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INSTITUTE OF CHEMICAL PROCESS FUNDAMENTALS OF THE ASCR

Electrical Conductivity of ILs and Their Mixtures

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COST CM 1206 EXIL. Workshop Prague April 21-22

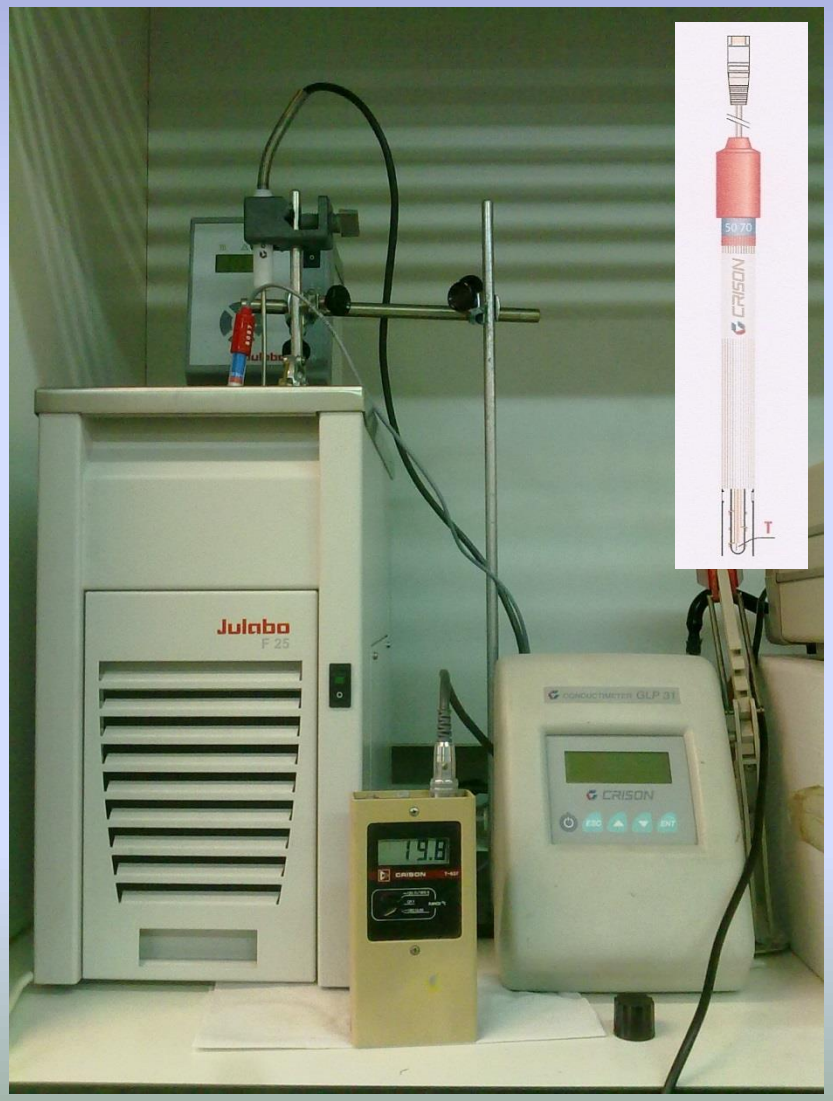
INTRODUCTION

- It is a fundamental characteristic of ILs
- Responsible for all charge transport process
- Not many experimental studies
- Nor theoretical or computational

Here I will tell you what we know about electrical conductivity in ILs,

and what is unknown…

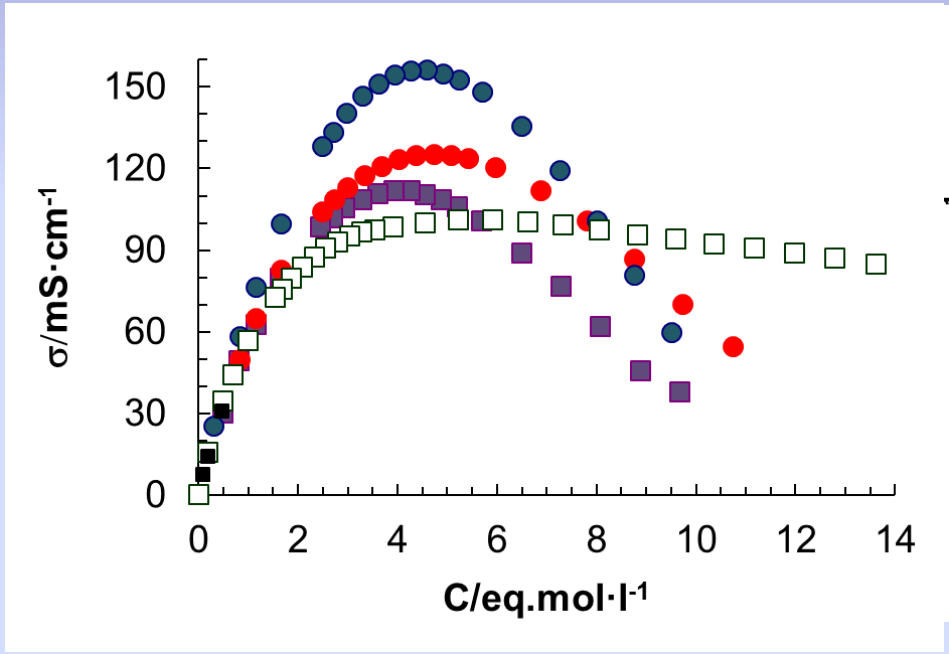
EXPERIMENTAL SET UP



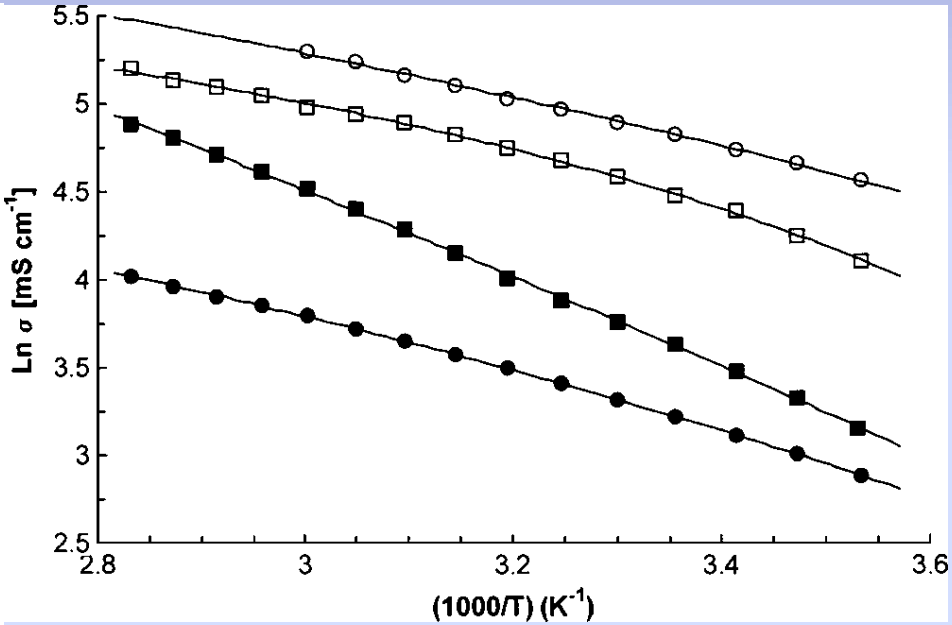
CRISON GLP 31 AND 31+

UNCERTAINTY < 1%
REPRODUCIBILITY < 4%

AQUEOUS SOLUTIONS OF Al SALTS UP TO SATURATION



Solid dots correspond to AlI_3, open dots to $AlBr_3$, solid squares to $AlCl_3$, and open squares to $Al(NO_3)_3$ vs. Al^{3+} concentration in aqueous solutions.



Logarithm of the electrical conductivity vs. 1000/T(K) for selected concentrations. Symbols represent the same solutions than figure at left. Lines are fits of VTF eq.

