On the Measurement of the Electrical Conductivity of Ionic Liquids

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10th IATP meeting, Santiago del Compostela, 2010
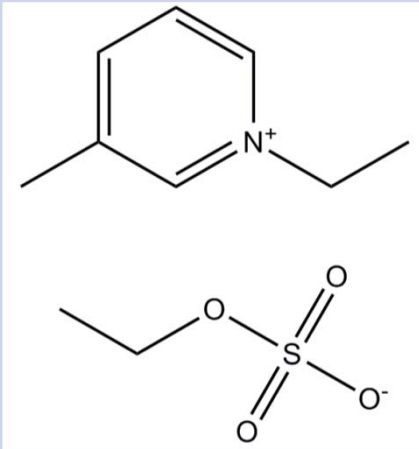
Introduction

- Room-Temperature Ionic Liquids (RTIL)
  - Salts that melt at or below room temperature;
  - $[EtNH_3]$-$[NO_3]$, first described in 1914 – melt. point: 12 °C;
  - RTILs have some physical properties that make them interesting as potential solvents for synthesis;

- Some potentially useful properties:
  - excellent electrochemical and thermal stability;
  - negligible vapor pressure;
  - a wide liquid range;
  - high electrolytic conductivity, κ

Introduction

- Electrolytic conductivity, κ
  - important for selecting a RTIL for electrochemical use;

- There is little or no data published for many RTILs;
  - Some times data are inconsistent or in poor agreement.

- Reasons for this disagreement in the reported values of κ for RTILs:
  - Inconsistent sample purity;
  - Presence of water:
    - water is everywhere;
    - even "hydrophobic" RTILs (not miscible with water) absorb water from the atmosphere;
    - the presence of water increases electrolytic conductivity, κ;
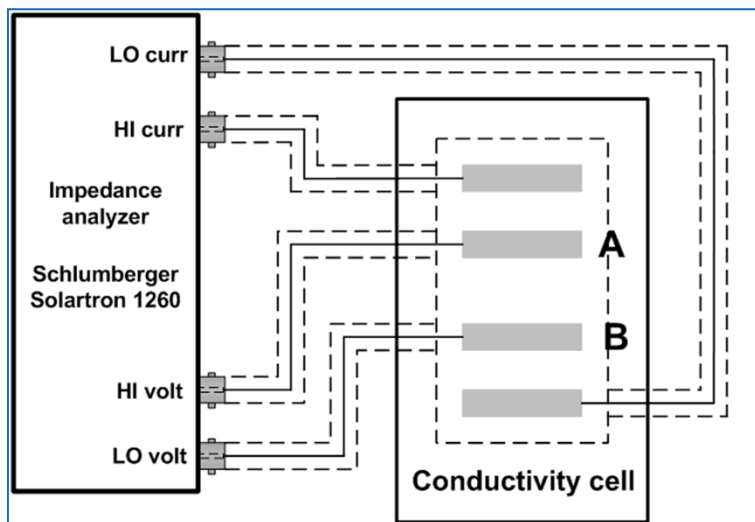   - trace levels of water could increase κ by lowering the viscosity, η

Objective

- Determination of the electrolytic conductivity of a RTIL by using a lock-in amplifier in a range of frequencies, and using an impedance analyzer to compare results:

  - Lock-in amplifier:
    - Signal Recovery model PE 7225

  - Impedance analyzer: Schlumberger Solartron 1260
    - Frequency resolution: 0.015ppm (1 in 65 million); resolution to 0.001dB, 0.01°; measures impedances > 100 MΩ.

  - Condutivity cell:
    - Schott LF 913 T, glass shaft, 5 platinum sensor rings, 30 KΩ NTC, cell constant: 65 m^{-1} ±10%.

Experimental

a)

b)

