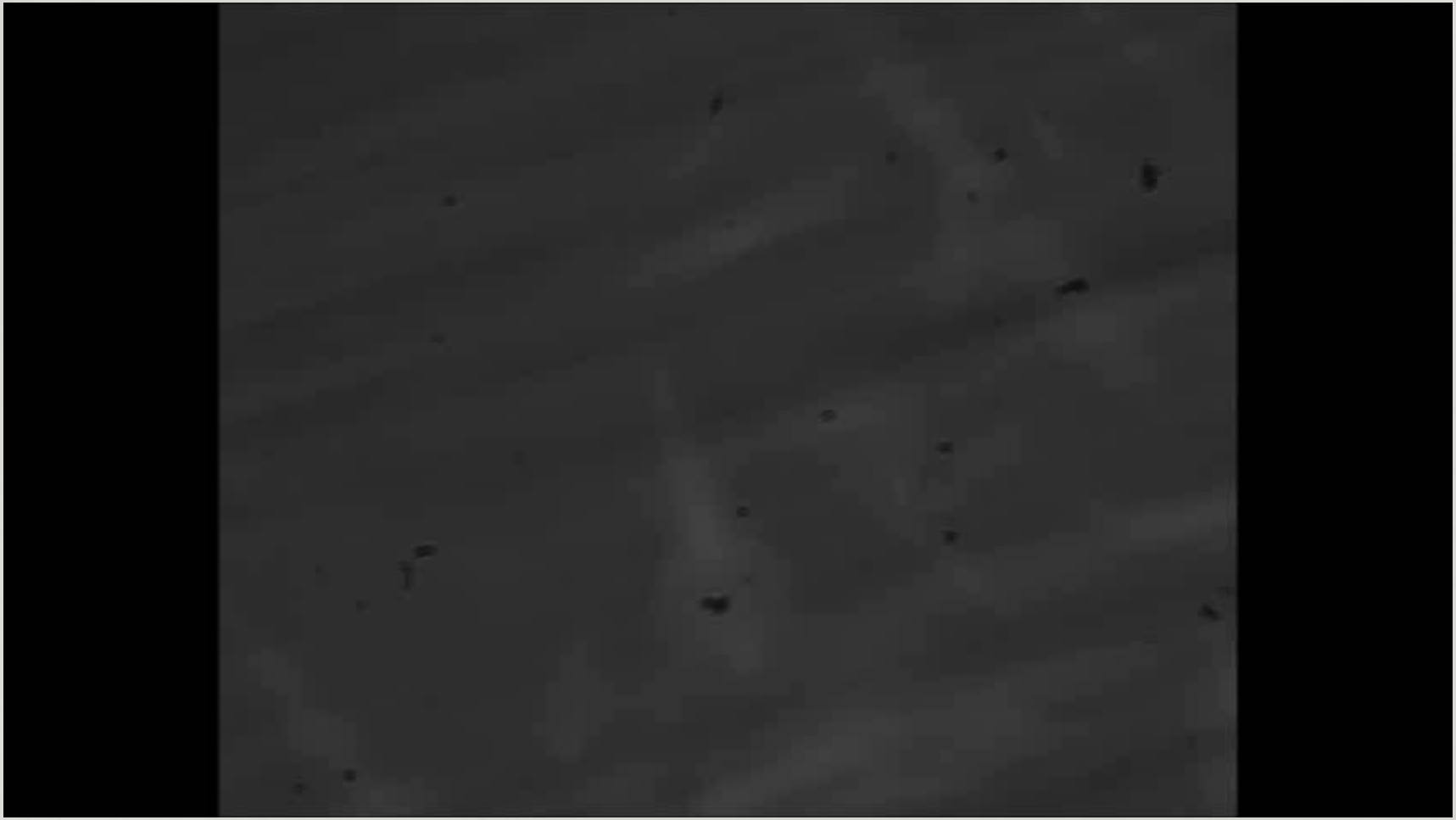
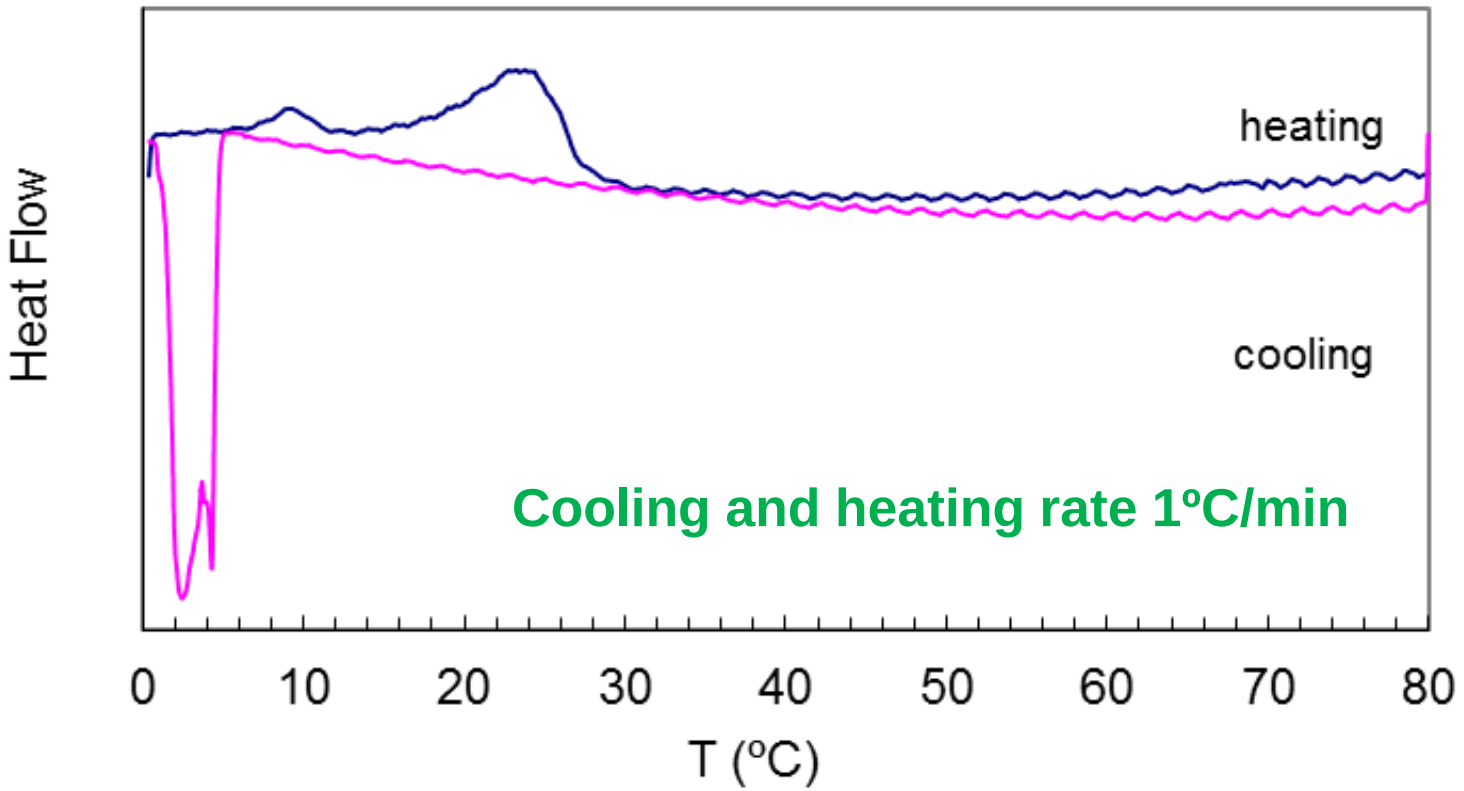
GELIFICATION FOR [EMIm][OSO_4] WHEN ADSORBING MOISTURE IN μm SCALE