J. Vila, E. Rilo, L. Segade, O. Cabeza and L.M. Varela. Electrical conductivity of aqueous solutions of aluminium salts. Physical Review E **71**, 31201-31208 (2005).

TEMPERATURE DEPENDANCE OF ILs

$$Ln\ \sigma = Ln\ \sigma_{\infty} - \frac{E_a}{k_B(T - T_g)}$$

VTF-type equation

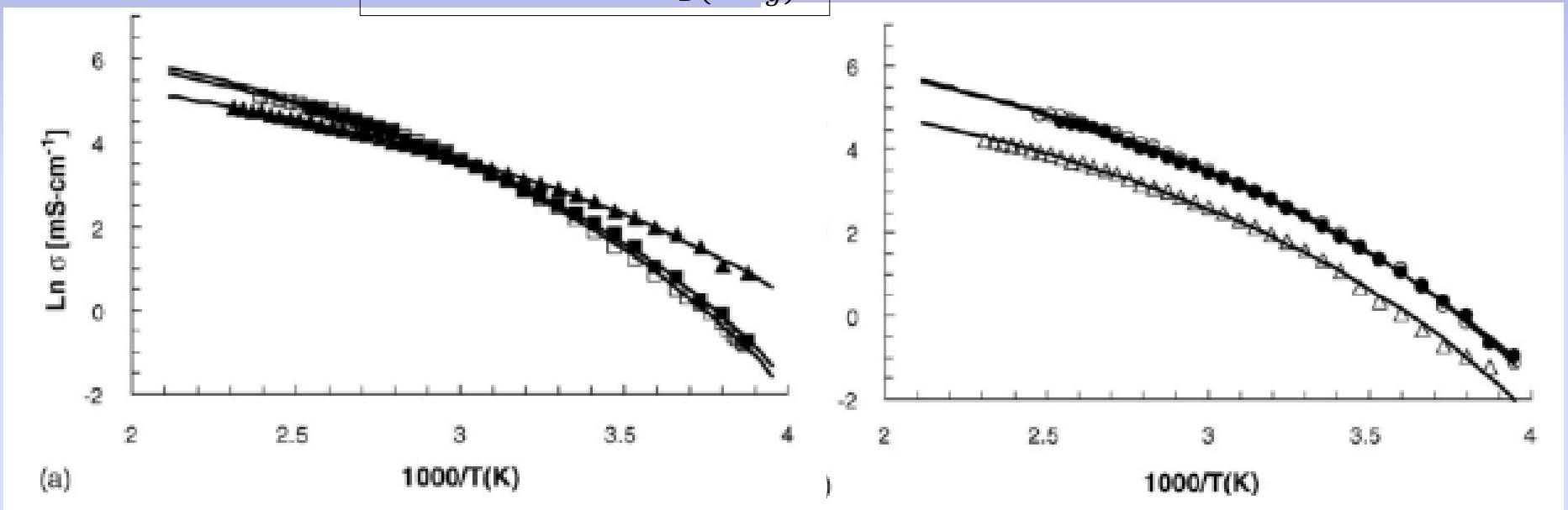
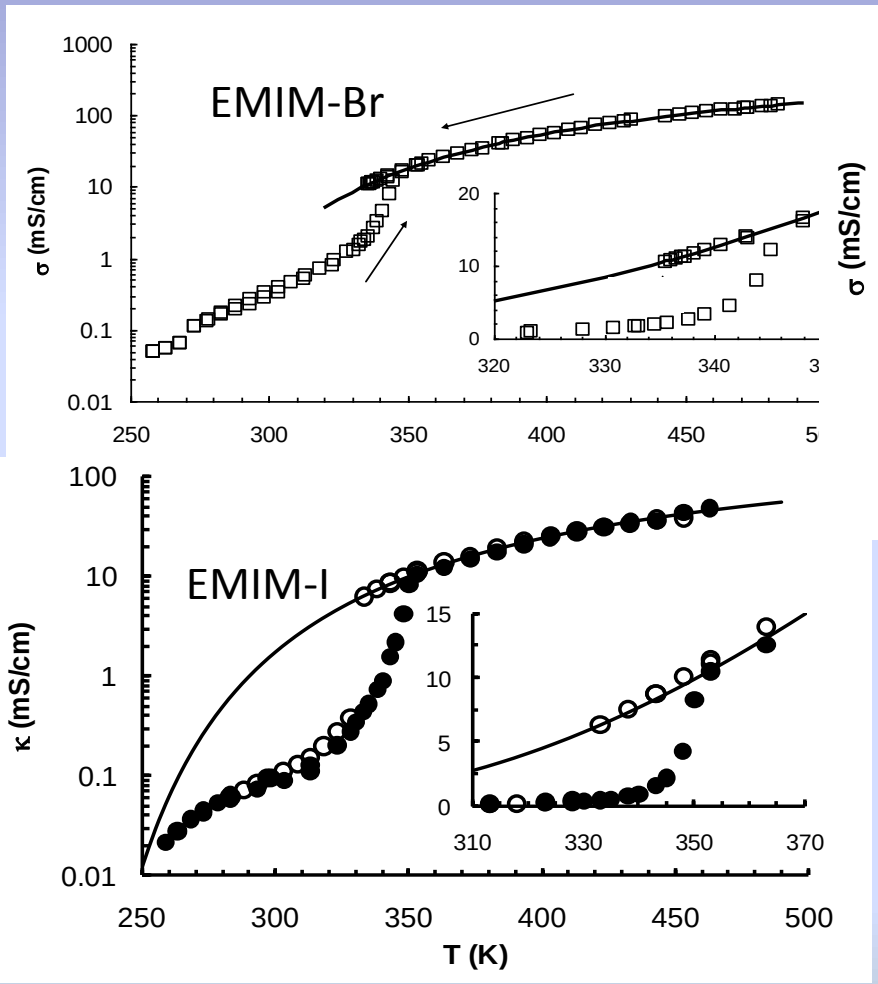
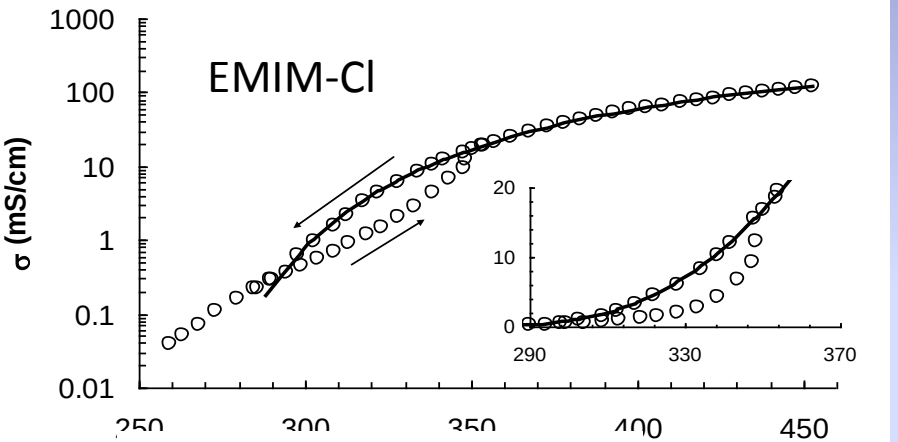


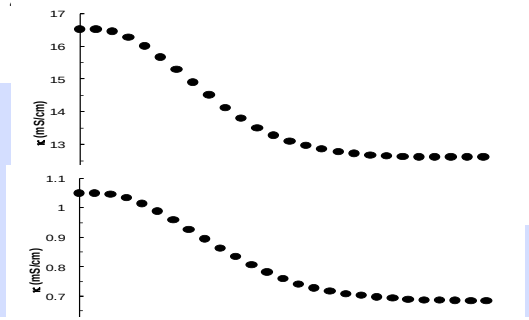
Figure 1. Logarithm of the electrical conductivity, Ln σ, vs.1000/T(K): (a) EMIM-$AlBr_3$ (x=0.30) (solid squares), EMIM-$AlBr_3$ (x=0.60) (open squares) and EMIM-BF_4 (solid triangles). At right, EMIM-$AlCl_3$ (x=0.33) (open circles), EMIM-$AlCl_3$ (x=0.60) (solid circles) and EMIM-ES (open triangles). Lines are the best fit of the **VTF-type** equation given

J. Vila, P. Ginés, J.M. Pico, C. Franjo, E. Jiménez, L.M. Varela and O. Cabeza. Temperatura dependence of electrical conductivity in EMIM-based ionic liquids. Evidence of Vogel-Tamman-Fulcher behavior. Fluid Phase Equilibria **242**, 141-146 (2006).