Max
Min

O'ring PTFE
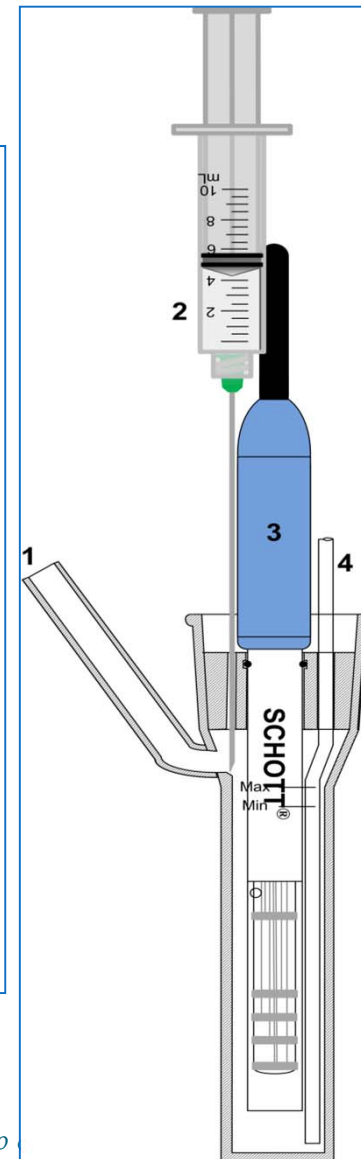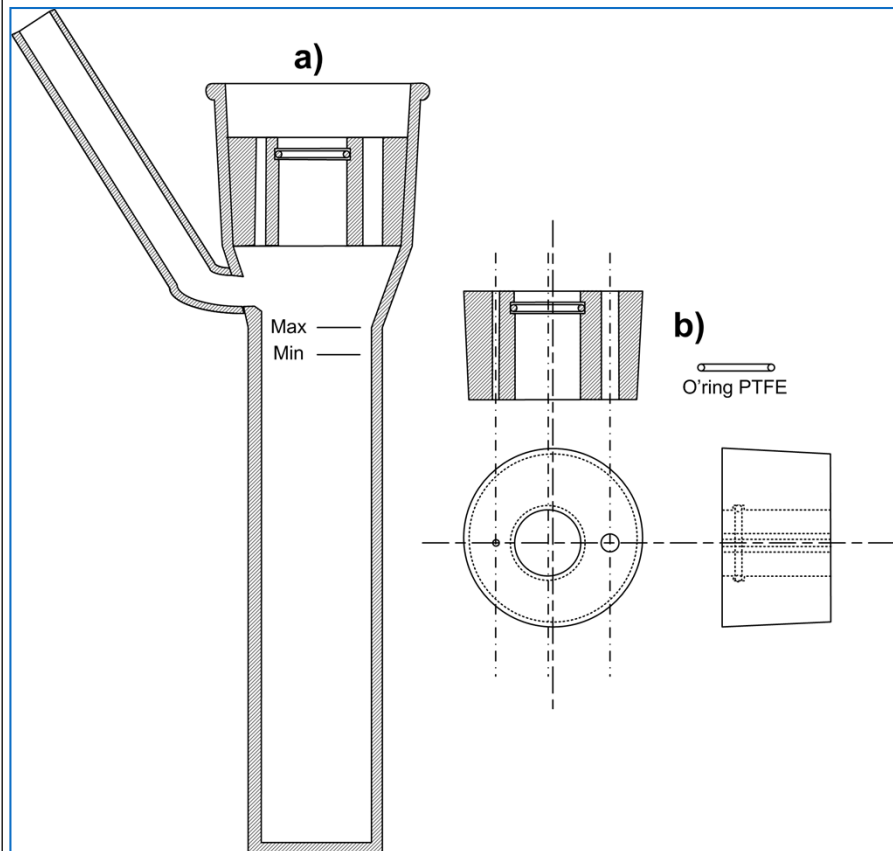
- 1 – Glass assembly for the condutivity cell
- 2 – syringe
- 3 – electrolytic conductivity cell
- 4 – PTFE tube for N_2

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Experimental

RT IL	Characteristics		Structure
[empy]$^+$[EtSO4]$^-$	Chem. formula	C$_{10}$H$_{17}$NO$_4$S	
	IUPAC name	1-ethil-3-methilpiridinium ethilsulphate	
	Molar mass (g·mol^{-1})	247,31	
	Purity (% m/m)	98 %	
	Risks	Corrosive	
	Manufacturer	Merck	
	CAS number	872672-50-9	
	Clorides (ppm)	Not detected	

