Investigating nano-structuring within imidazolium ionic liquids: A thermodynamic study using photochromic molecular probes

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Abstract

Following previous studies involving the thermal relaxation of spirocyclic compounds we extended our studies to investigate the formation of nano-structured domains in ionic liquids (ILs). Two compounds, spiropyran (**BSP**) and spirooxazine (**SO**) were added to imidazolium cation based ionic liquids with increasing chain lenghts (C_2 –C_{12}). Increasing side-chain length was found to have only minor effects on the rate of thermal relaxation of **BSP** and **SO**. **BSP** was found to be a suitable probe molecule as linear correlations in parameters were observed for this compound. This is believed to be due to the fact that **BSP-**IL interactions were based on hydrogen bonding between $\mathbf{MC_{BSP}}$ and the cation compared to $\mathbf{MC_{SO}}$ which is limited to electrostatic interactions thus enhancing the sensitivity of $\mathbf{MC_{BSP}}$ to the charged polar regions. Increasing the side-chain of the cation resulted in slight increases in **MC-BSP** activation energy from 96.93 kJ.mol^{-1} in [C_4mIm][NTf_2] to 105.27 kJ.mol^{-1} in [C_{12}mIm][NTf_2]. **MC-BSP** $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ values also increased with increasing side-chain. Expansion and dispersion of polar regions due to increasing non-polar interactions may be enhanced by introduction of the bulky probe molecule. The resulting reorganisation of the system produced positive entropies of activation, 13.79 J.K^{-1}.mol^{-1} for C_4mIm to 46.15 J.K^{-1}.mol^{-1} for C_{12}mIm, following an increase in disorder due to probe dye closure from **MC** to **BSP** and migration of dye to regions of preferential solvation. The ability for spirocyclic compounds to form both polar and non-polar isomers resulted in the ability to

analyse both solvent regions using a single probe dye. Ground state equilibrium, K_e, examined non-polar regions of the IL while equilibrium of activation, $K^{\ddagger}$, examined the polar regions. A linear response to side chain length to equilibrium of activation was believed to be due to the fact that polar regions were possibly expanding due to increasing influence of non-polar side chain interactions upon the over solvent structure. The result of such reordering and dispersion of polar regions reduces solvent-solute interactions which increases rate of **MC-BSP** relaxation.

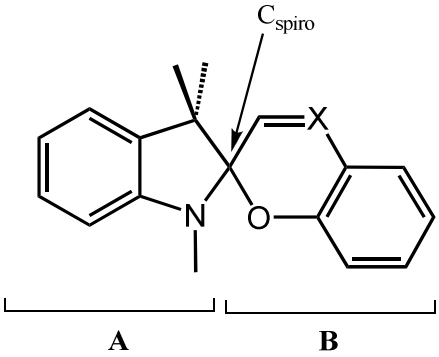
Introduction

Ionic liquids (ILs) are recieving increasing amounts of attention with regard to implementation as 'green' alternatives to current laboratory solvents. ILs consist entirely of ions in liquid state under 100ºC. The large range of ions available adds a 'designer' aspect to the liquids, meaning that such liquids could provide solvents with specific tailored properties. Proposed applications include recyclable solvents[1] and replacements to molecular solvents in catalysis,[2] electrochemistry,[3] synthesis[4] and elemental analysis[5]. Several reviews have provided detailed insight into ILs and have promoted their implementation was common laboratory solvents.[6] However, the lack of exact knowledge of the physical properties has resulted in their widespread application not being completely realised. Recent studies have proposed that imidazolium based ILs may form ordered systems resembling psuedo-crystalline systems based on stacking of mutual charges (aggregation) or ordered association of cation to surrounding anions and vice versa.[7] Theoretical modelling by Lopes et al examined the formation of such aggregates based on the imidazolium cation to investigate such ordering and its effect on the formation on nanostructured domains.[8] It is believed that imidazolium cations in ILs can be divided into two specific regions: a polar head group where the ion charge resides and a non-polar region where side groups extend into space (fig 1). These

polar head groups appear to interact preferentially with one another to form aggregates by three dimentional π-stacking and mutual association of the charged imidazolium rings with anion species to form polar regions. Alkyl side-chains extend away from these regions and through side-chain/van der Waal interactions form a complex network of non-polar regions.

Fig 1: Imidazolium cation C_6mIm showing polar (red) and non-polar (green) regions of the molecule based on findings and convention of identification by Lopes et al.

Our study intends to elaborate on these theoretical findings by the addition of two spirocyclic compounds to a range of imidazolium based ionic liquids. Both compounds, spiropyran (**SP**) and spirooxazine (**SO**) were previously employed to investigate the solvent-solute interactions of ILs.[9,10] The compounds have very similar core structures with the most significant changes being the nitrogen atom on the **B** fragment, differentiating **SO** and **BSP** (fig 2). Substituents on the right hand (**B)** side of each molecule are also varied. **BSP** contained a nitro group, known for its solvatochromic effect on the molecule[11] while **SO** contained a benzothiophene group which is believed to enhance metal chelation by assisting in the distribution of the charge interaction.[12]



Where X = **C** (pyran), N (oxazine)

Fig 2: Basic structure of spirocyclic compounds. Indoline (A) and pyran/oxazine (B) ring.

Photoswitching of spirocyclic compounds involves the use of light to induce cleavage of the SP_3 hybridised carbon of the indoline ring known as C_{spiro}. Initially, both **BSP** and **SO** are uncharged molecules with the indoline fragment (**A**) orthogonal to that of its respective pyran or oxazine fragment (**B**). Cleavage of this bond can occur by irradiation with UV light (typically around 365-375 nm) to form the merocyanine (**MC**) isomer. The **MC** isomer results from cis-trans isomerisation of the molecule, which results in a planar molecule with a charge distributed across the molecule. The process is also completely reversible by irradiation with white light. Photochromic compounds revert to their more stable 'ring closed' isomer known as thermal reversion and proceeds by removing heat from its surroundings to supply sufficient energy for the reorientation to occur, this process follows first order kinetics.

