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Doped ionic liquid crystals as effective weakly alignment media for polar solutes

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ABSTRACT

The ionic liquid crystal 1-dodecyl-3-methylimidazolium tetrafluoroborate slightly doped with water is presented as a promising NMR alignment medium for the measurement of residual dipolar couplings for polar molecules dissolved therein.

1. Introduction

Ionic liquid crystals (ILCs) are a fascinating class of molecular materials that combine the solvent properties of ionic liquids and the self-organization features of liquid crystals [1]. ILCs have been of considerable interest in recent years, both from the fundamental and applied point of view, and worldwide intense research activity in this field is presently going on [1–16]. They can be defined as a class of liquid–crystalline compounds containing anions and cations [1]. The ionic character means that some of the properties of the ILCs – *i.e.* electrical conductivity or ionic mobility – differ significantly from that of conventional liquid crystals. The ionic interactions tend to stabilize lamellar mesophases, but due to a combination of repulsive and attractive electrostatic forces, Van der Waals hydrophobic interactions and hydrogen bonding contacts, also uncommon molecular arrangements are found in ILCs [1,10].

Conventional LCs have been used for decades in NMR spectroscopy to measure anisotropic parameters (chemical shift anisotropy, indirect spin–spin coupling anisotropy, dipolar coupling, and quadrupolar splitting) from spectra of both the LC molecules and/or solute compounds dissolved therein [17–19]. Residual Dipolar Couplings (RDCs) proved, in particular, to be extremely powerful parameters for the constitutional, configurational and conformational analysis of small molecules. Their main limitation is, however, the high degree of orientational order they induce to a solute dissolved therein, giving rise to complex spectra that require dedicated software and, above all, a strong expertise to be analyzed. This is why research moved toward weakly ordered media [20–24], that induce a low ordering in the solutes. In such phases, the anisotropic NMR parameters are then significantly averaged, but not entirely, so that the size of the RDCs is reduced tremendously and the spectral quality of high-resolution NMR spectra is retained.

Many different weakly ordered media have been proposed for both non-polar and polar organic molecules, the most popular being lyotropic homopolypeptide liquid crystals (like poly-γ-benzyl-L-glutamate, PBLG) [25,26] and stretched polymer gels [27,28]. Sample preparation with these media is, however, often complicated because of the existence of a lower concentration limit, below which the liquid crystalline phase is disrupted, and because of the time needed sometimes for equilibration, respectively. Moreover, in both cases, effort has to be put in properly preparing the sample or in adequately compressing/stretching the gel to induce mechanical order.

Thanks to their mesophase behavior, ILCs might be suitable candidates as alternative orienting solvents for NMR measurements. Indeed, as most of traditional LCs, ionic liquid crystals are highly ordering media [1] and give then rise to complex second-order spectra. A first attempt to originate a weakly orienting medium starting from ILCs was recently made by Dama and Berger with the ionic liquid crystal *N*-dodecyl-*N*-methylpyrrolidinium bromide [C_{12}MPB] [29]. Using a 1:1:1:1 mixture of [C_{12}MPB]/*n*-decanol/D_2O/DMSO-d_6, the authors were able to measure the RDCs for a small polar solute dissolved therein. Following a different and

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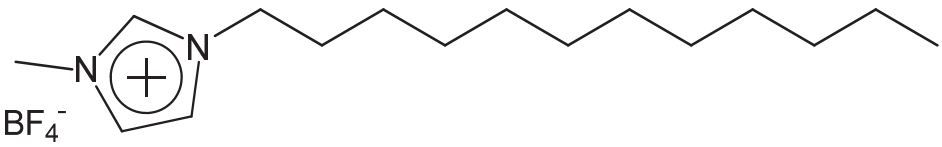

Fig. 1. Structure of the ionic liquid crystal 1-dodecyl-3-methylimidazolium tetrafluoroborate [C_{12}MImBF_4].

simpler strategy, we propose here a novel alignment medium based on the ILC 1-dodecyl-3-methylimidazolium tetrafluoroborate [C_{12}MImBF_4] (Fig. 1) slightly doped with D_2O. We show that a small addition of water is sufficient to generate an effective liquid crystalline phase, suitable to dissolve polar molecules and characterized by an extremely simple setup.

Among ILCs, 1-alkyl-3-methylimidazolium salts were chosen because they are examples of organic Room-Temperature Ionic Liquids (RTILs) [30]. The proposed structure for such phases contain hydrophobic regions of alkyl tails, and charge-ordered, hydrophilic head group regions [31]. The physical properties of 1-alkyl-3-methylimidazolium salts with alkyl chains (C_nH_{2n+1}) of different length and different counterions have been widely studied [30,32,33]. Results agree in observing liquid crystalline mesomorphism from $n = 12$ and highlight the key role of the counterion in influencing both the thermal behavior and the molecular organization.

