Solid-state NMR studies of hydrogen bonding networks and proton transport pathways based on anion and cation dynamics

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Proton dynamics in polymer electrolyte membranes are multifaceted processes, and the relative contributions of various mechanisms can be difficult to distinguish. Judicious choices of model systems can aid in understanding the critical steps. In this study, we characterize anion dynamics in a series of benzimidazole-alkyl phosphonate salts, and compare those dynamics to a membrane prototype, built on a decane backbone. The series of salts are characterized, using high resolution $^1$H solid-state magic angle spinning (MAS) NMR, DQ MAS NMR, and $^{31}$P centreband-only detection of exchange (CODEX) NMR spectroscopy, to determine the influence of the nature of the alkyl group on the rates and geometries of anion dynamics, and overall proton exchange processes. The alkyl group is shown to slow the correlation times for anion reorientation, when compared at ambient temperature. However, it is also apparent that the lowered lattice energy of the salt lowers the activation energy and allows good dynamics at intermediate temperatures in both the benzimidazolium ethylphosphonate and in the HBr adduct of 1,10-(1-H-imidazol-5-yl)decane phosphonic acid (Imi-d-Pa). Copyright © 2007 John Wiley & Sons, Ltd.

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INTRODUCTION

Proton exchange membrane materials

The choice of solid-state electrolytes for proton exchange membrane fuel cells (PEM-FCs) is currently dominated by polymer membrane systems. Many different polymer membranes exist, ranging from aromatic compounds to perfluorinated alkyl chains.1,2 Most proton exchange membranes rely heavily upon a liquid electrolyte to facilitate the ionic conduction process, as in the case of Nafion, a perfluorinated ionomer, where the hydration of the polymer promotes ionic conduction.3 Since the operating temperature range of Nafion is limited by the dew point of water in the membrane, a competing membrane design incorporates liquid phosphoric acid into polybenzimidazole (PBI), thus raising the achievable operating temperatures.4 Ultimately, the lifetime and performance of a fuel cell depends on any number of components; however, the loss of ionic carriers from the polymer electrolyte causes significant losses in ionic conductivity and thereby, a shortened lifetime of the fuel cell.5,6 In the case of PBI, low conductivity is often the result of phosphoric acid leaching out of the membrane and poisoning the catalyst.7–9 Over the lifetime of the device, the drop in ionic conductivity is attributed to the loss of participants in the vehicle-transport, which is presumed to dominate the conductivity of such systems.

To help alleviate the acid leaching problem in phosphoric acid-doped systems, new polymers have been synthesized, in which the acid functional groups are covalently tethered to the polymer backbone.10,11 By tethering the ionic carrier to the polymer backbone, it was thought that high ionic conductivity would be maintained, thereby eliminating the dependence on the liquid electrolyte. These polymer membranes used imidazole and phosphonic acid functional groups as ion carriers.10,11 This was a novel approach; however, the ionic conductivity of the membrane systems does not compare favourably to the more established liquid-based systems. Under dry conditions, the rigid and strong hydrogen bonding between the different units of the polymer inhibited the conduction of protons through these new membranes.

To better understand the mechanism of ion conduction in these polymer systems, the benzimidazole-alkyl phosphonate salts were prepared here as model compounds. The benzimidazole-alkyl phosphonates are chosen to represent a polymer system in which phosphonate is attached to an alkyl linker chain bonded to the polymer backbone. Three initial compounds were chosen, all having a similar cation, but varying the anion from phosphate, to methyl phosphonate, to ethyl phosphonate. Each of these three model compounds forms an extensive hydrogen-bonded network, structurally characterized by single crystal X-ray
Figure 1. Excerpts from the single crystal X-ray structure solutions show the hydrogen bonding of the three benzimidazole compounds with increasing alkyl chain length, (a) phosphate, (b) methyl phosphonate, (c) ethyl phosphonate. Highlighted in the structures are $\text{N} \cdots \text{H} - \text{O}$ hydrogen bonds as A and $\text{O} \cdots \text{H} - \text{O}$ hydrogen bonds as B. A similar hydrogen-bonding structure is observed for the alkyl phosphonates which have the same number of hydrogen-bonding partners. (d) Molecular structure of 1,10-(1-H-imidazol-5-yl)decanephosphonic acid, called Imi-d-Pa here.