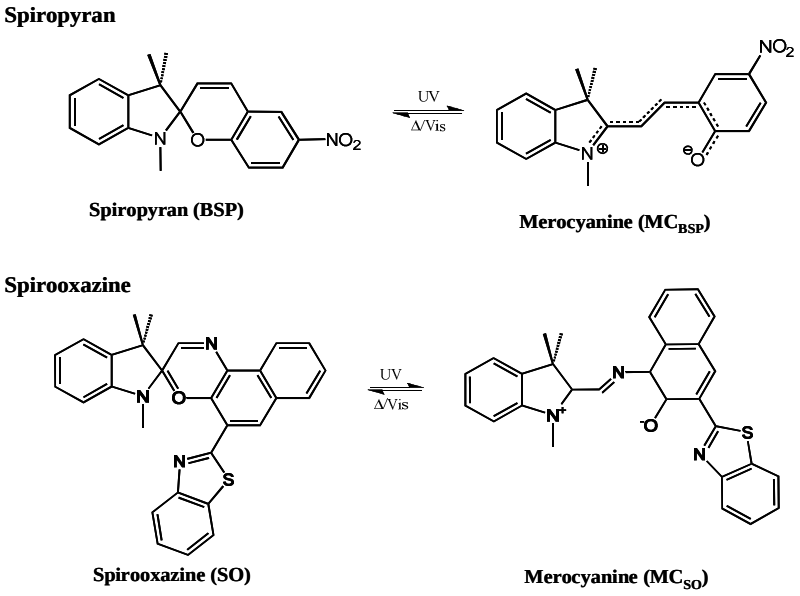


Fig 3: Spirocyclic compounds used in our studies and their photoswitchable states

The **MC** isomer is sensitive to its immediate molecular environment and these corresponding specific and non-specific interactions that occur mediate the compound's equilibrium between both isomers. Traditionally, polarity was the primary parameter with which rate constants were related, to predict trends in photoswitching and equilibrium. The MC isomer can also interact with specific metal ions, amino acids, DNA and organic ions.

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Estimates of IL physico-chemical properties has led to the re-evaluation of polarity as a macroscopic property that assumes that the entire solvent system acts as a continuous medium rather than a solution with molecular level properties.[13,14] Polarity probes, such as Reichardts dye, are quantified based on the intermolecular interactions between a probe molecule and solvent molecules through specific and non specific interactions with dye charge sites. For Reichardts dye, this is based upon an absorption shift due to solvent interaction with the zwitterionic sites of the compound and its subsequent effect on the excitation band gap of the molecule. To compliment such single parameter probe studies, the combination of three dyes (including Reichardt's) by Kamlet and Taft has allowed for hydrogen bonding of solvents to be examined.[15-17] Both single and multiparameter probe studies have seen considerable usage in evaluating ILs in an attempt to understand trends in their physico-chemical properties, but it appears ILs are much more complex solvent systems capable of undergoing many types of interactions. Characterizing them with a single 'polarity' term fails to describe the type and magnitude of individual interactions that make each IL unique..[4,18-20] Since spirocyclic compounds form zwitterionic compounds similar to those used in Reichardts studies, it was proposed that such compounds could possibly act as multi-parameter probes based on solvatochromic shifts of the MC isomer, rates of thermal relaxations of MC, and equilibrium constants.

In molecular solvents, the polarity-kinetic relationship is upheld for both **BSP** and **SO** with increasing kinetics observed with decreasing polarity. Kamlet-taft parameters showed that this was due to decreasing levels of hydrogen bonding between solvent and spirocyclic compounds.[9] **BSP** is known to form hydrogen bonds when in its **MC** form which meant that its rate of thermal relaxation could be directly affected by interactions with the solvent system. Experimentally, kinetic trends similar to that observed for molecular solvents were observed for the compound, which implied that **BSP** could act as a solvent sensitive probe. We recently reported the photo and solvatochromic properties of BSP in ILs containing $[NTf_2]^-$. It was found that the kinetics and thermodynamics of the SP-MC equilibrium was sensitive to the nature of the cation. It was also observed that the cation, $[emim]^+$ can even form a through-space orbital interaction with the merocyanine isomer, rather than a simple electrostatic interaction, thus inhibiting the merocyanine conversion back to the spirobenzopyran isomer. The same relationship was investigated in ILs using **SO** but similar trends were not apparent. It is believed that the bulky nature of the $\mathbf{MC_{SO}}$ and its substituents resulted in the association being restricted to electrostatic/non-specific interactions. **SO** was therefore chosen to act as a reference compound for comparing solvent structure as it relatively weak interactions meant that its process of thermal relaxation would be somewhat independent to that of the solvent system itself.

