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

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## *Abstract*

Molecular photoswitches have been used to investigate the possibility of nano-structured polar and non-polar domains in ionic liquids (ILs). Two photochromic compounds, spiropyran (**BSP**) and spirooxazine (**SO**) were added to imidazolium based ionic liquids containing the anion $[NTf2]^-$ and their photochromic behaviour was monitored with increasing side chain length ($C_2$ – $C_{12}$) of the imidazolium cation. Increasing side-chain length was found to have only minor effects on the rate of thermal relaxation of the merocyanine form of spiropyran ($\mathbf{MC_{BSP}}$) and spirooxazine ($\mathbf{MC_{SO}}$) to **BSP** and **SO,** respectively. **BSP** was found to be a suitable optical probe as linear correlations in parameters were observed for this compound. This is believed to be because **BSP**-IL interactions are based on hydrogen bonding between the $\mathbf{MC_{BSP}}$ and the ionic liquid cations, compared to $\mathbf{MC_{SO}}$, which is limited to electrostatic interactions. Hence, the sensitivity of $\mathbf{MC_{BSP}}$ is enhanced in the charged polar regions of the IL. Increasing the side-chain of the cation results in slight increases in $\mathbf{MC_{BSP}}$ to **BSP** relaxation activation energy from 96.93 $kJ.mol^{-1}$ in $[C_4mIm][NTf_2]$ to 105.27 $kJ.mol^{-1}$ in $[C_{12}mIm][NTf_2]$. $\mathbf{MC_{BSP}}$ to **BSP** relaxation $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ values also increase with increasing side-chain. The ability for spirocyclic compounds to switch between polar and non-polar forms appears to allow polar and non-polar regions in ILs to be probed dynamically using a single probe dye. It appears that the value of the ground state equilibrium constant, $K_e$, is dominated by the non-polar regions of the IL while the equilibrium constant of activation, $K^{\ddagger}$, is dominated by the polar regions. A correlation of side chain length to equilibrium constant of activation is believed to be because polar regions are possibly expanding

due to increasing influence of non-polar side chain interactions and compound insertion upon the overall solvent structure. The result of such reordering and dispersion of polar regions reduces solvent-solute interactions which increases the rate of $\mathbf{MC_{BSP}}$ to **BSP** relaxation.

## *Introduction*

Ionic liquids (ILs) are receiving increasing attention due to the large range of ions available adds a 'designer' aspect to the liquids, meaning that such liquids could provide solvents with specifically tailored properties. ILs consist entirely of ions in liquid state under 100ºC. Their 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 as common laboratory solvents.[6] However, the lack of detailed knowledge of the physico-chemical properties has resulted in their full potential not being completely realised.

Estimates of IL physico-chemical properties has led to the re-evaluation of solvent polarity as a macroscopic property that assumes the entire solvent system acts as a homogeneous medium rather than a medium that may possess nano-structured regions with dramatically different characteristics.[7,8] Polarity probes, such as Reichardts dye, can provide information about the polarity of a conventional solvent because of the absorption shift which accompanies the interaction of solvent molecules with the zwitterionic sites of the dye, as these interactions affect the excitation band gap of the probe molecule. To compliment such single parameter probe studies, the combination of three dyes (including Reichardt's) by Kamlet and Taft enabled hydrogen bonding behaviour of solvents to be examined.[9-11] 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..[4,12-14]

Photochromic materials based on spirocyclic compounds form merocyanines (**MC**) when exposed to UV irradiation, these zwitterions are similar in structure to those of betaine's used in Reichardts studies. It is proposed that such compounds could possibly act as multi-parameter probes based on

solvatochromic shifts of the **MC**, rates of thermal relaxations of **MC** to the spiro-form, and equilibrium constants $K_e$. Photoswitching of spirocyclic compounds (figure 1) 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.