Experimental

Impedance Analyzer

- range: 500 -20000 Hz
- step: 250 Hz
- Potentiostatic conditions: 10mV

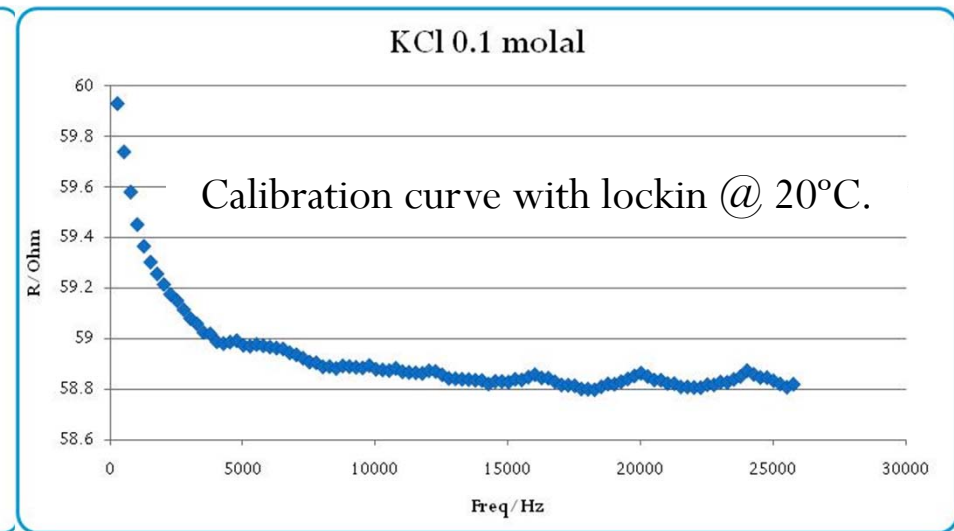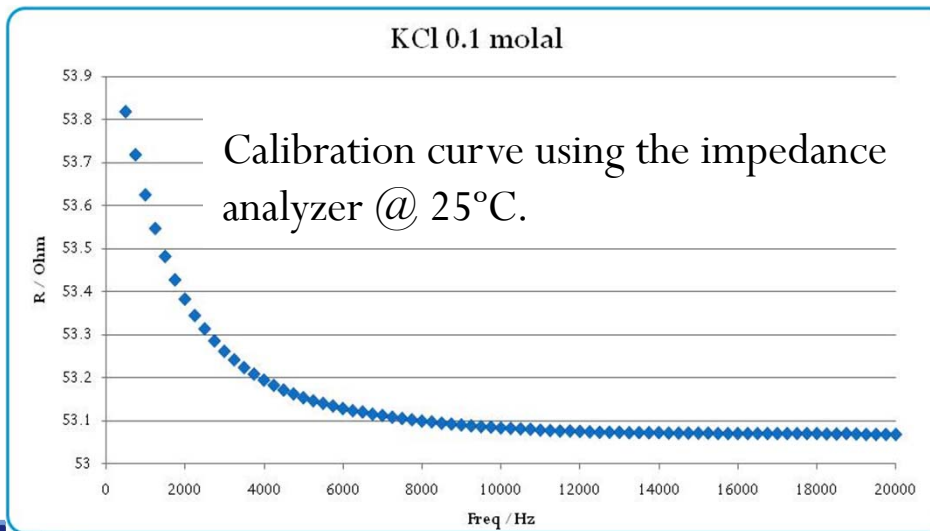at the *AB* terminals of the cell

Lock-in amplifier
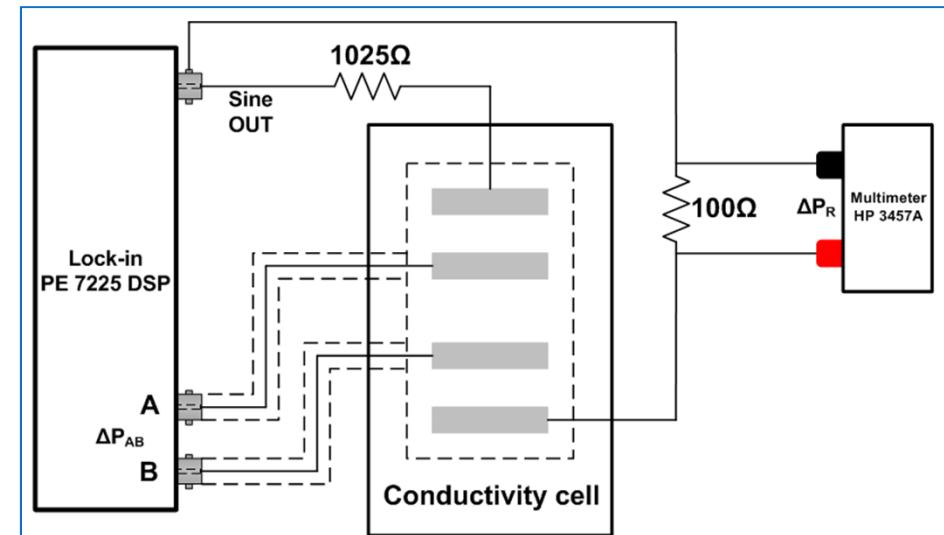
- range: 700 -25000 Hz
- step: 250 Hz
- Potentiostatic conditions: 10mV