LIQUID TO SOLID TRANSITION

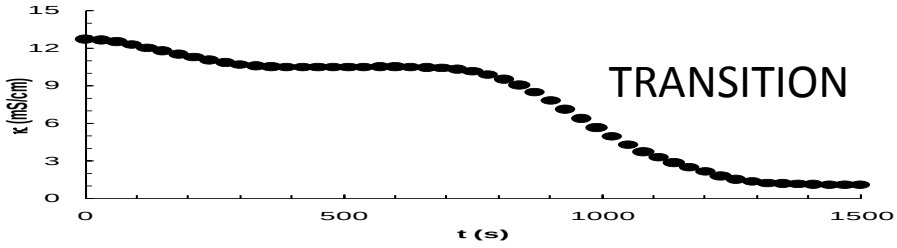






IONIC LIQUID

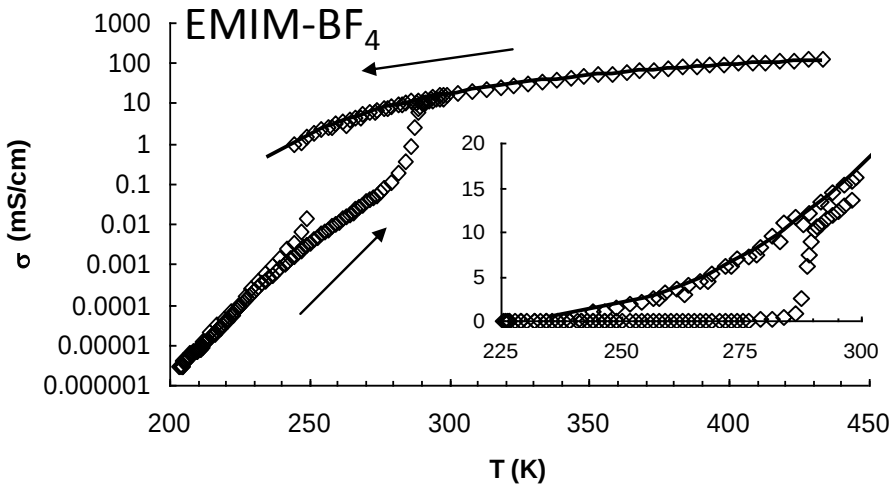
SOLID CRYSTAL

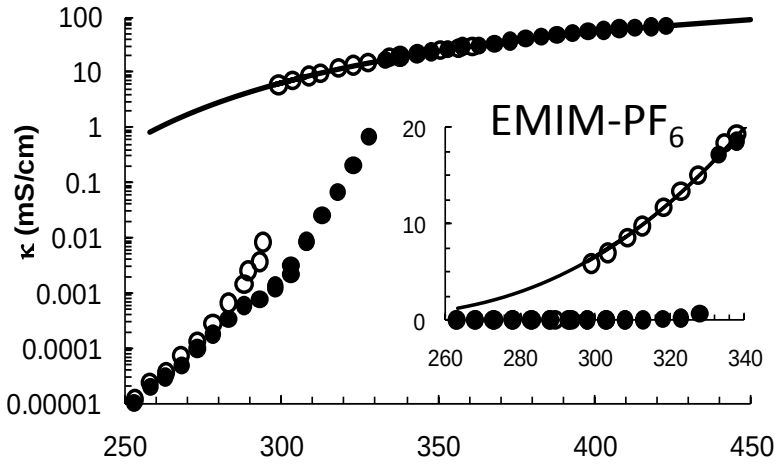


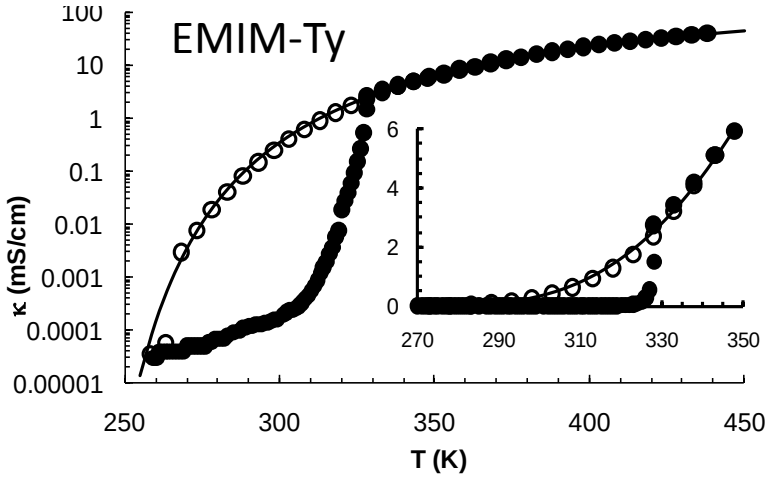
TRANSITION

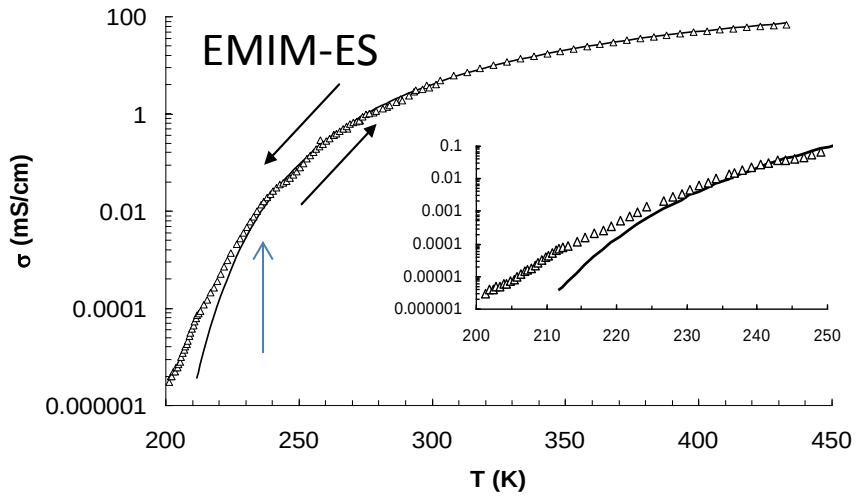
J. Vila, C. Franjo, J.M. Pico, L.M. Varela and O. Cabeza. Temperature behavior of the electrical conductivity of emim-based ionic liquids in liquid and solid states. Portugalae Electrochimica Acta **25**, 163-172 (2007).