Solid-state NMR strategies

Nuclear magnetic resonance (NMR) is a powerful tool that can be used to study the solid-state structure and dynamics of a material. This combination of structural and mobility information provides a unique perspective on materials performance. Fast magic angle spinning (MAS) is particularly valuable in achieving spectral resolution of $^1\text{H}$ NMR spectra in the solid-state, where the extensive homonuclear dipolar coupling network causes severe line broadening. Building upon the standard $^1\text{H}$ MAS NMR spectra, the full connectivity of the individual protons can be established via the 2D double quantum (DQ) pulse sequence, which is used to map out all the homonuclear dipolar coupled spin pairs in the material. The key advantage of 2D DQ MAS NMR for structural analysis is that the materials do not have to be crystalline to observe the connectivity of the different resonances in the spectrum. Thus, the 2D DQ MAS NMR correlation spectra can serve as a method to determine the local packing environment of amorphous materials. In this study, we use various DQ MAS NMR spectra to assign and propose a model for the hydrogen-bonded proton networks in the materials of interest.

Once the hydrogen-bonding network is structurally characterized, further NMR investigations allow for detailed characterizations of dynamics possible within that network. The dynamics of the proton and the anions in the model compounds are characterized here. In this study, we employ two types of NMR experiments to observe the dynamics of the different model compounds; variable temperature $^1\text{H}$ MAS NMR and $^{31}\text{P}$ centreband-only detection of exchange (CODEX) NMR experiments. The variable temperature experiments illustrate the effect of heating on the chemical environment through line narrowing, or coalescence processes. The line narrowing of a resonance with an increase in temperature is attributed to an increase in the effective transverse relaxation time, which, in these materials can be directly related to a change in the correlation time of a species owing to its increased mobility. The coalescence phenomena occurs when two or more spins are exchanging faster than the frequency difference between two different chemical shifts, representing unique chemical environments. When the frequency of the physical reorientation is faster than the frequency difference between the resonances, the resulting spectra exhibit only one resonance that is representative of the exchanging species.

The pulse program CODEX provides site specific determination of the geometry of the reorientation, and gives a measure of the timescale of the motion which can then be compared between the different materials. The CODEX pulse sequence refocuses the chemical shift anisotropy (CSA) to obtain this site specific information. Cross polarization is typically used to saturate the nuclei of interest and 180°
pulses are used every half-rotor period to recouple the CSA. Prior to the reconversion period, a mixing time is allowed for motion of the species to occur. Any motion of the ion causes a change in specific orientation of the CSA, which results in a decrease in the intensity of the refocused signal. The change of the CSA during the mixing time leads to attenuation of the echo and decays to the limit of 1/M, where M is the number of sites in the reorientation. For example, a rotation around a two-fold axis will lead to an attenuation of 50%. By varying the mixing time, a build-up curve can be constructed and fitted to an exponential function to obtain the jump rate.

EXPERIMENTAL

The crystals of benzimidazole model compounds were grown by adding 1:1 molar ratio of both the cation and the anion to a solution of dimethylsulfoxide. Any crystals not used for diffraction were ground and dried at 105 °C, to remove any residual solvent.¹³¹H MAS NMR and the ³¹P CODEX NMR experiments were conducted on a Bruker Avance 500. For the ¹H MAS NMR experiments, a 2.5 mm outer diameter rotor was used while spinning at 25 kHz. The bearing gas was used to heat the sample during the variable temperature experiments. Sample temperatures were calibrated for frictional heating using samarium stannate. The ³¹P CODEX NMR experiments were conducted using a 3000 µs contact time for cross polarization from ¹H to ³¹P, and 8 µs 180° ³¹P pulses were used during the pulse sequence. The MAS frequency used was 10 kHz on a 4 mm probe, which translates to 0.1 ms as the lowest increment for the mixing time. All other data points use a mixing time that is an integer number of 0.1-ms intervals. The reference spectrum was acquired using 0.1 ms for the mixing time and 3 s for the Z filter, while the completely attenuated spectra were obtained using 3 s for the mixing time and 0.1 ms for the Z filter.