at the *AB* terminals of the cell

$$R_L = \frac{\Delta P_{AB}}{I} = \frac{\Delta P_{AB} \cdot R_{100\Omega}}{\Delta P_R}$$

- The resistance of the liquid (R$_L$) is obtained with the eq. (Robinson and Stokes, Electrolyte Solutions, 2nd ed. rev, Butterworths, 1968).

$$R_L(f) = R_\infty + \frac{A}{f^c}$$

  - R$_\infty$ - resistance for infinite frequency;
  - *c = 1/2* or *c = 1* ➔ must be chosen to better adjust the experimental data.

Calibration curve using the impedance analyzer @ 25°C.

Calibration curve with lockin @ 20°C.

Experimental

- ## Calibration: KCl solutions @ 0.1 m e 0.01 m

method	Temperature
Lock-in	$17 - 45$ °C
Impedance analyser	25 °C

$$C_{cell} / m^{-1} = R_{\infty} / \Omega \times \kappa / S \cdot m^{-1}$$
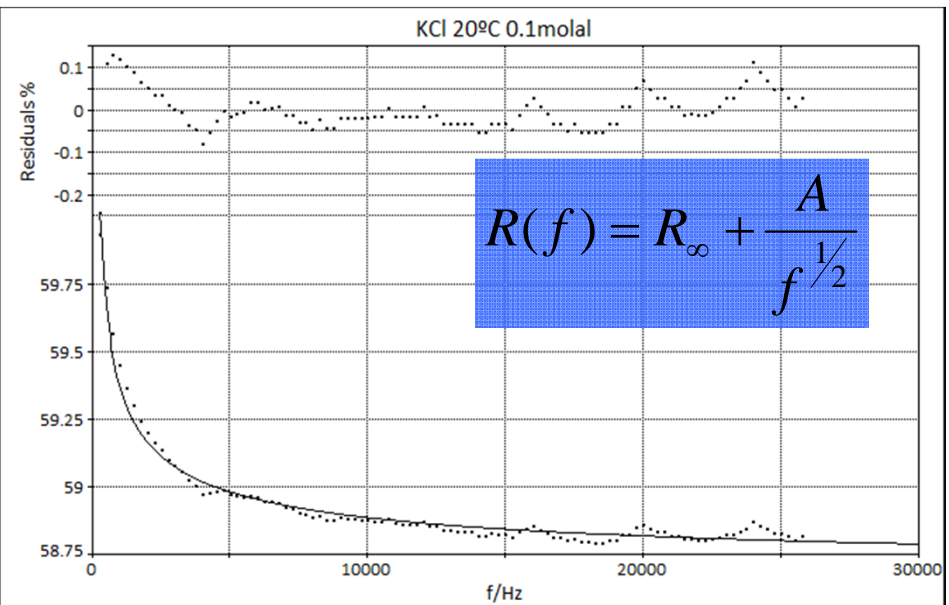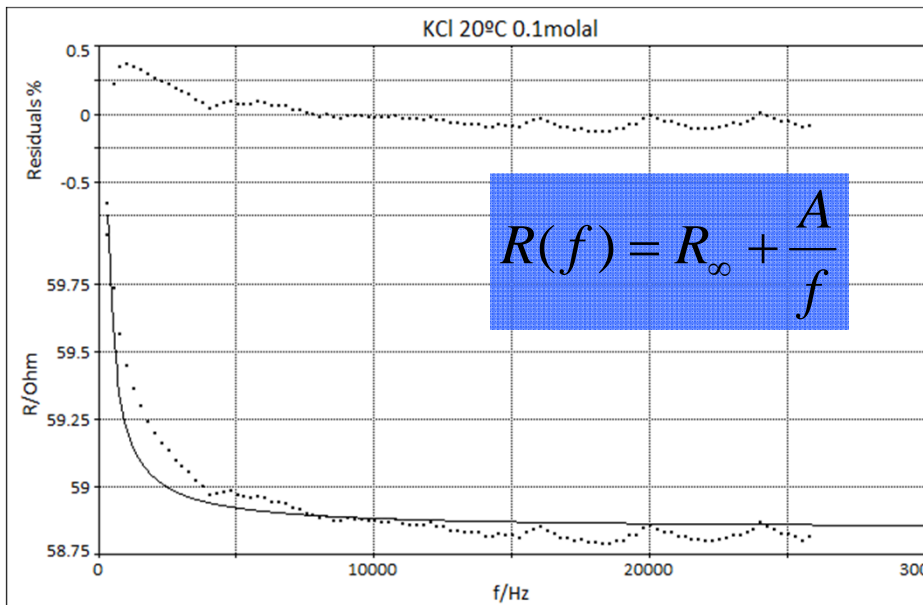
- ## Calibration: cell constant

