Photoswitchable Imidazolium based Spiropyrans- A physicochemical study

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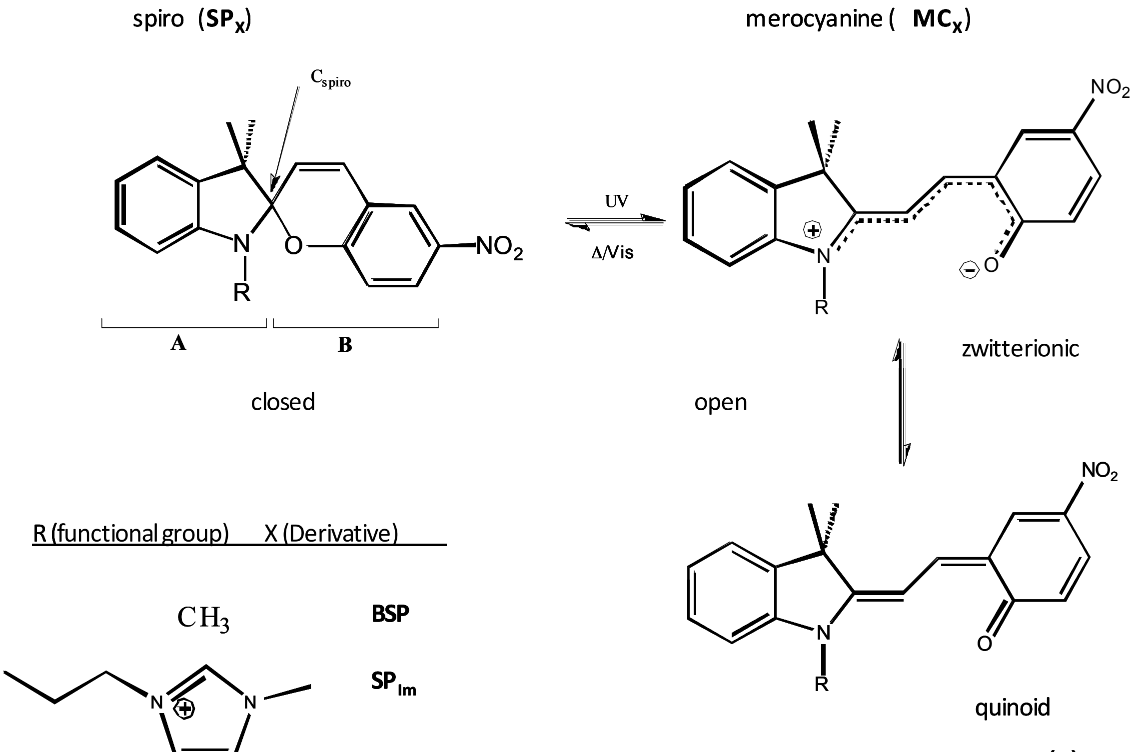
Abstract

We investigate the photo, solvate and thermochromic properties of a novel photoswitchable spiropyran derivative; **SP$_{\mathbf{Im}}$** in imidazolium based ionic liquids (ILs). **SP$_{\mathbf{Im}}$** was prepared by alkylation of the photoswitchable compound to an imidazolium cation and is added to imidazolium based ILs with increasing chain length to examine the stability of funtionalised cations its merocyanine **(MC)** and spiropyran **(SP)** forms and compared to standard spiropyran; **BSP**. The rate of thermal relaxation of the new derivative is found to be about ten times faster than that of **BSP** as reflected in rates of 13.9 $\times10^{-3}s^{-1}$ and 1.0 $\times10^{-3}s^{-1}$ for **SP$_{\mathbf{Im}}$** and **BSP** respectively in [C_6mIm][NTf_2]. Since ILs are believed to form nano-structured domains it is proposed that the covalent attachment of the imidazolium side group of **SP$_{\mathbf{Im}}$** fully integrates the photoswitchable moiety into the non-polar region through side-chain association. In contrast, unbound **BSP** is relatively free to migrate between both polar and non-polar regions and the **MC** form is more readily stablised by the IL charge via through space interactions and spontaneous movement to charged nano-domains leading to enhancement of the **MC** lifetime. At higher concentrations, rheological and transport properties were investigated to determine the impact of covalent attachment of the **BSP** fragment to an imidazolium cation had upon the ionic liquid structure. Ionic Conductivity was found to decrease by up to 23% for **SP$_{\mathbf{Im}}$** with effects increasing with cation side-chain length. Unlike **BSP**, the photoswitching of the **SP$_{\mathbf{Im}}$** did not affect conductivity or viscosity values. This may indicate that the mobility of the photoswitchable compound and the resulting disruption of such movement may be critical to the evolution of this physical property.

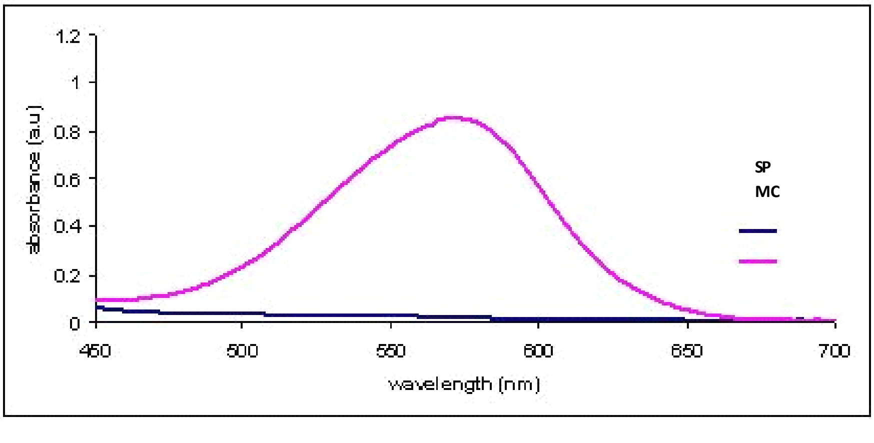
Introduction

The 'designer' aspect of ionic liquids (ILs) refers to the potential they offer to create new and versatile liquids with tunable characteristics and functionalities. This is primarily due to the ability form these liquids from an extensive range of cations and anions, thereby enabling the production of ionic liquids with specific properties. According to recent estimations, the number of potential anion-cation combinations available equates to around one trillion (10^{12}) different ILs.[1] Their proposed applications include recyclable solvents[2, 3], molecular solvent replacements for catalysis,[4] electrochemistry,[5] synthesis[6] and elemental analysis[7]. Past reviews have provided detailed insight into the synthesis and properties of ILs and have promoted their implementation as common laboratory solvents.[8] However, ILs may also provide suitable platforms for the production of functional materials with user-defined properties. Several groups have proposed the synthesis of 'task specific ionic liquids' based upon such liquids.(REFS) Ohno *et al* reviewed several such methods whereby IL properties were designed for specific end uses.(REF) Of particular interest was the formation of zwitterionic ionic liquids Recent studies of structuring within ionic liquids by our group employed spiropyran derivatives with polar and non-polar functional groups to encourage specific location within the liquid domains.[9] It was found that the interactions with the ions allowed for the spiropyran moiety to be located in distinctly different regions and report on them through thermodynamic and kinetic parameters. It is therefore intuitive that the next stage be the addition a functional group with matched the IL ions exactly and determine the effect of such integration into the liquid structure.