EXIL

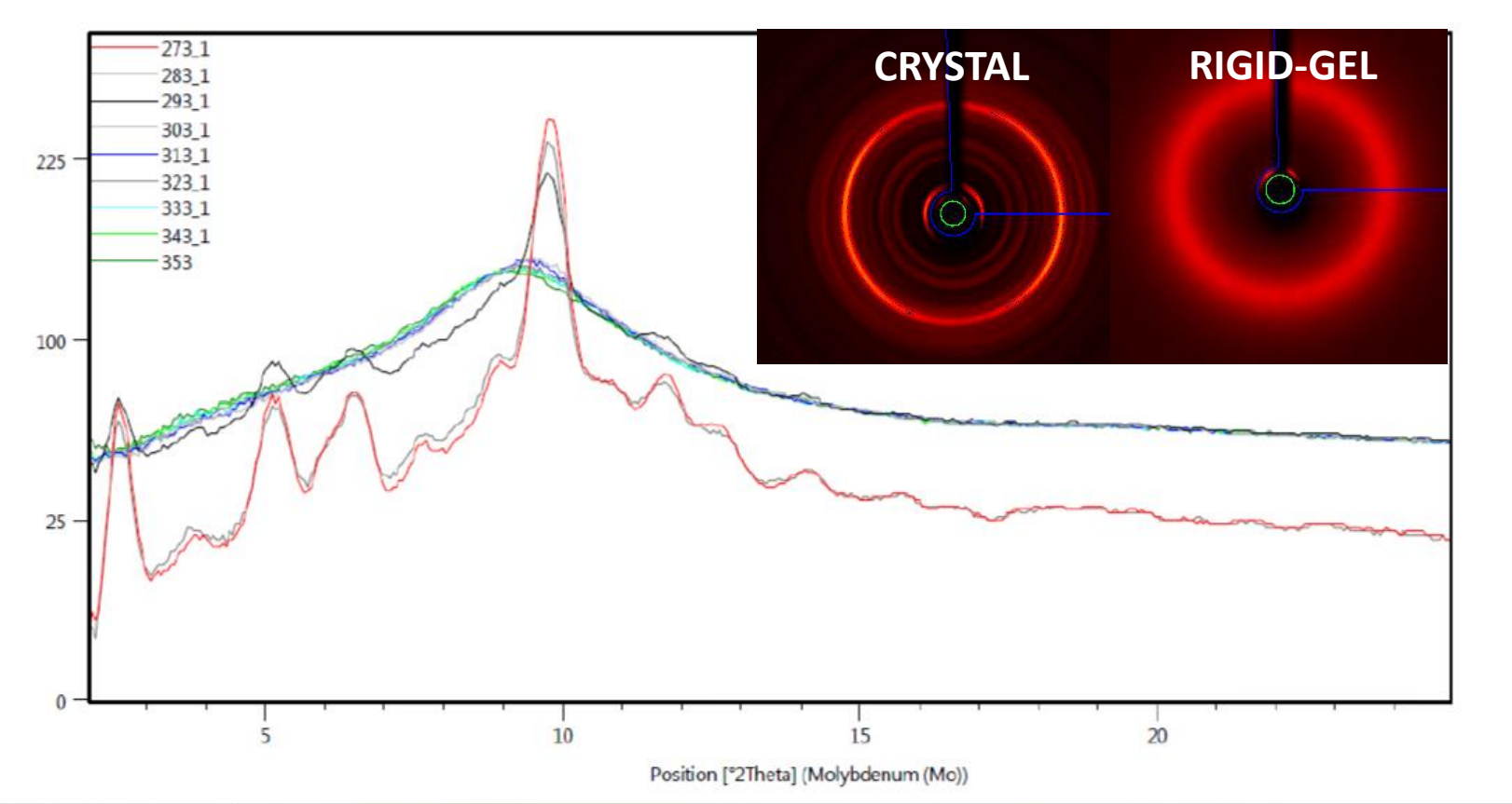
GELIFICATION FOR [EMIm][DSO_4] WHEN ADSORBING MOISTURE IN μm SCALE. SMECTIC-A MESOPHASE

DSC OF THE HYDRATED [EMIm][DSO_4]



No signal at 60ºC… Double peak when melting and crystallizing

X-RAY STUDY OF THE HYDRATED [EMIm][DSO_4]



X-Ray diffractogram (Mo) at different temperatures. Below 15 ºC it is a crystalline solid.

