Article

¹H NMR Relaxometry, Viscometry, and PFG NMR Studies of Magnetic and Nonmagnetic Ionic Liquids

Carla I. Daniel,[†] Fabián Vaca Chávez,[‡] Gabriel Feio,[§] Carla A. M. Portugal,[†] João G. Crespo,[†] and Pedro J. Sebastião*,[∥,‡]

[†]REQUIMTE/CQFB, Departamento de Química, Faculdade de Cieñcias e Tecnologia, Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal

[‡]Condensed Matter Physics Centre, University of Lisbon, Av. Prof. Gama Pinto 2, 1649-003 Lisbon, Portugal

[§]CENIMAT - Centro de Investigação em Materiais, Faculdade de Cieñcias e Tecnologia, Universidade Nova de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal

[∥]Departamento de Física, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

ABSTRACT: A study is presented of the molecular dynamics and of the viscosity in pure [Aliquat][Cl] ionic liquid and in a mixture of [Aliquat][Cl] with 1% (v/v) of [Aliquat][FeCl₄]. The ¹H spin−lattice relaxation rate, R_1, was measured by NMR relaxometry between 8 and 300 MHz. In addition, the translation self-diffusion, D, was measured by pulse field gradient NMR. The ILs' viscosity was measured as a function of an applied magnetic field, B, and it was found that the IL mixture's viscosity decreased with increasing B, whereas the [Aliquat][Cl] viscosity is independent of B. All experimental results were analyzed taking into account the viscosity's magnetic field dependence, assuming a modified Stokes−Einstein diffusion/viscosity relation. The main difference between the relaxation mechanisms responsible for R_1 in the two IL systems is related to the additional paramagnetic relaxation contribution associated with the ¹H spins−[FeCl₄] paramagnetic moments' interactions. Cross-relaxation cusps in the R_1 dispersion, associated with ³⁵Cl and ¹H nuclear spins in the IL systems, were detected. The R_1 model considered was successfully fitted to the experimental results, and it was possible to estimate the value of D at zero field in the case of the IL mixture which was consistent with the values of D measured at 7 and 14.1 T and with the magnetic field dependence estimated from the viscosity measurements. It was observed that a small concentration of [Aliquat][FeCl₄] in the [Aliquat][Cl] was enough to produce a "superparamagnetic"-like effect and to change the IL mixture's molecular dynamics and viscosity and to allow for their control with an external magnetic field.
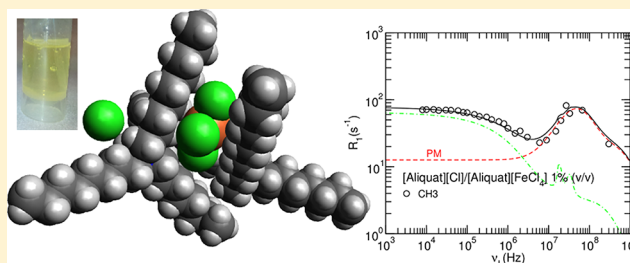
■ INTRODUCTION

Ionic liquids (ILs) belong to a class of liquids comprised of ions, recognized as novel solvents. The ILs are liquid salts over a wide range of temperatures, usually lower than 100 °C. In particular, those that are liquids at room temperature are designated room temperature ionic liquids (RTILs). ILs have extreme low volatility and are thermally stable, nonflammable, and reusable. They have gained interest for various applications in separation, electrochemistry, material science, as well as organic synthesis and catalysis, and it is expected that they can contribute to reduce or eliminate the hazards associated with the use of organic solvents. Depending on the application, ILs can be composed by different cation−anion combinations, and for this reason are called "designer solvents".[1] A new class of magnetically sensitive ionic liquids—magnetic ionic liquids (MILs)—has been recently synthetized and has gained interest due to their strong response to external magnetic fields.[2−4] MILs are ionic liquids comprised of metal−anion complexes having physical properties such as solubility, viscosity, surface tension, and/or molecular orientation that may be influenced

by applied magnetic fields.[2−5] Actually, the magnetic field influence on the IL solubility was confirmed by the dependence found between the concentration of MILs in binary water mixtures and the applied magnetic field strength.[2] The potential applications of MILs that have been presented recently include the development of magnetic fluids based on nanoparticles, the use of MILs in transport and separation of different solutes, in catalysis, in extraction processes, and in electrochromic devices.[6−12] The dependence between the magnetic field intensity and molecular orientation of MILs also suggests that the magnetic field can be used to control the distribution of charge density, solubility, or capacity to solvate different chemical species within the ILs, causing a significant impact on the solute transport through the IL media. For this, it is important to accquire a better comprehension about the influence of the magnetic field on the MIL magnetic behavior

and how it should be tuned in order to get the adequate MIL properties. Since the macroscopic properties of MILs are related to the microscopic structure, it is expected that the local magnetic structures play a key role in the MIL response to magnetic fields.[5]

The viscosity, η, which is larger in ILs than that of most common organic solvents, is one of the most important macroscopic properties of these materials. The IL viscosity depends essentially on the nature and combinations of cations and anions comprising IL structure. Since the viscosity is directly related to the relative diffusion of ionic species comprising the IL network, self-diffusion, it is important to study the dependence of both physical properties with the magnetic field and to get a better knowledge about their mutual relation in order to understand and optimize these systems for applications.

Nuclear magnetic resonance (NMR) is a well-known experimental technique used to study the molecular order and dynamics in different materials. In particular, the self-diffusion coefficient, D, can be measured directly by pulse field-gradient (PFG) NMR methods.[13]

It was reported that for ionic liquids the viscosity and translational self-diffusion relationship given by the Stokes–Einstein expression for conventional fluids is still valid provided some corrections to the original expression are considered.[14] In particular, molecular–polar interactions also determine the D vs η dependence.[15]

In view of the fact that in MILs the viscosity and the intrinsic diffusion of their ionic component species can be affected by external magnetic fields, a coherent estimate of both parameters requires the use of different experimental techniques to independently access each one of them. In fact, viscosity measurements using classical capillary viscometers can be made in the presence of magnetic fields up to 2 T; however, D is mostly measured directly by PFG NMR at much higher magnetic fields. Therefore, the D vs η dependence for the same magnetic field requires the estimate of D at low magnetic fields. As the spin–lattice relaxation time is sensitive to molecular motions, by using ^{1}H NMR relaxometry, it is possible not only to characterize the system from the molecular motions point of view but also to obtain the value of D at low magnetic fields.

The aim of this work is to study the influence of external magnetic fields on the molecular dynamics and on the viscosity of [Aliquat][Cl] and on the mixture [Aliquat][Cl]/[Aliquat]-[FeCl$_4$]. Viscosity measurements as a function of the magnetic field and proton spin–lattice relaxation measurements for the frequency range 10 kHz to 300 MHz (NMRD) were complemented by direct measurements of the self-diffusion coefficient by PFG NMR at magnetic fields of 7 and 14.1 T.

