Measurement of ionic liquids properties.

Dream or Nightmare?

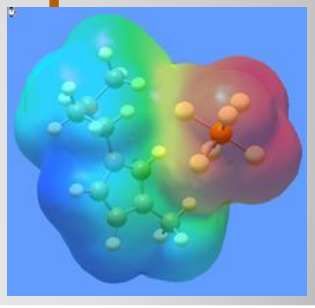
Carlos Nieto de Castro

Scope

- To try to answer to:
- Do we know how to measure the thermophysical properties of ionic liquids?
- And if we think we know, which type of care have we to take *a priori*?

Why Ionic Liquids?

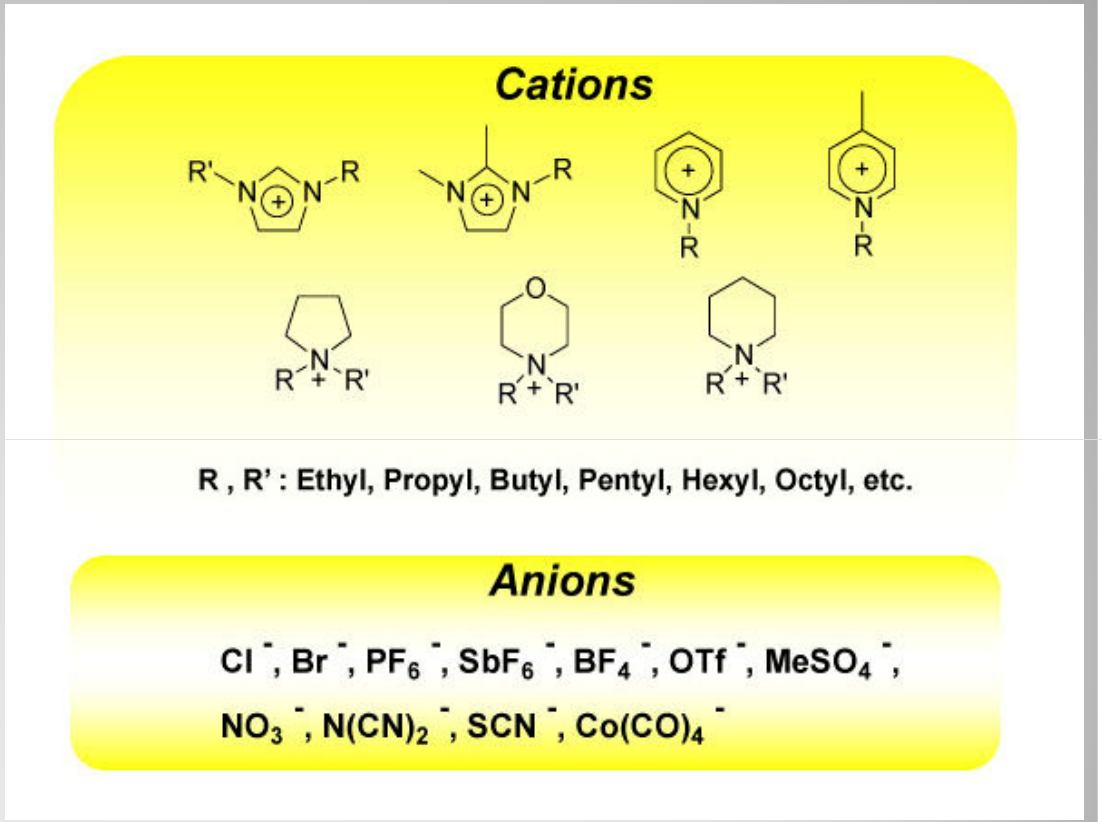
- Low temperature ionic liquids (LTIL's) are innovative fluids for chemical and materials processing, generally non-flammable and non-volatile at ambient conditions, and thus, perceived as "green" solvents.
- However, to implement new processes, it is necessary to prove that they are competitive with the traditional processes, not only from the point of view of final products, but for all the technological operations involved in the processes.
- The optimal technological design of new "green" processes requires the characterization of the ionic liquids used, namely values of their **thermodynamic, transport and dielectric properties**



[bmim][PF_6]

