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Investigation of the conduction properties of phosphoric and sulfuric acid doped polybenzimidazole

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When complexed with a strong inorganic acid such as sulfuric or phosphoric acid, films of polybenzimidazole (PBI) show two types of behaviour, depending on the time of immersion in the corresponding acid bath. The first type, prepared at shorter doping times, has conductivity in the range 10^{-5}–10^{-4} S cm^{-1}, whilst the second, of conductivity $>10^{-3}$ S cm^{-1} is formed after more prolonged immersion. The 'switch-over' from one state to the other is at 10–11 h in H_3PO_4, and 2–3 h in H_2SO_4. PBI has a remarkable capacity to concentrate H_3PO_4 and, even in an acid bath of concentration 3 mol dm^{-3}, the acid concentration within a PBI membrane is *ca.* 14.5 mol dm^{-3}. IR spectroscopy performed on hydrated PBI membranes as a function of temperature, and on acid-complexed membranes as a function of the amount of sorbed acid confirms proton transfer from H_3PO_4 to the imino groups of PBI and, at high doping levels, the presence of undissociated H_3PO_4.

Complexation of polymers or copolymers containing ether, amine or amide groups with strong acids leads to the formation of a new class of proton conductors.[1–6] These materials can be shaped into membranes and their use in electrochemical devices including electrochromic systems,[7–11] hydrogen sensors[12] and fuel cells[13,14] has been demonstrated. In comparison with usual liquid electrolytes such as aqueous phosphoric or sulfuric acid, the polymer/strong acid systems have obvious advantages in terms of reduced leakage and corrosion problems and they represent less costly alternatives to perfluorinated polymers.

Polybenzimidazole (PBI) is a basic polymer ($pK_a = 5.5$[13]) which can readily be complexed by a strong acid, to give a so-called acid-doped[5,6] system. The immersion of a PBI film in aqueous phosphoric acid leads to an increase both in its conductivity and its thermal stability.[15] An alternative method has been reported in which PBI films are cast directly from a solution containing phosphoric acid.[16] Depending on the quantity of acid in the complex PBI/H_3PO_4, such systems have a conductivity between 5×10^{-3} and 2×10^{-2} S m^{-1} at 130 °C, and even 3.5×10^{-2} S cm^{-1} at 190 °C.[5] Importantly, the electro-osmotic drag number of PBI/H_3PO_4 is almost zero, and can be compared with the higher values of Nafion-117^{TM} (0.6–2)[17,18]and Nafion-117^{TM}/H_3PO_4 (0.2–0.6).[19,20] This particular characteristic of the PBI/H_3PO_4 complex is important in the context of the complex problem of water management in a fuel cell. A low level of gas hydration can be used without drying-out of the membrane, which in general simplifies operation at temperatures above 100 °C, while also assisting in reducing reactant crossover, of particular importance in search for membranes suitable for direct methanol fuel cells.[14] Although it is known that the conduction properties depend on the doping level of phosphoric acid in PBI, this aspect seems not to have been investigated systematically. We have previously reported briefly[21]on the dependence of the conductivity of PBI/xH_3PO_4 as a function of the acid content x. Here, we compare this behaviour with that of the analogous complex formed with sulfuric acid, PBI/xH_2SO_4. In addition, in an attempt to better understand the nature of the interaction between the components, we have used IR spectroscopy to studied films of the PBI/xH_3PO_4 series at temperatures up to 230 °C using FTIR spectroscopy. Emphasis is placed on the interplay between immersion time of PBI films, concentration of the acid bath and acid uptake, and conductivity, and is complementary to a recent IR spectroscopic study[22] of anhydrous PBI/inorganic acid blends, including the temperature activation of their conductivity.

Experimental

Polybenzimidazole (Celazole, PBI), phosphoric acid (85%), sulfuric acid (96%) and dimethyl sulfoxide (DMSO, 99%) were purchased from Aldrich. DMSO was stored over molecular sieves.

Viscous solutions of PBI were prepared in DMSO. Typically, PBI (1 g) was added to DMSO (10 mL) and the suspension heated under reflux for up to 2 h until complete dissolution was achieved. Films, of thickness 50–100 µm for conductivity measurements, *ca.* 20 µm for IR spectroscopic study, were then drawn from this solution on glass plates, and dried in a vacuum oven at 120 °C for 5 h. The membranes were released from their support by immersion in water, and were washed in dilute (0.1 mol dm^{-3}) phosphoric acid for 2 h at 40 °C in order to remove traces of DMSO.