■ EXPERIMENTAL SECTION

Materials. The ILs selected for this study were the nonmagnetic [Aliquat][Cl] and its magnetic analogue [Aliquat][FeCl$_4$], where the [Cl] anions are substituted by iron anions [FeCl$_4$]. The IL and MIL were synthesized at the Faculdade de Farmácia, Universidade de Lisboa, according to the experimental procedure reported in the literature.[6,9] Their molecular weight, density, water content, and concentration of magnetic particles, at room temperature, are listed in Table 1. The ILs density was determined gravimetrically with a picnometer, the water content was measured by thermogravimetry, and the concentration of magnetic particles by inductively coupled plasma (ICP). Two samples were prepared: a sample

Table 1. IL Physical Parameters[a]

IL	molecular weight (g/mol)	density (g/cm³)	water content (% wt)
[Aliquat][Cl]	404.16	0.88	5.8
[Aliquat][Cl]/[Aliquat][FeCl$_4$]	405.8	1.03	5.5

[a]The molar concentration of [Aliquat][FeCl$_4$] in the [Aliquat][Cl]/[Aliquat][FeCl$_4$] mixture is 0.012 mol/L.

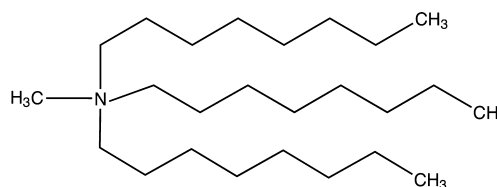of [Aliquat][Cl] and a mixture of [Aliquat][Cl]/[Aliquat]-[FeCl$_4$] 1% (v/v).

Figure 1. Molecular structure of the [Aliquat] cation.

Methods. *Viscosity Measurements.* The viscosity of the two IL systems was measured by capillary viscometry following the procedure reported in the literature.[16] The capillary used was manufactured and calibrated by Cannon - Instrument Company. The influence of an external magnetic field on the MIL viscosity was evaluated using a glass capillary Ubbelohde Viscometer − 3C and a GMW Dipole Electromagnet 3473-70 with a 75 mm poles gap by GMW Associates, USA. The measurements were carried out with the capillary viscometer placed between the electromagnet poles. The viscosity was measured for magnetic fields between 0 and 2 T. In order to decrease the experimental uncertainty, averages of six measurements were obtained with deviations from the mean smaller than ±0.2% at a room temperature of 22 °C.
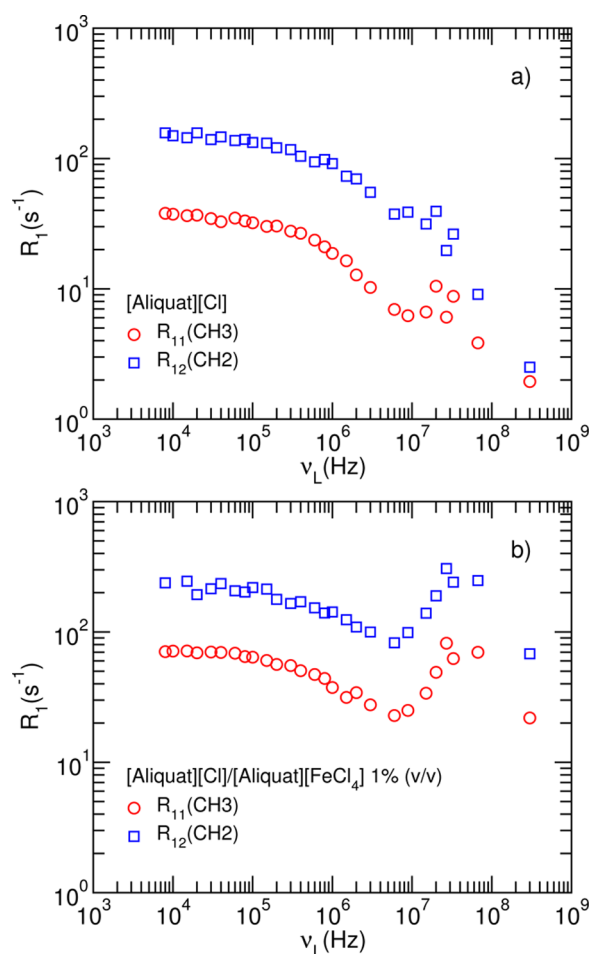
Nuclear Magnetic Resonance. The proton spin–lattice relaxation rate, R_1 ($\equiv 1/T_1$), was measured as a function of the Larmor frequency, $\nu_L = \gamma B/(2\pi)$, in the range 10 kHz to 300 MHz, using three different NMR instruments. In the range 10 kHz to 8.9 MHz, the data were obtained with a home developed fast field-cycling (FFC) spectrometer[17] operating with polarization and detection fields of 0.215 T and a switching time less than 3 ms. Between 10 and 91 MHz, a variable-field iron-core magnet equipped with a Bruker Avance II console was used. Bruker Avance II spectrometers were used for the self-diffusion and spin–lattice relaxation measurements at 300 MHz. For frequencies above 10 MHz R_1 was measured using the inversion recovery $((\pi)_x−\tau−(\pi/2)_{x,−x}−\text{Acq})$ sequence. All R_1 measurements were performed at 22 °C, and the experimental error for each R_1 was ±10%.

The diffusion coefficient, D, was measured using the stimulated spin–echo sequence[18] and a Bruker Diff 30 gradient unit at 7 T and a Bruker TCI CryoProbe at 14.1 T. D was obtained from the echo decay according to

$$I = I_o \exp\left[-\gamma^2 g^2 \delta^2 D\left(\Delta - \frac{\delta}{3}\right)\right] \tag{1}$$

where γ is the ^{1}H gyromagnetic ratio, g is the gradient strength, δ is the gradient length, and Δ is the delay between the gradients experiment. The values $\delta = 2$ ms and $\Delta = 50$ for the measurements at 7 T and $\delta = 6$ ms and $\Delta = 500$ ms in the case of 14.1 T were used.

Results. The ^{1}H NMR relaxometry results are represented in Figure 2 for the two IL systems. Obviously, the ^{1}H NMR

Figure 2. Larmor dependence of the proton spin−lattice relaxation rate R_1 for the studied systems: nonmagnetic ionic liquid [Aliquat][Cl] (a) and MIL [Aliquat][Cl]/[Aliquat][FeCl$_4$] 1% (v/v) mixture (b).

signal comes only from the cations, since the anions do not contain protons. The proton spin−lattice relaxation rate is presented, in a log−log scale, as a function of the Larmor frequency in the range 10 kHz to 300 MHz. For both samples, a biexponential decay of the time recovery of the longitudinal magnetization was observed, with two relaxation rates $R_{11} \equiv T_{11}^{-1}$ and $R_{12} \equiv T_{12}^{-1}$, in the whole frequency range. The two relaxation rates, R_{11} and R_{12}, were attributed to the CH$_3$ and CH$_2$ groups in the aliphatic chains, respectively. This assumption is reasonable in view of the fact that the interdigitation of aliphatic chains of different [Aliquat] cations might reduce significantly the mobility of the ethyl groups in comparison with the terminal methyl groups. The weighting factor for each component was fixed depending on the corresponding number of protons.

