On the Measurement of the Electrical Conductivity of Ionic Liquids

J. C. F. Diogo, D. R. C. Máximo, J.L. Correia da Mata, F. J. P. Caetano,
J. M. N. A. Fareleira, U.V. Mardolcar

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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

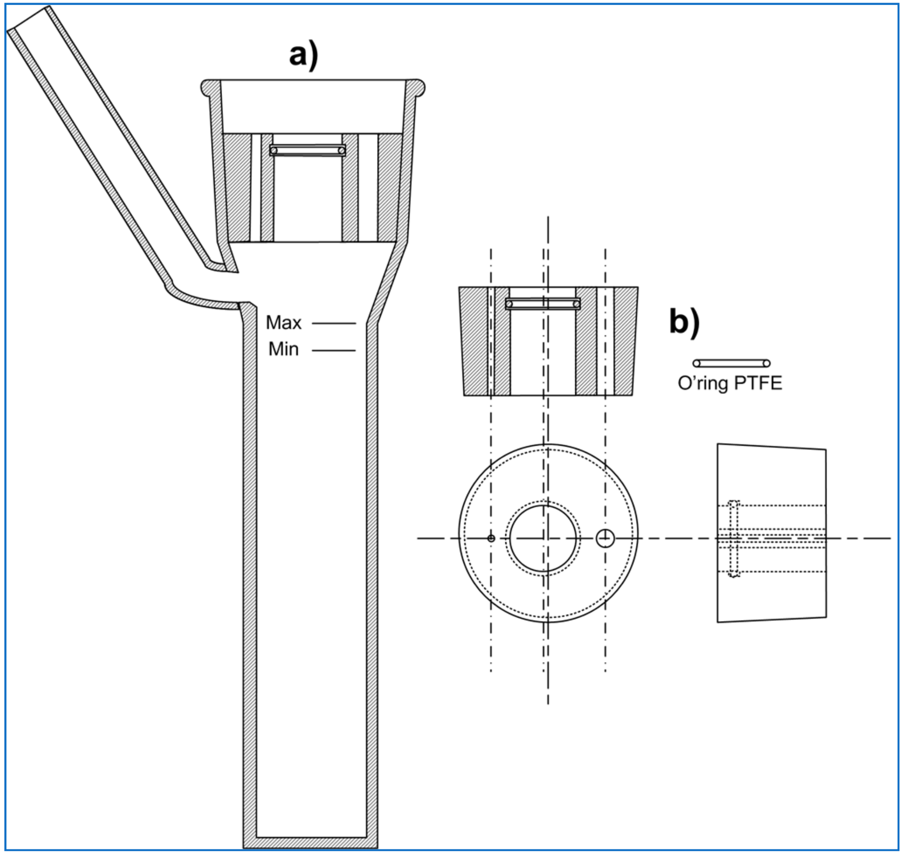
- Determination of the electrolytic conductivity of a RTIL by using a **lock-in amplifier in a range of frequencies**, and using an impedance analyzer to compare results:

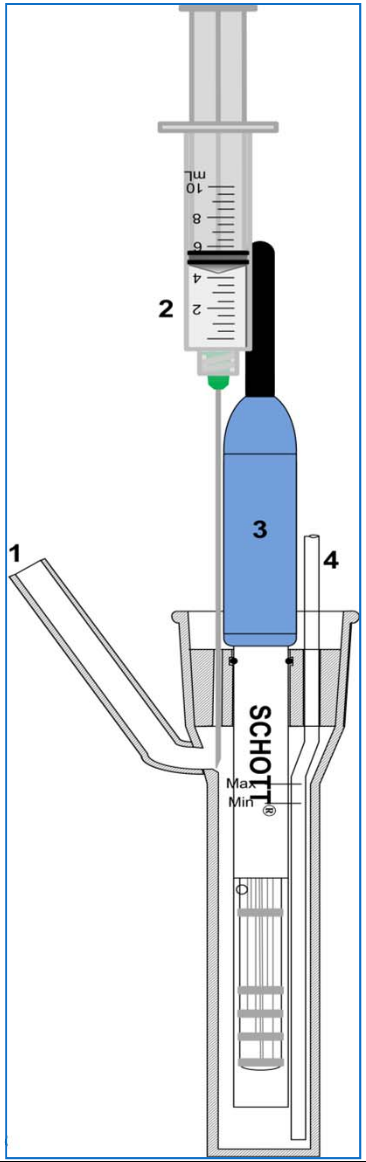
  - Lock-in amplifier:
    - Signal Recovery model PE 7225