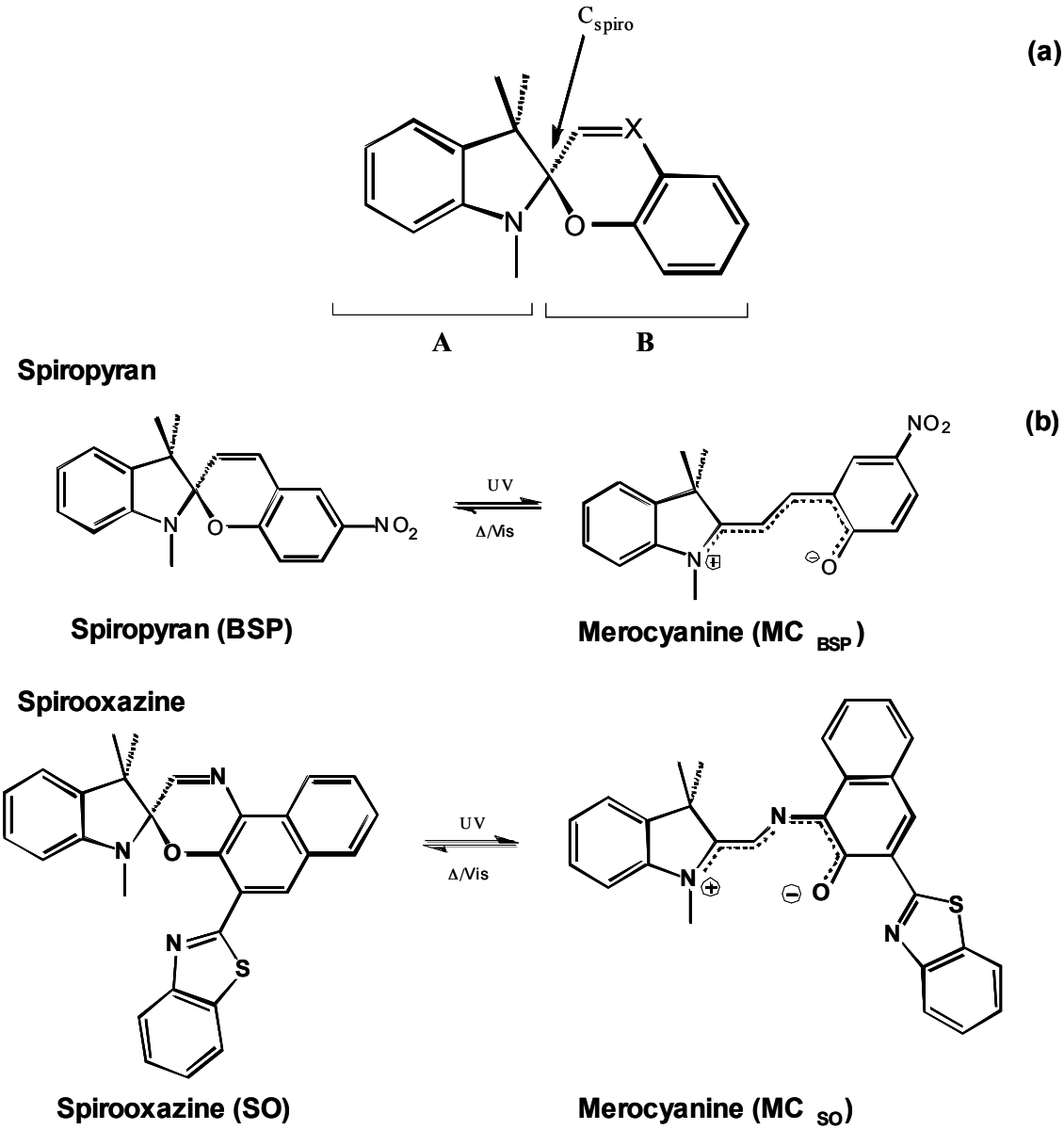



Fig 1: (a) Basic structure of spirocyclic compounds. Indoline (A) and pyran/oxazine (B) ring. Where X = **C** (pyran), N (oxazine)
(b) Spirocyclic compounds used in our studies and their photoswitchable states

The **MC** isomer arises from cis-trans isomerisation of the molecule, which results in a planar molecule with the charges largely delocalised across the molecule. The reorientation of the molecule results in the formation of several isomers, however, it is the cis-trans-cis (CTC) form which is most stable and produces the longest lifetime for solvent-solute interaction and thus use as a photochromic probe. The process is completely reversible by irradiation with white light. These photochromic compounds also revert spontaneously to their more stable 'ring closed' isomer through thermal reversion, in which the **MC** uses heat from its surroundings to supply sufficient energy for the reorientation to occur. This process follows first order kinetics.

The **MC** isomer is also sensitive to its immediate molecular environment and these corresponding specific and non-specific interactions that occur mediate the compound's equilibrium between both isomers.[15-18] In molecular solvents, the polarity-kinetic relationship was upheld for both **BSP** and **SO** with increasing rate constants observed with decreasing polarity.[19,20] Kamlet-taft parameters determined that this is due to decreasing levels of hydrogen bonding between solvent and spirocyclic compounds.[21] $\mathbf{MC_{BSP}}$ is known to form hydrogen bonds therefore inhibiting its rate of thermal relaxation. Similar trends to that observed in molecular solvents implies that **BSP** can act as a solvent sensitive probe in ionic liquids. 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 **BSP**-$\mathbf{MC_{BSP}}$ 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 BSP 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 restricted interactions with the IL ions to electrostatic/non-specific interactions. **SO** was therefore chosen to act as a reference compound for comparing solvent structure as the relatively weak interactions mean that its process of thermal relaxation would be somewhat independent of the solvent system used.

Recent studies have proposed that imidazolium based ILs may form ordered liquid systems resembling crystalline environments based on stacking of mutual charges (aggregation) or ordered association of cation to surrounding anions and vice versa.[22,23] Lopes *et al* examined the formation of nanostructured domains in ILs containing the imidazolium cation, it was found that certain 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 (figure 2). [24] 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 Waals interactions form a complex network of non-polar regions.

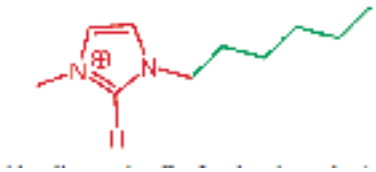


Fig 2: Imidazolium cation $C_6$mIm showing polar (red) and non-polar (green) regions of the molecule based on findings and convention of identification by Lopes et al.

The **MC** isomer of the two probe molecules provides a highly polar zwitterionic system which can interact with the opposing charges of the polar head groups of the solvent system, whereas the spiro isomer is known to be a neutral non-polar molecule and should reside in the non-polar region of the IL or at least at the interface of the region interfaces due to a marked reduction in solvent-solute interactions. As thermal relaxation occurs, the molecule would be expected to alternate their interactions between primarily polar and non-polar regions as the charged **MC** isomer reverts to the uncharged **SP** form and solvent reorganisation occurs. Previous spectroscopic studies of spiropyran in solutions containing lipid bilayers have exhibited diffusional believed to be due to the differing associations of each form of the compound.[25] The similarity between this ordering and the proposed ordering of ILs infers te possibility that similar mechanisms may be present with ILs which would allow the photochromic compounds to preferentially interact with specific regions thus probe the

existence of such structuring. The spirocyclic compounds themselves are bulky molecules which are quite large when compared to the size of the solvent molecules. The introduction of such molecules would therefore be expected to somewhat disrupt the ordering of the IL structure. However, the resulting reordering of the solvent molecules around the probe and the thermodynamic stability of the solvent molecules to physically accommodate the probe molecules will provide insight into the solvent system and the extent to which solvent/intramolecular ordering that occurs. Increasing the length of the non-polar side-chain of the imidazolium ion (figure 4) should affect the ordering of the IL at the molecular level due to 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 preferentially resides in 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 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. If nano-structuring exists in ILs we should observe a non-linear relationship between $K_e$ and thermal relaxation of the MC, due to the different molecular environments observed.