LIQUID TO SOLID TRANSITION



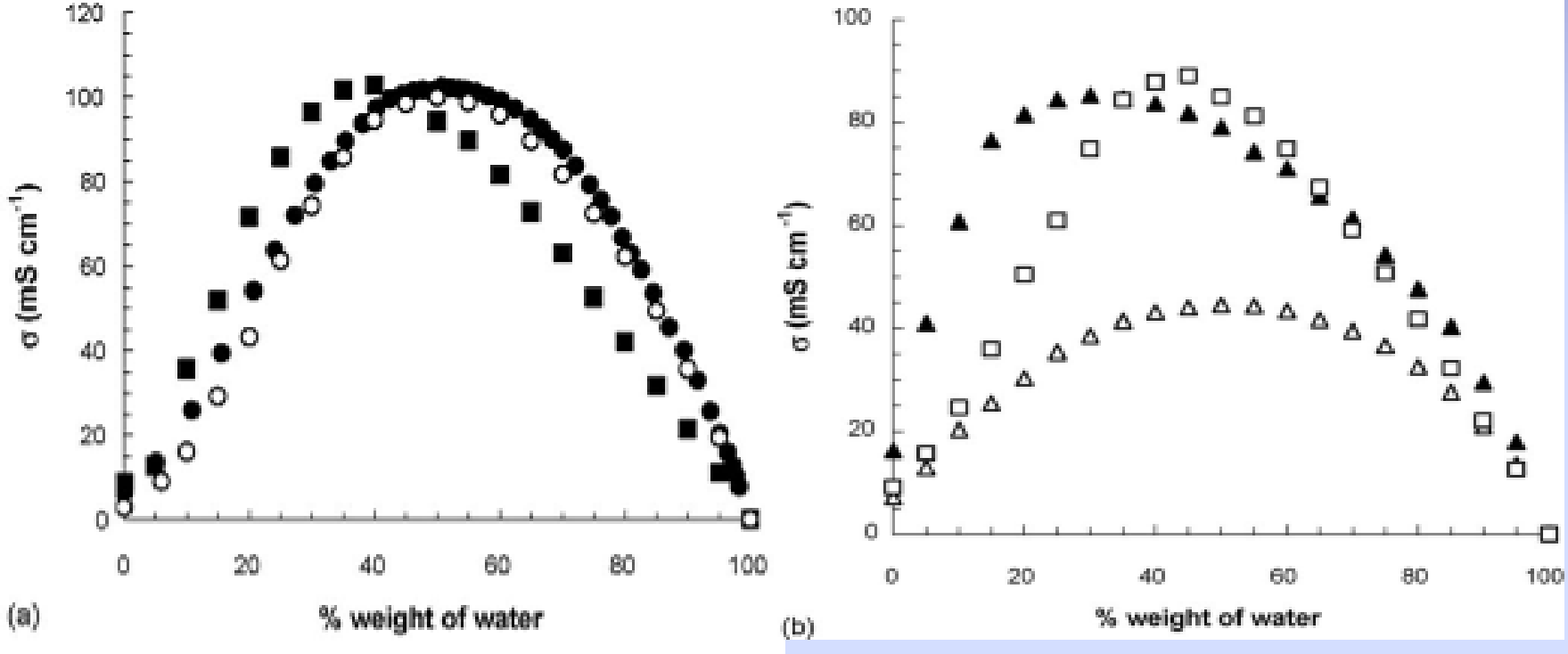






J. Vila, B. Fernández-Castro, E. Rilo, J. Carrete, M. Domínguez-Pérez, J.R. Rodríguez, M. García, L.M. Varela, O. Cabeza. Liquid-solid-liquid phase transition hysteresis loops in the ionic conduct. of ten imidazolium-based ionic liquids. Fluid Phase Equilibria **320**, 1-10 (2012)

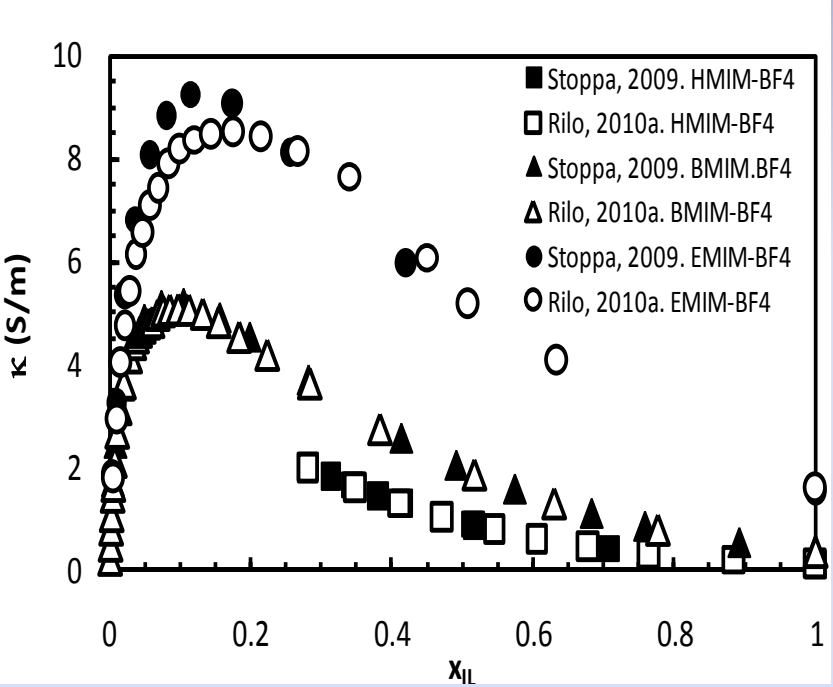
FOR AQUEOUS MIXTURES



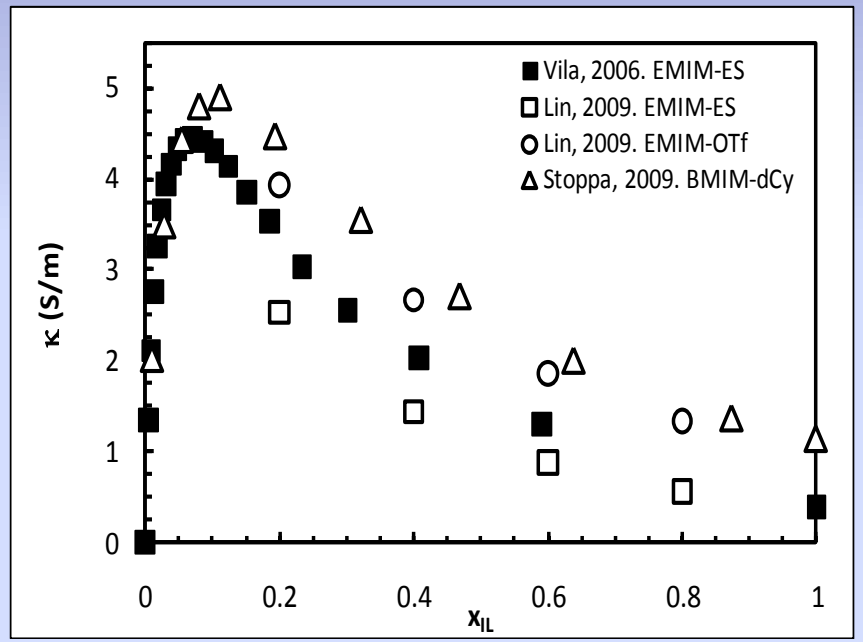
Electrical conductivity vs. the weight percentage of water in aqueous IL mixtures. (a) EMIM-$AlBr_3$ (x = 0.35) (solid dots), EMIM-$AlBr_3$, (x = 0.60) (solid squares) and EPYR-$AlBr_3$ (open dots). (b) EMIM-$AlCl_3$ (x = 0.33) (open squares), EMIM-BF_4 (solid triangles) and EMIM-ES (open triangles).

J. Vila, P. Ginés, E. Rilo, O. Cabeza , L.M. Varela. Great increase of electrical conduc. of ionic liquids in aqueous solutions. Fluid Phase Equilibria **247**, 32-39 (2006).

REVIEW ON EXPERIMENTAL DATA (2011)



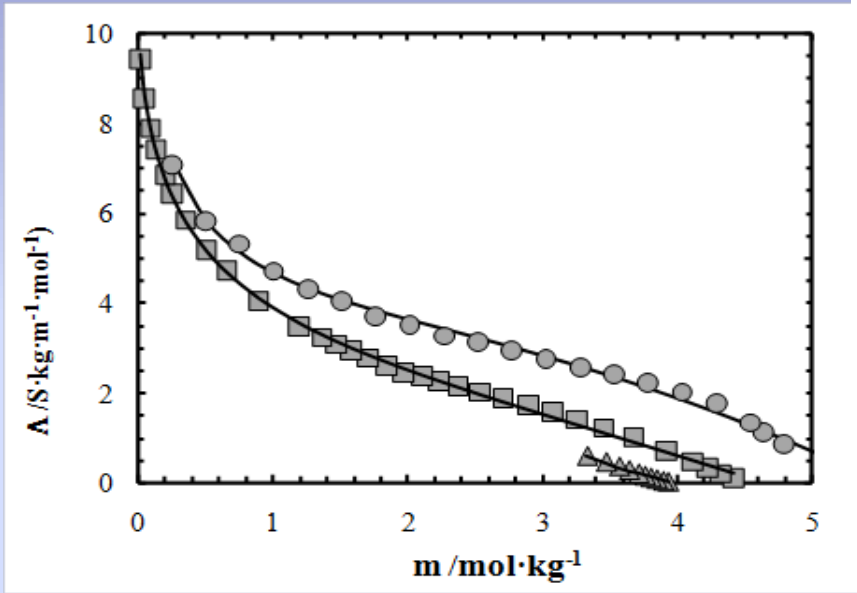
Electrical conductivity vs. IL molar fraction for three aqueous systems with tetrafluoro borate anions.