Photochromic materials based on the spirocyclic compound spiropyran are known to be photoactive, forming merocyanines (**MC**), when exposed to UV irradiation. Two derivatives (figure 1a) were chosen for our study, a well known commercially available spiropyran (**BSP**), and a novel derivative we synthesised (**SP$_{\mathbf{Im}}$**). **SP$_{\mathbf{Im}}$** is essentially **BSP** with an imidazolium cation attached to the nitrogen of the indoline (**A)** fragment of the compound. Photoswitching of spirocyclic compounds (figure 1a) involves the use of UV light (365-375nm) to induce cleavage of the SP_3 hybridised carbon of the indoline ring (known as C_{spiro}) and the adjoining oxygen of the pyran fragment (**B**). **BSP/SP$_{\mathbf{Im}}$** is an uncharged molecule with the indoline fragment (**A**) orthogonal to its pyran fragment (**B**). Cis-trans isomerisation of the molecule results in a planar molecule with a delocalised charge across the molecule forming a zwitterionic/quinoid system.[10] The resulting delocalisation of charge also shifts the absorbance of the molecule into the visible region of the spectum allowing for spectroscopic verification of the switching process (figure 1b). The compound can also be returned to its closed, colourless form by irradiation with white light or through thermal reversion in the dark. This type of relaxation occurs when the **MC** uses heat from its surroundings to supply sufficient energy for the reorientation to occur. The process of relaxation of the **MC** isomer to the closed spiro form follows first order kinetics.



(a)



(b)

Fig. 1 (a) Basic structure of spiropyran derivatives indicating indoline (A) and pyran (B) fragments and photoswitchingprocess between closed (**SP**) and open (**MC**) forms for each derivative (X) based on functional groups (R) added to base structure. (b) Ring opening and closing of $\mathbf{SP_{Im}}$ in C_4mIm NTf_2. Compound clearly transitions between colourless (**SP**) and coloured (MC) forms.

The **MC** isomer is sensitive to its molecular environment and the equilibrium between both isomers is regulated by specific and non-specific solvent-solute interactions.[11-14] In molecular solvents, a polarity-kinetic relationship is observed for **BSP** with increasing rate constants observed with decreasing polarity.[15] Kamlet-taft parameters determined that this is due to decreasing levels of hydrogen bonding between solvent and spirocyclic compounds.[16] $\mathbf{MC_{BSP}}$ is known to form hydrogen bonds therefore inhibiting its rate of thermal relaxation. Similar trends to those observed in molecular solvents imply that **BSP** can act as a solvent sensitive probe in ionic liquids.[17, 18] We previously reported the photo- and solvato-chromic properties of **BSP** in ILs containing $[NTf_2]^-$. It was found that the kinetics and thermodynamics of the $\mathbf{BSP}$-$\mathbf{MC_{BSP}}$ equilibrium was sensitive to the nature of the cation. It was also observed that the cation, $[C_2mIm]^+$ can form a through-space orbital interaction with the merocyanine isomer, rather than a simple electrostatic interaction, thus inhibiting the merocyanine conversion back to the **BSP** isomer.

Recent studies propose that imidazolium based ILs may form ordered systems resembling psuedo-crystalline systems based on stacking of mutual charges (aggregation) or ordered association of cations to surrounding anions and vice versa.[19, 20] Lopes et al computationally examined these nanostructured domains in ILs and found that the ILs can be divided into two specific regions: a polar region consisting of imidazolium head groups and anions and a non-polar region where side groups extend into space (figure 2).[21] The polar head groups are believed to interact with one another, forming aggregates by hydrogen bonding, electrostatic interactions, π-H interactions and π- π stacking resulting in three-dimensional arrangements. Alkyl side-chains are believed to interact with one another through van der Waals interactions to form a complex network of non-polar regions.

The **MC** isomer of both **BSP/SP$_{\mathbf{Im}}$** provides a highly polar system which can interact with the opposing charges of the polar head groups of the solvent system, whereas the closed, spiro isomer is known to be a neutral non-polar molecule and should reside in the non-polar region of the IL. As thermal relaxation occurs, the molecule would be expected to migrate from polar regions, to non-polar regions, as the charged **MC** isomer reverts to the uncharged **SP** form. This diffusion effect has been observed by spectroscopic monitoring of lipid bilayers in water.[22] The similarity between this ordering and the proposed ordering of ILs makes the migration process an ideal method to examine the existence of such regions and their effects on photochromic systems. Increasing the length of the non-polar side-chain of the imidazolium ion (figure 3) is believed to affect the ordering of the IL at the molecular level. This may be due to the increased volume of non-polar regions and related increased dispersion and corresponding expansion of polar regions arising from dissociation of imidazolium head groups from one another. Since the **MC** isomer is believed to interact with polar regions, it is anticipated that increasing the surrounding non-polar regions could possibly influence the equilibrium by favouring the **SP** form of the molecule. If structured polar domains exist, then their stabilising influence on **MC** should compete with such effects and thereby lead to much slower rates of thermal relaxation expected for liquids comprised of such long-chain, non-polar entities. We previously reported the application of designer molecular probes to locate themselves within specific nano-domains. In the case of **SP$_{\mathbf{Im}}$**, it can be hypothesised that the imidazolium functional group, now attached to the spiropyran, would interact fundamentally with the IL nano-structure. The imidazolium group should, in theory, associate and order itself within these polar nano-structured regions of the IL, and thus orientate the spiropyran fragment into the non-polar region. This ordering would in theory produce an inherently photoswitchable IL as the photochromic compound is now an essential component of the IL itself. Furthermore, this also should anchor the spiropyran in the non-polar region of the IL nano-structure which is not favourable to **MC** formation and inhibit its ability to migrate between regions of the IL.

