Reorientation phenomena in imidazolium methyl sulfonate as probed by advanced solid-state NMR

Gillian R. Goward, a,⁎ Kay Saalwächter, b Ingrid Fischbach, c and Hans Wolfgang Spiess c

a Department of Chemistry, McMaster University, 1280 Main St. W. Hamilton, ON, Canada L8S 4M1
b Institut für Makromolekulare Chemie, Universität Freiburg Stefan-Meier Str. 31, D-79104 Freiburg, Germany
c Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany

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Abstract

Evidence for reorientation of imidazolium rings in imidazolium methylsulfonate is demonstrated using solid-state NMR. This material is a model system for exciting new proton-conducting materials based on imidazole. Two advanced NMR methods, including ¹H–¹³C and ¹H–¹⁵N recoupled polarization transfer with dipolar sideband pattern analysis and analysis of the coalescence of ¹³C lineshapes are used to characterize the ring reorientation. The process is found to occur at temperatures well below the melting point of the salt, between 240 and 380 K, and is described by a single activation energy, of 38 ± 5 kJ/mol. This material is considered as a model system for quantifying the ring reorientation process, which is often proposed to be the rate-limiting step in proton transport in imidazole-based proton conducting materials.

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1. Introduction

Research into proton-conducting polymeric materials in recent decades has been driven by environmental concerns and the vision of developing a zero-emission vehicle based on polymer-electrolyte-membrane (PEM) fuel cells [1,2]. Current
membrane alternatives are extremely expensive, and moreover, incapable of operating in desirable temperature ranges. These perfluorinated ionic polymers operate on the principle of microphase domain segregation, with water or other acidic solvents acting as the proton-conducting media. Thus, the temperature range of fuel cell function is limited to that of the liquid phase of the proton solvent. To overcome this limitation, an innovative suggestion was recently proposed [3]. A family of materials based on imidazole tethered to ethylene oxide bridges (Imi-nEO) was prepared as a model material for PEM-fuel cells. In these materials imidazole acts as the proton solvent, and is covalently bonded to the polymer backbone, dramatically increasing the temperature range for effective proton conductivity. The pristine materials have been fully characterized using high-resolution 1H solid-state NMR under fast MAS conditions, together with DFT chemical shift calculations [4].

The pristine materials have insufficient conductivity to compete with other PEM candidates, thus small amounts of an acidic dopant such as triflic acid or methylsulfonic acid were added to achieve the desired conductivity by increasing the number of charge carriers in the system [3]. Imidazolium methylsulfonate is a crystalline material, which was prepared in order to investigate the fully-protonated variant of a common dopant for these proton-conducting materials [5]. Imidazole itself has been the focus of several recent investigations, due to the possibility of replacing water within proton-conducting membranes with this proton solvent [6]. The mechanism of proton transport continues to be a focus for both experimental and theoretical investigations [7–11]. As we demonstrate in this paper, imidazolium methylsulfonate exhibits molecular reorientations within the crystalline solid below the melting temperature. Such behavior is well documented in a variety of molecular crystals, and has recently been proposed as a desirable feature of ionic conductors for electrochemical applications [12–16]. An understanding of the ring reorientation process, which is found here to occur in imidazolium methylsulfonate, will provide deeper insight into one of the steps in proton transport in the imidazole-based polymers, of interest for PEM fuel cells. In particular, the ring-reorientation process is considered to be the rate-limiting step for proton transport in such systems, which rely on structural diffusion of the proton to facilitate conductivity, and as such, this study provides highly relevant information for continuing membrane development [3].

Several solid-state NMR measurements of imidazole itself are reported in the literature [7,8]. The lack of agreement between these studies points to the continuing uncertainty regarding the mechanism of proton transport in this material. We have recently described 1H NMR studies of imidazole, in which two hydrogen-bonded species were identified; one attributed to rigid rings, with a long spin-lattice relaxation time and a strong hydrogen bond, indicated by a high-frequency 1H chemical shift, and a second species, attributed to mobile rings, with short relaxation times and weak (or dynamically averaged) hydrogen bonds, represented by a lower frequency chemical shift. On the basis of these findings, we concluded that previous 15N exchange studies, which relied on and initial cross-polarization step, by their nature, selected only those imidazole units which were not involved in proton transport. Our ongoing studies in this area indicate that this two-phase phenomenon,
observed well below the melting point, is common to that characterized in ethylene-
oxide-tethered imidazole [4].