In the case of the [Aliquat][Cl], the two relaxation rates are very close at high frequencies and quite different at low frequencies. In view of the log−log scale used to represent the data in Figure 2a, it is clear that R_{11} is not simply proportional to R_{12} but is the result of a different combination of relaxation contributions. In Figure 2a, an enhancement on the proton relaxation rate can also be observed at frequencies around 20 and 30 MHz. This behavior was consistently observed for both

IL systems and cannot be associated with an increased scattering of data at these frequencies. In fact, it can be interpreted in terms of a cross-relaxation process between the ^{1}H and ^{35}Cl spin systems.[19]

In the case of the [Aliquat][Cl]/[Aliquat][FeCl$_4$] system, it is clear that for frequencies above 9 HHz the increase of R_1 with frequency is more pronounced than that observed for the [Aliquat][Cl] IL, meaning that, for this system, the spin−lattice relaxation is affected by additional relaxation mechanisms. The broad frequency peak observed in the relaxation rate (see Figure 2b) is similar to the ones reported for systems of aqueous colloidal suspensions of superparamagnetic particles. In systems of this type, the relaxation is induced by the local magnetic field gradient associated with the presence of the paramagnetic species and is called Curie relaxation.[20] This relaxation process becomes quite important in the high frequency range. The relaxation profiles presented here for the magnetic ionic liquid are consistent with those reported by Roch et al. in a suspension of magnetic particles.[21]

The additional increase of R_1 at specific Larmor frequencies in the range 20−30 MHz is also observed in the MIL system.

In Table 2 are presented the values measured for the viscosity, η, and the diffusion coefficients for the two IL

Table 2. Viscosity and Diffusion Experimental Results for the [Aliquat][Cl]/[Aliquat][FeCl$_4$] 1% (v/v) MIL (in Parentheses the Values for the [Aliquat][Cl] IL)

$B(T)$	η (Pa·s)	D (10^{-12} m^2 s^{-1})
~45 × 10^{-6}	1.26 (1.33)	
0.47	1.24 (1.33)	
1	1.22 (1.33)	
1.3	1.20 (1.33)	
1.8	1.17 (1.33)	
7		3.0 (1.3)
14.1		4.7

systems. For the sake of simplicity, the values for the [Aliquat][Cl] are presented in parentheses. Due to experimental constraints, it was not possible to measure the viscosity for magnetic fields above 2 T. In addition, it was not possible to measure the diffusion coefficient magnetic fields below 7 T. It is interesting to note that η decreases with increasing magnetic field for the MIL system. As expected, the viscosity of [Aliquat][Cl] does not change with the applied magnetic field. The viscosities of both IL systems at the earth magnetic field are similar.

■ ANALYSIS AND DISCUSSION

It is known that the frequency dependence of the proton nuclear magnetic spin−lattice relaxation rate is related with different molecular dynamic processes, such as rotational and translational diffusional mechanisms in isotropic fluids, and also with slow molecular motions in the case of mesomorphic materials.[22−24] In the case of isotropic fluids, rotations/reorientations of the molecules and translational self-diffusion are the motions that effectively modulate the dipolar spin interactions in the frequency range accessible by NMR. In particular, translational diffusion can become more important than molecular rotations/reorientations in the case of viscous fluids. In this case, the correlation times of the translational diffusion processes become larger than the correlation times of the rotational motions. This difference can be noticed in the R_1

dispersion, since at high frequencies R_1 is influenced more by the faster motions and at low frequencies R_1 is more sensitive to slow motions.

The ^{1}H NMR R_1 dispersions observed for the studied IL systems are dominated mainly by the relaxation mechanisms associated with the motions of the protonated cations, rotations/reorientations, and translational diffusion. Due to the presence of Cl in the IL anions, cross-relaxation between ^{1}H and ^{35}Cl might also be detected.

In the case of magnetic ionic liquid, the $[\text{FeCl}_4]^-$ anions might influence the proton spin−lattice relaxation through the coupling between the ^{1}H nuclear spin moments and the paramagnetic anions' magnetic moments. A contribution associated with these specific relaxation processes was detected in the high frequency range, as it was observed for aqueous colloidal suspensions of paramagnetic particles.[21]

Theoretical Models. *Translational Self-Diffusion.* In the case of isotropic liquids or isotropic phases of liquid crystal compounds, the contribution of translational self-diffusion (SD) to the relaxation can be expressed by the Torrey model[25] with

$$\left(\frac{1}{T_1}\right)_{\text{SD}} = C_d \frac{n\tau_D}{d^3}[\mathcal{T}(\omega\tau_D) + 4\mathcal{T}(2\omega\tau_D)] \tag{2}$$

where $\omega = 2\pi\nu_L$, $C_d = (1/2)(3\mu_0\gamma^2\hbar/(8\pi))^2$ is the strength of the dipolar interaction and $\mathcal{T}(\omega\tau_D)$ is a dimensionless analytical function that depends on the average time between diffusion jumps τ_D, the mean-square jump distance $\langle r^2 \rangle$, and the molecular width d. τ_D is related to the self-diffusion constant D by the relation $\langle r^2 \rangle = 6\tau_D D$. n is the density of ^{1}H spins.

Rotations/Reorientations. Molecular rotations/reorientations (Rot) may be characterized by one or more correlation times according to the number of independent rotational axes considered to describe this motion. Usually, rotations along the molecular long axis and rotations/reorientations along a molecular transverse axis have different correlations times and the most simple model used to describe this relaxation process is given a Rot$_1$ + Rot$_2$, where Rot$_i$ is given by the Bloemberger, Purcel, and Pound (BPP) model:

$$\left(\frac{1}{T_1}\right)_{\text{Rot}_i} = A_{\text{Rot}_i}\left[\frac{\tau_{\text{Rot}_i}}{1 + \omega^2\tau_{\text{Rot}_i}^2} + \frac{4\tau_{\text{Rot}_i}}{1 + 4\omega^2\tau_{\text{Rot}_i}^2}\right] \tag{3}$$

with $A_{\text{Rot}_i} = 9\mu_0^2\gamma^4\hbar^2/(128\pi^2 r_{i_{\text{eff}}}^6)$, where $r_{i_{\text{eff}}}$ is an effective interspin distance.[26]

Cross-Relaxation. ^{35}Cl has nuclear spin 3/2, and cross-relaxation (CR) between the proton spins and ^{35}Cl nuclear spins can occur. Cross-relaxation has indeed been observed between proton spins and nitrogen and also between proton spins and ^{35}Cl spins.[19,27,28] Cross-relaxation may become significant when the proton's Larmor frequency is close to each one of the quadrupole frequencies of the other nucleus. The relaxation rate can be expressed by[27]

$$\left(\frac{1}{T_1}\right)_{\text{CR}i} = A_{\text{CR}i}\frac{\tau_{\text{CR}i}}{1 + (\omega - \omega_i)^2\tau_{\text{CR}i}^2} \tag{4}$$

where ω_i, with $i = 1, 2, ...$, are the frequencies that correspond to the ^{35}Cl spin energy levels and $A_{\text{CR}i}$ are parameters related to the strength of the interaction.