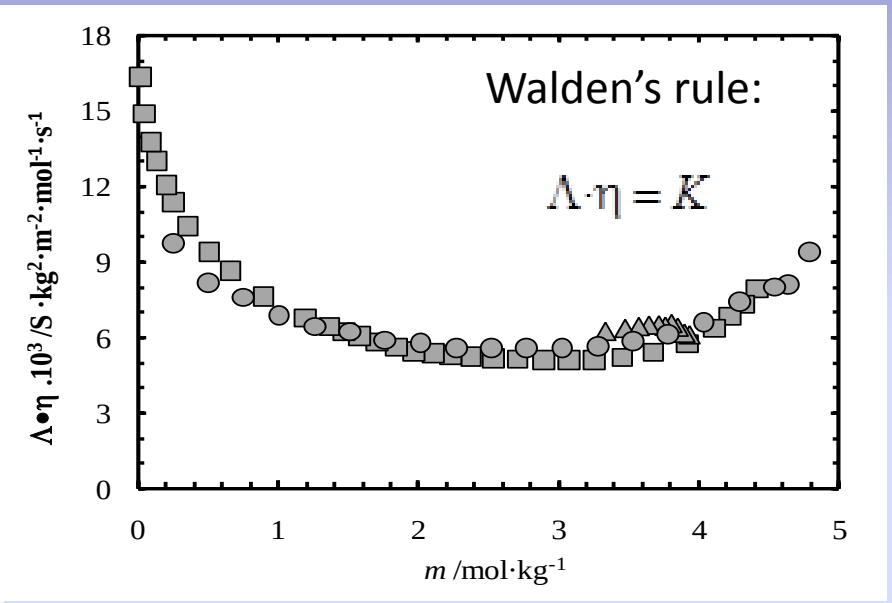
Electrical conductivity vs. IL molar fraction for four aqueous systems with different anions.

O. Cabeza, S. García-Garabal, L. Segade, M. Domínguez-Pérez, E. Rilo and L. M. Varela. Physical Properties of Binary Mixtures of ILs with Water and Ethanol. A Review, in "Ionic Liquids Theory, properties, new approaches" (Editor A. Kokorin). Pages 111-136 (2011). Ed. InTech. ISBN: 978-953-307-349-1

WALDEN'S RULE



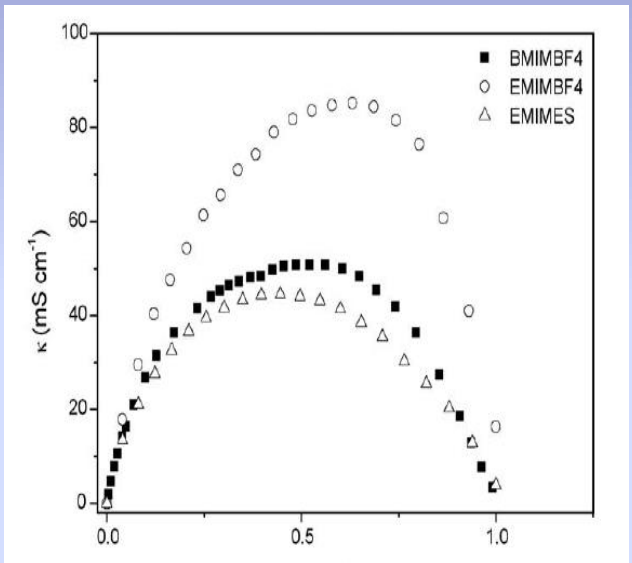
Molar conductivity vs. molality for **aqueous solutions** of C_2MIM-BF_4 (dot symbols), C_4MIM-BF_4 (square symbols) and C_6MIM-BF_4 (triangle symbols).

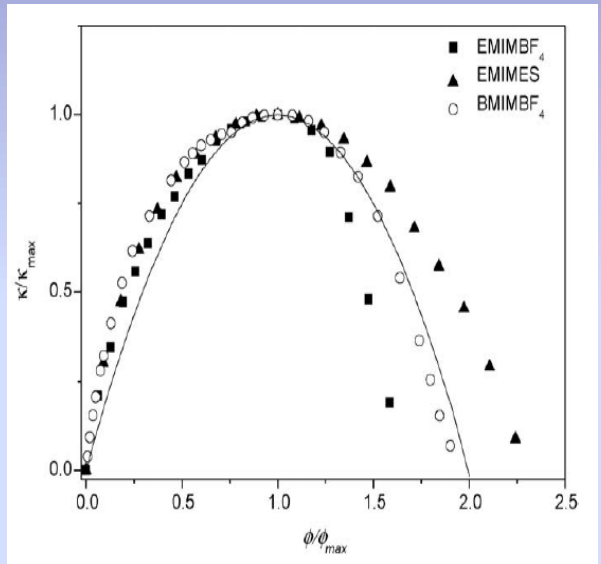


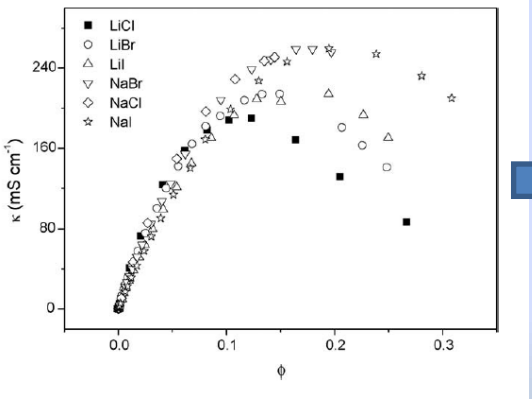
The product of molar conductivity by viscosity vs. molality for **aqueous solutions** for the same compounds than at left.
Walden's rule works for each m value!

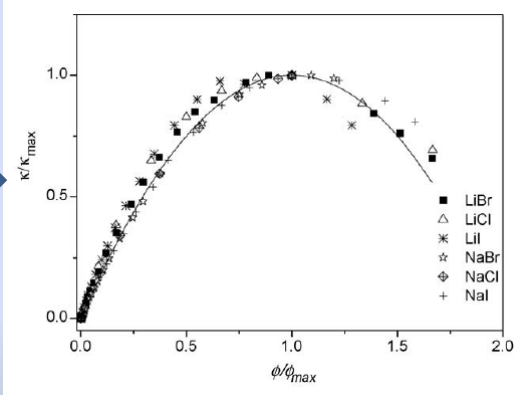
E. Rilo, J. Vila, J. Pico, S. García-Garabal, L. Segade, L.M. Varela, O. Cabeza. Electrical Conductivity and Viscosity of Aqueous Binary Mixtures of 1-Alkyl-3-methyl Imidazolium Tetrafluoroborate at Four Temperatures. Journal of Chemical Engineering Data **55**, 639-644 (2010).