Membranes were then treated at 20 °C by immersing them in baths of sulfuric and phosphoric acid, of concentration 0.1–10 mol dm^{-3} and, for each acid and each concentration, for periods of 1, 4, 8, 10, 12 and 24 h. Following this treatment they were rinsed briefly with water, and dried. Phosphorus and sulfur contents were determined by the Service Central d'Analyse Elémentaire of the CNRS at Vernaison, France. Water content was determined thermogravimetrically with a Stanton-Redcroft STA 781 balance using a heating rate of 5 °C min^{-1}. Thermal analysis with mass spectroscopic analysis of the decomposition products showed only water to be lost from PBI/H_3PO_4 blends below 400 °C.[23] IR spectra were recorded up to 230 °C on a Bomem DA8 FTIR spectrometer.

Membrane resistances were determined at 20 °C using a locally designed cell, which allows a column of liquid electrolyte (aqueous phosphoric or sulfuric acid) of variable length to be maintained between the film and the platinum black-surfaced platinum electrodes.[24] The cell constant was determined before each series of measurements using standard KCl solutions. The resistance $R_{\mathrm{cell/electrolyte}}$ of the (cell + liquid electrolyte), and the resistance R_{total} of the (cell + liquid electrolyte + membrane) were then measured for acid solutions of different concentrations or for different depths of electrolyte reservoir. The difference between R_{total} and $R_{\text{cell/electrolyte}}$ gives the membrane resistance R_m, in each case.

Results and discussion

Conductivity of PBI membranes in acid solution

The room temperature conductivity of PBI after soaking in H_3PO_4 of concentration up to 10 mol dm^{-3} for equilibration times of 1–16 h at 25 °C is shown in Fig. 1. In general, for all contact times, the conductivity increases rapidly at concentrations between 0 and 1 mol dm^{-3} before increasing more slowly and finally levelling off. However, the data of Fig. 1 show that under the conditions used, the PBI/H_3PO_4 complex clearly has two distinct types of behaviour, with an abrupt switch occurring for immersion times of more than 10–11 h. The cross-over to one or other of these two types of behaviour is independent of the concentration of the phosphoric acid bath and only depends on the duration of immersion. For contact times of <10 h, the conductivity attains a maximum value of *ca.* 5×10^{-5} S cm^{-1}, whilst above 10 h, a highly conducting state is reached with a conductivity of *ca.* 4×10^{-3} S cm^{-1}. The conductivity of PBI membranes in aqueous H_2SO_4 is represented in Fig. 2 as a function of the concentration of sulfuric acid, for different immersion times from 1 to 24 h. Insofar as two types of system are again observed, the PBI/H_2SO_4 complex resembles the phosphoric acid/PBI system, but the onset of the highly conducting state occurs at significantly shorter contact times, the switch occurring between 1 and 4 h. In the higher conductivity regime in each case, the membrane is very swollen, soft and flexible, and of limited mechanical strength. The highest conductivity observed both for sulfuric and phosphoric acid/PBI systems is comparable in magnitude to that of other polymer/acid blends, such as poly(acrylamide)/1.5H_3PO_4 (1.1×10^{-3} S cm^{-1}),[25] Nylon 6-10/2.5H_3PO_4 (1×10^{-3} S cm^{-1}),[26] and Elvamide/H_3PO_4,[27] and is consistent with values previously reported.[5,22]

Based on the results of Fig. 1 and 2, two immersion periods representative of the two states were chosen to study the conductivity of PBI over the electrolyte concentration range up to 14.7 mol dm^{-3} in H_3PO_4 (1 h, 16 h) and up to 10 mol dm^{-3} in H_2SO_4 (1 h, 5h), Fig. 3. The conductivity of the aqueous electrolyte is also reported for comparison, and is in agreement with literature data.[28] In all cases the conductivity both of the electrolyte and the membrane passes through a maximum. In phosphoric acid and for an immersion time of 1 h, there is little difference between the position of this maximum for aqueous H_3PO_4 solutions and for PBI/H_3PO_4. This implies that the concentration of H_3PO_4 within the membrane and that of the solution are very similar (see later), and also that the variation of the conductivity is determined by that of the absorbed acid. For this time of immersion, the conductivity of the PBI/H_3PO_4 complex is lower by a factor of 10^4 than that of phosphoric acid solutions at all concentrations. At a contact time of 16 h in phosphoric acid, the shape of the dependence of the conductivity is similar, but the maximum is displaced to higher acid concentration. In each case, for the membrane, the existence of a maximum in the conductivity dependence on concentration of electrolyte is characteristic of the presence of water (in addition to H_3PO_4 or H_2SO_4) in the membrane, and corresponds to an optimum solvation of cationic and anionic species. This effect was not observed in supposed anhydrous acid-doped PBI membranes, where the conductivity continuously increases with acid uptake.[22]