Ionic Liquid

- Ionic Liquids are most commonly defined as materials that are composed of cations and anions which melt at or below 100 ºC



In "Applications of ionic liquids in the chemical industry", Natalia V. Plechkova and Kenneth R. Seddon, Chem. Soc. Rev., 2008, 37, 123–150

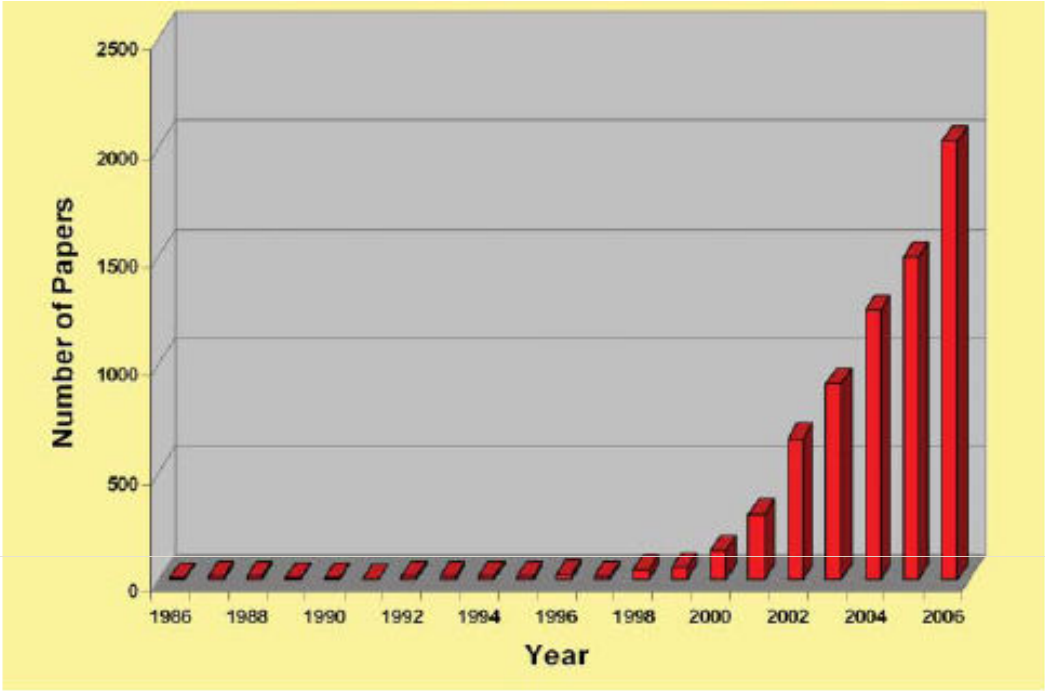


Fig. 15 Steeper than exponential growth of ionic liquid publications, 1986–2006.[59]

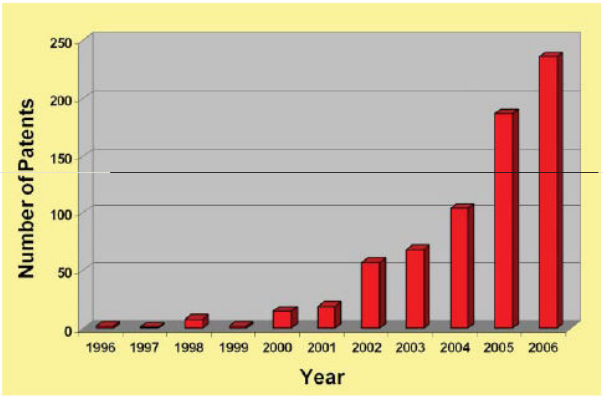


Fig. 16 Annual growth of ionic liquid patents, 1996–2006.[59]

World interest has grown exponentially in the last years

- **RTILs** possess a unique array of physico-chemical properties that make them suitable in numerous **task-specific applications** in which conventional solvents are non-applicable or insufficiently effective

- Such properties include:
  - high thermal stability,
  - high electrical conductivity,
  - high heat capacity per unit volume
  - wide range of viscosity
  - very good solvents properties
- As a result, ionic liquids are very popular materials and they enjoy a plethora of applications in various domains of physical science

IL Properties

- Most of the properties, namely thermophysical properties like viscosity and thermal conductivity have been measured using other liquids approach
- People forgotten about the structure and properties of ionic liquids and their impact in methods of measurement
  - Sample preparation and handling
  - Mathematical modelling
  - Chemical reactivity

Are Properties well measured?