Solid-state NMR is well known for the access it provides to site-specific structure
and dynamics of molecules in the solid state [17,18]. Research in the field is directed
in two distinct, but related branches: first, the development of new pulse sequences
which provide site-specific information via the effects of the structure or dynamics of
interest on dipolar couplings, chemical shielding anisotropies, or quadrupolar
couplings, within a material, and second, the application of these new methods to
materials of interest [19]. Many examples of the characterization of dynamics using
solid-state NMR are published in the literature. Phenyl ring flips in polycarbonate
are a classic example of a process observed and characterized by solid-state NMR
[20,21]. Other examples include studies using static 13C 2D exchange NMR to
describe helical jumps in polyethylene, polyethylene oxide, and isotactic poly-
propylene [19], and the deuterium NMR under static conditions for characterization
mobility of polyisobutane within a zeolite [22], through the effect of the motion on
the 2H quadrupolar coupling, to name a few.

Solid-state NMR of spin 1/2 nuclei under static conditions suffers from severe line
broadening on account of the anisotropy of dipolar couplings and chemical
shieldings in the solid state. Magic angle spinning (MAS) at tan−1 v2 is well
known for its ability to average anisotropic second rank tensors over the rotor
period. With the advent of fast MAS, even strong homonuclear 1H–1H couplings,
which occur in organic solids, can be successfully averaged [17]. However, as a
result of MAS, much valuable information is lost. An elegant and well-established
strategy for recovering relevant interactions selectively is known as recoupling [23].
A variety of sequences have been described, which accomplish recoupling of either a
dipolar coupling [24,25] or chemical shielding anisotropy [26,27]. Such pulse
sequences have been used to effectively characterize and quantify dynamics
processes. In this work, recoupled polarization transfer (REPT) [28], NMR pulse
sequences are implemented to characterize a motional process in imidazolium
methylsulfonate.

MAS heteronuclear dipolar recoupling sequences such as REDOR [24] have
classically been used to quantify internuclear distances between labeled spin pairs,
for example 13C–15N in biomolecules [29]. A new variant of the REDOR sequence
[30], called REPT, can be implemented to quantitatively extract dipolar coupling
constants [25,28,31]. The two variants used here are REPT-HSQC (heteronuclear
single quantum coherence) and REPT-HDOR (heteronuclear dipolar order). The
acquisition of rotor-encoded sidebands by incrementing the evolution time in
fractions of a rotor period leads to patterns which depend on the recoupling time and
dipolar coupling strength. These sideband patterns can be fitted or simulated to
obtain quantitative dipolar coupling constants, and thus characterize either an
unknown distance, or, as in this case, the effects of motional averaging on the
coupling on interest.

The pulse sequences utilized in this study, by their nature, probe different
timescales. The coalescence process, observed at low temperature, probes motions on
the millisecond timescale, whereas the REPT sequence samples heteronuclear dipolar
coupling constants on the timescale of tens to hundreds of microseconds, i.e. several rotor periods, under fast MAS conditions.

Motions which occur on the timescale of the pulse sequence can result in “relaxation” during spin evolution, leading to signal loss during a lengthy pulse sequence. This timescale, referred to as the intermediate motional regime (IMR) has been explored through experimental and theoretical investigations of dimethylsulfone [32]. IMR effects are observed in the high-temperature spectra presented here; however, we leave the full investigation of this phenomena, including simulations, to a future publication.

Here we characterize ring reorientations in imidazolium methylsulfonate using heteronuclear solid-state NMR recoupling. The results presented will provide the basis for further considerations of charge transport via hydrogen bonding and local molecular motion in novel proton-conducting materials.