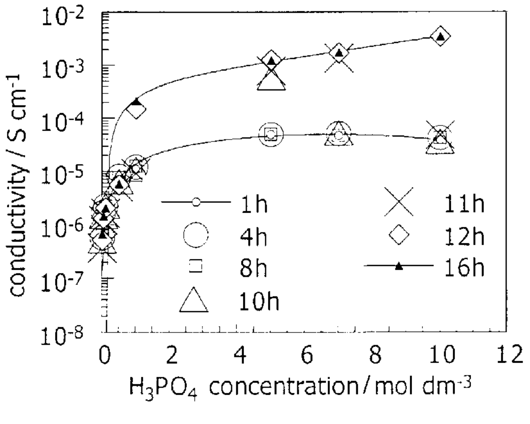

Fig. 1 Conductivity of PBI as a function of the H_3PO_4 concentration and for immersion times up to 16 h, 25 °C.

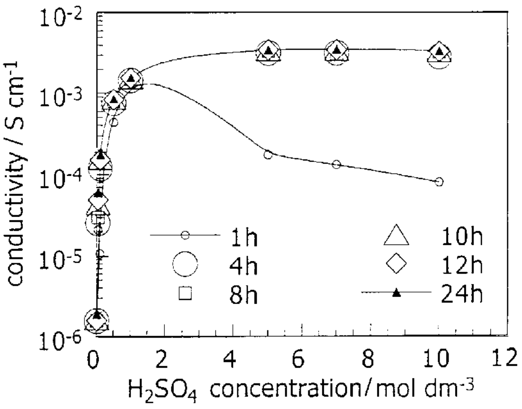

Fig. 2 Conductivity of PBI as a function of the H_2SO_4 concentration and for immersion times up to 24 h, 25 °C.

Doping level

Fig. 4 shows the uptake of phosphoric acid and sulfuric acid, expressed as the number of moles of electrolyte per polymer repeat unit, as a function of the acid concentration, for periods of immersion of 1 and 16 h (H_3PO_4) and 5 h (H_2SO_4). It can be seen that the uptake of phosphoric and sulfuric acid by PBI depends both on the acid concentration and on the duration of immersion, however it increases with increase in concentration of the acid bath for all immersion times studied. After 1 h, the number of moles of H_3PO_4 taken up lies between 0.02 (at phosphoric acid concentration 1 mol dm^{-3}) to 0.7 (10 mol dm^{-3}). For longer immersion times, the increase is more rapid and the number of moles of complexed H_3PO_4 attains 4.2 (10 mol dm^{-3}). These data complete and confirm those of Wainright *et al.*,[5,6] who have reported that after 16 h, 3.4 and 5 mol H_3PO_4 are taken up from acid baths of concentration 7 and 11 mol dm^{-3} respectively. The water content determined in membranes immersed in aqueous H_3PO_4 for 1 h (Fig. 4), decreases slightly from 1.8 to 1.3 H_2O per PBI repeat unit. After longer immersion times, the water uptake increases along with uptake of acid and, after 16 h of immersion the range determined experimentally is from 1.7 H_2O per PBI repeat unit (from 1 mol dm^{-3} H_3PO_4) to 4.7 H_2O per PBI (10 mol dm^{-3} H_3PO_4). The concentration of H_3PO_4 within the membrane may readily be calculated from these data, and is plotted in Fig. 5 as a function of the H_3PO_4 concentration of the acid solution for the two immersion times of 1 h and 16 h. After 1 h, the data points are distributed about a line of slope 1, which supports the variation of conductivity with acid concentration given in Fig. 3(a). For longer contact times however, the acid concentration in the membrane is systematically higher than that of the surrounding medium. For 16 h of immersion, this concentrating effect of PBI is particularly marked, and in fact above a solution concentration of 3 mol dm^{-3} the concentration of H_3PO_4 within the