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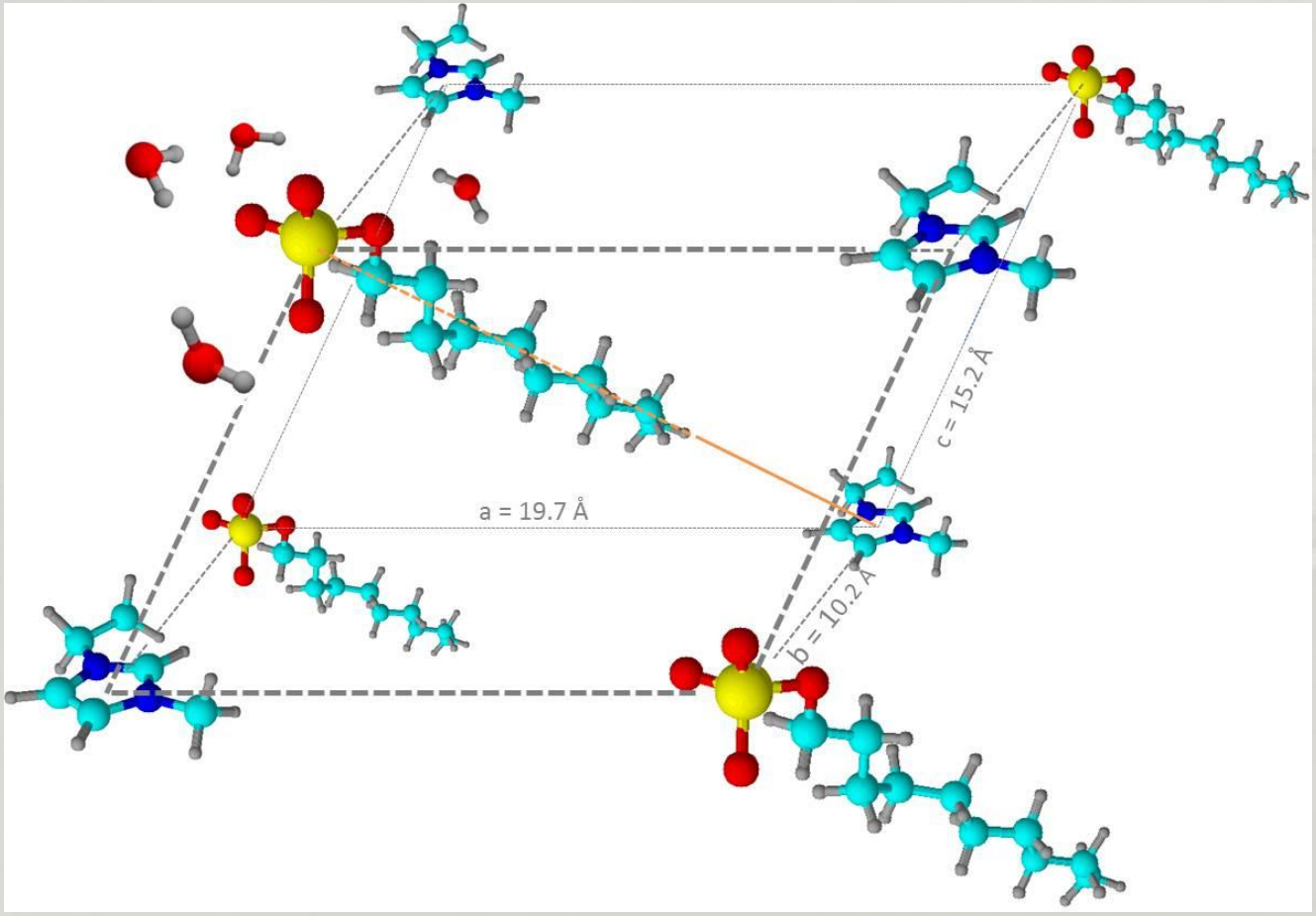
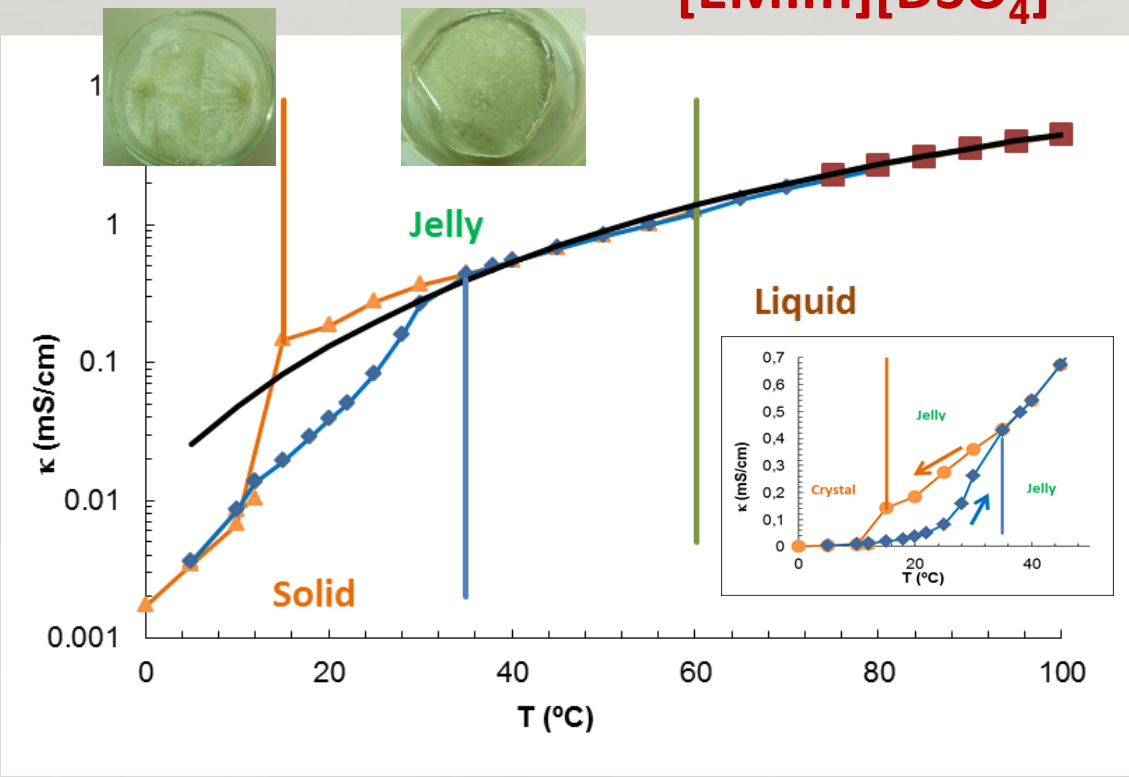
POSSIBLE MONOCLINIC P2/m STRUCTURE FOR HIDRATED [EMIm][DSO_4] ($\alpha = \gamma = 90º$, $\beta = 115º$)