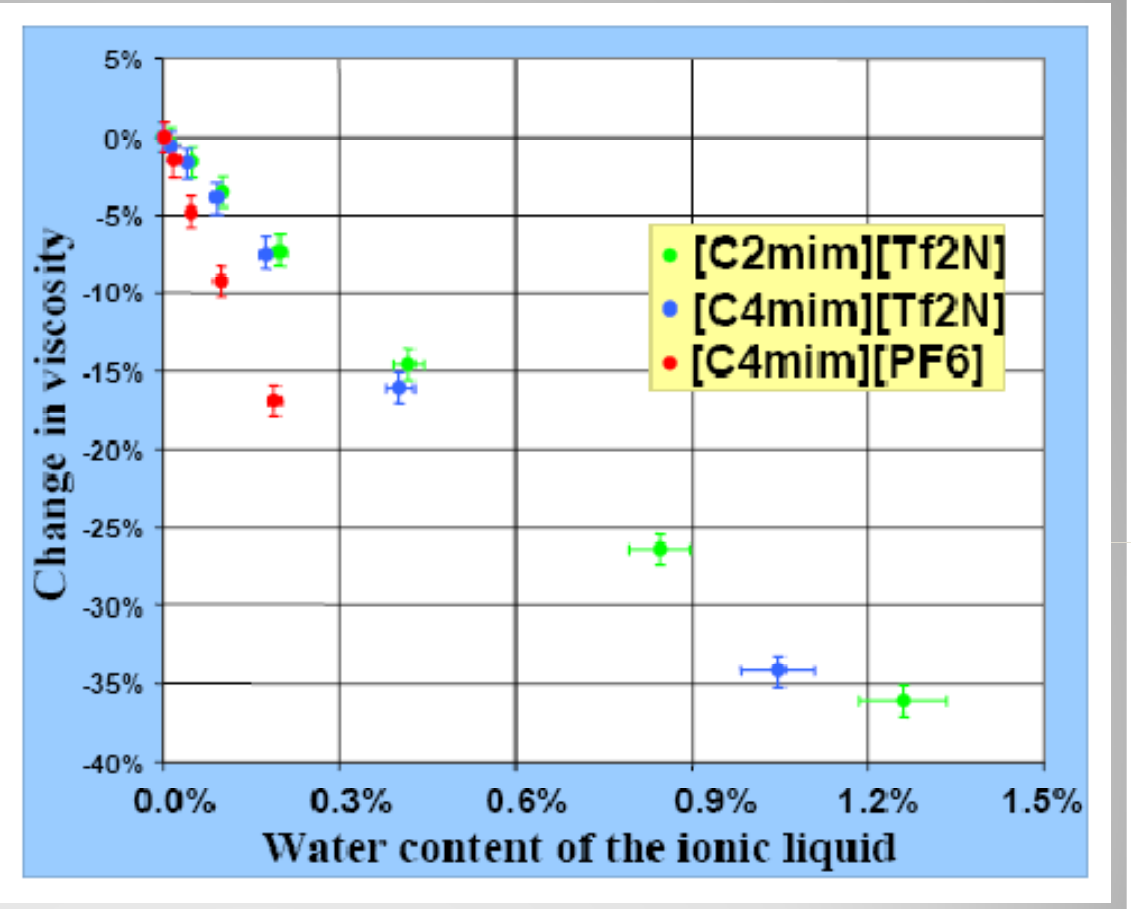
- Low to high viscosity, as the ions are not mutual independent, for most of the cases, and can form aggregates,
- Cations and anions have completely different sizes
- Reaction with water is possible,
- High solubility of water in IL's, affecting the properties,
- Moderate to high heat capacity per unit volume.

What characteristics of IL's can affect measurements?