THEORETICAL STUDIES ON IL MIXTURES







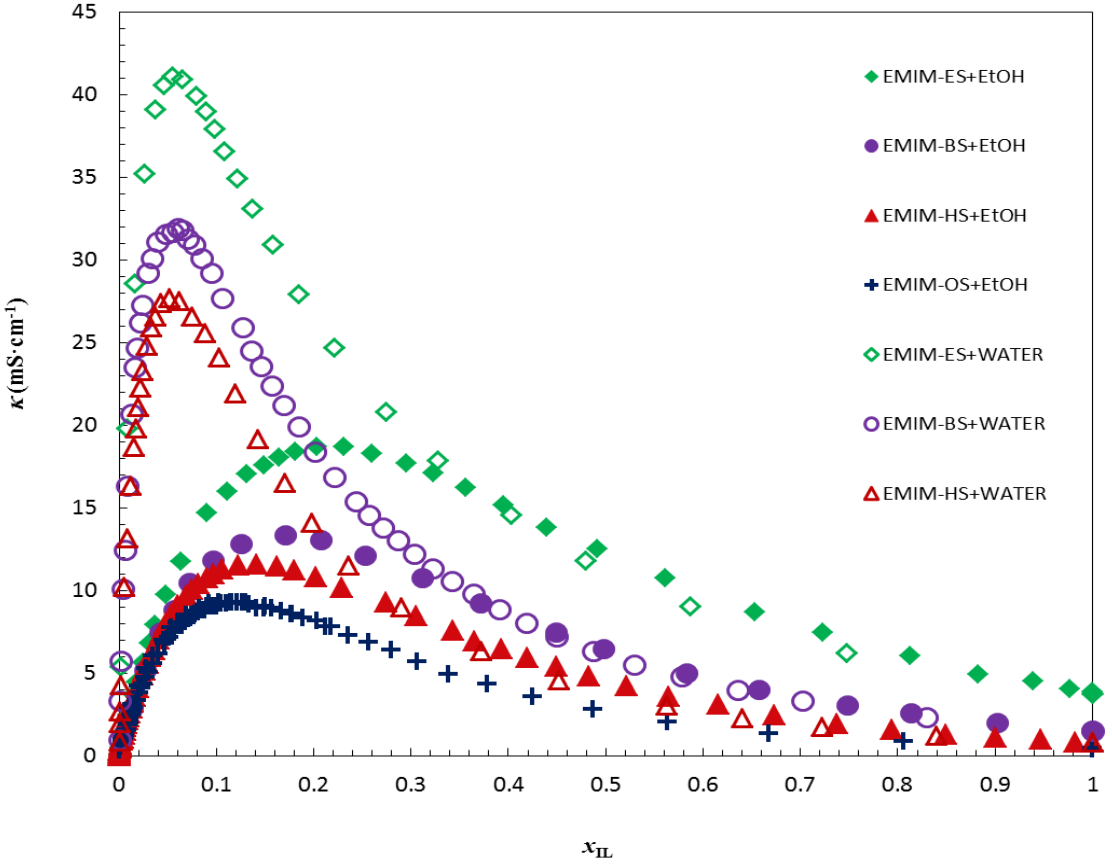


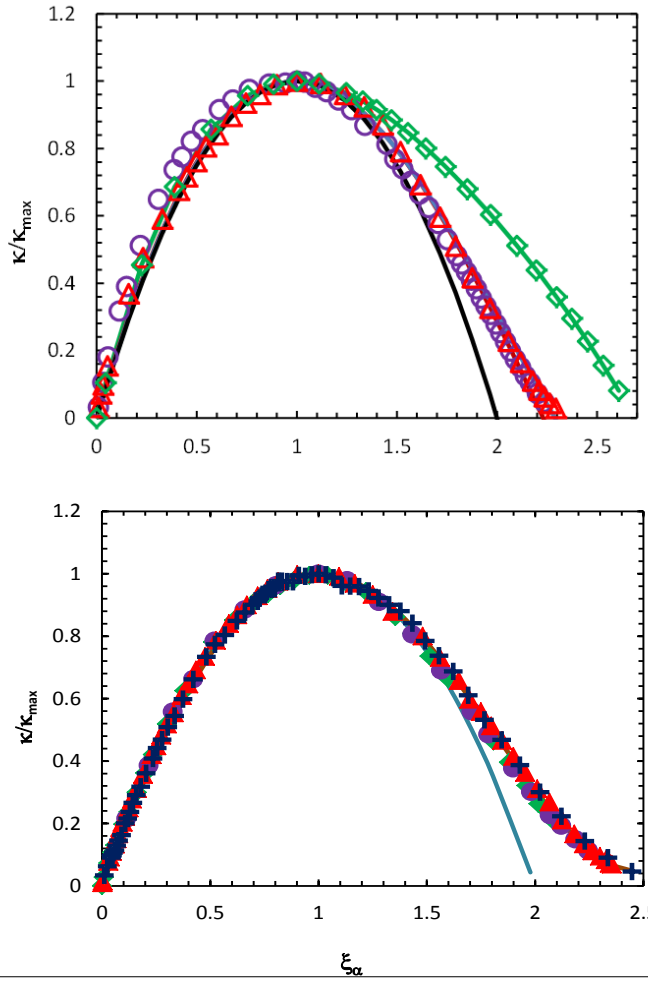
$$\frac{\kappa}{\kappa_{max}} = 2\xi_\alpha \left(1 - \frac{\xi_\alpha}{2}\right)$$

Universal Behavior!
No fitting parameters

L. M. Varela, J. Carrete, M. García, L.J. Gallego, M. Turmine, E. Rilo and O. Cabeza. Pseudo-lattice theory of charge transport in ionic liquid mixtures: corresponding states law for the electric conductivity. Fluid Phase Equilibria **298**, 280-286 (2010).

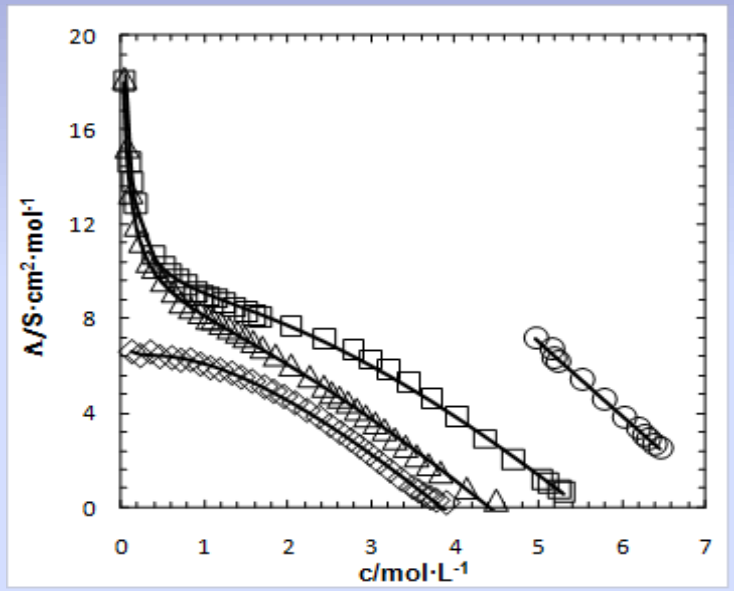
COMPARATION BETWEEN MIXTURES WITH WATER AND ETHANOL



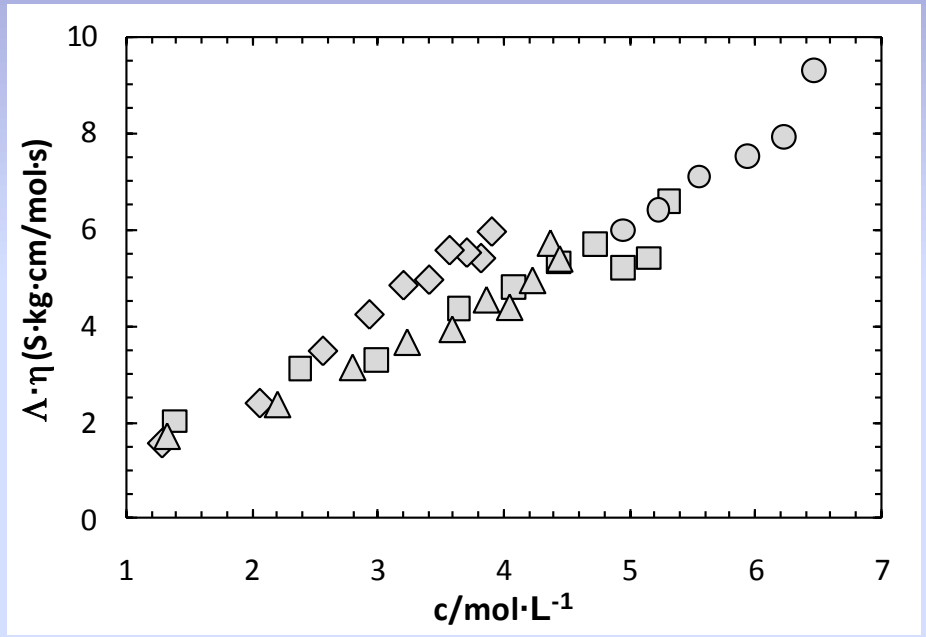


E. Rilo, J. Vila, S. García-Garabal, L.M. Varela and O. Cabeza. Electrical Conductivity of Seven Binary Systems Containing EMIM-Alkyl Sulfate Ionic Liquids with Water or Ethanol at Four Temperatures. The Journal of Physical Chemistry B **117**, 1411-1418 (2013).