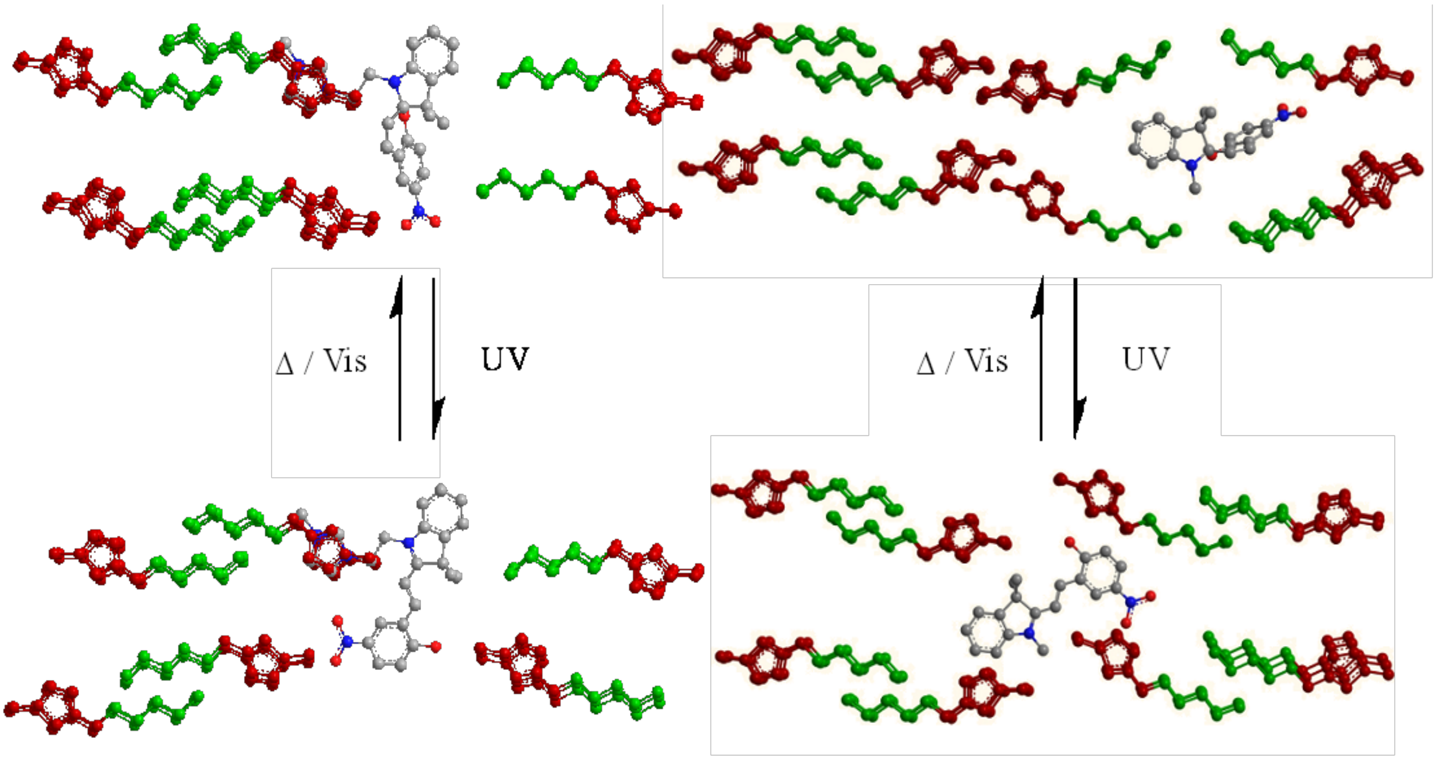


Fig. 2 Schematic of proposed 3D ordering of imidazolium cations with **SP$_{Im}$** (left) and **BSP** (right) in [C_6mIm][NTf_2] showing preferred residence of the MC (lower) and SP (upper) forms of the probe in polar (red) and non-polar regions (green), respectively.

Figure 2 illustrates such proposed effects whereby the increased interactions of the imidazolium moiety of **SP$_{Im}$** with the IL cations results in the restriction of the spiropyran moiety. As such, the photoswitching process of the spiropyran results in reordering of the liquid structure to accommodate the changes in conformation upon **MC$_{SPIm}$** formation. Because the photoswitchable moiety is anchored it its movement is inhibited and so the liquid is required to reorientate to associate with the resulting zwitterion charges. **BSP**, which has minimal complimentary associations is relatively free to migrate between polar and non-polar domains upon photoswitching to stabilise the different forms of the photoswitchable compound. The IL structure is therefore preserved since the **BSP** molecules are able to interact with the existing nano-structured domains of the liquid.

Thermodynamic and kinetic studies were carried out to examine the effect the integration of the photochromic compound into the IL structure has upon on rates of thermal relaxation, solvent reordering and the overall stability/equilibrium of both forms of the spiropyran derivatives.

R = ethyl: $[C_2mIm]^+$
butyl: $[C_4mIm]^+$
hexyl: $[C_6mIm]^+$
octyl: $[C_8mIm]^+$
decyl: $[C_{10}mIm]^+$
dodecyl: $[C_{12}mIm]^+$

Fig. 3 Cations and anion used in this study. 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide $[C_nmIm][NTf_2]$.

Cations with increasing chain lengths (figure 3) were chosen to examine the effect of increasing cation-cation interactions and dispersion of polar regions as proposed by Lopes *et al*[21] upon the thermodynamic and kinetic parameters of the integrated $\mathbf{SP_{Im}}$ molecules and comparison to **BSP** from similar experiments[23]

Experimental

ILs were synthesised and purified by metathesis of imidazolium cation and bis(trifluorosulfonyl)imide salts ($[C_4mIm]^+$-$[C_{12}mIm]^+$ and $[NTf_2]^-$) obtained from Sigma-Aldrich using previously reported techniques.[24] ILs were stored under argon due to the hygroscopic nature of these liquids. Spectrometric studies were carried out using a Perkin Elmer Lambda 900 spectrometer (Foss Ireland) with Perkin Elmer PTP-1 temperature controller. Samples were irradiated with UV light at 375 nm by UV LEDs (Roithner Lasertechnik, Vienna, Austria). Conductivity measurements were determined by electrochemical impedance between 10 MHz and 0.1 Hz on a Solartron SI 1296 Dielectric interface and Solartron SI 1270 frequency response analyzer. Viscosity measurements were determined using an Anton Paar AMVn rolling ball viscometer. 6-Nitro-1’,3’,3’-trimethylspiro[2H-1-benzopyran-2,2’-indolin] 1’,3’-Dihdro-1’,3’,3’-trimethyl-6-nitrospiro (**BSP**) (Sigma-Aldrich chemicals) was used as purchased and used with no further purification.

Synthesis and characterisation of SP_{Im}

NMR spectra were carried out on a Bruker AVANCE instrument using XWINMR software processed on a Silicon Graphics O2 workstation. The instrument operated at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Mass spectra were recorded on Bruker ESQUIRE LCMS instrument. TGA analysis was conducted using a Perkin-Elmer Pyris TGA in a flowing dry nitrogen atmosphere (50 mL / min.) between 25 and 800 °C with a heating rate of 10 °C / min. DSC traces are presented using the convention of endothermic as up and exothermic as down. All scans were carried out at a heating/cooling rate of 10 ^{o}C /min in the range of -150 ^{o}C – 200 ^{o}C using a TA Q100 series calorimeter.

