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Proceeding Paper

Structural Characterization by NMR Procedure of C_4C_1Pyrr TFSI Doped with Lithium TFSI Salt in Liquid and Gel States [†]

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Abstract: Ionic liquids represent a viable option as electrolytes for electrochemical applications such as energy storage devices, due to their high ionic conductivity and wide electrochemical window. However, liquid electrolytes present important problems of safety and performance, and encapsulation in a solid matrix can be a good solution to improve it. In this work, changes in the structure of the mixtures of ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide and lithium bis(trifluoromethylsulfonyl)imide against the concentration of the salt (0, 0.1, and 1.5 molal), and the effect of nanoconfinement through gelation process were studied using NMR technique.

Keywords: ionic liquid; nuclear magnetic resonance; electrolytes; gel; pyrrolidinium

1. Introduction

The future has as a challenge to achieve decarbonization, both in industry and of the economy, for a green and sustainable future. One of the main options is an ecological transition where fossil fuels are replaced by renewable ways of obtaining energy without carbon emissions into the atmosphere. This ecological transition brings new scientific and technical challenges such as the development and improvement of energy storage systems.

The current situation of electrolyte manufacturing is based on flammable and volatile mixtures that can put the operator's safety at risk when handling and assembling these into a commercial battery. This situation allows ionic liquids (ILs) and their mixtures with inorganics salts to be considered as a good alternative to replace the commercial electrolytes, due to their remarkable properties for electrochemical applications [1–3].

One of the main problems of common electrolytes, ILs among them, when handling and assembling in batteries, is their liquid condition, which complicates their manufacture when it comes to large-scale implementation. In the case of ILs, a solution could be the nanoconfinement of the ionic liquid in an organic matrix through sol–gel method [4] in order to keep its main properties intact obtaining a quasi-solid like material [5].

In this work, an NMR study was carried out with the main purpose to structurally analyze, with the salt addition and the effect of the gelling process, on the IL 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide C_4C_1Pyrr TFSI and lithium bis(trifluoromethylsulfonyl)imide (Li TFSI) against the concentration of the salt (0, 0.1 and 1.5 molal).

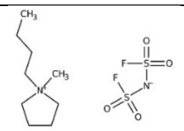
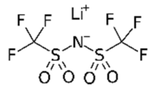
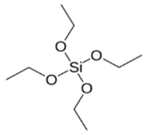
2. Materials and Methods

2.1. Chemicals

Three different mixtures of the ionic liquid C_4C_1Pyrr TFSI with the salt Li TFSI salt were prepared via stirring procedure (pure IL, 0.1 mol Kg^{-1} and 1.5 mol Kg^{-1}), being 1.5 mol kg^{-1} the saturated one.

In Table 1, a brief description of the chemical compounds used in this work can be found, where the molecular weight, structure, CAS number, supplier, and purity is indicated.

Table 1. Chemicals.

Name	Molecular Weight (g mol^{-1})	Structure	Abbreviation CAS Number	Provenance Purity
1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	422.41		C_4C_1Pyrr TFSI 223437-11-4	Iolitec >0.99
Lithium bis(trifluoromethylsulfonyl)imide	287.09		Li TFSI 90076-65-6	Acros Organics >0.99
Tetraethoxysilane	208.33		TEOS 78-10-4	Sigma Aldrich >0.98

2.2. Gelation Procedure

The sol-gel process for synthesizing the gel samples was an adaptation of the methodology reported by [6], which was carried out under acidic conditions. A brief description of the used method to gelling samples using volumetric proportions is:

A mixture of 2:1 volumetric parts of Formic Acid (FA):TEOS were stirred for 18 min at 40 °C in a flask. After this time, 4 volumetric parts of IL + lithium salt at desired concentration were added and stirred for 45 s more.

Finally, the pre-gel sample was deposited in a vial and stored at a room temperature for 24/48 h until full gelation. Once gelation is complete samples were submitted to high vacuum for 24 h.