Paramagnetic Relaxation. Proton spin−lattice relaxation can be affected by the presence of magnetic ions in two ways:

(i) the so-called *inner-sphere* relaxation, which occurs when relaxing protons bind temporarily to ions or ion complexes, and (ii) the *outer-sphere* relaxation, which applies to protons that do not bind but move or diffuse close to magnetic ions or particles.[29] This paramagnetic relaxation (PM) mechanism is here described using the outer-sphere approach whose relaxation equation is

$$\left(\frac{1}{T_1}\right)_{\text{PM}} = 6\tau_d c\left\{S_c^2 j_1(\omega, \tau_d, \tau_s \to \infty)\right.$$
$$\left.+ \left[S(S + 1) - S_c \cot g\frac{x}{2S} - S_c^2\right]j_1(\omega, \tau_d, \tau_s)\right\} \tag{5}$$

where S is the electronic spin along the applied magnetic field and c is a quantity proportional to the molar concentration of magnetized particles, $[\text{M}]$. r is the distance of closest approach between the anion and the protonated cation, $\tau_d = \langle r^2 \rangle/D$, D is the diffusion time constant, τ_s is the longitudinal electronic relaxation time, and ω is the proton Larmor frequency. S_c is given by

$$S_c = \frac{2S + 1}{2}\tanh^{-1}\left((2S + 1)\frac{\omega}{\omega_r}\right) - \frac{1}{2}\tanh^{-1}\left(\frac{\omega}{\omega_r}\right) \tag{6}$$

where $\omega_r = 2\gamma kT/(\hbar\gamma_S)$ and γ_S is the electron's gyromagnetic ratio. The corresponding spectral density for outer-sphere relaxation is[29]

$$j_1(\omega, \tau_d, \tau_s) = \text{Re}\left\{\frac{1 + \Omega^{1/2}/4}{1 + \Omega^{1/2} + 4\Omega/9 + \Omega^{3/2}/9}\right\} \tag{7}$$

where $\Omega = (i\omega + 1/\tau_s)\tau_d$.

Model Fits to the Experimental Results. The model used to analyze the R_1 experimental results can be expressed by a sum of different contributions—rotations/reorientation, self-diffusion, cross-relaxation, and paramagnetic relaxation—depending on the IL system:

$$R_1(\nu_L) = R_1^{\text{SD}}(\nu_L) + [R_1^{\text{Rot}_1}(\nu_L) + R_1^{\text{Rot}_2}(\nu_L)] + R_1^{\text{CR}}(\nu_L)$$
$$+ [R_1^{\text{PM}}(\nu_L)]_{\text{MIL}} \tag{8}$$

This model assumes that the relaxation mechanisms are statistically independent, as is often the case.[22,23] When fitting eq 8 to the experimental results, it was considered that $M \simeq 1.2 \times 10^{-2}$ mol/L, estimated by ICP, and $n \simeq 8 \times 10^{28}$ spins/m^3, estimated from the values of Table 1. d, τ_D, r, τ_d, τ_s, τ_1, A_{Rot_1}, τ_2, A_{Rot_2}, and a pair of $\tau_{\text{CR}i}$, $A_{\text{CR}i}$ for each cross-relaxation cusp in the R_1 dispersion were considered free fitting parameters.

Since for the $[\text{Aliquat}][\text{Cl}]/[\text{Aliquat}][\text{FeCl}_4]$ system the viscosity depends on the magnetic field, as observed in Table 2, the diffusion coefficient is expect to also be field dependent. Therefore, $\tau_D = \langle r^2 \rangle/(6D)$ is also field dependent. In order to include this file dependence on the theoretical R_1 model, it is convenient to have an analytical interpolating equation.

In Figure 3 are presented the viscosity values of Table 2 as a function of the magnetic field for the two ILs. η is independent of B in the case of $[\text{Aliquat}][\text{Cl}]$. In view of the field dependence of η for the $[\text{Aliquat}][\text{Cl}]/[\text{Aliquat}][\text{FeCl}_4]$ system, the empirical model

$$\eta = \frac{\eta_0}{1 + (\gamma B\tau_{\nu_1})^{P_1}} \tag{9}$$
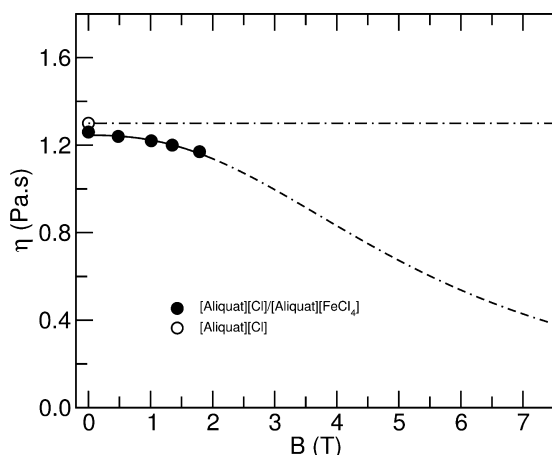
Figure 3. Viscosity measured for the [Aliquat][Cl] and [Aliquat][Cl]/[Aliquat][FeCl$_4$] systems. The solid line corresponds to the fit using eq 9. Dashed curves correspond to the extrapolated values of viscosity as a function of the magnetic field estimated using also eq 9.