A. **1-(3-bromoethyl)-2,3,3-trimethylindolenium bromide** was synthesized according to previously published procedure.[25]

B. **1́ - (3″-bromoethyl) - 3́,3́ – dimethyl - 6 -nitrospiro –[2*H*-1-benzopyran-2,2́-indoline] (SP-Br)**

A solution of 1-(3-bromoethyl)-2,3,3-trimethylindolenium bromide (2g, 5.76 mmol) and ethanol (15 ml) was added slowly to a suspension of 5-nitrosalicylaldehide (1g, 5.76 mmol) in ethanol (5 ml). To the reaction mixture was added triethyl amine (0.63g, 5.76 mmol). The reaction mixture was stirred and refluxed over 4 h under nitrogen. The solvent was removed under vacuum and the resulting crude dark brown compound was purified by silica/hexane:ethylacetae 10:1 to afford a bright light yellow compound, 0.23g, yield-10%. Analytical data; ^{1}H NMR (400 MHz) δ ($CDCl_3$): Analytical data; ^{1}H NMR (400 MHz) δ ($CDCl_3$): 1.11 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 3.31-3.61 (m, 4H, 2 x CH_2), 5.86 (d, H, J = 10.4 Hz, CH), 6.52 (d, H, J = 7.6 Hz, Ar-H), 6.67 (d, H, J = 9.2 Hz, CH), 6.85 (m, H, Ar-H), 7.04 (d, H, J = 7.2 Hz, Ar-H), 7.12-7.16 (m, 3H, Ar-H), 7.95 (m, 2H, Ar-

H), ^{13}C NMR ($CDCl_3$) δ (ppm): 19.83, 25.88, 29.83, 45.60, 53.00, 106.29, 106.54, 115.61, 118.48, 120.24, 121.75, 122.13, 122.88, 126.06, 127.90, 128.58, 135.84, 141.19, 145.95, 159.16. (m/z ion) calculated for 415.06 $(M+H)^+$ and found 415.2 $(M+H)^+$.

C. 1́ - (3″-methylimidazolioethyl) - 3́,3́ – dimethyl - 6 -nitrospiro –[2*H*-1-benzopyran-2,2́-indoline] bromide (SP-Imidazolium)(9).

1́ - (3″-bromoethyl) - 3́,3́ – dimethyl - 6 -nitrospiro –[2*H*-1-benzopyran-2,2́-indoline] (SP-Br) (1.11g, 2.67 mmol) was treated with 1-methyl imidazole (0.87g, 10.69 mmol) in (acetonitrile: DMF, 1:1) (15 ml). The reaction solution was heated to 100 ºC, and left to stir over 15 h. The resulting dark red solution was cooled down and washed with ether several times to remove starting material. The resulting light brown solid was filtered off and purified by silica/chloroform:methanol, 3:1, to afford a red neat compound, 0.8 g, yield -60 %. Analytical data; ^1H NMR (400 MHz) δ ($CDCl_3$): 1.07 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 3.64 (t, 2H, CH_2), 3.93 (s, 3H, CH_3), 4.50-4.65 (m, 2H, CH_2), 5.78 (d, H, $J =$ 12 Hz, CH), 6.37 (d, H, $J = 4$ Hz, Ar-H), 6.63 (d, H, $J = 8$ Hz, CH), 6.76 (m, H, Ar-H), 6.92 (d, H, $J =$ 8 Hz, Ar-H), 6.98-7.02 (m, 3H, Ar-H), 7.52 (s, H, Ar-H), 7.61 (s, H, Ar-H), 7.85-7.89 (m, 2H, Ar-H), 10.01 (s, H, Ar-H). ^{13}C NMR ($CDCl_3$) δ (ppm): 19.92, 26.02, 36.65, 44.38, 49.22, 52.61, 106.24, 106.48, 115.47, 118.44, 120.83, 121.13, 122.12, 122.97, 123.20, 123.54, 125.92, 127.83, 129.07, 135.71, 137.33, 141.04, 146.03, 158.99. (m/z ion) calculated for 497.11 $(M+H)^+$ and found 497.00 $(M+H)^+$, 417 $(M-Br)^+$, 335.20 $(M\text{-Imidazolium ring})^+$.

Differential scanning calorimetry: m.p: 138.6ºC

Thermogravimetric analysis: degradation temperature: 292ºC, water content: 4.4%

Results and Discussion

Photochromic properties

Samples were analysed at 298K in a temperature controlled UV-Vis spectrometer and irradiated at 375nm to induce ring opening and **MC** formation. **BSP** compounds were previously found to be solvatochromic due to solvent-solute interactions and resulting in the ability to estimate the solvent polarity based upon the extent of the shift observed (figure 5). Both probes exhibited about 10nm shifts on increasing side chain length from 4 carbons to 12. The similarity of solvatochromic shifts for each probe is believed to be due to the **MC** forms observing similar environments within each IL and that each spiropyran derivative locates in a specific region within the ILs. Slight shifts in **MC** λ_{max} are believed to be due to increasing influence of the surrounding non-polar side chains upon the stabilisation of the **MC** charge sites.

MC λ_{max} of **SP**$_{\mathbf{Im}}$ is observed to be red shifted to around 576 nm which would indicate that the region the compound was experiencing is non-polar (table 1) This agreements with the postulation that **SP**$_{\mathbf{Im}}$ is unable to migrate between the IL nano-structured domains due to its imidazolium cation functional group. The integration of this functional group into the liquid structure is believed to restrict the compound and the ordering within the liquid would be expected to arrange the photoswitchable fragment within the non-polar side chain domains. **BSP** however is believed to be free to migrate between these regions depending on whether the **SP** or **MC** isomer is predominant (**SP** preferring non-polar regions, **MC** preferring polar regions) and so can position itself in regions within the liquids which best suit the form of the compound and stabilisation of each form.