- Effect of water on the viscosity
- Thermal conductivity measured with non-isolated HW probe
- Available data (ILThermo)

Some examples

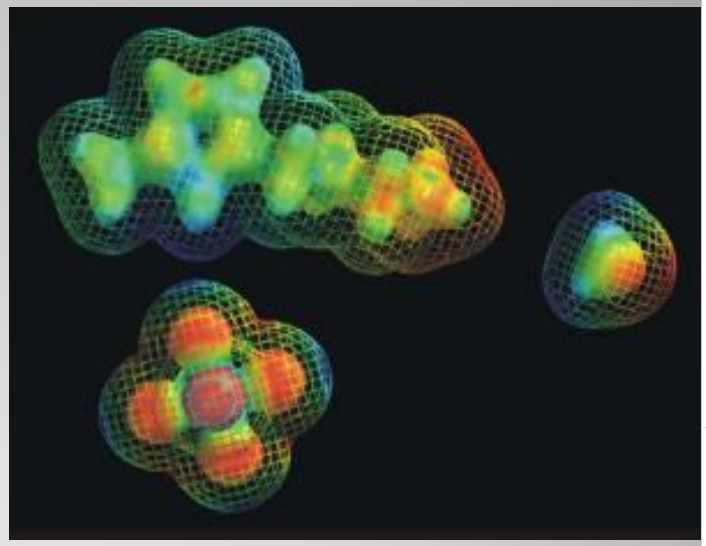
J. A. Widegren, A. Laesecke, J. W. Magee "*The effect of dissolved water on the viscosities of hydrophobic room-temperature ionic liquids*" Chem. Comm. (12): 1610-1612 (2005)



Effect of Water on Viscosity

- *Molecular "space filling" models demonstrate the difference in size for the positively charged "anion" (top image) and the negatively charged "cation" (bottom left) that combine to form a promising ionic liquid. It is still a mystery how the much smaller water molecule (right) can have such a large effect on the viscosity of such ionic liquids…*

[C4mim][PF_6]



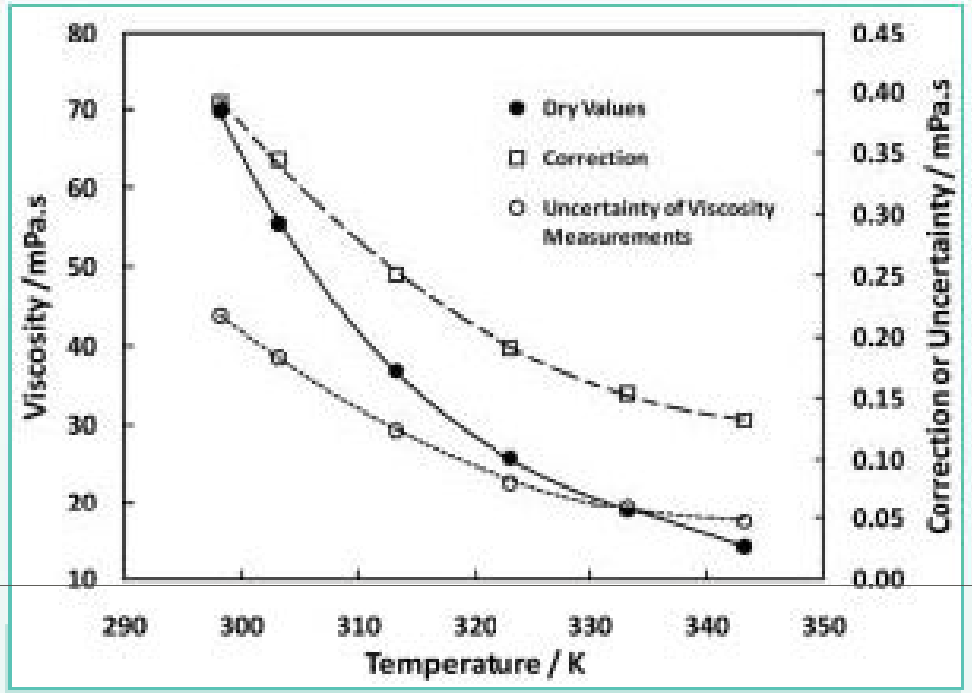


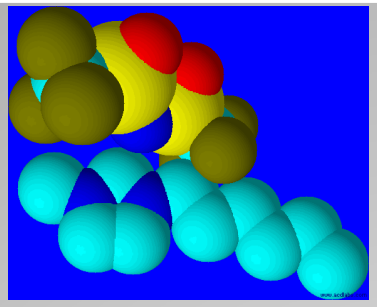
Figure 2. The viscosity of (hmim)(Tf2N) between 298 K and 343 K. Dry values mean experimental values corrected to zero water content in the sample, after (12). Lines are just trend quadratics