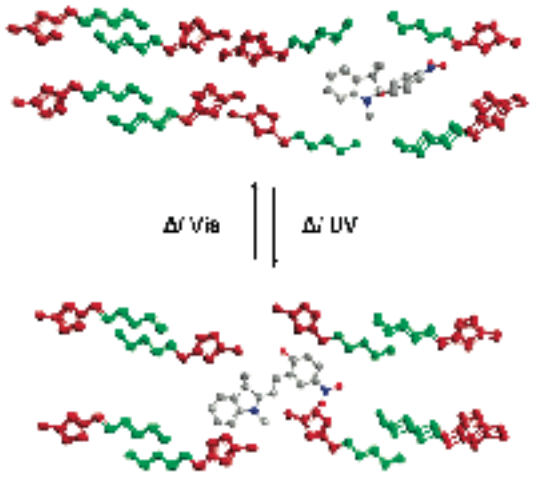
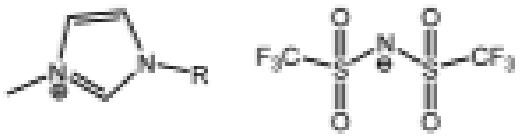



Fig 3: Schematic of proposed 3D ordering of imidazolium cations with **BSP** probe in $[C_6mIm][NTf_2]$ showing preferred residence of the MC (lower) and SP (upper) forms of the probe in polar and non-polar regions, respectively.

**Thermodynamic and kinetic studies were carried out to examine the extent of structuring in imidazolium based ILs based on equilibrium effects, rates of thermal relaxation and the effect upon solvent ordering due to the introduction of a bulky probe molecule.**




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

Fig 4: Cations and anion used in this study. 1-alkyl-3-methylimidazolium $[C_nmIm]^+$ and bis(trifluoromethanesulfonyl) amide $[NTf_2]^-$.

## *Experimental*

ILs were synthesised and purified in-house with salts obtained from Sigma-Aldrich using previously reported techniques.[26] The ILs produced were stored under argon to exclude uptake of 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 an in-house fabricated array based on 375nm UV LEDs (Roithner

Lasertechnik, Vienna, Austria). 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 supplied by Dr. Minkovska. All samples were prepared at room temperature.

## *Results and Discussion*

### Polarity and solvatochromic effects

All ILs were examined using the $ET_{30}$ scale as described previously.[21] 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 [$C_2$mIm][$NTf_2$] and 53.2 kcal.mol$^{-1}$ for [$C_6$mIm][$NTf_2$] were observed while similar chain lengths in molecular solvents with a polar region and extending non-polar side chain (e.g. alcohols) had $ET_{30}$ values of 51.9 kcal.mol$^{-1}$ and 48.8 kcal.mol$^{-1}$ for ethanol ($C_2$) and 1-hexanol ($C_6$) respectively.[7] As with $ET_{30}$ values, the observed solvatochromic 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 reducing the overall solvatochromic effect of the increasing alkyl chain length of the solvent. In addition to proposed reduction of polar region influence, the increasing chain length size also results in increasing size of non-polar domains and corresponding separation of polar regions from one another. Such increases would therefore produce a liquid system that would appear more non-polar throughout to spirocyclic compounds and thus result in solvatochromic shifts corresponding to such environments.

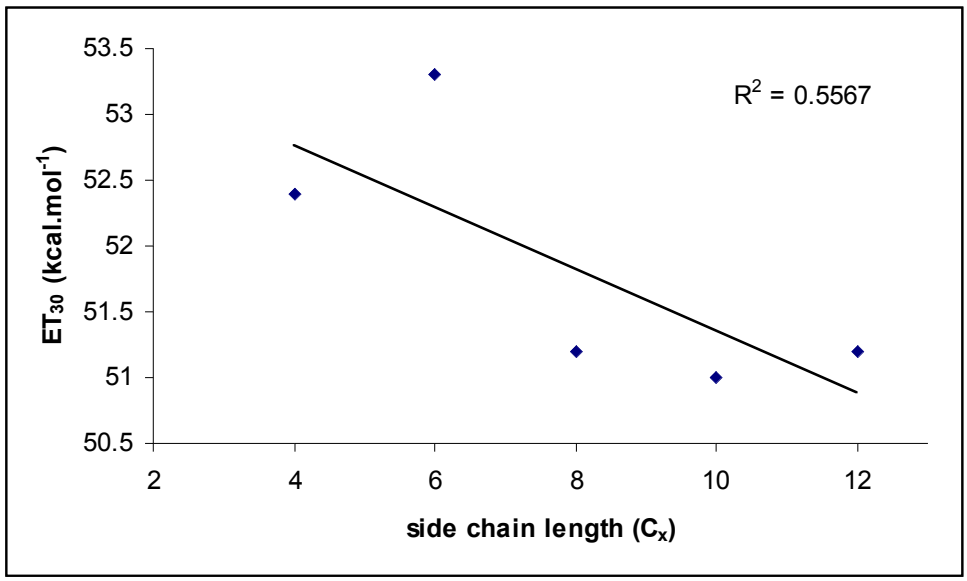



Fig 5: $ET_{30}$ values of ILs with increasing cation side-chain length.