Table 3. Relaxation Model Parameters Obtained for the Best Fit of eq 8 to the R_1 Experimental Results for the [Aliquat][Cl] and [Aliquat][Cl]/[Aliquat][FeCl$_4$] 1% (v/v) IL Systems, as Explained in the Text[a]

	[Aliquat][Cl]		[Aliquat][Cl]/[Aliquat][FeCl$_4$]	
	CH$_2$	CH$_3$	CH$_2$	CH$_3$
$\langle r^2 \rangle^{1/2}$ (10^{-10} m)	1.3 ± 0.2	1.9 ± 0.2	1.3 ± 0.2	1.9 ± 0.2
τ_{d_0} (10^{-9} s^{-1})			2.5 ± 0.2	2.8 ± 0.2
τ_s (10^{-10} s^{-1})		1.3 ± 0.1		
A_{Rot_1} (10^9 s^{-2})	3.0 ± 0.3	2.7 ± 0.2	3.0 ± 0.3	2.7 ± 0.2
τ_1 (10^{-10} s^{-1})	4.9 ± 0.5	2.4 ± 0.4	4.9 ± 0.5	2.4 ± 0.4
A_{Rot_2} (10^9 s^{-2})	0.4 ± 0.1		0.4 ± 0.1	
τ_2 (10^{-8} s^{-1})	3.2 ± 0.2		3.2 ± 0.2	
A_{CR1} (10^7 s^{-2})	2.5 ± 0.5			
τ_{CR1} (10^{-7} s^{-1})	3.9 ± 1.0	1.9 ± 0.3		
A_{CR2} (10^8 s^{-2})	2.6 ± 0.2	~0.2		
τ_{CR2} (10^{-8} s^{-1})	9.2 ± 1.1	~80		

[a]The follow fitting parameters are common for both IL systems: τ_{D_0} = (2.8 ± 0.2) × 10^{-9} s^{-1}, $d \simeq 7.3 \times 10^{-10}$ m, $M \simeq 0.012$ mol/L, $S \simeq 370 \pm 10$, $n = 8 \times 10^{28}$ spins/m^3, $p_1 \simeq 2.4$, and $\tau_{\nu_1} \simeq 7 \times 10^{-10}$, $p_2 \simeq 1.2$, and $\tau_{\nu_2} \simeq 9.3 \times 10^{-10}$ s, $\omega_1/(2\pi) \simeq 33$ MHz, and $\omega_2/(2\pi) \simeq 18$ MHz.

was considered to fit the available experimental results. η_0 is the viscosity at zero field and τ_{ν_1} and p_1 are the parameters that explained the decay of viscosity with B. Values of η_0 = 1.26 Pa·s, $\tau_{\nu_1} \simeq 7 \times 10^{-10}$, and $p_1 \simeq 2.4$ were determined.

The viscosity and self-diffusion coefficients are commonly related by the Stokes−Einstein equation. In the case of ionic liquids, it was found that this equation can be expressed as[14,15]

$$D = C\frac{T\sqrt{\alpha}}{\eta} \tag{10}$$

where $C = 7.48 \times 10^{-8} M_w^{1/2}/V^{0.6}$ depends on the MIL molar mass M_w and the molar volume V. α is an association degree often considered when relating the viscosity and diffusion in polar liquids. Assuming that α might depend on the magnetic field and combining eqs 9 and 10, we consider here that

$$D = D_0[1 + (\gamma B \tau_{\nu_2})^{p_2}] \tag{11}$$

where D_0 is the diffusion coefficient at zero magnetic field. Since $\nu_L = \gamma B/(2\pi)$, it is possible to include the field dependence of D in the relaxation model of eq 8.

Also, the model fitting parameters τ_d and τ_D must be expressed in terms of D_0, p_2, and τ_{ν_2}: $\tau_D = \tau_{D_0}/[1 + (\gamma B \tau_{\nu_2})^{p2}]$ and $\tau_d = \tau_{d_0}/[1 + (\gamma B \tau_{\nu_2})^{p2}]$.

In view of the fact that the measured spin−lattice relaxation rate reflects the molecular dynamics of the IL cations, some of the physical parameters considered in the relaxation model of eq 8 must be the same for both ILs studied. Therefore, eq 8 was fitted simultaneously to all experimental relaxation results using a nonlinear least-squares minimization procedure,[30] with a global minimum target. In this procedure, the values of the self-diffusion coefficients were also taken into account in order to obtain the values of ν_2 and p_2. The fitting parameters obtained for the best fit of eq 8 to the experimental results are presented in Table 3.

In Figure 4 are presented the best model fitting curves to the experimental spin−lattice relaxation results.

It is clear that for [Aliquat][Cl] the R_1 dispersion is well explained by the proposed relaxation model used. The R_{11} dispersion in Figure 4a is mainly described by a relaxation contribution with a short correlation time associated with rotations/reorientations of the [Aliquat][Cl] cations for frequencies above 10 MHz and by the translational self-diffusion relaxation contribution at lower frequencies. Clearly, the sharp cusps observed in the 10−40 MHz range are explained by the localized relaxation processes associated with the cross-relaxation mechanism between the ^{1}H and ^{35}Cl nuclear spins. The same basic relaxation features are present in the [Aliquat][Cl] R_{12} dispersion fit of Figure 4c. The main difference is the inclusion of a second rotation/reorientation contribution (Rot$_2$) with a much large correlation time than that of Rot$_1$. These features are compatible with the original assignment of R_{11} and R_{12} with the CH$_3$ and CH$_2$ cation groups, as it is reasonable to assume that the former groups can rotate faster that the latter ones. In fact, the interdigitation of the cations' chains might hinder conformational changes and restrict the CH$_2$ motions. Also, the CH$_2$ group motions might reflect overall molecular motions, necessarily slower than the motions of the methyl groups. It is also interesting to note that the mean-square jump distance associated with the translational displacements is small for both R_{11} and R_{12}, but it is larger in the case of the CH$_3$ groups. The translational diffusion seams to be an almost continuous process in both cases, but it reflects an additional mobility of the chain end groups. The cross-relaxation process between ^{1}H and ^{35}Cl nuclear spins is also localized in the frequency range 10−40 MHz, but the R_{12} cusps are worse resolved that in the case of R_{11}. From this point of view, it is possible to assume that R_{11} has an important contribution from the ^{1}H spins of the methyl group bonded to the nitrogen that are perhaps more spatially correlated with the ^{35}Cl spins in the anions.