Effect of water in the viscosity of $[C_6mim][Tf_2N]$ – Lisbon data

Experimental values with water contents between 119.3 ± 30 ppm and 196.4 ± 3 ppm, corrected to 10 ppm (dry samples) using NIST data

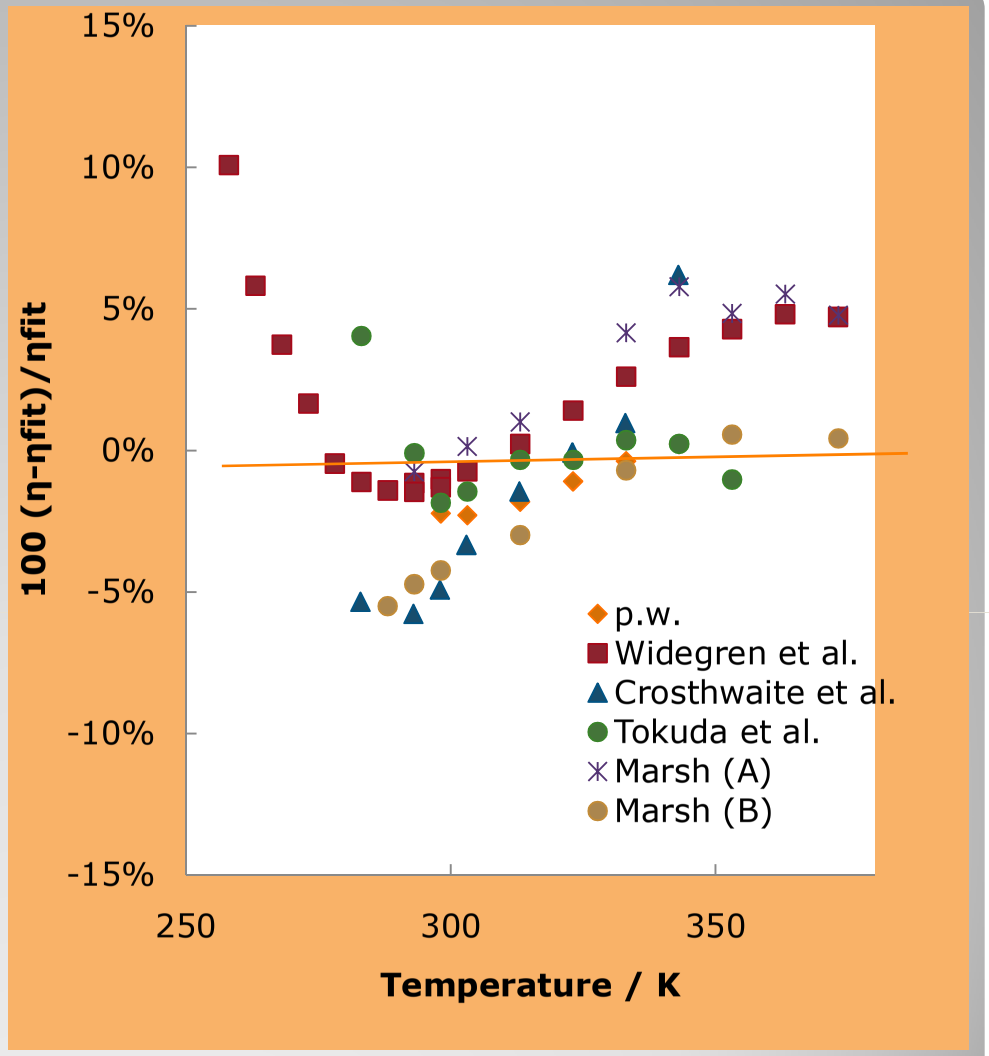
Nieto de Castro & Santos, Chemistry Today, 25, nº6, 20-23 (2007)