The DQ spectrum at 50.3 kHz MAS was acquired using a Bruker AMX 600 system. The 50.3 kHz ¹H MAS NMR spectrum was acquired using a prototype probe with rotors that have an outer diameter of 1.1 mm. The DQ spectrum was obtained using τ = τ. The 2D ¹H–¹H DQ MAS NMR spectrum was obtained with 64 scans and 64 slices in the indirect dimension with 1.8 µs ¹H pulse lengths. A separate cooling line that compensates for the frictional heating in this probe controlled the sample temperature to roughly 15 °C above ambient temperature.

High-field experiments were performed on the Bruker Avance II 900 MHz spectrometer, equipped with a 21.1 T magnet, at the National Ultrahigh Field NMR Facility for Solids in Ottawa, Canada. The experiments used rotors with an outer diameter of 2.5 mm while spinning at 30 kHz MAS, 90° pulse lengths were 2.5 µs.

RESULTS AND DISCUSSION

The model compounds of acid-doped PBI show many similarities to the polymer system; however, attention should be drawn to the fact that the ratio of phosphate to benzimidazole is 1:1 which would model the dynamics and structure of a polymer system with a low concentration of liquid electrolyte, compared to the doping rations typically reported for PBI membranes.¹ The model compounds simulate a material in which only the Grothuss mechanism (structural diffusion) is possible below the melting point. This is comparable to the polymers with tethered phosphonates, in which vehicle-transport is prohibited. The goal of tethering the acid group is to eventually reduce and eliminate the dependence of membrane performance on the presence of a liquid dopant.

Benzimidazole – Structure

The ¹H MAS NMR spectra of the three benzimidazole compounds can be divided into three regions; the hydrogen-bonded regions (18–9 ppm), aromatic region (9–5 ppm), and the aliphatic region (3–0 ppm) as shown as Fig. 2. The resonances are labelled A–D on each of the spectra where resonances labelled A represent N–H···O hydrogen bonds, resonances labelled B represent O···H–O hydrogen bonds, resonances labelled C represent aromatic protons, and resonances labelled D represent the methyl or ethyl protons. In the benzimidazole phosphate structure, both the oxygen atoms involved in the N–H···O hydrogen bonds also are hydrogen bonded to another phosphate. This leads to similar electronic environments for the two hydrogen-bonded protons in N–H···O hydrogen bonds, resulting in similar chemical shifts, A in Fig. 2(a). The inset of Fig. 2(a) shows the same A resonance acquired on a 900 MHz spectrometer, where the increased field strength reveals the two different N–H···O hydrogen bonds, A and A'. According to the X-ray diffraction data, these two hydrogen bonds only differ in bond length by 0.083 Å, making them very hard to resolve at a lower magnetic field. The A and A' resonances in Fig. 2(b) of the benzimidazole methyl phosphonate show the effect of a bifurcated oxygen on the chemical shift of its N–H···O hydrogen-bonded proton. The A resonance is assigned to the site without the oxygen split between two hydrogen bonds and the A' proton is bonded to the bifurcated oxygen and the imidazole ring, while the second hydrogen bond B is between two phosphates and shares the same oxygen atom as the A' proton. The aromatic protons are poorly resolved owing to the line-broadening contribution of the extra homonuclear dipolar couplings to the protons on the ethyl group. Nevertheless, the hydrogen-bonding arrangement is very similar in the alkyl phosphonate salts.

