Elucidating interactions of ionic liquids with polymer films using confocal Raman spectroscopy

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Received (in Cambridge, UK) 1st February 2005, Accepted 29th March 2005
First published as an Advance Article on the web 8th April 2005
DOI: 10.1039/b501507c

We report on the molecular interactions between room-temperature ionic liquids (RTILs) and Nafion® and PDMS membranes, proving that in contact with these polymers RTILs behave like electrolytes rather than solvents.

The combination of room-temperature ionic liquids and polymeric membranes has created unique barrier materials that have opened up the opportunity for cleaner separation processing technologies in the chemical and pharmaceutical industries,[1–3] as well as novel concepts where conductive transport barriers are required, such as in fuel cell technology.[4] For example, ionic liquids supported in a porous membrane structure yielded a separation selectivity for isomeric mixtures of amines otherwise not attainable,[1] while the immersion of charged Nafion® membranes in ionic liquids has been reported to result in membrane properties that could open up new strategies for the design of fuel cells.[5] While the use of polymer films in combination with room temperature ionic liquids (RTILs) has been recognized as opening up new opportunities for "green" processing, which are still in the beginning of being explored, the underlying interaction phenomena between ionic liquids and the membranes have not been elucidated hitherto. This can be attributed to the complex possible interactions, as ionic liquids consist of ions but possess a polarity in the range of polar organic solvents.[6] According to conventional understanding, this contradictory behaviour of ionic liquids impedes the prediction of the interaction of ionic liquids with other matrices, in particular with complex systems such as cross-linked membrane polymers.

For example, it was observed from swelling experiments that proton-conducting polymers such as those used for fuel cell applications apparently take up to 18–32% of ionic liquid, explained by electrostatic interactions and supposedly resulting in a new polymer–ionic liquid composite of improved ionic conductivity.[5] Non-charged polymers such as polydimethylsiloxane or polyvinylalcohol, however, apparently were not penetrated by ionic liquids.[2] So far, however, all observations have been merely macroscopic and do not provide any evidence, on the molecular level, on whether or how ionic liquids in fact dissolve into polymer matrices. Selecting two common membrane materials, we show for the first time that, despite being considered solvents, ionic liquids can behave as electrolytes and not as solvents when interacting with membrane polymers. This observation has significant impact on perceiving new separation processes involving both materials, as well as interpreting the occurring transport phenomena.

Confocal Raman spectroscopy allowed us to elucidate *in-situ* such interactions, taking advantage of the spatial resolution of the confocal microscope.[7] One of the most important advantages of confocal Raman microscopy is that the vibrational energy of the target solutes serves as a reporter, thereby avoiding the need for invasive monitoring aids such as molecular probes as is the case, for example, in confocal scanning laser microscopy.[7] Information on the relative concentration of a target solute at different depths inside a membrane polymer matrix can hence be gathered by simply moving the focalization spot across the membrane depth.[8] However, with increasing penetration of the membrane polymer the Raman signal typically diminishes strongly owing to the Raman scattering as well as attenuation of the excitation laser power. Although any attenuation was taken into account, the optical transparency of the materials which we selected for this work eliminated these inherent problems associated with confocal Raman spectroscopy. In this way, it was possible to focus the laser inside the membranes without damaging the polymer, while maintaining a high selectivity and sensitivity. The spatial resolution of the optical system employed allowed furthermore elimination of any signal from ionic liquid possibly adsorbed on the membrane surface.

The present study involved RTILs based upon the 1-n-butyl-3-methylimidazolium cation, $[BMIM^+][X^-]$, with X = PF_6 (hexafluorophosphate); BF_4 (tetrafluoroborate); NTf_2 (bis-((trifluoromethyl)sulfonyl)imide, $(CF_3SO_2)_2N$); and NO_3 (nitrate). These imidazolium-based RTILs were selected owing to the excellent resolution of their Raman spectra, high signal-to-noise ratio, and because their properties have been widely reported in the literature. RTILs were synthesized as reported elsewhere.[9] To obtain the Raman spectra of the membrane materials, thick slabs of membranes (about 130 μm in the case of Nafion® and about 160 μm in the case of PDMS) were placed horizontally between a microscope slide and a cover slip. A corresponding procedure yielded the Raman spectra of the RTILs. For studying the interaction of RTIL with the respective membrane, the latter was infused in the RTIL during about four days at room temperature, blotted carefully with a smooth tissue upon removal from the RTIL in order to discard any excess liquid, and subsequently prepared for analysis as mentioned above.