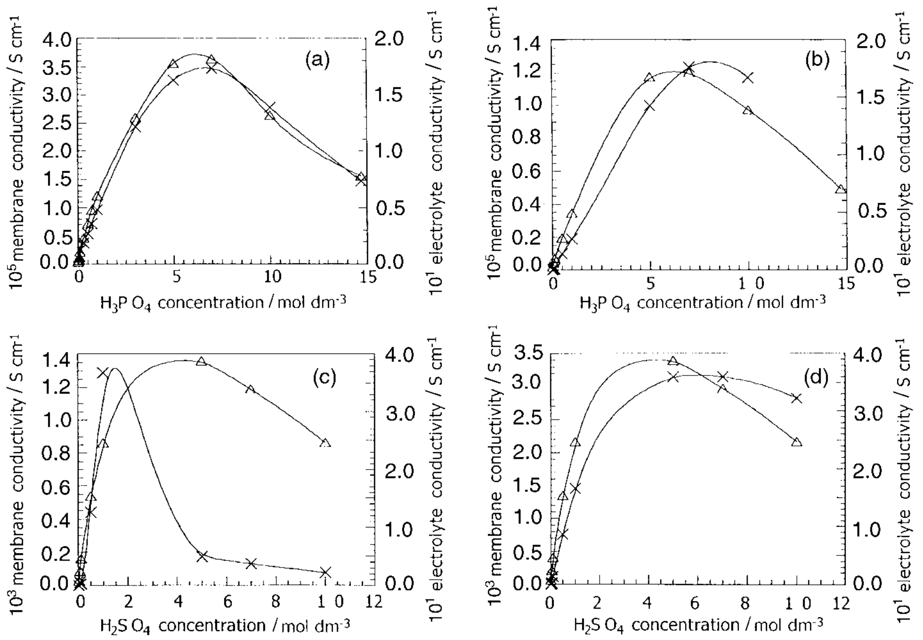

Fig. 3 Conductivity of PBI (○) and of aqueous electrolyte (×) as a function of electrolyte concentration, 25 °C: (a) H_3PO_4 1 h immersion; (b) H_3PO_4 16 h immersion; (c) H_2SO_4 1 h immersion; (d) H_2SO_4 5 h immersion.

membrane, 14.5 mol dm^{-3}, is close to that of concentrated phosphoric acid (H_3PO_4 85%: 14.7 mol dm^{-3}). Again, this is in agreement with the conductivity data of the membrane and bulk electrolyte of Fig. 3(b). The same concentrating effect of PBI with H_2SO_4 is observed after an immersion time of 5 h and is consistent with the shift of the conductivity maximum of the membrane with respect to the electrolyte solution reported in Fig. 3(d). The duration of immersion in phosphoric or sulfuric acid thus directly affects not only the amount of acid complexed, but also its resulting concentration in PBI.

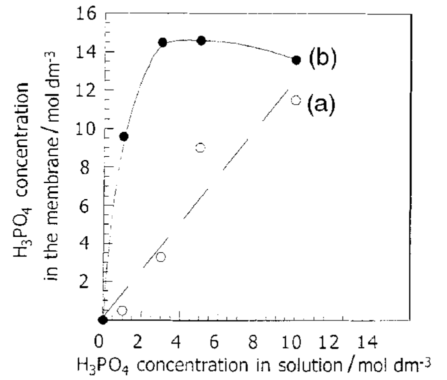

Fig. 5 Concentration of H_3PO_4 within a PBI membrane as a function of the concentration of the surrounding acid medium: (a) H_3PO_4, 1 h immersion; (b) H_3PO_4, 16 h immersion.

IR spectroscopic characterisation

Bouchet and Siebert[22] recently reported a complete IR spectroscopic study of anhydrous films of PBI/inorganic acid blends. The IR spectrum of PBI will be discussed before considering the changes brought about by hydration and complexation with H_3PO_4. The IR spectra of hydrated PBI recorded between 25 and 230 °C are shown in Fig. 6. Using the assignment published by Musto *et al.*,[29] the band at 3415 cm^{-1} can be attributed to the stretching vibration of free NH groups,

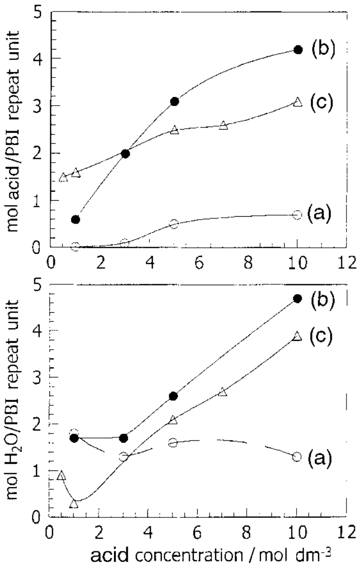

Fig. 4 Number of moles of (above) acid and (below) H_2O taken up per PBI repeat unit as a function of the concentration of the aqueous electrolyte: (a) H_3PO_4, 1 h immersion, (b) H_3PO_4, 16 h immersion, (c) H_2SO_4, 5 h immersion.