The connectivity of the hydrogen network in benzimidazole methyl phosphonate is observed in the 2D DQ MAS NMR spectra, which are shown as Fig. 3(a) and (b). These two spectra were acquired using 25 kHz and 50 kHz MAS respectively, and show the dramatic benefit of fast MAS. The greatest improvement of the increased spinning speed occurs in the resolved hydrogen-bonded region of the spectrum and the collapse of the alkyl linewidth reduces the overlap of the resonances. The A' couplings in the 25 kHz ¹H MAS NMR spectrum are not resolved and an assignment of the dipolar coupling to this environment is difficult; however, with the increase in MAS frequency, the two couplings (A'–B and A'–C) are resolved. The fast MAS in this case also reduces
Figure 2. The $^1$H MAS NMR spectra of the three benzimidazole compounds at 25 kHz MAS. (a) The inset to the phosphate spectrum is the same material recorded at 900 MHz (21 T magnetic field) and shows the separation of the two N···H–O hydrogen bonds. (b) The resonances of hydrogen bonding protons are shown above 11 ppm, (c) similar spectrum as (b), but with increased homonuclear dipolar broadening because of the additional protons of the ethyl group. The A, A’ resonances refer to N···H–O hydrogen bonds, while the B resonances refer to the O···H–O hydrogen bonds, C resonances refer to any protons that are bonded to the imidazole ring, and the D resonances refer to any alkyl protons.

Figure 3. The 2D DQ MAS NMR spectra of benzimidazole methyl phosphonate at (a) 25 kHz MAS and (b) 50 kHz MAS. The increased resolution of the fast MAS is observed, particularly, in the hydrogen-bonded and the aromatic regions of the spectrum.

coupling is observed in Fig. 3(b) as the A’–B correlation, thus the non-bifurcated hydrogen bond must be resonance A where no shared coupling is observed. The second key coupling is the B–D coupling which relates the O···H–O hydrogen bond to the methyl group. This hydrogen bond can be uniquely identified as the hydrogen between two phosphonate anions, on account of its strong coupling to the methyl groups. By process of elimination, the resonance labelled A’ in the spectra must be the bifurcated N–H···O hydrogen bond. The structure of the benzimidazole ethyl phosphonate is similar to that of the methyl analogue, where a single oxygen in the asymmetric unit has a single bifurcated oxygen leading to two different N–H···O and one O–H···O hydrogen bonds. Through the use of 2D DQ MAS NMR, the assignment of the different resonances can be...
made, using the short-range contact information provided by the homonuclear dipolar couplings.

The 2D DQ MAS NMR spectrum in Fig. 3(b) has many other dipolar couplings that are resolved at this higher MAS frequency. Many of the couplings can be identified from the crystal structure for example, the coupling of the \( \text{A/A}' \) resonances to the resonance at 9 ppm which corresponds to the proton in the two position on the imidazole ring. Also observed is a coupling from the B resonance to a C resonance at 7 ppm; this dipolar coupling results from the O–H–O hydrogen-bonded proton and an adjacent phenyl ring proton. A dipolar coupling from the A hydrogen bond to the methyl protons is observed in the spectrum, while it is not present for the A' resonance because of their respective proximity in the crystal structure. This is also the reason that no A–A' correlation is observed, as the hydrogen-bonded protons are on opposite sides of the benzimidazole ring. In summary, the 2D DQ NMR spectrum acquired at 50 kHz MAS provides a wealth of structural information which complements that obtained from diffraction studies, and provides new insights into the hydrogen-bonding network in the salt.

**Benzimidazole – dynamics**

The chemical effect of adding longer aliphatic chains is to decrease the lattice energy and lower the melting point of the material. This effect is observed in the differential scanning calorimetry (DSC) curves of the three benzimidazole compounds shown in Fig. 4. The DSC curve in Fig. 4(a) of the benzimidazole phosphate shows the melting point of the powder material at 430 K. Similarly, for the methyl and ethyl analogues (Fig. 4(b), (c)), the melting points decrease to 417 and 393 K, respectively. The DSC trace for the phosphate shows a strong exothermic behaviour after the phase transition, attributed to phosphate dehydration. The lowered melting point of both the methyl and ethyl analogues suggest that the increased chain length will facilitate fast dynamics to these solids at lower temperatures. The DSC traces of the methyl and ethyl analogues both have a stable liquid region at high temperatures above the melting point. The methyl analogue does go through an exothermic transition after the melting point, though not to the same degree as the thermal dehydration that the phosphate undergoes. The latter dehydration occurs under dry conditions for similar materials.30