**BSP**, due to its nitro group, exhibits solvatochromic effects due to a wavelength shift of the $\mathbf{MC_{BSP}}$ absorption maximum. Linear bathochromic (red) shifts were observed with increasing cation side-chain lengths as previously established in molecular solvents of decreasing polarity.[27] Similar effects were not observed for **SO** as the equivalent $\mathbf{MC_{SO}}$ does not exhibit solvatochromic behaviour.

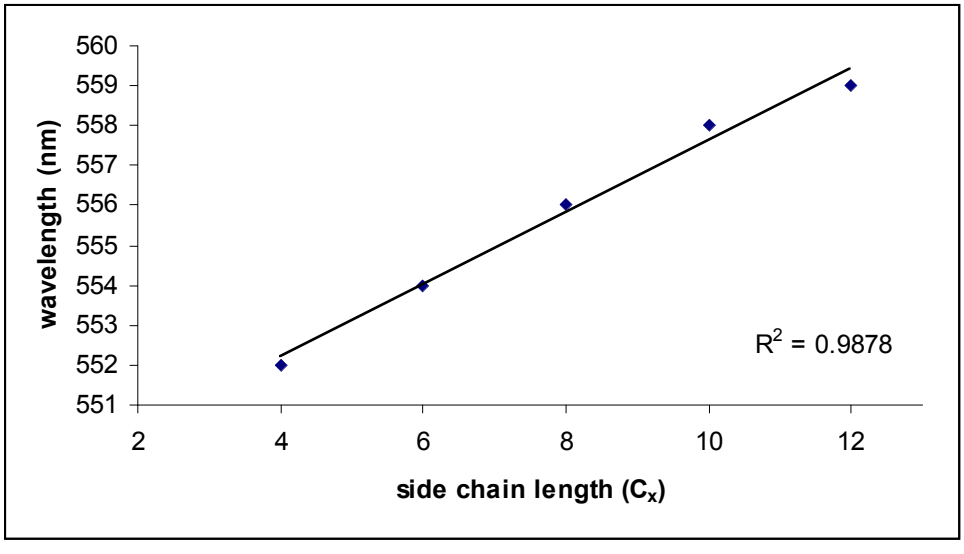


Fig 6: $\mathbf{MC_{BSP}}$ solvatochromic shift versus cation side-chain length.

## Kinetic parameters

Samples were placed in thermostatically controlled UV-Vis spectrometer and were irradiated in-situ using an LED array to induce ring opening and **MC** formation. Upon removal of the UV light source**,** the thermal relaxation first order decay curves were then examined using equation **(1)**.

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

The rates of thermal relaxation were recorded at 298K and 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 $1.0\text{x}10^{-3}\text{s}^{-1}$ to $2.0\text{x}10^{-3}\text{s}^{-1}$ (fig 7a). Since lengthening of the side-chains would be expected to promote more inter-chain interactions it is believed that such interactions place a strain upon the mutual interactions of the polar head groups. This strain in turn may cause the polar head groups separate further from each other, increasing the size of the polar region while reducing the overall charge density within the region to accommodate the solute molecules.[28] Early investigations into IL structuring observed deviations from traditional correlations between viscosity and diffusion for the diffusion coefficients of solutes within 'wet' or hydrated ILs.[29] Further studies concluded that this could be explained through the IL system swelling to accommodate the solvent molecules, as had been observed previously in studies involving IL/molecular solvent binary mixtures, such as [bmIm][$PF_6$] and naphthalene.[30] We propose that the addition of spirocyclic compounds, particularly those when predominantly in the charged/polar **MC** form, are integrated into the IL

structure in a similar manner in addition to the size of the **BSP** physically disrupting the regions when added to the ILs. If separation of head groups occurs upon such integration, then the distance between the imidazolium ring charge and the C2 proton of the **MC** isomer would be lengthened. This would imply a reduction in the ability of the **MC** molecules to stabilise polar guests. Rates of thermal relaxation of $\mathbf{MC_{BSP}}$ were found to increase with increasing chain length, and we believe this is due to a reduction in the effectiveness of interactions in polar regions, while the impact of non-polar regions is enhanced, favouring the conversion to **BSP**.

**SO** was found to have similar relaxation rates of approximately $2.3x10^{-2}s^{-1}$ within all ILs (fig 7b), the increasing chain length having no apparent effect. This agreed with our previous findings and is believed to be due to the solvent-solute interactions being predominantly electrostatic, and its influence was therefore similar in each IL.[21] Further support for this hypothesis comes from the rates of thermal relaxation, which were ten times faster than that observed for the **BSP** system. This would be expected, due to considerably weaker interactive forces stabilising the $\mathbf{MC_{SO}}$. The relatively weak electrostatic forces also means that **SO/** $\mathbf{MC_{SO}}$ molecules are relatively free to move within the IL due to the absence of any strong direct interactions in polar or non-polar nano-regions in the IL. **SO** molecules may therefore migrate to an intermediate region between the two regions and where variations in side chain length and head group interaction would have less impact.