The main difference between the R_1 model fits of [Aliquat][Cl] and [Aliquat][Cl]/[Aliquat][FeCl$_4$] observed in Figure 4 is the notable presence of the paramagnetic relaxation mechanism dominant in the high frequency region. This relaxation mechanism is characterized by the existence of a maximum relaxation rate in the frequency region above 1 MHz. It was possible to fit R_{11} for both [Aliquat][Cl] and [Aliquat][Cl]/[Aliquat][FeCl$_4$] using the same Rot$_1$, Rot$_2$,
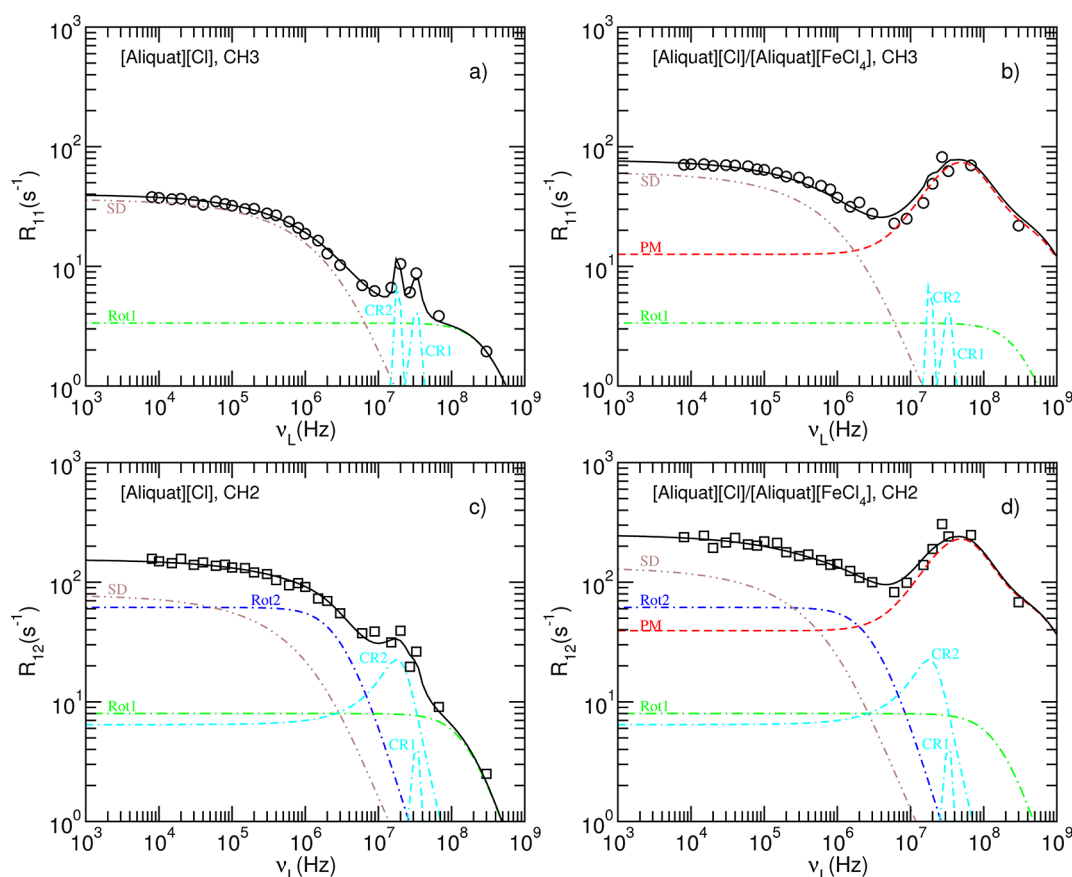
Figure 4. Experimental results and model fitting curves for the two spin−lattice relaxation rates as a function of frequency for the IL systems, as explained in the text.

and CR relaxation contributions. However, the translational self-diffusion presented slightly different contributions in the two IL systems. It is clear that the cross-relaxation is masked by the strong dominating PM contribution. Nevertheless, this contribution was also considered in the [Aliquat][Cl]/[Aliquat][FeCl$_4$] model fit to the R_{11} and R_{12} experimental results. Therefore, the effect of local order changes due to the presence of magnetic anions is detected mainly in the cations' self-diffusion, in comparison with dynamics in the [Aliquat]-[Cl].

One important aspect of the model fit analysis is the fact that the SD contribution to the relaxation rate is approximated by $R_1(\nu_L) \sim \nu_L^{-2}$ for frequencies above 2 MHz and becomes negligible for frequencies above 10 MHz in comparison with the dominant contributions of the other relaxation mechanisms. Therefore, the magnetic field effect on the [Aliquat][Cl]/[Aliquat][FeCl$_4$] viscosity and consequently on the diffusion coefficient is not important for the SD relaxation contribution for frequencies above 2 MHz. For lower frequencies, the magnetic field effect on D is expected to be small in view of the small effect on the measured viscosity in the range 0−0.5 T (i.e., between 0 and 20 MHz), as it can be observed in Figure 3.

It is interesting to observe that from the values of A_{Rot} it is possible to estimate the two values of r_{eff}, $r_{eff1} \simeq 2.5 \times 10^{-10}$ associated with a correlation time τ_1 of the order of 10^{-10} s and $r_{eff2} \simeq 3.4 \times 10^{-10}$ associated with a correlation time τ_2 of the order of 10^{-8} and present only in the analysis of the spin−lattice relaxation rate associated with the CH$_2$ [Aliquat] chain protons. τ_2 might therefore be related with rotations/reorientations involving the [Aliquat] chains as a whole, since

r_{eff2} is larger than r_{eff1}, which is associated with the faster moving CH$_3$ groups.

The value of the paramagnetic spin S obtained from the model fit, presented in Table 3, is considerably larger than the value of the [FeCl$_4$] anion spin $S = 5/2$ associated with the Fe^{3+} ion.[20] Large values of S ($S > 25$) are usually associated with superparamagnetic particles, with dimensions much larger than ∼5 nm. The spin−lattice relaxation rate dispersions obtained for the [Aliquat][Cl]/[Aliquat][FeCl$_4$] system are similar to the ones observed for aqueous solutions of superparamagnetic particles in what concerns the broad peak in the high frequency region.[21] Therefore, it is reasonable to conclude that the collective alignment process of the paramagnetic spins, associated with the superparamagnetic spin's concept, is also observed in the [Aliquat][Cl]/[Aliquat][FeCl$_4$] system. Indeed, domains formed by the ensemble of [Aliquat][Cl]/[Aliquat][FeCl$_4$] iron anions, required to produce a superparamagnetic spin $S \simeq 370$, might exist and influence the cations' ^{1}H spin−lattice relaxation including those within these regions. In the [Aliquat][Cl]/[Aliquat][FeCl$_4$] system, we found that the process of paramagnetic relaxation depends only on the value of S, in contrast with the paramagnetic relaxation in aqueous solutions of superparamagnetic particles where both the radius of the particles and S are important.[21]

The large effective paramagnetic spin estimated might also be associated with the noticeable viscosity's magnetic field dependence observed for the [Aliquat][Cl]/[Aliquat][FeCl$_4$] system. The decrease of viscosity with increasing magnetic field might be a consequence of the interaction between the magnetic field and the delocalized charge in the [FeCl$_4$] anion,

which might weaken the average ionic interaction, thus favoring the molecular diffusion.