  - 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%.

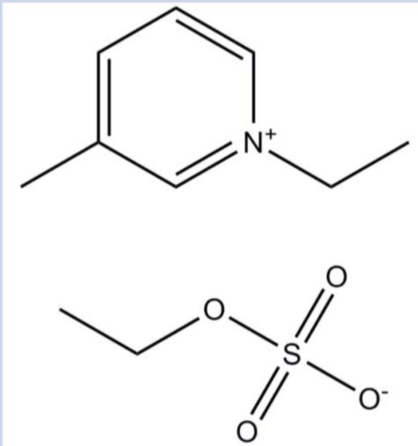
Experimental





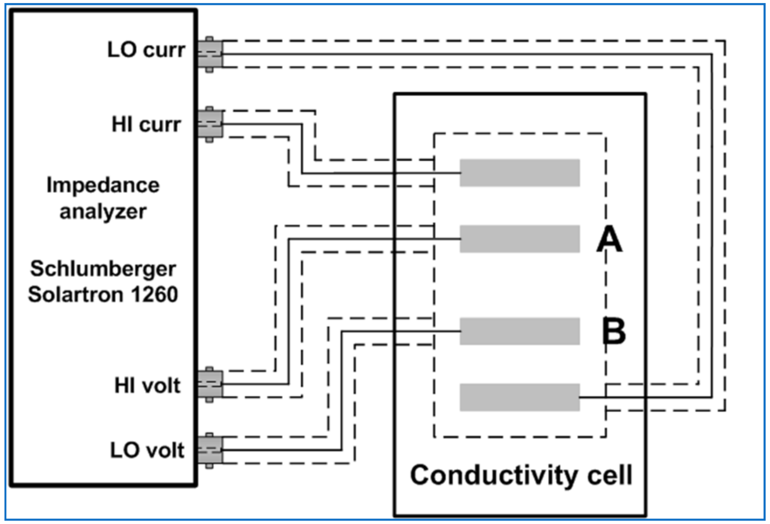
- 1 – Glass assembly for the condutivity cell
- 2 – syringe
- 3 – electrolytic conductivity cell
- 4 – PTFE tube for N_2

Experimental

RT IL	Characteristics		Structure
$[empy]^+[EtSO4]^-$	Chem. formula	$C_{10}H_{17}NO_4S$	
	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