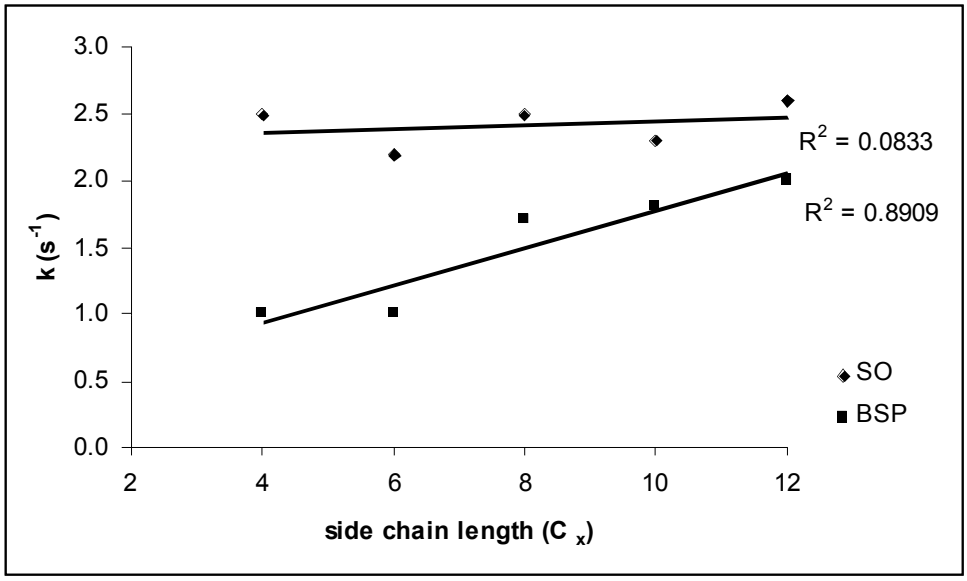


Fig 7: Rate of thermal relaxation of MC isomer to **BSP** / **SO** versus cation side-chain length.

## Thermodynamic parameters

The dependence of the rate of thermal relaxation with temperature was investigated 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.[31] The thermodynamic parameters found are 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 = Planck's constant
$k_b$ = Boltzmann constant

$\Delta S^{\ddagger}$ 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 is a measure of the amount of reorientation of the system during the thermal relaxation from **MC** to **BSP** within the IL, and it is related to the rigidity of the

solvent and the overall thermal stability of the **$MC_{BSP}$-BSP** system. Positive values imply that the IL-solute system undergoes significant reorientation during thermal relaxation from **$MC_{BSP}$** to **BSP**. The observed increase in values may be due to increasing ordering of non-polar regions as increasing chain length will strengthen interactions in the non-polar regions. Steric effects from solvent-solvent and solvent-**$MC_{BSP}$** interactions could result in expansion of polar regions, allowing an easier transfer of the probe molecule during **$MC_{BSP}$-BSP** conversion. At short chain lengths ($C_2$mIm), it would be expected that little ordering exists and the IL ions are in random motion much like molecular solvents. Since ordering is enhanced as chain lengths increases, the IL may adopt a more structured form at the nano-scale, with polar and non-polar regions between which the **$MC_{BSP}$** and **BSP** molecules can move dynamically as the equilibrium shifts. The introduction of the spirocyclic compound and its subsequent transition from **$MC_{BSP}$** (charged) to **BSP** (uncharged) should also result in considerable reorientation of the IL ions around the guest molecules. Furthermore, the physical size of the probe molecule itself is expected to significantly disrupt the established IL structure. Movement of the probe molecules during their transition from the **MC** form to their respective **BSP/SO** forms should also involve molecular reorientation to accommodate the probe molecules, thus increasing the entropy of the system. Positive entropies also imply that the interactions between the IL ions is weak enough for the spirocyclic compound to disrupt the system. This means that the IL structure itself is 'fluid' enough to facilitate dynamic movement of the probe molecules between the IL polar/non-polar regions. **SO** once again showed no clear correlation between the entropies of activation and chain length, which suggests that for the **$MC_{SO}$-SO** thermal relaxation in the various ILs is relatively independent of the nano-structure of the IL.