3. Experimental Procedure

NMR sample were placed in 5 mm diameter tubes. A spectrometer Bruker DRX500 de 11.74 T (500 MHz resonance of ^{1}H) were used to analyze both gel and liquid samples at 313.15 K, equipped by:

- Reverse detection probe 1H/13C/15N (standard tube 5 mm) with Z gradient.
- 1H/X multinuclear reverse detection probe (standard tube 5 mm) with Z gradient.
- X/1H multinuclear probe for 10 mm diameter tube.
- BACSTM 50-sample robot sample changer.
- Two waveform generators for selective pulses.
- Liquid N_2 cooling device for low temperature experiments.
- Top Spin control software v. 1.3 under Linux Red-Hat Enterprise 5.1 Operating System.

4. Results

Figure 1 shows ^{1}H spectra for the C_4C_1Pyrr TFSI + Li TFSI mixtures in liquid and gel forms. The relative position of CH_3 corresponding to the butyl chain of the IL has been adjusted to the value provided by Pavel et al. [7]. Regarding multiplet information of the different present peaks, the resolution reached was not enough to determine with exactitude what kind of splitting is present. Peak shift was indicated in ppm and can be found in Table 2. As can be seen, both the salt addition and the gelation procedure keep the peak position at a similar value (shift) compared to the pure sample; this indicates that the structure remains constant without a significant change in the structural arrangement. The most remarkable result, in both ^{1}H and ^{13}C (Figure 2) spectra, is the apparition of new peaks due to the impurities during the gelation procedure on the saturation concentration. These impurities were impossible to extract during the annealing or vacuum.

As it can be seen in Table 3, nanoencapsulation of the IL translates in a widening of the FWHM (full width at half maximum) both ^{1}H and ^{13}C spectrum, this is due to a slight slowdown in molecular dynamics of the ionic liquid [8], but this widening is not enough to consider it as a solid, so the nanoencapsulated IL keeps its properties as liquid-like, inside the organic matrix.