	Cell const /cm^{-1}	Uncertainty (2σ) /%	$(C_{Lockin} - C_{IA})/C_{IA}$ / %
Lockin	0.6934	0.2441	0.19
Impedance Analyzer	0.6921	0.0068	

- Electrolytic conductivity for the calibration obtained from interpolation from the CRC- Handbook of Chemistry and Physics (85th ed.) "Standard KCl Solutions for Calibrating Conductivity Cells" table;

- (Cell const (Imp. Analyser)) - 6.5% difference from the cell constant indicated which has an uncertainty of 10%;

Calibration:

Lock-in

c	Parameters	Value	RMSD/%
1	R_∞	58.804	0.006
	A	388.511	4.507
1/2	R_∞	58.641	0.009
	A	24.662	1.667

$$R(f) = R_\infty + \frac{A}{f^c}$$

KCl 20ºC 0.1molal

$$R(f) = R_\infty + \frac{A}{f}$$

KCl 20ºC 0.1molal

$$R(f) = R_\infty + \frac{A}{f^{1/2}}$$

Experimental

Calibration:

Impedance Analyzer

c	parameters	Value	RMSD/%
1	R_∞	53.051	0.0054
	A	490.795	14.98
1/2	R_∞	52.882	0.011
	A	21.641	1.872

$$R(f) = R_\infty + \frac{A}{f^c}$$

$$R(f) = R_\infty + \frac{A}{f}$$

$$R(f) = R_\infty + \frac{A}{f^{1/2}}$$
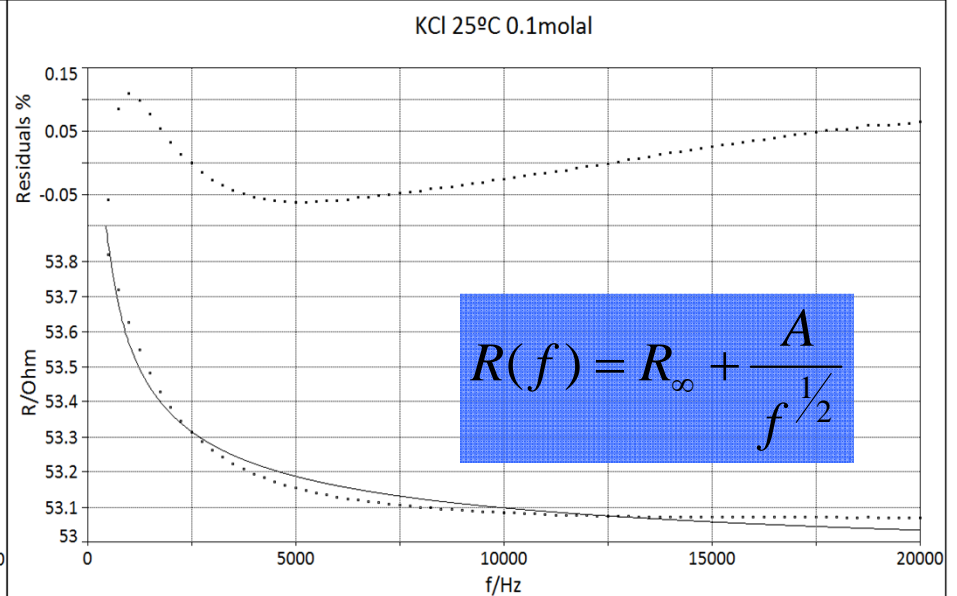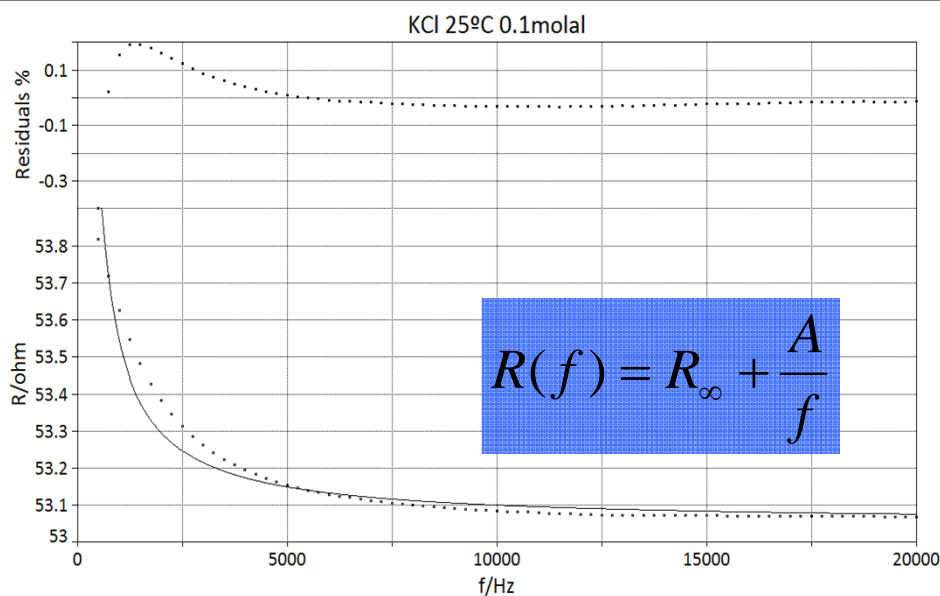
• Experimentaly the eq. seems to adjust better to the results when using 1/f