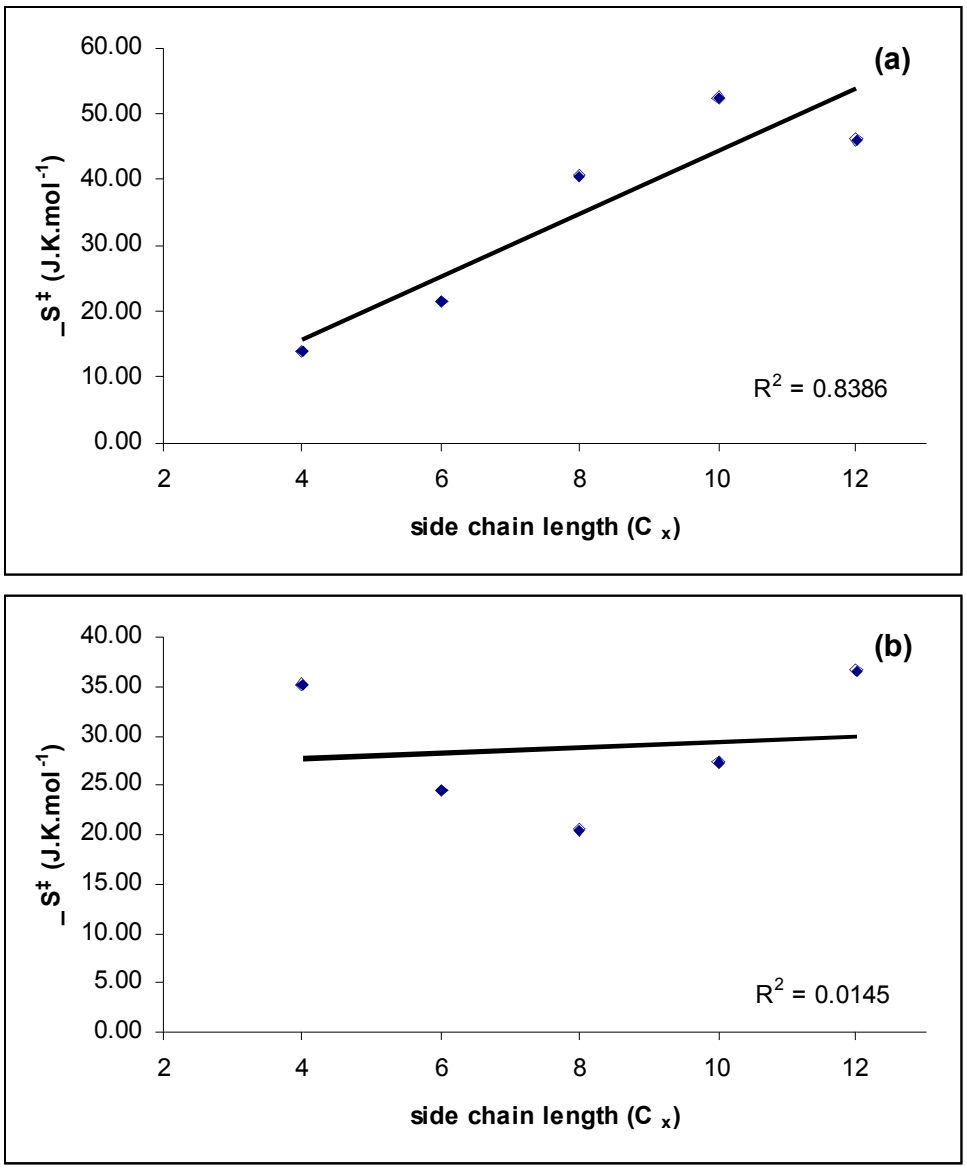



Fig 8: Entropies of activation of **BSP** (a) and **SO** (b) versus cation side-chain length.

The related parameters of activation energies ($E_a$) and enthalpies of activation ($\Delta H^{\ddagger}$) were also found to slightly increase with increasing chain length. Initially, this appears to be contradictory, as increasing energy barriers would be expected to yield slower rates of relaxation. However, this could arise due to compensation for the increased separation of charged sites as the chain length is increased. Such changes in the solvent system would be expected to produce an environment that is generally less polar than that of shorter chain cations, and therefore less favourable to **MC** stability. Since imidazolium cations are known to interact through charge association (coordinated by anions in the polar region), ion pairing, hydrogen bonding and, to a lesser extent, pi-stacking, it

would be expected that *intra*-molecular interactions would dominate.[22,32] The expansion of such systems therefore reduces these interactions, and may in fact facilitate *inter*-molecular interactions (**MC**-IL). Such interactions would result in an increased stability of the **MC** form of the probe molecule, and thus increase the energy barrier required for thermal relaxation to occur. However, the thermal relaxation process provided far greater energy than 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 is the overall effect observed.

In contrast, 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 is proposed that the process of thermal relaxation is also somewhat independent of the nature of the IL, provided the charged centre remains unchanged, as is the case in this study. The bulky nature of the **SO** substituents may provide sufficient steric hindrance to prevent hydrogen bonding which would influence the relaxation process. The ability of the **SO** and **MCso** molecules to move somewhat freely between the IL nanostructured regions also means that the $\mathbf{MC_{SO} \Rightarrow SO}$ conversion could occur with relatively little interaction with the IL ions. As a result, the process for thermal relaxation is similar in all ILs tested, and is independent of chain length.

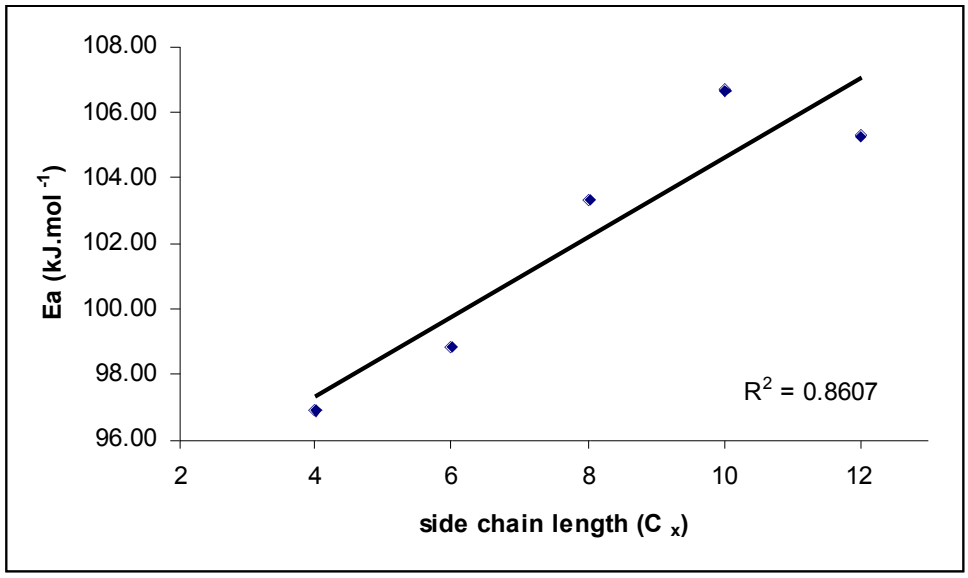



Fig 9: Activation energy of **MC-BSP** thermal relaxation versus cation side-chain length.

The ground state equilibrium, $K_e$, and transition state equilibrium, $K^{\ddagger}$, were also examined to determine the effects of chain length and IL nanostructure on the $\mathbf{MC_{SO}}$**-SO** and $\mathbf{MC_{BSP}}$**-BSP** equilibria. Ground state equilibria were determined using equation **(5)**

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

Where,
C = concentration of **BSP/SO**
ε = extinction coefficient. $3.5\text{x}10^4 M^{-1}cm^{-1}$ for **BSP**[33] and $7.85\text{x}10^4 M^{-1}cm^{-1}$ for **SO** (obtained experimentally by Dr. Minkovska).