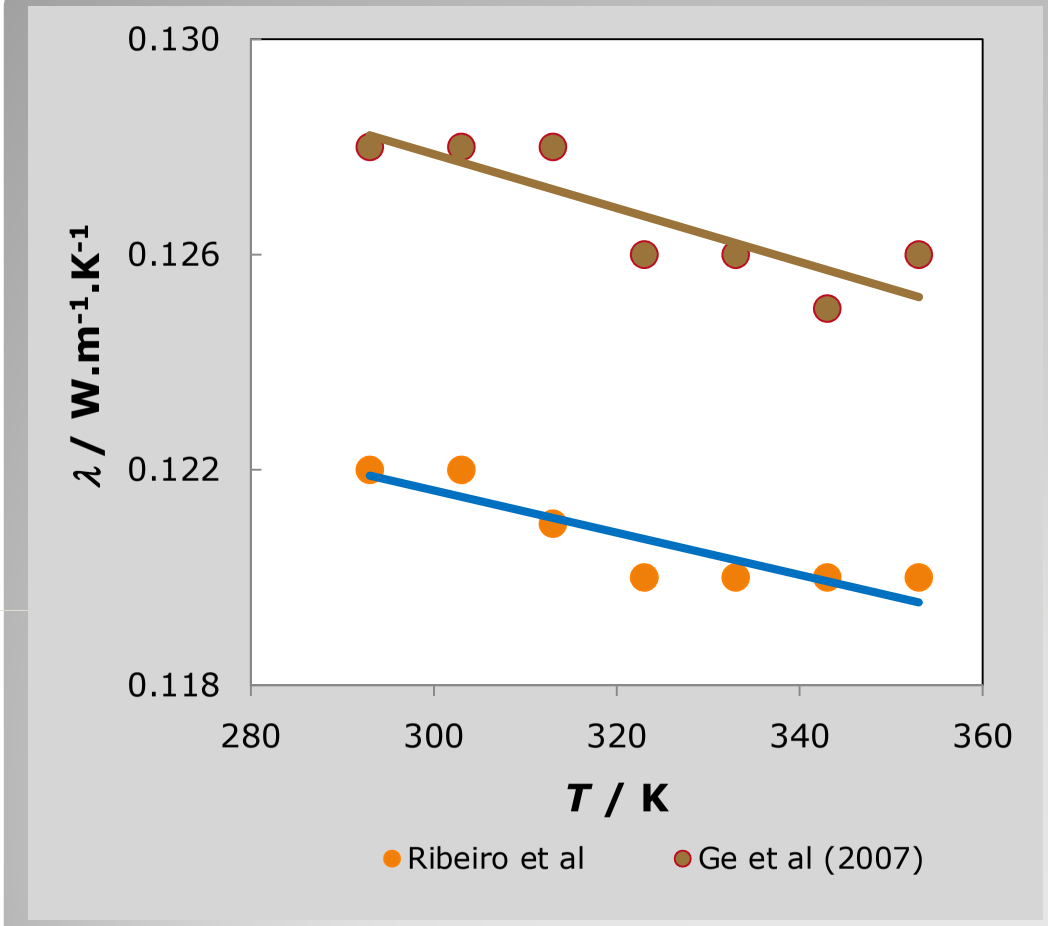
$[C_6mim][Tf_2N]$ – our data



- IUPAC project liquid
- All the participants aware of water absorption problem!
- But…

$[C_6mim][Tf_2N]$





- Measurements made with the same equipment, with (Ribeiro *et al* (2008) and without (Ge *et al*, 2007) insulated probe

Thermal conductivity of $[C_6mim][Tf_2N]$

Getting data from ILThermo

- Data bases are very useful
- Let us look to density of $[C_6mim][Cl]$

T / K	ρ / kgm-3 /uncert.	Method	Ref
298.15	1041 / 3%	VT	Gomes et al (2006) PCL
298.15	1040 /2.7%	VT	Gomes et al (2006) (JCED)
298.15	1030 /10%	Pycno.	Huddleston et al (2001)

Getting data from ILThermo

- Data bases are very useful
- Let us look to viscosity of $[C_6mim][Cl]$

T / K	η / Pa.s /uncert.	Method	Ref
298.15	1809 /2%	Capillary	Gomes et al (2006) (JCED)
298.15	0.716 /10%	Capillary	Huddleston et al (2001)

Same Liquid?