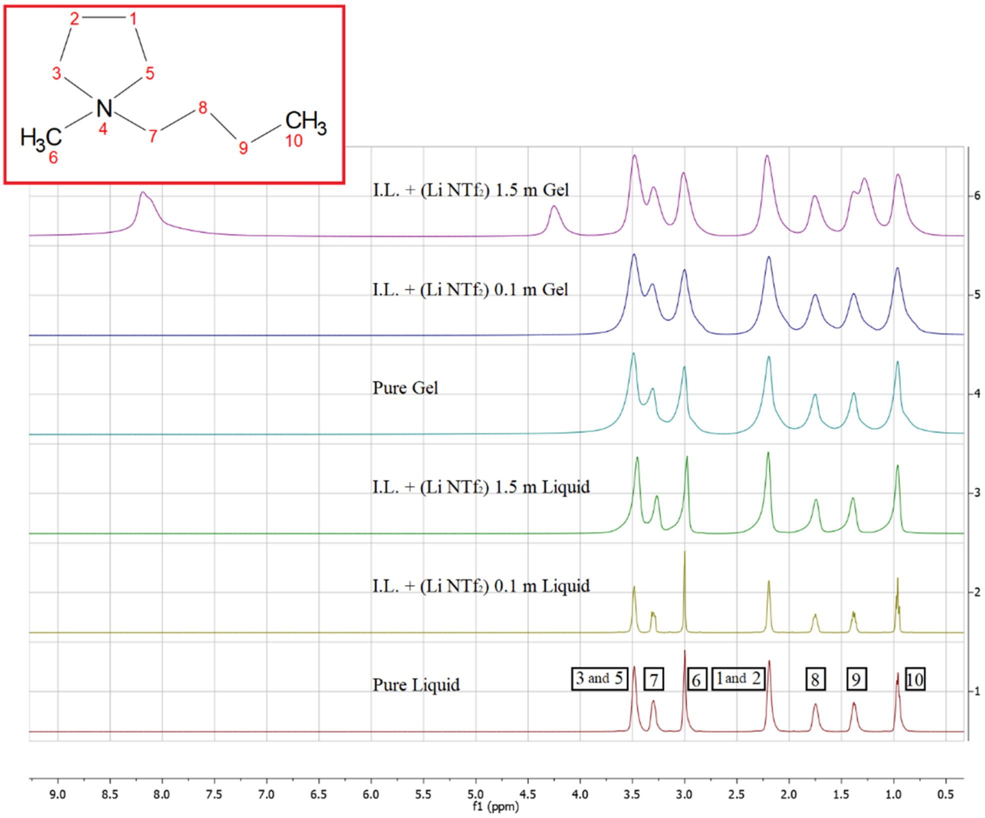


Figure 1. The ^{1}H spectra of analyzed samples. Inset shows C_4C_1Pyrr cation with the corresponding numbered atomic bonds. The Y-axis is measured in arbitrary units (AU).

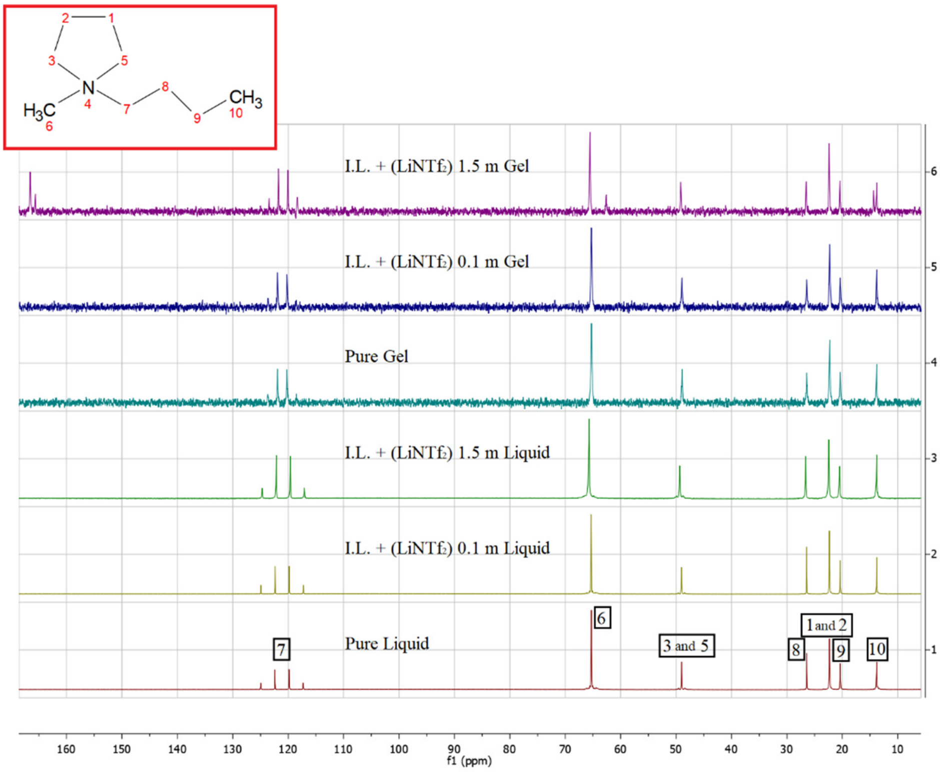


Figure 2. The ^{13}C spectra of analyzed samples. Inset shows C_4C_1Pyrr cation with the corresponding numbered atomic bonds. The Y-axis is measured in arbitrary units (AU).

Table 2. Peak shift (in ppm) of liquid and gel mixtures for ^{1}H and ^{13}C spectrum.