From the values of τ_{D_0} and τ_{d_0} in Table 3, it is possible to estimate the values of D_0 for the IL systems using the expressions $\tau_{D_0} = \langle r^2 \rangle / (6D_0)$ and $\tau_{D_0} = \langle r^2 \rangle / (D_0)$, respectively. The values $D_0 = (1.6 \pm 0.5) \times 10^{-12}$ m² s⁻¹ and $D_0 = (1.0 \pm 0.3) \times 10^{-12}$ m² s⁻¹ corresponding to [Aliquat][Cl] and [Aliquat][Cl]/[Aliquat][FeCl₄] ILs, respectively, are presented in Figure 5. In this figure are also presented the values of D
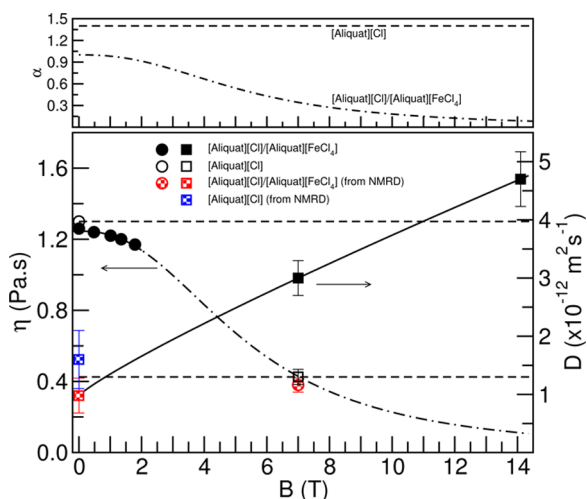
Figure 5. Viscosity (full and empty black circles) and translational self-diffusion (full and empty black sqaures) measured for the [Aliquat]-[Cl] and [Aliquat][Cl]/[Aliquat][FeCl₄] systems. The patterned squares (red and blue) refer to the estimated diffusion values from the model fit of eq 8, as explained in the text. Flat dashed curves correspond to the extrapolated values of viscosity and diffusion as a function of the magnetic field. The dashed-dot curve and the red patterned circle were obtained using eq 9. The self-diffusion coefficients measured at 7 and 14.1 T were fitted together with the value at zero field obtained from NMRD. The phenomenological magnetic field dependences of α for both [Aliquat][Cl] and [Aliquat][Cl]/[Aliquat][FeCl₄] are also plotted.

measured by PFG NMR at 7 and 14.1 T. The fitting $D(B)$ curve obtained using eq 11 is also shown. On the basis of the founding that τ_{ν_1} and p_1 are different from τ_{ν_2} and p_2, it can be inferred from eq 9 to eq 11 that the association parameter is also magnetic field dependent. The phenomenological dependence obtained for α is shown in the top of Figure 5.

The values of α estimated for [Aliquat][Cl] and [Aliquat]-[Cl]/[Aliquat][FeCl₄] at zero field, using eq 10, were $\alpha = 1.4 \pm 0.3$ and $\alpha = 1.0 \pm 0.2$, respectively. The difference between these two values might be due to the different nature of the [Cl] and [FeCl₄] anions. In Figure 5 are presented the phenomenological magnetic field dependence of α for the two IL systems.

With the values of η_0, D_0, and D at 7 T, it is possible to estimate the value of viscosity at 7 T. The value obtained, $\eta_{7T} \simeq 0.38$ Pa s, is coherent with the extrapolated values obtained from the phenomenological model fitting curve of the viscosity measured between 0 and 2 T.

■ CONCLUSIONS

This work presents a molecular dynamics study of two ionic liquids: a nonmagnetic ionic liquid, [Aliquat][Cl], and an ionic liquid mixture of [Aliquat][Cl] with its analogue [Aliquat]-[FeCl₄]. The two systems were studied by viscometry, ¹H NMR relaxometry, and pulse field gradient NMR.

The viscosity results showed that at zero magnetic field both IL systems presented basically the same viscosity, although the [Aliquat][Cl] viscosity was slightly larger that that of [Aliquat][FeCl₄]. For increasing magnetic fields, the viscosity of [Aliquat][Cl] remained constant. However, for the [Aliquat][Cl]/[Aliquat][FeCl₄], a clear viscosity decrease for increasing magnetic fields was observed.

The spin−lattice relaxation time was measured over a broad frequency range from 10 kHz to 300 MHz at 22 °C. A biexponential decay in the time recovery of the longitudinal magnetization was detected for both IL systems, revealing the presence of two spin subsystems in the samples. One spin−lattice relaxation rate, R_{11}, was associated with the CH₃ and the other, R_{12}, to the CH₂ groups.

Both R_{11} and R_{12} relaxation rates revealed a peculiar frequency dependence in the case of the [Aliquat][Cl]/[Aliquat][FeCl₄] ionic liquid with a broad peak in the high frequency region between 10 and 300 MHz. In the case of [Aliquat][Cl], these broad peaks where not observed, but in the frequency region 20−30 MHz, some sharp cusps where detected.

The experimental viscosity results obtained as a function of the magnetic field were analyzed in terms of a phenomenological curve that considers a maximum value for zero field and a Lorentzian-like decay with the magnetic field. The viscosity and diffusion coefficients were assumed to be inversely proportional according to a modified Stokes−Einstein relation that considers an association degree in order to take into account the polar character of the fluids. The diffusion coefficient magnetic field dependence was introduced in the relaxation model used to analyze the spin−lattice relaxation results.

The relaxation model considered includes the contributions of rotations/reorientations, translational self-diffusion, and cross-relaxation between the ¹H and ³⁵Cl nuclear spins. In the case of the [Aliquat][Cl]/[Aliquat][FeCl₄] system, the broad relaxation peak in the frequency range 10−300 MHz was interpreted in terms of a relaxation mechanism associated with the paramagnetic relaxation involving the ¹H spins and the paramagnetic [FeCl₄] magnetic moments. The model fit to all experimental relaxation rate results is very good. The values of the diffusion coefficient corresponding to zero magnetic field were obtained from the fits and were compatible with the diffusion coefficients measured by PFG NMR at 7 and 14.1 T within the frame of the magnetic field dependence used for the viscosity/diffusion.

In view of the independent measurements of viscosity and self-diffusion, it is concluded that the modified Stokes−Einstein, which considered a molecular association factor, is needed to relate both quantities. Moreover, it was found that this association factor is also magnetic field dependent for the [Aliquat][Cl]/[Aliquat][FeCl₄] system.

It was possible to estimate the viscosity for a magnetic field of 7 T, that otherwise would be difficult to obtain with the available experimental setups.

In spite of the small concentration of [Aliquat][FeCl₄] in the [Aliquat][Cl]/[Aliquat][FeCl₄] mixture, it was enough to change its molecular dynamics and viscosity and to control both with an external magnetic field.

It can be concluded that the MIL mobility can be modulated by the presence of a magnetic field. The tuning of the MIL properties and the increase of the diffusion in the presence of a magnetic field might be an advantage, for example, in the case of transport of molecular species across the MILs.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: pedro.jose.sebastiao@ist.utl.pt.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Han, D.; Row, K. H. Recent Applications of Ionic Liquids in Separation Technology. *Molecules* **2010**, *15*, 2405−2426.

(2) Lee, S. H.; Ha, S. H.; Ha, S.-S.; Jin, H.-B.; You, C.-Y.; Koo, Y.-M. Magnetic Behavior of Mixture of Magnetic Ionic Liquid [Bmim]FeCl4 and Water. *J. Appl. Phys.* **2007**, *101*, 09J102.