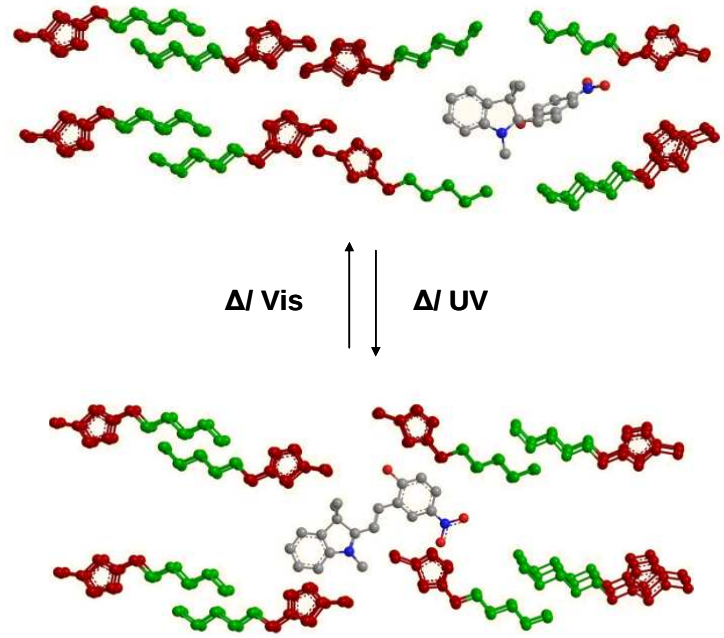

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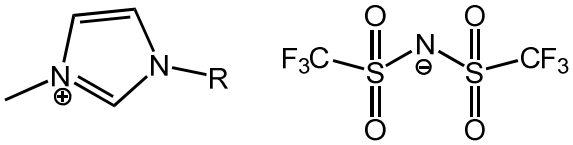
Fig 4: Schematic of proposed 3D ordering of imidazolium cations with **BSP** probe in [C_6mIm][NTf_2].

It is proposed that spirocyclic compounds ability to form two distinctive conformations may be used to examine both regions with the ILs similar to above (fig 4). Thermodynamic and kinetic studies were carried out to examine the extent of structuring in the ionic liquids based on equilibrium effects, rates of thermal relaxation and the effect upon solvent ordering due to the introduction of a bulky probe molecule.

The merocyanine (**MC**) form of the molecules provide a highly polar zwitterionic system which can interact with the opposing charges of the polar head groups of the solvent system. Upon thermal relaxation, the molecule returns to its spiro (**BSP/SO**) form which presents a neutral, non-polar molecule. If nano-structuring exists in ILs then it is would be expected that each form of the compound would reside in very different regions within the solvent based upon stability of the conformer. As thermal relaxation occurs, the molecule would be expected to migrate from one region to another in the

solvent system. By increasing the length of side-chain it is proposed solvent structure could result in changes to the order of the system itself. This could be related to increased dispersion and a corresponding expansion of polar regions themselves by dissociation of imidazolium head groups from one another and in response to increasing non-polar regions. Since **MC** preferentially resides in polar regions it was anticipated that increasing the surrounding non-polar regions could possibly influence the equilibrium by shifting it towards the closed spiro form of the molecule. If structured polar domains exist, then their stabilising influence on **MC** should reduce the effect of these non-polar regions and subsequently provide rates of thermal relaxation much slower than that expected for long-chain, non-polar molecules.



R = ethyl: C_2mIm
butyl: C_4mIm
hexyl: C_6mIm
octyl: C_8mIm
decyl: C_{10}mIm
dodecyl: C_{12}mIm

Fig 5: Cations and anion used in this study. 1-alkyl-3-methylimidazolium $[C_nmIm]^+$ andbis(trifluoromethanesulfonyl) amide $[NTf_2]^-$.

Experimental

ILs were synthesised and purified in-house with salts obtained from Sigma-Aldrich using previously reported techniques.[21] ILs produced were stored under argon to exclude absorption of atmospheric water. 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 375nm using in-house fabricated LED (Roithner Lasertechnik, Vienna,

Austria) array. Reichardts dye 30 (Sigma-Aldrich chemicals) and 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) were used as purchased with no further purification. 1,3,3-trimethyl-5'-(2-benzothiazolyl)-spiroindoline-2,3'-naphtho(2,1-b)(1,4) oxazine (**SO**) was previously synthesized and used as supplied. All samples were prepared at room temperature.

Results and Discussion

Polarity and solvatochromic effects

Solvent polarity was examined using the ET_{30} scale by previously explained procedures.[9] Spectroscopic shifts relating to solvent-dye interactions were found to have a linear response in ET_{30} with increasing side-chain length. The linear decrease in polarity was however minor when compared to that of molecular solvents of similar chain lengths. ET_{30} values of 52.6 $kcal.mol^{-1}$ for $[C_2mIm][NTf_2]$ and 53.2 $kcal.mol^{-1}$ for $[C_6mIm][NTf_2]$ were observed while similar chain length molecular solvents with a polar region and extending non-polar side chain (i.e alcohols) had ET_{30} values of 51.9 and 48.8 for ethanol (C_2) and 1-hexanol (C_6) respectively.[13]

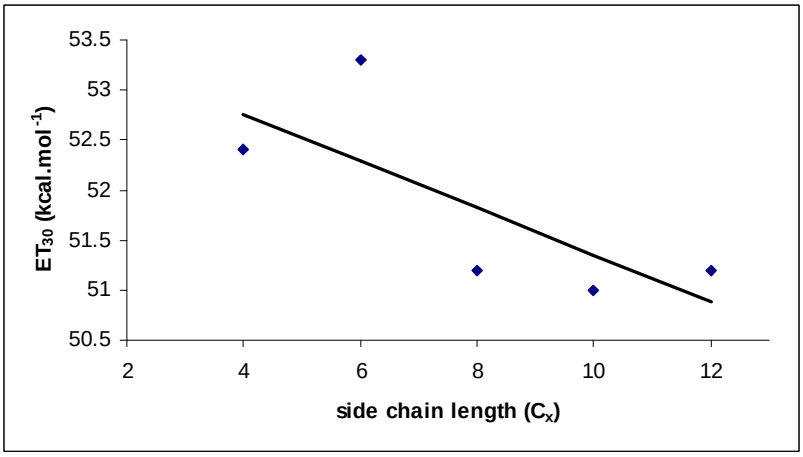


Fig 6: ET_{30} values of ILs with iincreasing cation side-chain length.

BSP due to its nitro group exhibited solvatochromic effects which allowed for analysis of solvent polarity based upon the wavelength shift of the **MC** absorption maximum. Linear hchromic (red) shifts were observed with increasing cation side-chain lengths as previously established in molecular solvents of decreasing polarity.[22] Similar solvatochromic effects were not observed for **SO** as the compound did not contain a solvatochromic moiety.