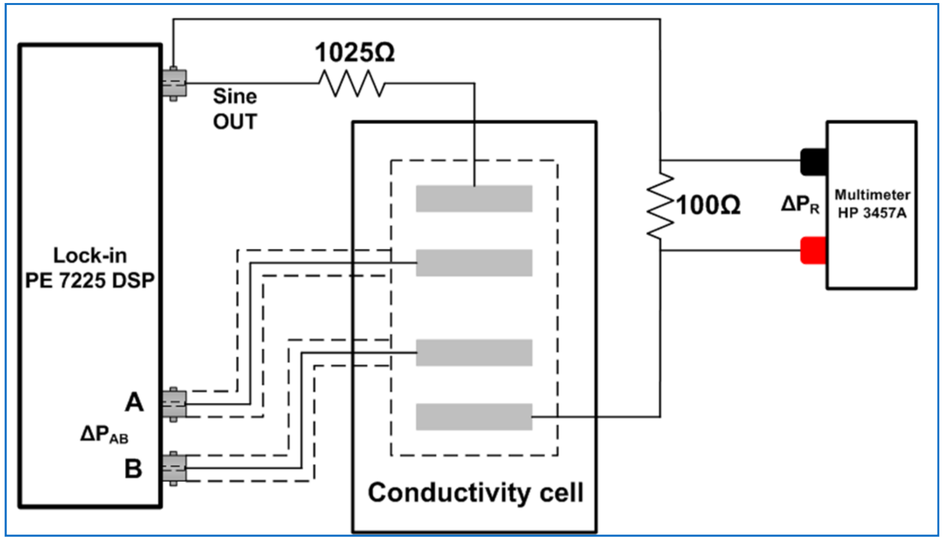
Impedance Analyzer



- 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

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

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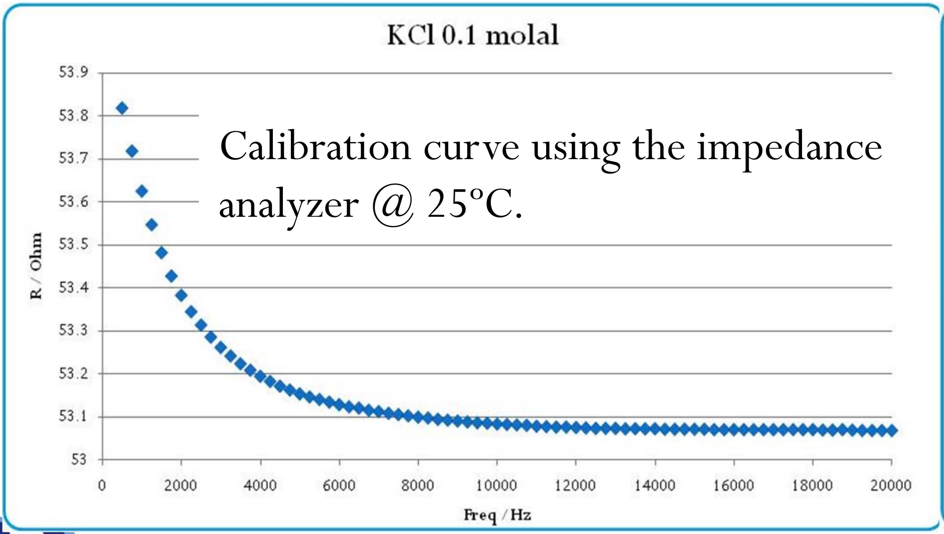
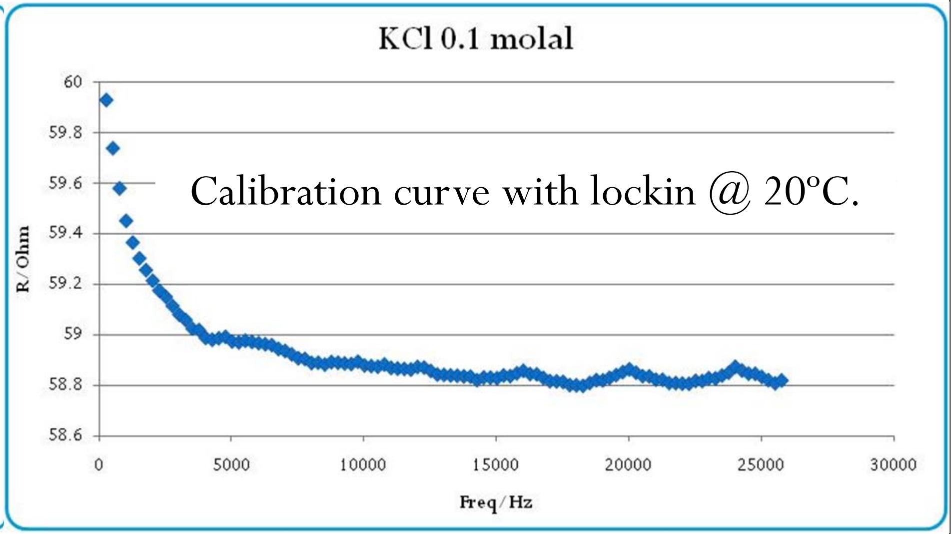
Experimental