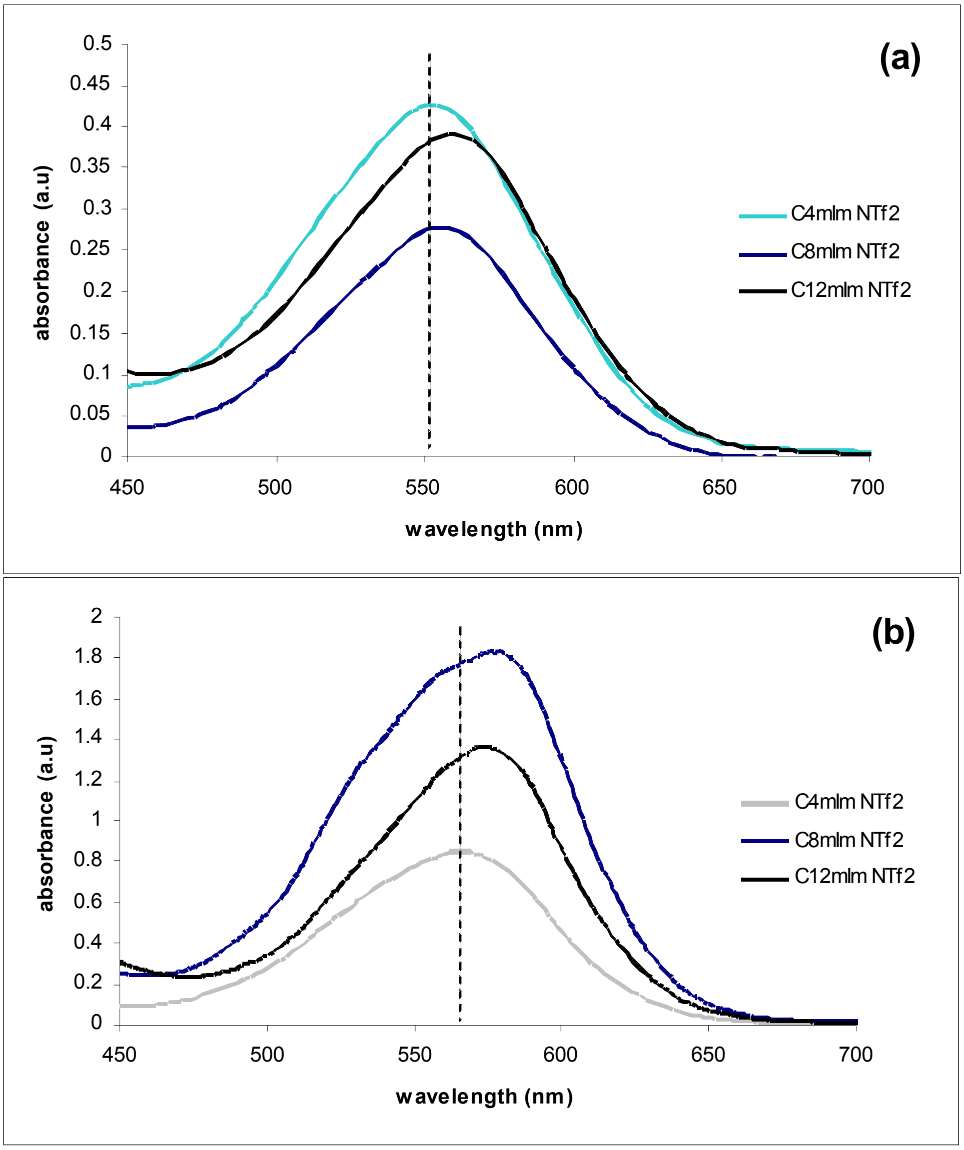


Fig. 5 UV-Vis spectra showing solvatochromic shift of **MC** form of (a) **BSP** and (b) **SP$_{\mathbf{Im}}$**. Samples irradiated for 30 seconds at 375nm at 298K.

Kinetic Parameters

After irradiation, the resulting first order decay curves (figure 6) were analysed using equation **(1)** to determine the rates of thermal relaxation, *k*, at 298 K (table 2).

$$\ln\frac{[A]}{[A_0]} = -kt \qquad (1)$$

Rates are found to be approximately an order of magnitude faster and relatively constant for **SP$_{\mathbf{Im}}$**

at around 13.5x10^{-3}s^{-1} in each of the ILs, compared to that of **BSP** which had rates slightly increasing from 1.0x10^{-3}s^{-1} to 2.0x10^{-3}s^{-1} from [C$_4$mIm][NTf$_2$] to [C$_{12}$mIm][NTf$_2$]. Once again, these results can be interpreted in terms of its ability to migrate between the IL nano-structured regions. As **BSP** is believed to be relatively mobile it can migrate to more polar regions within the ILs and thus stabilise the charge sites through electrostatic interactions and hydrogen bonding to the phenolate oxygen.[17] The increase in rate constants for **MC$_{BSP}$** → **SP$_{BSP}$** may be due to the cation inter-chain interactions, which at longer side-chain lengths, are believed to put strain upon the mutual interactions of the polar head groups. The result is that the weakened polar regions dissociate, reducing the overall charge density within the region to accommodate the solute molecules in addition to the region being expanded by the solute itself upon its introduction.[26-28] This would lead to a reduction in the liquid's polar region to facilitate the **MC$_{BSP}$** and stabilise the compound in this form.

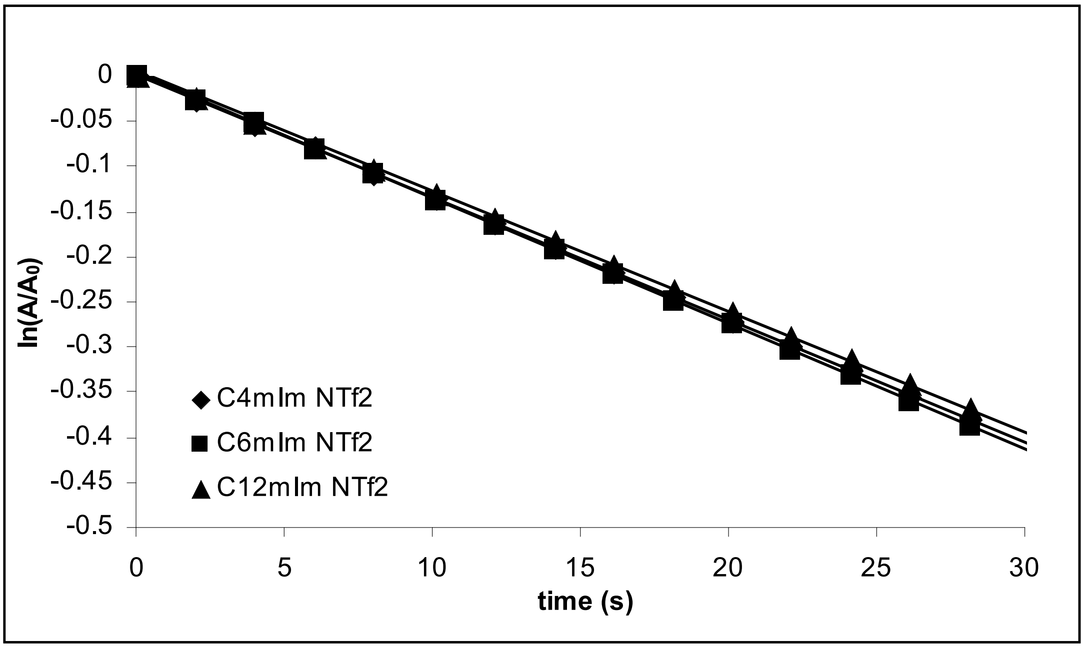


Fig. 6 First order plots of thermal relaxation on SP_{Im} in ILs.

The large increase in relaxation rates observed for $\mathbf{SP_{Im}}$ (approx $13.5x10^{-3}s^{-1}$) is believed to be attributed to the functionalisation of spiropyran with the imidazolium ring. The ring would be expected to associate with the neighbouring rings through π-stacking, anion-cation associations and hydrogen bonding. As a result, the spiropyran fragment would be expected to become located within the non-polar regions of the IL through organisation similar to that seen in the bulk liquid where head group interaction results in the remaining side chains organising into separate domains. Non-polar molecular solvents shift the equilibrium of spiropyran to its closed form due to lack of charge stabilisation and similar effects are seen for $\mathbf{MC_{SPIm}}$ with the aliphatic side-chains of the ILs with resulting order of magnitude increase in kinetics would appear to support this reasoning. In addition to the large increase in rates of thermal relaxation it is also found that the rate of relaxation did not vary significantly; remaining at around $13.5x10^{-3}s^{-1}$ for each IL with for $\mathbf{SP_{Im}}$. This differed from **BSP** with rates observed to double from $1x10^{-3}s^{-1}$ to $2x10^{-3}s^{-1}$ from $[C_4mIm][NTf_2]$ to $[C_{12}mIm][NTf_2]$ respectively. If $\mathbf{SP_{Im}}$ is immobilised within the non-polar regions of the ILs then the environment it observes has little variation beyond increasing chain lengths which is not detected by the molecules and so the level of interaction remains similar in each IL.