EXIL

IONIC CONDUCTIVITY MEASUREMENT FOR THE HYDRATED [EMIm][DSO_4]



Electrical Conductivity of the hydrated [EMIm][DSO_4] vs. T. The black line represents the best fit of a VTF equation: $\kappa = A \bullet \exp\{-B/(T(K)-T_0)\}$ (for data above 35ºC). Vertical lines indicate the transition temperatures. Observe the thermal hysteresis loop in the gel-solid transition (at 15ºC) and solid-gel (at 35ºC).

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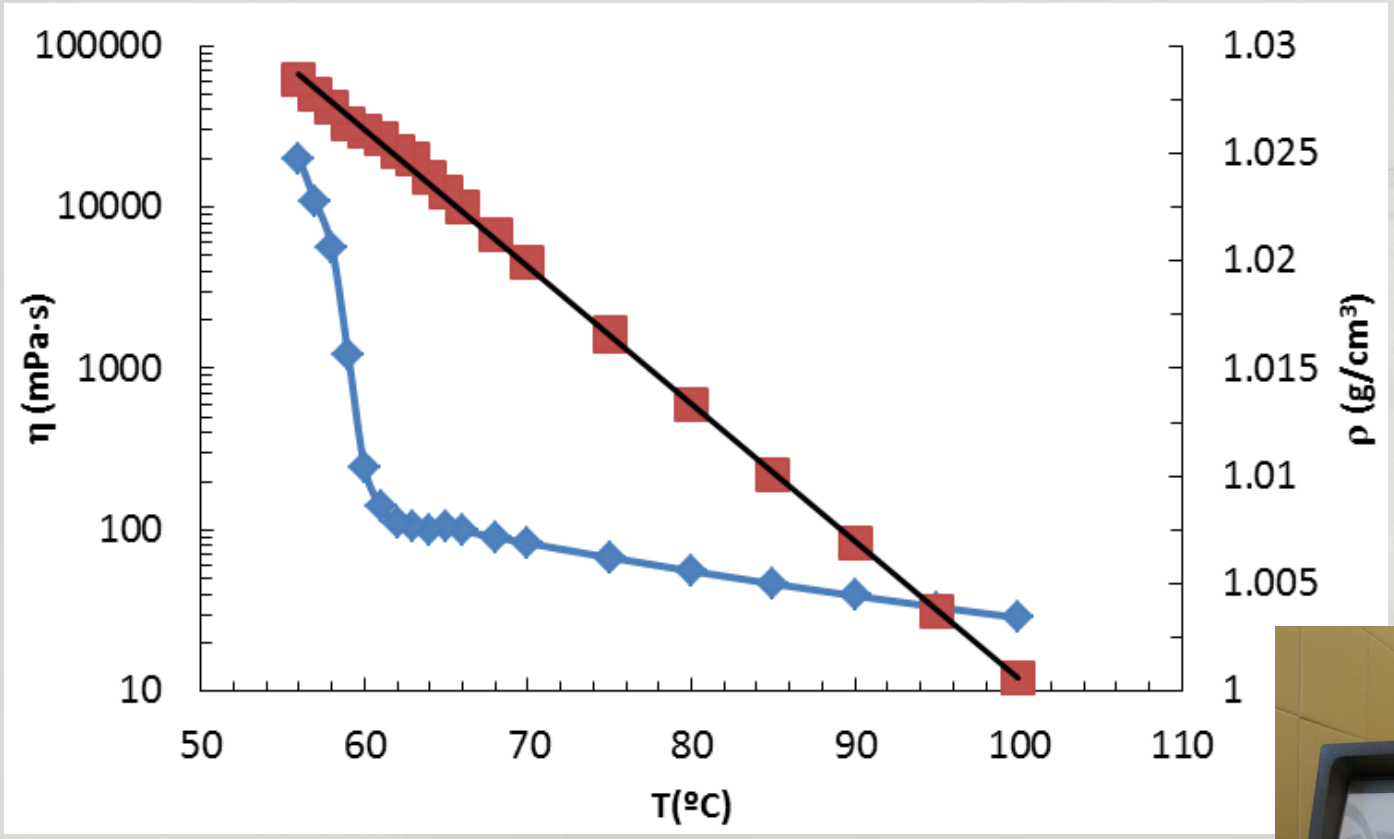
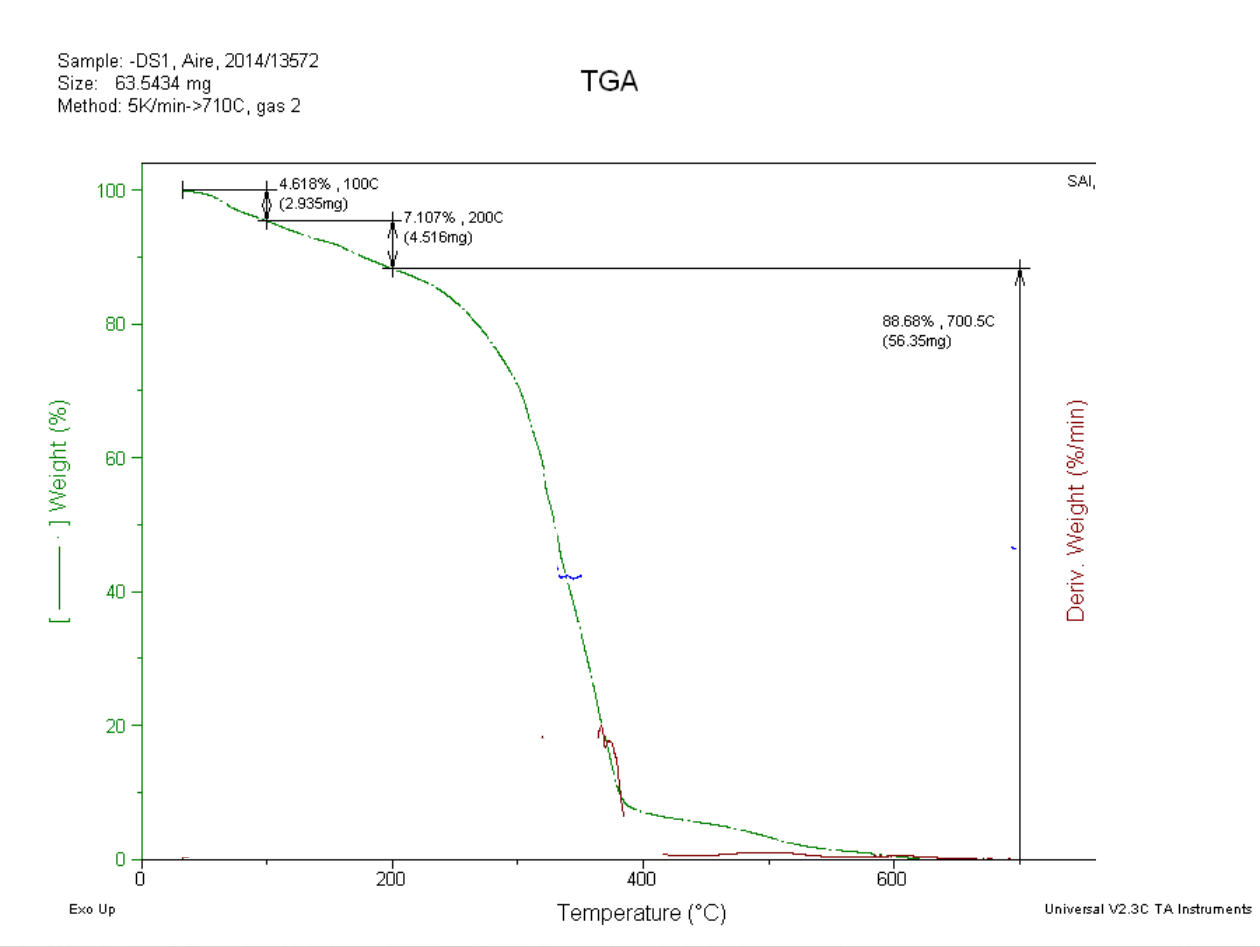
VISCOSITY AND DENSITY OF HYDRATED [EMIm][DSO_4]



We use a viscodensimeter Anton Paar Stabinger SVM 3000. The only one adequate for measurement this samples

Viscosity, η, (rhombus) and density, ρ, (squares) of hydrated [EMIm][DSO_4] in function of temperature. Black line represents the best linear fit to density.

TGA OF HYDRATED [EMIm][DSO_4]



At the beginning sample loses the water, and then, about 300ºC it decomposes.

FUTURE WORK

- LOOK FOR NEW GEL FORMER ILs
- ADD RELEVANT SALTS FOR ELECTROCHEMISTY
- STUDY PROPERTIES OF NEW PURE AND SALTED HYDRATED JELLYS
- USE THEM FOR REAL DEVICES AND PROCESSES

THANKS FOR YOUR ATTENTION

FROM "MESTURAS" GROUP AND COWORKERS