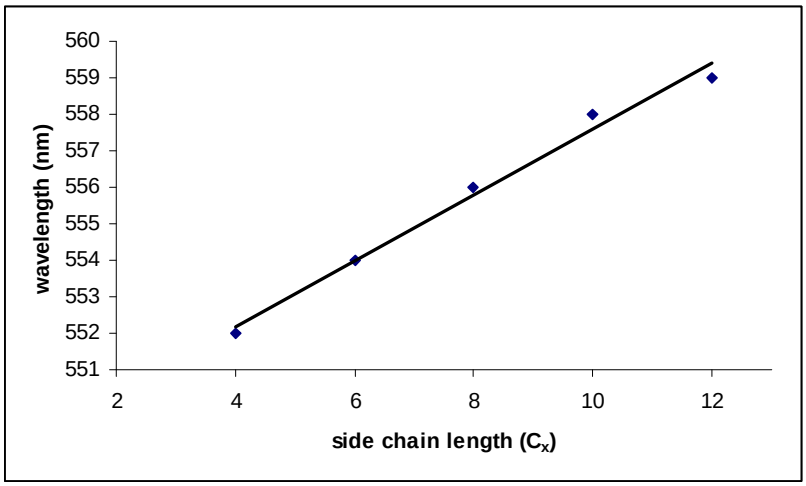


Fig 7: $\mathbf{MC_{BSP}}$ solvatochromic shift versus cation side-chain length

As with ET_{30} values, the observed shifts were subtle compared to those observed in molecular solvents. Such subtleties may be due to the fact that the polar regions of the ILs may somewhat retain their stabilising influence upon the **MC** even with increasing chain length thus buffering or reducing the overall effects of the increasing non-polarity of the solvent.

Kinetic parameters

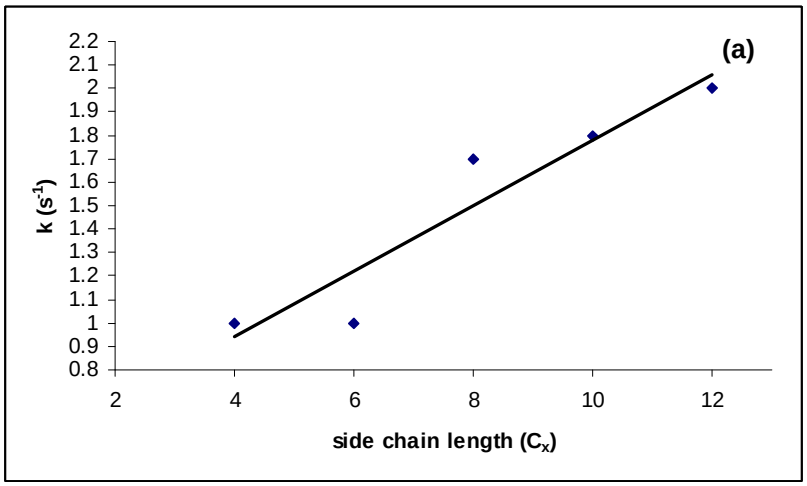
Samples were placed in thermostat controlled UV-Vis spectrometer and was irradiated in situ using an LED array to induce cleavage and **MC** formation. Once UV light source was removed, the subseqent first order decay curves were then examined using equation **(1)** to find the rates of thermal relaxation.

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

The rates of thermal relaxation were recorded at 298K and were summarised in table 1. Slight increases in rates of relaxation were observed with increasing chain length when **BSP** was added to the ILs. Increasing chain length resulted in rates of thermal relaxation doubling from $1.0x10^{-3}s^{-1}$ to $2.0x10^{-3}s^{-1}$ (fig 8a). Since lengthening of the side-chains would be expected to promote more inter-chain interactions it is believed that such enteractions place a strain upon the mutual interactions of the polar head groups. Such strain may cause restrictions which would result in the head groups having to move away from oneanother increasing the size of the polar region while reducing the overall charge density within the region to accommodate the solute molecules.[23] Early investigations into IL structuring observed deviations from traditional correlations between viscosity and diffusion for the diffusion coefficients of solutes within 'wet' ILs.[24] Further studies concluded that this could be explained as the IL system swelling to accommodate the solvent molecules as observed for studies involving IL/molecular solvent binary mixtures such as [bmIm][PF_6] and naphthalene.[25] It is now proposed that the addition of spirocyclic compounds, particularly those photoswitched to the polar **MC** form, are integrated into the IL structure in a similar manner. If dissolution of head groups is occuring upon such integration then the resulting proximity of both the imidazolium ring charge and the C2 proton to the **MC** would be lengthened.

This would imply a reduction in the polar stabilisation of the **MC** molecules. Rates of thermal relaxation were found to increase and is believed to be due to this reduction in polar interactions while the non-polar regions would be anticipated to further enhance the conversion to **BSP**.

SO was found to have similar relaxation rates of approximately $2.3x10^{-2}s^{-1}$ with no correlation in all ILs (fig 8b). This agreed with our previous findings and was believed to be due the the fact that the solvent-solute interactions were predominently electrostatic and its influence was similar in each IL.[9] Further support for this hypothesis came from the rates of thermal relaxation which were ten times faster than that oberved for **BSP.** This would be expected due to considerably weaker interactive forces stabilising the $\mathbf{MC_{SO}}$. The relatively weak electrostatic forces also meant that **SO** was free to move within the solvent system with minimal direct interactions with it. **SO** may therefore migrate to an intermediate region between the two regions and was therefore less sensitive to side chain length and head group interaction.