BSP appears to retain the ability to migrate within the regions resulting in a compound that is more sensitive to the subtle changes in liquid structuring. Since $\mathbf{MC_{BSP}}$ will preferentially associate with polar regions, changes in the system are believed to affect these regions which would in turn be expected to alter the relaxation of the compound to its closed form. As side chain length increases and polar regions become dispersed this decreases their ability to interact and stabilise the $\mathbf{MC_{BSP}}$ to the same extent. Also, as side chain lengths increase it would be expected that the increasing size of the non-polar regions would have an increasing attraction to the relaxing molecules (which are returning to the uncharged spiro form) and facilitate faster closure.

Thermodynamic parameters

Thermodynamic properties such as activation energy (E_a), entropy of activation ($\Delta S^\ddagger$), enthalpy of activation ($\Delta H^\ddagger$) and Gibbs energy of activation ($\Delta G^\ddagger$) were determined by Arrhenius and Eyring plots (figure 7) and using equations **(2)** and **(3)**. Equation **(4)** allowed for the manipulation of the Eyring dependency to derive the transition state equilibrium.[29] Samples were heated between 283K and 303K and results are summarised in table 1. **BSP** values were determined in previous studies.[17]

$$\ln k = E_a / RT + \ln A \qquad (2)$$

$$\ln (k/T) = -\Delta H^\ddagger/RT + \ln (k_B/h) + \Delta S^\ddagger/R \qquad (3)$$

$$k = (k_B T/h)K^\ddagger \qquad (4)$$

where,
R = gas constant
h = Planck’s constant
k_b = Boltzmann constant

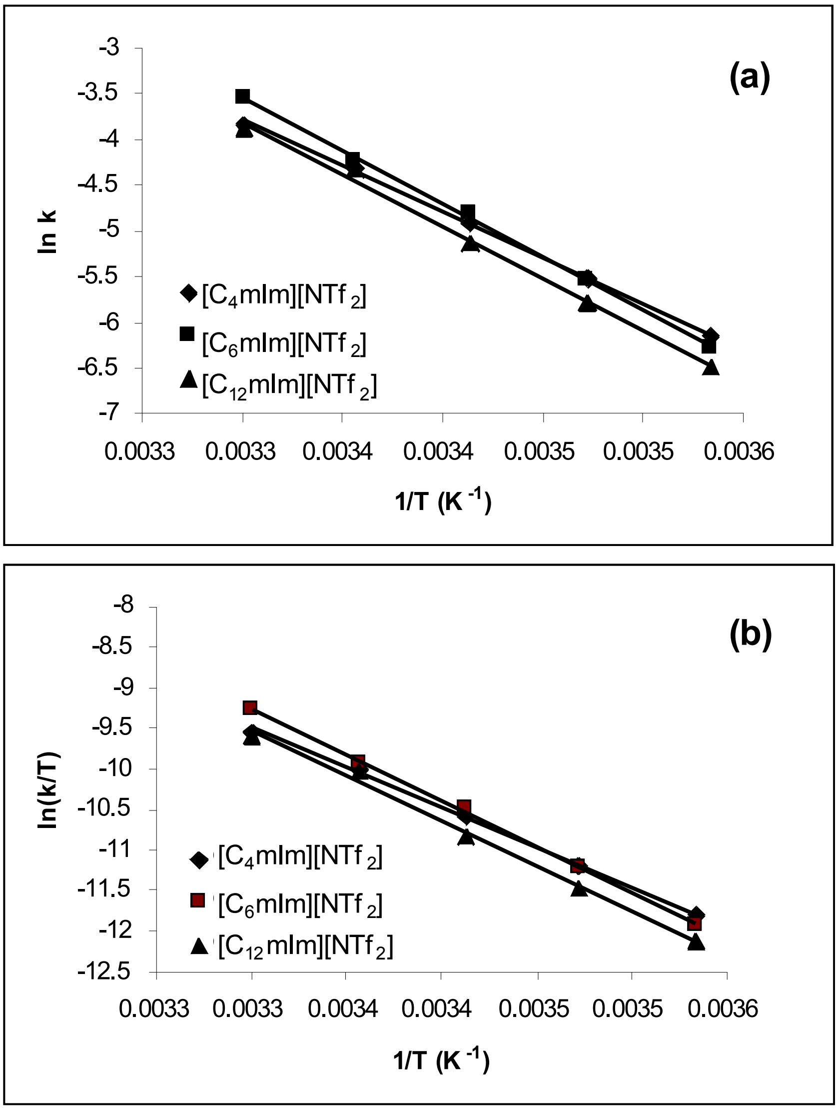


Fig. 7 Arrhenius (a) and Eyring (b) plots of $\mathbf{SP_{Im}}$ in ILs.

The entropy of activation, $\Delta S^{\ddagger}$ values for both derivatives were found to increase with chain length. **BSP** values are found to be larger, ranging from 13.79 - 46.15kJ.mol^{-1}, compared to $\mathbf{SP_{Im}}$ with values of -7.86 - 29.87kJ.mol^{-1} and overall reductions of around 10-15 J.K.mol^{-1} in each IL for the latter. The slight negative entropy of activation is observed for $\mathbf{SP_{Im}}$ in [C$_4$mIm][NTf$_2$] of -7.86kJ.mol^{-1} implies that the IL-$\mathbf{SP_{Im}}$ systems are more rigid than that of **BSP** and this complied with the initial hypothesis that the imidazolium fragment of $\mathbf{SP_{Im}}$ integrated into the cation ordering of the ILs. This integration into the system initially adds rigidity by becoming part of the liquid structure itself while the tethering of the spiropyran fragment to the cation ensured that any diffusion properties of the spiropyran fragment were limited or eliminated. Locating the spiropyran fragment in the non-polar region also reduced the ability of the **MC** form to interact with polar regions and thus reducing the polar region reorientations observed in response to such interactions. Similarly, activation energies (E_a) are found to decrease about 10 kJ.mol^{-1} when the imidazolium fragment is introduced to the spiropyran molecule (table 1). **BSP** is found exhibit activation energies ranging from 96.93 – 105.27 kJ.mol^{-1} while **SP$_{\mathbf{Im}}$** has lower energies at 83.84 – 85.33kJ.mol^{-1} for [C$_4$mIm][NTf$_2$] to [C$_{12}$mIm][NTf$_2$] respectively. Reduction in energies at transition states would imply that much of the solvent interaction had occurred at equilibrium upon integration into the IL due to **SP$_{\mathbf{Im}}$** becoming immobilised within the liquid nano-structure . The thermal relaxation process that follows therefore involves less interaction of the between **MC$_{\mathbf{SPIm}}$** and the IL ions and therefore the energy barriers observed where not as large as those seen for the thermal relaxation of **MC$_{\mathbf{BSP}}$.** Since **BSP** is free to move within the IL structure, allowing the molecules to interact to a certain degree with the polar regions at equilibrium. The ring opening process may also result in the formation of solvent-solute interactions which did not exist when **BSP** is in its closed form. These interactions therefore create increased stabilisation and increased energy barriers to be overcome during the thermal relaxation process. Interestingly the reduction in activation energies are relatively small when compared to the resulting increase in rates of thermal relaxation between **BSP** and **SP$_{\mathbf{Im}}$**. This may indicate that the spiropyran molecule is sensitive to such energy requirements and the influence of such barriers may be critical to the control of thermal relaxation and thus stabilisation of the photochromic compounds in either form. Lower enthalpies of activation $\Delta H^{\ddagger}$ and Gibbs energy of activation $\Delta G^{\ddagger}$ of about 10 kJ.mol^{-1} and 5 kJ.mol^{-1} respectively are also observed in **SP$_{\mathbf{Im}}$** when compared to **BSP** (table 1). For [C$_6$mIm][NTf$_2$] **SP$_{\mathbf{Im}}$** was found to have a $\Delta H^{\ddagger}$ of 86.28kJ.mol^{-1} compared to 96.41kJ.mol^{-1} for **BSP** and $\Delta G^{\ddagger}$ values of 83.61kJ.mol^{-1} and 90.01kJ.mol^{-1} respectively. Since these parameters are analogous to that of activation energy, such reductions would be exepected and provided further insight into the system's overall role in the relaxation process.

