Microporous and Mesoporous Materials xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Molecular transport in ionic liquids under confinement studied by low field NMR

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ARTICLE INFO

Keywords:
Gels
Films
Mobile NMR
Single sided NMR
Porous systems
Ionic liquids

ABSTRACT

Films from aqueous gelatin solutions following the addition of several types of ionic liquids were studied. The water was allowed to evaporate until the films reached their final steady condition, while the ionic liquids remained in the matrix structure because of their negligible vapor pressure. Transversal and longitudinal relaxation times and diffusion coefficient were determined with the help of a single-sided mobile nuclear magnetic resonance scanner. Conductivity measurements were performed in addition. The results reveal different dynamics of the ionic liquids under confinement in the gelatin film porous matrix. The films become rigid and opaque using anions containing Fluor, while they are more flexible and semitransparent, when dicyanimide anion is used. The effect of the geometrical restrictions of the gel matrix on the dynamics of the solvent is more pronounced for the case of the flexible films, while the conductivity remains close to the bulk.

1. Introduction

The development of materials based on polymeric matrices combined with room temperature ionic liquids (RTILs) has gained considerable interest during recent years due to their applications as electrolytes in conducting films [1] with application in batteries and other related energy-storage systems. The functionality and properties of these materials can be adjusted using different types of RTILs and hosting polymers. In particular, their combination with biopolymers expands these applications towards the field of biosensors [2]. The knowledge of dynamical and physicochemical properties in these systems is necessary in order to characterize the microscopic transport properties of the mobile ions responsible for the electrical conductivity [3,4,5].

Gelatin is a water-soluble denatured protein obtained by the partial hydrolysis of collagen. During film preparation, the gelatin in solution with water is first heated at ~ 50°C, and later cooled below the coil/helix transition temperature (40 °C). In this process, some of the molecular chains conforming the gelatin combine with each other to form a partial collagen-like triple helix. The combination of dicyanamide-based ILs with gelatin have been used recently to prepare conducting films [6].

Single-sided mobile NMR scanners [7] allow the study of films, both during formation in an open environment [8,9], and after their formation process is completed. The high field gradient strength of the devices permits the discrimination between the two different nuclei ^{1}H and ^{19}F, changing the relative position of the sample respect to the magnet [10] (see Fig. 1). This is particularly suitable because in many RTILs, ^{1}H and ^{19}F are found in different ions.

In this contribution, ILs and water are used as solutions to dissolve gelatin and prepare films. Due to the low volatility of ILs, they will remain in the final film, while the water evaporates with only a small irreducible water fraction remaining. Arising questions are: What is the mobility of the confined IL in comparison to their bulk values? Could the film be used as a conducting film? The focus is put on the characterization of the dynamics of the ILs and trying to answer those questions.

2. Materials and methods

The RTIL 1-butyl-3-methylimidazolium dicyanamide ($Bmim^{+}DCA^{-}$), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($Emim^{+}Tf2N^{-}$),1-Ethyl-3-methylimidazolium tetrafluoroborate ($Emim^{+}BF4^{-}$), were used. The detailed procedure of the preparation of the films are given in Supplementary Contents.

For the sample Gel-$EmimBF_4$, 1 ml of $EmimBF_4$ was used. In the case of the Gel-EmimTf2N, two samples were prepared, one containing 1.5 ml of EmimTf2N (1:1.5) and the other one, 2.5 ml of EmimTf2N

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https://doi.org/10.1016/j.micromeso.2017.11.050
Received 15 January 2017; Received in revised form 21 September 2017; Accepted 28 November 2017

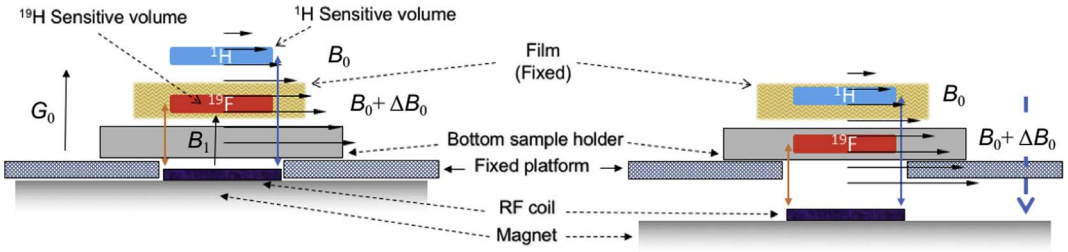

Fig. 1. Scheme of the single-sided NMR set-up showing both, the sensitive regions corresponding to the ^{1}H and ^{19}F resonance. The sensitive volumes remain at a fixed distance from the surface of the magnet, which can be moved in the vertical direction (B_0, magnetic field; B_1, radiofrequency field; G_0, magnetic field gradient). The distance between the sensible volumes of ^{1}H and ^{19}F is 1300 μm.

(1:2.5). The Gel-BmimDCA sample contains 2.5 ml of BmimDCA.

A single-sided NMR scanner operated at a ^{1}H Larmor frequency of 18.7 MHz, with a static magnetic field gradient of 21.6 T/m. was employed. More details are included in Supplementary Contents.