The primary mechanism of ionic conduction in this family of materials is hypothesized to be the rotation of the anion and not the ring flip of the cation. This analysis is based on previous \(^{13}\)C CODEX NMR comparison of imidazolium methyl sulfonate to benzimidazolium methyl phosphonate, which yielded correlation times of 29 ms for imidazolium at 273 K and 4.2 s for benzimidazolium at 298 K, and thereby ruled out the two-site ring flip for benzimidazolium cations.13

The decreasing melting points in the series of compounds is consistent with the dynamics of the material becoming more efficient at lower temperatures for materials with a longer alkyl chain length. To investigate the compound behaviour of the compounds with temperature and the resulting coalescence of any NMR resonances, variable temperature NMR spectra of the materials were recorded over the temperature range of our MAS probe. The variable temperature NMR data are shown as Fig. 5. The local mobility within these compounds is clearly related to the length of the material’s alkyl substitution. The phosphate spectra shown in Fig. 5(a) have no observable chemical shift changes or line narrowing within the temperature range of our instrument. The methyl analogue undergoes coalescence of the two hydrogen bonds that share the same oxygen atom, as shown as a function of temperature in Fig. 5(b). This coalescence shows that the interchange of these two protons is favoured in the alkyl analogue. The reorientation of the methyl phosphonate indicates that Grothuss style transport of protons in these or similar materials is facilitated, via the hydrogen-bonding network of the material.

This trend is further reinforced by the variable temperature spectra of the ethyl analogue, shown in Fig. 5(c). A
new resonance at \( \sim 13 \) ppm can be observed in the variable-temperature spectra; this resonance occurs prior to any extreme narrowing in the aromatic region. The new resonance occurs at the average chemical shift of resonances A’ and B, which implies that the new resonance originates from spins located in those two sites at 350 K. At this temperature, only a fraction of the anions produce a successful jump which interchanges the spins, represented in the spectrum as the appearance of the new resonance. If only the A’ and B sites were exchanging, the coalescence would follow the same pattern as the methyl phosphonate. If, however, all three hydrogen-bonding resonances were undergoing coalescence, the new resonance would reach the average chemical shift of all three hydrogen-bonded sites. As the temperature increases past 350 K, the new resonance shifts from 13.07 to 13.81 ppm by the maximum temperature of 360 K. At 353 K, the new resonance has reached the average of the A’ and B resonances at 13.42 ppm. As the chemical shift increases, the contribution of the A hydrogen bond to the exchange increases, and at 356 K, the resonance reaches 13.70 ppm. At lower temperatures, the anion facilitates the exchange of A’ and B protons through a three-fold rotation, as shown in the \(^{31}P\) CODEX data below. A similar mechanism has been outlined in our previous work for the methyl phosphonate. By 358 K, the material is nearing its melting point, however, full isotropic rotation is not yet achieved, as the \(^1H\) MAS NMR spectrum does not differ significantly from the spectrum at 356 K. At 360 K, the resonances have narrowed considerably, as a result of the isotropic tumbling. Surprisingly, the onset of local dynamics is observed by NMR well below the melt transition observed by DSC, at 393 K. This is consistent with the ability of NMR to probe molecular level process before the onset of macroscopic behaviour, and warrants further investigation. Upon cooling, the material returns to its earlier state, and reproduces the spectrum shown in Fig. 2(c). Before the material melted, the onset of phosphonate dynamics, followed by the benzimidazole ring reorientation at higher temperatures, give evidence that the ionic conduction by a process resembling the Grothuss mechanism is viable and can lead to ionic transport.