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





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 $_{\text{(Imp. Analyser)}}$) - 6.5% difference from the cell constant indicated which has an uncertainty of 10%;

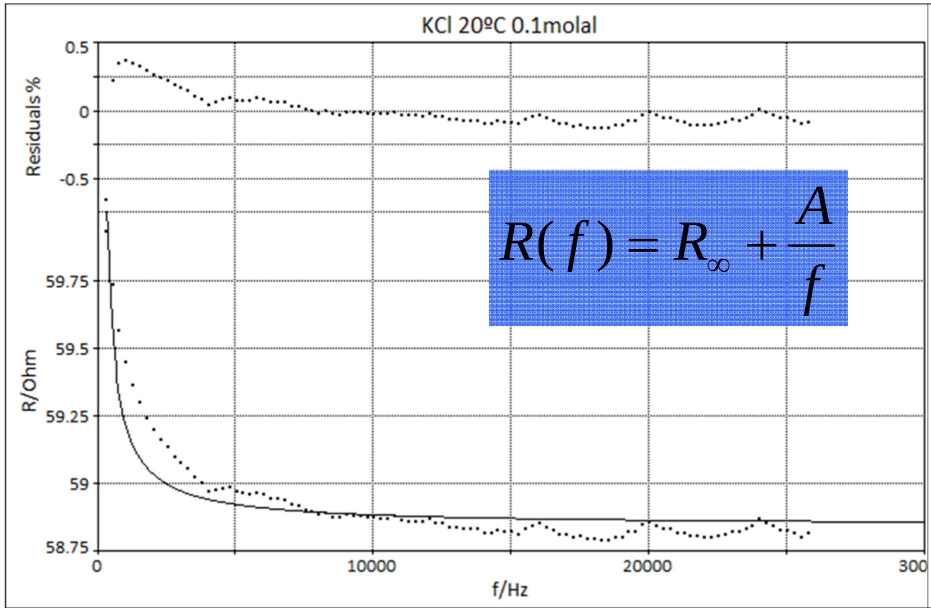
Experimental

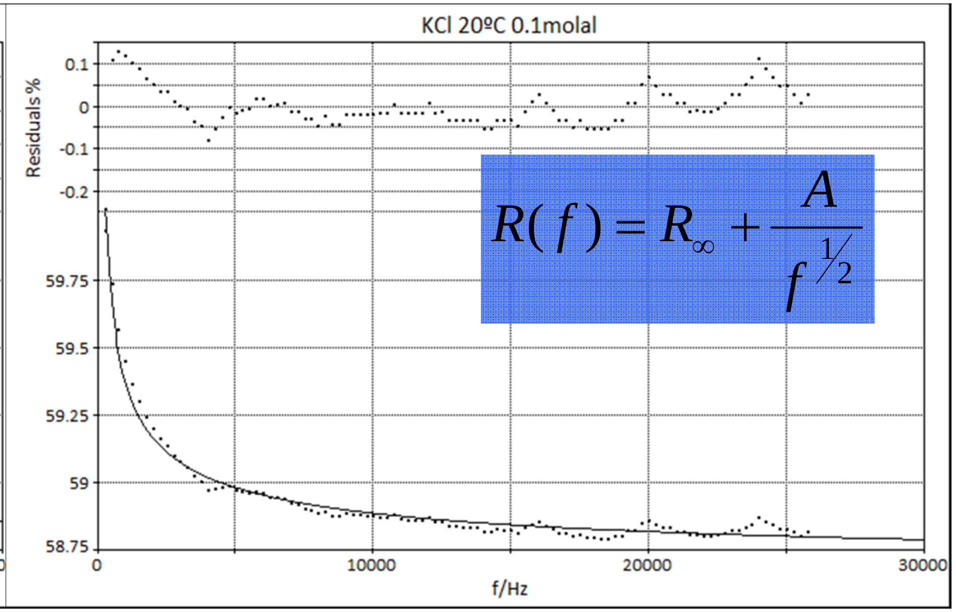
Calibration:

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

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



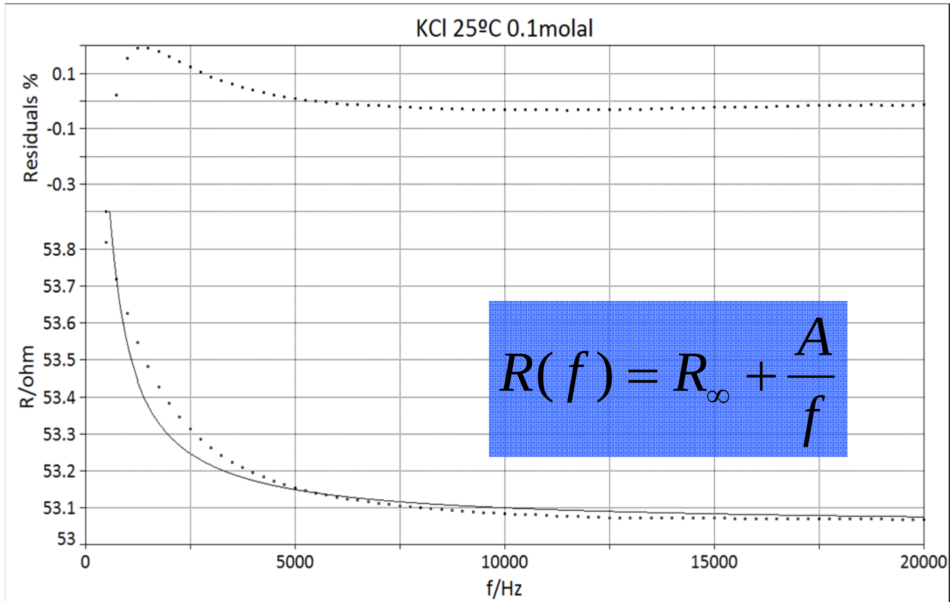


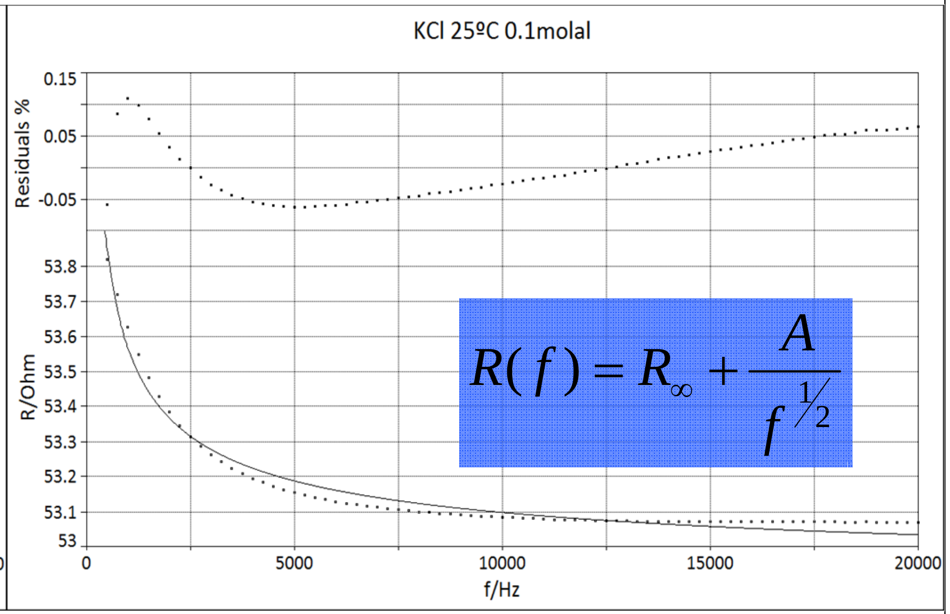
Experimental

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