Experimental

- Ionic liquid: [empy]$^+$[EtSO4]$^-$
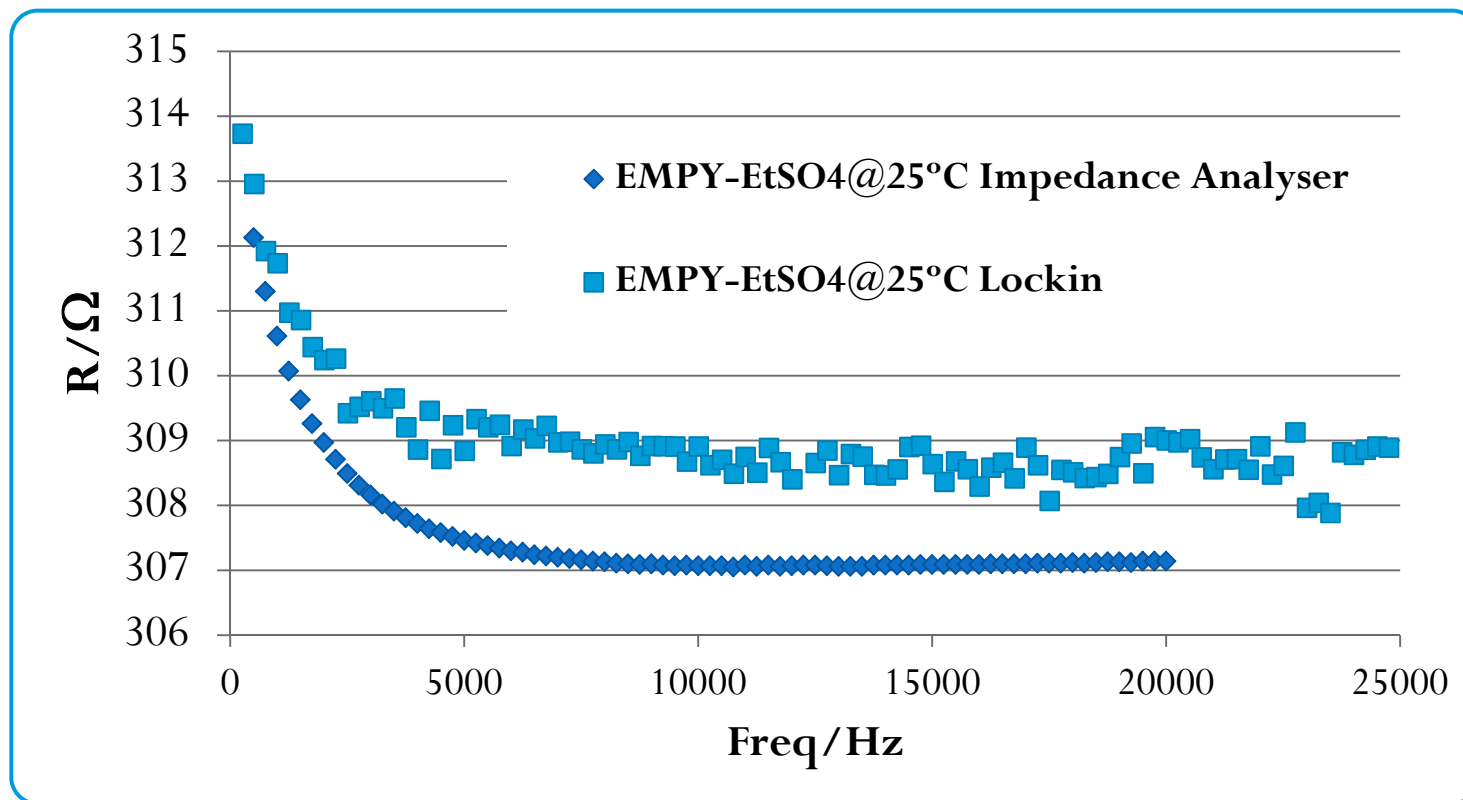 - electrolytic conductivity