The benefit of acquiring a DQ MAS NMR spectrum at higher temperatures is that only resonances with dipolar couplings that have a lifetime that is longer than the rotor period appear in the spectrum. Any resonance that does not meet this specification is removed from the DQ MAS NMR spectrum. The application of the DQ MAS pulse sequence as a mobility filter has been used previously and depends on the MAS frequency to determine the jump frequency of the species of interest. The new resonance at \( \sim 13 \) ppm is removed from the 1D \(^1H\)–\(^1H\) DQ MAS NMR spectrum at temperatures \( \geq 354 \) K. Given the MAS frequency of 25 kHz, and a recoupling period of one rotor period, this implies a jump rate between sites of equal to or greater that 40 \( \mu s \). As the temperature increases beyond 354 K, the benzimidazole ring becomes mobile, which causes the narrowing of the aromatic resonances. Consistent with the conclusion of our earlier \(^{31}P\) CODEX study, the anion rotation rate far exceeds the rate of the two-site reorientation of the benzimidazole ring flip, as witnessed by the appearance of the new hydrogen-bonding resonance prior to the narrowing of the aromatic resonances.

To measure the reorientation of the anions the CODEX pulse sequence was employed to determine the type of reorientation and the jump frequency. If a reorientation occurs during the mixing time, the CSA changes and the magnetization is not refocused, resulting in attenuation of the detected signal. The exchange curves from the three different anions are shown in Fig. 6. The plateau of the exchange curve is determined by the geometry of the reorientation. The phosphate shown in Fig. 6(a) shows a four-fold reorientation that leads to a plateau of 75%, while the alkyl phosphonates in Fig. 6(b), (c) have a three-fold motion that leads to a plateau of 66%. Three exchange curve data sets have been acquired using different lengths of the refocusing period, chosen within the plateau region of the data set (data not shown). Spin diffusion would be detected as a bi-exponential build-up of the exchange intensity; however, the fits of these data sets gave an error bar of 5 ms for single exponential functions, indicating that spin-diffusion is not playing a role here. Moreover, attempts to fit the data to a bi-exponential function results in large error bars for the correlation times. The correlation times obtained for the different species are \( 56 \pm 5 \) ms for the phosphate, \( 75 \pm 5 \) ms for the methyl phosphonate, and \( 101 \pm 5 \) ms for the ethyl phosphonate. The correlation times from the fits reveal that, as the length of the chain increases, the rotation of the phosphate slows...
down. The phosphate, having no constraints on the type or direction of the isotropic reorientation of the tetrahedron, has the quickest reorientation time, while the restriction to an anisotropic three-fold motion slows the alkyl phosphonates. The variable temperature data supports the conclusion that the motion of the ethyl phosphonate will possess the lowest activation energy, and phosphate the highest, of the materials studied here, as evident from their variable temperature response observed in Fig. 5. This implies that the tethered phosphonate will not inhibit structural diffusion driven conductivity mechanisms of the polymer by any significant amount. The increased dynamics of the alkyl phosphonates at higher temperatures may lead to higher ionic conductivity and would mean that any polymer membrane based on the phosphonate may have increased performance at higher temperatures relative to the acid salt. Tethering the phosphate does limit the group’s ability to provide a second mechanism of conductivity by vehicle-transport, however, increasing the chain length may improve this mode of conductivity.

**Imi-d-Pa – structure**

By tethering the acid group to the backbone of the polymer system, the need for a strongly protic liquid electrolyte may decrease. A model for this system is the Imi-d-Pa, which has both imidazole and phosphonate groups. The structure of this compound is shown in Fig. 1(d). Both end groups are known for their solid-state mobility, as characterized by solid-state NMR. Unsurprisingly, the model compound of Imi-d-Pa does not form a highly ordered system and a crystallographic structure solution is not available. To understand the structure of this novel material and the connectivity of the hydrogen bonds, the solid-state structure was determined quantitatively using the 2D DQ MAS NMR spectrum at 60 kHz MAS. The spectrum is shown in Fig. 7(a). The assignment of the resonances was determined through heteronuclear correlations. The solid-state structure of the Imi-d-Pa with four different hydrogen bonds and their connectivities are shown in Fig. 7(b). For comparison, a derivative of the Imi-d-Pa was produced which had a doubly protonated imidazole ring through the addition of HBr. The addition of HBr removes the imidazole ring as a hydrogen-bonding acceptor and reduces the compound’s ability to form multiple hydrogen bonds between different molecules.