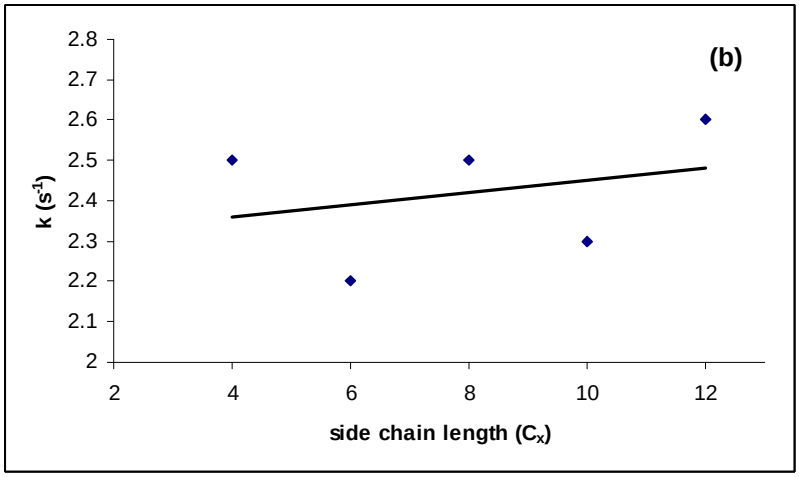


Fig 8: Rate of thermal relaxation of (a) **BSP** and (b) **SO** versus cation side-chain length.

Thermodynamic parameters

The linear dependence of temperature to the rate of thermal relaxation was plotted using equations **(2)** and **(3)** to find the activation energy (E_a), entropy of activation ($\Delta S^{\ddagger}$), enthalpy of activation ($\Delta H^{\ddagger}$) and Gibbs energy of activation ($\Delta G^{\ddagger}$). An alternative form of the eyring equation **(4)** was also employed to derive the equilibrium of the activated complex of the transition state theory.[26] The thermodynamic parameters found were summarised in table 1.

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

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

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

where,

R = gas constant
h = plancks constant
k_b = Boltzmann constant

BSP was found to have linear correlations between its thermodynamic parameters and rates of thermal relaxation but such changes were deemed to be minor due to relatively small observed changes. $\Delta S^{\ddagger}$ values were positive and increased with chain length (table 1). Changes in this parameter were obvious for **BSP** with entropies from 13.79 $J.K^{-1}.mol^{-1}$ in $[C_4mIm][NTf_2]$ to 46.15 $J.K^{-1}.mol^{-1}$ in $[C_{12}mIm][NTf_2]$. Entropy of activation was a measure of the amount of reorientation of **BSP** within the system relating to the rigidity of the solvent and the overall thermal stability of the system. Positive values implied that the system is therefore temperature dependent and **BSP** undergoes significant reorientation during thermal relaxation from **MC**. The observed increase in values may be due to increasing ordering of non-polar regions as increasing chain lengths would imply increasing intra-molecular interactions. Steric effects from solvent-solvent and solvent-**MC** interactions could result in expansion of polar regions allowing for more apparent molecular movements during **MC-BSP** conversion. At short chain lengths (C_2mIm), it would be expected that little ordering exists and solvent molecules are in random motion much like molecular solvents. Since ordering occurs at longer chain lenghts, the solvent system is believed to lean towards structuring similar to that of a solid but still retaining increased freedom of molecular motion . The introduction of a spirocyclic compound and its subsequent transition from **MC** (charged) to **BSP** (uncharged) would result in considerable reorientation of the solvent system around the charge sites. The physical size of the molecule itself would also cause significant change to the solvent system by forcefully inserting itself into the solvent system and subsequently disrupt the established structure. Movement of the molecules during their transition from **MC** to **BSP/SO** would also involve reorganisation to accommodate the active solute molecules and so increasing the entropy of the system. Positive entropies would also imply that the interactions of the solvent molecules was weak enough for the spirocyclic compound to disrupt the system. This meant that the liquid structure itself was ‘fluid’ enough to facilitate solute movement and acted

similar to traditional molecular solvents. **SO** once again showed no clear correlation in entropies of activation which implied that similar reorientation processes occurred for **MC-SO** thermal relaxation in all ILs and the the process was somewhat independent of the solvent system itself.

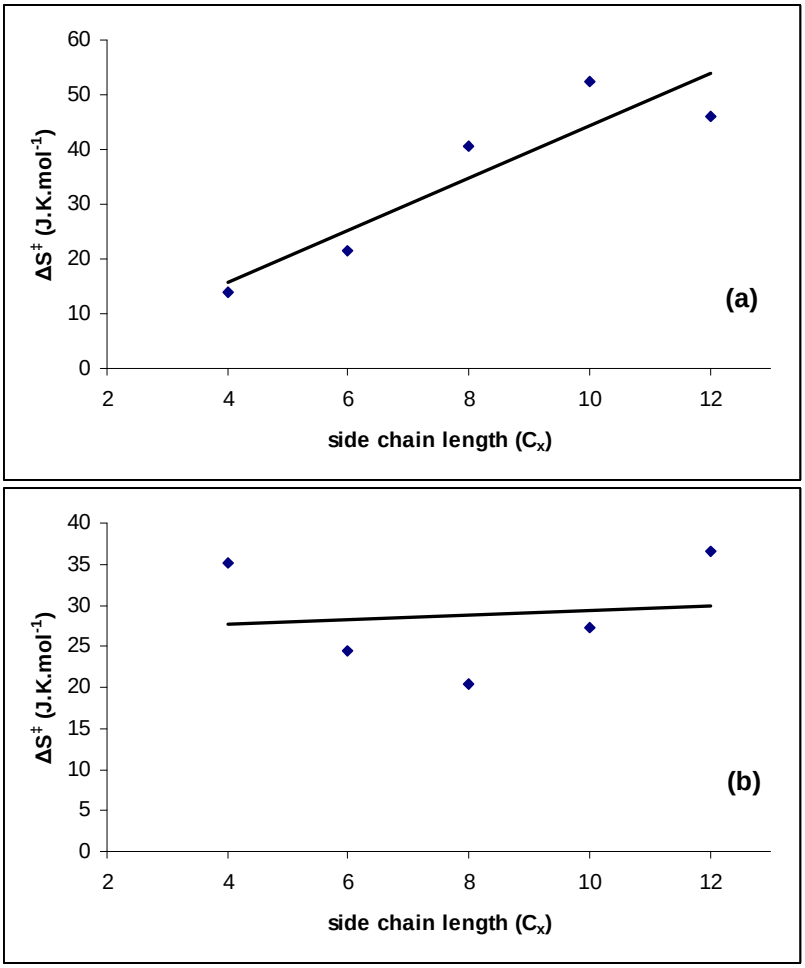


Fig 9: Entropies of activation of **BSP** (a) and **SO** (b) versus cation side-chain length.