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





- Experimentaly the eq. seems to adjust better to the results when using 1/f

Experimental

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

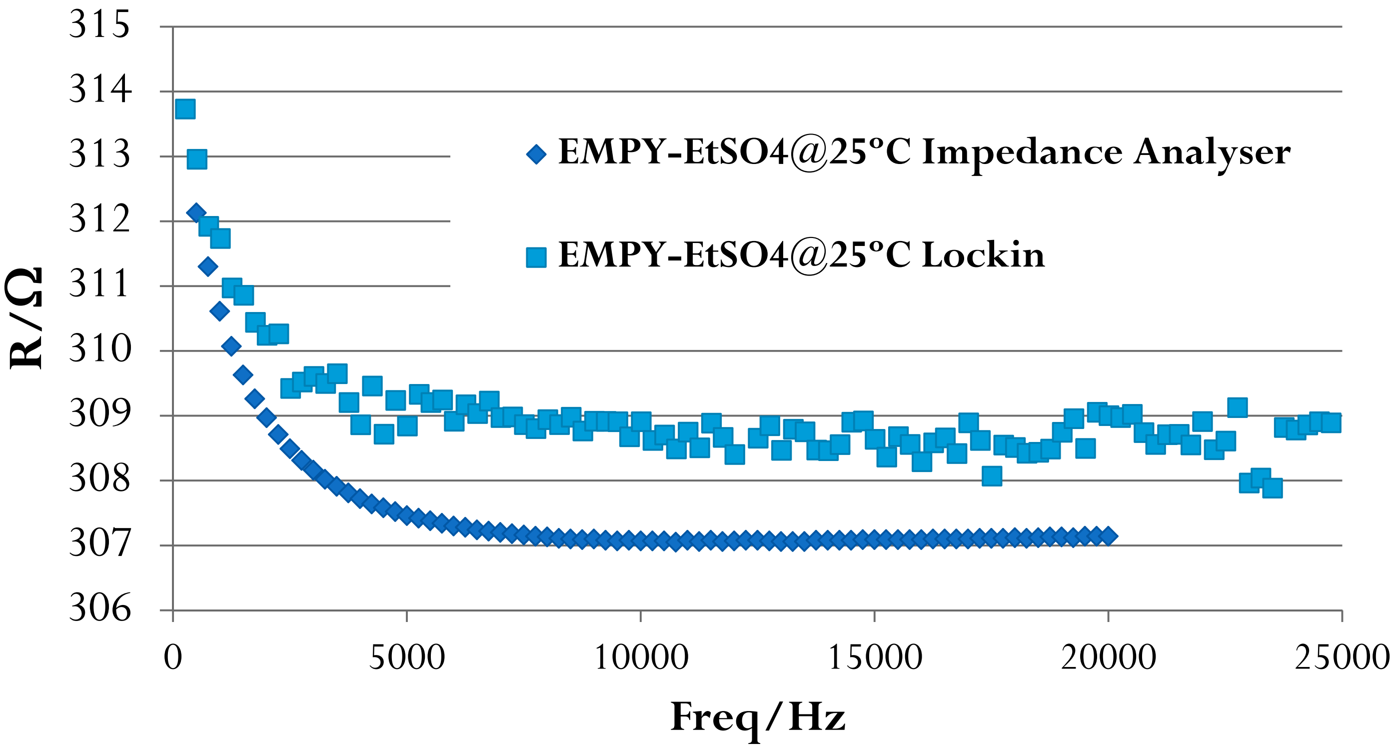
$$\kappa / S \cdot m^{-1} = \frac{c_{cell} / m^{-1}}{R_\infty / \Omega}$$