$$\kappa / S \cdot m^{-1} = \frac{c_{cell} / m^{-1}}{R_{\infty} / \Omega}$$

- Water content (Karl-Fischer Metrohm 831 KF Coulometer)

	Before the measurements (ppm)	After the measurements (ppm)
Impedance analyser	<10	n.a.
Lock-in	<10	<30

EMPY-EtSO4

Impedance analizer vs Lock-in

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EMPY-EtSO4

Lock-in

c	parameters	Value	RMSD/%
1	R_∞	308.650	0.02
	A	1801.893	5.10
1/2	R_∞	307.798	0.02
	A	104.728	3.35

$$R(f) = R_\infty + \frac{A}{f^c}$$

EMPY-EtSO4 25ºC

$$R(f) = R_\infty + \frac{A}{f}$$

EMPY-EtSO4 25ºC

$$R(f) = R_\infty + \frac{A}{f^{1/2}}$$

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EMPY-EtSO4

Impedance Analizer

c	parameters	Value	RMSD/%
1	R_∞	306.885	0.01
	A	3199.742	2.68
1/2	R_∞	305.815	0.02
	A	138.113	2.68

$$R(f) = R_\infty + \frac{A}{f^c}$$

EMPY-EtSO4 25ºC

$$R(f) = R_\infty + \frac{A}{f}$$

EMPY-EtSO4 25ºC

$$R(f) = R_\infty + \frac{A}{f^{1/2}}$$

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Results
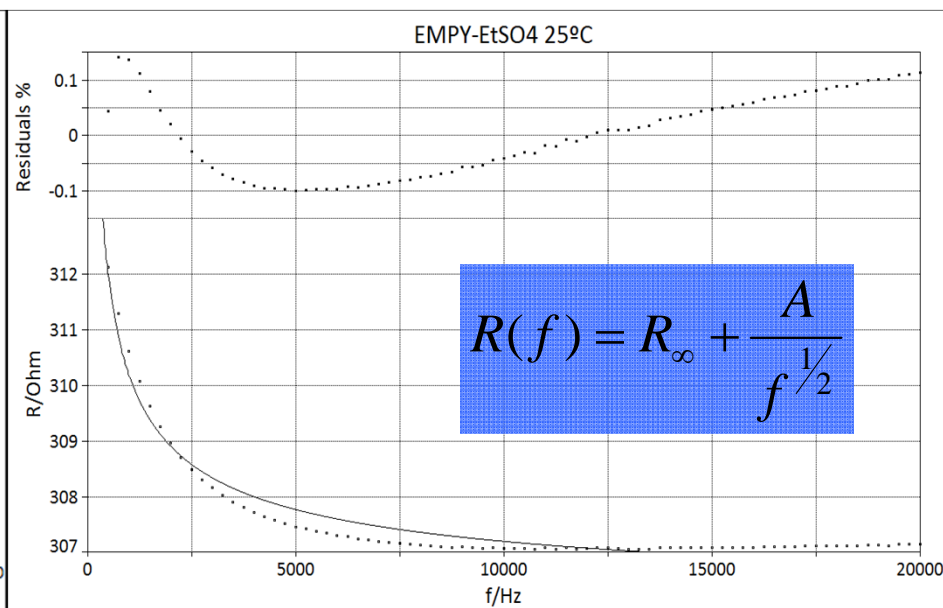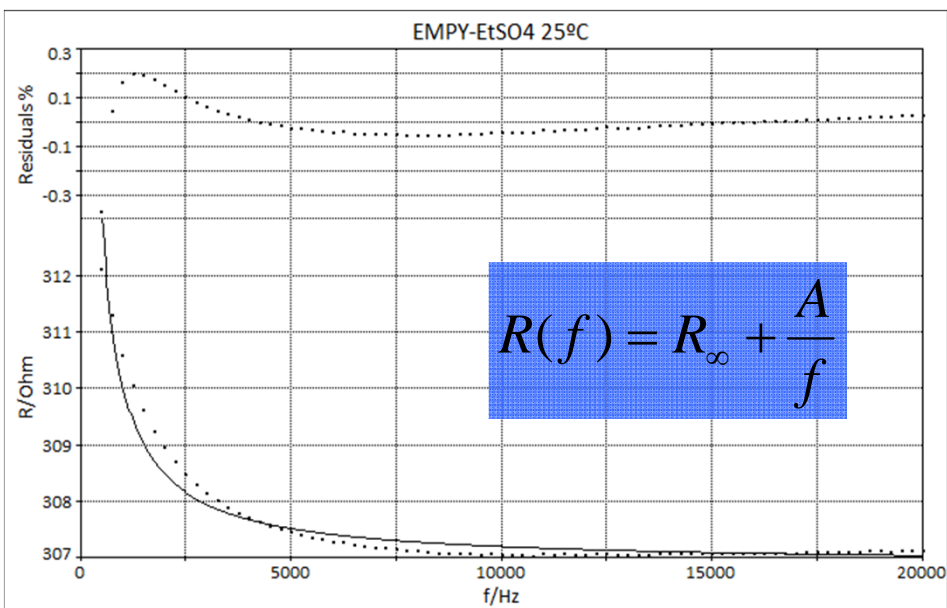
EMPY-EtSO4: Electrolytic conductivity

	T / °C	κ /S.m-1	Uncertainty (2σ)/%
Lockin	20.03	0.172	0.216
	24.84	0.225	0.058
	29.78	0.288	0.010
	34.84	0.366	0.056
	39.80	0.452	0.004
Impedance Analyzer	25.67	0.225	0.047
	30.66	0.290	0.002

Results

- Comparison of the electrolytic condutivity values, obtained with the two methods