Both the Nafion® and the PDMS membranes proved to be transparent to laser; in the case of Nafion®, no appreciable absorption of radiation by the material was observed across the whole membrane thickness. For both membrane materials, the characteristic Raman lines could therefore be detected with similar intensity from the surface of the membrane (0 mm) to its interior (about 65 μm). The practical in-depth resolution of the confocal

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Raman system was obtained by using the classical calibration method.[10] The axial resolution of the optical equipment was measured at the air/silicon interface as a function of the experimental conditions and determined to be in the order of 9 μm, thus, signals from more than 4.5 μm beyond the confocal plane did not affect the actual signal. It should be pointed out that this resolution is not identical to the optical resolution of the confocal microscope, which is far lower. It is rather a measure of how much the signals from beyond the confocal plane contribute to the signal of interest, which is not of primary interest for the more common biological applications of the method, but in this work is indispensable information.

Fig. 1 presents the spectra of the four RTILs studied. In all spectra the vibrational lines of the cation appeared at approximately the same frequencies as previously reported such that common cation lines could be distinguished from the different anion frequencies.[11] For [BMIM$^+$][PF$_6^-$] (Fig. 1A) and [BMIM$^+$][BF$_4^-$] (Fig. 1B), the predicted strong Raman vibration lines for the anion in each case appear at 743 cm^{-1} and 766 cm^{-1}, respectively, as expected.[12] For [BMIM$^+$][NTf$_2^-$] (Fig. 1C), the number of lines deriving from vibrational modes of the anion is higher due to the complexity of the molecule and major lines can be observed at 750, 1142, and 1249 cm^{-1} that are tentatively assigned to a strong vibration line from the CF$_3$ group;[12,13] to a symmetric SO$_2$-stretching as well as a C–F stretching;[14,12] a symmetric SO$_2$-stretching in sulfonyl fluorides,[12] respectively. For [BMIM$^+$][NO$_3^-$], a strong nitrate band can be observed at 1043 cm^{-1} identical to that determined for nitrate in aqueous solution.[12,15]

Two membranes were investigated in this work, namely Nafion®, a sulfonated polytetrafluoroethylene, and polydimethylsiloxane (PDMS). These membranes were chosen due to their different physico-chemical characteristics: PDMS, a non-charged, hydrophobic membrane polymer commonly used in separations and microdevices,[16–18] is not penetrated by electrolytes but swollen by organic solvents;[16] Nafion®, on the other hand, is an example of an ion-conducting membrane that, depending on the degree of crosslinking, can possess a low permeability for non-charged organic molecules.[19] After contact with the ionic liquids, these two membrane polymers were analyzed with regard to uptake of ionic liquid with the confocal Raman microscope. The spatial resolution of the optical system was in the order of 9 μm (depth of focus) which allowed detection of the presence of ionic liquids within the membrane (at about 65 μm) without the signal being affected by residues of RTIL inevitably remaining adsorbed on the membrane surface during preparation of the sample. In Nafion®, all bands representing BMIM$^+$ could be clearly identified, suggesting a considerable uptake of [BMIM$^+$][PF$_6^-$] (Fig. 2B). However, the band of PF$_6^-$ was not detected (743 cm^{-1}). Because Nafion® presents a band at a similar frequency (733 cm^{-1}, Fig. 2A), it remained unclear whether the band for PF$_6^-$ was masked by that of the membrane polymer, or whether it was in fact absent. We therefore verified the possible absence of the anion

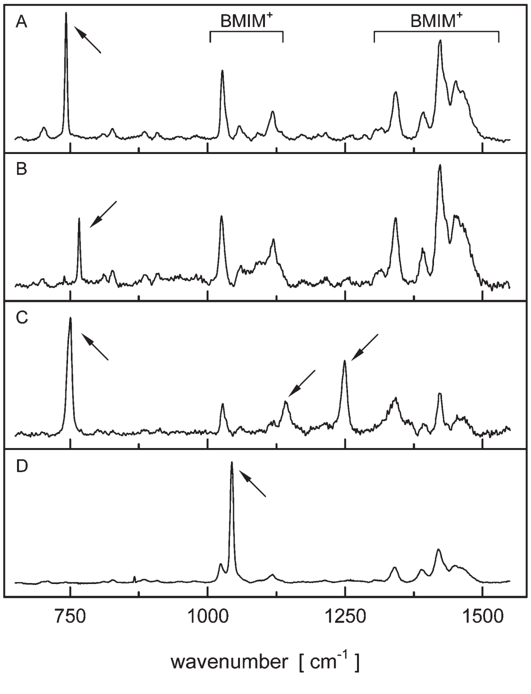

Fig. 1 Raman spectra of the four ionic liquids studied: A: BMIM$^+$ PF$_6^-$; B: BMIM$^+$ BF$_4^-$; C: BMIM$^+$ NTf$_2^-$; D: BMIM$^+$ NO$_3^-$. The typical groups of bands of the BMIM$^+$ cation are indicated while bands corresponding to the anion are emphasized by arrows.