				^{1}H Spectra				
Sample	**10**	**9**	**8**	**1, 2**	**6**	**7**	**3, 5**	
Pure IL (liquid)	0.93	1.35	1.72	2.16	2.97	3.27	3.45	
IL+Li TFSI 0.1m (liquid)	0.93	1.34	1.72	2.16	2.97	3.27	3.45	
IL+Li TFSI 1.5m (liquid)	0.93	1.36	1.71	2.17	2.95	3.24	3.42	
Pure IL (gel)	0.93	1.35	1.72	2.16	2.97	3.28	3.46	
IL+Li TFSI 0.1m (gel)	0.93	1.35	1.72	2.16	2.97	3.28	3.45	
IL+Li TFSI 1.5m (gel)	0.93	1.36	1.73	2.18	2.98	3.27	3.45	
				^{13}C Spectra				
Sample	**10**	**9**	**1,2**	**8**	**3, 5**	**7**	**6**	**CF_3**
Pure IL (liquid)	13.40	19.99	21.92	26.03	48.59	64.90	64.95	120.73 (Q)
IL+Li TFSI 0.1m (liquid)	13.40	20.00	21.93	26.04	48.62	64.93	64.98	120.70 (Q)
IL+Li TFSI 1.5m (liquid)	13.40	20.10	22.04	26.21	48.93	65.28	65.38	120.47 (Q)
Pure IL (gel)	13.40	19.98	21.88	26.03	48.52	64.87	UNDEF	120.68 (Q)
IL+Li TFSI 0.1m (gel)	13.40	19.97	21.89	26.02	48.55	64.90	UNDEF	120.68 (Q)
IL+Li TFSI 1.5m (gel)	13.40	20.03	21.99	26.14	48.75	65.14	UNDEF	120.51 (Q)

Table 3. FWHM (in Hz) of liquid and gel mixtures for ^{1}H and ^{13}C spectrum.

				^{1}H Spectra			
Sample	**10**	**9**	**8**	**1, 2**	**6**	**7**	**3, 5**
Pure IL (liquid)	19.29	25.26	28.19	20.49	12.49	25.37	22.59
IL+Li TFSI 0.1m (liquid)	13.89	21.06	23.67	15.56	6.64	19.92	16.55
IL+Li TFSI 1.5m (liquid)	24.66	32.62	35.26	24.86	15.81	31.94	32.72
Pure IL (gel)	58.75	65.47	68.43	62.56	42.89	58.75	72.13
IL+Li TFSI 0.1m (gel)	87.65	100.87	99.37	99.43	88.85	105.36	106.75
IL+Li TFSI 1.5m (gel)	80.54	84.10	79.83	104.22	72.43	108.05	100.13

				^{13}C Spectra				
Sample	**10**	**9**	**1,2**	**8**	**3,5**	**7**	**6**	**CF_3**
Pure IL (liquid)	9.2	9.4	10.3	6.8	9.7	6.7	5.7	5.8; 5.4; 5.2; 5.2
IL+Li TFSI 0.1m (liquid)	5.5	5.7	6.7	4.3	9.1	5.3	6.2	3.9; 3.6; 3.5; 3.5
IL+Li TFSI 1.5m (liquid)	13.2	16.2	18.0	10.9	17.6	8.3	21.6	13.9; 9.4; 8.7; 11.6
Pure IL (gel)	23.7	30.8	31.2	33.4	28.8	40.3		21.3; 25.8; 25.6; 29.1
IL+Li TFSI 0.1m (gel)	27.8	33.6	33.4	39.2	35.6	41.7		23.1; 25.3; 23.9; 25.5
IL+Li TFSI 1.5m (gel)	21.9	24.1	23.1	24.3	27.0	30.8		24.8; 21.3; 23.6; 21.0

5. Conclusions

This work reports ^{1}H and ^{13}C NMR spectra for mixtures of an IL, C_4C_1Pyrr TFSI and its mixture with Li TFSI and their gelation via sol-gel process. Slight differences have been found except for saturated mixture on gel sample, which shows impurities versus the rest of samples, liquid and gel.

The most remarkable result is that nanoencapsulated IL keeps its properties as liquid-like, inside the organic matrix.

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Conflicts of Interest: The authors declare no conflict of interest.

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