Due to the strong gradient and the frequency of excitation, both ^{1}H and ^{19}F nuclei fulfill the condition $\omega_0 = \gamma_H B_0 = \gamma_F(B_0 + \Delta B_0)$ inside the field of view of the scanner, above the radiofrequency (RF) coil (see Fig. 1), with $\Delta B_0 = B_0\left(\gamma_H/\gamma_F - 1\right)$. In this way, a selection of either ^{1}H or ^{19}F can be made when the thickness of the film is less than the distance between the location of ^{1}H and ^{19}F resonances. The height of the effective sensitive volume of the device is around 240 μm. In Fig. 1, the regions corresponding to the ^{1}H and ^{19}F resonance frequency are shown with the values of B_0 and $B_0 + \Delta B_0$, respectively. These values of the field change in the sample when the magnet is moved down. The corresponding ^{1}H Larmor frequency is $\omega_0/2\pi = 18.7$ MHz. The film, together with the platform remain fixed. In the left-hand side of the drawing, only the fluorine nuclei inside the sample are at resonance with the frequency ν_0. On the right side, the magnet is moved downwards, allowing only the proton nuclei in the sample to be at resonance with ν_0. The vertical arrows indicate the distance between the position of the sensitive volume and the RF coil for ^{1}H and ^{19}F nuclei, in the range of 3.0 mm and 1.7 mm, respectively.

3. Results and discussion

Fig. 2a shows the profile of the sample gel-EmimTf2N (1:1.5), from which a thickness of around 750 μm can be obtained. The ratio of the area under the profiles scales approximately with the number of ^{1}H and ^{19}F atoms in the IL molecules (11–6, respectively). In order to control whether the scanner is introducing any error in this measurement, a profile of the bulk IL EmimTf2N was measured, filling all the volume on top of the scanner. This profile shows up as a step-wise function proportional to the number of nuclei in the sample (Fig. 2b). A correlation between the signal-proportions and the number of nuclei is obtained. This result is not taking into account possible deviations due to the fact that (i) the signal is related to the specific NMR sensitivity of the atom and, (ii) in NMR unilateral sensors there is a dependence of the B_1 power to the distance of the sensitive volume from the coil.

Table 1
Relaxation times and diffusion values of the sample gelatin-EmimTf2N (1:1.5). The values of the distances are relative to the bottom of the sample holder (see Fig. 2a). For example, the heights 2000 μm and 1400 μm represent the same height in the sample, encoded in two different sensitive volumes corresponding to ^{19}F and ^{1}H nuclei. The last two rows show the bulk values of EmimTf2N.

Distance from bottom surface (μm)	T_2 (ms)	T_1 (ms)	D(10^{-11} m^2/s)
2600 (^{19}F)	347 ± 31	694 ± 62	3.7 ± 0.2
2300 (^{19}F)	389 ± 35	640 ± 32	4.2 ± 0.2
2000 (^{19}F)	412 ± 37	706 ± 66	3.4 ± 0.2
1400 (^{1}H)	388 ± 27	483 ± 39	4.9 ± 0.2
1100 (^{1}H)	325 ± 16	470 ± 19	5.4 ± 0.1
800 (^{1}H)	306 ± 15	517 ± 21	5.0 ± 0.1
Bulk EmimTf2N (^{1}H)	409 ± 10	431 ± 8	5.0 ± 0.1
Bulk EmimTf2N (^{19}F)	656 ± 10	763 ± 10	4.1 ± 0.1

In order to study the dynamics and effect of interaction between the molecules of IL and gelatin in the sample, relaxation and diffusion measurements were performed at three different heights in the film. The results are summarized in Table 1. Due to the relatively large error in the relaxation time values, no significant differences of T_1 and T_2 can be distinguish in different layers of the film.

The diffusion coefficients were measured at a diffusion time of 2 ms. No systematic dependence on depth is found. No significant differences between the confined and the bulk values at this diffusion time are found.

Fig. 3 shows the profile of the same material with a different ratio, sample gel-EmimTf2N (1:2.5), with a thickness of around 340 μm, and the diffusion coefficients as a function of the diffusion time. In the center of the film, the relaxation times are $T_2 = (327 \pm 9)$ ms for the

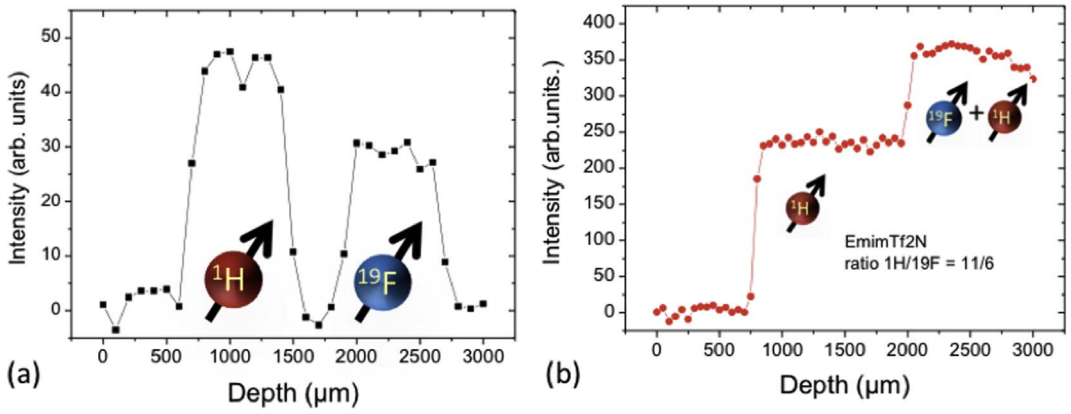

Fig. 2. (a) Profile of the sample Gel-EmimTf2N (proportion gel-IL 1:1.5). (b) Profile test measurement of the bulk IL EmimTf2N. Below 2000 μm, only the 1H signal is detected.