(3) de Pedro, I.; Rojas, D. P.; Blanco, J. A.; Rodriguez Fernandez, J. Antiferromagnetic Ordering in Magnetic Ionic Liquid Emim[FeCl4]. *J. Magn. Magn. Mater.* **2011**, *323*, 1254−1257.

(4) de Pedro, I.; Rojas, D. P.; Albo, J.; Luis, P.; Irabien, A.; Blanco, J. A.; Rodriguez Fernandez, J. Long-Range Magnetic Ordering in Magnetic Ionic Liquid: Emim[FeCl4]. *J. Phys.: Condens. Matter* **2010**, *22*, 296006.

(5) Hayashi, S.; Saha, S.; Hamaguchi, H. O. A New Class of Magnetic Fluids: bmim[FeCl4] and nbmim[FeCl4] Ionic Liquids. *IEEE Trans. Magn* **2006**, *42*, 12−14.

(6) Albo, J.; Santos, E.; Neves, L. A.; Simeonov, S. P.; Afonso, C. A. M.; Crespo, J. G.; Irabien, A. Separation Performance of CO2 through Supported Magnetic Ionic Liquid Membranes (SMILMs). *Sep. Purif. Technol.* **2012**, *97*, 26−33.

(7) Wang, H.; Yan, R.; Li, Z.; Zhang, X.; Zhang, S. Fe-Containing Magnetic Ionic Liquid as an Effective Catalyst for the Glycolysis of Poly(ethylene terephthalate). *Catal. Commun.* **2010**, *11*, 763−767.

(8) Branco, A.; Branco, L. C.; Pina, F. Electrochromic and Magnetic Ionic Liquids. *Chem. Commun.* **2011**, *47*, 2300−2302.

(9) Del Sesto, R. E.; McCleskey, T. M.; Burrell, A. K.; Baker, G. A.; Thompson, J. D.; Scott, B. L.; Wilkes, J. S.; Williams, P. Structure and Magnetic Behavior of Transition Metal Based Ionic Liquids. *Chem. Commun.* **2008**, 447−449.

(10) Okuno, M.; Hamaguchi, H.-o.; Hayashi, S. Magnetic Manipulation of Materials in a Magnetic Ionic Liquid. *Appl. Phys. Lett.* **2006**, *89*, 132506.

(11) Jiang, Y.; Guo, C.; Liu, H. Magnetically Rotational Reactor For Absorbing Benzene Emissions by Ionic Liquids. *China Particuol.* **2007**, *5*, 130−133.

(12) Deng, N.; Li, M.; Zhao, L.; Lu, C.; de Rooy, S. L.; Warner, I. M. Highly Efficient Extraction of Phenolic Compounds by Use of Magnetic Room Temperature Ionic Liquids for Environmental Remediation. *J. Hazard. Mater.* **2011**, *192*, 1350−1357.

(13) Callaghan, P. *Principles of Nuclear Magnetic Resonance Microscopy*; Oxford University Press: New York, 2003.

(14) Morgan, D.; Ferguson, L.; Scovazzo, P. Diffusivities of Gases in Room-Temperature Ionic Liquids: Data and Correlations Obtained Using a Lag-Time Technique. *Ind. Eng. Chem. Res.* **2005**, *44*, 4815−4823.

(15) Wilke, C. R., J. S.; Chang, P. Correlation of Diffusion Coefficients in Dilute Solutions. *AIChE J.* **1955**, *1*, 264−270.

(16) Tao, R.; Xu, X. Reducing the Viscosity of Crude Oil by Pulsed Electric or Magnetic Field. *Energy Fuels* **2006**, *20*, 2046−2051.

(17) Sousa, D.; Domingos Marques, G.; Cascais, J. M.; Sebastião, P. J. Desktop Fast-Field Cycling Nuclear Magnetic Resonance Relaxometer. *Solid State Nucl. Magn. Reson.* **2010**, *38*, 36−43.

(18) Price, W. S. Pulsed-Field Gradient Nuclear Magnetic Resonance as a Tool for Studying Translational Diffusion. 1. Basic Theory. *Concepts Magn. Reson.* **1997**, *9*, 299−336.

(19) Anoardo, E.; Pusiol, D. J., D. J.; Aguilera, C. Nmr-Study of the T(1) Relaxation Dispersion in the Smectic Mesophase of 4-Chlorophenyl 4-Undecyloxybenzoate. *Phys. Rev. B: Condens. Matter* **1994**, *49*, 8600−8607.

(20) Gueron, M. Nuclear-Relaxation in Macromolecules by Paramagnetic-Ions - Novel Mechanism. *J. Magn. Reson.* **1975**, *19*, 58−66.

(21) Roch, A.; Muller, R. N.; Gillis, P. Theory of Proton Relaxation Induced by Superparamagnetic Particles. *J. Chem. Phys.* **1999**, *110*, 5403−5411.

(22) Dong, R. *Nuclear Magnetic Resonance of Liquid Crystals*; Springer: New York, 1997.

(23) Sebastião, P. J.; Cruz, C.; Ribeiro, A. C. Advances in Proton NMR Relaxometry in Thermotropic Liquid Crystals. In *Nuclear Magnetic Resonance Spectroscopy of Liquid Crystals*; Dong, R. Y., Ed.; World Scientific Publishing Co. Pte. Ltd.: Singapore, 2009; pp 129−167.

(24) Neves, L. A.; Sebastião, P. J.; Coelhoso, I. M.; Crespo, J. G. Proton NMR Relaxometry Study of Nafion Membranes Modified with Ionic Liquid Cations. *J. Phys. Chem. B* **2011**, *115*, 8713−8723.

(25) Torrey, H. C. Nuclear Spin Relaxation by Translational Diffusion. *Phys. Rev.* **1953**, *92*, 962−969.

(26) Bloembergen, N.; Purcell, E. M.; Pound, R. V. Relaxation Effects in Nuclear Magnetic Resonance Absorption. *Phys. Rev.* **1948**, *73*, 679−712.

(27) Kimmich, R.; Winter, F.; Nusser, W.; Spohn, K. H. Interactions and Fluctuations Deduced from Proton Field-Cycling Relaxation Spectroscopy of Polypeptides, Dna, Muscles, and Algae. *J. Magn. Reson.* **1986**, *68*, 263−282.

(28) Pusiol, D. J.; Humpfer, R.; Noack, F. Nitrogen Nuclear-Quadrupole Resonance Dips in the Proton Spin Relaxation Dispersion of Nematic and Smectic Thermotropic Liquid-Crystals. *Z. Naturforsch., A: Phys. Sci.* **1992**, *47*, 1105−1114.

(29) Gillis, P.; Roch, A.; Brooks, R. A. Corrected Equations for Susceptibility-Induced T2-Shortening. *J. Magn. Reson.* **1999**, *137*, 402−407.

(30) Sebastião, P. J. 2009; http://fitteia.org.