The related parameters of activation energies (E_a) and enthalpies of activation ($\Delta H^{\ddagger}$) were found to also slightly increase with increasing chain length. This appeared contradictory as increasing

energy barriers would be expected to yield slower rates of relaxation. This could be possibly be explained as a compensation for the dispersion of charge sites with increasing non-polar influence on solvent structure. Such changes in the solvent system would be expected to produce an environment that was generally less polar that that of shorter chain cations and less favourable to **MC** stability. Since imidazolium cations are known to interact through pi-stacking and charge association (corodinated by anions in polar region) it would be expected that *intra*-molecular interactions wold dominate. The exansion of such systems therefore reduces these interations. This may allow for *inter*-molecular interactions (**MC**-IL) to occur more readily than previously possible. Such interactions would result in increased stability of the **MC** form of the compound and thus increase the energy barrier required for thermal relaxation to occur. However, the thermal relaxation process provided far greater energy that this energy barrier and so, although the activation energy and the enthalpies of activation increase, the overall equilibrium has a dominating influence on the process and so increasing rates of relaxation with increasing side chain length was observed.

For **SO** the thermodynamic parameters showed little or no variance with increasing chain length. Since **SO** is believed to interact with the ILs primarily through electrostatic interactions it was proposed that the process of thermal relaxation was also somewhat independent of the IL itself. The bulky nature of the substituents of **SO** may have provided sufficient hindrence to avoid interactions (hydrogen bonding) of close enough proximity to influence the relaxation process. The ability for the molecule to move somewhat freely in the solvent would have also meant that the could reorgnise itself with relatively low interaction with the solvent. As a result, the process for thermal relaxation is similar in all ILs

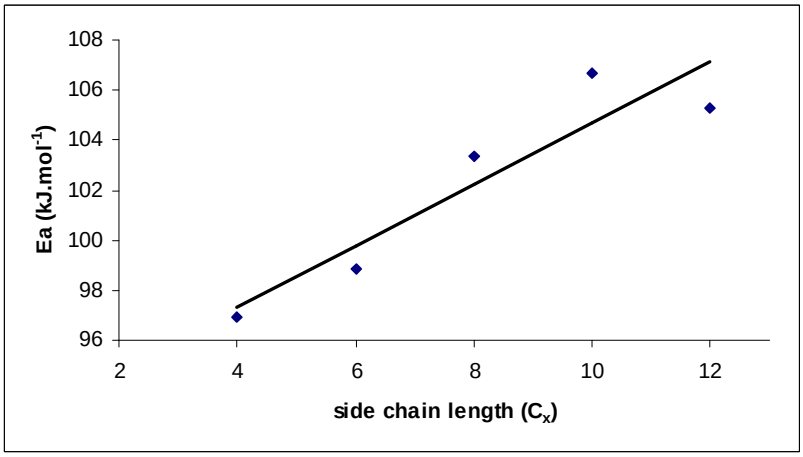


Fig 10: Activation energy of **MC-BSP** thermal relaxation versus cation side-chain length.

The ground state equilibrium, K_e, and transition state equilibrium, $K^{\ddagger}$, were also examined to determine the effects of chain length and solvent order on the form that the spirocyclic compounds were predominently stabilised as. Ground state equilibria were determined using equation **(5)**

$$K_e = \frac{[MC]}{[BSP]} = \frac{A}{\varepsilon \times C - A} \qquad (5)$$

Where,
C = concentration of **BSP/SO**
ε = extinction coefficient. $3.5x10^4 M^{-1}cm^{-1}$ for **BSP**. $7.85x10^4 M^{-1}cm^{-1}$ for **SO**.

Ground state equilibrium constants were not found to be inconsistent in relation to increasing side-chain length of cation for both **BSP** and **SO**. K_e values around $7x10^{-3}$ for **BSP** and $5x10^{-3}$ for **SO** were observed in each of the ILs. This implies that the spirocyclic compounds remained in their closed form in each of the ILs. Since the closed, spiro forms of the comounds had a lower energy level than that of **MC** it would be expected that at equilibrium that the compound would be primarily in its closed form. However, polar regions within the solvents would be expected to have

shifted the equilibrium towards the open form. Examination of the shorter chain (more polar) ILs showed little change in equilibrium compared to that of long chain cations. This would appear to reinforce the existence of domains within the solvent system. If the spirocyclic compounds are residing in the non-polar region when in their spiro forms then it would appear that changing the size of such region had little effect as the compound thermodynamically favoured this form and so resided in similar regions in each IL.