**Imi-d-Pa – dynamics**

The $^1$H MAS variable temperature NMR spectra for Imi-d-Pa and the HBr adduct are shown in Fig. 8(a), (b). The $^1$H MAS variable temperature NMR experiments of Imi-d-Pa show no changes in the hydrogen-bonded region of the spectrum. This indicates that the material is rigid and the strong hydrogen bonding in this material would prevent effective transport of protons. The $^1$H NMR variable temperature response of the HBr adduct is different because of the lowered lattice energy. The narrowing of the aromatic resonances occurs at a lower temperature due to the ease of the imidazole ring flip about its $C_2$ axis. This can be seen in Fig. 8(b). It is notable that this differs significantly from the behaviour of the benzimidazole salts, where no aromatic ring flip is observed.

Coalescence of the lower frequency $\text{N–H} \cdot \cdot \cdot \text{O}$ and $\text{O–H} \cdot \cdot \cdot \text{O}$ hydrogen bonds in the HBr adduct begins at 350 K. At high temperature, the high frequency $\text{N–H} \cdot \cdot \cdot \text{O}$ hydrogen bond (16 ppm) becomes dynamic, and on the NMR timescale, shares the same chemical environment as the other hydrogen bonds. This is consistent with the significant line narrowing of the aromatic resonance of the imidazole rings, which indicates that the imidazole ring flip is occurring rapidly. The benzimidazole ring flip is highly temperature dependent and does not participate in the conduction of ions at lower temperatures. In contrast, Imi-d-Pa and other imidazole-based materials show facile cation dynamics, at temperatures comparable to those where phosphonate anion dynamics are observed.
The dynamics present in the HBr adduct are determined by the motion of the phosphonate group and imidazole ring. An illustration of the structure and the motion at higher temperature is shown as Fig. 9. The structure is governed by the hydrogen bonding of the imidazole rings and phosphonate groups. It is noteworthy that these dynamics again begin well below the documented melting point of >413 K for the HBr adduct. The proposed dynamics are based on the present study of alkyl phosphonate dynamics, where the mechanism is inferred, by analogy with the methyl and ethyl phosphonates, to be a $C_3v$ geometry. Similarly, the two-site imidazole ring flip has been characterized in related salts, and is thereby inferred here again. Interestingly, the variable temperature $^1$H MAS NMR spectra indicate simultaneous onset of these two dynamics processes, based on the synchronous line narrowing observed across the spectra.

CONCLUSION

Structural details of complex hydrogen-bonding motifs in a family of benzimidazole-alkyl phosphonate salts are deduced from $^1$H solid-state DQ MAS NMR data, achieved under fast MAS. Alkylation of the phosphate group is demonstrated to decrease the rate of reorientation of the anion in a series using $^{31}$P CODEX NMR. Additionally, the trend from an isotropic four-site motion of the phosphate itself, to an anisotropic three-fold reorientation about the carbon–phosphorus bond, common among the alkyl phosphonates studied to date. The promising indicator, for the further development of analogous anhydrous proton-conducting membranes, is the lowering of the lattice energy of the salts as the alkyl chain is lengthened, as measured by DSC. This correlated well with the earlier onset of line narrowing of the $^1$H NMR resonances, associated with proton exchange processes, as temperature was increased in the ethyl salt.

Finally, a model for the dynamics processes active in the HBr adduct of Imi-d-Pa is proposed on the basis of the combination of the imidazole ring flip and phosphonate three-fold reorientation. This correlation of the dynamics in prototype membrane materials such as Imi-d-Pa with model salts, such as benzimidolium methyl phosphonate, demonstrates the value of studies that probe the details of the dynamic process governing proton transport.
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