2. Experimental

Materials were prepared by combining imidazole with methylsulfonic acid, and were provided by M. Schuster. Solid-state NMR experiments were performed at a $^1H$ Larmor frequency of 700 MHz (16.44 T). Heteronuclear $^1H$--$^{13}C$ and $^1H$--$^{15}N$ dipolar sideband patterns were acquired for samples packed in 2.5 mm rotors, spun at 25–30 kHz. Hard $\pi/2$ pulses of 2 $\mu$s were used. Recoupling times of 4 rotor periods were used for $^1H$--$^{13}C$ measurements, while 6 rotor periods were used for $^1H$--$^{15}N$ measurements. The $^1H$--$^{13}C$ dipolar sideband patterns were acquired at 30 kHz MAS using the REPT-HSQC sequence, with 164 increments in the indirect dimension, of 144 transients each, with time increments of 1.12 $\mu$s, giving a sweep width of 448 kHz in the indirect dimension. At low temperature, the sideband patterns were acquired at 25 kHz MAS with 164 increments of 2 $\mu$s with 144 transients each. The $^1H$--$^{15}N$ dipolar sideband patterns were acquired at 30 kHz MAS using the REPT-HDOR sequence with 96 increments of 1.04 $\mu$s, with 64 transients each, in the indirect dimension. At low temperature, the sideband patterns were acquired at 25 kHz MAS with 60 increments of 2 $\mu$s with 64 transients each.

Fast MAS is known to induce significant sample heating, due to the frictional forces present under these conditions. Using Sm$_2$Sn$_2$O$_7$ as a shift reference, temperature calibrations were performed, as described in Ref. [33]. All temperatures reported here are corrected accordingly, for MAS heating effects.

3. Results and discussion

The crystal structure of imidazolium methyl sulfonate was elucidated using standard single-crystal X-ray diffraction methods [5]. The material crystallizes in the orthorhombic space group, Pbcn, with cell parameters of $a=7.918\ \text{Å}$, $b=11.040\ \text{Å}$, and $c=16.086\ \text{Å}$. A portion of the unit cell is shown in Fig. 1, together with a schematic of the molecular structure. The relative orientations of the C–H and N–H
bonds with respect to the $C_2$ reorientation axis of the imidazolium ring are indicated in the figure. The hydrogen bonding arrangement of the neutral parent imidazole [6,34] is interrupted in this structure by the interaction which arises between the positively charged imidazolium rings and the negatively charged methyl sulfonate units. The solid-state NMR study described here focuses on the protonated imidazole rings (imidazolium units). The relevant heteroatoms are described by their
ring positions: carbons found at apical and basal positions, and two nitrogen sites. At low temperature, the basal carbon positions become inequivalent, with a splitting of 113 Hz. A series of variable temperature 1D $^{13}$C spectra are shown in Fig. 2(a). The coalescence process is clearly visible, and is characterized by the lineshape analysis and corresponding correlation times shown in Fig. 2(b) [35].

These data were collected using the one-dimensional version of REPT, which is better known under the acronym TEDOR [24,30], and utilizes a coherent pathway for magnetization transferred between protons and carbon nuclei. An interesting consequence of this choice of pulse sequence is observed at elevated temperatures, although still well below the melting temperature of the solid ($T_m > 130^\circ$C). As is evident in Fig. 2, at 360 K, the coalesced resonance of the basal carbons vanishes. Indeed the signal-to-noise (S/N) ratio of the entire spectrum is decreasing with increasing temperature. This reflects the fact that the pulse sequence relies on the $^1$H–$^{13}$C dipolar coupling. Further evidence of the unequal influence of temperature on the apical and basal resonances is given in Fig. 3, which shows a section of the 2D $^1$H–$^{13}$C REPT correlation spectra acquired at 330 and 360 K, respectively. The absence of the basal resonance in the spectrum acquired at 360 K is attributed to a ring reorientation about the $C_2$-axis of the imidazolium units in the crystal lattice.

Fig. 2. (a) 1D variable temperature $^1$H–$^{13}$C REPT spectra. (b) Lineshape analysis of coalescence process for basal $^{13}$C resonances.
This reorientation is hypothesized to average the basal $^1$H–$^{13}$C dipolar interactions, while not (or negligibly) averaging the apical $^1$H–$^{13}$C dipolar coupling. The relative orientations of these two C–H bonds, with respect to the axis of the 180° ring flip, are proposed to give rise to this difference.