The equilibrium of activation, $K^{\ddagger}$,was examined for both **MC** forms to determine the stability of the charged forms of the derivatives and their ability to return to the more stable ground state/closed forms. **SP$_{\mathbf{Im}}$** is found to exhibit $K^{\ddagger}$ values an order of magnitude larger than the equivalent **BSP** indicating that **SP$_{\mathbf{Im}}$** favours conversion to the **SP** form from the transition state more than **BSP** (table 1). For example, in [C_6mIm][NTf_2] $K^{\ddagger}$ is found to be $2.23 x 10^{-15}$ for **SP$_{\mathbf{Im}}$** and $1.65 x 10^{-16}$ for **BSP**. This further supports the hypothesis that the ability to migrate freely within the ILs is critical for stabilisation of the **MC**/**SP** form. Integrating **SP$_{\mathbf{Im}}$** in the cation-cation association structures and the resulting restriction of the spiropyran molecule produces unfavourable conditions for **MC$_{\mathbf{SPIM}}$** formation which in turn shifted the equilibrium towards the closed form. $K^{\ddagger}$ values agree with such hypothesis with equilibrium of activations around ten times larger for **SP$_{\mathbf{Im}}$** than that of **BSP**. Such values imply that at the transition state the solvent-solute interactions are less for **SP$_{\mathbf{Im}}$** than **BSP** which results in less stabilisation of the **MC$_{\mathbf{SPIM}}$** form.

Addition of 1 mol% of each derivative to the ILs allows for optical determination of the extent of solvent-solute interactions and equilibrium effects (figure 8). The addition of the imidazolium side chain in **SP$_{\mathbf{Im}}$** and its restrictive properties upon the spiropyran fragment is confirmed by the formation of colourless/yellow liquids which indicates that the **SP$_{\mathbf{Im}}$** exists primarily in the **SP** form of the compound due to the established lack of solvent mediated stabilisations by the non-polar side-chains and the spiropyran fragment. **BSP** in imidazolium based ILs is found to exist in its coloured **MC$_{\mathbf{BSP}}$** form indicating that **MC** stabilisation in the polar regions enhances the open form of the compound. Since **BSP** is free to associate with all regions within the IL depending on the form (**BSP↔MC**) it is possible that the compound could easily associate at specific locations within the liquid which would stabilise the compound. As shown previously, the attraction to charged/polar regions would be greater than that of the non-polar domains since specific interactions such as hydrogen bonding present in the polar regions would be greater than that of diffuse/non-specific van der Waals forces and thus encourage ring opening.[18]

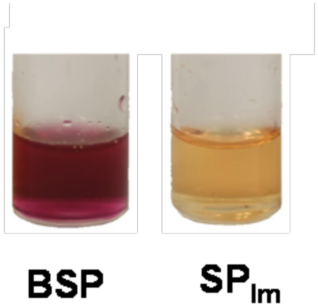


Fig. 8 equilibrium of each derivative clearly visible. **BSP** is stabilised towards its coloured **MC** form while **SP$_{Im}$** exists in its closed, colourless SP form.

The effects observed are similar to those found for spiropyran compounds in polar protic molecular solvents.[15] Non-polar solvents are found to enhance the formation of the closed form at equilibrium while the rates of thermal relaxation are quite large. Conversely, in polar solvents the stabilization of the **MC** form results in increased lifetimes of this form and measurable concentrations of **MC** at equilibrium. However, in molecular solvents, such shifts in equilibrium are only observed in each case by changing the molecular solvent itself. In the case of ionic liquids, the changes were observed within the same IL in each case. It is believed that this is due to the differing interactions the spiropyran derivatives experience within the liquids and thus influence which region the spirocyclic component resides in. This agrees with the proposed migration of spiropyran between the regions of the ILs and further supports the existence of such nano-structuring within the ILs. Interestingly, such large shifts in the equilibrium of the photochromic compounds may provide insight into the creation of photoswitchable systems with enhanced lifetimes of both closed and open states. The addition of tailored functional groups may allow the compounds to be ‘trapped’ within the IL region of choice extending the existence of either form for longer periods of time. The irradiation of UV/visible light could provide the energy required to switch between each state and locate the compound in specific regions thereby stabilising the particular isomer. Functional groups could then interact with the reciprocal regions thus ‘hooking’ the spiropyran molecules to the region of initial affinity and limit the diffusional effects of the molecules, extending the lifetimes of each form.[9]

Viscosity and Conductivity effects

Addition of higher concentrations of the spiropyran derivatives (1mol%) also allows for the effect of photoswitching upon IL viscosity and conductivity to be examined (table 2). Previous studies of **BSP** in phosphonium based ILs at similar and higher concentrations (5mol%) have found that the introduction and photoswitching of the compound can result in light mediated rheological and conductivity changes to the ILs themselves.[30] The addition of spirocyclic compounds to ionic liquids is believed to induce disruption of the liquid structure due to the bulky nature of the photochromic compound. It has been suggested that the anion-cation association within polar regions form worm-like ion channels[21]. Photoswitching of spirocyclic compounds and the resulting migration of the compound into these domains could therefore be disrupting these sensitive structures critical to the physical properties of the ILs and so inducing changes in viscosity and conductivity. Positive $\Delta S^{\ddagger}$ values imply that solvent reoganisation occurs upon **MC** formation which supports the belief that photoswitching the compound would further affect the overall properties of the ILs and their structuring. $\Delta S^{\ddagger}$ values are found to be consistently lower for **SP$_{\mathbf{Im}}$** which implies that the system observed is more rigid. Since the photoswitchable moiety is immobilised within the cation structure, it would be expected that the molecules are restricted and unable to migrate between domains and so results in less disruption. Comparison of **BSP** and **SP$_{\mathbf{Im}}$** can therefore determine the proposed importance of the restriction/freedom of solute migration upon the physical properties of ILs.

Analysis of viscosity effects found that negligible changes in the properties are observed upon addition and photoswitching of both **BSP** and **SP$_{\mathbf{Im}}$**. At 1 mol% the concentration of the photoswitchable compound is still relatively small compared to that of the bulk liquid which could result in the liquid itself masking the rheological effects as any changes related to photoswitching would be localised and dispersed within the IL system. Initial addition of the spiropyran derivatives should result in increased solvent-solute interactions such as hydrogen bonding and electrostatic interactions with the subsequent formation of the **MC** forms further increasing the available sites for said solvent-solute interactions.