Among the 1-alkyl-3-methylimidazolium salts, [C_{12}MImBF_4] was particularly interesting because it exhibits thermotropic liquid crystalline behavior at a reasonable temperature [1,32]. The mesophase has been identified as a modified form of a smectic A phase, the so-called smectic A_2 phase (SmA_2), that is an interdigitated bilayer smectic A phase where the molecules are in repeating bilayer units [30]. It has a negative anisotropy of the magnetic susceptibility [15], with the director of the phase oriented perpendicularly to the magnetic field of the NMR spectrometer.

In the following we describe how the addition of small amounts of D_2O makes [C_{12}MImBF_4] a promising easy-to-use candidate as weakly ordering alignment medium for polar solutes.

2. Results and discussion

To evaluate the effect of doping the ILC with water, 410 mg (86.3% w/w) of [C_{12}MImBF_4] and 65 mg of D_2O (13.7% w/w) were directly weighted into an NMR tube and mixed well and allowed to equilibrate. ^{2}H NMR spectra were recorded at different temperatures on cooling from the isotropic temperature and are reported in Fig. 2, together with the corresponding deuterium quadrupolar splitting for the solvent D_2O signal.

The magnitude of the quadrupolar splitting of D_2O is compatible with the range expected for a weakly water-based alignment medium [34–36]. Note for comparison that the deuterium quadrupolar splitting for the previously reported mixture of [C_{12}MPB] with D_2O (25% w/w) was significantly higher and only the use of a ternary 1:1:1 mixture of [C_{12}MPB]/D_2O/decanol (33.3% w/w) or a quaternary 1:1:1:1 mixture of [C_{12}MPB]/DMSO-d_6/D_2O/decanol (25% w/w) allowed the measurement of smaller quadrupolar splittings of 84 and 52 Hz, respectively [29].

The evidence of the weak alignment of water encouraged then the use of the D_2O-doped [C_{12}MImBF_4] ILC for dissolving and weakly orienting a small polar solute. Based on this motivation, theophylline was chosen as test compound to study the alignment properties of the medium. Theophylline (see figure in Table 1) is a methylxanthine drug, like caffeine and theobromine, and it is commonly used for asthma and various respiratory diseases.

A sample was prepared by dissolving 19.4 mg of theophylline in 761 mg of [C_{12}MImBF_4]. Note that, as previously mentioned, [C_{12}MImBF_4] behaves as a highly ordering liquid crystal when used as it is. This implies that the ^{1}H NMR spectrum of theophylline will result in a classical, very complex, second-order spectrum, requiring the help of a suitable graphical package to be analyzed. Moreover, theophylline it is only sparingly soluble in the ILC. Therefore, a doping with D_2O was carried out. To investigate the effect of increasing doping on the solute's order, small amounts of D_2O, from 3.1% w/w to 8.8% w/w, were progressively added directly in the NMR tube. After each addition, the mixture was heated and shaken for few minutes until it was homogeneous and cooled back to rt. As a consequence of the progressive doping, the transition

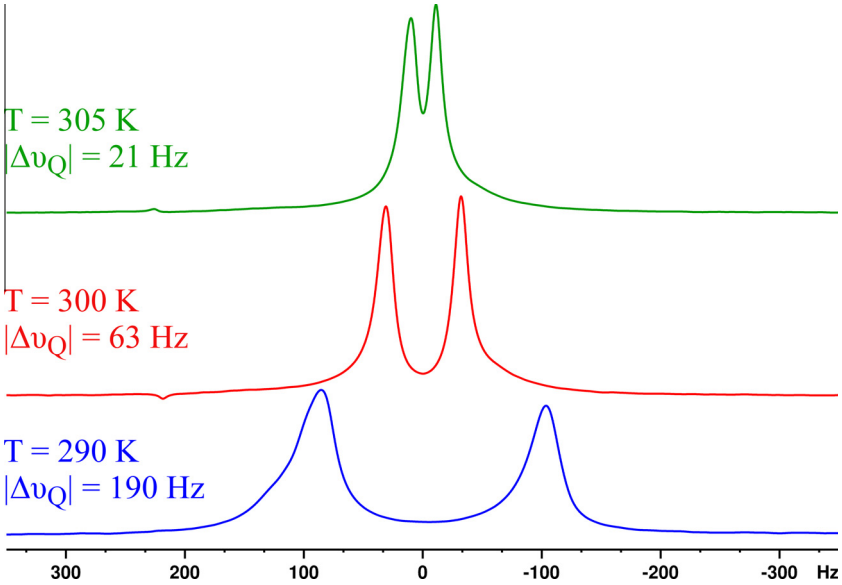

Fig. 2. ^{2}H NMR spectra of [C_{12}MImBF_4] doped with D_2O at 13.7% w/w at different temperatures. Spectra were recorded using 16384 points and 16 scans and processed using an exponential filter (LB = 5.0 Hz).