SYSTEMATIC STUDIES ON ILs (2007-2013)



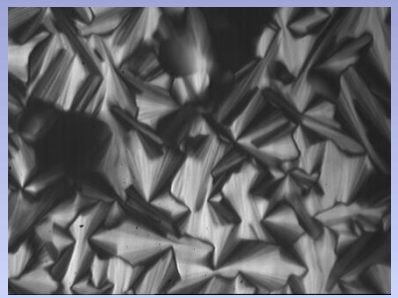
Molar conductivity vs. ionic liquid concentration for binary **mixtures of ethanol** with $C_2MIM\text{-}BF_4$ (dots), $C_4MIM\text{-}BF_4$ (squares), $C_6MIM\text{-}BF_4$ (triangles) and $C_8MIM\text{-}BF_4$ (rhombus symbols).

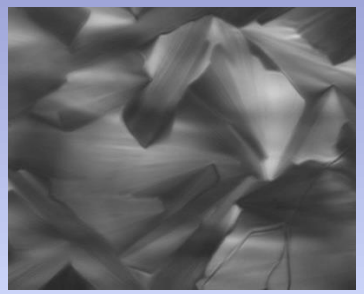


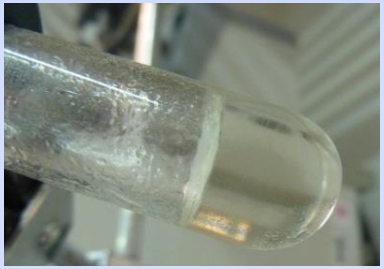
The product of molar conductivity by viscosity vs. molality for **mixtures with ethanol** for the same compounds than at left. Walden's rule also works.

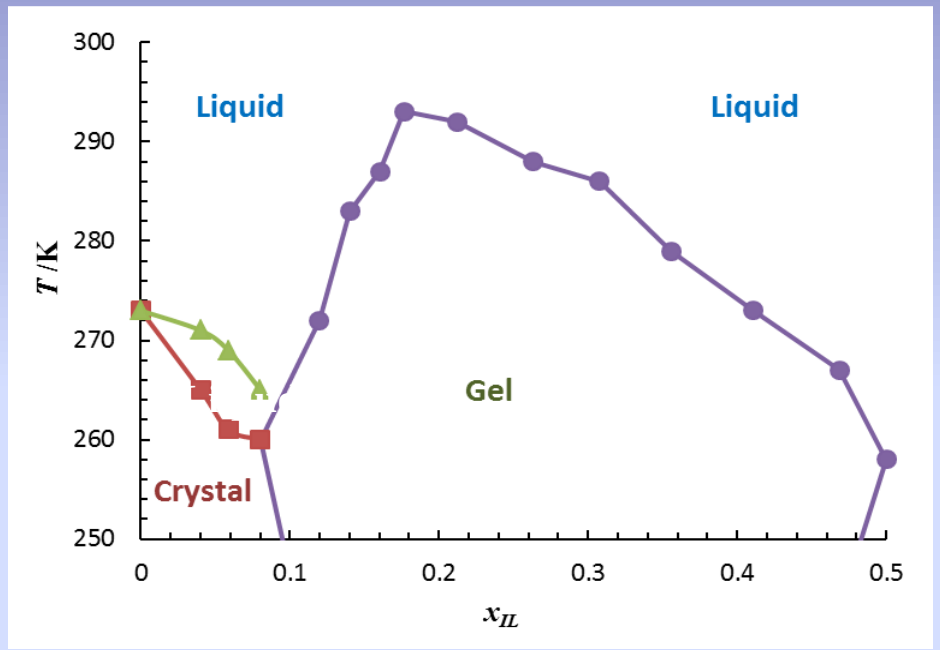
E. Rilo, J. Vila, M. García, L. M. Varela and O. Cabeza. Viscosity and electrical conductivity of binary mixtures of CnMIM-BF4 with ethanol at 288 K, 298 K, 308 K and 318 K. Journal of Chemical Engineering Data **55**, 5156-5163 (2010).