Such cohesive nature of the interactions should in theory result in a decrease in solvent freedom and the reduction in movement and an increase in viscosity. The lack of apparent changes with photoswitching is most likely again due to 1 mol% concentrations being insufficient to affect the bulk properties of the ILs. This could also explain inconsistencies in results such as slight positive results where negative results were expected.

Interestingly, conductivity effects yielded some unexpected results whereby the reduction in conductivity due to **BSP** is smaller than that of **SP$_{\mathbf{Im}}$** introduction. The largest effect for **BSP** is a decrease of around 10% in conductivity in [C_{12}mIm][NTf_2] which is about 13% less that that of **SP$_{\mathbf{Im}}$** in the same IL. Since **SP$_{\mathbf{Im}}$** is believed to integrate within the IL structure, it is possible that the extent of **SP$_{\mathbf{Im}}$** ordering and restriction within the liquids may be integral to conductivity effects. **BSP,** with its lack of interactive functional groups is envisaged to have much more freedom within the IL systems and as such should be able to interact with both polar and non-polar regions more readily than that of the tethered derivative. **BSP** appeared to cause negligible changes to both viscosity and conductivity both with introduction and photoswitching. In contrast, the introduction **SP$_{\mathbf{Im}}$** is found to steadily decrease the conductivity of the ILs with increasing side chain lengths. This could be attributed a dispersal of the ion channels with increasing sizes in non-polar domains. The addition of spiropyran, due to its bulky nature, could disrupt the side-chain, Van der Waals interactions and as such may ‘push’ the cations further apart producing a more dispersed IL system. The augmentation of the IL nano-structure could result in an increase in anion-cation distances and so lowering the efficiency of electron transfer and the resulting conductivity of the liquid.

The viscosity of the imidazolium based ILs is found to be considerably lower than that of the phosphonium based ILs where photorheological effects were previously observed for **BSP**.[30] Since increasing the side-chain lengths of the imidazolium cations was also found to correspond to an increase in viscosity, the corresponding increase in conductivity effects observed with **SP$_{\mathbf{Im}}$** addition may imply that the liquids inherent viscosity is important for the ability to produce or detect such physical changes. In addition to the lower viscosity of the imidazolium based liquids, positive entropies of activation imply that the ions themselves have the ability to move when the derivaties are added and photoswitched within the ILs. This may reduce the ability of the spiropyran derivatives to disrupt the ion channels and the transport system may even be able to 'move around' the spiropyran molecules. As viscosity increases this freedom is reduced and so the introduction of the molecules and their effects become more apparent. Indeed, in [C_{12}mIm][NTf_2] the reduction in conductivity with **SP_{Im}** addition is found to be almost 25%. Changes due to **BSP** were not as large and it is found that the entropies of activation are reduced by around 15 $J.K^{-1}.mol^{-1}$ in [C_{12}mIm][NTf_2] when **SP_{Im}** is added compared to **BSP**. This is probably due to the increase rigidity that results from the integration of the **SP_{Im}** molecules into the IL itself and the more direct changes it has upon the liquid structure. Since more impressive photorheological effects produced in previous studies[30] were observed in ionic liquids with far higher viscosities and much more negative entropies of activation, we propose the rigidity of the phosphonium based systems described be these physical and thermodynamic properties allow this class of ILs to exhibit the light mediated properties which cannot be seen in imidazolium based ILs. Finally, the solubility limit of imidazolium based ILs for the spiropyran derivatives is reached at 1 mol% additions and so it is unclear whether concentration increases would have any effect to enhance the photorheological effects such as those found for 5 mol% concentrations of **BSP** in phosphomium based ILs.

Conclusions

We have successfully characterised the effects if integration of a photoswitchable spiropyran moiety in imidazolium based ILs. Based upon increasing evidence of structuring within ILs we have examined the extent to which interaction with such ordering could have upon the photoswitching properties of spiropyran derivatives. It was found that the integration of the spirocyclic compound, **SP_{Im}** into the liquid resulted in a significant shift in equilibrium towards the closed (**SP**) form. This is believed to be due to enhanced interactions between the IL cations and the imidazolium groups covalently attached to the spiropyran molecules resulted restriction of the compounds movement and permanent orientation of the spiropyran fragment into the non-polar region of the IL. The compound was unable to move to regions which stabilise the open (**MC**) form and resulted in lower activation energies and faster relaxation times. Such effects would appear to support the existence of nanostructured polar and non-polar domains. Addition of the derivatives to ILs with increasing side-chain length resulted in moderate changes to thermodynamic parameters.

Comparison to ILs containing **BSP** suggests that this molecule may dynamically transfer between the polar and non-polar nano-structured domains within ILs and aid in the stabilisation of each form (**SP/MC**) of the compound. Slower rates of thermal relaxation implied that the **BSP** form was more stabilised than that of **SP$_{\mathbf{Im}}$** and that **BSP** has stronger interactions with the polar regions of the ILs. Thermal relaxation rates were found to be similar for **SP$_{\mathbf{Im}}$** in all of the ILs indicating that the environment showed little variation. **BSP** exhibited increasing rates with chain length which implied that polar regions and the interaction of the compound with non-polar regions was more influential. Equilibria of activation values were similar regardless of the IL cation chain length for **SP$_{\mathbf{Im}}$**, which suggests that stabilisation effects are similar for each form of the probe molecule in each IL. This further supported the belief that similar structuring was observed within non-polar regions in each IL and that the effect of increasing side-chain length may be limited to polar regions. The lack of significant variation in activated complex parameters reinforces this interpretation, as similar interactions would logically result in similar levels of stabilisation of the respective forms of the spirocyclic compound. Positive $\Delta S^{\ddagger}$ values mean that the compound undergoes significant reordering within the solvent system during thermal relaxation. This implies that the spirocyclic probe disrupts the IL nanostructure and when **BSP** was introduced and positions itself dynamically within each of the nanostructured regions. The process is not observed to the same extent for **SP$_{\mathbf{Im}}$** with lower entropy values found in all ILs. This is believed to be because of the restriction of the molecules due to the integration of the imidazolium functionalisation into the IL structure. Previous studies have found that phosphonium based ILs present rigid systems with negative entropies of activation, which suggests that the structuring of imidazolium based ILs is due to π-π stacking and various non-specific interactions. This in contrast to that of phosphonium ILs, whose interactions like van der Waals forces generate stronger inter-molecular bonds, which is reflected in the higher viscosities observed for these ILs. Addition of 1 mol% of spiropyran derivatives to ILs produced minimal rheological effects. Conductivity effects were found to increase significantly (up to 23%) for $\mathbf{SP_{Im}}$ with increasing side chain lengths. Smaller effects were found for **BSP** addition with decreases in conductivity up to 10% found in [C_{12}mIm][NTf_2] while neither compound was found to endow photoswitchable rheological effects. Slight trends observed for $\mathbf{SP_{Im}}$-IL systems due to increasing chain length, viscosity and decreases in IL entropies (compared to **BSP**) may provide insight into the future creation of photoactive rheological fluids similar to those observed in phosphonium based IL systems.

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