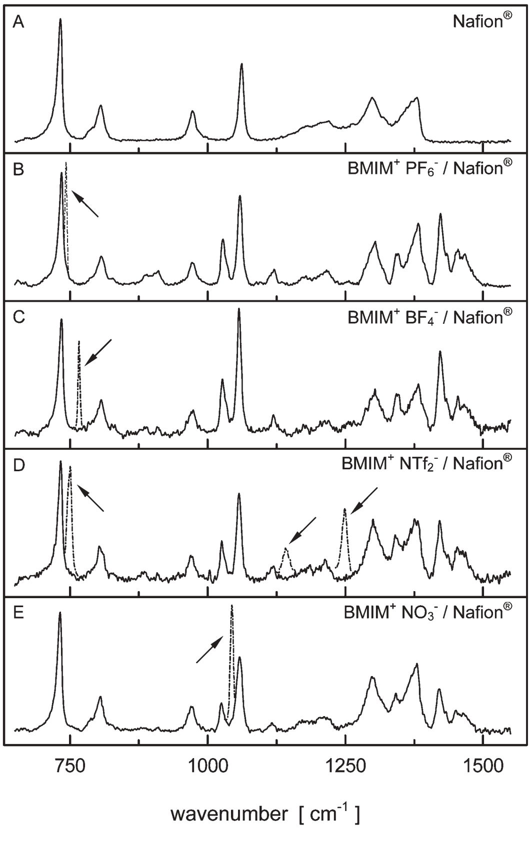

Fig. 2 Raman spectra of Nafion® membrane alone, and Nafion® containing each of the four ionic liquids studied. A: Nafion®; B: BMIM$^+$ PF$_6^-$ in Nafion®; C: BMIM$^+$ BF$_4^-$ in Nafion®; D: BMIM$^+$ NTf$_2^-$ in Nafion®; E: BMIM$^+$ NO$_3^-$ in Nafion®. The spectra show the typical bands for both Nafion® and the cation BMIM$^+$ (solid lines) while no bands for the anions could be detected inside the membrane polymer. The theoretical positions of the anion bands are shown as dotted lines and indicated by arrows.

in the membrane using ionic liquids of the same cation $BMIM^+$ but containing anions whose bands are clearly distinct from those of Nafion®, namely BF_4^-, NTf_2^-, and NO_3^-.

Figs. 2C–E clearly demonstrate that the cation $BMIM^+$ is present inside the membrane, whereas the respective anion is absent (dotted lines). This observation proves that a cation-exchange process takes place between the counter-cation of the membrane and the ionic liquid cation. Such an observation contradicts what has been stated previously in the literature,[5] namely that ionic liquids dissolve as a whole in ion-exchange membranes such as Nafion®, presumably owing to cluster formation.

When in contact with a non-charged hydrophobic polymer, such as PDMS which is known to be unpermeable to electrolytes,[16,18] it might be expected that RTILs still dissolve owing to their solvent-like properties. It should be noted that PDMS is reported to dissolve non-charged molecules up to the size of chrysene ($C_{18}H_{12}$).[20] Interestingly, after contacting PDMS with the RTILs, no evidence for the presence of either the anions or the cation was found in PDMS membranes. This demonstrates for the first time at the molecular level that RTILs may not penetrate non-charged polymer networks where electrostatic interactions cannot be established, at least not in detectable amounts.

Our study proves that RTILs in contact with membrane polymers may behave exclusively as electrolytes and not as organic solvents despite sharing the properties of both when in the pure state. For emerging clean separation processes involving the recovery of solutes from RTILs by non-charged polymeric membranes, such as polydimethylsiloxanes, this implies facing the unique situation that the bulk solvent (the RTIL) does not affect the chemical stability and transport properties of the separation barrier; the separation process can hence be entirely tailored to the target solutes, which is a significant advantage over conventional separation processes employed until today. When RTILs are contacted with ion-conducting polymers, an ion-exchange process must be anticipated rather than the formation of novel composites, an observation which also has an impact in fuel cell and sensor applications.‡

This work was supported by the Fundação para a Ciência e a Tecnologia, Portugal by project grant POCTI/QUE/39061/2001 as well as by post-doctoral grants BPD/14414/2003 (R.D.P.) and BPD/7172/2001 (T.S.); we thank C. A. M. Afonso for kindly providing samples of the RTILs.

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Notes and references

‡ The Nafion® membrane was a Nafion® 117 purchased from FuelCellStore, USA, and used in its protonated form. PDMS-membranes were prepared from Dehesive® 942 (Wacker, Germany) according to the manufacturer's instructions. Raman spectra were measured at room temperature with 413 nm cw excitation using a Kr^+ laser (Coherent Innova 302). The excitation power was *ca.* 3 mW at the sample. The spectra were recorded in a LabRAM HR confocal Raman spectrometer (Jobin Yvon), equipped with a liquid nitrogen cooled CCD camera. The resolution was set to 3 cm^{-1}, and one scan of 60 s was the total accumulation time of the spectra measured. The increment per data point was 0.5 cm^{-1}. Raman spectra were obtained by using an objective (WD = 470 μm) with a magnification power of 50x and a numerical aperture of NA = 0.75.

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