Correlation eq.: $\kappa(S \cdot m^{-1}) = a + b \cdot T(^oC) + c \cdot T(^oC)^2$

a	b	c
0.06544899	0.00085615	0.00022

T / °C	κ / S·m^{-1}		Diff. / %
	exp.(Imp.Analyzer)	Lock-in (corr)	
25.67	0.225	0.234	-3.68
30.66	0.290	0.301	-3.65

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Conclusions

- Measurements done with a Lock-in for a range of frequencies and compared with an impedance analyzer;
  - The measurements with KCl aquous solutions are satisfactory.

- However, the tests performed with EMPY-EtSO$_4$ were not conclusive ➔ we need to improve the measuring method:
  - reduce random noise in measurements with lock-in;
  - optimize the procedures regarding control of water contamination ➔ logistic difficulties: the equipments are located in different buildings…

- The frequency dependency of the resistance may induce a significant deviation to the results obatained with lock-in

- We still need to recalibrate with certified standard solutions.

- Thank you for your attention

	Constant Cell (cm^{-1})		Diff (%)
	c = 0.5	c = 1	
Lockin	0.6908	0.6921	-0.2508
Impedance Analyzer	0.6904	0.6934	-0.3783

- physical properties that make them interesting as potential solvents for synthesis
  - Good solvents for a wide range of both inorganic and organic materials;
  - They have the potential to be highly polar and yet noncoordinating solvents;
  - Immiscible with a number of organic solvents and provide a nonaqueous, polar alternative for two-phase systems.