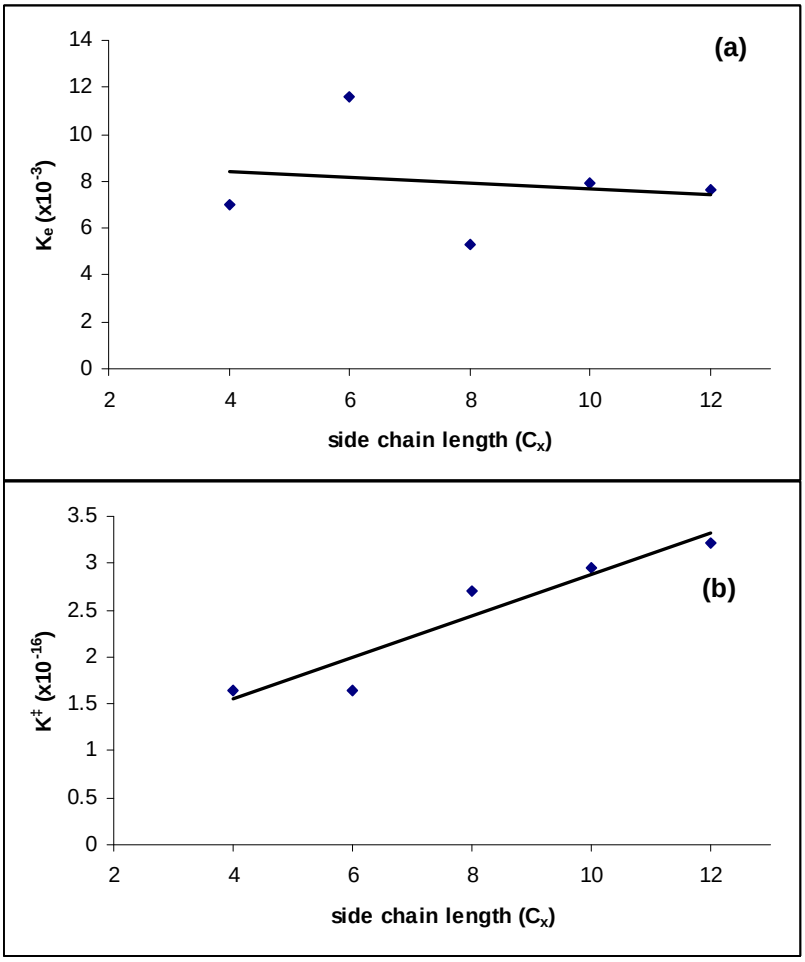


Fig 11: (a) Ground state equilibria and (b) equilibria of activation of **BSP** versus cation side chain length

To examine polar regions of the ILs, the transition state equilibrium, $K^{\ddagger}$, was determined. The equilibrium is based on the thermodynamic interconversion between **MC** to **BSP/SO** and the process of relaxation based upon which is the prefered state of the molecule. **MC,** due to its zwitterionic nature is believed to reside in the region of the polar head groups and migrate to non-polar regions as it thermally relaxes to its closed spiro form. Therefore the transition state equilibrium was based on the molecule residing in the polar region of the solvent. A linear increase in equilibrium constant was found with increasing chain lengths which implied that increasing structuring and distribution of polar regions had a significant effect on the **MC** relaxation process. Unlike the ground state equilibrium constants, where the compound was in its most stable (closed) form predominantly, the **MC** form is inherently unstable and favourably relaxes to its closed form as **MC** molecules are at a thermodynamically higher energy and will therefore preferentially relax. This results in effects due to the interactions of the **MC** with the polar regions and the competing influence of the non-polar regions upon the equilbrium and the corresponding rates of relaxation. Since the closed form of the molecule requires significant energy to form **MC,** the ground state equilibrium is somewhat biased to the closed form by the availability of non-polar regions. This may explain why there is little relationship between the rate constants and the equilibrium constants. In the case of **MC** thermal relaxation**,** the opposite occurs as the compound must now relax to its closed form from its higher energetic state. The influence of the equilibrium is apparent as the levels of interaction and availability of polar regions with respect to non-polar regions can slow down or increase the rate of this thermal relaxation. With increasing chain length, structuring within the solvent would be expected to disperse the polar regions and weaken their relative strengths of interaction. Theoretical models by Lopes agreed with this convention with $[C_{12}mIm]^{+}$ based ILs showing a majority of non-polar regions compared to that of $[C_4mIm]^{+}$ ILs. Reduction in the strength of **MC**-IL interactions results in reduced

stability and greater influence by non-polar regions upon the compound. This would in turn shift the equilibrium toward the closed form of the compound. This was observed with increasing $K^{\ddagger}$ values from $1.65x10^{-16}$ in $[C4mIm]^{+}$ to $3.22x10^{-16}$ in $[C12mIm]^{+}$. For **SO** the response in $K^{\ddagger}$ values due to chain length was not as clear as that observed for **BSP**. This was believed to be due to the passive nature of $\mathbf{MC_{SO}}$ -IL interactions and the relatively independent nature of the relaxation process resulting from this.