Ground state equilibrium constants were found to be consistent in relation to increasing IL cation side-chain length for both **BSP** and **SO**. $K_e$ values around $7\text{x}10^{-3}$ for **BSP** and $5\text{x}10^{-3}$ for **SO** were observed in each of the ILs. This implies that the spirocyclic compounds remained in their closed (**BSP/SO**) form in preference to the respective **MC** form in each of the ILs. Since the closed, spiro forms of the compounds have a lower energy level than of the respective **MC** form, it would be expected that they would be primarily in the closed form at equilibrium. However, polar regions within the ILs may shift the equilibrium towards the **MC** form. Examination of the shorter chain

(more polar) ILs showed little change in equilibrium constants compared to that of the longer chain cations. This would appear to reinforce the existence of domains within the solvent system, as increasing the chain length of the IL cation should favour the formation of the spiro form. If the spirocyclic compounds are residing in the non-polar regions in their closed form then it would appear that changing the size of such regions has little effect upon the equilibrium. Since spirocyclic compounds thermodynamically favour residing in such regions due to the uncharged nature of their closed form (and its lower thermodynamic energy level), intuitively it would be expected that the contribution of the non-polar regions of each IL to the equilibrium constant would be similar or equivalent in each of the ILs.

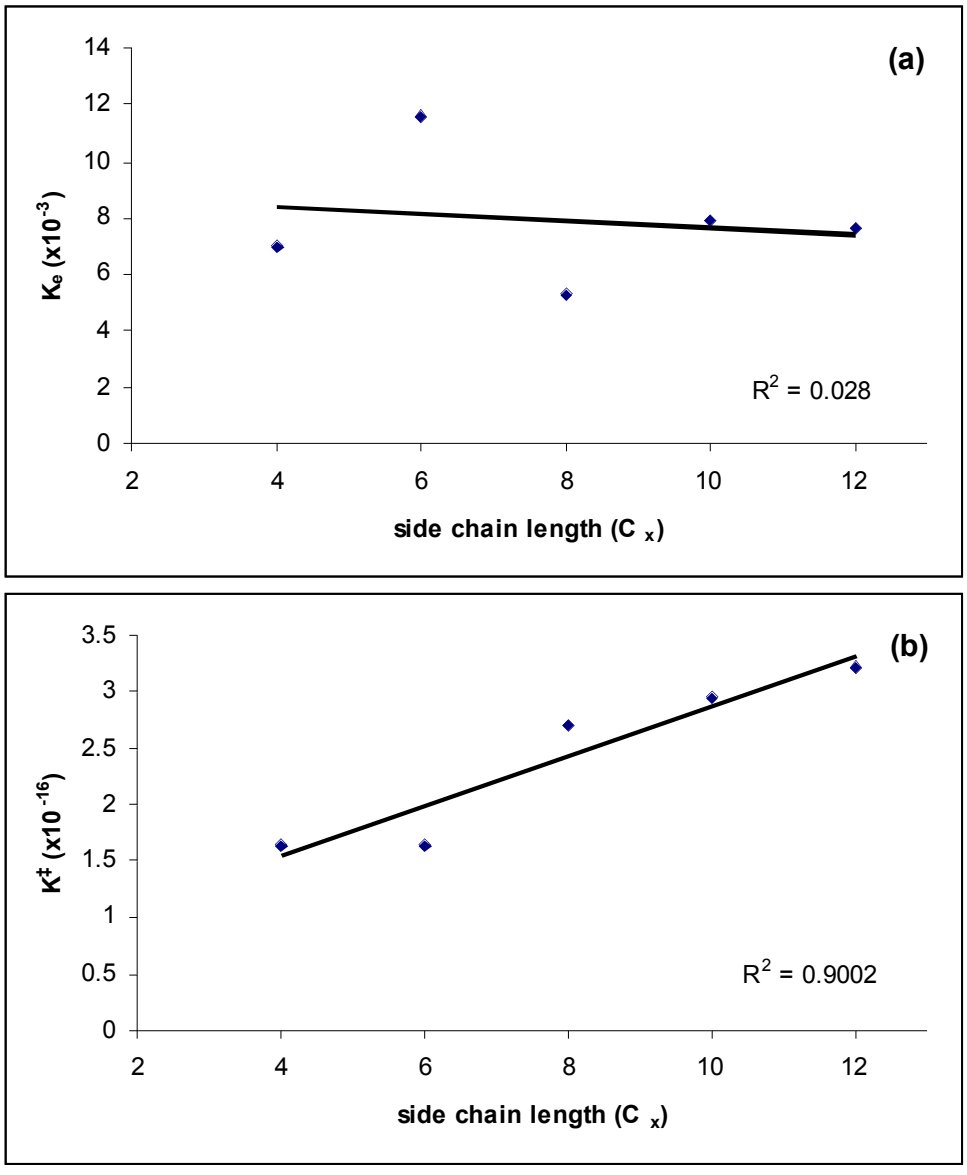



Fig 10: (a) Ground state equilibria and (b) equilibria of activation of **BSP** versus cation side chain length

To examine the effect of polar regions of the ILs, the transition state equilibrium, $K^{‡}$, was determined. The equilibrium is based on the thermodynamic interconversion between **MC** and the respective **BSP/SO** forms, and the process of relaxation is based upon which is the preferred state of the molecule. The transition state equilibrium determines whether the process of relaxation preferentially occurs. At this transition state (**MC‡**) the compound is in the process of relaxation to **BSP/SO.** However, sufficient interaction with the IL system will increase the stability of the **MC** form which compete with one another during the process. Unlike the ground state equilibrium constants, where the compound is predominantly in its most stable, ground state (closed) form , the compound is now in its **MC** form which is inherently unstable as such isomers are at a thermodynamically higher energy state. The spirocyclic compounds in their excited states therefore preferentially relax to their ground state but the ability to do so is based upon the equilibrium of the system. The transition state equilibrium, in particular, examines which isomer of the compound is preferred at the transition state, which is related to the relative interactions of the **MC** form with the IL polar regions and the competing influence of the non-polar IL regions favouring the closed form. The result is that any changes in the equilibrium is therefore sensitive on changes to the system which can only be observed when the spirocyclic compounds are in the process of thermal relaxation and migrating within the IL. Since the ground state (closed) form of the probe molecules require energy to form their respective **MC** isomers**,** the ground state equilibrium $K_e$, is somewhat biased towards the closed form and so the compound resides consistently in the non-polar regions of the ILs. This may explain why there is little relationship between the rate constants and the ground state equilibrium constants. In the case of **MC** thermal relaxation and the transition state equilibrium**,** the opposite occurs as the compound must now relax to the spiro form from its higher energetic state.