- 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

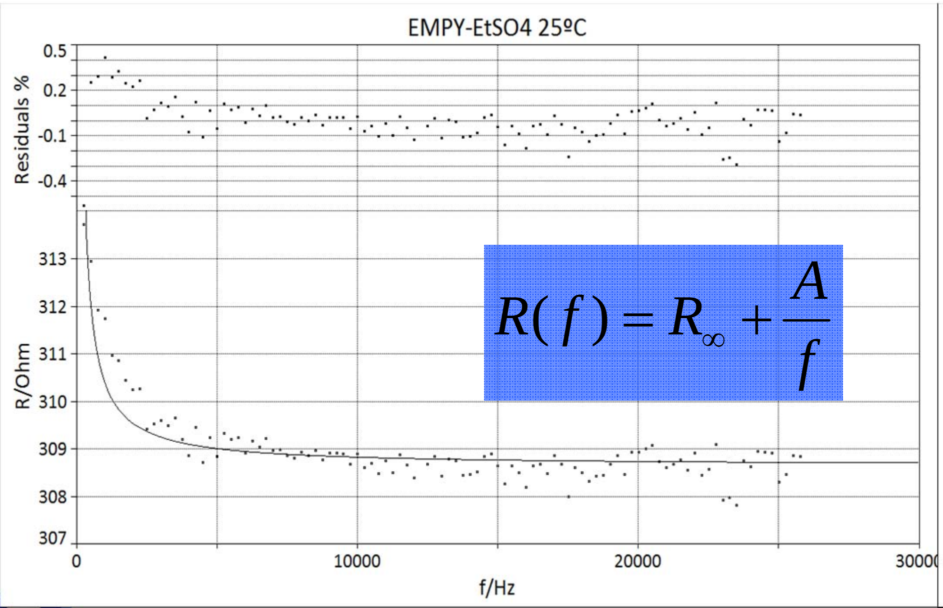
Impedance analizer vs Lock-in

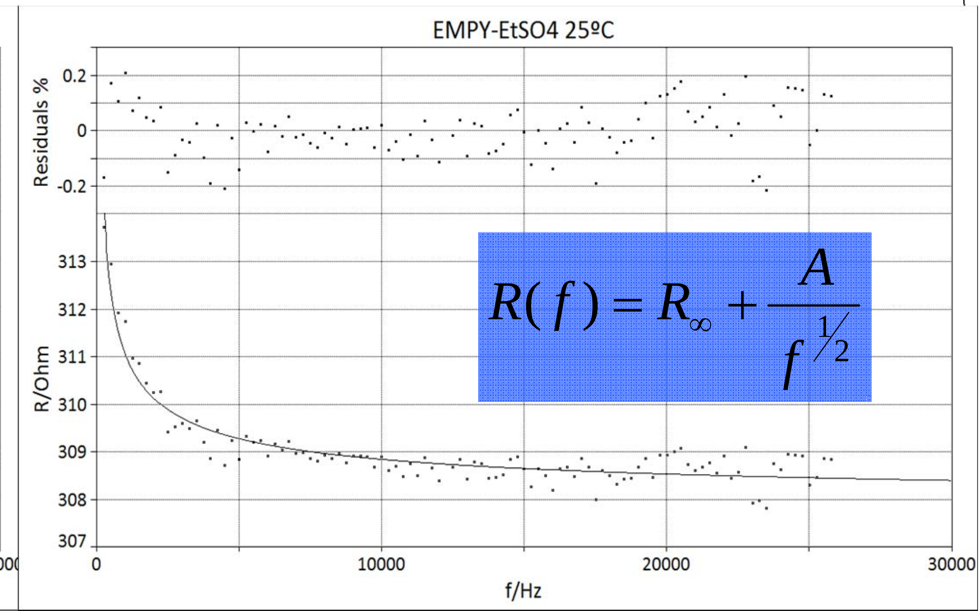


EMPY-EtSO4
Lock-in

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

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

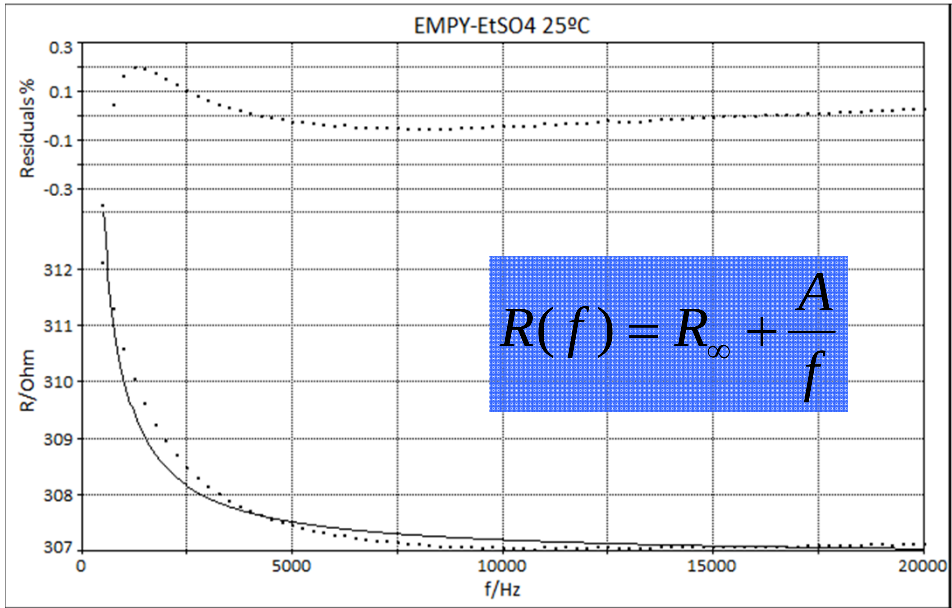


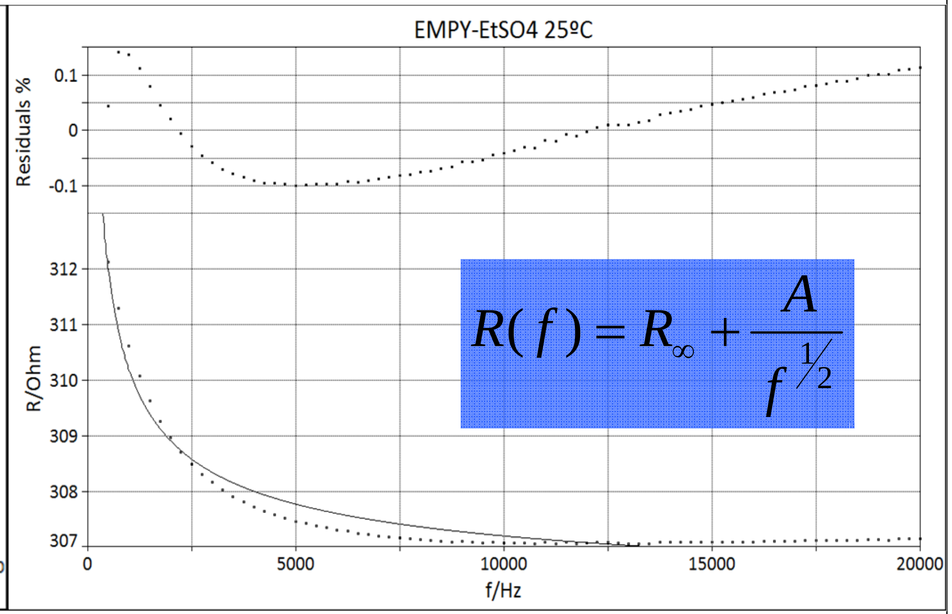


EMPY-EtSO4
Impedance Analizer

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

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





Results

EMPY-EtSO4: Electrolytic conductivity

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

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

Conclusions

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