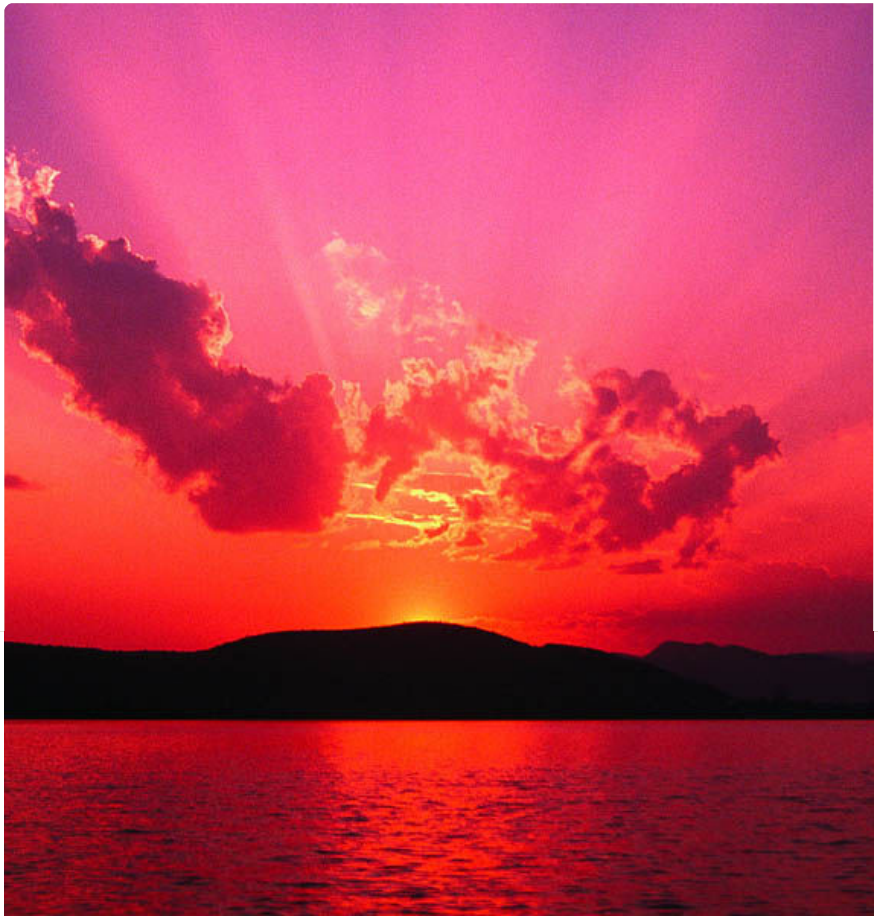
Getting data from ILThermo

- Data bases are very useful
- Let us look to surface tension of $[C_6mim][Cl]$

T / K	σ kgm-3 /uncert.	Method	Ref
298.15	0.0425 / 3%	Ring Tensiometer	Huddleston et al (2001)
298.15	0.0411 /5%	Pycno.	Ghatee &Zolghadr (2008)

- It is evident that:
  - **Accurate measurements of the thermal properties**, namely thermal conductivity of ionic liquids and nanomaterials, are a must
    - Probably new methods are needed, namely for solid aggregates
    - Transient-hot wire, with isolated wires (or polarizing techniques) can be used to ionic liquids and nanofluids, including "bucky" gels
  - **Standardization/Intercomparisons** are also necessary, namely for ionic liquids and nano-carbons – IUPAC Project
  - **Chemical and physical characterization of the samples** to be used is a must, while handling in controlled atmospheres can be necessary for some ionic liquid systems
  - **Systems are much more complex than the ones used before. It is therefore necessary to have an interdisciplinary approach, where physics, chemistry and molecular sciences have to work together**

Conclusions?



Dream?

Nightmare?

It can be either!

Acknowledgment

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- Ana Paula Ribeiro (PhD student)

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