With increasing chain length, structuring within the solvent is proposed to disperse and weaken the relative interactions of the polar regions. 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 of the **MC** form and further enhance the formation of the closed form which shifts the equilibrium toward the closed form of the compound. This is 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 is 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.

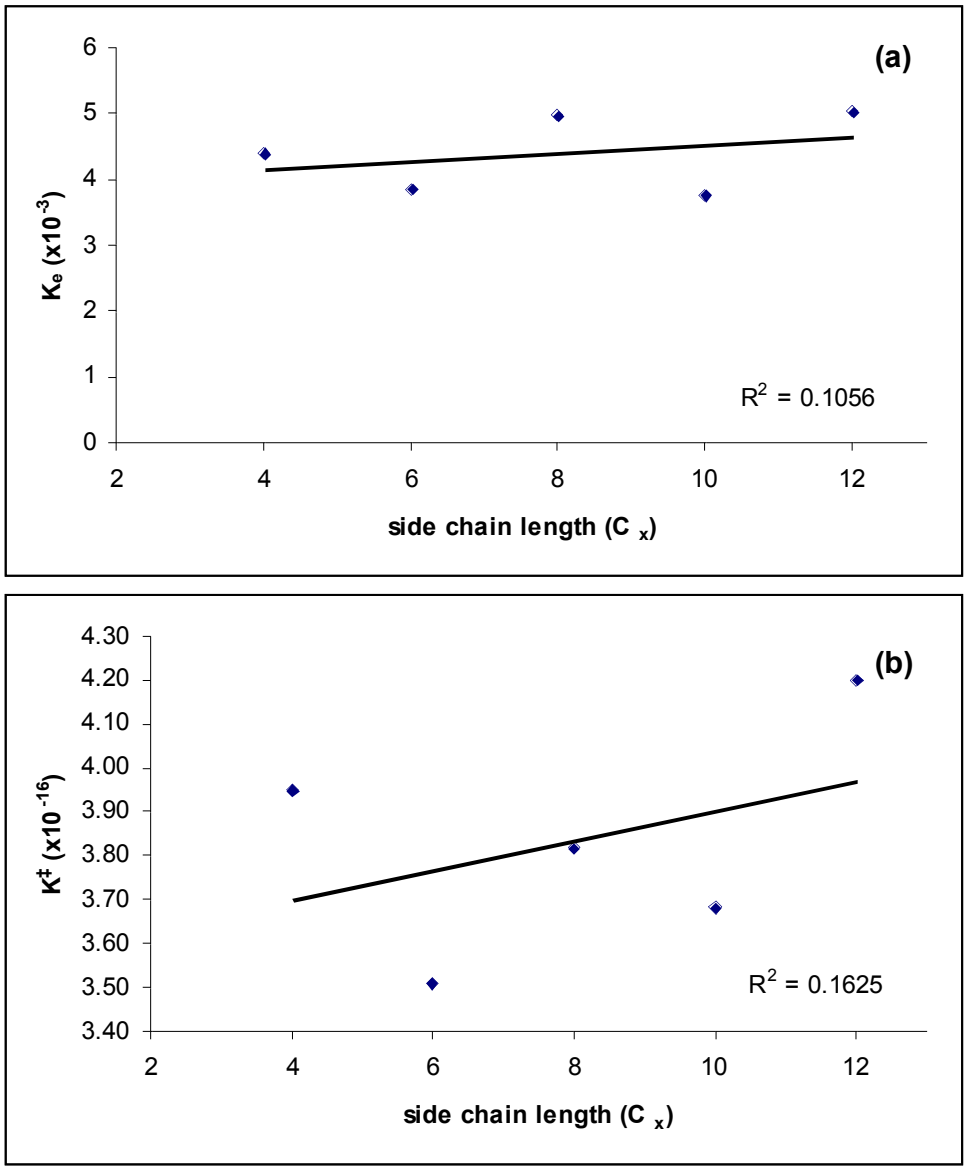


Fig 11: (a) Ground state equilibria and (b) energy of activation of **SO** versus cation side-chain length.

## *Conclusions*

Imidazolium based ILs appear to present nanostructured polar and non-polar domains. Spirocyclic compounds added to ILs with a non-polar side chain of increasing length resulted in moderate changes to thermodynamic parameters possibly due to enhanced structuring of the nano-domains. **BSP** was found to be sufficiently sensitive to quantify thermodynamic and kinetic parameters due to its intimate interaction with the imidazolium 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 with the IL. Probing of ILs with **BSP** suggests that the molecule may dynamically transfer between the polar and non-polar nano-structured domains in the IL. Ground state equilibria values were similar regardless of the IL cation chain length, which suggests that stabilisation effects are similar for each form of the probe molecule 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 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. Interestingly, positive $\Delta S^{\ddagger}$ values mean that the compound undergoes significant reordering within the solvent system during thermal relaxation. This further implies that the spirocyclic probe disrupts the IL nanostructure when it is introduced, and it migrates dynamically between the nanostructured 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.

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