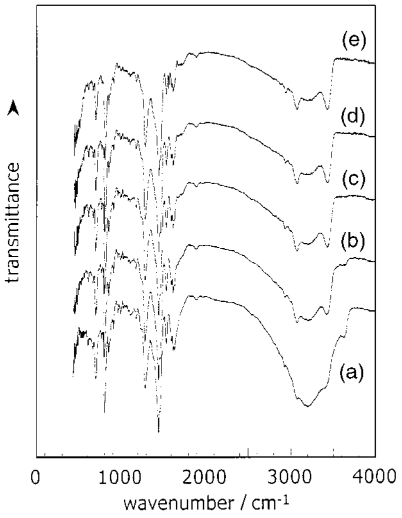

Fig. 6 IR spectra of a hydrated PBI film (a) at 25 °C, and after heating to (b) 50 °C, (c) 80 °C, (d) 120 °C and (e) 230 °C.

and the broad absorption centred at *ca.* 3145 cm^{-1} to hydrogen bonded NH groups. To higher frequencies, the band at 3625 cm^{-1} arises from the water of hydration of PBI. In this spectral range also, a weak band at 3063 cm^{-1} arises from the stretching vibration of aromatic C–H groups. In the mid-wavenumber domain, the region 1500–1650 cm^{-1} is characteristic of benzimidazoles,[30] in particular the C=C/C=N stretch at 1612 cm^{-1} and modes characteristic of the conjugation of benzene and imidazole (1590 cm^{-1}). Strong absorption at 1443 and 1543 cm^{-1} results from in-plane deformation of benzimidazole. The breathing mode of the imidazole ring gives a broad band at 1280 cm^{-1}. In-plane C–H deformation vibrations characteristic of substituted benzimidazoles are seen between 1230 and 1090 cm^{-1}. Two strong absorptions at 801 and 705 cm^{-1} are characteristic of heterocycles. As the temperature of the membrane is increased, the only significant changes are observed in the high wavenumber region. Thus the absorption at 3625 cm^{-1} progressively disappears and is absent at 80 °C and, concomitantly, the broad band assigned to hydrogen bonded NH stretching vibrations loses intensity. Loss of water thus reduces hydrogen bonding interactions N–H$\cdots$OH$_2$, although residual breadth at 230 °C shows the presence of self-associated –NH groups.[29]

The IR spectra of PBI/xH$_3$PO$_4$ with $x = 0.02$, 0.09, 0.5, 0.7 (1 h of immersion) and 4.2 (16 h immersion) are shown in Fig. 7. The uptake of phosphoric acid leads to profound spectral modification, in particular in the regions 2000–3500 and 800–1300 cm^{-1}, where wide spectral domains are obscured by absorption due to hydrogen bonding and vibrations of hydrogen phosphate groups, respectively. The regions 1250–1750 and 500–800 cm^{-1} are free of H$_3$PO$_4$ absorption, and can be analysed for more specific modification attributable to interactions between the two components, *e.g.* proton transfer or hydrogen bonding. Protonation of nitrogen on PBI will lead to the formation of H$_2$PO$_4^-$, the differentiation of which from H$_3$PO$_4$ in the region of the stretching vibrations ν(PO) is not easy. However, the absorptions at 870 {ν_s[P(OH)$_2$]}, 986 {ν_{as}[P(OH)$_2$]}, 1075 [ν_s(PO$_2$)], 1120 [ν_{as}(PO$_2$)] and 1173 cm^{-1} [ν_{as}(PO$_2$)] are all compatible with the presence of H$_2$PO$_4^-$. The further addition of H$_3$PO$_4$ ($x = 4.2$) leads to a spectrum very similar to that given by pure phosphoric acid with characteristic maxima at 890 and 1004 cm^{-1}.[31,32]

In the high frequency region (2000–3500 cm^{-1}), the intensity of bands assigned above to free and hydrogen bonded NH groups diminishes with addition of H$_3$PO$_4$, before becoming masked by the strong absorption ν(OH) of H$_3$PO$_4$ or its anions.