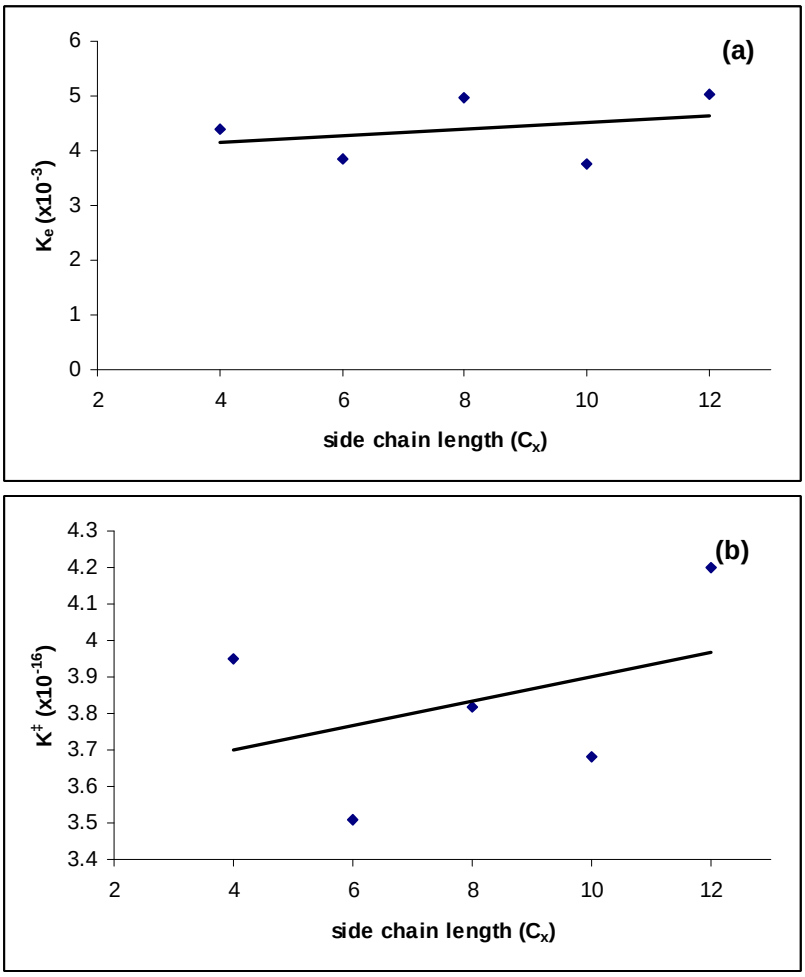


Fig 12: (a) Ground state equilibria and (b) equilibria of activation of **SO** versus cation side-chain length.

Conclusions

Imidazolium based ILs appeared to present themselves as pseudo-crystalline systems consisting of distinct polar and non-polar domains. Spirocyclic compounds added to ILs of increasing side chain length to investigate their ability to probe such domains resulted in moderate changes due to possible increases in structural integredy with chain length. **BSP** was found to be sufficiently sensitive to quantify thermodynamic and kinetic parameters due to its intimate interaction with the cation when in its zwitterionic **MC** form. **SO** failed to achieve the same effect and this was believed to be due to its inability to form hydrogen bonds and its restriction to electrostatic interactions. Probing of ILs with **BSP** found that the molecule was able to reside in each region of the solvent. Ground state equilibria found that the closed form of the molecule was similar regardless of size of polar region which implied that such regions may have been of similar size in each IL. This may have implied that the ratio of anion:cation was the same in each IL but that the structuring of the IL with increasing chain length resulted in strain and possible dispersion or expansion of such regions from $[C_2mIm]^+$ to $[C_{12}mIm]^+$. The lack of great variation in activated complex parameters reinforced this theory as similar interactions would logically result in similar levels of stabilisation of the respective forms of the spirocyclic compound. Interestingly, positive dS values meant that the compound underwent significant reordering within the solvent system during thermal relaxation. This implies that the spirocyclic probe was disrupting the solvent system upon its introduction and migration throughout the regions. This interaction with the ILs may be a reason why rates of relaxation of relaxation are found to be slow in ILs compared to molecular solvents. Previous studies have found that phosphonium based ILs present rigid systems with negative entropies of activation and so this may imply that the structuring of imidazolium based ILs is due to pi-pi stacking and various non-specific interactions. This in great contrast to that of phosphonium ILs where specific interations such as Van Der Waals produced stronger

systems and was reflected in the solvents viscosity.

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Table 1

Physicochemical properties of spirocyclic compounds in molecular solvents and ionic liquids. Reference values in parenthesis

SO

					Arrhenius		*Eyring*			
IL	*λmax MC*	k_{25}	ET_{30}	K_e	E_a	*A*	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}_{25}$	$K^{\ddagger}$
	(nm)	*($x10^{-2}$ s^{-1})*	(kcal.mol^{-1})	*($x10^{-3}$)*	*(kJ.mol^{-1})*		*(J.K^{-1}.mol^{-1})*	*(kJ.mol^{-1})*	*(kJ.mol^{-1})*	*($x10^{-15}$)*
C_2mIm NTf_2	642	2.3	52.6(52.6)	6.62	95.23	1.11E+15	34.92	92.80	82.39	3.68
C_4mIm NTf_2	642	2.5	52.4(50.0)	4.38	95.18	1.14E+15	35.20	92.75	82.26	3.95
C_6mIm NTf_2	644	2.2	53.3(51.9)	3.84	92.35	3.16E+14	24.52	89.91	82.61	3.51
C_8mIm NTf_2	646	2.5	51.2(51.1)	4.97	90.79	1.91E+14	20.31	88.35	82.30	3.82
C_{10}mIm NTf_2	644	2.3	51.6(51.0)	3.77	92.87	4.39E+14	27.23	90.44	82.33	3.68
C_{12}mIm NTf_2	646	2.6	51.2	5.03	95.32	1.34E+15	36.48	92.89	82.02	4.20

BSP

					Arrhenius		*Eyring*			
IL	*λmax MC*	k_{25}	ET_{30}	K_e	E_a	*A*	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}_{25}$	$K^{\ddagger}$
	(nm)	*($x10^{-3}$ s^{-1})*	(kcal.mol^{-1})	*($x10^{-3}$)*	*(kJ.mol^{-1})*		*(J.K^{-1}.mol^{-1})*	*(kJ.mol^{-1})*	*(kJ.mol^{-1})*	*($x10^{-16}$)*
C_2mIm NTf_2	552	1.2	52.6(52.6)	8.66	106.69	6.43E+15	49.55	104.26	89.49	2.02
C_4mIm NTf_2	552	1.0	52.4(51.6)	7.02	96.93	8.71E+13	13.79	94.49	90.38	1.65
C_6mIm NTf_2	554	1.0	53.3(51.9)	11.60	98.84	2.67E+14	21.48	96.41	90.01	1.65
C_8mIm NTf_2	556	1.7	51.2(51.1)	5.31	103.34	2.18E+15	40.55	100.90	88.82	2.71
C_{10}mIm NTf_2	558	1.8	51.6(51.0)	7.94	106.68	1.02E+16	52.42	104.24	88.62	2.96
C_{12}mIm NTf_2	559	2.0	51.2	7.63	105.27	5.73E+15	46.15	102.14	88.39	3.22