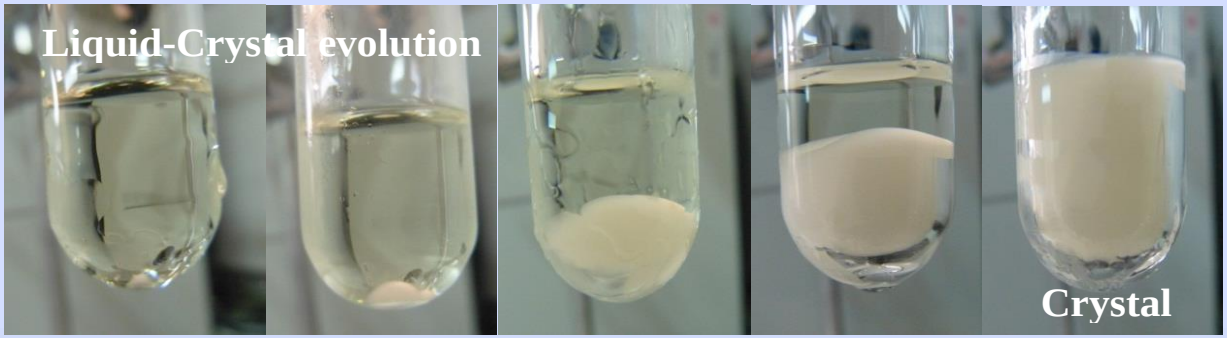
PRESENT AND FUTURE WORK





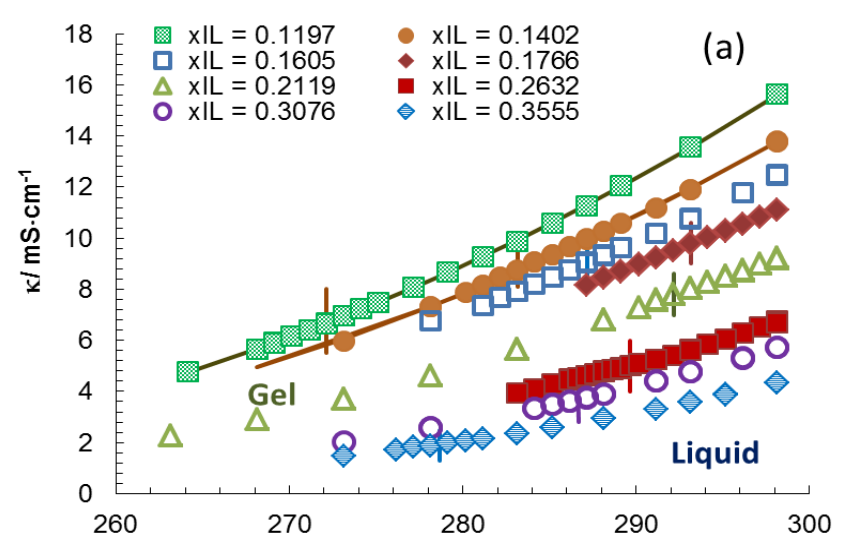


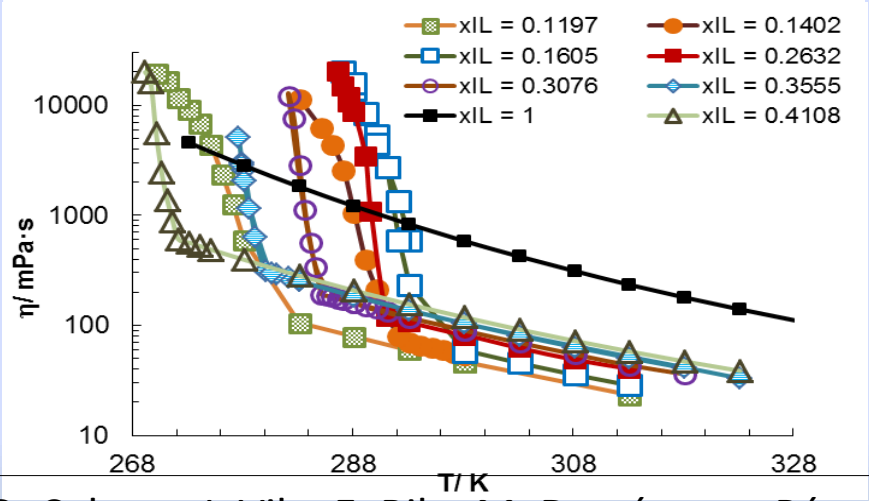


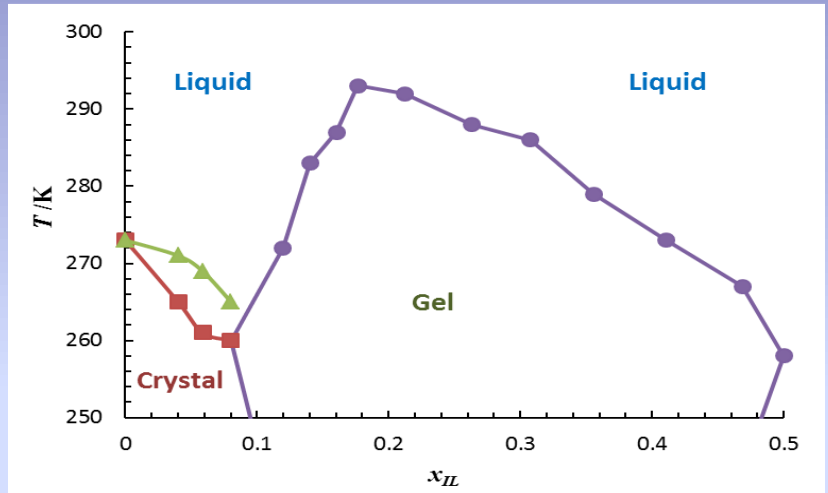


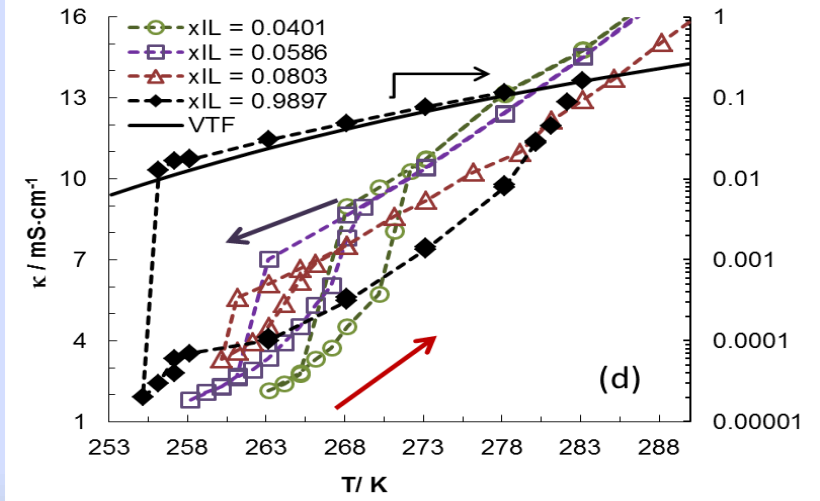
O. Cabeza, J. Vila, E. Rilo, M. Domínguez-Pérez, L. Otero-Cernadas, E. López-Lago, T. Méndez-Morales and L.M. Varela. Physical properties of aqueous mixtures of the ionic liquid 1-ethyl-3-methyl imidazolium octyl sulfate: a new ionic rigid gel. The Journal of Chemical Thermodynamics **75**, 52-57 (2014)

PRESENT AND FUTURE WORK









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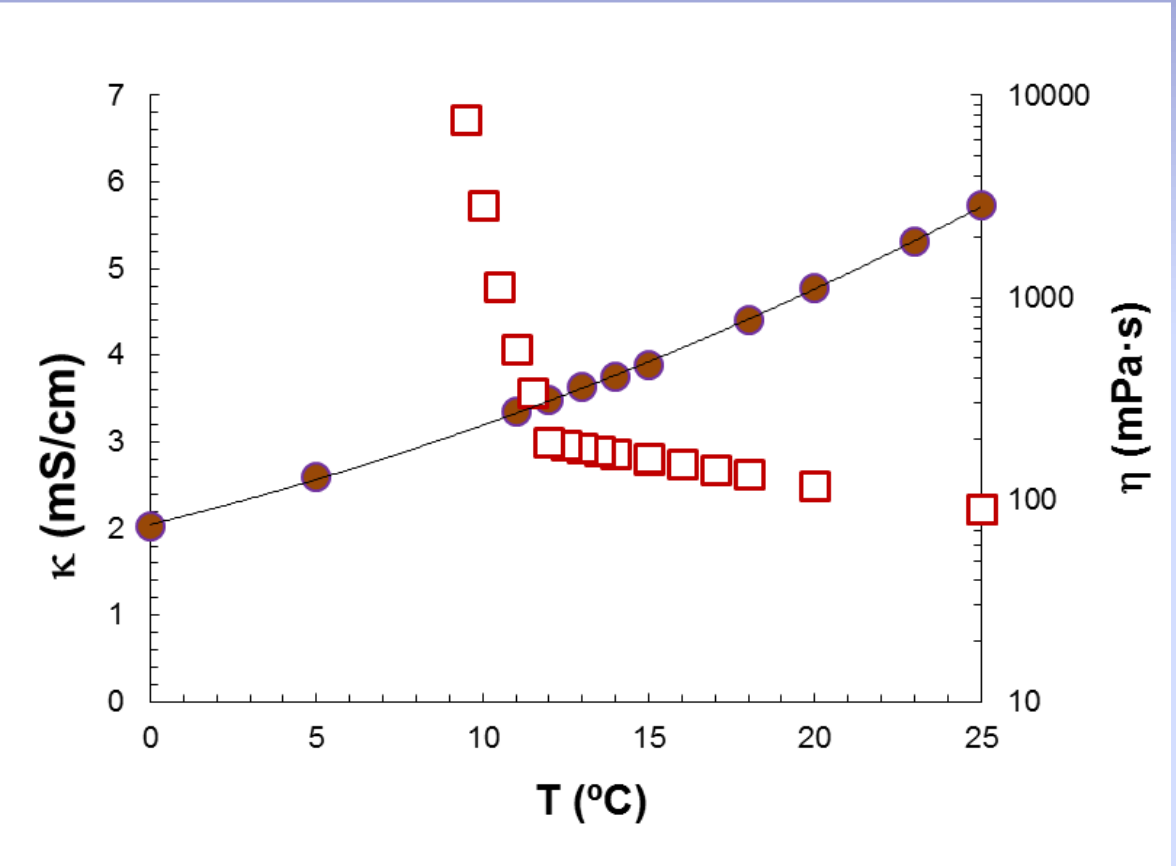
PRESENT AND FUTURE WORK



Walden's rule does not work at all…!

Is it still valid ionic conduction as unique charge transport mechanism?

PRESENT AND FUTURE WORK

- To continue studying rigid-gel state and applications, including optical ones
- To elucidate ionic transport mechanism role from theoretical and experimental points of view
- Computational MD simulations of transport properties (polarizable potential)
- Conductivity of ILs with added salts (first results where presented yesterday by M. Turmine)
- ILs as base compound for new electrolytes
- To begin studying electrical conductivity in DES (Deep Eutectic Solvents)

ACKNOWLEDGEMENT

All authors of any of the papers mentioned, and to Mr. Manuel Cabanas for many wonderful measurements

THANKS FOR YOUR ATTENTION