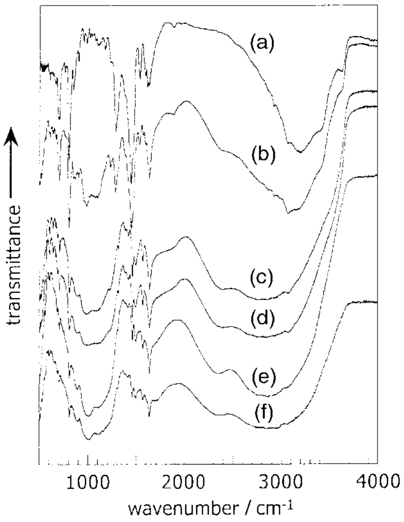

Fig. 7 IR spectra of (a) PBI, (b) PBI/0.02H$_3$PO$_4$, (c) PBI/0.09H$_3$PO$_4$, (d) PBI/0.5H$_3$PO$_4$, (e) PBI/0.7H$_3$PO$_4$ and (f) PBI/4.2H$_3$PO$_4$ recorded at 25 °C.

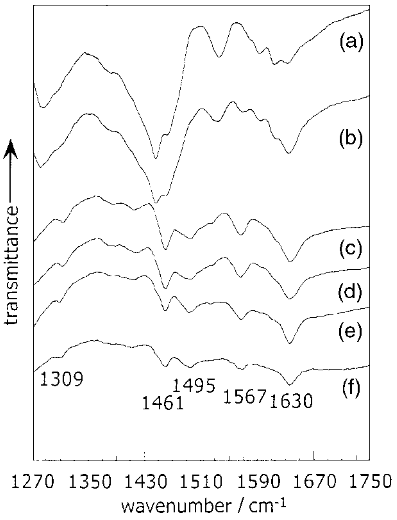

Fig. 8 IR spectra of (a) PBI, (b) PBI/0.02H$_3$PO$_4$, (c) PBI/0.09H$_3$PO$_4$, (d) PBI/0.5H$_3$PO$_4$, (e) PBI/0.7H$_3$PO$_4$ and (f) PBI/4.2H$_3$PO$_4$ in the region 1270–1750 cm^{-1} recorded at 25 °C.

The breadth towards the lower limit of this frequency range indicates the formation of strong hydrogen bonds between NH groups, H$_2$PO$_4^-$ ions and H$_3$PO$_4$.

Wasmus *et al.*[33] have suggested that protonation of PBI by phosphoric acid takes place on the imino nitrogen group of the polymer. In agreement with this, a shoulder to broad band near 2400 cm^{-1} can possibly be attributed to the stretching vibration NH$^+$.[34] The addition of phosphoric acid also induces an increase in intensity of bands at 1309, 1461, 1567 and 1630 cm^{-1}, and the appearance of a new signal at 1495 cm^{-1}, Fig. 8. This latter band can be attributed to the vibration ν(C=N) of the C=NH$^+$ group, resulting from protonation of the imino nitrogen atom. The absorptions at 1309, 1461 and 1567 cm^{-1} result from strong coupling between δ(NH) and ν(CN) as predicted by calculation of the potential energy distribution.[29] The presence of these five bands indicates modification of the electronic structure and electron delocalisation, made possible only by the protonation of the imino nitrogen site. These results are in agreement with the conclusions from ^{13}C and ^{31}P NMR spectroscopy published by Wasmus *et al.*[33]

In the above analysis, the presence of water has not, so far, been taken into consideration. As described above, water is associated with the phosphoric acid molecule, and can also contribute to its ionisation, with concomitant formation of oxonium ions. The absorption band at 3625 cm^{-1} assigned above to the stretching vibration of water is only observed at low doping levels of H$_3$PO$_4$. Above $x = 0.09$, this band is lost in the broad massif given by ν(OH) of H$_3$PO$_4$ and its anions. In super-cooled phosphoric acid, around 10% of the H$_3$PO$_4$ molecules are dissociated into H$_2$PO$_4^-$ and H$_4$PO$_4^+$[35,36] ions and proton conduction involves principally the former. In PBI/H$_3$PO$_4$ complexes, the protonation of imino sites increases the ionisation of phosphoric acid, with formation of H$_2$PO$_4^-$. However, in the most highly doped systems, and even in the presence of water, undissociated phosphoric acid is in equilibrium with ionic species, and the mechanism of proton transfer should be expected to be close to that of concentrated solutions or pure phosphoric acid.

Acknowledgements

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