To further investigate this process, rotor-encoded REPT patterns were acquired at three temperatures. An example of the 2D spectra, together with the extracted sideband patterns acquired at 330 and 350 K are presented in Fig. 4. The data are fitted using an analytical simulation routine, to acquire coupling constants for the $^1$H–$^{13}$C dipolar couplings at each temperature. These data are listed in Table 1. A
visual inspection of the spectra reveals the equivalence of the two couplings at low temperature, as well as at ambient temperature, in which cases both the apical and basal 1H–13C couplings are on the order of 19±0.5 kHz. The reduced coupling of 8.4±0.2 kHz observed at 350 K is immediately evident in the weaker sideband pattern observed for the basal carbon resonance at this temperature. The dipolar coupling for this basal resonance is reduced by more than a factor of two relative to that of the apical carbon, which remains relatively unchanged, at 18.9±0.2 kHz. The low signal-to-noise ratio of the basal resonance as compared to the apical resonance can be understood when assuming that the flip motion is in the IMR with flip rates
on the timescale of the experiment. This IMR is usually characterized by a significant reduction of the S/N ratio [32]. The lack of any strong even order sidebands in the REPT sideband patterns, as well as the spacing between imidazolium units due to the coordination with the methyl sulfonate groups in the crystalline lattice both indicate that the spin-pair approximation is valid in this case.

Fig. 5 shows the experimental, fitted, and simulated $^1$H–$^{15}$N REPT sideband patterns acquired under HDOR conditions, where, as opposed to the HSQC variant, the chemical-shift information in the indirect ($^1$H) dimension is sacrificed in favor of reduced experimental times. A single $^1$H–$^{15}$N correlation is observed under all experimental conditions. At low temperature, the agreement between the experimental and fitted sideband patterns is very good. Fitting the higher-order sidebands only, a coupling constant of $9.4 \pm 0.2$ kHz is obtained. The onset of molecular reorientation on the time scale of the pulse sequence, predicted to occur at or below 360 K, based on the $^{13}$C–$^1$H results, is found to have a much less significant effect on the $^1$H–$^{15}$N sideband pattern, even at temperatures as high as 380 K. The fit of this

![Figure 5](image-url)

Fig. 5. (a) $^1$H–$^{15}$N REPT dipolar sideband patterns acquired using the HDOR variant of the pulse sequence, for $t_{\text{exc}} = 6t_r$ (280 and 380 K). Fitted patterns are shown in red, offset from the experimental spectra. (b) Sideband patterns obtained from simulations based on the molecular geometry of the imidazolium ring under static and fast dynamics conditions.
sideband pattern yields a coupling constant of \( 7.5 \pm 0.2 \text{ kHz} \), which is not substantially reduced, relative to the \( 9.4 \pm 0.2 \text{ kHz} \) coupling observed for the rigid rings. The lack of a significant change in the S/N ratio in spectra acquired at high temperature, relative to those acquired at ambient temperature is accounted for by the fact that this material is 99\% enriched in \(^{15}\text{N} \), and thus the signal intensity remains strong, even in the case of some degree of motion in the IMR.

Using the “rigid” dipolar coupling constants obtained from the spectra at low temperatures it is now possible to simulate the sideband patterns for a fast 180\(^\circ\) ring flip around the \( C_2 \) symmetry axis. For this purpose it is necessary to consider the angle between the flip axis and the respective bond vector of the coupled nuclei. The angles were determined from the crystal structure data assuming that the \( C–H \) bond vector bisects the internal \( C–C–N \) angle of the imidazolium ring and the \( N–H \) bond vector bisects the internal \( C–N–C \) angle of the imidazolium ring as is shown in Fig. 1(a). We obtained 35.6\(^\circ\) for the angle between the flip axis and the \( C–H \) bond vector and 72.0\(^\circ\) for the angle between the flip axis and the \( N–H \) bond vector. The resulting sideband patterns for fast dynamics are shown in Fig. 4(c) (\(^{1}\text{H}–^{13}\text{C}\)) and in Fig. 5(a) (\(^{1}\text{H}–^{15}\text{N}\)). These simulated patterns correspond to averaged dipolar coupling constants of \( D_{\text{IS}}=9.7 \pm 0.2 \text{ kHz} \) (\(^{1}\text{H}–^{13}\text{C}\)) and \( D_{\text{IS}}=7.9 \pm 0.2 \text{ kHz} \) (\(^{1}\text{H}–^{15}\text{N}\)). The agreement between simulated and experimental data is reasonable.

At first sight it seems to be surprising that the \(^{1}\text{H}–^{13}\text{C} \) dipolar coupling constant is much more strongly reduced than the \(^{1}\text{H}–^{15}\text{N} \) dipolar coupling constant, since the angle between the \( N–H \) bond vector and the flip axis is much bigger than that between the \( C–H \) bond vector and the flip axis. Here, it becomes evident that the tensorial nature of the dipolar coupling must be regarded. The rigid dipolar coupling tensor is traceless and symmetric (\( \eta_0 = 0, D_{\text{IS}} = -1/2 \delta_0 \)). Motional averaging leads to a dipolar coupling tensor which is generally not symmetric any longer (\( \eta_{\text{avg}} \neq 0 \)). This observation is well known from the quadrupolar interaction tensor \[36\]. A calculation of the averaged interaction tensors for the 180\(^\circ\) ring flip yields:

\[
\delta_{\text{avg}}/\delta_0 = 0.5 \quad \text{and} \quad \eta_{\text{avg}} = 0.97 \quad \text{for the basal} \quad ^{1}\text{H}–^{13}\text{C} \text{ dipolar coupling},
\]

\[
\delta_{\text{avg}}/\delta_0 = 0.86 \quad \text{and} \quad \eta_{\text{avg}} = 0.16 \quad \text{for the} \quad ^{1}\text{H}–^{15}\text{N} \text{ dipolar coupling},
\]

which are in good agreement with the experimental observations. The differences between the spin-pair fitted patterns and the simulated patterns can be attributed to the fact that the spin-pair fit results assume an \( \eta \) value of 0, whereas the simulations take into account that the tensor becomes asymmetric under reorientation. These differences are not pronounced, since dipolar sideband patterns are not very sensitive to the value of \( \eta \) \[32\].

From the \(^{1}\text{H}–^{13}\text{C} \) sideband patterns, we estimate that ring reorientation occurs on the timescale of 1–2 rotor periods, i.e. 33–67 \( \mu \text{s} \). We combine these data with the correlation times obtained from analysis of the coalescence process in the next section, to determine whether each measurement probes the same reorientation process.

In Fig. 6 the relevant correlation times obtained from REPT, and coalescence measurements are plotted together against inverse temperature. The resulting
straight-line relationship is accurately described by a single Arrhenius function, consistent with a single two-site imidazolium ring reorientation process, measured by all methods. The activation energy for this process is determined to be $38 \pm 5 \text{kJ/mol}$. The data fit to one straight-line function with Arrhenius behavior, and thus represent the same 2-site ring reorientation process.

A final observation is drawn from the comparison of previously reported activation energies for proton transport in glassy Imi-nEO materials, measured both through conductivity and $^1\text{H}$ NMR line width studies. The activation energies determined there were in the range of $52 \pm 5 \text{kJ/mol}$ [4]. From this possibly coincidental similarity, we infer that the ring reorientation process is also the rate-limiting step in proton transport in these novel proton-conducting materials. This interpretation is not unexpected, and has been predicted based on a variety of other measurements as well, dating as far back as 1970 [6]. Nevertheless, conclusive proof of the nature of proton transport, even in model systems, remains elusive.

4. Conclusions

Imidazolium ring reorientation in imidazolium methylsulfonate has been clearly demonstrated using coalescence analysis and REPT dipolar sideband pattern analysis. These unique measurements point to a single reorientation process, with an activation energy of $38 \pm 5 \text{kJ/mol}$. This material is considered as a model system for the reorientation process which is proposed to be rate-limiting for proton transport.
in a new class of proton-conducting materials. We have confirmed this activation energy for the ring reorientation process using CODEX [26,37] measurements, which will be the subject of a forthcoming publication.

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